

IMPERIAL

ON MODELLING THE CHEMO-MECHANICAL COUPLED RESPONSE OF STARCH HYDROGEL DURING HUMAN GASTRIC DIGESTION

A thesis submitted for the degree of Doctor of Philosophy of Imperial College London
and the Diploma of Imperial College London

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Feb 2026

Declaration of Originality

I hereby declare that this thesis is entirely my own work. All material that is not my own has been clearly acknowledged, and appropriate references have been provided in accordance with departmental requirements.

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Abstract

Glucose homeostasis is essential for human survival, yet is frequently disrupted by hyperglycaemia, which is closely associated with non-communicable metabolic disease such as obesity and type-2 diabetes. A key dietary contributor to hyperglycaemia is the widespread consumption of highly processed starch-based foods with high glycaemic index values. Industrial processing disrupts food structure and alters mechanical properties, making these foods rapidly broken down in the gastrointestinal tract, increasing enzyme accessibility, and accelerating gastric emptying and intestinal glucose absorption.

Therefore, the importance of understanding and engineering the chemo-mechanical properties of starch-based systems for controlled digestion is emphasised. Among starch-based foods, starch hydrogels provide a biocompatible and tunable system for nutritional design and drug delivery. However, their digestion involves coupled enzymatic hydrolysis, mechanical degradation, and large deformation, which is still not fully understood.

To bridge this gap, this thesis combines *in vitro* experimentation with *in silico* modelling. Starch hydrogels prepared under different processing conditions were characterised by microscopy, thermal analysis, and extensive mechanical tests, revealing constitutive behaviour governed by the polymer network formed during gelatinisation and retrogradation. Compression tests after enzymatic hydrolysis were employed to characterise mechanical property changes due to degradation, and diffusion tests were conducted to quantify the enzyme transport properties. The experimental result provides the basis for model development and calibration.

A chemo-mechanical constitutive model was proposed to capture hyperelasticity, time-dependent viscoelasticity, retrogradation-induced pseudoelasticity, and enzymatic degradation. Implemented in the Finite Element Method, the model successfully reproduced the coupled diffusion-reaction-deformation behaviour observed

experimentally. The framework was extended using the Coupled Eulerian-Lagrangian method to simulate gastric digestion under peristalsis and fluid-solid interactions, and the results were compared with dynamic *in vitro* digestion tests.

Overall, this thesis establishes a unified experimental-computational approach for quantifying and predicting starch hydrogel digestion, providing an intuitive and quantitative tool for nutritional and biomedical applications.

Keywords:

Starch hydrogel, Gastric digestion, Enzymatic hydrolysis, Chemo-mechanical behaviour, Hyper-pseudo-viscoelastic constitutive model, Diffusion-reaction-deformation process, Coupled Eulerian-Lagrangian Finite Element Method

Acknowledgements

When I received the admission offer from Imperial College London, I was filled with excitement and anticipation. Four years have passed quickly, and my doctoral study is now drawing to a close. It has been a demanding yet invaluable experience, marked by an unfamiliar research direction, a steep learning curve, and the challenges of adapting to a new environment. Along the way, I gained significant expertise in mechanics theory, numerical modelling, programming, experimental techniques, and many related areas. Throughout this journey, I have been fortunate to receive support from many individuals, to whom I express my sincere gratitude.

First and foremost, I thank my supervisor, Professor Maria Charalambides, with deep appreciation for her meticulous guidance and support. Her broad knowledge, rigorous research approach, and commitment to academic excellence have profoundly shaped my development as a researcher. She offered generous intellectual freedom while providing clear and constructive advice whenever I faced setbacks. Under her supervision, I completed a highly challenging, multidisciplinary project. Her professionalism and dedication have set a standard I will continue to follow in my future academic career.

I am deeply grateful to my master's supervisors, Professor Xiaohu Yao and Professor Mokarram Hossain, whose guidance laid the foundation for my academic path and trained me to become an independent researcher. Their continued advice, support, and collaboration during my PhD have strengthened my determination to pursue a long-term career in scientific research.

My sincere thanks go to Professor Maria Papathanasiou from the Department of Chemical Engineering for her guidance on the chemical aspects of the project and for her insightful suggestions during our meetings; Dr Chaiwut Gamonpilas from the National Metal and Materials Technology Center, Thailand, for his support with the design and operation of dynamic *in vitro* digestion experiments; and Dr Aygul Dagbasi, Dr

ACKNOWLEDGEMENTS

Aaron Lett, and Professor Gary Frost from the Department of Metabolism, Digestion and Reproduction for their advice on the biological and nutritional aspects of this work.

I particularly thank Dr Dimitrios Bikos, Dr Tian Yuan, and Dr Wei Fan for their academic discussions and advice. I am grateful to Mr Alexandros Makrypidis, whose close collaboration in this project has been essential to the progress. I further thank Dr Ruth Brooker and Dr William Megone for laboratory induction, safety guidance, and technical assistance. I also appreciate the support and discussions from all members of the Soft Solids Group. My heartfelt thanks go to Dr Kaka Cheng, whose companionship has been invaluable. I am also thankful to my friends in London, whose shared moments have helped relieve stress and made my time here both enjoyable and memorable.

Finally, I am deeply grateful to my parents, my sister, my uncle and his family, for their unwavering encouragement. Their trust and support have sustained me through difficult times, and I remain profoundly thankful for their presence throughout this journey.

Research Output

Publications related to this thesis are listed below:

[1] Liao, Z., Makrpidis, A., Charalambides, M., Papathanasiou, M. (2025). On the pseudoelastic-viscoelastic behavior of starch hydrogels at various degrees of gelatinization and retrogradation. *Physics of Fluids*, 37 (2), 027185. DOI: [10.1063/5.0251424](https://doi.org/10.1063/5.0251424)

[2] Liao, Z., Dagbasi, A., Yap, K., Yang, J., Makrpidis, A., Yuan, T., Lett, A., Masen, M., Papathanasiou, M., Dini, D., Frost, G., Charalambides, M., On the chemo-mechanical behaviour of starch hydrogels under α -amylase hydrolysis. *Ready for submission*

[3] Liao, Z., Makrpidis, A., Charalambides, M. In silico simulation of gastric digestion of starch hydrogels. *In preparation*

Part of publication [1] is presented in [Chapter 2](#).

Part of publication [2] is presented in [Chapter 3](#) and [Chapter 4](#).

Part of publication [3] is presented in [Chapter 5](#).

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Acronyms

(NH₄)₂CO₃ ammonium carbonate. [85](#)

1D one-dimensional. [106](#), [107](#), [110](#), [130](#), [131](#), [133](#), [167](#)

2D two-dimensional. [148](#), [153](#), [154](#), [167](#), [168](#), [189](#)

3D three-dimensional. [16](#), [147](#), [153](#), [168](#), [176](#), [184](#), [189](#), [196](#)

ACW antral contraction wave. [5](#)

ADP adenosine diphosphate. [97](#)

ATP adenosine triphosphate. [97](#)

BCA bicinchoninic acid. [100](#), [102](#)

BSA bovine serum albumin. [102](#)

CaCl₂ calcium chloride. [208](#)

CEL Coupled Eulerian-Lagrangian. [viii](#), [19](#), [21](#), [168](#), [171](#), [174](#), [176](#), [183](#), [186](#), [196](#), [198](#), [202](#), [214](#), [216](#), [220](#), [221](#)

CFD Computational Fluid Dynamic. [18](#), [19](#), [168](#)

CPU central processing unit. [217](#)

CT Computed Tomography. [189](#)

DEM Discrete Element Method. [18](#), [19](#)

DENT double edge notched tension. [30](#)

DI deionised. [32](#), [39](#), [58](#), [81](#), [82](#), [207](#)

DIC Digital Image Correlation. [60](#), [61](#), [63](#)

DN double-network. [16](#)

DOG degree of gelatinisation. [24](#), [25](#), [26](#), [27](#), [29](#), [31](#), [32](#), [39](#), [47](#), [48](#), [49](#), [50](#), [52](#), [76](#)

DOR degree of retrogradation. [26](#), [29](#), [31](#), [32](#), [35](#), [36](#), [39](#), [52](#), [69](#), [76](#)

DP degree of polymerisation. [8](#)

DSC Differential Scanning Calorimetry. [25](#), [26](#), [31](#), [32](#), [35](#)

EOS equation of state. [184](#)

EWF essential work of fracture. [30](#)

F/P fluorescein to protein. [100](#), [101](#)

FDM finite difference method. [106](#), [107](#), [108](#), [109](#), [110](#)

FE Finite Element. [113](#), [138](#), [146](#), [147](#), [168](#), [169](#), [171](#), [190](#), [214](#)

FEM Finite Element Method. [vii](#), [18](#), [19](#), [20](#), [30](#), [109](#), [139](#), [141](#), [146](#), [156](#), [167](#), [220](#)

FITC fluorescein isothiocyanate. [100](#), [101](#), [103](#)

FSI fluid-solid interaction. [19](#), [21](#), [221](#)

FVM Finite Volume Method. [18](#)

G6PDH glucose-6-phosphate dehydrogenase. [98](#)

GES gastric electrolyte secretion. [207](#), [208](#)

GI gastrointestinal. [vii](#), [1](#), [2](#), [3](#), [6](#), [7](#), [8](#), [14](#), [16](#), [17](#), [18](#), [19](#)

GIP glucose-dependent insulintropic peptide. [7](#)

GLP-1 glucan-like peptide. [7](#)

H₂O water. [85](#), [208](#)

HCl hydrochloric acid. [82](#), [85](#), [86](#), [207](#)

HK hexokinase. [97](#)

IPN interpenetrating-network. [16](#)

KCl potassium chloride. [85](#), [208](#)

KH₂PO₄ potassium dihydrogen phosphate. [85](#)

MgCl₂ magnesium chloride. [85](#)

Na₂CO₃ sodium carbonate. [83](#), [100](#)

NaCl sodium chloride. [85](#), [208](#)

NADP⁺ nicotinamide adenine dinucleotide phosphate. [98](#)

NADPH nicotinamide adenine dinucleotide phosphate. [98](#)

NaHCO₃ sodium bicarbonate. [85](#), [100](#)

NCD non-communicable metabolic disease. [vii](#), [1](#), [7](#)

ODE ordinary differential equation. [18](#), [20](#)

PAHBAH P-hydroxybenzoic acid hydrazide. [83](#)

PBPK Physiologically Based Pharmacokinetics. [18](#), [20](#)

PBS Phosphate Buffered Saline. [83](#)

PDE partial differential equation. [139](#), [153](#), [156](#)

PTFE polytetrafluoroethylene. [87](#)

RDS rapidly digestible starches. [12](#)

RS resistant starches. [13](#)

SDF simulated digestion fluid. [207](#)

SDS slowly digestible starches. [12](#)

SEM Scanning Electron Microscopy. [17](#), [29](#), [31](#), [33](#), [76](#)

SGF simulated gastric fluid. [85](#), [86](#), [96](#), [97](#), [110](#)

SPH Smoothed Particle Hydrodynamics. [18](#), [19](#), [168](#), [169](#)

SQP sequential quadratic programming. [157](#)

SSE sum of squared errors. [157](#)

T2D type-2 diabetes. [vii](#), [1](#), [7](#), [8](#)

UMAT user material subroutine. [139](#), [146](#), [147](#), [151](#), [153](#), [155](#), [165](#), [175](#)

VDISP user displacement subroutine for explicit solver. [183](#), [195](#), [198](#)

VEXTERNALDB user external database subroutine for explicit solver. [194](#), [195](#), [198](#)

VUMAT user material subroutine for explicit solver. [175](#), [176](#), [196](#)

XRD X-ray Diffraction. [25](#), [26](#)

Nomenclature

Chapter 2

A	Newly created surface area during fracture
A_0	Initial cross-sectional area
b	Width of wire-cutting sample
d	Diameter of wire
D_{int}	Dissipation energy density
$D_{\text{int}}^{\text{neq}}$	Dissipation energy density due to viscoelasticity
$D_{\text{int}}^{\text{peq}}$	Dissipation energy density due to pseudoelasticity
$\dot{\varepsilon}$	Engineering strain rate
ε	Nominal strain
ε_V	Volumetric nominal strain
ε_X	Axial nominal strain
ε_Y	Lateral nominal strain
ε_{eq}	Equivalent strain
$\varepsilon_{\text{true}}$	True strain (Hencky strain)
F	Force
Γ	loading-unloading path of nominal strain
γ	Shear strain
Γ_1	loading-unloading path of nominal strain for the primary cycle

Γ_2	loading-unloading path of nominal strain for the reloading cycle
γ_R	Apparent shear strain at the outer radius
G	Strain energy release rate
G_c	Fracture toughness
ΔH_{Gel}	Enthalpy change of gelatinisation
ΔH_{Ret}	Enthalpy change of retrogradation
h	Height of the specimen
L_0	Initial gauge length
μ	Friction coefficient
P	Nominal stress
θ	Angular displacement
ρ_{gel}	Density of starch hydrogel
ρ_s	Density of starch powder
R	Radius of the specimen (outer radius)
r	Radial position in the specimen
σ	True stress (Cauchy stress)
σ_y	Yield stress
σ_{eq}	Equivalent stress
τ	Shear stress
τ_R	Apparent shear stress at the outer radius
T	Torque
U	Total potential energy
u	Displacement
V	Current volume
V_0	Initial volume

Chapter 3

$[A^-]$	Concentration of conjugate base of the acid
A_1	Baseline UV-Vis absorbance measured before the assay
A_2	UV-Vis absorbance measured after the incubation step of the assay
A_{280}	UV-Vis absorbance measured at 280 nm
A_{495}	UV-Vis absorbance measured at 495 nm
C	Concentration
C^*	Normalised concentration
C_{eq}	Equilibrium concentration
D	Diffusion coefficient
$E_{280}^{0.1\%}$	UV-Vis absorbance at 280 nm of the protein at 0.1% w/v concentration
f_{enz}^*	Enzyme saturation ratio
f_{enz}	Total amount of enzyme within the sample
$[HA]$	Concentration of the acid
$[H^+]$	Concentration of hydrogen ion
h	Height of the diffusion test sample
V	Volume of the diffusion test sample
$\mathbf{J}$	Diffusion flux vector
K_a	Acid dissociation constant
$f_{F/P}$	Molar ratio of fluorescein to protein
m	Number of temporal nodes
M_{enz}	Molar mass of enzyme
M_{mal}	Molar mass of maltose
n	Number of spatial nodes
ΔR	Spatial step size
R	Normalised spatial coordinate

r	Radial position
r_0	Sample radius
ΔT	Temporal step size
T	Normalised temporal coordinate
t	Time

Chapter 4 Constitutive model

a_α	Enzyme specific activity
$\bar{\mathbf{C}}$	Isochoric right Cauchy-Green strain tensor
$\bar{\mathbf{C}}_{\max}$	Maximum historical isochoric right Cauchy-Green strain tensor
$\mathbf{C}$	Right Cauchy-Green strain tensor
$\mathbf{C}_{e,j}$	Elastic right Cauchy-Green strain tensor of the j -th Maxwell element
$\mathbf{C}_{v,j}$	Viscous right Cauchy-Green strain tensor of the j -th Maxwell element
C_{enz}^0	Reference enzyme concentration constant
c_1, c_2, c_3	Hyperelastic material parameters (shear moduli)
C_S	Mass concentration of substrate
$c_{p,1}, c_{p,2}, c_{p,3}$	Pseudoelastic material parameters (shear moduli)
C_{S_0}	Initial mass concentration of substrate
$c_{v,j}$	Shear modulus of the j -th Maxwell element
$\bar{C}_E$	Effective enzyme mass concentration
$\mathbf{d}_{v,j}$	Viscous deformation rate tensor of the j -th Maxwell element
$\mathcal{D}_{\text{int}}$	Internal dissipation energy density
$\mathcal{D}_{\text{int}}^{\text{chem}}$	Chemical internal dissipation energy density
$\mathcal{D}_{\text{int}}^{\text{neq}}$	Non-equilibrium internal dissipation energy density
$\mathcal{D}_{\text{int}}^{\text{peq}}$	Pseudo-equilibrium internal dissipation energy density
$[\text{ES}]$	Enzyme-substrate complex concentration

$[E]$	Enzyme concentration
$[E]_0$	Initial enzyme concentration
η	Softening factor
η_j	Viscosity of the j -th Maxwell element
$[\bar{E}]$	Effective enzyme molar concentration
$\bar{\mathbf{F}}$	Isochoric part of the deformation gradient tensor
$\bar{\mathbf{F}}_{\max}$	Maximum historical value of the isochoric deformation gradient
$\mathbf{F}$	Deformation gradient tensor
$\mathbf{F}_{e,j}$	Elastic deformation gradient tensor of the j -th Maxwell element
$\mathbf{F}_{v,j}$	Viscous deformation gradient tensor of the j -th Maxwell element
ϕ_l	Volume fraction of liquid phase
f	Chemical interaction variable, substrate ratio
$\bar{I}_1$	First invariant of the isochoric right Cauchy-Green strain tensor
$\bar{I}_{1,\max}$	Historical maximum value of the isochoric first strain invariant $\bar{I}_1$
$\mathbb{I}$	Fourth-order identity tensor
$\mathbf{I}$	Second-order identity tensor
I_1	First invariant of the right Cauchy-Green strain tensor
$I_{1,\max}$	Maximum historical value of the first strain invariant I_1
$I_{1e,j}$	First invariant of the elastic right Cauchy-Green strain tensor of the j -th Maxwell element
J	Jacobian determinant of the deformation gradient
$\tilde{K}_S$	Michaelis-Menten constant related to the substrate concentration
$\tilde{K}_{\text{enz}}$	Michaelis-Menten constant related to the enzyme concentration
$k_{\text{cat},\max}$	Maximum catalytic reaction rate constant
k_{cat}	Catalytic rate constant of the enzymatic reaction
K_m	Michaelis-Menten constant

k_{+1}	Forward rate constant of the enzymatic reaction
k_{-1}	Backward rate constant of the enzymatic reaction
λ	Deformation (stretch) ratio
$\lambda_{e,j}$	Deformation (stretch) ratio of the elastic part of the j -th Maxwell element
$\lambda_{v,j}$	Deformation (stretch) ratio of the viscous part of the j -th Maxwell element
l	Specimen deformed length
l_0	Specimen initial length
$\lambda_{\max}$	Historical maximum of the deformation ratio λ
$[M]$	Concentration of the maltose
m	Portion of the hydrolysis part retained in the solid
m_{enz}	Mass of enzyme
m_s	Mass of substrate
M_{enz}	Molar mass of the enzyme
$[P]$	Product concentration
$\mathbb{P}$	Fourth-order projection tensor
$\mathbf{P}$	First Piola-Kirchhoff stress tensor
$\tilde{\mathbf{P}}^{\text{eq}}$	Equilibrium part of the first Piola-Kirchhoff stress tensor with chemical dependence
$\tilde{\mathbf{P}}_j^{\text{neq}}$	Non-equilibrium part of the first Piola-Kirchhoff stress tensor of the j -th Maxwell element with chemical dependence
$\tilde{\mathbf{P}}^{\text{peq}}$	Pseudo-equilibrium part of the first Piola-Kirchhoff stress tensor with chemical dependence
$\tilde{P}^{\text{eq}}$	Equilibrium part of the nominal stress with chemical dependence
$\tilde{P}_j^{\text{neq}}$	Non-equilibrium part of the nominal stress of the j -th Maxwell element with chemical dependence
$\tilde{P}^{\text{peq}}$	Pseudo-equilibrium part of the nominal stress with chemical dependence
P	Nominal stress
p	Hydrostatic pressure

P^{eq}	Equilibrium part of the nominal stress excluding chemical dependence
P^{neq}	Non-equilibrium part of the nominal stress excluding chemical dependence
P_j^{neq}	Non-equilibrium part of the nominal stress of the j -th Maxwell element excluding chemical dependence
P^{peq}	Pseudo-equilibrium part of the nominal stress excluding chemical dependence
P_0^{peq}	Pseudo-equilibrium nominal stress for a perfectly crosslinked network
ρ_{gel}	Density of the starch hydrogel
ρ_{liq}	Density of liquid phase
R, M, β	Pseudoelastic material parameters
r	Reaction rate consuming substrate
r_{∞}	Limiting reaction rate
$[S]$	Substrate concentration
$\bar{\mathbf{S}}^{\text{eq}}$	Isochoric equilibrium part of the second Piola-Kirchhoff stress tensor excluding chemical dependence
$\bar{\mathbf{S}}^{\text{peq}}$	Pseudo-equilibrium part of the fictitious second Piola-Kirchhoff stress tensor excluding chemical dependence
$\bar{\mathbf{S}}_0^{\text{peq}}$	Pseudo-equilibrium part of the fictitious second Piola-Kirchhoff stress tensor for a perfectly crosslinked network
$\bar{\mathbf{S}}_j^{\text{neq}}$	Non-equilibrium part of the fictitious second Piola-Kirchhoff stress tensor of the j -th Maxwell element excluding chemical dependence
$\hat{\mathbf{S}}_j^{\text{neq}}$	Intermediate fictitious stress tensor of the j -th Maxwell element
$\mathbf{S}$	Second Piola-Kirchhoff stress tensor
$\mathbf{S}_{\text{vol}}$	Volumetric part of the second Piola-Kirchhoff stress tensor
$\tilde{\mathbf{S}}$	Fictitious isochoric second Piola-Kirchhoff stress tensor with chemical dependence
$\tilde{\mathbf{S}}^{\text{eq}}$	Fictitious isochoric equilibrium part of the second Piola-Kirchhoff stress tensor with chemical dependence
$\tilde{\mathbf{S}}_j^{\text{neq}}$	Fictitious isochoric non-equilibrium part of the second Piola-Kirchhoff stress tensor of the j -th Maxwell element with chemical dependence

$\tilde{\mathbf{S}}^{\text{peq}}$	Fictitious isochoric pseudo-equilibrium part of the second Piola-Kirchhoff stress tensor with chemical dependence
$\tilde{\mathbf{S}}^{\text{eq}}$	Equilibrium part of the second Piola-Kirchhoff stress tensor with chemical dependence
$\tilde{\mathbf{S}}_j^{\text{neq}}$	Non-equilibrium part of the second Piola-Kirchhoff stress tensor of the j -th Maxwell element with chemical dependence
$\tilde{\mathbf{S}}^{\text{peq}}$	Pseudo-equilibrium part of the second Piola-Kirchhoff stress tensor with chemical dependence
$\tilde{\mathbf{S}}_{\text{iso}}$	Isochoric part of the second Piola-Kirchhoff stress tensor with chemical dependence
τ_j	Relaxation time of the j -th Maxwell element
v	Reaction rate generating product
V_{gel}	Volume of gel phase
V_{liq}	Volume of liquid phase
ω_{S}	Concentration of the substrate at a certain location of the sample and at a given time for hydrolysis
ω_{S_0}	Initial mass concentration of the substrate
$\mathbf{X}$	Reference position
$\mathbf{x}$	Current position of a material point
ψ	Helmholtz free energy density function, or specific strain energy function
Ψ^{eq}	Equilibrium part of the strain energy function excluding chemical dependence
Ψ^{neq}	Non-equilibrium part of the strain energy function excluding chemical dependence
Ψ^{peq}	Pseudo-equilibrium part of the strain energy function excluding chemical dependence
Ψ_0^{peq}	Pseudo-equilibrium strain energy function for a perfectly crosslinked network
$\Psi_{\text{max}}^{\text{peq}}$	Maximum historical value of Ψ_0^{peq} over the loading history
Ψ_{vol}	Volumetric part of the strain energy function
$\tilde{\Psi}^{\text{eq}}$	Equilibrium part of the strain energy function with chemical dependence

$\tilde{\Psi}^{\text{neq}}$	Non-equilibrium part of the strain energy function with chemical dependence
$\tilde{\Psi}^{\text{peq}}$	Pseudo-equilibrium part of the strain energy function with chemical dependence
$\tilde{\Psi}_{\text{iso}}$	Isochoric part of the strain energy function with chemical dependence

Chapter 4 Finite element method

$[\mathbf{B}]$	Geometric (strain-displacement) matrix of the element
$\mathbf{b}_0$	Body force vector per unit reference volume
$[\mathbf{C}^{[e]}]$	Voigt notation matrix of the material tangent moduli tensor of the e -th element
$\bar{\mathbb{C}}$	Intermediate isochoric tangent moduli tensor
$\bar{\mathbb{C}}^{\text{eq}}$	Isochoric equilibrium part of the referential tangent moduli tensor
$\bar{\mathbb{C}}_j^{\text{neq}}$	Isochoric non-equilibrium part of the referential tangent moduli tensor for the j -th Maxwell element
$\bar{\mathbb{C}}^{\text{peq}}$	Isochoric pseudo-equilibrium part of the referential tangent moduli tensor
$\mathbb{C}$	Spatial Jaumann tangent moduli tensor
$\mathbb{C}^{\text{eq}}$	Isochoric equilibrium referential tangent moduli tensor excluding chemical effects
$\mathbb{C}_j^{\text{neq}}$	Isochoric non-equilibrium referential tangent moduli tensor of the j -th Maxwell element excluding chemical effects
$\mathbb{C}^{\text{peq}}$	Isochoric pseudo-equilibrium referential tangent moduli tensor excluding chemical effects
$\mathbb{C}^{[e]}$	Fourth-order material tangent moduli tensor of the e -th element
$\mathbf{C}_{\mathbf{v},j}^{[i+1]}$	Updated viscous right Cauchy-Green tensor at iteration $i + 1$
$\mathbf{C}_{\mathbf{v},j}^{[i]}$	Viscous right Cauchy-Green tensor at iteration i
$\tilde{\mathbb{C}}^{\text{eq}}$	Chemical-dependent isochoric equilibrium tangent moduli tensor
$\tilde{\mathbb{C}}_j^{\text{neq}}$	Chemical-dependent isochoric non-equilibrium tangent moduli tensor of the j -th Maxwell element
$\tilde{\mathbb{C}}^{\text{peq}}$	Chemical-dependent isochoric pseudo-equilibrium tangent moduli tensor
C	Mass concentration used in mass diffusion analysis

C_i	Local enzyme concentration of the integration point i
c_p	Heat capacity
$C_{S,i}$	Local substrate concentration of the integration point i
$\mathbb{C}_{\text{iso}}$	Isochoric part of the referential material tangent moduli tensor
$\mathbb{C}_{\text{vol}}$	Volumetric part of the referential material tangent moduli tensor
$[\mathbf{D}]$	Material stiffness matrix in Voigt notation
δ^j	Nodal displacement variation vector of the j -th node
δ_i^j	Generalised displacement coefficient for the i -th component in the j -th basis function
$\mathbf{d}$	Spatial rate of deformation tensor
$\{\delta^{[e]}\}$	Element nodal displacement vector of the e -th element
D	Mass diffusivity in Fick's law
$\delta_k^{[e]}$	Component of the nodal displacement vector of the e -th element
ϵ	Tolerance
ϵ_j	Tolerance for condition j
$\{\epsilon^{[e]}\}$	Voigt notation vector of the small-strain tensor in the e -th element
$\{\mathbf{F}^{[e]}\}$	Voigt notation vector of the deformation gradient tensor in the e -th element
f_{enz}^*	Global enzyme ratio
f_S^*	Global substrate ratio
$\mathbf{J}$	Mass flux vector
$\hat{J}$	Independent volumetric degree of freedom used in hybrid elements, read from STRESS(NTENS+1)
$[\mathbf{K}^{[e]}]$	Linear stiffness matrix of the e -th element
$[\mathbf{K}_T^{[e]}]$	Tangent stiffness matrix of the e -th element
$\hat{K}$	Bulk modulus associated with the hybrid element volumetric degree of freedom
κ	Material bulk modulus used to define the volumetric strain energy function

k	Thermal conductivity used as an analogue of mass diffusivity
$[\mathbf{L}]$	Differential operator matrix relating displacements to strains or deformation measures
M	Number of displacement components (spatial dimensions)
$[\mathbf{N}]$	Shape function matrix of the element
$\mathbf{N}$	Outward unit normal vector on the boundary of the reference configuration
$\mathbf{N}_j$	Shape function vector of the j -th node
N	Total number of basis functions / finite elements (context-dependent index)
n_{int}	Total number of integration points
$N_{i,j}$	Scalar basis (shape) function associated with the j -th node for the i -th displacement component
Ω_0	Reference configuration
$\Omega_0^{[e]}$	Reference configuration of the e -th finite element
$\partial\Omega_0^{[ee']}$	Interface boundary between elements $[e]$ and $[e']$ in the reference configuration
$\partial\Omega_{t0}$	Portion of the boundary with prescribed traction forces
$\partial\Omega_{t0}^{[e]}$	Traction boundary of the e -th element in the reference configuration
$\bar{\mathbf{P}}$	Traction force on the boundary
Π	Total potential energy functional
$\Pi^{[e]}$	Total potential energy functional of the e -th element
$\tilde{\mathbb{P}}$	Modified projection operator used in the isochoric elasticity tensor
$\{\mathbf{P}_{\text{ext}}^{[e]}\}$	Equivalent external nodal force vector of the e -th element
$\{\mathbf{P}_{\text{int}}^{[e]}\}$	Equivalent internal nodal force vector of the e -th element
$\{\mathbf{P}^{[e]}\}$	Voigt notation vector of the first Piola-Kirchhoff stress tensor
$\{\mathbf{P}_0^{[e]}\}$	Equivalent nodal force vector due to interface tractions from neighbouring elements
$\mathbf{q}$	Heat flux vector
$\{\mathbf{R}^{[e]}\}$	Residual nodal force vector of the e -th element

$\sigma_{FE,j}$	Stress data set predicted by the finite element model for condition j
$\sigma_{Test,j}$	Stress data set measured in experiments for condition j
SSE_j	Sum of squared errors for condition j
$\{\sigma\}$	Voigt notation vector of the Cauchy stress tensor used in Abaqus UMAT
$\{\sigma^{[e]}\}$	Voigt notation vector of the Cauchy stress tensor in the e -th element
Δt	Time increment
T	Temperature field used as an analogue of mass concentration
$\mathbf{u}$	Displacement vector
$\mathbf{u}^{[e]}$	Displacement vector field within the e -th element
$\{\mathbf{u}^{[e]}\}$	Element displacement vector (assembled from nodal displacements) of the e -th element
u_i	i -th component of the displacement vector
u_i^0	Prescribed displacement component on the essential boundary
V_i	Volume of the integration point i
$\mathbf{w}$	Spatial spin tensor
$\Psi^{[e]}$	Strain energy density function of the e -th element

Chapter 5

a	Lower point defining the rotation axis in the part instance
β	Shape parameter in the Elashoff function
b	Body force per unit mass
b	Upper point defining the rotation axis in the part instance
c	Point defining the local x - y plane for the coordinate system
c	Speed of sound in the material
c_0	Reference bulk sound speed
c_{eff}	Effective specific heat capacity
c_w	Peristaltic wave propagation speed

C_{10}	Shear modulus parameter of the Neo-Hookean stomach wall material
$\mathbf{d}$	Rate of deformation tensor
D_1	Compressibility parameter of the stomach wall material
d_k	Offset distance of the k -th wavelet from the first
E	Material tangential modulus
e	Internal energy density
E_s	Young's modulus of the starch hydrogel
Φ	Flux associated with the field variable
ϕ	Generic scalar or vector field variable
$f(t)$	Fraction of ingesta remaining in the stomach at time t
f_i	Effective volume fraction of material in the i -th Eulerian element
Γ_0	Grüneisen parameter at reference state used in the EOS
$h(x, t)$	Spatio-temporal propagation function of the peristaltic wave
$\mathbf{k}$	Unit vector along the rotation axis
k_{eff}	Effective thermal conductivity
$k_{y1}, \dots, k_{y6}$	Polynomial coefficients describing the stomach wall profile
$\lambda(x, t)$	Contraction ratio of the stomach wall
$\lambda_0, \lambda_1, \lambda_2$	Parameters defining the contraction ratio amplitude profile
$\lambda_p(t)$	Time-dependent contraction ratio of the pylorus
$\lambda_{\text{max}}(x)$	Amplitude of the contraction ratio along the centreline
l_c	Characteristic element length
l_w	Wavelet length
$l_x^n(x)$	Lagrangian interpolation function defining pyloric radial variation
l_p	Length of the pylorus segment
l_{w0}	Initial wavelet length at the start of the stomach
l_{wf}	Final wavelet length at the distal stomach region

$l_w(s)$	Wavelet length as a function of the curvilinear coordinate s
l_{w0}, l_{wf}	Initial and final wavelet lengths along the centreline
ν_l	Poisson's ratio used in the pseudo elastic-plastic liquid model
ν_s	Poisson's ratio of the starch hydrogel
n_1	Exponent (controlling pyloric shape sharpness)
n_2	Exponent controlling sharpness of the peristaltic wavelet
n_p	Exponent controlling spatial sharpness of pyloric contraction
$\bar{p}$	Weighted average pressure over Eulerian elements
p_i	Pressure of the i -th Eulerian element
$p_{\max}$	Maximum pressure among all relevant Eulerian elements
θ	Rotation angle used in Rodrigues' formula
$\mathbf{r}$	Radius vector from the centreline to the node position
$\mathbf{r}_0$	Initial radius vector of a stomach wall node
$\Delta\mathbf{r}$	Radial displacement vector of a stomach wall node
$\mathbf{R}$	Rotation matrix constructed from local-global direction cosines
ρ	Mass density
ρ_l	Density of the gastric liquid
ρ_s	Density of the starch hydrogel
ρ_w	Density of the stomach wall material
r_x, r_y, r_z	Components of the radius vector $\mathbf{r}$
$\boldsymbol{\sigma}$	Cauchy stress tensor
γ_{ij}	Engineering strain component
$\mathbf{S}$	Source term in the Eulerian conservation equation
ε_{ij}	Tensor component of strain
$\{\boldsymbol{\sigma}\}$	Vector notation of the Cauchy stress tensor used in Abaqus VUMAT

s	Curvilinear coordinate defined as the normalised arc length along the stomach centreline
s	Linear Hugoniot slope coefficient in the EOS
s_0	Starting curvilinear coordinate of the peristaltic wave
$s_b(t)$	Curvilinear coordinate of the wave back at time t
s_s	Curvilinear coordinate marking the end of the stomach region of interest
$\mathbf{t}$	Translation vector applied during coordinate transformation
Δt	Time increment used in the explicit central difference method
t_0	Initial time of pylorus contraction
t_{de}	Initial time point when the sleeves are in a deflated state
$t_{1/2}$	Half-emptying time of the stomach
t_p	Time required for pylorus closure
t_{step}	Time interval between consecutive wavelets
$\mathbf{v}$	Material velocity vector
$\mathbf{v}_{global}$	Global coordinate vector after transformation
$\mathbf{v}_{local}$	Local coordinate vector of a node
$\mathbf{x}_n$	Global position vector of a surface node
$\mathbf{x}_c$	Position vector on the stomach centreline corresponding to curvilinear coordinate
ξ	Local coordinate measured from the wave back
x_0	Left boundary of the fitted stomach wall segment
x_1	Left boundary of the simplified rear stomach region
x_2	Centreline location marking the transition of contraction amplitude
$x_b(t)$	Position of the wave back of each peristaltic wavelet
x_l	Length of the simplified stomach centreline
x_i	Centreline coordinate at the pylorus exit
x_p	Centreline coordinate at the pylorus entrance

NOMENCLATURE

x_s	Midpoint coordinate of the pylorus
Δy	Displacement in the y -direction due to peristaltic contraction
Δy_c	Final peristaltic contraction displacement
Δy_p	Additional displacement due to pyloric contraction
y_0	Initial distance from the stomach centreline at $t = 0$
y_i	Radius at the pylorus ends
y_p	The Narrowest radius of the pylorus

Chapter 1

Introduction

1.1 Background

Glucose homeostasis is a physiological feedback mechanism that maintains the dynamic equilibrium of blood glucose levels. This equilibrium is indispensable for human survival, since glucose is the primary energy source for all organisms (Frayn & Evans, [2019](#)). Starch, the primary source of dietary glucose (Bantle et al., [1983](#)), contributes the highest percentage of the average caloric intake (Wang et al., [2015](#)) and is the key energy source for humans (Zheng et al., [2019](#)). However, excessive and rapid consumption of starch can cause hyperglycaemia, i.e., a persistently high blood glucose level. Hyperglycaemia leads to the development of non-communicable metabolic diseases (NCDs), such as obesity, as well as type-2 diabetes (T2D), a chronic non-communicable metabolic disease caused by long-term disturbance of glucose homeostasis (Augustin et al., [2002](#); Gandasi et al., [2018](#); Petersen & Shulman, [2002](#); Poti et al., [2017](#); Schwingshackl & Hoffmann, [2013](#)).

One culprit of hyperglycaemia is highly processed starch-based foods (Björck et al., [1994](#); Brand et al., [1985](#); Edwards et al., [2019](#)), which have a high glycaemic index, i.e., the relative ability to raise postprandial blood glucose levels (Jenkins et al., [1981](#)). Industrial processing disrupts the hierarchical structure of raw foods and alters their mechanical properties (AlShaalan, [2019](#); Jeong et al., [2019](#)). As a result, processed foods are easier to break down in the gastrointestinal (GI) and more readily accessible to digestive enzymes, leading to rapid gastric emptying into the small intestine, rapid glucose absorption into the bloodstream, and disruption of glucose homeostasis. To maintain relatively stable glucose homeostasis for the prevention and treatment of the diseases mentioned above, there is a strong demand for controllable digestion, with slower breakdown of starch-based foods

and slower gastric emptying.

The controlled digestion of starch also facilitates its application in the pharmaceutical industry. As a biomaterial compatible with the human body, starch is nontoxic, nonirritant, and biodegradable, and is therefore widely used in conventional tablets and capsules as a binder, disintegrant, or lubricant (Builders & Arhewoh, 2016). Moreover, it has been reported that the material properties of starch-based systems, including mechanical properties, chemical properties, and digestibility, can be modulated through variations in heating time, temperature, moisture content, formulation, and processing methods (AlShaalan, 2019; Gamonpilas et al., 2009a; Gamonpilas et al., 2009b; Lund & Lorenz, 1984; Wang et al., 2015). This high degree of tunability enables starch to be engineered as a drug delivery vehicle, allowing controlled and targeted drug release within the gastrointestinal tract. Such systems are beneficial for the treatment of diseases such as colorectal pathologies (Builders & Arhewoh, 2016; Koev et al., 2020, 2022).

Accordingly, the properties of starch-based foods or drug-delivery carriers can be tailored through appropriate processing to achieve controlled digestion. However, the digestion of starch-based foods is a complex process. During digestion in the GI tract, the food bolus, i.e., a rounded mass of chewed food that is swallowed, undergoes both mechanical and chemical breakdown processes simultaneously (AlShaalan, 2019; Jeong et al., 2019). The mechanical breakdown of food is primarily induced by mechanical loads such as mastication in the oral cavity and peristaltic contractions in the stomach and intestine. In contrast, chemical breakdown arises from the diffusion of saliva, gastric, and intestinal fluids into the food bolus and the subsequent enzymatic reactions. In starch-based foods, the enzymatic hydrolysis of starch molecules catalysed by α -amylase progressively softens the food bolus, leading to mechanical property degradation and facilitating mechanical breakdown, which in turn increases the surface area exposed to the enzyme. From a physical standpoint, this process can be represented as a coupled diffusion-reaction-deformation system involving the transport of enzymes, the chemical breakdown of polymeric networks in starch-based foods, and the concurrent mechanical response under large deformation up to failure. However, the connection between the properties of starch-based foods and digestive behaviour is not well understood. Interdisciplinary research is required, including expertise in digestive physiology, the material science of starch-based foods, solid and fluid mechanics, enzyme chemistry, and related areas. To address this knowledge gap, the chemo-mechanical properties of starch-based foods and their influence on breakdown behaviour during digestion in the GI tract, particularly in the stomach, need to be

investigated.

In the following sections, the physiology of human digestion, focusing on the gastric phase ([Section 1.2](#)), the chemistry and structure of starch ([Section 1.3](#)), and the research methods employed in digestion studies ([Section 1.4](#)) are briefly introduced to provide the necessary background for our research. The research gap will then be discussed in [Section 1.5](#), and the outline of this thesis is summarised at the end of this chapter ([Section 1.6](#)).

1.2 Physiology of human digestion

1.2.1 Gastrointestinal tracts of humans and gastric digestion process

The human GI tract comprises four major sections, including the mouth, stomach, small intestine, and colon, as shown in [Figure 1.1](#). Oral processing is the first step of food digestion. In this phase, foods undergo three main processes: mastication, lubrication, and enzyme hydrolysis. When foods are ingested, they are broken down by mastication, mainly 15 to 20 cyclic loads (Bornhorst et al., [2016](#)) in the form of cutting, crushing, and grinding by the teeth (AlShaalan, [2019](#)). The applied force varies from around 50–150 N, depending on the mechanical properties of the food products (Mioche & Peyron, [1995](#)). Meanwhile, salivary glands excrete neutral pH saliva, which contains mucins for lubrication (Chen, [2009](#)) as well as α -amylase for preliminary degradation of carbohydrates (Gouseti et al., [2019](#)). Along with repositioning and mixing by the tongue, a viscous food bolus is formed for safe swallowing (Bornhorst et al., [2016](#); Kong & Singh, [2008](#)).

The food bolus is then swallowed through the oesophagus and the cardia (the entrance of the stomach) and enters the stomach. The stomach is an organ with an average capacity of 1500 mL in adults (Standring, [2016](#)), and it has a flexible geometry that can accommodate ingested food from a J-shaped tube to a dilated bag (Kuiken et al., [1999](#)). As shown in the inset of [Figure 1.2](#), the stomach wall is stacked with multiple layers (Bauer et al., [2020](#); Boland, [2016](#); Kristensen et al., [2021](#)). These layers serve different functions:

- mucosa secretes gastric fluid and interacts with ingested foods,
- submucosa connects the mucosa and muscular layers,
- muscular layers (including circular, longitudinal, and oblique layers) provide stiffness and generate active movement anisotropically, and

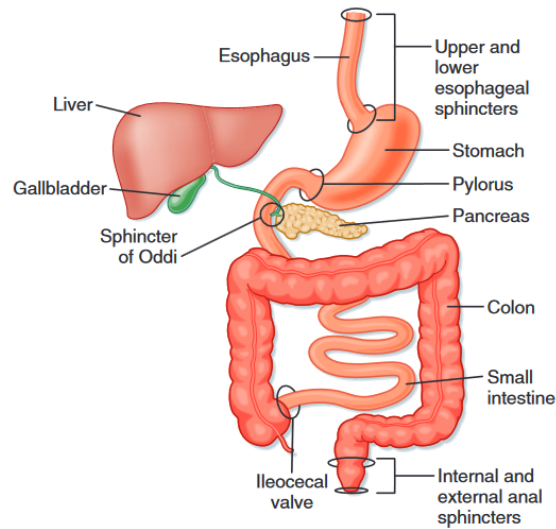


Figure 1.1. Gastrointestinal tract system (Stanton & Berne, 2017).

- serosa offers smoothness to the stomach. They occur in varying thicknesses across different regions, contributing to heterogeneity of the stomach wall (Bauer et al., 2020).

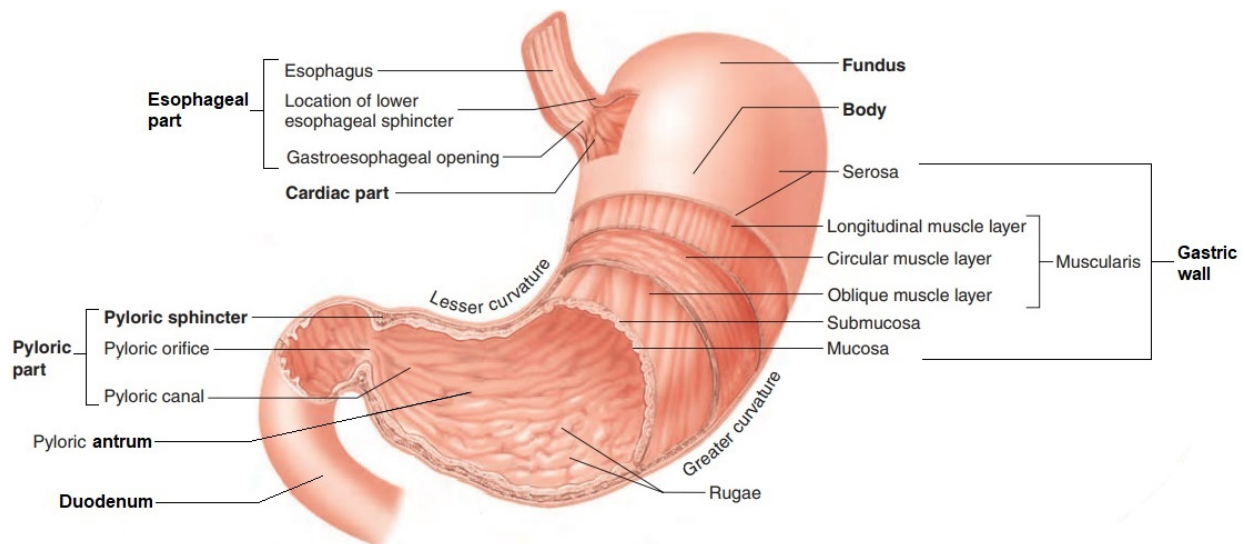


Figure 1.2. A profile of stomach sections and stomach wall (HijamaLife, 2020).

The heterogeneity and the anisotropy of the stomach wall enable different functions in different regions of the stomach wall. According to the functions, the stomach can be divided into several main parts, as shown in Figure 1.2, including:

- cardia, the exit of the oesophagus and the entrance of the stomach,
- fundus, the upper part of the stomach connected to the cardia,
- corpus (stomach body), the middle part of the stomach,

- antrum, the distal part of the stomach connected to the pylorus, and
- pylorus, the exit of the stomach.

The distensibility of the stomach is attributed to the wavy muscle layers in the fundus part. The fundus has the thickest longitudinal layer among the three parts (Burdan et al., 2012), serving as a reservoir for food storage (Bauer et al., 2020). The longitudinal layer is thinner in the corpus and negligible in the antrum. In comparison, the circular layer is thicker in the corpus and significantly thicker in the antrum (Bauer et al., 2020), allowing the antrum to provide strong peristaltic waves to grind and mix food. (Bellmann et al., 2016). The pyloric sphincter contains strong circular muscles that can control whether the sphincter is closed or open and therefore can control the emptying of food. The fundus and corpus contain chief and parietal cells, which secrete gastric liquid, including lipase, pepsin, and acid (Bellmann et al., 2016). Combined with the saliva liquid, gastric secretions are mixed with the food bolus in the antrum to promote the hydrolysis of the food bolus.

The gastric processes exhibit distinct patterns in the fed (postprandial) and fasted (intermeal) states, regulated by neurohormonal feedback influenced by food digestibility and the mechanical properties of gastric contents (Ferrua & Singh, 2010). In the fed state, the stomach generates regular peristaltic antral contraction waves (ACWs) at approximately three cycles per minute. There are generally three different phases during the fed state (Bellmann et al., 2016; Ehrlein & Schemann, 2005), as illustrated in [Figure 1.3](#), including:

- the propulsion phase, during which the pyloric sphincter is closed, and digesta (food being digested) is pushed from the corpus to the distal antrum due to peristalsis,
- the retropulsion phase, during which the pyloric sphincter is closed, and the digesta at the distal antrum is pushed back to the proximal antrum and corpus, and
- the emptying phase, during which the pylorus opens slightly and functions as a sieve. Water and food particles in diameters of around 1–2 mm pass to the small intestine, while larger digesta is retropulsed to the antrum for further breakdown.

The propulsion and retropulsion phases grind, mix, and progressively reduce the particle size and mechanical properties of the digesta, and followed by the emptying phase. The fasted state, which occurs after the fed state, starts with a long phase of quiescence around half an hour, followed by an irregular low amplitude of contractions around 1.5 hours, and ends with housekeeper waves, i.e., a burst of waves to clean the remaining digesta in the stomach in less than 20 minutes on average with the pylorus open (Bellmann et al., 2016).

In the small intestine (composed of the duodenum, jejunum, and ileum), the chyme (digesta passed from the stomach to the intestine) is subjected to both mechanical and

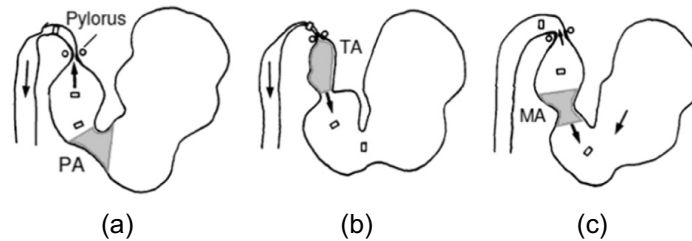


Figure 1.3. Three gastric phases during the fed state (Bellmann et al., 2016). (a) Propulsion phase, (b) retropulsion phase, and (c) emptying phase.

chemical actions. Peristaltic transport of chyme is generated by coordinated contractions of the intestinal smooth muscle layers (Brasseur et al., 2007). Propagating peristaltic waves drive axial transport, while localized contractions promote mixing of chyme with digestive secretions and enhance nutrient release (Bornhorst et al., 2016). The gallbladder and pancreas secrete digestive enzymes for further hydrolysis of nutrients into low molecular weight molecules, including monosaccharides, amino acids, and fatty acids (Boland, 2016). In addition, pancreatic juice containing bicarbonate ions neutralises the pH, maximising enzyme activity in this phase (Boland, 2016; Guyton & Hall, 2010). This process enables these nutrients to be absorbed via the intestinal wall into the bloodstream (Santos et al., 2019).

After most bioaccessible nutrients are absorbed in the small intestine, the indigestible residuals of the chyme are transferred through the ileocecal valve to the colon (i.e., large intestine). The presence of microbiota allows for the anaerobic fermentation of the residual chyme to produce short-chain fatty acids and methane (Boland, 2016). The residual chyme is also dehydrated while water and electrolytes are absorbed again from the colon to maintain homeostasis (Guyton & Hall, 2010). The residuals (i.e., faeces) are stored in the second half of the colon. The peristaltic movement of the colon facilitates the transport and defecation of faeces (Kristensen et al., 2021).

1.2.2 Glucose homeostasis regulation

The human body employs integrated neurohormonal feedback mechanisms in response to food intake, allowing the GI tract to communicate with metabolic organs such as the pancreas and liver (Stanton & Berne, 2017). These mechanisms operate through endocrine, paracrine, and neurocrine pathways that together coordinate digestive and metabolic functions. In the endocrine regulation, enteroendocrine cells in the GI tract sense chemical and mechanical stimuli from ingested food and release hormones that

circulate through the bloodstream to act on distant organs such as the pancreas, liver, and brain. Through paracrine regulation, these sensing cells instead release mediators that act locally on neighbouring cells within the GI environment, regulating functions such as gastric acid secretion and water absorption. By contrast, neurocrine regulation involves neural stimuli that trigger sensory neurones to release neurotransmitters directly onto the effector cells they innervate.

One result of neurohormonal regulation is glucose homeostasis. Typically, blood glucose levels in a fasted state are 4–5.9 mmol/l and are less than 7.8 mmol/l two hours after meals (AlShaalan, 2019). This homeostasis is achieved through the regulation of two glucoregulatory hormones, insulin and glucagon, secreted by the pancreas in response to blood glucose levels (Röder et al., 2016). In a fed phase, intestinal absorption causes an increase in blood glucose levels, which stimulates the secretion of incretin hormones in the GI tract, such as glucan-like peptide (GLP-1) and glucose-dependent insulintropic peptide (GIP), accounting for a large part of the postprandial insulin response (AlShaalan, 2019). Acting through endocrine signalling, incretins enhance insulin secretion from pancreatic β -cells. Insulin, as a glucoregulatory hormone, then promotes glucose uptake in the liver, adipose tissue, and skeletal muscle, where glucose is stored as glycogen via glycogenesis or converted into lipids via lipogenesis (Berg et al., 2019). Meanwhile, insulin suppresses hepatic glucose production, thereby lowering blood glucose levels. During the fasted state, blood glucose is gradually consumed via glycolysis to provide energy for daily use. Falling glucose levels trigger pancreatic α -cells to secrete glucagon, another glucoregulatory hormone, which restores circulating glucose from glycogen by stimulating glycogenolysis and, when glycogen stores are depleted, gluconeogenesis from non-carbohydrate precursors (Röder et al., 2016). Together, insulin and glucagon form a complementary negative feedback system that stabilises blood glucose across fed and fasted phases and maintains metabolic homeostasis.

Glucose homeostasis can be disrupted by long-term, unhealthy lifestyle habits. Diets high in processed foods and sedentary behaviour tend to maintain chronically elevated postprandial glycaemic levels, which in turn drive sustained insulin secretion. Prolonged exposure to high glucose and insulin concentrations is strongly associated with the development of NCDs (Augustin et al., 2002; Poti et al., 2017). Obesity may arise because persistently high insulin levels inhibit lipid utilisation and promote fat storage. T2D can subsequently develop, as chronic hyperinsulinaemia leads to downregulation of insulin receptors and thus insulin resistance. In this state, β -cells continue to secrete

insulin in response to rising glucose levels, but peripheral tissues respond poorly, leading to sustained hyperglycaemia (Jenkins et al., 1981). Processed foods, which stimulate rapid and excessive glycaemic responses, therefore contribute to obesity and T2D. A potential mitigation strategy is to design foods whose internal structure slows glucose release while maintaining satiety. This strategy motivates the present research, which examines the digestion and breakdown behaviour of a type of starch-based food, starch hydrogel, within the GI tract.

1.3 Starch chemistry and structure

1.3.1 Dietary carbohydrates

Food is a complex system composed of diverse nutrients, ranging from macromolecules such as carbohydrates, proteins, and lipids to micronutrients including minerals, vitamins, and water (Singh & Gallier, 2014). Among these nutrients, dietary carbohydrates are the primary exogenous source of glucose and are directly linked to the regulation of glucose homeostasis (AlShalan, 2019). Carbohydrates can be categorised, according to their degree of polymerisation (DP), into three main groups: sugars (mono- and disaccharides, DP = 1, 2), oligosaccharides (intermediate DP with short chains), and polysaccharides (high DP, long-chain polymers).

D-glucose is the most abundant naturally occurring monosaccharide (Domb et al., 1998). It has the molecular formula $C_6H_{12}O_6$ and contains six carbon atoms, giving rise to multiple stereoisomers. In aqueous solution, glucose exists in several interconvertible forms, including:

- the acyclic (open chain) form, in which C-1 (carbon 1, see the indexing in Figure 1.4) functions as an aldehyde group (Figure 1.4(a)),
- the five-membered furanose form (glucofuranose, Figure 1.4(b)), and
- the six-membered pyranose form (glucopyranose, Figure 1.4(c) and Figure 1.4(d)).

Cyclisation occurs through a nucleophilic addition of the C-4 or C-5 hydroxyl group to the C-1 aldehyde, forming a hemiacetal linkage. In solution, the pyranose form dominates, accounting for approximately 99% of all glucose molecules. The C-1 hydroxyl can be orientated either trans (on opposite sides) to the C-5 substituent, giving α -D-glucose (Figure 1.4(c)), or cis (on the same side), offering β -D-glucose (Figure 1.4(d)). Interconversion between these anomers, known as mutarotation, significantly influences the digestibility and structural properties of the polysaccharides they form. Variations in

the orientation and position of functional groups on the carbon skeleton yield numerous other monosaccharide stereoisomers. Biologically relevant examples include fructose and mannose.

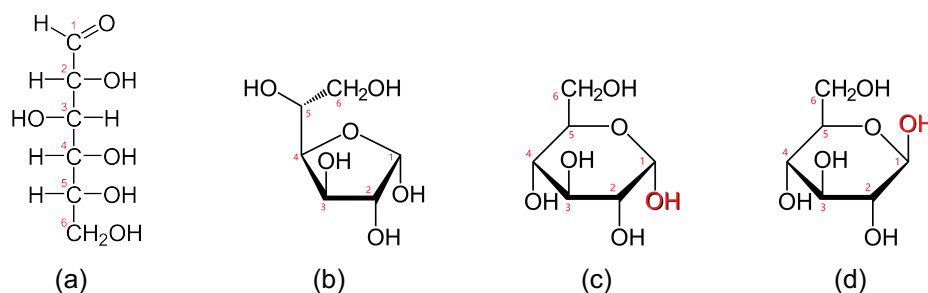


Figure 1.4. Different forms of D-glucose. (a) Acyclic form α -D-glucose, (b) α -D-glucopyranose, and D-glucopyranose: (c) α -D-glucopyranose, (d) β -D-glucopyranose.

Monosaccharides polymerise through a dehydration condensation reaction, in which the hemiacetal group at C-1 of one monomer reacts with a hydroxyl group of another, forming a glycosidic bond. A $1 \rightarrow 4$ glycosidic linkage is formed between C-1 and C-4 of two saccharide units (Figure 1.5(a)), whereas a $1 \rightarrow 6$ linkage connects C-1 and C-6 (Figure 1.6(b)). Glycosidic bonds are further classified as α or β depending on the stereochemistry at the anomeric carbon relative to the reference stereo-centre (Varki et al., 2022). An α -glycosidic bond forms when the two linked anomeric centres have the same configuration, while a β -glycosidic bond forms when they differ (Berg et al., 2019). These stereochemical differences are illustrated by disaccharides (Figure 1.5). Maltose consists of two α -D-glucose monomers joined by an $\alpha - (1 \rightarrow 4)$ bond, placing both units in the same orientation (Figure 1.5(a)). In contrast, cellobiose is formed from two β -D-glucose monomers connected by a $\beta - (1 \rightarrow 4)$ bond, giving opposite orientations (Figure 1.5(b)). Other important disaccharides include lactose (galactose-glucose) and sucrose (glucose-fructose).

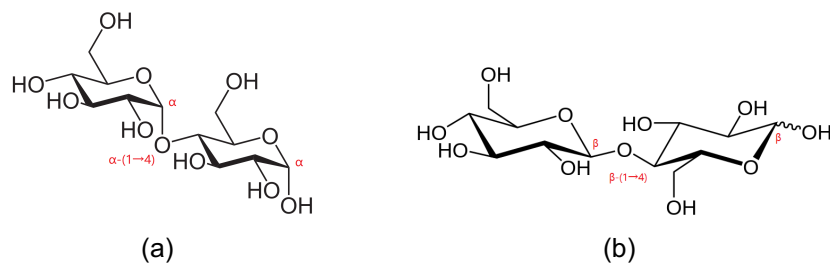


Figure 1.5. Two types of commonly seen disaccharides: (a) maltose and (b) cellobiose.

A further polymerisation of monosaccharides produces oligosaccharides and

polysaccharides. Oligosaccharides are short carbohydrates with low molecular weights, including maltotriose, dextrin, limit dextrin, etc. Polysaccharides are long-chain carbohydrates with high molecular weights and are generally divided into storage and structural types. Among storage polysaccharides, starch originates from plants and is composed of two glucose polymers (Lovegrove et al., 2017):

- Amylose (Figure 1.6(a)), a largely linear and helical chain of α -D-glucose linked by $\alpha - (1 \rightarrow 4)$ glycosidic bonds, with only limited $\alpha - (1 \rightarrow 6)$ branching.
- Amylopectin (Figure 1.6(b)), a highly branched polymer formed by both $\alpha - (1 \rightarrow 4)$ and $\alpha - (1 \rightarrow 6)$ linkages.

Note that native (natural and unmodified) starch also contains small amounts of phytoglycogen, lipids, phosphate monoesters, and proteins/enzymes. Apart from starch, glycogen is an animal storage polysaccharide, an analogue of amylopectin that is more highly branched and compacted (Blanco & Blanco, 2017). Cellulose (Figure 1.6(c)) is a plant structural polysaccharide composed of $\beta - (1 \rightarrow 4)$ -linked β -D-glucose units forming extended fibrillar straight chains with high tensile strength due to more hydrogen bonds (Pinto et al., 1993).

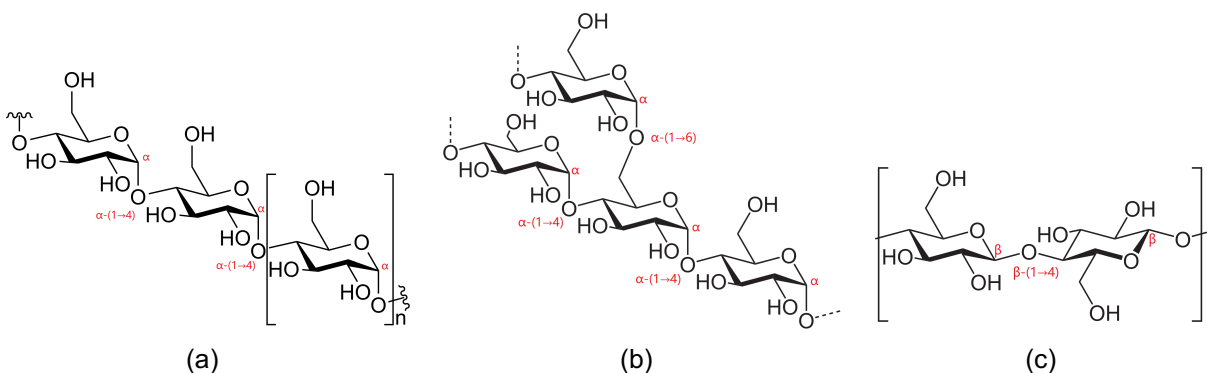


Figure 1.6. Three types of commonly seen polysaccharides. (a) Amylose, (b) amylopectin, and (c) cellulose.

The concentrations of many sugars are determined using assays based on their reducing properties. A reducing sugar is a sugar that can act as a reducing agent because, in solution, it can convert into an open-chain form containing a free aldehyde or ketone group. All common monosaccharides and most disaccharides are reducing sugars, while sucrose and trehalose are examples of non-reducing disaccharides because both of their hemiacetal groups are involved in glycosidic bonding.

1.3.2 Polysaccharide hydrolysis

The chemical composition of polysaccharides is a key factor influencing their digestibility. As polysaccharides are formed through dehydration condensation reactions that create glycosidic bonds, their digestion proceeds in the opposite direction: the glycosidic linkages are cleaved by hydrolysis, a reaction in which water molecules are consumed to break chemical bonds, as illustrated in [Figure 1.7](#).

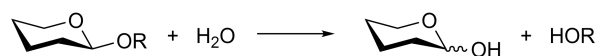


Figure 1.7. Hydrolysis of a glycosidic bond.

These processes are catalysed by enzymes known collectively as glycoside hydrolases, or glycosidases. [Figure 1.8](#) illustrates the hydrolysis of starch by different enzymes. Among them, α -amylase is a key glycosidase secreted by the salivary glands and pancreas. It cleaves $\alpha - (1 \rightarrow 4)$ glycosidic bonds at random positions along the starch (or glycogen) chain, as shown in [Figure 1.9](#), producing glucose, maltose, maltotriose, and various dextrans. Dextrans contain both $\alpha - (1 \rightarrow 4)$ and $\alpha - (1 \rightarrow 6)$ linkages and can be further hydrolysed into smaller saccharides. Because α -amylase cannot cleave $\alpha - (1 \rightarrow 6)$ linkages, hydrolysis stops at branch points, yielding limit dextrans (Blanco & Blanco, 2017). In addition, the enzyme does not act on $\alpha - (1 \rightarrow 4)$ linkages immediately adjacent to a branch point and therefore cannot hydrolyse maltose or maltotriose (Frayn & Evans, 2019). As a result of the random but constrained cleavage pattern, the frequency of glucose release is lower than that of maltotriose, and both are markedly lower than that of maltose (Brandam et al., 2003). Limit dextrans, disaccharides, and trisaccharides are further hydrolysed into monosaccharides (glucose) at the brush border of the small intestine by enzymes such as glucoamylase (maltase) and isomaltase, ensuring that the released glucose can be absorbed and utilised by the human body for energy storage and metabolism.

Note that cellulose, despite being a polysaccharide, contains $\beta - (1 \rightarrow 4)$ linkages that cannot be cleaved by human glycosidases. On the other hand, cellulase, the enzyme required for this reaction, is absent in the human body (Pinto et al., 1993). Therefore, glycosidic bond configuration fundamentally determines polysaccharide digestibility.

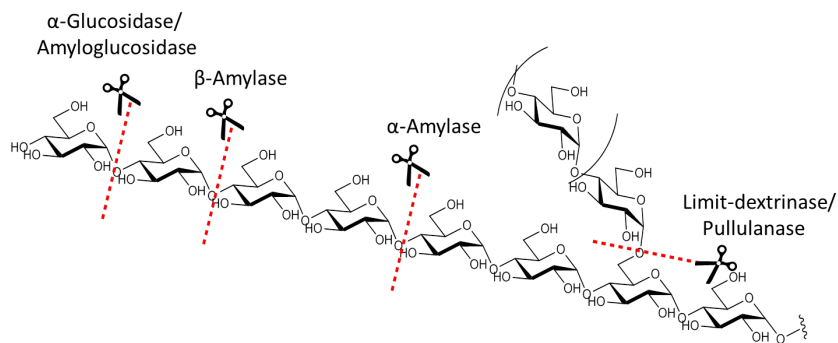


Figure 1.8. Starch hydrolysis by different enzymes (Megazyme, 2022).

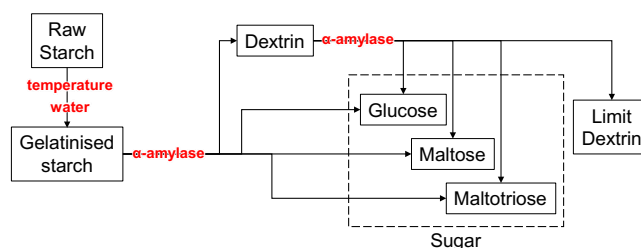


Figure 1.9. Starch hydrolysis by α -amylase (Brandam et al., 2003).

1.3.3 Native starch microstructure and digestibility

Native starches are organised in granule form, with a semi-crystalline hierarchical structure, and typically range in diameter from 1 to 100 μm depending on the botanical source (Wang & Copeland, 2013). As shown in Figure 1.10 (Wang & Copeland, 2013), the granules display a characteristic concentric architecture consisting of an amorphous core surrounded by alternating semi-crystalline and amorphous growth rings. The amorphous core comprises predominantly amylose (in non-waxy starches), which adopts mainly single helical conformations, together with disordered amylopectin chains. The amorphous rings are similarly composed of disordered or extended amylopectin side chains interspersed with amylose chains. Each semi-crystalline growth ring contains alternating crystalline and amorphous lamellae. The amorphous lamellae consist mainly of amylopectin branch points, non-helical amylopectin segments, and long linear amylopectin chains that interconnect adjacent clusters. The crystalline lamellae, by contrast, comprise double helices formed between neighbouring amylopectin chains (Bertoft, 2017). These helices behave as biopolymer crystals (Raguin & Ebenhö, 2017), stabilising adjacent chains and assembling into either A-type (orthogonal) or B-type (hexagonal) packing arrangements (AlShaalan, 2019; Raguin & Ebenhö, 2017).

Starches are classified into Rapidly digestible starches (RDS), Slowly digestible starches

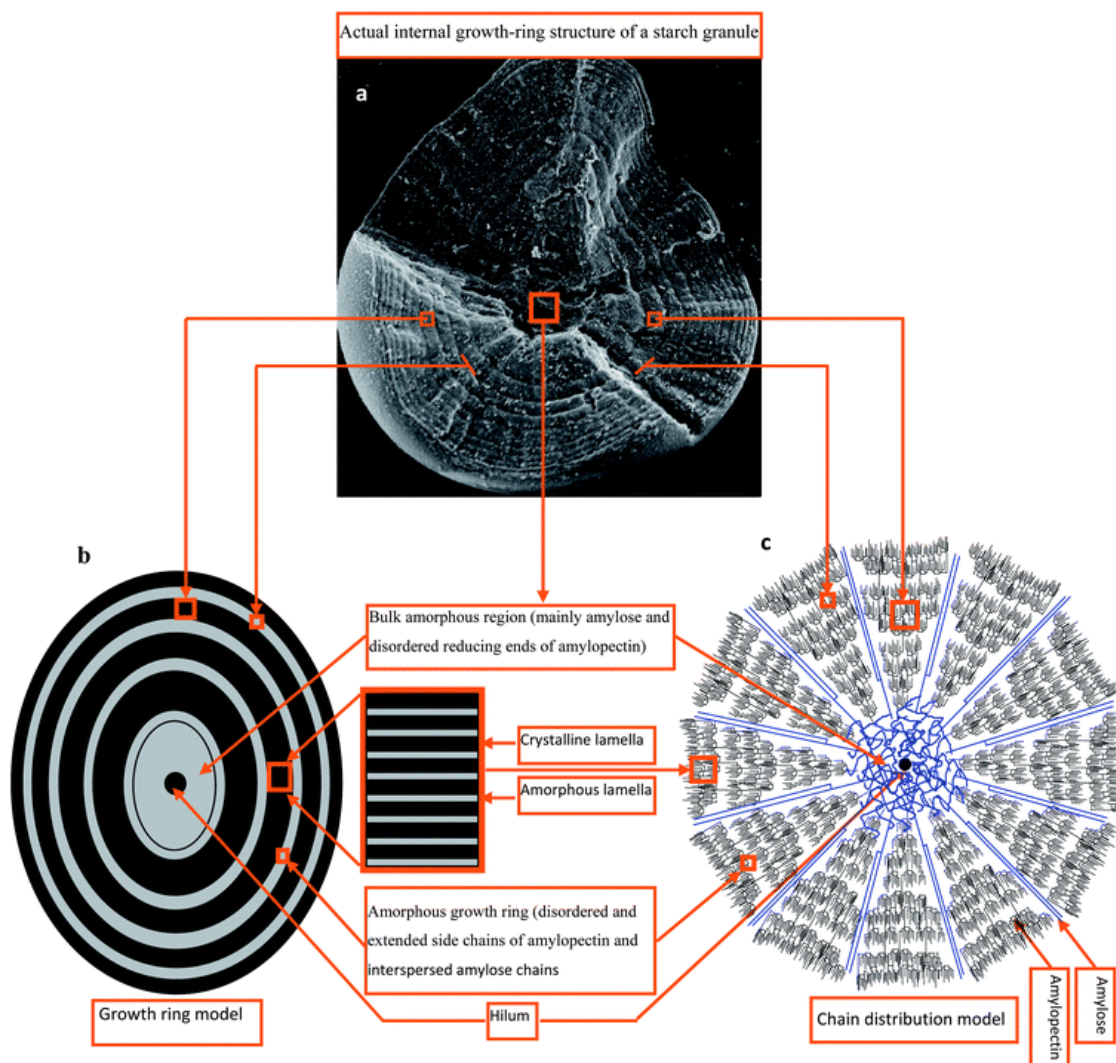


Figure 1.10. Starch granule structure, obtained from Wang and Copeland (2013).

(SDS), and Resistant starches (RS) according to the digestibility (AlShaalan, 2019; Nguyen & Sopade, 2018). Starches from different botanical sources, such as potato, wheat, maize, rice, and pea, exhibit marked differences in granule size, shape, crystalline pattern, pore structure, and amylose-to-amylopectin ratio, all of which influence their digestibility (Gallant et al., 1992; Nguyen & Sopade, 2018; Sjöö & Nilsson, 2018). In native starches, the single helical amylose forms the amorphous domains and is therefore more susceptible to enzymatic hydrolysis. Amylopectin, by forming densely packed double helices within semi-crystalline regions, exhibits much lower susceptibility to amylolysis (hydrolysis by amylase). As a result, native ungelatinised high-amylose starches tend to be more digestible (Lovegrove et al., 2017). Processing markedly alters starch structure and, consequently, digestibility (He et al., 2025). Gelatinisation during

heating with water disrupts crystalline order, swells granules, and produces a largely amorphous polymer network in which the amylose-to-amylopectin ratio has minimal influence on enzymatic susceptibility. Subsequent cooling induces gelation and retrogradation (recrystallisation), reducing digestibility, while amylopectin retrogrades more slowly and remains more accessible than amylose (AlShaalan, 2019). These factors will be further introduced in Chapter 2. Food processing also modifies the matrix surrounding starch. For instance, milling breaks granules and cell walls, reduces particle size, and effectively substitutes for part of the mechanical disintegration occurring in the GI tract, thereby accelerating digestion (Oghbaei & Prakash, 2016).

1.3.4 Starch hydrogel

A hydrogel is a semi-solid system consisting of a hydrophilic, three-dimensional, crosslinked network spanning the entire liquid phase, allowing it to behave as a solid without flow (Ferry, 1980). Many starch-based staple foods, such as noodles, rice, and pasta, can be regarded as starch-based hydrogels (Cui et al., 2022b; Koshenaj & Ferrari, 2024; Larrea-Wachtendorff et al., 2022; Vieira et al., 2023). When native starch is heated in water and subsequently cooled, the starch molecules associate through physical interactions to form a self-assembled, physically crosslinked hydrogel network (Gamonpilas et al., 2009a; Gamonpilas et al., 2009b; Koev et al., 2020; Larrea-Wachtendorff et al., 2022; Qamruzzaman et al., 2021). This structure is formed from hydrogen bonding among the abundant hydroxyl groups on starch molecules (Nasri-Nasrabadi et al., 2014). As the crosslinked network is formed by physical interactions, such as hydrogen bonding, rather than chemical crosslinks, which usually require toxic reagents (Cui et al., 2022a), physically crosslinked hydrogels are often safe, healthy, biocompatible, biodegradable, eco-friendly, economical, and readily available (Qamruzzaman et al., 2021). Therefore, physically crosslinked starch hydrogels are a suitable alternative bio-based hydrogel to the synthetic hydrogels (Koshenaj & Ferrari, 2024; Pulgarín et al., 2023), and have been widely explored for applications in food engineering, biomedicine, pharmaceuticals, and cosmeceuticals (Cui et al., 2022a; Qamruzzaman et al., 2021; Vieira et al., 2023; Xue et al., 2025). In addition to physically crosslinked starch hydrogels, chemically modified starch-based hydrogels have been developed to enhance material properties and broaden application potential. These systems are typically produced through chemical crosslinking reactions such as etherification, where hydroxyl groups are substituted with carboxymethyl or other ether groups, or by grafting vinyl monomers onto the starch (Qamruzzaman et al., 2021; Xue

et al., 2025). Furthermore, incorporating additional components, such as solvents, salts, nanoparticles, fillers, or fibres (e.g., cellulose nanofibres Nasri-Nasrabadi et al., 2014) into the starch matrix can significantly improve the mechanical strength, stability, and functional performance of starch-based hydrogels (Koshenaj & Ferrari, 2024; Qamruzzaman et al., 2021; Xie, 2024).

The applications of starch hydrogels are versatile. One direct application is in food engineering. In food processing, starch hydrogels are used as low-fat substitutes and multifunctional texture modifiers, and their tunable gelation behaviour enables the stabilisation of food matrices and improves sensory quality and mouthfeel (Xue et al., 2025). Starch hydrogels are also employed in food packaging as edible biodegradable films and coatings that provide moisture control and antioxidant or antimicrobial protection, thereby extending the shelf life of perishable foods and reducing food waste (Koshenaj & Ferrari, 2024; Qamruzzaman et al., 2021; Xue et al., 2025), such as the pH-sensitive dual-network starch hydrogel reported by Cui et al. (2023).

Starch hydrogels are also widely used in pharmaceutical and biomedical applications. Owing to their controllable swelling and diffusion behaviour, they can be designed (e.g., altering the amylose-to-amylopectin ratio Koev et al., 2020) to absorb aqueous metabolites and nutrients, while simultaneously encapsulating and protecting bioactive molecules (Bhatia et al., 2013; Xue et al., 2025). Consequently, starch hydrogels serve as effective drug-delivery carriers capable of loading, stabilising, and gradually releasing therapeutic agents, enabling controlled or stimuli-responsive drug release with improved therapeutic efficacy and reduced side effects (Abd El-Ghany & Mahmoud, 2021; de Stéfano et al., 2020; Koev et al., 2022). In addition, starch hydrogels can function as haemostatic and wound-healing dressings by maintaining a moist environment, absorbing exudates, preventing infection, and delivering antibacterial or bioactive compounds, and thus promoting tissue regeneration and accelerating wound healing (Abd El-Ghany & Mahmoud, 2021; Cui et al., 2022b; Xue et al., 2025). The high absorbency, biocompatibility, and ability to carry active ingredients of starch hydrogels also make them suitable for skincare and hygiene products (Qamruzzaman et al., 2021). The high water-absorption capacity and biodegradability of starch hydrogels make them suitable for environmental applications, such as wastewater treatment, where they can adsorb heavy metals and organic pollutants (Qamruzzaman et al., 2021; Xue et al., 2025). The release-controlled properties also enable their use in agriculture for soil moisture retention and as carriers for fertilisers or pesticides, enhancing water efficiency and reducing negative environmental impact (Qamruzzaman et al., 2021).

Modifying a starch hydrogel matrix through the in-situ polymerisation of a second polymer network, which is crosslinked chemically or ionically, generates double-network (DN) or interpenetrating-network (IPN) architectures, which endows the hydrogels with high stretchability and toughness (Cui et al., 2023; Li et al., 2025; Lin et al., 2021; Zeng et al., 2021; Zhao et al., 2024). These architectures provide deformation compatibility for intimate contact with human skin, as well as impact resistance and protective functionality (Sarmah & Karak, 2022). Furthermore, incorporating conductive components, e.g., salts, ionic liquids, metal ions, and carbon-based fillers, into the starch hydrogel matrix can significantly enhance its ionic or electrical conductivity, enabling stable signal transduction under deformation. These additives also confer additional functional properties, including transparency, self-adhesion, self-healing, moisture retention, and anti-freezing performance (de Stéfano et al., 2020; Lu et al., 2022; Xie, 2024; Xue et al., 2025; Zhao et al., 2022). Because of their combined mechanical and functional advantages, these modified starch hydrogels are extensively used in flexible wearable sensors, soft electronic components, and bio-interfaces, where they serve as the active sensing layer for detecting strain, pressure, motion, humidity, or temperature for health monitoring.

Traditional starch-based materials can be processed using several moulding methods, such as extrusion and casting (Yu et al., 2021). With their tunable rheological properties and shear-thinning behaviour, starch hydrogels are also compatible with advanced manufacturing techniques like 3D printing, enabling the fabrication of complex structures with enhanced functionality (Xue et al., 2025). These 3D printed starch-based hydrogels have promising applications in food printing, offering cost-efficient, customised fabrication of foods with tailored shapes and nutrition (Vieira et al., 2023; Zheng et al., 2019, 2023). In the context of biomedical and tissue engineering, they are applied as printable scaffolds that mimic natural extracellular matrices and support cell growth, as well as for the development of personalised implants for tissues such as liver, lung, nerve, cartilage, and bone (Xue et al., 2025).

Among these applications, the digestion behaviour of starch hydrogels for food processing and drug delivery in the GI tract is of particular interest in this thesis. Understanding how the hydrogel influences mechanical response, enzymatic hydrolysis and glucose release kinetics can inform the design of functional foods and drug delivery carriers.

1.4 Analysis method for digestion behaviour

Among various ways to investigate food digestion, *in vivo* analysis involves experiments within the living body to determine how food behaves in the GI tracts of living organisms, where it is under real hormonal regulation. It can be classified into two main categories: human studies and animal studies (Kristensen et al., 2021). The human *in vivo* analysis provides direct information on the human digestive process, including gastric emptying rate, intestinal transit time, and nutrient absorption. However, these techniques have limitations. Firstly, this method is inconvenient for retrieving and measuring the mechanical properties of digesta. In addition, variation among individuals impedes variable control and reduces experimental repeatability. Furthermore, as these experiments are performed on humans, safety and ethical concerns are involved. Mammalian animals, such as pigs, are similar to humans in their digestive systems and are often used as alternatives for digestive research (Hasjim et al., 2010; Le Feunteun et al., 2014; Picot & Sauvant, 2004; Weber & Ehrlein, 1998; Ziegler et al., 2016). Animal experiments involve relatively less ethical consideration, so that intubation during surgical experiments can be applied. However, there are still differences in feeding habits, GI tract anatomy, and other physiology that cannot be ignored.

Given the practical and ethical challenges associated with conducting digestion studies *in vivo*, researchers often turn to *in vitro* experiments, which mimic digestion responses outside the living body and are more controllable. There are two types of *in vitro* digestion models: static and dynamic models. Static *in vitro* models simulate a particular digestive environment of the oral, gastric, and intestinal phases by controlling pH, temperature, enzyme concentration, electrolytes, and mixing conditions (Bornhorst et al., 2016). Because *in vivo* environments are complex, *in vitro* studies require complex protocols to yield authentic results. The recently established INFOGEST protocol has greatly improved reproducibility and comparability across studies (Brodkorb et al., 2019; Minekus et al., 2014). Compared with *in vivo* and dynamic *in vitro* approaches, static models are simpler, less costly, and allow highly controlled and repeatable experiments, facilitating detailed structural analyses of digesta (e.g., SEM investigation) (Aleixandre et al., 2021; Almeida et al., 2019). However, because static tests are typically performed in beakers or tubes under fixed conditions, they cannot reproduce the dynamic variations in pH, enzyme activity, motility, and flow that occur *in vivo*, limiting their physiological realism. Dynamic models aim to reproduce the time-dependent motility, flow, mass transfer, and compartmental structure of the GI tract. In some cases, dynamic models incorporate feedback control to mimic neurohormonal regulation (Dupont et al., 2019;

Gouseti et al., 2014). Systems such as TIMagc replicate the geometry and peristaltic behaviour of the stomach, while multi-compartmental models simulate the oral, gastric, and intestinal phases in a single setup (Bellmann et al., 2016; Minekus et al., 1995; Wang et al., 2022). These models provide more physiologically relevant data and better approximate *in vivo* digestion than static tests. Nonetheless, they require complex, expensive equipment, are time-consuming to operate, and, even with sophisticated design, cannot fully reproduce the intricacies of human digestion, thereby limiting their applicability to specific conditions.

While static and dynamic *in vitro* models provide valuable insight into digestive behaviour, they remain limited by experimental constraints. They cannot fully capture the complexity of *in vivo* physiology. To overcome these limitations, *in silico* approaches, i.e., numerical simulations performed on computers, have become an increasingly acceptable alternative. These methods aim to develop mathematical models with assumptions to remove unnecessary details that can be solved by computers, allowing researchers to model digestive processes without interfering with the human body or constructing complex artificial organs, and enabling flexible, cost-efficient exploration of scenarios that are impractical or impossible to test experimentally. Two major *in silico* methodologies are employed in digestion research. The first type is commonly used in medical and biochemical studies, including ordinary differential equation (ODE)-based kinetic models, compartment models, and Physiologically Based Pharmacokinetics (PBPK) models. These approaches focus on biochemical reactions and digestion kinetics, typically without resolving geometry or spatial mechanics or using highly simplified representations of the GI tract. For example, PBPK models represent each digestive compartment through systems of differential equations in which geometry and environmental conditions are incorporated implicitly via parameters (Le Feunteun et al., 2021b; Peters, 2011). Although computationally efficient, they offer limited spatial resolution and cannot visualise the dynamic digestion process.

In contrast, the second type consists of mechanics-based numerical simulation methods that explicitly resolve spatial and temporal variations in geometry, material properties, and boundary conditions via the governing mechanical and physical equations. These include Computational Fluid Dynamic (CFD) methods such as Finite Volume Method (FVM) (mesh-based) and Smoothed Particle Hydrodynamics (SPH) (particle-based and meshless), solid mechanical methods such as Finite Element Method (FEM) (mesh-based) and Discrete Element Method (DEM) (particle-based), as well as hybrid combinations of these techniques (Brandstaeter et al., 2019; Kristensen et al., 2021; Liu

et al., 2024; Palmada et al., 2023). Computational Fluid Dynamic (CFD) methods treat food materials as fluids and are particularly suitable for simulating the flow and mixing of liquid or semi-liquid foods, but are limited in their ability to represent solid mechanics. SPH are sometimes employed to model large deformations and fragmentation of solids including food materials. However, they are less effective in accurately capturing tensile behaviour, which may appear during digestion. Among solid mechanical methods, DEM is mainly applied to granular materials, such as powders, sands, and food fragments, whereas its applicability to continuum solids is limited. In contrast, FEM is increasingly used due to its versatility in handling solids with complex geometries, heterogeneous materials, and multi-physics couplings. By discretising realistic geometries into finite elements and directly solving the governing laws, FEM provides intuitive spatio-temporal visualisation of digestion phenomena. However, it is less suited for modelling large deformations of solids and fluid flow. For digestion simulations that involve both fluid and solid phases, such as the interaction between solid food bolus, gastric fluid, and gastric peristalsis, FSI methods that couple CFD and FEM are employed to capture the complex interplay between fluid flow and solid mechanics (Ghosh et al., 2025). Coupled Eulerian-Lagrangian (CEL) FEM is a special FEM method that enables the treatment of fluid-structure interaction within the FEM framework (Benson, 1992; Skamniotis et al., 2020). It is worth noting that the aforementioned methods primarily resolve digestion processes at the macroscopic length scale. Microstructural modelling approaches, such as molecular dynamics (Yang et al., 2024b) or coarse-grain modelling (Chen et al., 2019; van der Laan et al., 2025), have also been applied to investigate the behaviour of starch at the molecular level, but they are not the focus of this thesis. A more detailed review of FEM for digestion simulation is provided in Chapter 5.

1.5 Research objectives

Although there have been extensive applications of starch hydrogels in food engineering and pharmaceuticals, as reviewed in Section 1.3.4, and various methods have been developed to investigate digestion behaviour, as discussed in Section 1.4, a systematic understanding of the breakdown behaviour of starch hydrogels in the human stomach is still lacking. Studies closely related to this thesis, such as Gamonpilas et al. (2009a) and Gamonpilas et al. (2009b), examined the mechanical properties of starch hydrogels but did not consider enzymatic hydrolysis, and their numerical analyses did not simulate digestion in the GI tract. Skamniotis and Charalambides (2020) and Skamniotis et al. (2020) modelled both in vitro experiments and in vivo digestion of starch-based food

bolus using an FEM framework. Still, their constitutive model did not account for coupling among diffusion, reaction, and deformation, and the stomach geometry was simplified, neglecting gravity. Other studies on starch digestion or starch hydrogels mainly focus on *in vitro* experiments or *in silico* studies of ODE based kinetic models or PBPK models, without considering the mechanical behaviour of the hydrogel or its interaction with the digestive environment (Drechsler & Ferrua, 2016; Le Feunteun et al., 2021a; Meraz et al., 2022; Moxon et al., 2017).

To achieve the goal of designing starch hydrogels with controlled digestion behaviour for glucose homeostasis regulation and drug delivery, and to address the research gap outlined above, it is essential to understand their breakdown behaviour in the human stomach. Our aim in this study is to develop an *in silico* framework for this purpose. This requires an *in vitro* comprehensive characterisation of the chemo-mechanical behaviour of starch hydrogels prepared under various conditions and an understanding of how this behaviour evolves during enzymatic hydrolysis. A constitutive law reproducing the chemo-mechanical responses under enzymatic hydrolysis is proposed and calibrated. The constitutive model is implemented within the FEM to capture the diffusion, reaction, and deformation of starch hydrogels and to simulate their *in vivo* breakdown within an anatomically realistic human stomach geometry. In addition, dynamic *in vitro* digestion experiments are conducted as a complementary component of this study. Overall, this work establishes a systematic approach for investigating the complex digestion processes occurring in the human stomach and provides reliable computational tools for the design and optimisation of starch-based foods.

1.6 Thesis outline

In addition to the present section, which provides a general introduction to digestion and starch hydrogels, this thesis is structured as follows. Chapter 2 investigates the mechanical properties of starch hydrogels prepared under different conditions, including gelatinisation, retrogradation, and varying water contents. Microscopy characterisation, thermal analysis, and comprehensive mechanical experiments, including compression, tension, rheology, and wire-cutting tests, are conducted. The mechanical properties during enzymatic hydrolysis are then studied in Chapter 3 through uniaxial compression tests, revealing degradation in mechanical behaviour with increasing reaction extent. The enzyme diffusivity within the hydrogel matrix is also quantified.

Using the experimental results from Chapter 2 and Chapter 3, and informed by the

microstructural characteristics of starch hydrogels, a chemo-mechanical coupled constitutive model is proposed and implemented in a finite element framework to simulate the diffusion-reaction-deformation process in [Chapter 4](#). This constitutive model is further applied in [Chapter 5](#) to simulate human gastric digestion, accounting for FSI using the CEL approach. The numerical predictions are validated against dynamic *in vitro* digestion experiments. Finally, [Chapter 6](#) summarises the key findings and future research. More detailed introductions and literature reviews are provided at the beginning of individual chapters where appropriate. Note that, throughout this thesis, unless otherwise specified, square brackets [•] are used to indicate grouping (precedence), whereas parentheses (•) denote function arguments. This convention is adopted to avoid ambiguity.

Chapter 2

Comprehensive material characterisation and mechanical experiments on starch hydrogel.

2.1 Introduction

Starch hydrogel is a significant component of many staple foods that are heated in the presence of water, such as rice, noodles, pasta, and cereal porridge (Cui et al., [2022b](#); Koshenaj & Ferrari, [2024](#); Larrea-Wachtendorff et al., [2022](#); Vieira et al., [2023](#)). Preparation of these foods involves factors such as cooking conditions (including water content, heating time, and heating temperature), storage history (including storage duration and refrigeration temperature), and botanical sources (that determine the amylose-to-amylopectin ratio). The variations of these preparation factors have been shown to influence the mechanical properties of the resulting hydrogels (Chung et al., [2006](#); Wang et al., [2015](#)), and these mechanical properties, in turn, affect their enzymatic hydrolysis and digestion behaviour (Dome et al., [2020](#); Drechsler & Bornhorst, [2018](#); Gamonpilas et al., [2009b](#); Skamniotis et al., [2019](#); Skamniotis & Charalambides, [2020](#); Wang et al., [2015](#)). Therefore, investigating the factors that govern the mechanical properties of starch hydrogels, as well as the relationships between these factors and the corresponding mechanical responses, is essential for understanding their digestive behaviour and for designing starch hydrogels with desirable digestive characteristics. These key factors are introduced below.

2.1.1 Factors affecting the properties of starch hydrogels

2.1.1.1 Degree of gelatinisation (DOG)

At room temperature, native starch granules are insoluble, and their structure is stable. Cooking native starch in excess hot water leads to gelatinisation, the irreversible disruption of the molecular order within starch granules. During heating above the gelatinisation temperature (initiation temperature of gelatinisation) (Morris, 1990), the granules undergo hydration and swelling (Lovegrove et al., 2017). As hydrogen bonds between polymer chains are disrupted and replaced by interactions with water molecules, the tightly bound crystalline regions formed by the short branches of amylopectin begin to dissociate and melt (Yu & Christie, 2005), leading to an increase in molecular randomness within the granule. Due to the mutual immiscibility of amylose and amylopectin, phase separation occurs (Goesaert et al., 2005; Yu & Christie, 2005), and amylose molecules in the core region leach into the surrounding water (BeMiller, 2011). The further swelling of the granule and spread of the amylopectin chains causes a noticeable increase in the viscosity of the starch suspension (Goesaert et al., 2005; Wang & Copeland, 2015), and the suspension is opaque (Nagasaki et al., 2021). Under continued shear mixing, the swollen granules eventually disintegrate, and the amylose becomes fully dissolved, resulting in a viscosity decrease approaching that of water. At the same time, the liquid becomes transparent, indicating that density fluctuations disappeared, and the homogeneity increases (Nagasaki et al., 2021). The resulting viscoelastic liquid mass consists of a continuous phase of polymer network and a discontinuous phase of swollen granule fragments (BeMiller, 2011; Miles et al., 1985). The gelatinisation process disrupts the ordered structure and disperses the starch molecules, yielding a homogeneous system. It can be seen that gelatinisation is an entropy-rise process. Thus, an increase in temperature accelerates the rate of gelatinisation (Lund & Lorenz, 1984). Upon cooling (gelation and retrogradation, see Section 2.1.1.2), this liquid transforms into a solid-state starch hydrogel. Note that in addition to gelatinisation with heating in excess water, high hydrostatic pressure to disrupt the starch granule structures can also lead to gelatinisation (Buckow et al., 2007; Larrea-Wachtendorff et al., 2022; Liu et al., 2020; Papathanasiou et al., 2015).

The degree of gelatinisation (DOG) quantifies the extent of gelatinisation in starch samples. Various methods have been developed to characterise the DOG. As starch granules contain highly orientated crystalline regions, they exhibit birefringence under polarised light microscopy, appearing as a dark Maltese cross pattern that represents the degree of order within the starch granule (Rumpold, 2005; Zobel, 1988). Therefore, the

loss of birefringence during gelatinisation indicates partial or complete gelatinisation of the starch granule (Papathanasiou et al., 2015). Thus, optical microscopy can be used to characterise the DOG by the change of birefringence before and after gelatinisation (Buckow et al., 2007; Papathanasiou et al., 2015; Pei-Ling et al., 2012; Rumpold, 2005; Zobel, 1988). In addition to optical methods, thermal analysis techniques are widely used to characterise the DOG. As gelatinisation involves the melting of crystallites within starch granules, the heat flow associated with this endothermic process can be measured using techniques such as the Differential Scanning Calorimetry (DSC) (Cooke & Gidley, 1992; Fu et al., 2013; Liu et al., 2020; Pei-Ling et al., 2012; Xu et al., 2021; Yan et al., 2021; Zhang et al., 2014), where the difference of heat flows between the sample and a reference sample as a function of temperature and time is determined. For fully gelatinised starch, the enthalpy of gelatinisation is zero, while for partially gelatinised starch, the enthalpy of gelatinisation is proportional to the remaining crystallinity. Therefore, the DOG can be calculated by comparing the enthalpy of gelatinisation of the sample with that of the native starch (Wang & Copeland, 2013). Similarly, X-ray Diffraction (XRD) can be used to measure the diffraction change due to crystallinity changes, where a narrower and higher peak characterises higher crystallinity. Therefore, XRD is also used to obtain the DOG (AlShaalan, 2019; Baks et al., 2007; Fu et al., 2013). Interestingly, Ai and Jane (2015), Fang et al. (2020), and Torres et al. (2018) characterised the DOG by rheological tests, as the mechanical properties change with a varying DOG.

2.1.1.2 Degree of retrogradation (DOR)

Upon cooling of the liquid-state gelatinised starch mass, gelation occurs, forming a solid starch hydrogel, which is a three-dimensional polymer network swollen with water (Ferry, 1980). Gelation is the transition from a liquid to a solid gel state when the crosslinking density reaches a critical value, the gel point (Winter & Chambon, 1986). Note that gelation, the formation of a solid from a liquid, is to be distinguished from gelatinisation, which breaks down the granule structure and releases the starch molecules. Gelation occurs as the dispersed starch molecules (dominantly amylose) reassociate via hydrogen bonds, forming a crosslinked network (Tako et al., 2014; Zobel, 1984). As it is an exothermic process, hydrogen bonds form upon cooling. The network formation by amylose molecules is called short-term retrogradation and determines the initial stiffness (or hyperelasticity, discussed later) of the starch hydrogel (Yan et al., 2021). A higher amylose content leads to a denser crosslinked network and a stiffer hydrogel (Wang

et al., 2015). The short-term formation of the polymer matrix by the amylose is irreversible (Miles et al., 1985).

Over longer storage times, the amylopectin side chains of the starch hydrogel tend to form more hydrogen bonds between the hydroxyl groups (-OH), and eventually recrystallisation and phase separation occur, which is known as retrogradation (BeMiller, 2011; Rumpold, 2005; Yan et al., 2021). This recrystallisation process is long-term compared to the short-term amylose gelation, which takes several days or weeks and is reversible (BeMiller, 2011; Miles et al., 1985). Due to the reassociation of the polymer chains, the retrogradation process is accompanied by the syneresis effect, i.e., the tendency of water expulsion from the gel network (Rumpold, 2005). In addition, as retrogradation proceeds, the starch hydrogel transitions from transparent to opaque (Yan et al., 2021), indicating the formation of crystallites. The crystallites formed by amylopectin together with granule remnants act as fillers in the polymer network, reinforcing the hydrogel and enhancing its mechanical strength (Miles et al., 1985; Morris, 1990). Therefore, the degree of retrogradation (DOR) significantly influences the mechanical properties of starch hydrogels. The recrystallisation process is a non-equilibrium exothermic (energy released) thermodynamic process (BeMiller, 2011; Jang & Pyun, 1997), which is dependent on the rate of crystallite nucleation and the rate of crystal growth (Jang & Pyun, 1997), hence longer storage time (Jang & Pyun, 1997; Wang et al., 2015) and lower storage temperature give rise to stronger retrogradation (Aguirre et al., 2011; Lovegrove et al., 2017; Wang et al., 2015).

As the retrogradation process involves the recrystallisation of amylopectin chains, and these crystallites melt again upon reheating (Morris, 1990), techniques that characterise crystallinity changes, similar to characterising the DOG, are commonly used to measure the DOR, such as DSC (Jang & Pyun, 1997; Rumpold, 2005) and XRD (Aguirre et al., 2011; Miles et al., 1985).

2.1.1.3 Water content

Water in starch and starch hydrogels can be classified into monolayer, multilayer, and condensed water, based on their binding strength and interactions with starch molecules (Lv et al., 2011; Mannheim et al., 1994). The monolayer water, adsorbed directly onto polar sites such as hydroxyl or amide groups through strong molecular forces, constitutes the first layer of binding and exhibits the strongest hydrogen bonding. It is mainly associated with crystalline regions, which possess a higher monolayer capacity than amorphous domains (Lv et al., 2011). Multilayer water forms through hydrogen

bonding between adjacent water molecules and starch functional groups, representing a weaker but still structured mode of association. Beyond these bound layers, condensed water exists as physically adsorbed or capillary water within interstitial spaces or pores (Mannheim et al., 1994).

Water plays a crucial role in the gelatinisation and retrogradation processes of starch. During gelatinisation, the melting of crystalline regions disrupts strong hydrogen bonds and decreases monolayer capacity (Lv et al., 2011). As more amorphous structures are formed, weaker hydrogen bonds associated with multilayer water become predominant, owing to the exposure of additional binding sites (Lv et al., 2011). In contrast, the amount of condensed (free) water decreases as these molecules participate in new, weaker interactions. No water is expelled from the hydrogel during compression in our following findings due to the presence of these interactions. The predominant multilayer water is responsible for the dehydration behaviour of the hydrogel when exposed to air. Consequently, water acts as a plasticiser in the amorphous regions (BeMiller, 2011), enhancing chain mobility and flexibility of the hydrogel matrix and converting the initially rigid granules into a softer, more flexible hydrogel material (Waigh et al., 2000).

The water content or starch mass fraction significantly influences the process of gelatinisation and retrogradation behaviour of starch. The gelatinisation temperature decreases with increasing water content in starch suspensions, reflecting the facilitation of hydrogen bond disruption and polymer chain mobility by sufficient hydration (Rumpold, 2005). Nagasaki et al. (2021) reported that the rate of gelatinisation varies considerably with water content (or starch mass fraction). At lower water content, a faster progression of gelatinisation is found, attributed to the limited mobility of water molecules and enhanced molecular interactions at higher solid contents. Nevertheless, the DOG decreased with increasing starch mass fraction or decreasing water content (Rumpold, 2005), due to the insufficient swelling and breakdown of the granule (Wang & Copeland, 2013). The water content or starch mass fraction also affects the gelation and retrogradation behaviour. Goesaert et al. (2005) and Morris (1990) found that starch gelation occurs at concentrations above 6% (w/w). It requires a sufficient number of polymer chains to overlap and interconnect, which requires a specific concentration of starch molecules so that the intermolecular distance is comparable to the molecular size. The extent of retrogradation was found first to increase and then decrease with increasing water content between 20% and 90%, showing a parabolic trend (Wang et al., 2015). At very low water levels, the limited mobility of starch chains suppresses recrystallisation, while at excessively high water contents, excessive molecular spacing

and dilution prevent effective chain reassociation.

2.1.1.4 Amylose-to-amylopectin ratio

According to the previous sections, amylose leads to the formation of an irreversible amorphous network during gelatinisation, reinforced by thermo-reversible crystallites formed by amylopectin together with granule remnants (Morris, 1990). Therefore, starch gels can be regarded as composite systems with intrinsic structural heterogeneity (Koev et al., 2020). It is well established that higher amylose levels raise the gelatinisation temperature by restricting granule swelling and suppressing structural breakdown (Yan et al., 2021). When gelatinisation is sufficient, starch with a higher amylose content generally produces a stronger network, while starch with a higher amylopectin content (waxy) forms softer, weaker gels but exhibits enhanced retrogradation (Wang et al., 2015). In addition, the crystalline lamellae within amylopectin clusters increase in size with amylose content, and the rigidity of starch granules is proportional to their amylose level but inversely proportional to the degree of swelling (Yan et al., 2021).

Therefore, the amylose-to-amylopectin ratio, determined by the botanical origin of the starch, strongly influences the gelatinisation and retrogradation behaviour and thus governs both the structural and mechanical properties of starch hydrogels. Leloup et al. (1991) assessed the amylose-to-amylopectin ratio using the iodine-starch test due to the strong iodine affinity of the amylose helix. They reported that a higher amylose fraction yields hydrogels with greater mechanical stiffness under uniaxial compression, thermal resistance (lower solubility in hot water), and resistance to acid hydrolysis and enzymatic amylolysis. Koev et al. (2020) further demonstrated that low-amylose starches form weaker gels with greater swelling capability, higher chain mobility, and more pronounced viscoelasticity due to the less densely crosslinked network formed by amylose molecules. Consistently, Pulgarín et al. (2023) showed that amylose-rich starches are more resistant to gelatinisation and swelling, and are more prone to dehydration and retrogradation, exhibiting lower chain mobility. AlShaalán (2019) further observed that starches with higher amylose content exhibit slower *in vitro* digestion and therefore a reduced glucose release rate.

In this study, we focus on potato starch with a stable amylose-to-amylopectin ratio from the same commercial product. The influence of this ratio on mechanical properties will be investigated in future work by comparing starches sourced from different botanical origins.

2.1.2 Current in vitro mechanical experiments on starch hydrogels

Generally, the gelatinisation process enables amylose to form a physical crosslinked polymer network via hydrogen bonds (Yan et al., 2021), which provides the fundamental matrix hyperelasticity. Meanwhile, the imperfections of the polymer network, i.e., dangling chains that are not attached to the network at both ends and solvated chain fractions that are trapped in pore water, provide viscoelasticity (Koev et al., 2020; Mazurek et al., 2019), as their movement causes internal friction. Furthermore, the retrogradation process enables amylopectin chains to form crystallites within the network (Yan et al., 2021), which serve as particle reinforcement. The amylose and amylopectin chains collectively tailor the mechanical properties of the starch hydrogel as a filled polymer (Morris, 1990). The mechanical behaviour of filled polymers has been investigated extensively (Li et al., 2019; Mazurek et al., 2019; Stricher et al., 2015). The fillers are the reinforcement phase that strengthens the material. However, once the filler ruptures or detaches from the matrix, the reinforcement is lost, leading to stress softening, or the so-called Mullins effect (Liao et al., 2020c; Mohammed et al., 2013; Mullins, 1948). As the DOG is influenced by the cooking temperature and time, and the DOR is affected by the storage time and temperature, these factors have an impact on the mechanical properties, which in turn influence the digestion process.

Research on the mechanical properties of food materials has been widely conducted. Early studies investigated the uniaxial compression behaviour of bread dough and highlighted the influence of platen friction (Charalambides et al., 2005), while wire-cutting tests were used to characterise fracture behaviour in cheese (Goh et al., 2005). Comprehensive mechanical characterisation of bread dough under tension, compression, and shear was later performed by Mohammed et al. (2013), who developed a hyper-viscoelastic constitutive model and combined experiments with finite element simulations to analyse extrusion processes. The micromechanical behaviour of brittle food materials has also been explored. For example, Mohammed et al. (2014) combined uniaxial compression tests with Scanning Electron Microscopy (SEM) and X-ray tomography to link the micro- and macrostructural responses of confectionery wafers, supported by finite element simulations of failure responses. The tensile strength of potato starch was characterised using diametric compression tests by Horabik et al. (2019). Chocolate has been extensively studied in terms of its thermal and mechanical properties, and modelling frameworks have been developed to simulate its breakdown during oral processing (Bikos et al., 2021, 2022a, 2022b; Bikos et al., 2023; Samaras et al., 2020, 2023, 2024). Other studies have examined the rate-dependent compression

behaviour of food materials with different internal structures, such as pea seeds (Petropoulou et al., 2020). Starch-based food products have received particular attention. Skamniotis et al. (2016, 2017, 2018) and Skamniotis (2017) characterised the constitutive behaviour of starch-based pet food using uniaxial tensile and compression tests and determined the essential work of fracture (EWF) via double edge notched tension (DENT) tests, supported by viscoplastic-damage finite element simulations of wire-cutting and mastication. Subsequent studies investigated the mechanical properties and digestion behaviour of starch-based biscuits using a combination of compression and cutting tests (Skamniotis & Charalambides, 2020; Skamniotis et al., 2020). Wire-cutting tests have also been widely applied to characterise fracture properties of food materials (Gamonpilas et al., 2009a; Goh et al., 2005; Kamyab et al., 1998; Skamniotis & Charalambides, 2020).

The investigation of the mechanical properties of starch hydrogels remains limited. In most studies, the focus has not been on the mechanical properties. For mechanical tests, the tests were mainly rheological and aimed at determining viscosity or dynamic moduli (Fabek et al., 2014; Iqbal et al., 2021; Torres et al., 2018; Yan et al., 2021; Zheng et al., 2023), which did not provide a comprehensive understanding of the mechanical response history of the material. Besides rheological tests, Leloup et al. (Leloup et al., 1991) reported a positive correlation between the elastic moduli and the amylose-to-amylopectin ratio. Drechsler et al. (Drechsler & Bornhorst, 2018; Drechsler & Ferrua, 2016) performed uniaxial compression tests via a texture analyser to obtain the strength, tangent modulus, and toughness. They also performed bulk compression tests via a Universal Test Machine. One of the most relevant studies was conducted by Gamonpilas et al. (Gamonpilas et al., 2009b). They performed a relatively comprehensive study on the compression and wire-cutting experiments on starch hydrogels. A hyperelastic constitutive model was used to characterise the mechanical response by fitting the stress-strain curve. The model was then implemented into FEM to predict the mechanical behaviour of the starch hydrogel during cutting (Gamonpilas et al., 2009a).

Among the aforementioned studies, Skamniotis et al. (2020) and Gamonpilas et al. (2009b) are the two most important and relevant works to the present research. The mechanical testing methodologies and simulation framework reported by Skamniotis et al. (2020), together with the material preparation procedures, mechanical characterisation, and inverse analysis approach described by Gamonpilas et al. (2009b), provide key methodological references and form the basis for the experimental and

modelling strategies adopted in this thesis.

However, except for these studies, there is no report on the dependence of mechanical properties on key hydrogel factors, including the DOG, DOR, and water content. Specifically, comprehensive loading-unloading data, which are essential for material model development and *in silico* simulations of the digestion of starch foods, are absent from the literature. Also, due to the brittle nature of starch hydrogels, performing tension tests is challenging, and to the best of our knowledge, no reports on tensile testing of starch hydrogels exist.

Therefore, there is a clear need for comprehensive experimental characterisation of the mechanical response and failure behaviour of starch hydrogels, with particular emphasis on key factors such as DOG, DOR, and water content. Such characterisation will be conducted under multiple loading conditions, including compression, tension, shear, and wire-cutting. These data are essential for the development of accurate constitutive models capable of predicting the mechanical behaviour of starch hydrogels under a range of conditions.

2.1.3 Chapter outline

This chapter aims to investigate the relationship between the preparation conditions simulating cooking and storage and the mechanical properties of starch hydrogels. By focusing on pure starch, we try to isolate and understand its unique contributions to starch-based foods. In this chapter, in addition to the current Introduction section, [Section 2.2](#) describes the preparation of starch hydrogel specimens. Microscopy characterisations, including optical microscopy and SEM, are presented in [Section 2.3](#). [Section 2.4](#) presents the DSC results to characterise the DOG and DOR of starch hydrogel specimens prepared under different cooking and storage conditions. Subsequently, the main mechanical experimental results are presented in [Section 2.5](#), where uniaxial compression loading-unloading tests are performed to investigate the cyclic loading behaviour ([Section 2.5.2](#)), strain rate and temperature dependence ([Section 2.5.3](#)), and the influence of the key factors of hydrogel formation on the mechanical properties of starch hydrogels including the DOG ([Section 2.5.4](#)), DOR ([Section 2.5.5](#)), and water content ([Section 2.5.6](#)). The uniaxial tension and shear test data are presented in [Section 2.6](#) and [Section 2.7](#), respectively, to complement the compression tests. The fracture behaviour of the starch hydrogel is investigated via wire-cutting tests in [Section 2.8](#), and the post-failure behaviour is analysed by

compression tests of crushed and reformed specimens in [Section 2.9](#). Each section presents the experimental setup, results, and discussion. Finally, [Section 2.10](#) summarises the key findings of this chapter.

2.2 Starch hydrogel preparation

Potato starch powder (S2004, Sigma-Aldrich) was used in this study. Such powdered starch was extracted from tubers, which typically involves crushing, filtration, sedimentation and drying (Ahmed et al., [2024](#); Dorantes-Fuertes et al., [2024](#)). Starch suspensions with a mass fraction of 20% (w/w), i.e., 80% (w/w) moisture content, were prepared by mixing native starch powder with deionised (DI) water in a beaker. The suspension was stirred continuously and heated in a 90°C water bath with a heating time of 40 minutes, which is sufficient to obtain fully gelatinised samples (Papathanasiou et al., [2015](#); Zheng et al., [2019](#)). The cooked liquid was then swiftly poured into specimen moulds at ambient temperature (i.e., 20°C), including those for compression, shear, tensile, and wire-cutting tests. The liquid in the moulds was left to cool down to ambient temperature for the formation/gelation of solid specimens. The hydrogel specimens were then gently demoulded, wrapped in cling film, and stored in a sealed plastic bag to prevent dehydration. The samples were stored at ambient temperature (20°C) for 48 hours (2 days) to allow a constant degree of retrogradation before mechanical testing. Note that other heating times, storage times, and storage temperatures were also used to obtain samples with different DOGs, DORs, and water contents for mechanical tests (see details in [Section 2.5.1](#)). The average density of the starch hydrogel samples was measured as $\rho_{\text{gel}} = 0.996 \pm 0.064 \text{ g/cm}^3$ by dividing the sample mass by its volume. In the following sections, the density of the hydrogel is assumed to be constant at $\rho_{\text{gel}} = 1.00 \text{ g/cm}^3$. These specimens were typically used for mechanical experiments and for optical and scanning electron microscopy. For DSC (see details in [Section 2.4.1](#)), the starch powder suspension was prepared in the DSC pans sealed with lids and subsequently tested to investigate the gelatinisation properties. We denote the 20% w/w fully gelatinised starch hydrogels, with a cylindrical geometry of 20 mm diameter and 20 mm height, stored for 48 hours at 20°C, as the benchmark material state, unless otherwise specified.

2.3 Microscopy characterisation

2.3.1 Optical Microscopy

An optical microscope (Carl Zeiss Axio Imager A2m) was used to observe the morphology of the starch suspensions and the gelatinised starch. A droplet of starch suspension or a small piece of starch hydrogel sample was placed on a glass slide and covered with a coverslip, respectively. The glass slide was placed on a thin hotplate and heated to 90°C under the microscope. The change in the morphology of the starch sample from a granule to a hydrogel during the gelatinisation process was observed *in situ* under the microscope.

The ungelatinised 20% w/w starch suspension was observed by OM, as shown in [Figure 2.1\(a\)](#). The starch granules appeared elliptical, with sizes ranging from 5 μm to 60 μm . The suspension was heated to 90°C *in situ* under the OM to observe the gelatinisation process. From [Figure 2.1\(b\)](#) to [Figure 2.1\(d\)](#), as the temperature increased to 90°C, the starch granules gradually swelled due to water absorption, lost their elliptical shape, and finally disappeared within 5 minutes. During this process, the crystallites within the granules melted, and the polymer chains dissolved, causing the suspension to become transparent as density fluctuations disappeared (Nagasaki et al., [2021](#)), indicating a homogeneous suspension.

2.3.2 Cryo Scanning Electron Microscopy (Cryo-SEM)

Higher magnification images of the microstructure of the gelatinised starch hydrogel were obtained via Cryo-SEM (Tescan Mira, Czech Republic). The samples were frozen in liquid nitrogen, transported to the vacuum preparation chamber, sublimated to remove surface ice, and fractured to expose the internal structure. The fractured samples were coated with a thin layer of platinum using a sputter coater within the chamber. The coated samples were then transferred to the SEM chamber for imaging.

[Figure 2.2\(a\)](#) and [Figure 2.2\(b\)](#) show that a compact and disordered polymer network was formed. The pore size is on the scale of 100 nm. Its morphology is comparable to that of other gel materials reported in the literature (Djabourov, [1991](#)), where a gelatin gel network of 2% concentration exhibited a length scale between 20 nm and 100 nm, and a 10% gel between 10 nm and 30 nm.

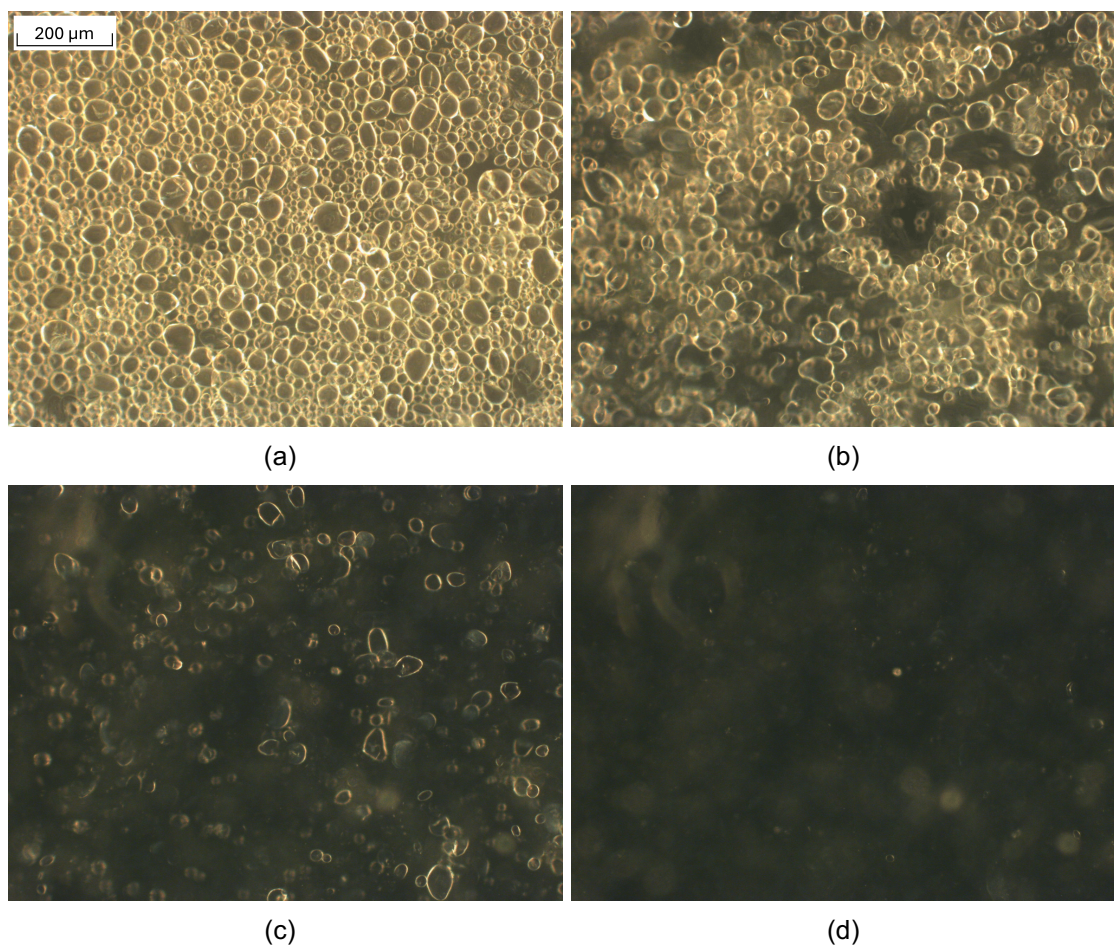


Figure 2.1. *In situ* optical microscopy images (200 times magnification) of the gelatinisation process of 20% w/w starch suspension heated at 90°C for (a) 0 minutes, (b) 1 minute, (c) 2 minutes, and (d) 3 minutes.

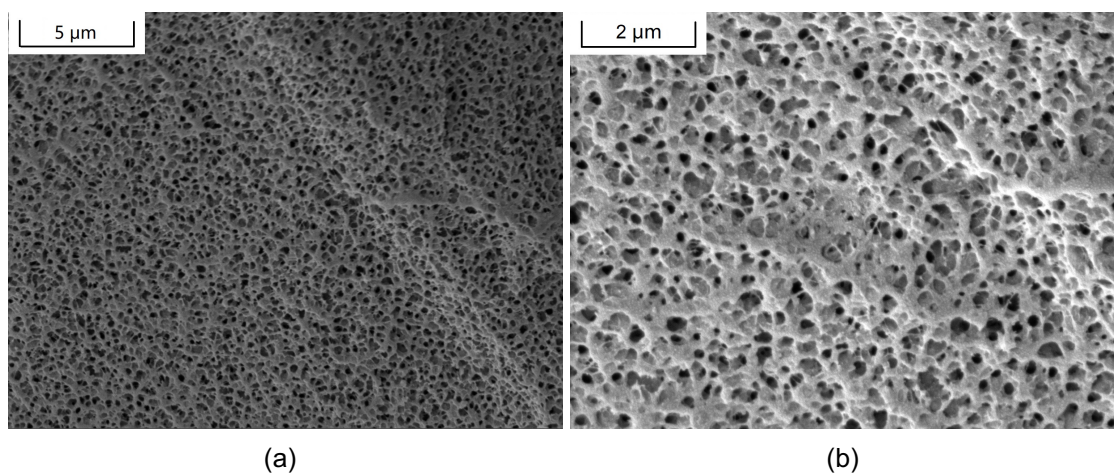


Figure 2.2. Cryo-SEM image of starch hydrogel prepared at benchmark conditions. (a) 20,000 times magnification, and (b) 40,000 times magnification.

2.4 Characterisation of degree of retrogradation using Differential Scanning Calorimetry

2.4.1 DSC experimental procedure

The thermal properties of the starch hydrogels were tested using DSC (DSC250, TA Instruments, New Castle, DE, USA). A 20% w/w suspension of starch powder, referred to as a raw sample, at 20°C (as described in [Section 2.2](#)) was placed in a hermetically sealed aluminium pan, and an identical but empty sealed aluminium pan was used as a reference. The samples were heated from 20°C to 90°C at a heating rate of 10°C/min, during which gelatinisation occurs, and then cooled down to 20°C for a heating-cooling cycle. An immediate second heating-cooling cycle was also imposed on some samples for comparison. The normalised heat flow (heat flow normalised by mass) was recorded as a function of temperature change. The endothermic enthalpy (ΔH) was calculated by integrating the normalised heat flow curve with respect to time from the starting temperature T_s to the ending temperature T_e , as shown in the shaded area in [Figure 2.3\(a\)](#). The enthalpy of gelatinisation is denoted as ΔH_{Gel} .

After the heating-cooling cycles, to study retrogradation, the gelatinised samples in the sealed pans were stored at 20°C for storage times of 24, 48, 96, 192, and 480 hours. After storage, the pans were heated again in the DSC, and the enthalpy of retrogradation, denoted as ΔH_{Ret} , was calculated. DOR is defined as the percentage of the enthalpy of the sample after retrogradation ΔH_{Ret} to the enthalpy of the native starch suspension ΔH_{Gel} , i.e.,

$$\text{DOR} = \frac{\Delta H_{\text{Ret}}}{\Delta H_{\text{Gel}}} \times 100\%. \quad (2.1)$$

Here, we assume that the maximum level of retrogradation is reached when $\Delta H_{\text{Ret}} = \Delta H_{\text{Gel}}$. Note that the DSC tests on the raw samples (to investigate gelatinisation) and the gelatinised samples for various storage times (to investigate retrogradation) were each repeated at least five times.

2.4.2 DSC experimental results and discussion

[Figure 2.3\(a\)](#) shows the normalised heat flow (heat per unit mass) versus temperature. The solid black curve represents the first heating process, while the dashed black curve represents the second heating process. During the first heating, the starch granule structure broke down, and the crystallites absorbed heat and melted. Thus, a valley can

be observed in the black curve. The enthalpy of gelatinisation is calculated by integrating the valley area with respect to time, which is proportional to the shaded area. The average enthalpy was found to be 4.11 J/g (indicated by the black dot in [Figure 2.4\(a\)](#)). Since the starch was fully gelatinised, the second heating (dashed curve) yielded a flat line with an enthalpy of 0. The average peak temperature (temperature of heat flow peak) was 68.1°C (illustrated by the black dot in [Figure 2.4\(b\)](#)). In previous studies (Wang & Copeland, [2013](#); Xu et al., [2021](#); Yan et al., [2021](#); Zhang et al., [2014](#)), peak temperatures ranging from 62°C to 67°C for potato starch have been reported. Note that, as crystallites melt during heating and the cooling path is not relevant to the enthalpy calculation, only the heating path is shown in [Figure 2.3\(a\)](#) and [Figure 2.3\(b\)](#).

After gelatinisation, the specimens were stored at 20°C for 24, 48, 96, 192, and 480 hours. Their enthalpies were measured by heating the samples from 20°C to 90°C, as shown in [Figure 2.3\(b\)](#). The enthalpy versus storage time curves are illustrated in [Figure 2.4\(a\)](#), along with the gelatinisation enthalpy of the raw samples for comparison. For the 24-hour specimens, only a negligible melting enthalpy was observed. As storage time increased, the enthalpy gradually rose, approaching the gelatinisation enthalpy of the raw samples. During storage and retrogradation, the amylopectin chains in starch hydrogels recrystallised. As this process occurred, the hydrogel released energy. Upon reheating, the newly reformed crystallites melted again. With longer storage time, more crystallites formed, leading to greater energy absorption during melting and, consequently, higher enthalpy values. Using [Equation 2.1](#), the values of the DORs for samples stored for different times were calculated (see [Figure 2.4\(a\)](#)).

Unlike the raw starch granules, where the crystallites before gelatinisation were relatively regular, the crystallites formed in starch hydrogel during retrogradation exhibited different morphologies and melted at different temperatures (Pei-Ling et al., [2012](#); Stute et al., [1996](#)). As a result, the enthalpy valleys of [Figure 2.3\(a\)](#) and [Figure 2.3\(b\)](#) span different ranges with different starting temperatures ranging from 45 °C to 50°C and ending temperatures ranging from 75°C to 85°C compared to [Figure 2.3\(a\)](#). Additionally, [Figure 2.4\(b\)](#) shows an increasing trend in the peak temperature over time.

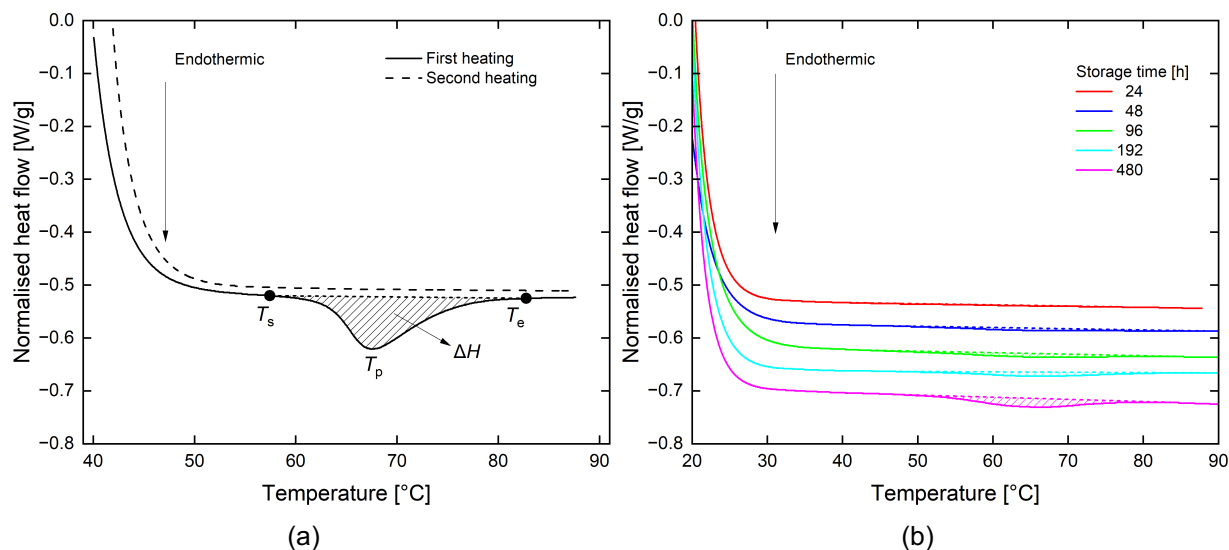


Figure 2.3. (a) DSC curve of the gelatinisation process (first heating), where a 20% w/w suspension of raw starch sample transformed into a hydrogel, in comparison to the curve of the second heating. (b) DSC curves of the fully gelatinised starch hydrogels, which were stored at 20°C for various storage times before the DSC test. Note that the cooling path is omitted and the curves are vertically offset for visual clarity.

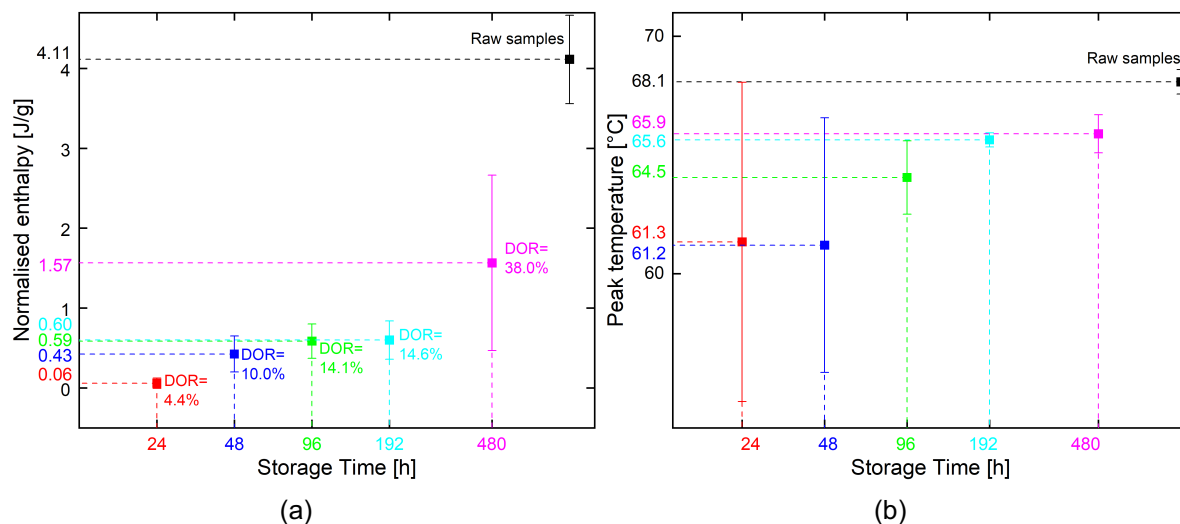


Figure 2.4. (a) Normalised enthalpy versus storage time of the gelatinised samples in comparison to the raw samples. The values of the DOR were calculated from Equation 2.1. (b) Peak temperature versus storage time of the gelatinised samples in comparison to the raw samples.

2.5 Compression mechanical tests on starch hydrogels

2.5.1 Mechanical experiments preparation for uniaxial compression tests

A Universal Testing Machine (Instron 5543, USA) was used to perform the uniaxial compression on the starch hydrogel specimens (as well as tension tests in [Section 2.6](#) and wire-cutting tests in [Section 2.8](#)). A 100 N load cell was used for all these tests. For the uniaxial compression tests, the hydrogel specimens with a diameter of 20 mm and a height of 20 mm were formed in a cylindrical aluminium mould with a smooth, polished cavity. The hydrogel specimens were placed between two horizontal flat platens, as shown in [Figure 2.5](#). As friction can adversely affect the validity of experimental results (Charalambides et al., 2005), silicone oil (Ultimate Racing) with a viscosity of 10 Pa·s was applied between the specimen surfaces and the platens. This approach minimised friction, prevented the specimen barrelling effect, as evidenced in [Figure 2.5](#), and ensured a relatively ideal uniaxial loading condition. To verify that the size effect was insignificant, additional tests were conducted using lubricated samples of a smaller aspect ratio (diameter 20 mm and height 15 mm) and a reduced size (diameter 12.5 mm and height 12.5 mm), and it was confirmed that the stress-strain results were consistent across these sample sizes (results not shown).

The uniaxial compression tests were the primary focus of the experimental investigation in this chapter. Nominal stress and nominal strain were recorded during the tests. The nominal stress is defined as $P = F/A_0$, where F is the force obtained by the load cell, and A_0 is the initial area of the cross-section. The nominal strain is defined as $\varepsilon = u/l_0$, where u is the cross-head displacement, and l_0 is the initial height of the sample. The nominal stress and strain are negative in compression and positive in tension. However, as a common practice, the absolute values of nominal stress and strain are presented in the following sections. By default, tests at each condition were replicated at least five times to ensure the repeatability of the results.

We denote the following as the **benchmark condition**, unless otherwise specified: mechanical tests performed at a nominal strain rate of 0.01 s^{-1} , at 20°C and 50% relative humidity, comprising two-cycle loading-unloading tests to a nominal strain of 0.2 and a monotonic loading test to failure. The material state used for this benchmark is a starch hydrogel with a starch mass fraction of 20% w/w, prepared by heating at 90°C for 40 minutes (fully gelatinised) and stored at 20°C for 48 hours. These parameters will be

varied to investigate their influence on the mechanical behaviour of the starch hydrogel.

Firstly, loading-unloading tests with various primary loading nominal strains (0.20, 0.16, 0.12, and 0.08) and corresponding reloading nominal strains (0.16, 0.12, 0.08, and 0.04) were performed to investigate the constitutive behaviour, including energy dissipation and strain softening. Then, the strain rate and temperature dependence were evaluated by varying the nominal strain rate (ranging from 0.02 /s to 0.0002 /s) and the testing temperature (ranging from 5°C to 40°C). Subsequently, the influence of key factors of hydrogel formation was studied, including the DOG altered by changing the heating time (1–50 minutes), the DOR altered by changing storage conditions (storage duration from 1 hour to 1 month, and storage temperatures of 5°C, 20°C, and 40°C), and water content (50%, 60%, 70%, and 80%). Furthermore, the water absorption and retention capacity of the starch hydrogel were assessed through hydration tests, in which specimens were immersed in DI water for various durations to allow water uptake, and dehydration tests, in which specimens were placed at room temperature and exposed to air for controlled durations. Weight change was recorded using a precision balance (Pioneer PX Series, OHAUS, USA) with a data-logging capability.

The detailed test conditions of the uniaxial compression experiments are summarised in [Table 2.1](#). The benchmark conditions for the material state and mechanical tests are highlighted in **bold**. The figures presenting the results for each test condition are also listed in the table for reference.

Table 2.1. Experimental conditions of uniaxial compression tests. The benchmark condition is highlighted in **bold**, and the corresponding figures present the results.

Specimen size		Heating temperature	Testing humidity	Testing mode
Height	Diameter			
20 mm	20 mm	90°C	50%	Two-cycle loading-unloading at strain 0.2 Monotonic loading until failure Multistep loading-unloading test Figure 2.7 Two-cycle test with various cyclic strains Figure 2.8

Testing temperature [°C]	Strain rate [1/s]	Heating time[min]	Storage time[h]	Storage temperature [°C]	Starch mass fraction (Moisture content) [%]
5, 20 , 40, 60 Figure 2.9 – Figure 2.11	0.001, 0.002, 0.01 , 0.02 Figure 2.12	1 – 50, 40 Figure 2.13 – Figure 2.15	0.1 – 768, 48 Figure 2.16 – Figure 2.18	5, 20 , 30 Figure 2.19	20 (80) , 30 (70), 40 (60), 50 (50) Figure 2.21 – Figure 2.25

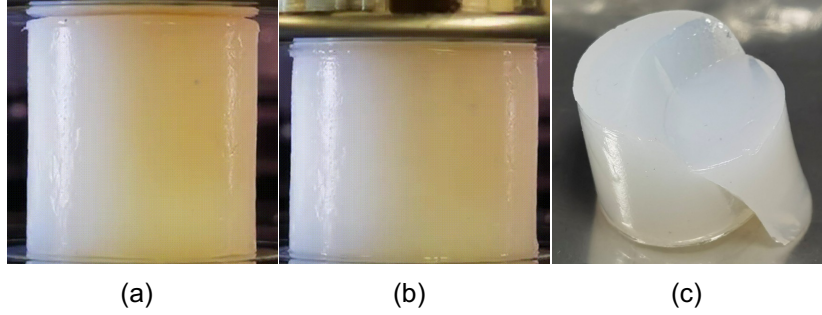


Figure 2.5. Image of a sample for compression tests at (a) the initial state and (b) strain 0.15. No obvious barrelling phenomenon is observed on the specimen. (c) shows the sample after fracture.

2.5.2 Loading-unloading cyclic tests, viscoelasticity, and pseudoelasticity

To investigate the constitutive behaviour of the starch hydrogel, cyclic loading-unloading tests were performed. The path of the unloading curve and the difference between the loading and second cycles provide essential information on identifying mechanical behaviour and distinguishing plasticity, viscoelasticity, and pseudoelasticity (Ogden & Roxburgh, 1999).

Figure 2.6 shows two-cycle loading-unloading tests on a 20% w/w starch hydrogel prepared under the benchmark condition, with a loading strain rate of 0.01 /s, at 20°C and at 50% humidity. As the residual strain is negligible at the end of each cycle, the material does not undergo plastic deformation. Additionally, dissipation energy density is observed over a cycle. Here, we define D_{int} as the dissipation energy density (energy dissipation per unit volume in a cycle) accumulated along the loading path, calculated by

$$D_{\text{int}} = \int_{\Gamma} P d\varepsilon, \quad (2.2)$$

where Γ is the loading-unloading path of nominal strain, P is the nominal stress, and ε is the nominal strain. Thus, D_{int} represents the area enclosed between the loading and unloading paths. However, both dissipation and stress level decreased significantly from the primary loading (the 1st cycle) to the reloading cycle (the 2nd cycle), indicating a progressive loss of material stiffness. This phenomenon is called stress-softening behaviour, or the Mullins effect (Mullins, 1948). Since there is a difference in stress levels between primary loading and reloading, the material does not exhibit true elasticity. However, when the maximum historical strain is not exceeded, the unloading paths of

both cycles nearly coincide (see Figure 2.6), behaving elastically. Therefore, a material with such a stress-softening behaviour is also called a pseudoelastic material (Ogden & Roxburgh, 1999). A multistep loading-unloading cyclic test, shown in Figure 2.7, which is commonly used for characterising the Mullins effect, was also performed. The loading paths were cycles with increasing strain levels at each step, as illustrated in the inset of Figure 2.7. Stress softening can be observed at the reloading path of each step, as the stress required to reach the same strain is lower than in the previous step. Thus, stress softening proceeds once the historical maximum strain level increases.

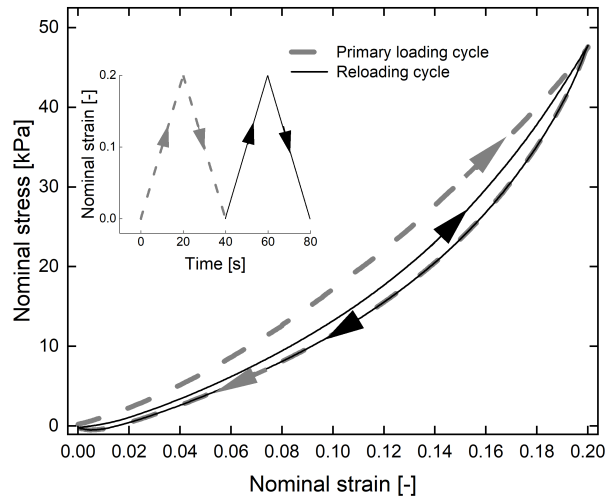


Figure 2.6. Two-cycle loading-unloading tests at the strain level of 0.2 on the starch hydrogel prepared under the benchmark condition.

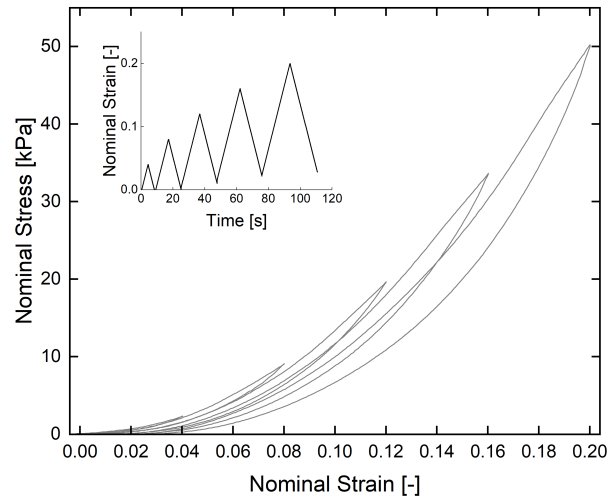


Figure 2.7. A multistep loading-unloading test on starch hydrogels prepared under the benchmark condition. The loading-unloading path was performed with increasing strain levels as shown in the inset.

The stress-softening behaviour becomes more pronounced with increasing maximum strain history. To verify this, two-cycle loading-unloading tests with varying strain levels were performed on starch hydrogels prepared under the benchmark condition. The two cycles are plotted separately. The first (primary) loading-unloading cycles for specimens from #1 to #4, loaded to different maximum nominal strains of 0.20, 0.16, 0.12, and 0.08, respectively, are shown in Figure 2.8(a). Immediately after each primary cycle, a second (reloading) cycle was applied to the same specimen at a strain level equal to or lower than its primary loading. The reloading curves at 0.08 strain are presented in Figure 2.8(b). Reloading curves at 0.04, 0.16, and 0.20 strain were also obtained, and these data were used to construct Figure 2.8(c), discussed later. Figure 2.8(b) shows that as the maximum strain level of the primary loading increases, the stress level at the reloading cycle decreases, indicating more pronounced stress softening. As mentioned

in [Section 2.1](#), stress softening is a typical behaviour of a particle-reinforced polymer (Diani et al., 2009). This behaviour is found to be caused by the detachment or breakdown of the particles from the polymer network. Upon loading, the polymer network observed in [Figure 2.2](#) deforms and provides the basic elasticity, while the particles provide reinforcement. However, once the particles detach from the network, the reinforcement is lost, leading to stress softening. A larger historical maximum strain leads to more intense detachment and, therefore, a weaker stress response during reloading (Li et al., 2019). Stress softening is also observed in some natural rubbers and is related to crystallinity (Diani et al., 2009). Similarly, in the case of the starch hydrogel, the crystallites serve as particle reinforcement, and the corresponding stress softening results from their detachment or breakage. Note that [Figure 2.8\(a\)](#) and [Figure 2.8\(b\)](#) show the error bands of the stress-strain curves, which are the standard deviations of the stress-strain curves of the five repeated tests.

Once stress softening occurs, the stress level does not recover to its original level, leading to a decrease in dissipation during reloading cycles compared to the first cycle. The dissipation that remained in the reloading cycles is an indicator of the viscoelasticity of the material. [Figure 2.8\(c\)](#) illustrates the dissipation energy density levels with respect to different historical maximum strains. Here, each legend symbol represents a different reloading strain level, among which the circle symbols (emphasised in a box) represent the strain of 0.08 obtained from [Figure 2.8\(b\)](#). It can be seen that at a specific reloading strain, the dissipation energy density during reloading cycles remains stable, regardless of the historical maximum strain levels reached in the primary loading cycles. Although the stress level decreases due to stress softening (pseudoelasticity), viscoelasticity remains stable, indicating that viscoelasticity and pseudoelasticity (stress softening) are independent responses. As mentioned in [Section 2.1](#), viscoelasticity arises from imperfections in the polymer network, such as dangling chains and solvated chain fractions, which depend on the level of crosslinking. It can be inferred that the density of crosslinks is influenced by gelatinisation but is not affected by the change in the maximum historical strain. Here, we argue that the dissipation during the primary loading cycle is caused by both stress softening and viscoelasticity ([Figure 2.8\(a\)](#)), whereas the dissipation during the reloading cycle is mainly caused by viscoelasticity ([Figure 2.8\(b\)](#)). Therefore, the viscoelastic dissipation is calculated as the enclosed area of the reloading cycle, and the stress softening dissipation is obtained by subtracting the enclosed area

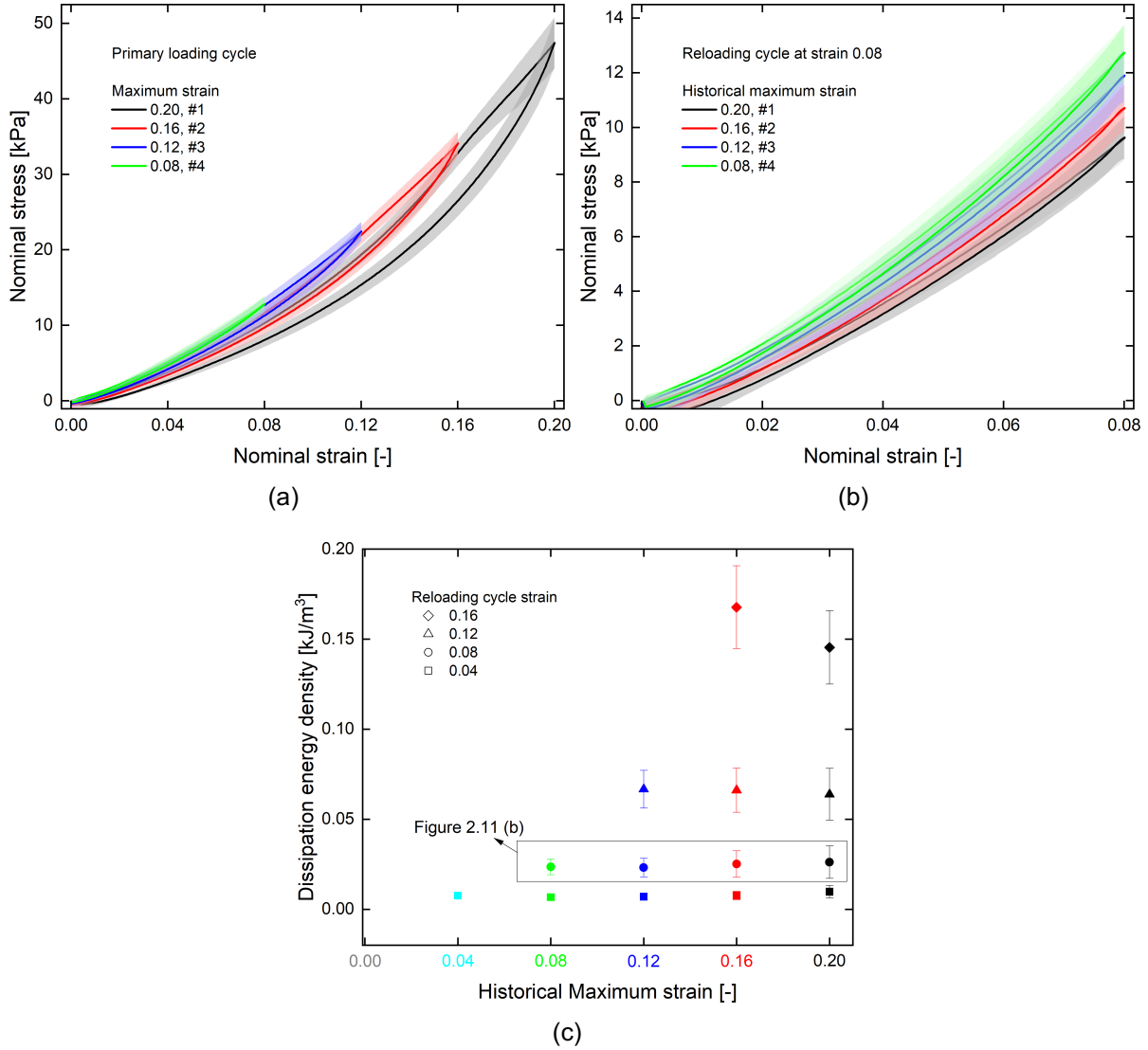


Figure 2.8. Two-cycle loading-unloading tests on starch hydrogels prepared under the benchmark condition. (a) The primary loadings (the first cycles) of specimens #1 to #4 at maximum strain levels of 0.20, 0.16, 0.12, and 0.08, respectively. (b) The reloadings (the second cycles) of specimens #1 to #4 at the same strain level of 0.08. (c) Dissipation energy density of the reloading cycles with respect to the historical maximum strain reached in primary loading cycles. Reloading strain levels are at 0.04, 0.08 ((b)), 0.16, and 0.2. Note that stress-strain curves of reloading at strain levels of 0.04, 0.16, and 0.2 are not shown.

of the reloading cycle from that of the primary loading cycle, i.e.,

$$D_{\text{int}}^{\text{neq}} = \int_{\Gamma_2} P d\varepsilon, \quad D_{\text{int}}^{\text{peq}} = \int_{\Gamma_1} P d\varepsilon - \int_{\Gamma_2} P d\varepsilon \quad (2.3)$$

where $D_{\text{int}}^{\text{neq}}$ and $D_{\text{int}}^{\text{peq}}$ are the viscoelastic dissipation energy density (also called non-equilibrium dissipation) and pseudoelastic dissipation (also called pseudo-equilibrium dissipation or stress softening dissipation), respectively, Γ_1 and Γ_2 are the loading-unloading paths of the primary loading cycle and the reloading cycle, respectively.

Note that the hyper-pseudoelastic-viscoelastic response discussed above is caused by the polymer network structure of the starch hydrogel, and therefore can be altered during enzymatic hydrolysis, which will be addressed in [Chapter 3](#). In addition, although the starch hydrogels may also possess poroelastic properties, as shown in [Figure 2.2](#), this occurs at a much longer timescale (several hours) than the experiments we considered here (around two minutes). This is because the water in the starch hydrogel after gelatinisation is bound more strongly to the starch molecules compared to free water (Lv et al., [2011](#)). It is also observed that water absorption and expansion are not evident during a compression test, as discussed in [Section 2.5.6](#). Therefore, poroelasticity is not investigated in this study.

2.5.3 Rate dependence and temperature dependence

For viscoelastic polymeric materials, rate and temperature dependence are often observed. In this section, the rate dependence and temperature dependence of the starch hydrogel are investigated. Compression tests were performed on hydrogel specimens at 5°C, 20°C, 37°C, 50°C, and 60°C, with other conditions identical to the benchmark condition. Specimens were stored at the target temperatures for 1 hour to ensure a homogeneous temperature field within the samples. These temperatures correspond to the range of temperatures for food storage and human consumption in daily life, such as in a domestic refrigerator (around 5°C), in an ambient environment (20°C), within the human body (37°C), or just after cooking (50 and 60°C). The results are shown in [Figure 2.9](#). It is shown that the overall stress level and the dissipation energy density of both cycles decrease with temperature, as shown by the area in the loading-unloading cycle. The results indicate that the starch hydrogel is temperature-dependent. This temperature dependence is typically considered an entropic-elastic property of polymer materials (Holzapfel & Simo, [1996](#)). As the

temperature decreases, the network entropy decreases, leading to fewer possible chain configurations and, consequently, a stiffer response.

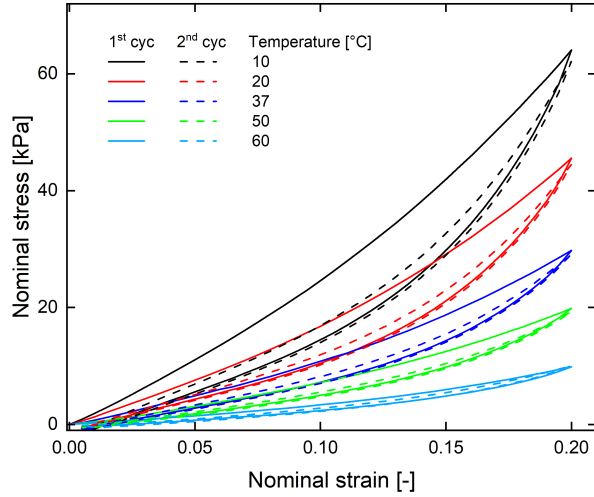


Figure 2.9. Two-cycle loading-unloading tests on starch hydrogels at different temperatures.

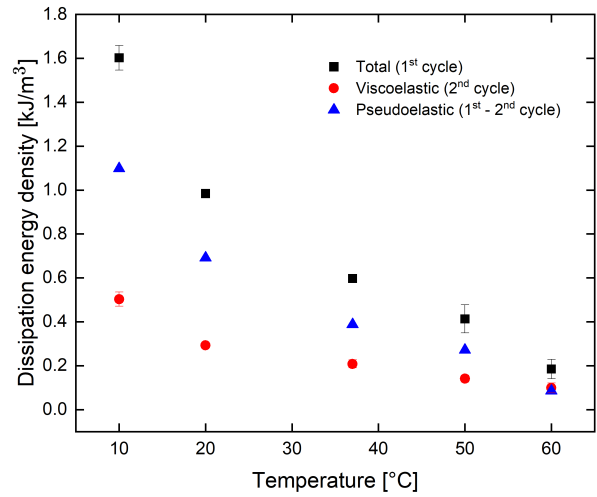


Figure 2.10. Dissipation energy density of compression tests at a temperature of 20 °C.

The dissipation energy density was also calculated following Equation 2.3 to separate the viscoelastic dissipation and pseudoelastic dissipation at different temperatures, as shown in Figure 2.10. It is shown that both types of dissipation decrease with temperature. However, an interesting phenomenon is observed: the pseudoelastic dissipation decreases more rapidly than the viscoelastic dissipation as temperature increases, which may be due to a decrease in crystallite content at higher temperatures, driven by melting.

The fracture behaviour of the starch hydrogels at different temperatures was also investigated using monotonic loading tests, as shown in Figure 2.11. It is shown that the ultimate strain, the strain when failure occurs (corresponding to the maximum stress), increases slightly with temperature, while strength, the maximum stress before failure, decreases with temperature, as illustrated in Figure 2.11(a) and Figure 2.11(b), respectively. The failure points, the points in the stress-strain space where the material fails, are plotted in Figure 2.11(c) with dotted curves corresponding to the monotonic loading paths at the same temperatures.

The strain rate dependence of the starch hydrogel was investigated by compression tests performed at different strain rates of 0.0002 /s, 0.001 /s, 0.002 /s, 0.01 /s, and 0.02 /s, with other conditions the same as the benchmark condition. The results are shown in Figure 2.12. The loading-unloading curves do not show an evident trend with varying

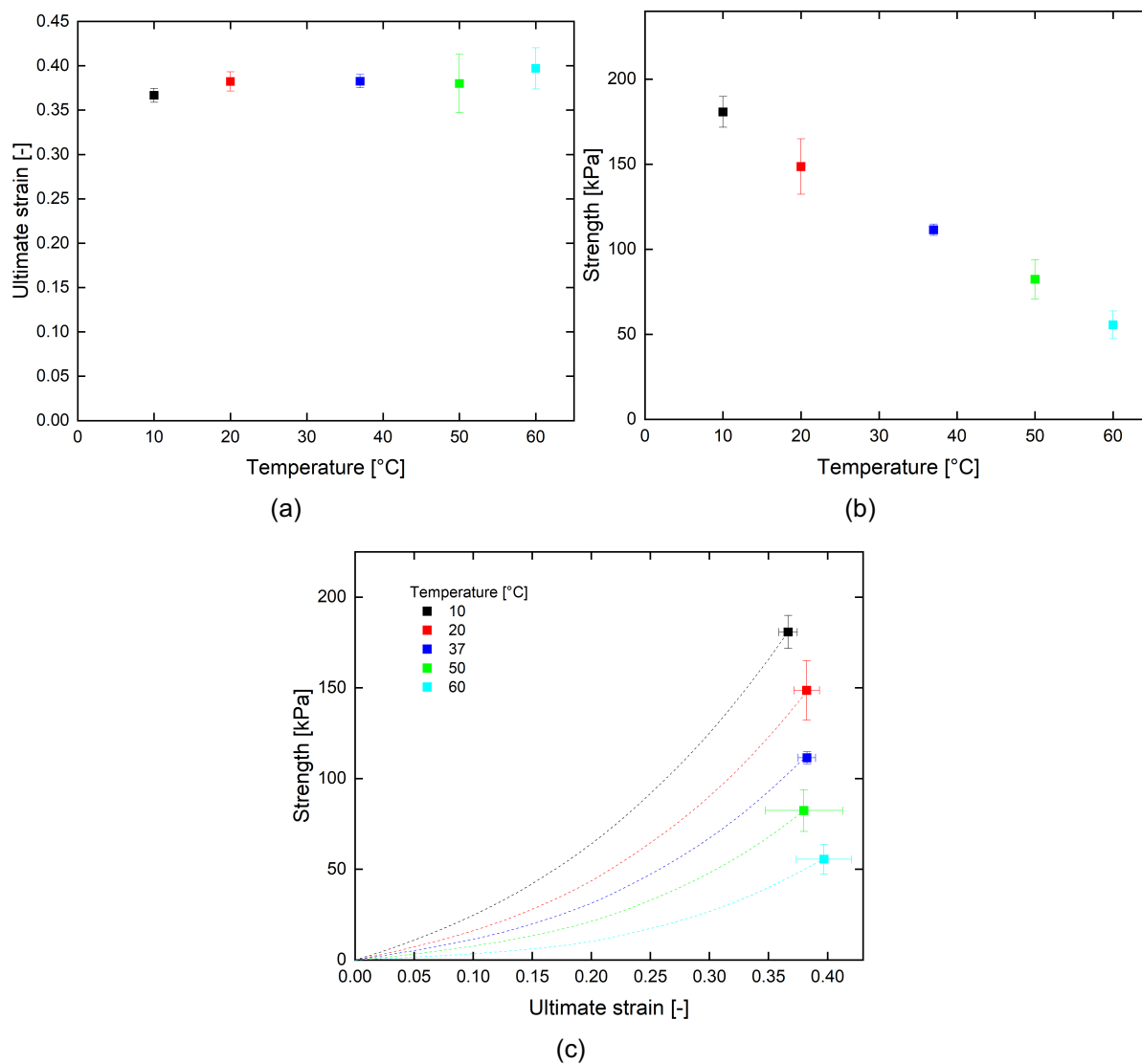


Figure 2.11. Fracture behaviour of starch hydrogels at different temperatures. (a) Ultimate strain, (b) strength, and (c) failure point, with example monotonic loading curves at corresponding temperatures.

strain rates, indicating that the rate dependence is less significant than the temperature dependence, consistent with the findings of Gamonpilas et al. (2009b). However, hysteresis was still observed in Figure 2.12, and the slight residual strain was not permanent, indicating that viscoelastic behaviour remains.

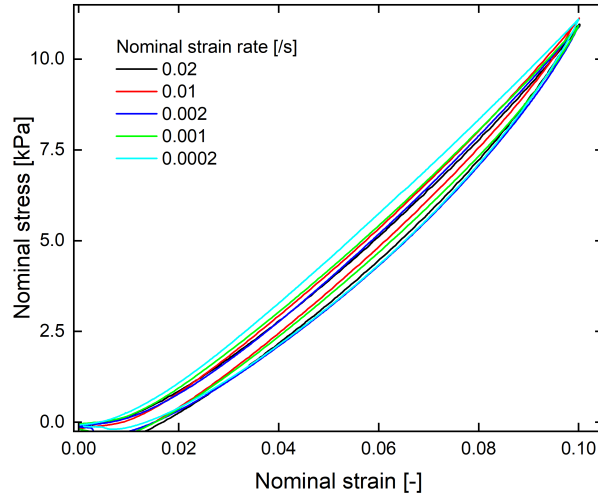


Figure 2.12. Loading-unloading tests on starch hydrogels at different strain rates.

It is noteworthy that Gamonpilas et al. (2009b) further observed, by contrast, that the failure points were strain-rate dependent, with both ultimate strain and strength decreasing with higher strain rate. The rate dependence of the failure point could be due to the stress wave effect.

2.5.4 Dependence of mechanical properties on the DOG

Heating the suspension of starch powder induces gelatinisation, and longer heating times generally result in a higher DOG. To investigate the influence of heating time on the DOG, compression tests were performed on specimens prepared with different heating times during the gelatinisation process. The timing was initiated when the beaker containing the starch suspension was placed in a 90°C water bath, and the heating time was recorded until the liquid mixture was injected from the beaker into the specimen mould using a heated syringe. As mentioned in Section 2.1.1.1, the initially opaque liquid mixture gradually became completely transparent, which was typically observed after approximately 5 minutes.

The target heating times were spaced at 15-second intervals from 1.5 to 5 minutes, 1-minute intervals from 5 to 10 minutes, and 10-minute intervals after 20 minutes. Before 1.5 minutes, the starch granules were not sufficiently gelatinised. As a result, insufficient

crosslinking prevented the material from retaining its shape and forming a solid hydrogel. Therefore, no compression tests were performed for heating times shorter than 1.5 minutes. As the transfer of the mixture into the moulds was performed manually and required time, the actual heating times deviated slightly from the target values. These slight deviations could lead to differences in the DOG and, consequently, in the mechanical properties. Therefore, the actual heating time of each specimen was recorded at the moment the mixture finished being injected into the moulds. Because the manual transfer introduced slight but unavoidable deviations from the target heating times, statistical averaging at a specific heating time was not practical. Instead, the entire heating procedure, which lasted 1 hour, was repeated 5 times. In each repeat, the mixture was injected at the same set of target heating times, while the actual heating times were recorded and allowed to vary naturally. All individual data points are presented in the following figures to show the scattering arising from these variations and to illustrate the overall trend of mechanical properties with heating time.

It should also be noted that the gelatinisation rate depended on the mixing efficiency. Magnetic stirring was found to be insufficient compared with manual stirring using a spatula. Hence, manual stirring was employed in all experiments to ensure adequate mixing and uniform heating of the suspension during gelatinisation. However, manual stirring introduced slight variations in mixing intensity among specimens, which may also have affected the DOG and the mechanical response.

Two-cycle loading-unloading tests were performed on specimens prepared with different heating times, as shown in [Figure 2.13](#), while all other conditions were kept identical to the benchmark. [Figure 2.13\(a\)](#) presents the collective stress-strain curves (only the first cycles of the two-cycle tests are shown), with colours corresponding to the heating times indicated by the colour scale. The blue curves, representing heating times below 3 minutes, exhibit relatively low stress levels but significant variations, reflecting differences in the DOG. The green curves, corresponding to heating times of 3–5 minutes, show a moderate increase in stress levels, whereas the yellow and red curves, corresponding to heating times above 5 minutes, display slightly higher, but stabilised, stress responses. [Figure 2.13\(b\)](#) presents selected results for further illustration. It can be observed that from 2 to 3 minutes (purple, yellow, cyan, and green curves), the stress levels increase significantly, whereas at 5 minutes and beyond (blue, red, and black curves), the curves nearly overlap, indicating that the DOG has stabilised. These observations suggest that the gelatinisation process is almost complete after approximately 5 minutes of heating at 90°C, beyond which further increases in the DOG

are minimal. This finding is consistent with the optical microscopy observations in [Section 2.3](#) and with the previously described sample preparation procedure, where the suspension became completely transparent after around 5 minutes of heating.

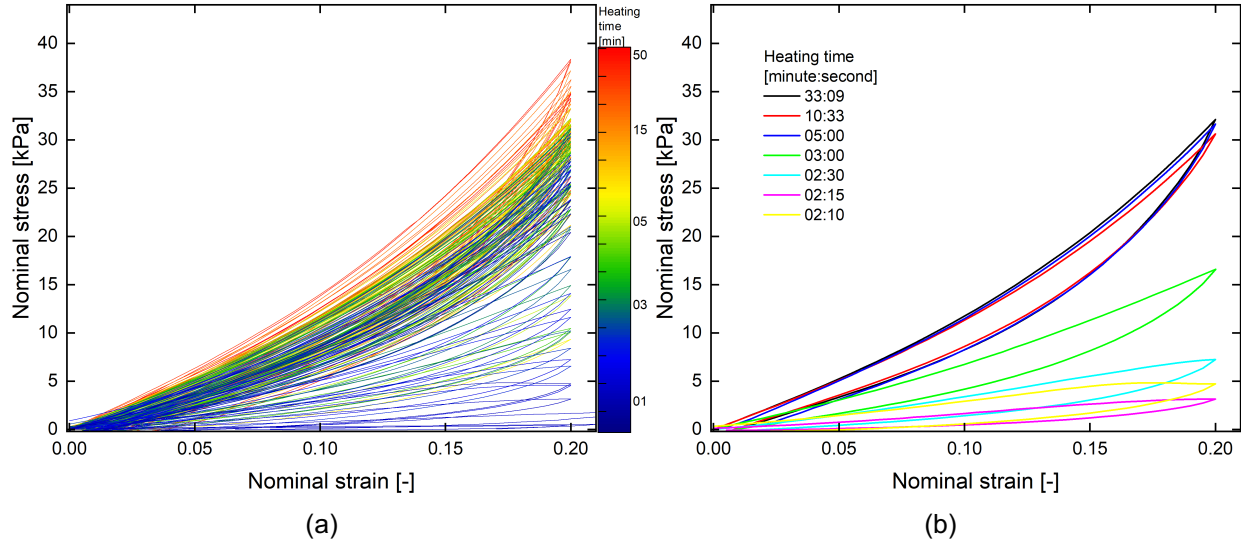


Figure 2.13. Loading-unloading compression test of starch hydrogels with different heating times. Only the first cycles of the two-cycle tests are shown. (b) Collective results for heating times ranging from 1.5 minutes to 50 minutes, shown on the colour scale. (a) Selected results with heating time, where the colours only distinguish individual experiments.

In addition, the dissipation energy density of both cycles was calculated and is presented in [Figure 2.14](#). It can be observed that both the viscoelastic dissipation (second cycle) and the pseudoelastic dissipation (first cycle minus second cycle) increase rapidly with heating time up to approximately 5 minutes (dashed vertical line in [Figure 2.14](#)), after which they stabilise with a slight increase. This trend aligns with the stress-strain curve observations in [Figure 2.13](#), indicating that the DOG increases with heating time until around 5 minutes, beyond which it remains relatively constant.

During gelatinisation, the starch granule swells and the crystallites are melted down, as mentioned in [Section 2.4.1](#). The granule structure is disrupted, and amylose and amylopectin leach out, allowing hydrogen bonds to form between water molecules and polymer chains. A stronger DOG means a more sufficient release of the polymer chains, allowing for more hydrogen bonding with water molecules. This interaction results in a more robust network with a higher density of crosslinks, leading to greater hyperelasticity. In addition, more released polymer chains allow for a higher density of dangling chains and solvated chain fractions, leading to greater viscoelastic dissipation

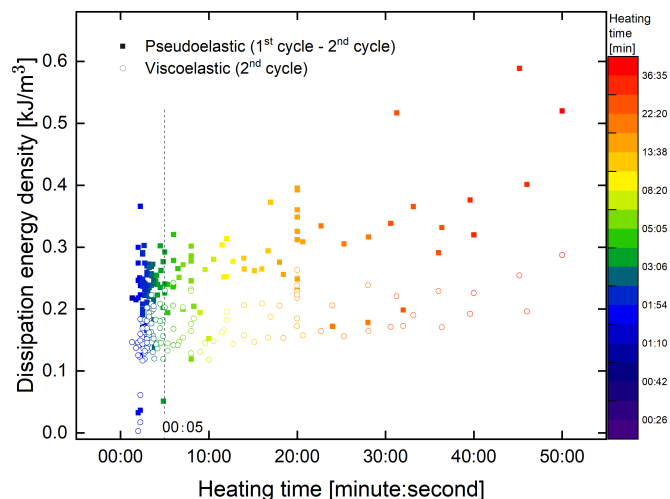


Figure 2.14. Viscoelastic dissipation energy density (second cycle) and the pseudoelastic dissipation energy density (first cycle minus second cycle). The total dissipation energy density (first cycle) is not shown for clarity. The colour scale is the same as Figure 2.13(a).

and a higher concentration of crystallites formed during retrogradation, resulting in stronger stress softening. This process explains the higher overall stress levels and primary loading dissipation observed at higher DOG values, as shown in Figure 2.13, and strong dissipation energy density in Figure 2.14.

The fracture behaviour of starch hydrogels with different heating times was also investigated through monotonic loading tests, as shown in Figure 2.15. Note that the colour map indicating the heating time of Figure 2.15 is also identical to that of Figure 2.13(a). As illustrated in Figure 2.15(b), the strength increases with heating time up to approximately 5 minutes, after which it stabilises. This trend is expected, as a higher degree of DOG results in a stronger network structure. The ultimate strain (see Figure 2.15(a) and Figure 2.15(c)) firstly decreases between 1.5 and 2 minutes (e.g., data points within the dashed box in Figure 2.15(c)), followed by an increase until about 5 minutes, beyond which it remains relatively constant. As discussed earlier, before 1.5 minutes of heating, the starch granules are insufficiently gelatinised, leading to an inadequate network unable to retain its shape. At this stage, the material behaves as a highly viscous liquid. After approximately 1.5 minutes, a network structure begins to form. Still, it remains incomplete, and the hydrogel exhibits a plastic-like behaviour characterised by a large ultimate strain and significant permanent deformation due to plastic flow. With an increasing DOG, plastic flow becomes restricted while the network structure remains relatively weak, and therefore, the ultimate strain decreases. As heating continues, the ultimate strain increases again as the network structure becomes more complete, allowing it to sustain larger deformations before failure. The failure

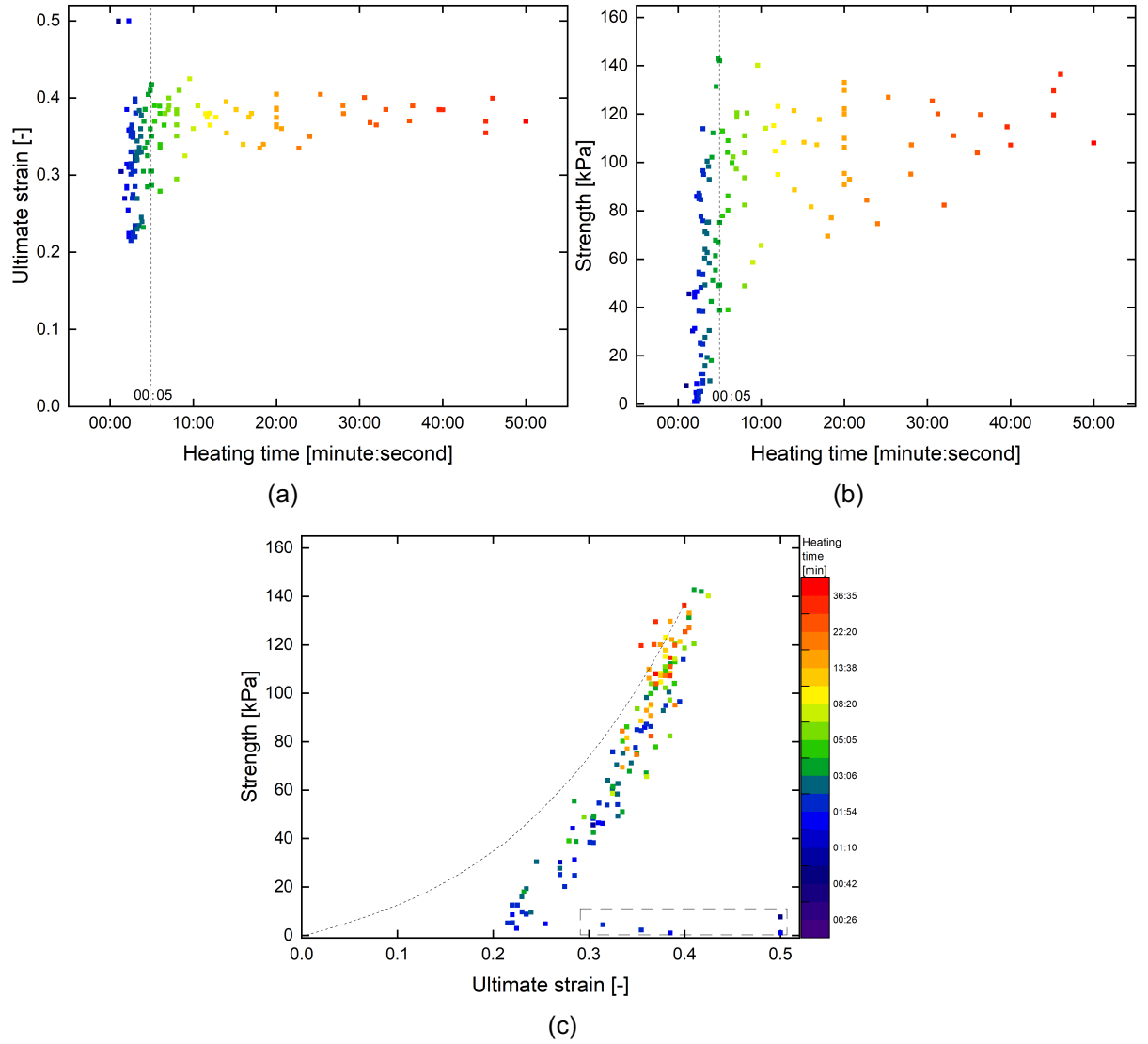


Figure 2.15. The failure behaviour of starch hydrogels with different heating times. (a) The ultimate strain, (b) strength, and (c) failure point, with an example of a monotonic loading curve with a heating time of 45 minutes. The colour scale indicating heating time is the same as that in Figure 2.13(a).

points in the stress-strain space are shown in [Figure 2.15\(c\)](#), together with an example stress-strain curve indicated by a dotted line. This trend is consistent with the previous observations of the stress-strain behaviour and the dissipated energy density, further confirming that the DOG increases with heating time up to approximately 5 minutes, beyond which it remains nearly constant.

2.5.5 Dependence of mechanical properties on the DOR

When the fully gelatinised starch suspension is injected into the mould, the initially transparent hydrogel gradually becomes opaque. In the meantime, gelation occurred as the hydrogel solidified. This process is attributed to retrogradation. The DOR was controlled by both the storage time and storage temperature and was characterised by the DSC method as discussed in the previous section. The change in mechanical properties with the DOR is investigated in this section. Two-cycle loading-unloading tests were performed on starch hydrogels with storage periods ranging from 0.1 hours (6 minutes) to 768 hours (32 days, around 1 month), with other conditions identical to the benchmark condition. The stress-strain curves in [Figure 2.16](#) show that the overall stress increases with a longer storage time.

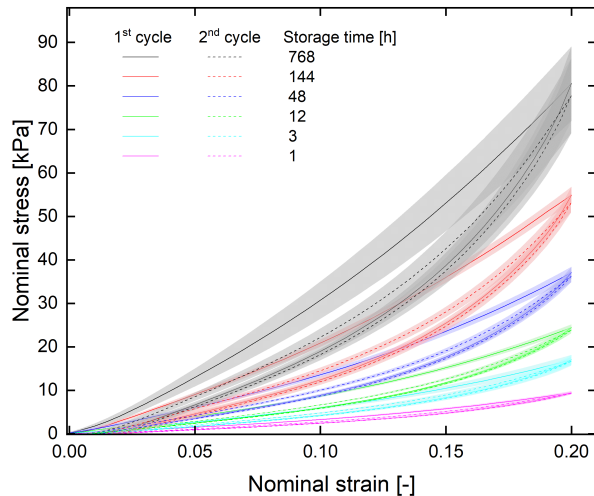


Figure 2.16. Stress-strain curves with error bands of two-cycle loading-unloading tests on starch hydrogels with different storage times.

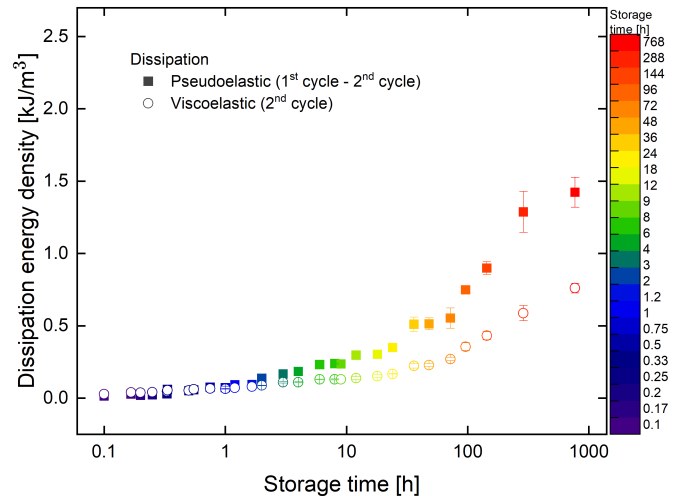


Figure 2.17. Dissipation energy density of compression tests with respect to storage time. The colour scale indicates the storage times.

The values of the dissipation energy density are further depicted in [Figure 2.17](#) with respect to storage time on a logarithmic scale. It is found that both the viscoelastic and pseudoelastic dissipation increase with increasing storage time. As mentioned in

Section 2.4, the polymer chains recrystallise with time during retrogradation. As the crystallites serve as filler reinforcement of the polymer network, the overall stress level and the pseudoelastic dissipation increase with storage time. Note that the increase in stress can also be attributed to syneresis (Rumpold, 2005), in which starch chains interact strongly with water molecules, leading to a more compact polymer network, a higher density of crosslinks in the hydrogel, and, consequently, a stronger stress response. With this more compact network, the viscoelastic dissipation also increases with storage time.

An increase in brittleness of the starch hydrogel with increasing storage time is also observed in the monotonic loading tests, as shown in Figure 2.18. The strength increases with storage time, as illustrated in Figure 2.18(b), while the ultimate strain illustrated in Figure 2.18(a) decrease with storage time. This indicates that the starch hydrogels were reinforced by the crystallites formed during retrogradation, whereas their ductility decreased due to internal stress concentration around the crystallites. The failure points in the stress-strain space are shown in Figure 2.18(c), with the colour scale indicating storage time, and an example stress-strain curve (dotted line) shows that the failure point falls within a linear envelope.

We further investigated the mechanical properties of the starch hydrogel stored at different temperatures, as illustrated in Figure 2.19. It is also observed that the decrease in storage temperature enhances the retrogradation of the starch hydrogel, similar to the effect of an increase in storage time in Figure 2.16. The overall stress levels, dissipation of the primary loading cycles, and dissipation of the reloading cycles increase at a lower storage temperature. Since crystallite formation is an energy-releasing process, lower temperatures facilitate this process, thereby accelerating retrogradation (Aguirre et al., 2011; Lovegrove et al., 2017; Wang et al., 2015).

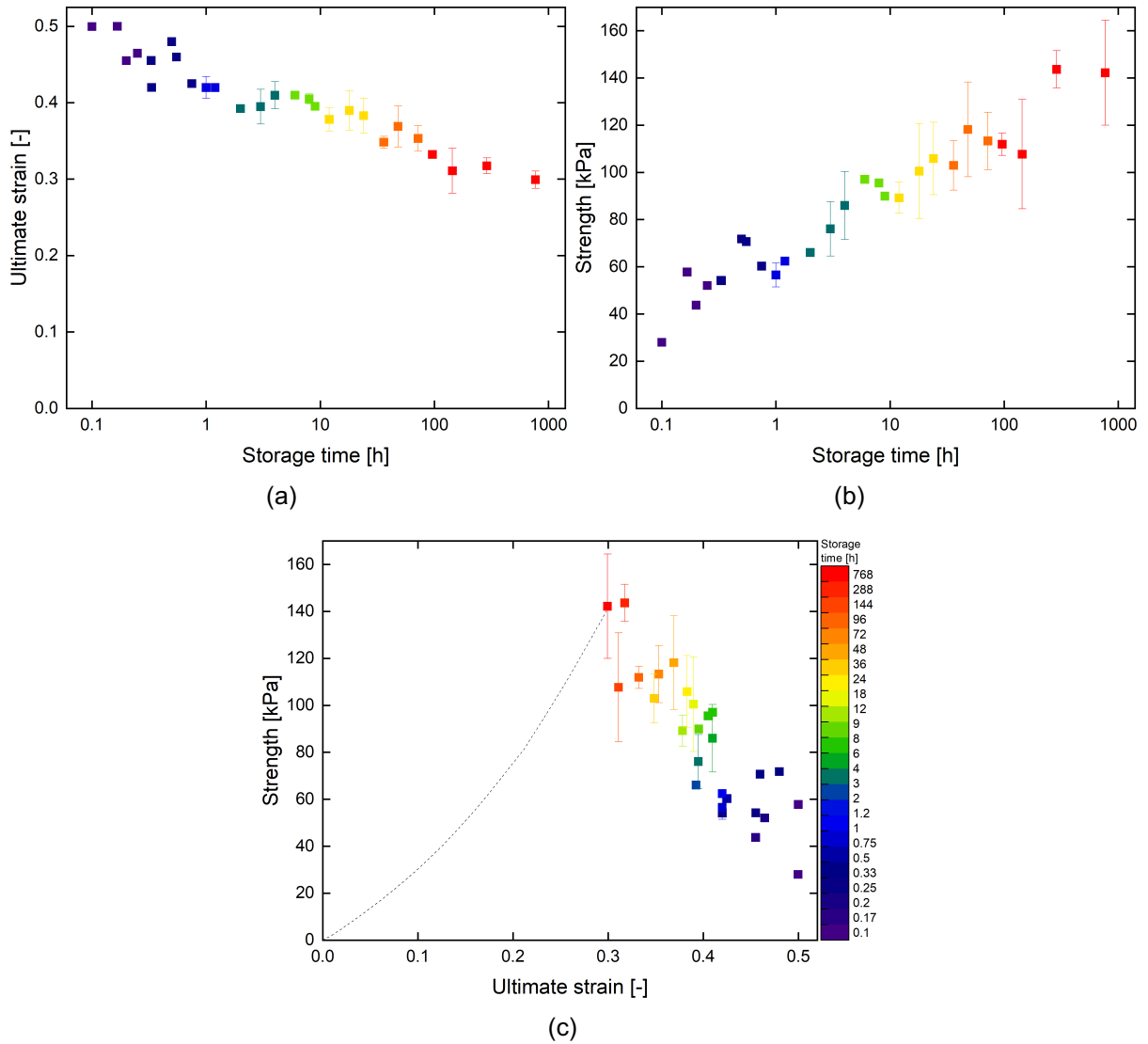


Figure 2.18. The failure behaviour of starch hydrogels with different storage times. (a) The ultimate strain, (b) strength, and (c) failure point (with an example of a monotonic loading curve with a storage time of 768 hours). The colour scale indicating storage time in (c) is the same as that in Figure 2.17.

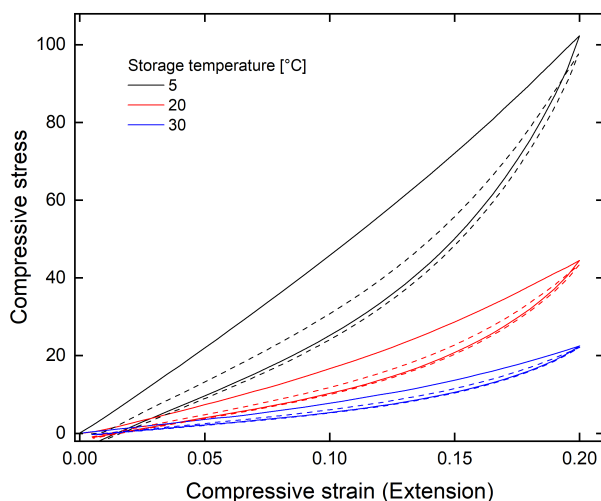


Figure 2.19. Two-cycle loading-unloading tests at different storage temperatures.

2.5.6 Dependence of mechanical properties on water content

During the preparation of starch hydrogels, as in common cooking processes, variations in water content can markedly affect the final texture of the product, as water is a major constituent of hydrogel materials. It is therefore natural to expect that the moisture content would influence the mechanical properties of starch hydrogels. To investigate this effect, compression tests were performed on starch hydrogels with different moisture contents (starch mass fractions), including 50% (50%), 60% (40%), 70% (30%), and 80% (20%) w/w, achieved by adjusting the initial water-to-starch powder mass ratio during sample preparation. Note that moisture contents below 50% led to incomplete gelatinisation and early gelation during heating, producing inhomogeneous samples. Conversely, for moisture contents of around 90% or higher, the polymer chain density was too low to form a stable solid hydrogel, and the material remained in a highly viscous liquid state. Therefore, no tests were performed for moisture contents below 50% or above 80%. To allow for retrogradation, samples were stored for 2, 24, and 48 hours before testing.

Figure 2.20 presents the stress-strain curves of starch hydrogels with different moisture contents at storage times of 48 hours (Figure 2.20(a)) and 2 hours (Figure 2.20(b)). It can be observed that the overall stress level decreases with increasing moisture content. A higher moisture content results in a lower density of polymer chains per unit volume, leading to a less dense network structure with fewer crosslinks, thereby reducing the overall stress response. This finding is consistent with the statement that water acts as a plasticiser, softening starch in starch hydrogels (BeMiller, 2011). Figure 2.21 further illustrates the stress-strain curves for starch hydrogels with different storage times, with

fixed moisture contents of 50% (Figure 2.21(a)) and 60% (Figure 2.21(b)), respectively. As expected, for each moisture content, the stress level and dissipation increase with storage time, consistent with the finding from the 80% hydrogels in Section 2.5.5.

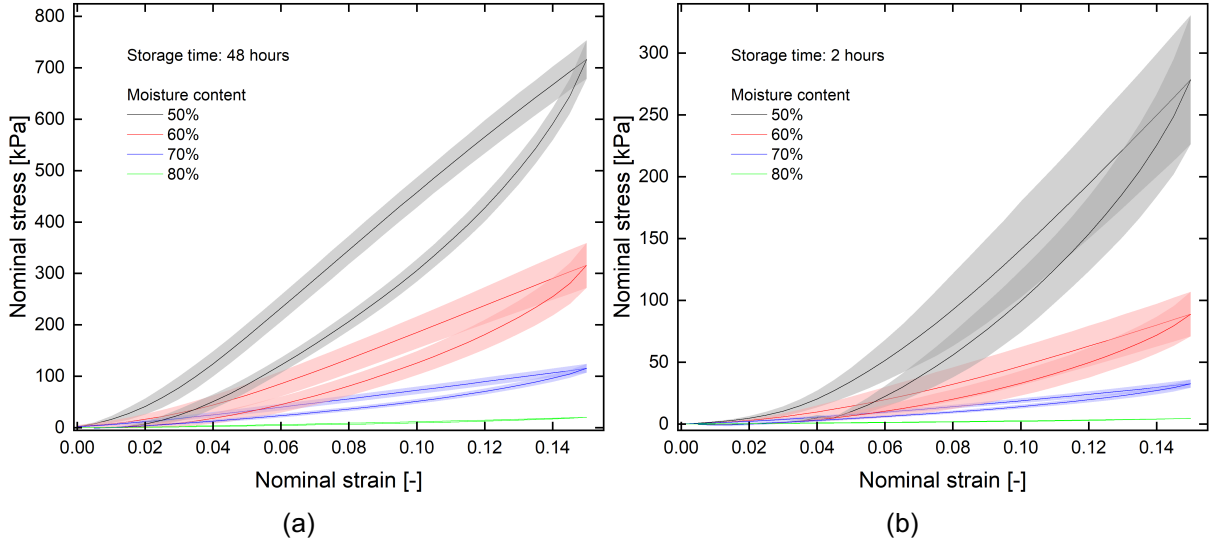


Figure 2.20. Cyclic compression test for starch hydrogel of various moisture content and with storage times of (a) 48 hours and (b) 1 hour.

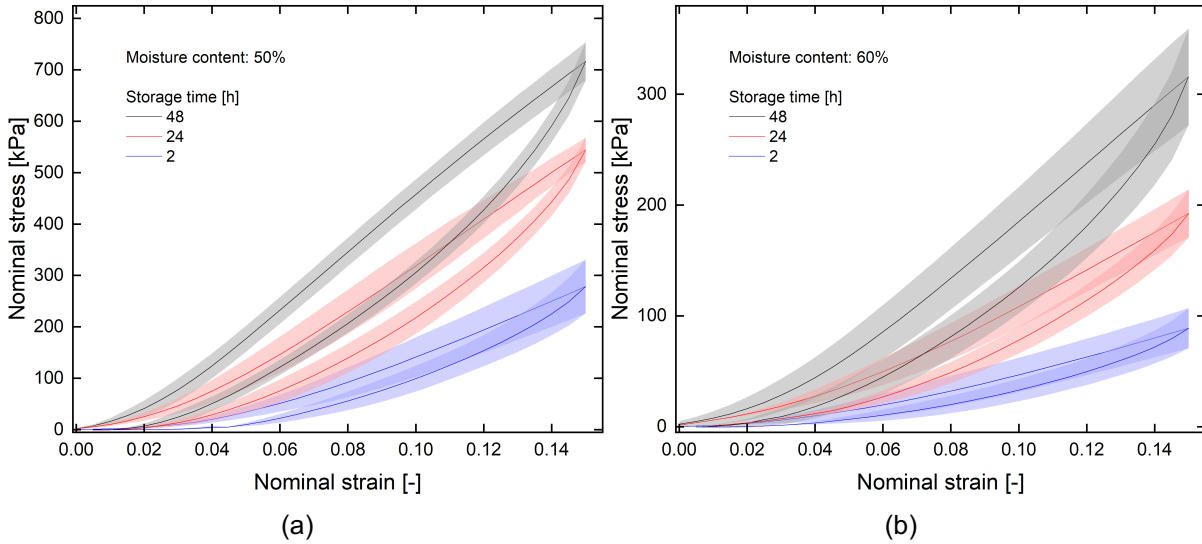


Figure 2.21. Cyclic compression test for starch hydrogel at various storage times with moisture content of (a) 50%, and (b) 60%.

The fracture behaviour in monotonic loading tests is illustrated in Figure 2.22. It is shown that the ultimate strain (Figure 2.22(a)) decreases with decreasing moisture content, whereas strength (Figure 2.22(b)) increases with decreasing moisture content, indicating that starch hydrogels with a lower moisture content are more brittle as the chain density

increases. The failure points in the stress-strain space are shown in Figure 2.22(c) with an example stress-strain curve indicated by a dotted line. Furthermore, for each moisture content, the ultimate strain decreases with storage time, while the strength increases with storage time, consistent with the findings in Section 2.5.5 that retrogradation toughens the starch hydrogel but reduces its ductility.

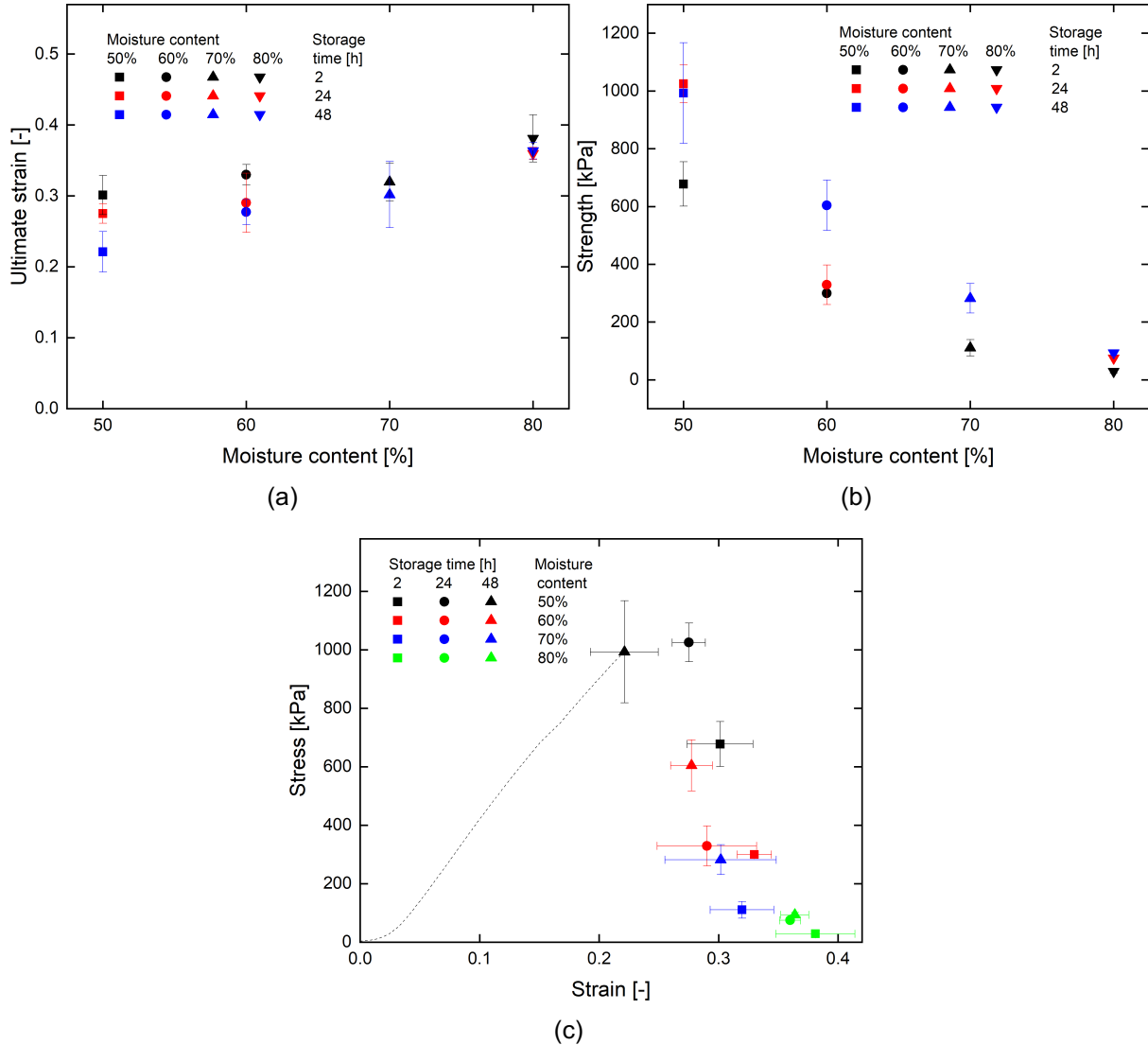


Figure 2.22. Failure behaviour of starch hydrogels with different moisture contents. (a) The ultimate strain, (b) strength, and (c) failure point (with an example of a monotonic loading curve of 50% moisture content with a storage time of 48 hours).

As mentioned in Section 2.2, the sample was stored in a sealed bag because it lost moisture during storage when exposed to air. After gelatinisation by heating and solidification in the sample mould, the starch hydrogel was demoulded and placed on the

balance, exposed to air at room temperature (around 20°C) and a relative humidity of around 50%. The mass of the sample was recorded by the balance against time, as shown in Figure 2.23. It is shown that the mass ratio, defined as the current mass divided by the initial mass, decreases rapidly in the first two hours, then decreases slightly thereafter. As Figure 2.24 shows, the sample lost water from the surface first while the inner part remained hydrated. The loss of water causes shrinkage of the material, and the different moisture loss rates between the surface and inner part lead to non-uniform shrinkage and shear strain. Therefore, along with moisture loss, cracks initiated at the surface and propagated inward. Note that we did not perform relaxation tests to investigate the rate dependence in Section 2.5.3, as the sample would lose moisture during the long period of relaxation tests, leading to a change in the measured mechanical response.

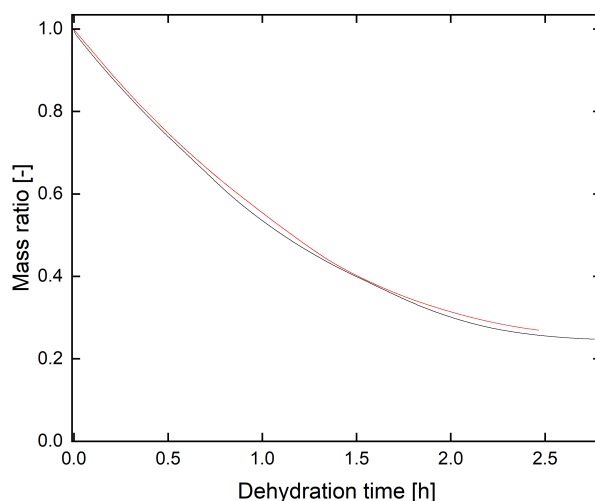


Figure 2.23. Mass ratio of starch hydrogels during the dehydration process (two repeated tests).



Figure 2.24. Image of samples at 2.5 hours of dehydration.

The hydration process was also investigated by immersing the 20% w/w samples stored for 24 hours of retrogradation in a sealed bag into DI water at room temperature (around 20°C). The mass ratio change during the hydration process is shown in Figure 2.25(a).

It is shown that the mass ratio increase is insignificant, and after 30 hours of hydration, it reaches only 1.1. The stress-strain behaviour of the hydrated samples is illustrated in Figure 2.25(b). It is shown that the overall stress level increases slightly with hydration time, within the error bars. This increase could be attributed to retrogradation, so the contribution of swelling of the hydrogel network upon water absorption is not significant. The low absorption capacity may be due to the starch hydrogel initially having a high moisture content of 80% (w/w), and to the network being well crosslinked, which resists further hydration and swelling.

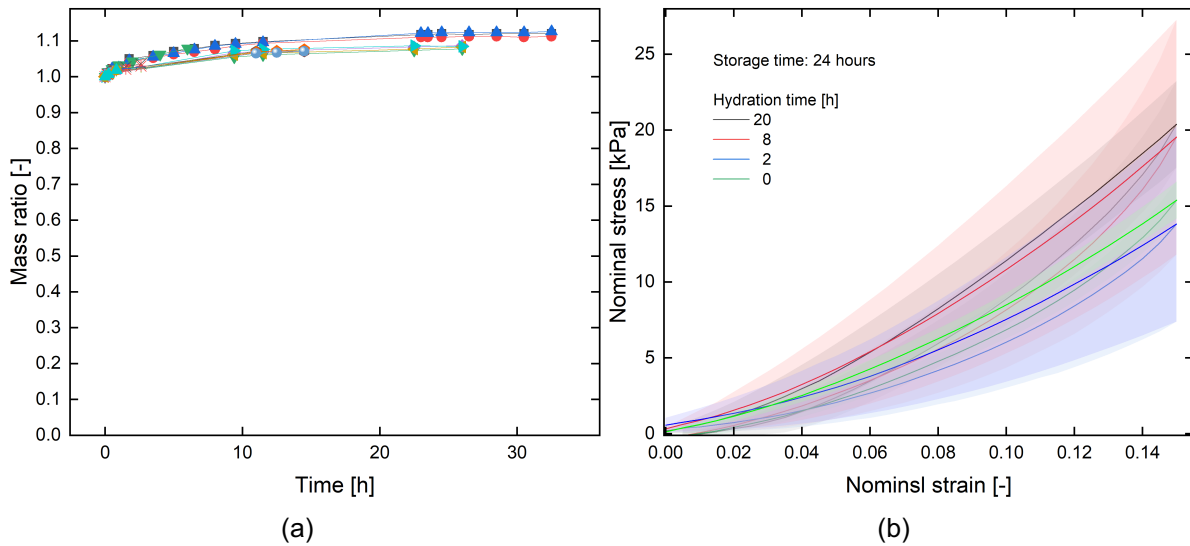


Figure 2.25. Uniaxial compression behaviour of the starch hydrogels under various hydration times. (a) Mass ratio change, in which different colours represent different repeats. (b) stress-strain behaviour.

2.6 Uniaxial tensile tests

2.6.1 Dumbbell sample preparation

In the literature, oat-based bolus samples have demonstrated the presence of tensile and shear stress states (Skamniotis et al., 2019, 2020) during the oral process and the gastric process. Similarly, uniaxial tension and shear tests were also performed to characterise the tensile and shear behaviour of the starch hydrogel. This section focuses on uniaxial tensile tests, while shear tests are presented in Section 2.7. Uniaxial tensile tests were performed using dumbbell specimens loaded monotonically at a strain rate of 0.01 /s until failure, with storage time including 4 hours, 48 hours, and 96 hours, as shown in Figure 2.26. The fully gelatinised 20% w/w hydrogel specimens were moulded

into the dumbbell shape using a silicone mould, with a gauge length of 20 mm, a width of 3 mm in the gauge section, and a thickness of 3 mm. The dumbbell shape was used to mitigate stress concentrations and prevent fractures near the grips. The length-to-width or length-to-thickness ratio is greater than 5 to ensure an uniaxial state during testing. As the sample was in a dumbbell shape, the deformation near the shoulder of the sample would be non-uniform, and therefore, the crosshead displacement cannot be used to obtain accurate strain measurements. Hence, Digital Image Correlation (DIC) analysis was employed (Liao et al., 2019). The specimens were sprayed with a white background and black speckles on the front surface. With the irregular shapes of speckles, the surface displacement can be tracked, and therefore, the strain field during the tests can be measured. Specimens were carefully mounted between two grips, and the length direction was aligned with the loading axis.

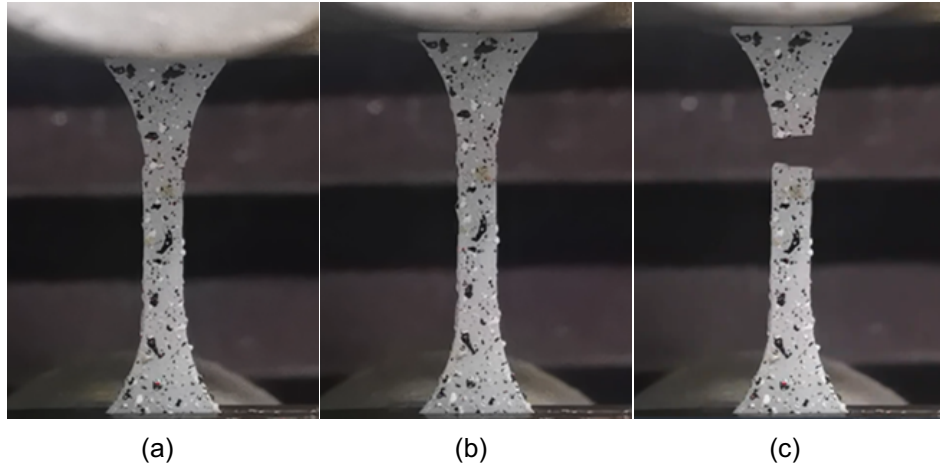


Figure 2.26. Image of a sample for tension tests at (a) the initial state, (b) strain 0.1 and (c) after fracture.

2.6.2 Experimental results of uniaxial tensile tests

The DIC measurement of axial strain ε_X and lateral strain ε_Y at different times is illustrated in Figure 2.27 and Figure 2.28, respectively. It can be observed that the contours of the strain field are not perfectly uniform, as the speckle paint has a different stiffness from the starch hydrogel. In particular, the black speckles are relatively stiffer, leading to less local deformation. As the technique tracks speckle displacements, the overall strain can be measured from the length change between two speckles. For example, in the images of Figure 2.27, the length between two speckles, facet point 1 and facet point 2, is joined to form a line segment. The strain in the axial direction (X direction) is calculated, and the

results are presented on the left of the image. Similarly, the lateral strain in the Y direction is calculated by the length change between facet point 3 and facet point 4, as well as between facet point 5 and facet point 6, as shown on the left of Figure 2.28. Note that using this method, the noise in Y direction strain is stronger than that in X direction strain, as the distance in Y direction is significantly smaller than that in X direction. To reduce the noise, the strain is averaged over multiple line segments (only two were presented in the figures).

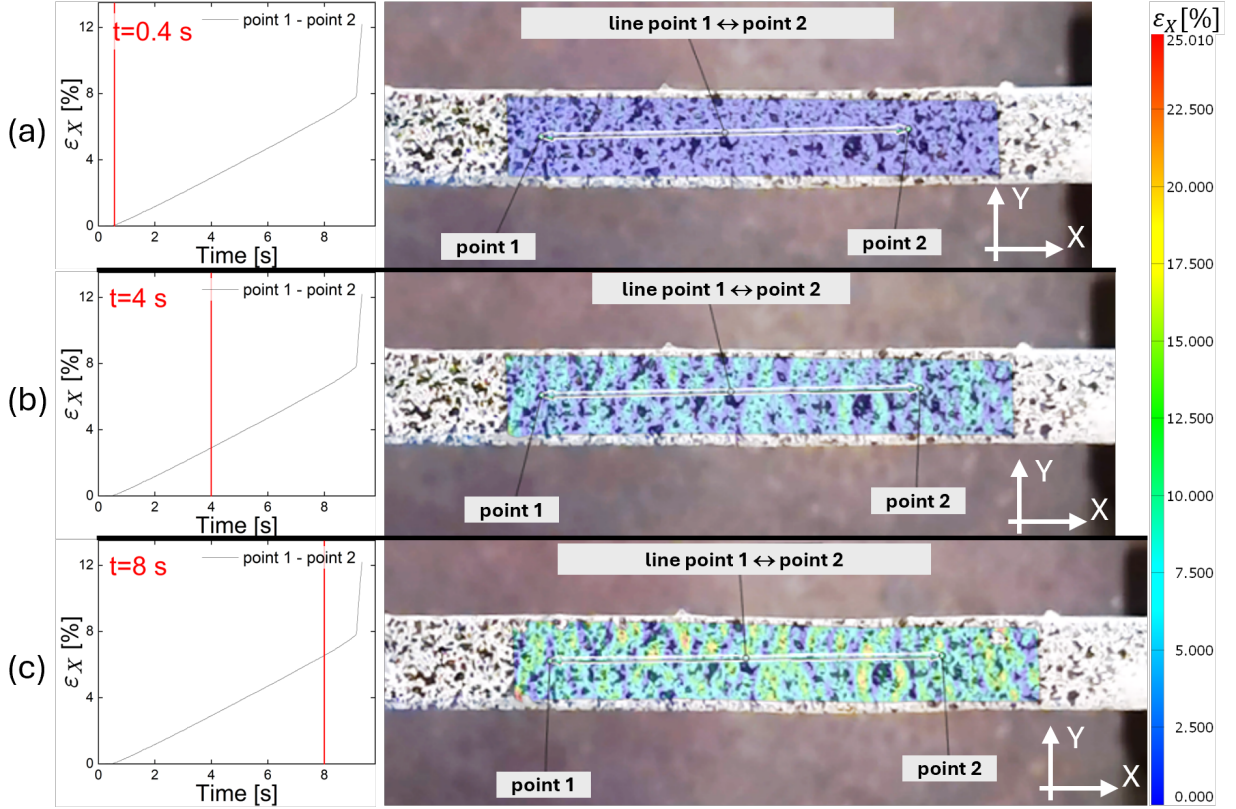


Figure 2.27. DIC measurement of axial strain ε_X of the specimen parallel section at experiment time (a) $t=0.4$ s, (b) $t=4$ s, and (c) $t=8$ s. Note that the vertical loading direction is along the X axis (the image has been rotated horizontally).

Since we obtained both axial and lateral strains from DIC measurements, and knowing that for uniaxial tension, the lateral strains are identical in both lateral directions ($\varepsilon_Y = \varepsilon_Z$), the volumetric strain can be calculated as:

$$\varepsilon_V = \frac{V - V_0}{V_0} = [1 + \varepsilon_X][1 + \varepsilon_Y][1 + \varepsilon_Z] - 1 = [1 + \varepsilon_X][1 + \varepsilon_Y]^2 - 1. \quad (2.4)$$

The volumetric strain measurement results according to DIC analysis are shown in Figure 2.29. It can be observed that the volumetric strain remains close to zero with a

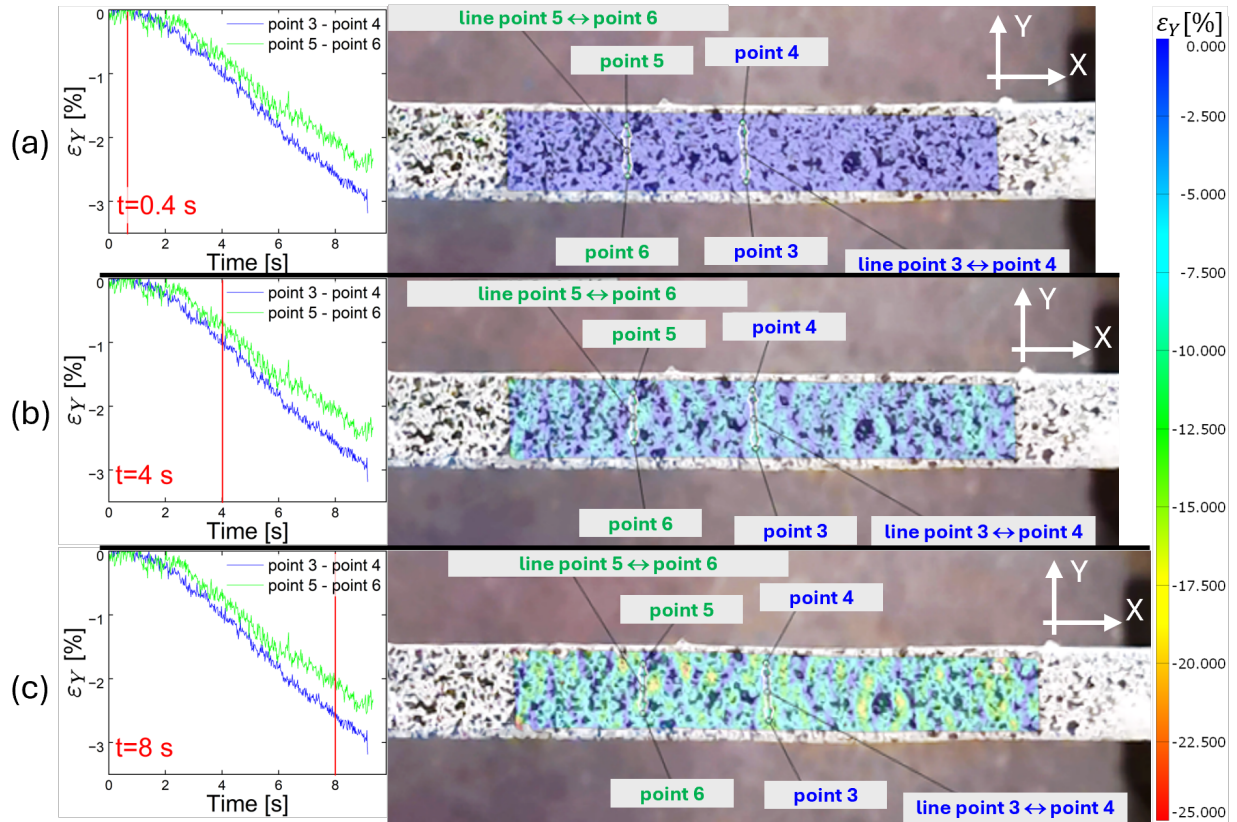


Figure 2.28. DIC measurement of lateral strain ε_Y of the specimen parallel section at experiment time (a) $t=0.4$ s, (b) $t=4$ s, and (c) $t=8$ s. Note that the vertical loading direction is along the X axis (the image has been rotated horizontally).

slight increase throughout the tensile test, indicating that the starch hydrogel behaves nearly incompressible under uniaxial tension.

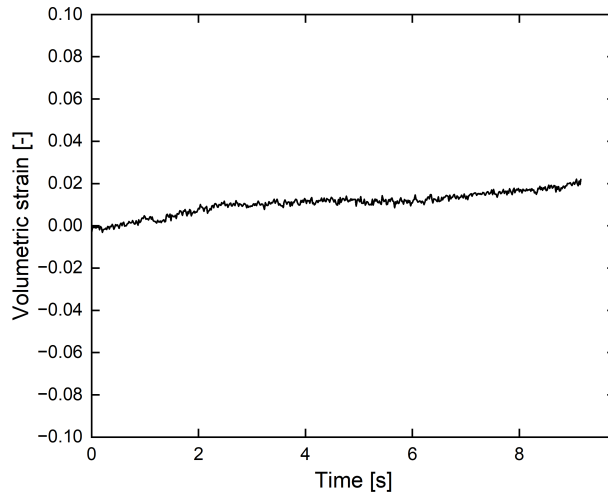


Figure 2.29. Volumetric strain measurement results according to DIC analysis.

Then the stress-strain curves were obtained, using the strain from DIC measurements, as shown in [Figure 2.30](#). The curves are almost linear in all monotonic loadings. The repeated tests are also plotted, showing good reproducibility of the slopes and stress levels, while the failure points are more scattered. Imperfect specimen geometry or imperfect alignment during testing can lead to stress concentrations due to the brittle nature of the starch hydrogel, resulting in variability in failure points. The failure of tension is generally less than the nominal strain of 0.12, smaller than those in compression tests, as shown in [Figure 2.18](#), which are usually above the nominal strain of 0.3. The difference is more significant when comparing the true strain. Comparing results at different storage times, the overall stress level increases with storage time, consistent with the findings from compression tests in [Section 2.5.5](#). A two-cycle loading-unloading test was also performed on the tensile specimen with a storage time of 4 hours, as shown by the blue curve with square symbols. It showed stress softening between the primary loading and reloading cycles and viscoelastic dissipation during the reloading cycle, as observed in the compression tests.

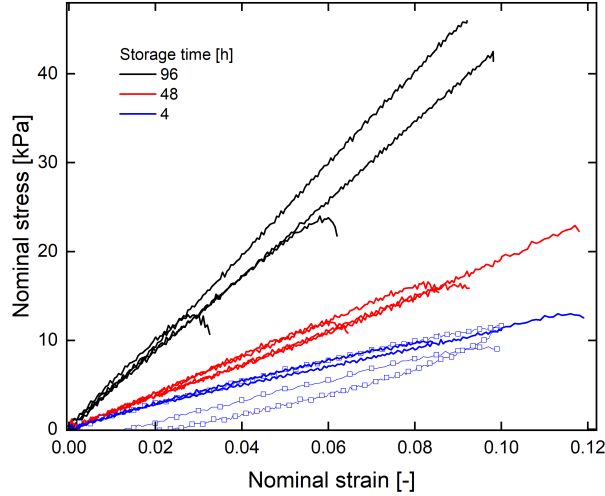


Figure 2.30. Uniaxial tensile tests of starch hydrogels with different storage times, at a strain rate of 0.01 /s.

2.7 Rheometric shear tests

2.7.1 Experimental preparation for rheometric shear tests

To investigate the shear behaviour of the starch hydrogel, rheometric shear tests were performed using a rheometer (H20, TA Instruments). The hydrogel specimens were moulded into a cylindrical shape with a diameter of 25 mm and a height of 5 mm. The specimens were placed between two parallel flat platens, as shown in [Figure 2.32](#). For shear tests, the top surface of the specimen is expected to rotate with the top surface of the upper platen, while the bottom surface is fixed with the bottom platen, which requires minimising the relative slip between the specimen and the platens. Therefore, the sample was glued to sandpaper (grit 120) and taped to the platens to avoid slippage during shear tests. A compressive preload of 1 N was applied to ensure complete contact between the specimen and the platens. The upper platen was then rotated according to the prescribed angular displacement. The torque and angular displacement were recorded during the test, from which the shear stress and shear strain were calculated. Noting that both shear stress and shear strain are defined as positive in the clockwise direction and negative in the anticlockwise direction.

The calculation of shear stress and shear strain is illustrated in [Figure 2.31](#). It is assumed that, for a small angular displacement θ applied at the upper platen, each cross-section of the specimen remains planar and perpendicular to the axis of rotation throughout the deformation. The rotation varies linearly along the specimen height, from 0 at the fixed bottom to θ at the top. Under these classical torsion assumptions, each radial line in

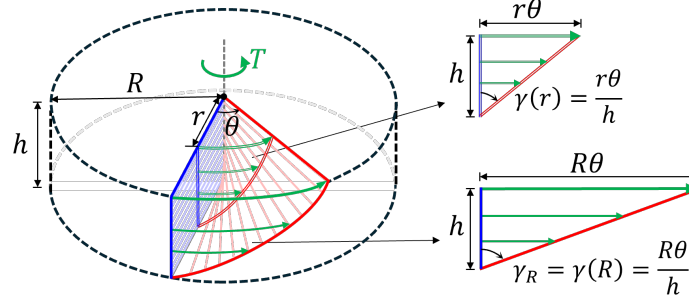


Figure 2.31. Schematic of the engineering shear strain γ obtained from the rheometer shear test.

the cylindrical specimen, shown in blue in Figure 2.31, remains straight after rotation and moves to the position indicated by the red lines. Therefore, the curved cross-section at the radius r and the curved surface at the outer radius R , indicated by the black arrows, undergo simple shear, as illustrated by the two plane projections in Figure 2.31. A material point at the radius r on the top surface travels an arc length of $r\theta$. The engineering shear strain at the radius r and at the outer radius R is defined as

$$\gamma(r) = \frac{r\theta}{h}, \quad \gamma_R = \gamma(R) = \frac{R\theta}{h}, \quad (2.5)$$

where h is the specimen height. This expression shows that the shear strain varies linearly with the radius. For small strains, the stress-strain response is approximately linear, and thus the shear stress also varies linearly with radius, such that $\tau(r)/r = \tau_R/R$, where τ_R is the shear stress at the outer radius. When a torque T is applied to the upper platen, the torque-stress relationship for a solid cylinder becomes

$$T = \int_0^R \tau(r) r 2\pi r \, dr = \frac{\pi R^3}{2} \tau_R, \quad \Rightarrow \quad \tau_R = \frac{2T}{\pi R^3}. \quad (2.6)$$

The quantities γ_R and τ_R obtained above are defined as the apparent shear strain and apparent shear stress, respectively. These apparent measures correspond to the values evaluated at the outer radius following the classical torsion assumption. Note that, according to Afandi (2012), during large deformations, the stress state is no longer pure shear, and the stress-strain relation becomes nonlinear. Therefore, additional geometric corrections may be required. In the present study, only the apparent shear stress and shear strain are presented. An example of a shear test sample is shown in Figure 2.32. The tests were performed on the benchmark samples at a shear strain rate of 0.01 /s. Cyclic loadings were performed with shear strains of 0.15 at the first cycle and 0.20 at the second cycle, followed by monotonic loading until failure. Here, a cycle consists of

loading to a positive strain, then to a negative strain of equal magnitude, and finally returning to the initial state.

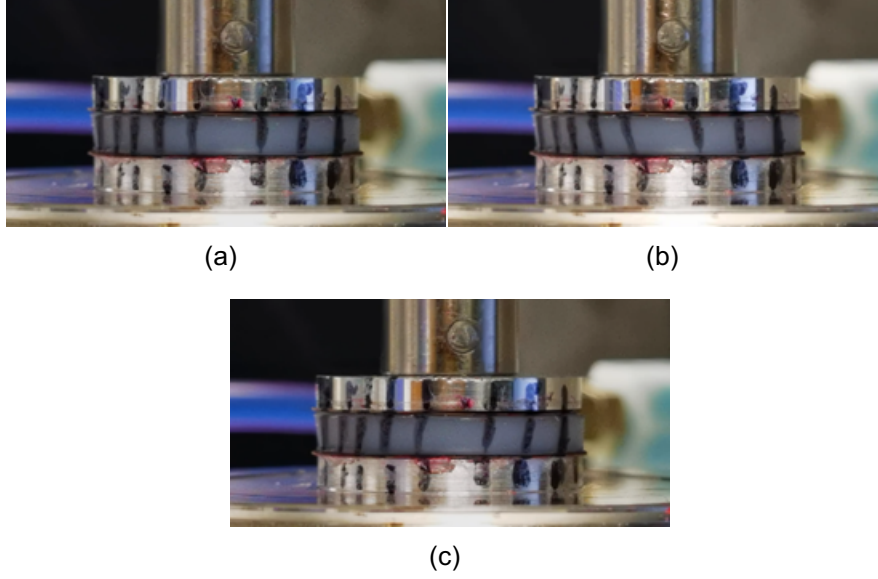


Figure 2.32. Image of a sample for shear tests at (a) the initial state, (b) clockwise and (c) anti-clockwise loadings.

2.7.2 Experimental results of rheometric shear tests

The rheometer shear test on starch hydrogels is illustrated in Figure 2.33, with the loading history shown in the inset. The test includes the first cycle (shear first clockwise, then anticlockwise) to strain 0.15 and the second cycle to strain 0.2, followed by a monotonic shear loading. Similar to the compression and tensile tests, stress softening is observed between the primary loading and reloading cycles, and viscoelastic dissipation is observed during the reloading cycle.

Finally, a comparison of the true stress-strain curves of compression, tensile, and rheometer shear tests of starch hydrogels with a storage time of 48 hours. In order to compare the stress-strain behaviour under different loading modes, variable conversions are performed. First, the nominal stress and strain from the experiments are converted to true stress and strain. For uniaxial tension and compression, the true stress (Cauchy stress) σ and true strain ε_{true} (Hencky strain) are calculated as:

$$\sigma = P(1 + \varepsilon), \quad \varepsilon_{true} = \ln(1 + \varepsilon) \quad (2.7)$$

Note that for compression, the stress and strain are negative (although we use their

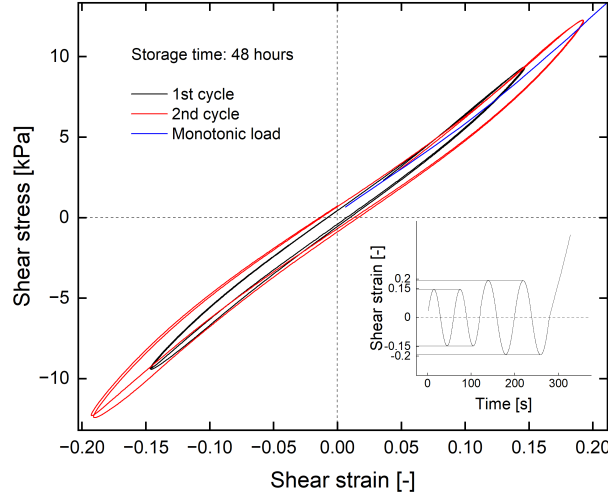


Figure 2.33. Rheometer shear tests of starch hydrogels at a strain rate of 0.01 /s.

absolute values for plotting in earlier sections), while for tension, they are positive. For simple shear, the stress and strain definitions remain the same. The true stress and true strain are further converted to equivalent stress σ_{eq} and equivalent strain ε_{eq} following Skamniotis and Charalambides (2020). For uniaxial tension and compression, the equivalent stress and equivalent strain are:

$$\sigma_{eq} = |\sigma|, \quad \varepsilon_{eq} = |\varepsilon_{true}|. \quad (2.8)$$

For simple shear, they reduce to:

$$\sigma_{eq} = \sqrt{3} \tau, \quad \varepsilon_{eq} = \frac{1}{\sqrt{3}} \gamma. \quad (2.9)$$

The comparison of the equivalent stress-strain curves from the three loading modes is shown in Figure 2.34. The equivalent stress-strain curves from the three loading modes are relatively consistent.

2.8 Wire-cutting tests

2.8.1 Wire-cutting tests setup

To investigate fracture behaviour, wire-cutting tests were performed on starch hydrogels using the method of Goh et al. (2005). According to Goh et al. (2005), when a wire of diameter d cuts through a soft material of width b , and the force F is recorded, the cutting

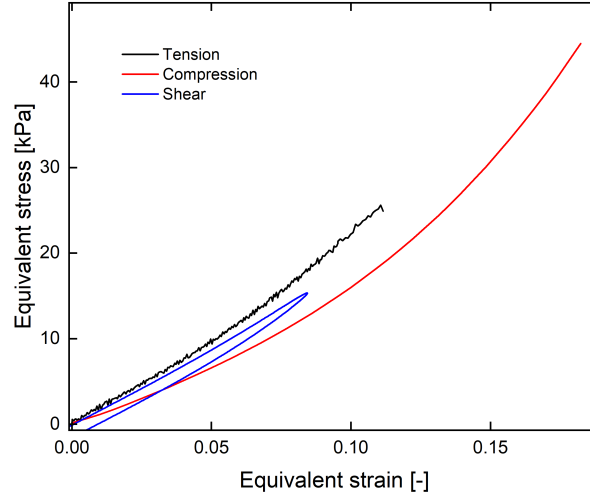


Figure 2.34. Comparison of equivalent stress-strain curves of compression and tensile tests of starch hydrogels and the rheometer simple shear test.

force per unit width F/b can be expressed as:

$$\frac{F}{b} = G_c(\dot{\epsilon}) + \sigma_y(\dot{\epsilon})[1 + \mu]d, \quad (2.10)$$

where G_c is the fracture toughness of the material, σ_y is the yield stress of the material (the stress at the tip of the wire), μ is the friction coefficient between the wire and the material being cut, and $\dot{\epsilon}$ is the strain rate during cutting. Both σ_y and G_c may depend on the strain rate $\dot{\epsilon}$ during cutting, leading to a rate-dependent cutting force. The fracture toughness G_c is defined as the energy required to create a unit area of new surface during fracture, which is an intrinsic material property independent of the test method. The strain energy release rate G is defined as

$$G = -\frac{\partial U}{\partial A} = -\frac{1}{b} \frac{\partial U}{\partial a}, \quad (2.11)$$

where U is the total potential energy, A is the newly created surface area, and a is the crack length, reaches G_c , fracture occurs. Therefore, G_c is a fundamental parameter characterising the fracture behaviour of materials. When G is less than G_c , the crack remains stable. When

$$G \geq G_c, \quad (2.12)$$

the driving force exceeds the material toughness, and the crack propagates. Therefore, by performing wire-cutting tests with different wire diameters and plotting F/b against d , the fracture toughness G_c can be obtained from the intercept at $d = 0$.

The wire-cutting tests were performed using a customised wire-cutting rig mounted on the Universal Testing Machine (Instron 5543, USA). The samples were stored for durations

of 4, 48, and 144 hours before testing to allow for varying DOR. The hydrogel specimens for wire-cutting tests were formed in a rectangular aluminium mould during gelation from liquid state to solid state. The sample dimensions were 30 mm in length, 12 mm in width, and 12 mm in height. Note that the length is large enough to ensure no curling occurs near the edges during cutting and to eliminate edge effects (Kamyab et al., 1998). The diameters of the cutting wire of 0.03 mm, 0.06 mm, 0.075 mm, 0.1 mm, 0.125 mm, 0.2 mm, 0.25 mm, and 0.6 mm were used to investigate the effect of wire diameter on the cutting behaviour. The hydrogel specimens were placed on a flat platen, with their length perpendicular to the cutting wire, as shown in Figure 2.35. The wire was mounted on the rig and positioned just above the top surface of the specimen, aligning with the centre cross-section perpendicular to the length. During the test, the wire was moved downwards at a constant speed to cut through the specimen. Test speeds of 0.1 mm/s, 1 mm/s, and 10 mm/s were used to investigate the strain rate dependence of the wire-cutting behaviour. The force exerted on the wire was recorded during the test. The wire-cutting test is shown in Figure 2.35. All other conditions remained identical to the benchmark.

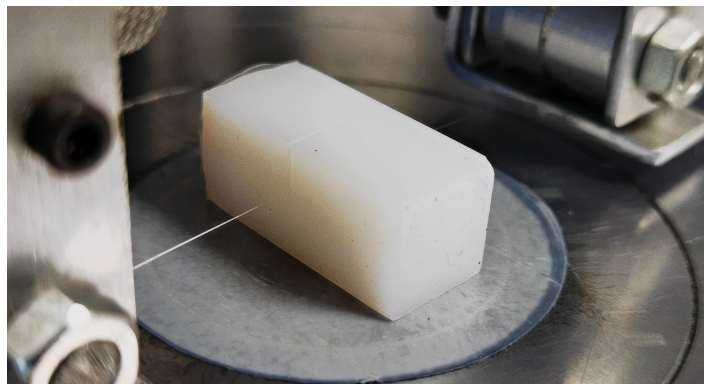


Figure 2.35. Image of a sample for wire-cutting tests.

2.8.2 Experimental results of wire-cutting tests

Typical force-displacement curves for starch hydrogels are shown in Figure 2.36, using tests with 0.06 mm wire diameter and various cutting speeds as examples. The curves exhibit an initial linear increase in force corresponding to indentation and elastic deformation before cutting occurs. Once the essential work to initiate surface fracture is reached, the force drops as the wire penetrates the sample. Subsequently, the cutting force stabilises as the wire advances through the hydrogel. This steady-state force was recorded for further analysis.

The stable wire cutting forces F divided by the specimen width b (i.e., the width of the

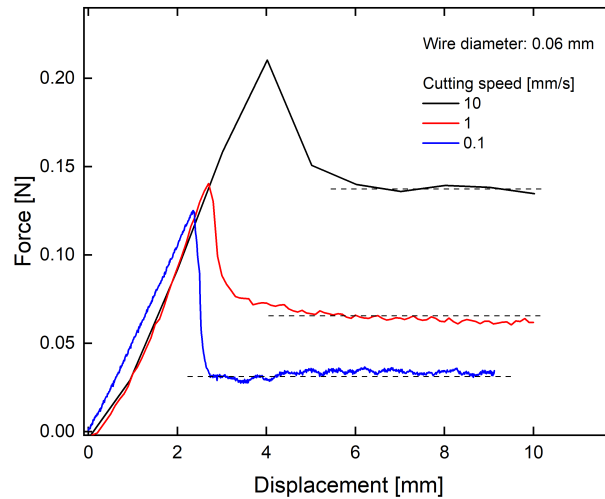


Figure 2.36. Wire cutting test results for starch hydrogels with 0.06 mm wire diameter and various cutting speeds, as an example of obtaining the stable cutting force.

region in contact with and being cut by the wire) are plotted in [Figure 2.37\(a\)](#), [Figure 2.37\(b\)](#), and [Figure 2.37\(c\)](#), for starch hydrogels with storage times of 4 hours, 48 hours, and 144 hours, respectively. Following Goh et al. (2005), the F/b data were fitted by linear regression and extrapolated to zero wire diameter d , and the intercepts were taken as the fracture toughness, G_c . The resulting G_c obtained from the intercepts is summarised in [Figure 2.37\(d\)](#) as a function of storage time and cutting speed. It is observed that the intercepts increase with both cutting speed and storage time. The positive rate dependence is consistent with the findings of Goh et al. (2005), and the increase with storage time indicates that fracture toughness rises with retrogradation. Similar to the crushed and reformed hydrogel discussed in [Section 2.9](#), viscosity contributes to the rate-dependent behaviour. It enhances the plastic and viscous dissipation during cutting, resulting in higher apparent fracture toughness at higher cutting speeds and larger wire diameters. The data obtained in this study are of the same order of magnitude as those reported by Gamonpilas et al. (2009a) and Goh et al. (2005), and these data will help model the fracture behaviour of starch hydrogels in future studies.

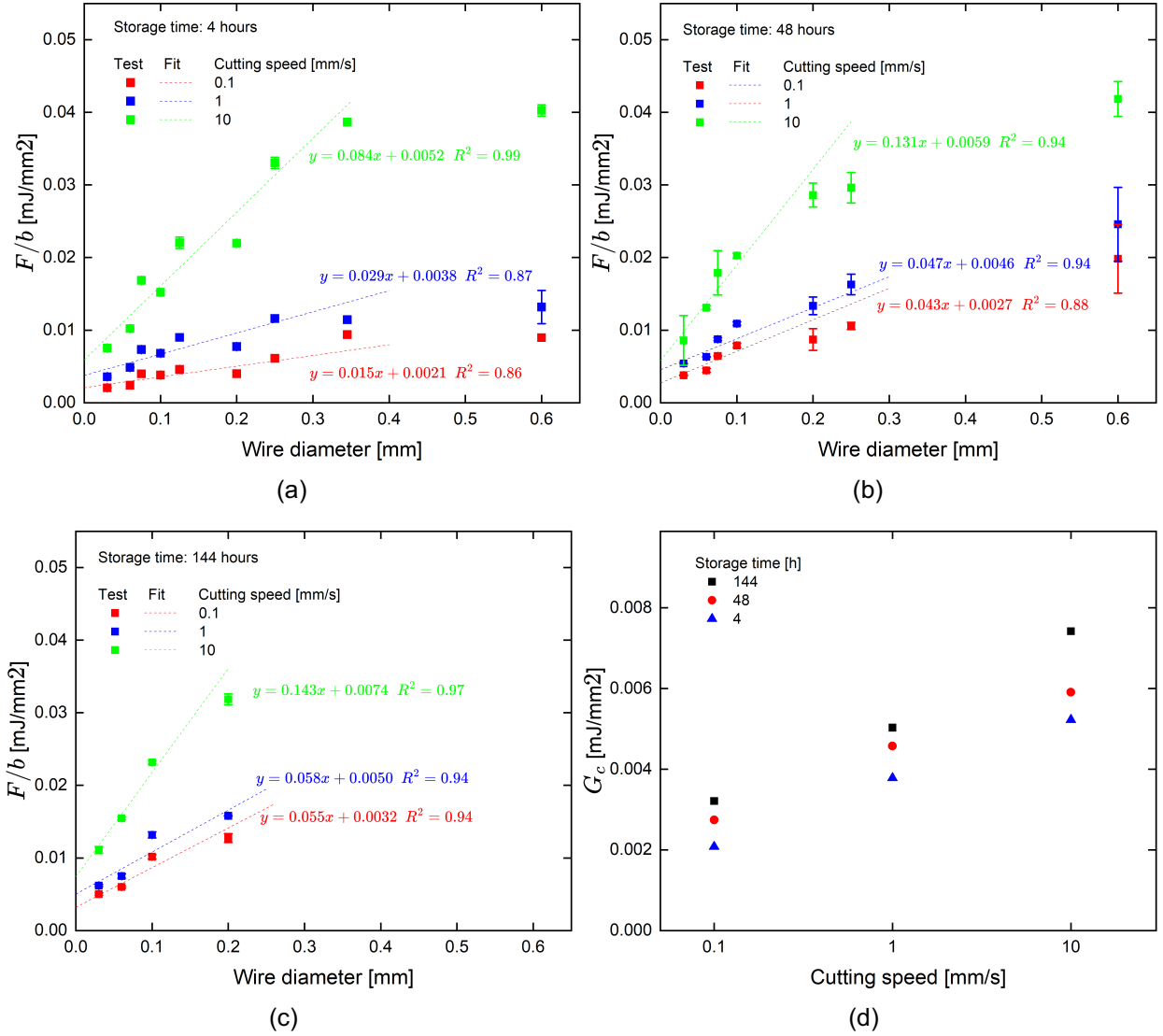


Figure 2.37. Stable wire cutting force for starch hydrogels with different diameters and cutting speeds, with storage times of (a) 4 hours, (b) 48 hours, and (c) 144 hours, and the fracture toughness G_c (d).

2.9 Mechanical behaviour of the crushed and reformed hydrogels

2.9.1 Preparation of crushed and reformed hydrogels

We also perform compression tests on crushed and reformed (post-failure) hydrogel samples, which mimic starch-based food boluses after mastication. The hydrogel samples, prepared as described in [Section 2.5.1](#), were first crushed into small pieces using a blender for 3 minutes, a duration chosen to ensure a comparable degree of fragmentation across all samples, placed in the same cylindrical moulds in [Section 2.5.1](#), then reformed by confined compression within the moulds using a cylindrical indenter. The crushed hydrogel formed a cohesive sample during reforming. The reformed samples were tested immediately after reforming to avoid dehydration. A crushed and reformed sample is shown in [Figure 2.38](#). Note that factors of the blending process, including the blender geometry, blending time, and blending speed, can influence the size and morphology of the crushed hydrogel fragments, potentially affecting the mechanical behaviour of the crushed and reformed hydrogel. To eliminate this source of variability, the blending process was standardised in this study, and the effects of individual blending parameters were not investigated. It was found that, after the sample was reformed using the indenter, the resting time did not affect its mechanical behaviour (results not shown), provided that the moisture content was maintained by using cling film. This indicates that cohesiveness forms immediately upon reforming and is not time-dependent. Nevertheless, as the indentation was applied manually, the degree of cohesiveness may vary between samples due to variability in the applied indentation force. This limitation could be addressed in future studies through controlled or instrumented indentation procedures.

Various loading conditions were applied to these samples, including loading-unloading tests with a nominal strain of 0.3 at strain rates of 0.001 /s, 0.01 /s, and 0.1 /s ([Figure 2.39\(b\)](#)), multicycle loading-unloading tests at various strain levels, including 0.05, 0.1, 0.2, and 0.3 at a strain rate of 0.01 /s ([Figure 2.39\(c\)](#)), monotonic loading to strain over 0.5 at strain rates of 0.01 /s ([Figure 2.39\(c\)](#) and [Figure 2.39\(d\)](#)), and multistep loading-unloading tests with a strain step of 0.05 to strain 0.2 and a step of 0.1 to strain 0.4 at a strain rate of 0.01 /s ([Figure 2.39\(d\)](#)). These tests aim to investigate rate dependence, the Mullins effect, and the large-strain behaviour of the crushed-reformed hydrogel samples.

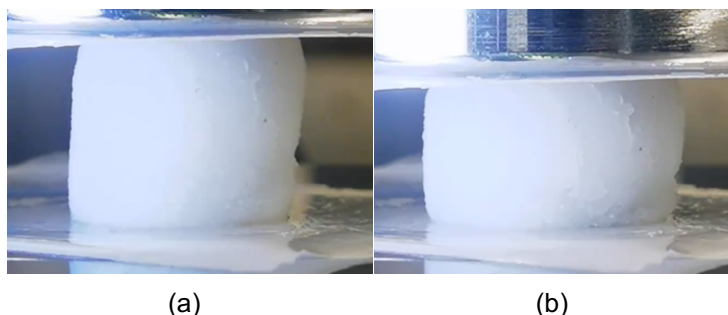


Figure 2.38. Image of a sample for compression tests at (a) the initial state, and (b) a strain larger than 0.2.

2.9.2 Experimental results of compression tests on crushed and reformed hydrogels

The mechanical behaviour of the crushed and reformed starch hydrogels is illustrated in Figure 2.39. A comparison between the crushed-reformed hydrogel and the original hydrogel is shown in Figure 2.39(a). The crushed-reformed hydrogel exhibits a significantly lower stress than the original hydrogel, indicating a substantial loss of mechanical strength after crushing and reformation. The strain-rate dependence observed during the loading-unloading tests is shown in Figure 2.39(b). The overall stress level increases with increasing strain rate, indicating a strain rate dependence. In comparison, as discussed in Section 2.5.3, the original hydrogel samples presented in Figure 2.5(a) in Section 2.5.3 showed insignificant rate dependence. Permanent residual strains were observed after unloading in Figure 2.39(b). Accordingly, the crushed and reformed hydrogel can be regarded as a viscoplastic material. After being crushed, the hydrogel fragment exhibited a sticky texture, allowing it to adhere to itself through intermolecular interactions. During compression, these cohesive fragments rearrange and slide relative to each other, leading to plastic energy dissipation and pronounced rate dependence.

Cyclic loading-unloading tests at different strain levels were further performed, as shown in Figure 2.39(c). At strain levels below 0.1, the stress-strain curves exhibit behaviour similar to that of the original hydrogel, with hyper-pseudo-viscoelastic characteristics, negligible residual strain after unloading, stress softening during reloading, and hysteresis loops in reloading cycles. When the strain exceeds 0.1, the residual strain becomes pronounced, and the hysteresis loops at different strain levels (blue and green curves) appear nearly identical. This behaviour is further confirmed by the stepwise cyclic loading test (red curve in Figure 2.39(d)), where each loop shows a consistent

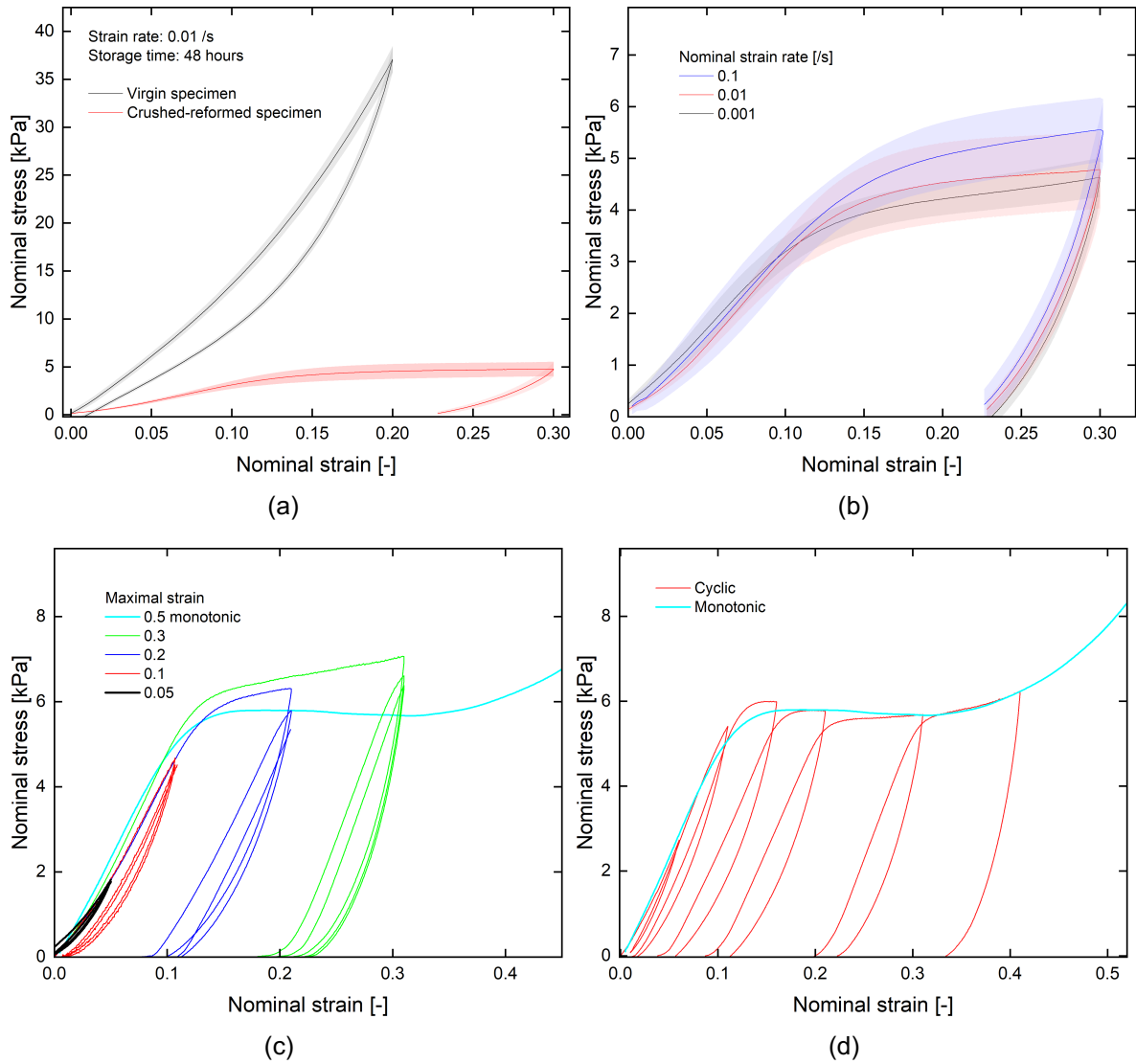


Figure 2.39. The mechanical behaviour of crushed and reformed starch hydrogels. (a) comparison with the original hydrogel. (b) Strain rate dependence (with error bands). (c) cyclic loading behaviour at different strain levels. (d) stepwise cyclic loading behaviour compared with a monotonic loading test.

response. For all the compression tests on the crushed and reformed hydrogels in [Figure 2.39](#), a distinct change in slope occurs at a loading strain (or reloading strain increment) of approximately 0.1. The slope before these turning points is similar to that of their unloading path (slightly different due to viscoelasticity), and the strain levels of all these unloading paths are all close to 0.1, indicating that this turning point corresponds to the yield point. The material flows plastically beyond yielding, and upon unloading, the elastic deformation is recovered while the plastic strain remains permanent. It is found that the loading curve in the subsequent cycle resembles that of the initial loading, except for the offset due to residual strain. For the crushed and reformed hydrogel samples, after unloading, if the residual deformed configuration is taken as the new reference configuration, each material point can be regarded as being in a mechanically equivalent state to its initial state before loading. This is because the internal microstructure has not undergone irreversible changes beyond the permanent set arising from relative slippage between the re-agglomerated cohesive fragments. In other words, if a reloading strain increment is applied from the residual strain, with the strain origin redefined at that point, the resulting reloading stress response coincides with the initial loading response, regardless of the residual strain.

A monotonic loading test was also performed and compared with the cyclic tests shown in [Figure 2.39\(c\)](#) and [Figure 2.39\(d\)](#). In some specimens, such as those in [Figure 2.39\(b\)](#) and the cyclic tests in [Figure 2.39\(c\)](#), no strain softening was observed. In contrast, the monotonic test (cyan curve) and the cyclic test (red curve) shown in [Figure 2.39\(d\)](#) exhibited strain softening beyond the yield point. This behaviour can be attributed to inhomogeneities introduced during the reforming process, with some fragments not adhering well and internal voids remaining. The collapse of these voids, or the sudden slippage and rearrangement of fragments, could cause stress drops during loading, or in other words, strain softening. Another notable observation is the occurrence of stress hardening at large strains (beyond 0.4). This arises because, at large deformations, the specimen is no longer under an actual uniaxial compression state. The sample may bulge outward or develop cracks due to biaxial (lateral) deformation of the cross-section, while lateral confinement may also occur at high compression levels. Consequently, results obtained beyond a strain of 0.4 are not considered to represent the uniaxial compression behaviour of the material.

2.10 Conclusions

In this chapter, we conducted a comprehensive experimental investigation of the mechanical properties of starch hydrogels, considering various material parameters and loading conditions. First, the gelatinisation process of the starch hydrogel was observed by optical microscopy, where starch granules swell and eventually break down, and become transparent. The microstructure of the starch hydrogel was further characterised by cryo-SEM, which revealed a compact, disordered polymer network. The gelatinisation and retrogradation processes were characterised by differential scanning calorimetry, which showed that the melting enthalpies of the crystallites decreased after gelatinisation and increased with storage time, indicating greater retrogradation. The DOR was characterised by the melting enthalpies of the crystallites using the DSC method.

Cyclic uniaxial compression tests showed that starch hydrogels exhibit pseudoelasticity with stress-softening behaviour, as well as viscoelastic behaviour with strong temperature dependence and mild strain-rate dependence. The stress levels and dissipation energy density were found to be negatively correlated with temperature. The dependence of mechanical properties on the DOG, DOR, and water content was also investigated. It is found that stress, total energy dissipation density, and strength increase with higher DOGs, DORs, and lower water content. The ultimate strain first decreased and then increased with DOG, decreased with increasing DOR, and decreased with decreasing water content.

We propose that the material can be regarded as a filler-reinforced composite polymer. The polymer network matrix formed during gelatinisation provides elasticity and viscoelasticity. A higher DOG results in a more crosslinked network as well as imperfections such as dangling chains and solvated chain fractions, leading to higher stress levels. Meanwhile, the crystallites formed during retrogradation act as fillers, reinforcing the material and leading to pseudoelasticity. A higher DOR caused by longer storage time or lower storage temperature increases the filler content and enhances the reinforcement of the polymer, leading to higher stress levels and more substantial dissipation caused by stress softening. Furthermore, water acts as a plasticiser, softening the polymer network and reducing the overall stiffness and strength.

Mechanical responses under uniaxial tension and shear were also investigated, showing viscoelastic and pseudoelastic behaviour similar to that observed in compression tests. Stress levels increase with storage time, consistent with findings from compression tests. However, the failure strains in tension are significantly smaller than those in compression, indicating a more brittle behaviour under tension. The compression, tension, and shear

test data provide a complete characterisation of the mechanical behaviour of the starch hydrogels under different stress conditions.

Wire-cutting tests were performed to investigate the fracture toughness of the starch hydrogels. The fracture toughness increased with both cutting speed and storage time, indicating rate dependence and retrogradation-induced enhancement. The viscosity contributes to rate-dependent behaviour and enhances plastic and viscous energy dissipation during cutting, resulting in a higher apparent fracture toughness at higher cutting speeds. Finally, compression tests were performed on crushed and reformed hydrogel samples, mimicking starch-based food boluses after mastication. The crushed and reformed hydrogel exhibits pronounced rate dependence and viscoplastic behaviour due to the rearrangement and sliding of fragments during compression, leading to plastic energy dissipation. A distinct yield point was observed at a strain of approximately 0.1, beyond which the material flows plastically, resulting in permanent residual deformation upon unloading.

The experimental results presented in this chapter provide a comprehensive understanding of the mechanical behaviour of starch hydrogels under various material parameters reflecting different cooking procedures and loading conditions. These findings lay the foundation for developing constitutive models to accurately describe the complex mechanical responses of starch hydrogels, which will be discussed in [Chapter 4](#).

Chapter 3

Diffusion and mechanical property degradation of starch hydrogel under enzymatic hydrolysis

3.1 Introduction

In the human gastrointestinal tract, digestion of food involves both mechanical and chemical breakdown. Mechanical breakdown occurs during mastication in the mouth and peristalsis in the stomach wall, while chemical breakdown is facilitated by the diffusion and reaction of gastric fluids. Particularly for starch-based foods, e.g., starch hydrogel, on the one hand, the hydrolysis of the starch molecules catalysed by the α -amylase in gastric fluids ([Figure 1.7](#)) softens the food bolus, leading to mechanical property degradation and facilitating mechanical breakdown. On the other hand, mechanical breakdown increases the surface area that is exposed to enzymes. Hence, the chemo-mechanical properties of starch foods are key factors influencing the breakdown and digestion rate of starch foods.

Given that starch digestion involves both mechanical and chemical processes, it is argued that the investigation of the chemo-mechanical properties of starch hydrogels remains limited. The most physiologically relevant chemo-mechanical research method is human *in vivo* experiments. However, as discussed in [Section 1.4](#), *in vivo* experiments are limited by ethical issues and the difficulty of controlling the experimental conditions. Instead, *in vitro* experiments are more controllable and reproducible and therefore widely utilised by researchers (Nadia et al., [2021](#)). The key to *in vitro* tests is to mimic the human

in vivo digestion conditions as closely as possible. A large volume of *in vitro* studies exists on the digestion of starch, including *in vitro* characterisation of enzymatic hydrolysis (Dhital et al., 2017; Edwards et al., 2014; Freitas et al., 2018; Goñi & Saura-Calixto, 1997; Korompokis et al., 2021; Pallares Pallares et al., 2018; Papathanasiou et al., 2015; Van Hung et al., 2016) and acidic hydrolysis (Pinto et al., 1993) of starch molecules by testing the concentration of glucose. However, these studies mainly focused on the hydrolysis process and kinetics. As mentioned in Section 2.1, the mechanical properties of starch hydrogels have been investigated in several studies, including Fabek et al. (2014), Iqbal et al. (2021), Jeong et al. (2016), Leloup et al. (1991), Ring (1985), Torres et al. (2018), Yan et al. (2021), and Zheng et al. (2023). However, only a few studies account for the effect of enzymatic hydrolysis. Drechsler and Ferrua (2016) applied a texture analyser to perform uniaxial compression and bulk compression tests on starch hydrogels made from different botanical origins and moisture content after enzymatic hydrolysis by simulated gastric fluids. They used peak force as a measure of food hardness and found that hardness decreased with hydrolysis time, with different hydrolysis rates across starch sources. Later, Drechsler and Bornhorst (2018) further applied similar test methods to investigate the failure strength, toughness, apparent modulus, and hardness of potato cubes, all of which decrease with enzymatic hydrolysis. However, in their study, the complete mechanical performance under loading and unloading was not investigated, and the effect of enzyme diffusion in the starch hydrogel was not considered. Several studies have further examined the influence of acid diffusion (Mennah-Govela et al., 2015) or enzyme diffusion (Edwards, 2014) on starch hydrolysis. However, the enzyme diffusivity was not quantified in these studies. In particular, enzyme diffusion within solid food matrices, such as starch-based systems, has rarely been investigated. Moreover, the coupling between the chemical and mechanical behaviours of starch hydrogels has also received limited attention.

Therefore, gaps remain in understanding the chemomechanical behaviour of starch hydrogels under hydrolysis. The chemo-mechanical response of starch hydrogels during enzymatic hydrolysis has yet to be experimentally characterised. The diffusivity of starch hydrogels has yet to be quantified by a more direct and accurate method. In this chapter, the chemomechanical behaviour of starch hydrogel under enzymatic hydrolysis by α -amylase is investigated. We first prepare the starch hydrogel specimens and the enzyme solution in Section 3.2. Then we perform enzymatic hydrolysis of the starch hydrogel specimens and conduct uniaxial compression tests to determine the mechanical properties after hydrolysis in Section 3.3, where the influence of pH on the enzymatic hydrolysis is also investigated. The diffusivity of the enzyme in the starch

hydrogel is measured using fluorescein in [Section 3.4](#). Finally, the conclusions of this chapter are drawn in [Section 3.5](#).

3.2 Materials

This section describes the preparation of starch hydrogels and the enzyme solution for hydrolysis.

3.2.1 Starch hydrogel preparation

The preparation procedure for starch hydrogel is the same as described in [Section 2.2](#). Suspensions of starch with a 20% w/w mass fraction were prepared by mixing potato starch powder (S2004, Sigma-Aldrich) in DI water. They were gelatinised by heating at 100 °C for 40 min until transparent and low viscosity. After cooling at 20 °C in cylindrical specimen moulds, solid hydrogel specimens were obtained and stored in sealed bags at 20 °C. To investigate the influence of retrogradation on hydrolysis, the samples were kept for varying storage times, including 8, 18, 48, and 192 hours. Another batch of samples was kept for 48 hours to ensure a consistent degree of retrogradation. For the mechanical tests in [Section 3.3](#), three sizes of specimens are used for investigating the size effect in [Section 3.3.2](#), including 20 mm diameter and 20 mm height specimens, 12.5 mm diameter and 12.5 mm height specimens, and 5 mm diameter and 5 mm height specimens, as shown in [Figure 3.1\(a\)](#), and they are referred to as large, medium, and small specimens, respectively. Other mechanical tests were performed on the medium-sized specimens. For the diffusivity tests in [Section 3.4](#), samples were prepared with a diameter of 10 mm and a thickness below 1 mm by pipetting a droplet of the hot unsolidified starch hydrogel (also referred to as a starch paste) immediately after gelatinisation onto a Petri dish and placing a round glass slide with a diameter of 20 mm, as shown in [Figure 3.1\(b\)](#). When the sample cooled down and solidified, it was found to adhere tightly to the glass slide and the Petri dish. For the α -amylase activity tests described in [Section 3.2.2.2](#), a 0.05% w/w starch suspension was prepared using the same heating temperature and duration as the solid hydrogel samples, but at a much lower concentration, so that a liquid-state starch paste was obtained upon cooling Morris ([1990](#)). The starch paste enabled homogeneous mixing with the enzyme and decoupled diffusion effects, following the approach of Minekus et al. ([2014](#)).

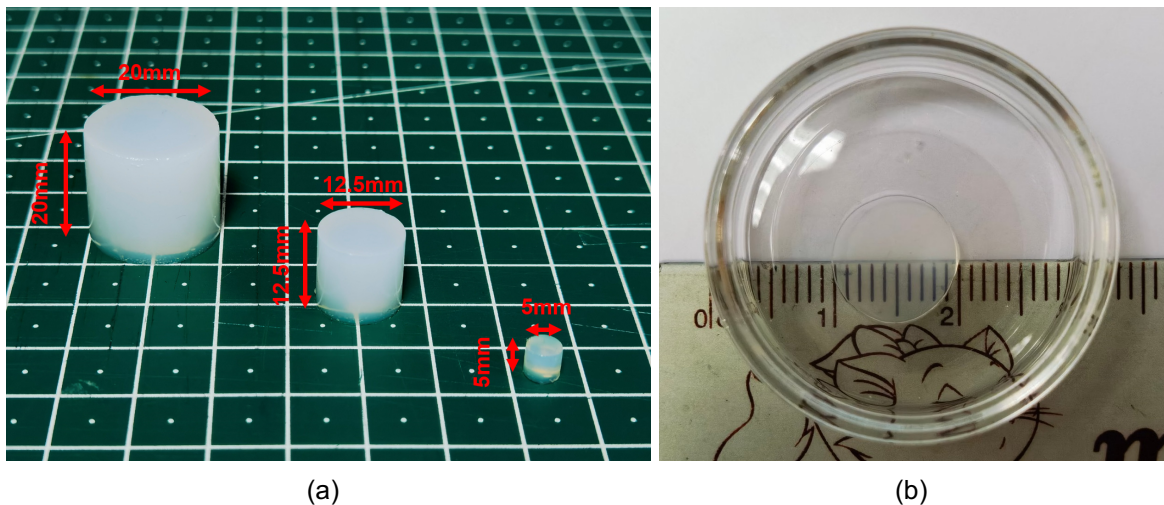


Figure 3.1. Starch hydrogel samples. (a) Large, medium, and small cylindrical samples for uniaxial compression tests. (b) A sample for the diffusivity test.

3.2.2 Hydrolysis Solution preparation

Tests with different hydrolysis conditions were conducted, including acidic hydrolysis, enzymatic hydrolysis under varying acidic conditions, and hydrolysis in simulated gastric conditions, as described below.

3.2.2.1 Acidic condition preparation

To reproduce the varying acidic conditions of the human stomach and examine their influence on starch hydrogel degradation, three hydrochloric acid (HCl) solutions were prepared at target pH values using a 1 M HCl stock solution. Each solution was diluted with DI water to a total volume of 200 mL. The required HCl concentration for each pH value was determined based on the dissociation relationship of a strong acid:

$$\begin{aligned}
 [\text{H}^+] &= [\text{HCl}] = 10^{-\text{pH}} \text{ mol/L}, \\
 \text{pH} &= -\log_{10}[\text{H}^+] = -\log_{10}[\text{HCl}].
 \end{aligned}
 \tag{3.1}$$

pH values of 1.0, 2.0, and 3.0 were used for the acidic hydrolysis tests. pH values of 1.0, 5.0, 6.0, and 7.0 were used for the enzymatic hydrolysis tests. pH values around 5.0, 7.0, and 8.0 were used for the simulated gastric fluid tests.

3.2.2.2 α -amylase preparation and activity test

The enzyme used in this study is α -amylase (A3176 Sigma-Aldrich) from porcine pancreas as a model of human enzyme, following Edwards et al. (2014). It catalyses the hydrolysis of internal α -1,4-glycosidic linkages of D-glucose units of polysaccharide. An α -amylase solution with a concentration of 1.18 g/L within 0.1 M Phosphate Buffered Saline (PBS) (P4417 Sigma-Aldrich) was used following Mackie and Pangborn (1990) and Mennah-Govela et al. (2015). The corresponding molar concentration was therefore 22.5 $\mu\text{mol/L}$. According to the product information of the α -amylase, the molecular mass of the enzyme M_{enz} is around 51–54 kDa (1 Da = 1 g/mol) with a pH range for activity of 5.5–8.0 and an optimum at pH 7. Also, the specific enzyme activity is labelled over 5 U/mL at 20 °C and pH 6.9. However, the activity at 37 °C and pH 7.0 is expected to be higher and needs to be tested. Note that 1 U (= 1 unit = 1 $\mu\text{mol/min}$) is defined as one micromole of substrate that reacts/converts per minute under the catalysis of enzymes (under a specified assay condition) (Labuda et al., 2018). As the molar mass of maltose, M_{mal} , is 342.297 g/mol, 1 U of amylase corresponds to the amount that liberates 1 mg of maltose from starch in 3 minutes.

The activity test was performed as follows. A 0.05% w/w starch suspension was heated to 90°C for 40 minutes for gelatinisation. A volume of 5 mL of the starch substrate was then cooled to 37°C and stored in a tube. A quantity of 5 μL of α -amylase was weighed and solubilised in 5 mL of PBS to prepare the working solution. Microcentrifuge tubes with 100 μL stop solutions containing 0.3 M sodium carbonate (Na_2CO_3) (Sigma, S7795) were prepared for enzyme deactivation. As illustrated in Figure 3.2, in step 1, 100 μL of the starch substrate was pipetted directly into a tube of stop solution to serve as blank (no hydrolysis) samples. In step 2, hydrolysis was initiated by adding 100 μL of the working enzyme solution to the starch substrate, followed immediately by storing this tube in a rotary mixer (Thermo Scientific HulaMixer) at 37°C. Subsequently (steps 3–6), 100 μL of the starch and enzyme mixture was pipetted subsequently into separate stop solutions of microcentrifuge tubes at predetermined hydrolysis times (3, 6, 9, and 12 minutes) to deactivate the enzyme. The entire procedure was repeated three times for reproducibility. Therefore, including one blank and four hydrolysis time points, a total of 15 microcentrifuge tubes of aliquots were collected and centrifuged. After centrifugation, the supernatant was diluted to ensure the absorbance fell within the measurable range, mixed with the P-hydroxybenzoic acid hydrazide (PAHBAH) reagent in a multi-well plate to initiate the chromogenic reaction (step 7), and finally analysed by spectrophotometry to measure the absorbance at 405–425 nm. Here, the PAHBAH assay quantifies reducing sugars by

measuring the yellow chromophore formed when aldehyde groups reduce PAHBAH under heating (AlShaalan, 2019; Lever, 1972).

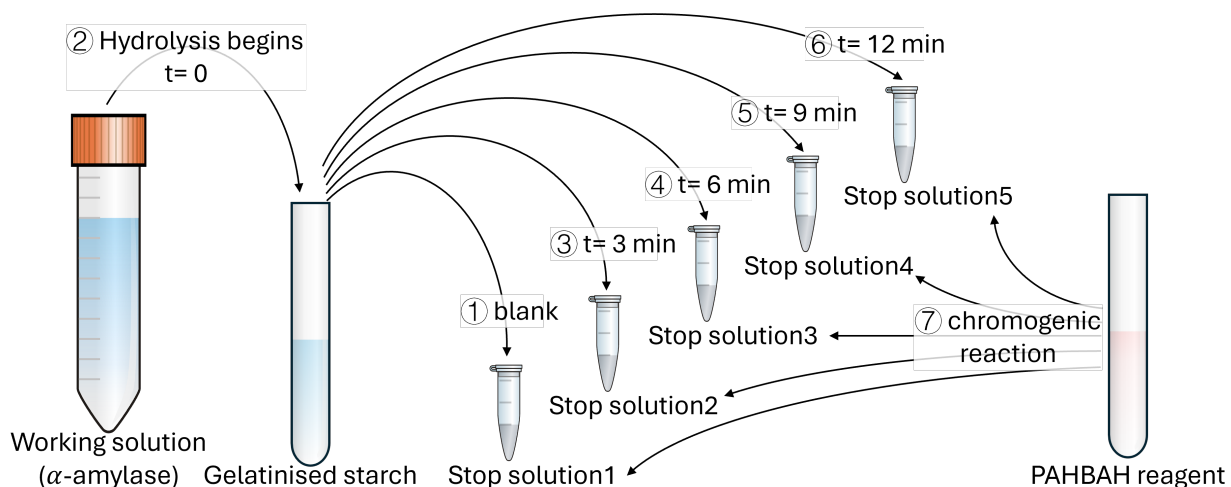


Figure 3.2. Schematic of the experimental setup for the amylase activity test.

Standard colour reaction experiments were performed on maltose solutions with known concentrations beforehand, and the light absorbance is a linear function of maltose concentration, as is illustrated in Figure 3.3. The sugar concentration at each time point

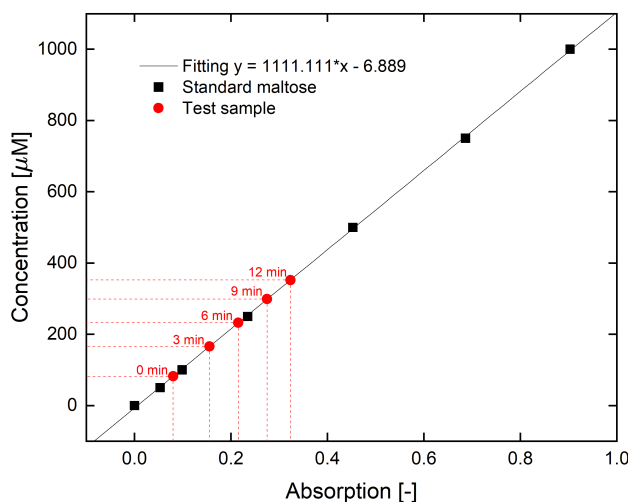


Figure 3.3. Light absorbance of the starch solution during hydrolysis, compared with the standard maltose solution. Note that the data has subtracted the reading of a blank control group to eliminate the background effect.

during digestion can be determined using the standard light absorbance function. As the time interval is known, simply by dividing the increment of sugar concentration by the interval, the reaction rates were obtained, as is shown in Table 3.1. The specific activity

of α -amylase, $a_\alpha = 1896$ U/mg, was obtained, similar to Dhital et al. (2014). According to the INFOGEST standard, the measured amylase activity is valid for use for 1 month. Note that the specific activity of an enzyme could be a function of temperature, pH, or other factors according to our experiments in Section 3.3 and the literature (Bessler et al., 2009; Brandam et al., 2003; Rosenblum et al., 1988). However, in this study, we take it as a constant for simplicity.

Table 3.1. Result of amylase activity test (M: mol/L; U: μ mol/min).

Time [min]	Sugar concentration [μ M]	Time interval [min]	Reaction rate [μ M/min]	Specific amylase activity
0	3285			
3	6625	0 to 3	1113	45513 U/mL
6	9296	3 to 6	890	(stock 24 mg/mL)
9	11944	6 to 9	882	1896 U/mg
12	14088	9 to 12	715	

3.2.2.3 Simulated gastric fluid preparation

The simulated gastric fluid (SGF) solution was prepared for investigating its effect on starch hydrolysis. The preparation was performed according to the INFOGEST protocol (Minekus et al., 2014), while pH values of less than 5.0, 7.0, and around 8.0 were adjusted using HCl and measured with pH indicator strips to represent progressively neutralised gastric conditions. Note that CaCl_2 was not used, as it caused precipitation. We did not use

Table 3.2. Composition of SGF used in this study.

Constituent	Stock conc. [g/L]	Stock conc. [mol/L]	Conc. in SGF [mmol/L]
KCl	37.3	0.5	6.9
KH_2PO_4	68.0	0.5	0.9
NaHCO_3	84.0	1.0	25.0
NaCl	117.0	2.0	47.2
$\text{MgCl}_2 \cdot (\text{H}_2\text{O})_6$	30.5	0.15	0.1
$(\text{NH}_4)_2\text{CO}_3$	48.0	0.5	0.5

pH 3.0 because enzyme activity was significantly reduced at this pH. Before dissolving HCl into the SGF, the solution was alkaline with a pH of around 8.0. To reach a lower pH, the required volume of hydrochloric acid (1M) was calculated using the Henderson-Hasselbach equation, as a bicarbonate buffer system is created on addition of NaHCO_3

to the solution:

$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]}\right),$$

$$[\text{HCl}] = [\text{HA}] = [\text{A}^-] \times 10^{\text{p}K_a - \text{pH}}, \quad (3.2)$$

where K_a is the acid dissociation constant with a value of $\text{p}K_a = 6.1$ (Boron & Boulpaep, 2016), $[\text{HA}]$ is the concentration of the acid, and $[\text{A}^-]$ is the concentration of the conjugate base. For a 200 mL solution that contains a total $[\text{HCO}_3^-]$ of 25 mM, it yields the equation $5.0 = 6.1 + \log_{10}(5.0 - x)/x$, where x is the concentration of acid added. Therefore, around 4.63 mmol HCl, i.e., 4.63 mL of 1 M HCl was required to add to the SGF to reach a pH of 5.0.

3.3 Uniaxial compression properties of starch hydrogel under hydrolysis

3.3.1 Chemo-mechanical tests setup

The hydrogel samples were prepared according to the methodology described in Section 3.2.1. The α -amylase whose activity was measured in Section 3.2.2.2 was used for the hydrolysis. The α -amylase hydrolysis of the starch hydrogel was performed by immersing the starch hydrogel samples with different degrees of retrogradation and sizes in the enzyme solution at 37°C at various pH values for different hydrolysis times. SGF described in Section 3.2.2.3 was also used for hydrolysis, after which the sugar concentration was measured for validation of the hydrolysis in Section 3.3.4. Table 3.3 summarises all experimental parameters for sample preparation prior to the uniaxial compression tests.

Table 3.3. Experimental parameters regarding sample preparation before uniaxial compression tests.

Hydrolysis condition	pH [-]	Hydrolysis temp. [°C]	Enzyme conc. [g/L]	Hydrolysis time [min]	Storage time [h]	Specimen size	Section
Enzymatic hydrolysis	7.0	37	1.18	0, 30, 60, 90, 120	48	Large, Medium, Small	3.3.2
	7.0			0, 60, 120	8, 18, 48, 192	Medium	3.3.3
	5.0, 6.0, 7.0			180	48	Medium	3.3.4
Acidic hydrolysis	1.0, 2.0, 3.0	37	0	180	48	Medium	3.3.4
SGF hydrolysis	< 5.0, 7.0, $\approx$ 8.0	37	1.18	180	48	Medium	3.3.4

The mechanical properties of starch hydrogels were measured before (no hydrolysis) and after the hydrolysis using uniaxial compression tests. A Universal Test Machine (Instron 5543, Instron, Norwood, MA, USA) was used to perform the compression tests. A 100 N load cell was used for all the tests. Following [Section 2.5.1](#), silicone oil (Ultimate Racing) with a viscosity of 10 Pa·s was used to reduce the friction between the specimen surfaces and the platens in order to obtain relatively ideal uniaxial loading conditions. The platens were coated with polytetrafluoroethylene (PTFE) tape to protect the metal from chemical attack. The nominal stress and nominal strain were recorded during the tests, following [Section 2.5.1](#). The nominal strain rate (rate of nominal strain) of all tests was set to 0.01 /s. The tests were performed at 20 °C, and 50% relative humidity was maintained in the laboratory. The compression included two types of loading paths: cyclic and monotonic. The cyclic loading was performed to investigate the energy dissipation, while the monotonic loading was performed to obtain failure properties of the starch hydrogel.

3.3.2 Degradation of the mechanical properties of starch hydrogels by α -amylase hydrolysis

The time-dependent degradation of the mechanical properties was investigated by immersing hydrogel specimens of three different sizes in the enzyme solution for varying durations (0, 30, 60, 90, and 120 minutes). Compression tests were subsequently performed on these specimens, as illustrated in [Figure 3.4](#) and [Figure 3.5](#). A progressive degradation of the mechanical response was observed across all sample sizes, as shown in [Figure 3.4](#). The general stress level, the initial stiffness, and the tangential stiffness at a particular strain level decreased with increasing hydrolysis time, whereas the dissipation energy density (defined in [Equation 2.2](#)) increased with hydrolysis time. Moreover, smaller samples exhibited a more pronounced degradation, indicating a size-dependent degradation behaviour, as further confirmed in [Figure 3.5](#). Initially, as [Figure 3.5\(a\)](#) illustrates, the mechanical responses of all three samples were nearly identical and fell within the experimental error band, suggesting no size dependence before hydrolysis. However, as hydrolysis progressed, the decrease in stiffness became more evident in the smaller samples than in the larger samples. In particular, in [Figure 3.4\(c\)](#), the tangential stiffness of the small samples transitioned from increasing to decreasing with strain, indicating that hydrolysis induced additional structural damage during deformation.

The observed size dependence results from the diffusion-reaction process. At the

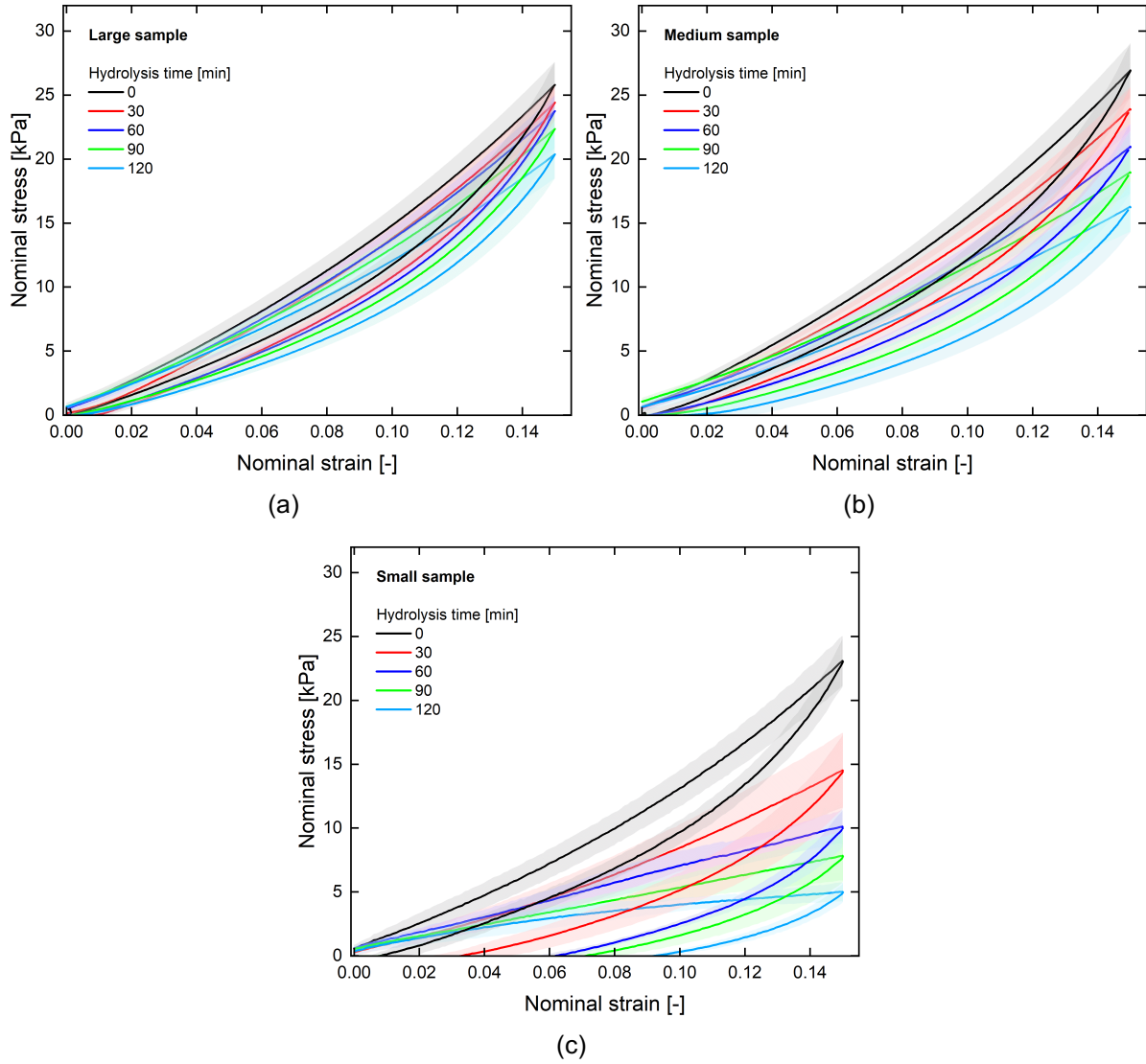


Figure 3.4. Loading-unloading behaviour for different periods of hydrolysis. (a) Large samples. (b) Medium samples. (c) Small samples.

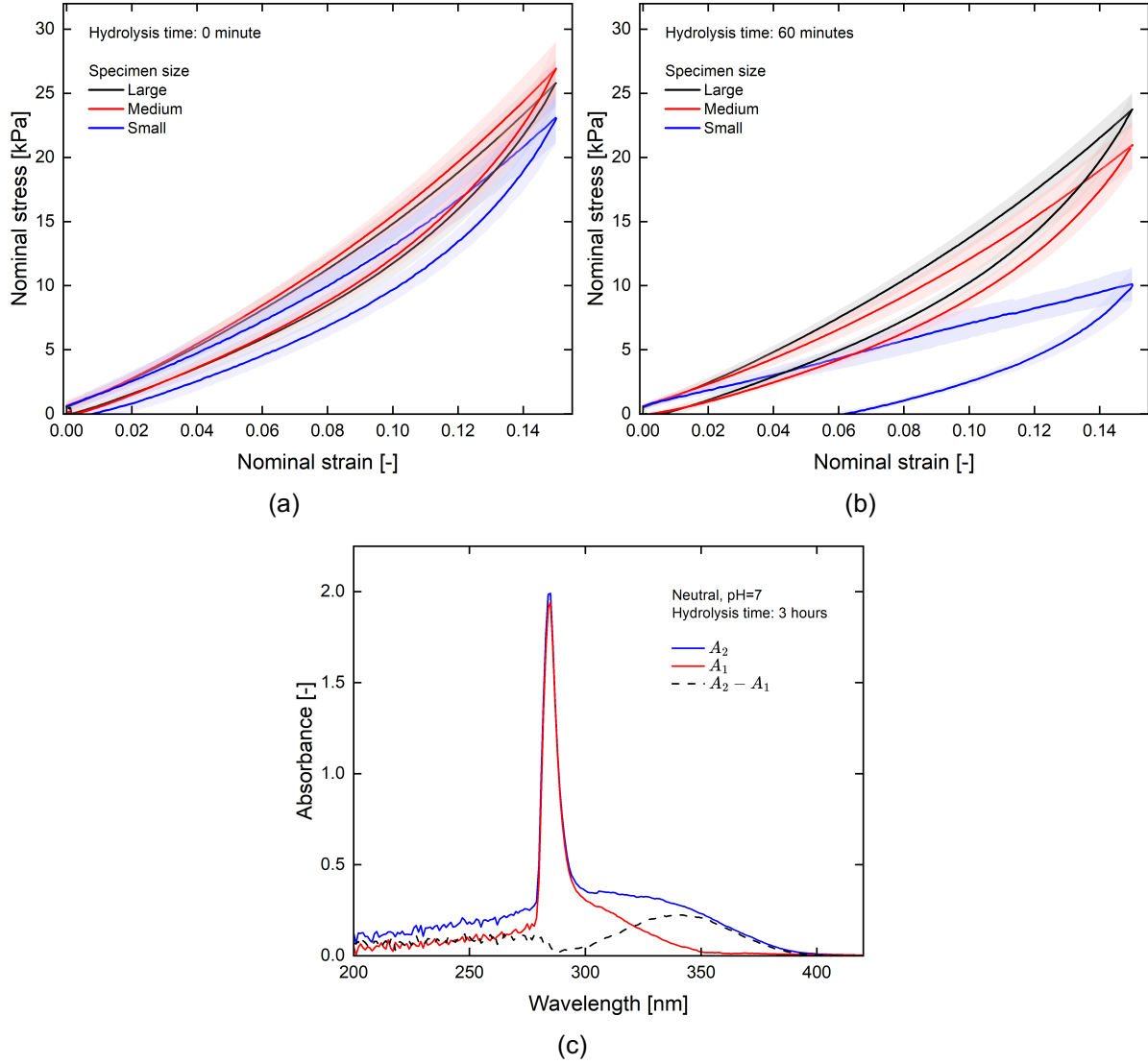


Figure 3.5. Loading-unloading behaviour of different sample sizes. (a) No hydrolysis. (b) Hydrolysis for 60 minutes. (c) Hydrolysis for 120 minutes.

beginning, the enzyme was present only on the sample surface, and hydrolysis occurred only at this external surface. As hydrolysis proceeds, the enzyme diffuses into the starch hydrogel, and hydrolysis occurs in the presence of the enzyme. The diffusion process is illustrated in [Figure 3.6](#). As shown, with the same diffusion coefficient and diffusion-reaction time, a higher ratio of sample volume in the small specimen containing the enzyme results in a higher degree of hydrolysis. The reaction is more homogeneous as the enzyme spreads throughout the sample, whereas in the larger sample it mainly occurs near the surface. The inhomogeneous reaction leads to spatially varying mechanical properties throughout the sample, which in turn result in an inhomogeneous stress distribution under uniaxial compression.

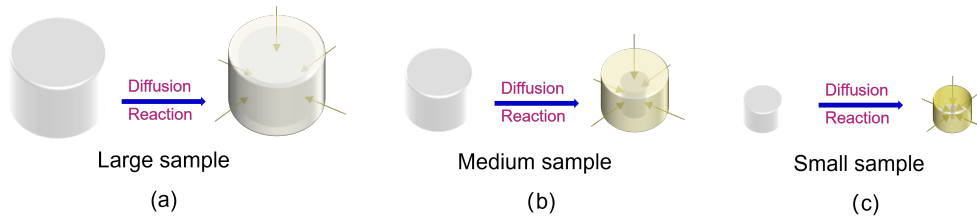


Figure 3.6. Schematics of the diffusion reaction process of different sample sizes, with white colour indicating no enzyme and yellow indicating enzyme presence. (a) Large sample. (b) Medium sample. (c) Small sample.

The dissipation energy density (defined in [Equation 2.2](#)) is calculated and plotted in [Figure 3.7\(a\)](#). There is a slight trend that the dissipation increased with the hydrolysis time for each sample size. As the dissipation can be related to viscoelasticity caused by internal friction between chains (Li et al., 2019; Stricher et al., 2015), the increase of dissipation may be related to the chain breakage and increase of chain mobility as a result of the hydrolysis. The peak stress at the first cycle is also plotted in [Figure 3.7\(b\)](#), which shows a clear trend that the peak stress decreases with increasing hydrolysis time. The polymer network provides the stiffness of the starch hydrogel, and hydrolysis breaks the polymer chains, leading to a decrease in the stress response and, consequently, the stress at maximum strain. It can also be seen that the decline is more pronounced in smaller samples than in larger ones, as smaller samples have a higher enzyme volume fraction and therefore stronger degradation.

The failure properties of the starch hydrogel after different hydrolysis times were also investigated via monotonic loading tests, as shown in [Figure 3.8](#). The ultimate strain is plotted in [Figure 3.8\(a\)](#), which shows a slight increase with the hydrolysis time. The strength is plotted in [Figure 3.8\(b\)](#), which shows a significant decrease with increasing hydrolysis time. The failure point, as a stress-strain coordinate, is demonstrated in

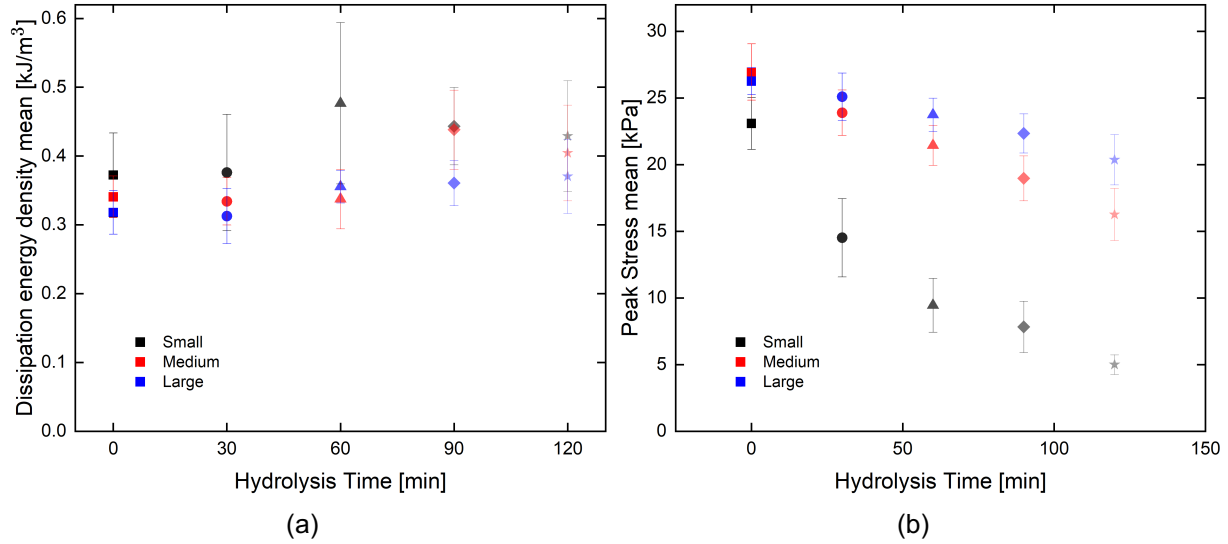


Figure 3.7. Comparison of cyclic response under different hydrolysis times. (a) Dissipation energy density. (b) Peak stress at first cycles.

Figure 3.8(c), with a monotonic loading curve indicated by a dotted line. The decrease in strength can be explained by the breakage of polymer chains as a result of hydrolysis, which weakens the polymer network. The slight increase in the ultimate strain is due to the increased motility of polymer chains after partial chain breakage, as mentioned above.

3.3.3 Retrogradation reinforcement of the hydrolysis resistance of the starch hydrogels

In Section 2.5.5, it was found that the degree of retrogradation increases with the storage time, leading to an increase of stiffness and strength of the starch hydrogel. Here, the influence of retrogradation on the hydrolysis resistance of the starch hydrogel was further investigated. Storage times of 8, 18, 48, and 192 hours were considered. The hydrolysis was performed for 0, 60, and 120 minutes. The stress-strain responses of the samples are illustrated in Figure 3.9.

It is observed that the stiffness of the starch hydrogel increases with storage time, consistent with the findings in Section 2.5.5, and the stress level remained higher throughout the hydrolysis process for samples with longer storage time. The peak stress at a strain of 0.2 is plotted in Figure 3.10(a), which shows a decrease with the hydrolysis time for all storage times. Since hydrolysis leads to the breakage of polymer chains, it is assumed that the stress response is proportional to the number of effective polymer

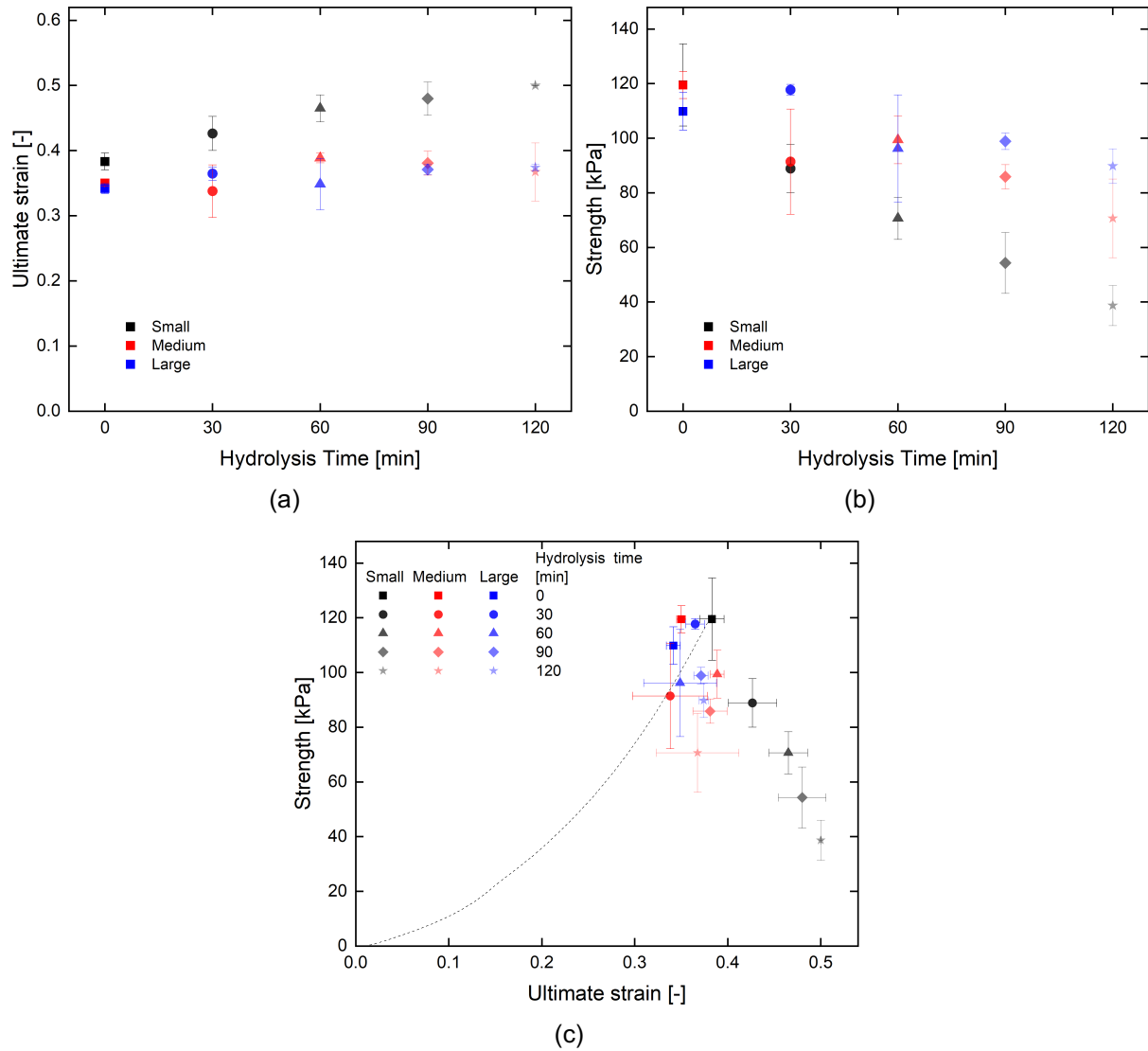


Figure 3.8. Comparison of the failure behaviour under different hydrolysis times. (a) Ultimate strain level, (b) Strength, (c) Failure points plotted as stress-strain coordinates. The dotted line shows a monotonic loading curve example of a small sample without hydrolysis.

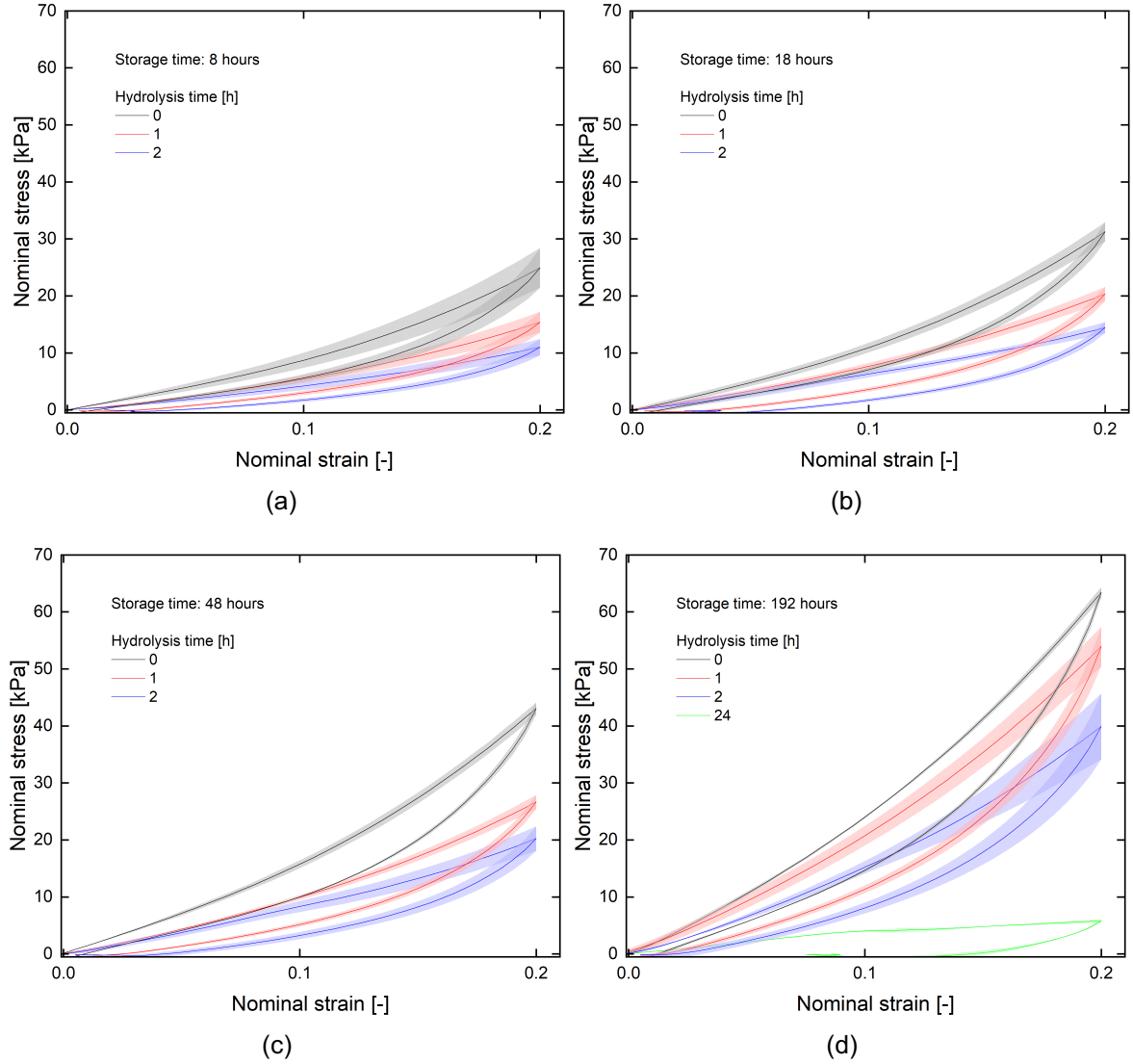


Figure 3.9. Stress-strain response of starch hydrogels with varying storage time at different levels of hydrolysis. (a) 8 hours of storage, (b) 18 hours of storage, (c) 48 hours of storage, (d) 192 hours of storage.

chains that bear the load. The peak stress ratio, i.e., the ratio of the peak stress after hydrolysis to that before hydrolysis, can be regarded as an indicator of the hydrolysis resistance and is plotted in Figure 3.10(b). The peak stress ratio increases with storage time, indicating that retrogradation enhances the hydrolysis resistance of the starch hydrogel. As mentioned in Chapter 2, the retrogradation creates structures of crystallites, which are compact and more resistant to enzyme diffusion as well as enzymatic hydrolysis, and therefore lead to a lower speed of degradation.

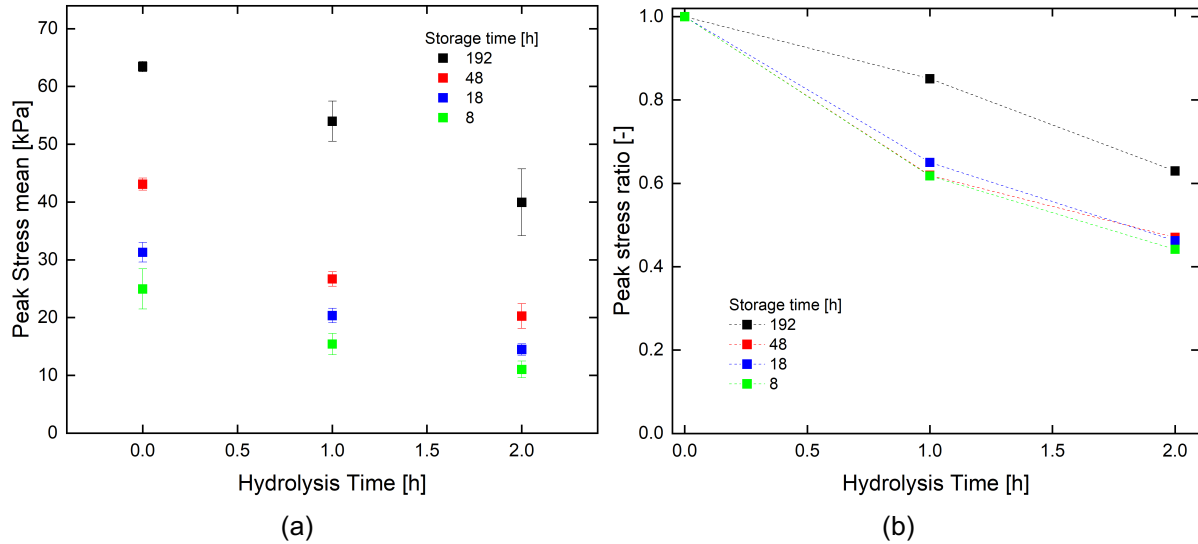


Figure 3.10. Comparison of the first peak stress and the peak stress ratio of starch hydrogels with varying storage time with respect to hydrolysis time. (a) First peak stress, (b) Peak stress ratio.

The failure properties of the starch hydrogel after different hydrolysis times and storage times were also investigated via monotonic loading tests, as shown in Figure 3.11. Consistent with Section 3.3.2, for all storage times, the ultimate strain plotted in Figure 3.11(a) decreases with storage time. It also shows a slight increase with the hydrolysis time. The strength, plotted in Figure 3.11(b) shows a decrease with the hydrolysis time. The failure point is plotted as a stress-strain coordinate in Figure 3.11(c), with an example of a monotonic loading curve shown as a dotted line. For longer storage time, due to stronger retrogradation, the stress levels remained higher throughout the hydrolysis process, consistent with the peak stress in the cyclic test mentioned above, which results from increased crystallinity and reduced chain mobility, while the ultimate strain remained lower.

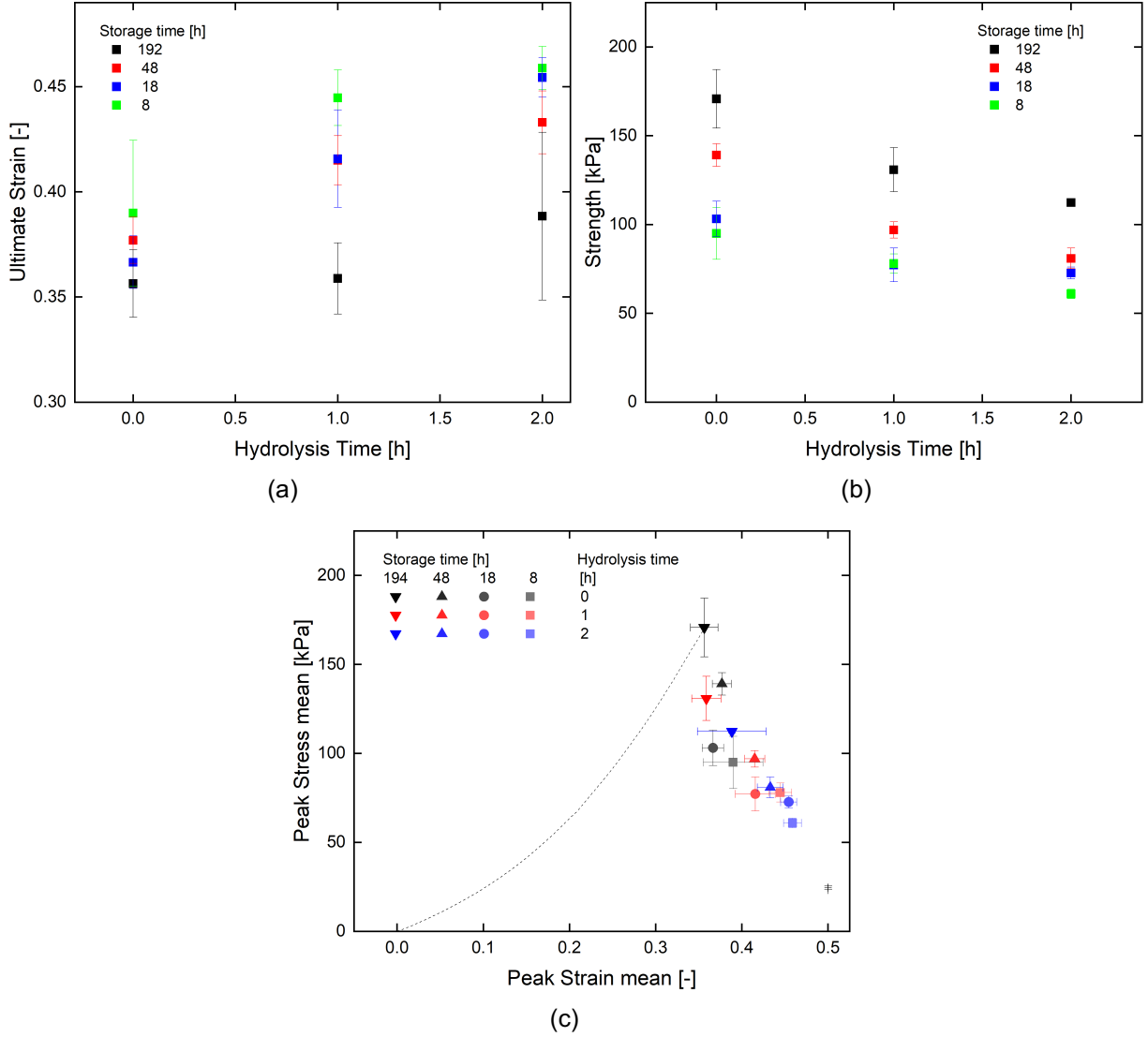


Figure 3.11. Comparison of the ultimate strain and failure stress of starch hydrogels with varying storage time with respect to hydrolysis time. (a) Ultimate strain, (b) strength, (c) failure point. The dotted curve is an example of a monotonic loading curve of a sample with 194 hours of retrogradation time without hydrolysis.

3.3.4 Effect of pH on enzymatic degradation of the mechanical properties of starch hydrogels

The pH value is a key factor influencing enzyme activity and, consequently, the hydrolysis process. In this study, the effects of acidic hydrolysis and pH on the degradation of mechanical properties of starch hydrogels during enzymatic hydrolysis (with pure enzyme or with SGF and enzyme) were investigated. The hydrolysis time was fixed at 180 minutes across all conditions. The stress-strain responses of the samples after acidic hydrolysis are shown in Figure 3.12. The variation in the mechanical response across different pH values was minimal, with all curves falling within the experimental error band. The results under acidic conditions were comparable to those under neutral conditions (see the control group in the green dashed line in Figure 3.12), indicating that no significant acidic hydrolysis occurred in the starch hydrogels.

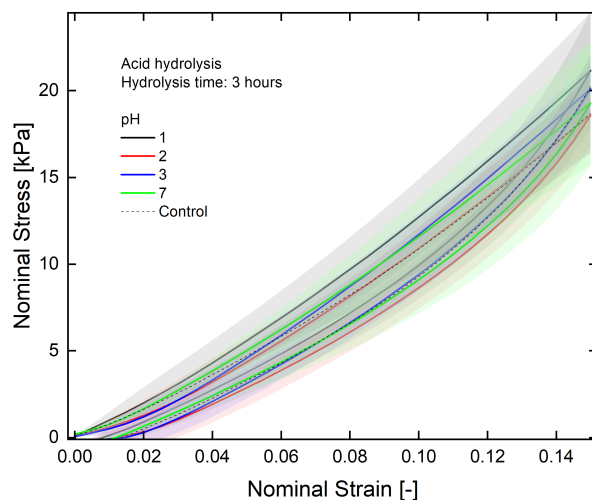


Figure 3.12. Compression behaviour under acidic hydrolysis at different pH values after 3 hours of hydrolysis. The green dashed line indicates the control group at neutral pH.

The stress-strain responses of the samples after enzymatic hydrolysis at different pH values are illustrated in Figure 3.13. It is found that the stress increases with decreasing pH, indicating that the enzymatic hydrolysis is less effective at lower pH. This is consistent with the fact that the activity of α -amylase is maximised at a pH of around 7. Below pH 5, enzyme activity drops significantly, leading to reduced hydrolysis efficiency and, consequently, a stress response similar to that of the control group (samples without hydrolysis). This is also confirmed by the mechanical test of samples after hydrolysis in SGF at different pH values, which simulated more physiologically realistic environments by incorporating acid, salts, and enzymes, as illustrated in Figure 3.14. The stress response at $\text{pH} < 5$ does not differ significantly from the control group,

whereas neutral pH (pH 7) conditions exhibit the most pronounced reduction in stress response. The alkaline conditions of pH 8 show a less pronounced reduction. Note that the solution of the hydrogel hydrolysis in SGF was kept for glucose concentration validation in [Section 3.3.5](#).

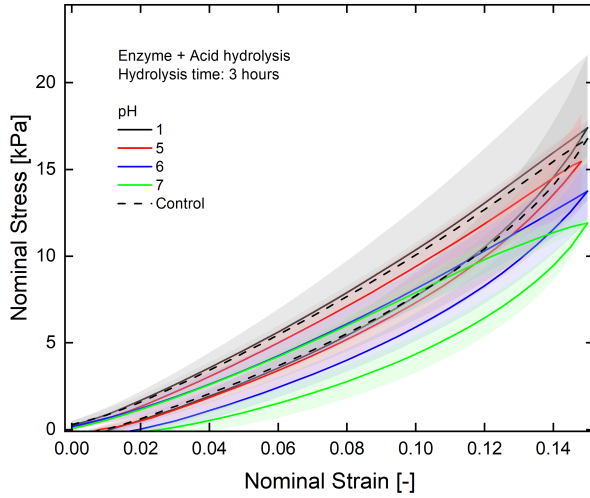


Figure 3.13. Compression behaviour under enzymatic hydrolysis at different pH values after 3 hours of hydrolysis. The dashed line indicates the control group without the enzyme.

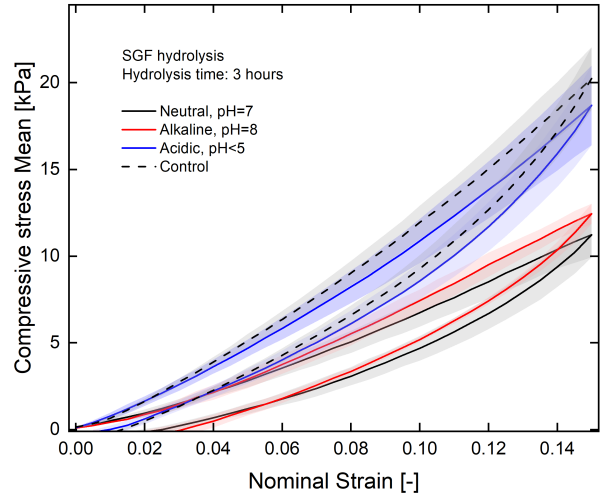
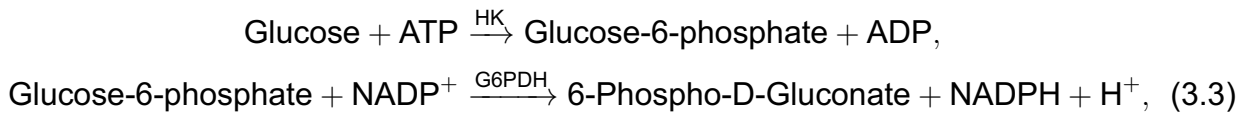


Figure 3.14. Compression behaviour under SGF hydrolysis at different pH values after 3 hours of hydrolysis. The dashed line indicates the control group without SGF.

3.3.5 Glucose concentration during hydrolysis

The UV-Vis spectrophotometer (UV-2600i, Shimadzu, Japan) was used to quantify the D-glucose concentration released from the starch hydrogel samples after hydrolysis. UV-Vis spectrophotometry measures the amount of ultraviolet or visible light absorbed by a substance. By directing light through the post-hydrolysis solution and measuring absorbance at specific wavelengths, the analyte concentration can be determined quantitatively. The protocol provided by the D-glucose assay kit (AK00031, NZYtech) was used to quantify glucose (Minekus et al., [2014](#)). According to the protocol, the following reactions occur:



where D-glucose is first phosphorylated by hexokinase (HK) in the presence of adenosine triphosphate (ATP) to form glucose-6-phosphate and adenosine diphosphate

(ADP). Subsequently, glucose-6-phosphate is oxidised by glucose-6-phosphate dehydrogenase (G6PDH) in the presence of nicotinamide adenine dinucleotide phosphate (NADP^+) to form 6-phospho-D-gluconate and nicotinamide adenine dinucleotide phosphate (NADPH).

The concentration of NADPH product is stoichiometrically equivalent to the amount of D-glucose present in the original solution, and NADPH can be quantified by measuring absorbance at 340 nm. To determine the glucose concentration in the hydrolysed samples, the UV-Vis absorbance measured in the assay was baseline-corrected and subsequently compared with a calibration curve generated from standard D-glucose solutions with known concentrations. The correction approach, identical to that used in the enzyme activity tests described in [Section 3.2.2.2](#), subtracts the baseline absorbance measured before the assay, A_1 , from the absorbance measured after the incubation step of the assay, A_2 , as illustrated in [Figure 3.15\(a\)](#). The resulting corrected absorbance $A_2 - A_1$ for the samples (solid curves) and for the standard solutions (dotted curves) is shown in [Figure 3.15\(b\)](#). The absorbance values at 340 nm were extracted and plotted in [Figure 3.15\(c\)](#), where the standard data are shown as open squares and the samples as closed squares. The standard data were fitted using a linear function (solid line in [Figure 3.15\(c\)](#)), which was subsequently used to determine the glucose concentrations of the hydrolysed samples. The glucose concentration during hydrolysis at different pH values is plotted in [Figure 3.15\(d\)](#). It can be observed that, in all cases, glucose concentration increases over time. In addition, glucose production decreases as pH decreases. This chemical evidence supports the mechanical findings presented in [Figure 3.13](#), namely that more active enzymes lead to stronger hydrolysis and, consequently, greater degradation of mechanical properties. The glucose concentration at pH 7 is the highest, as the enzyme is most active around neutral pH, while the glucose concentration at an alkaline pH of 8 is lower. The glucose concentration at $\text{pH} < 5$ is close to zero, indicating that the enzyme is almost inactive at that pH. This confirms that the degradation of the starch hydrogel was caused by enzymatic hydrolysis.

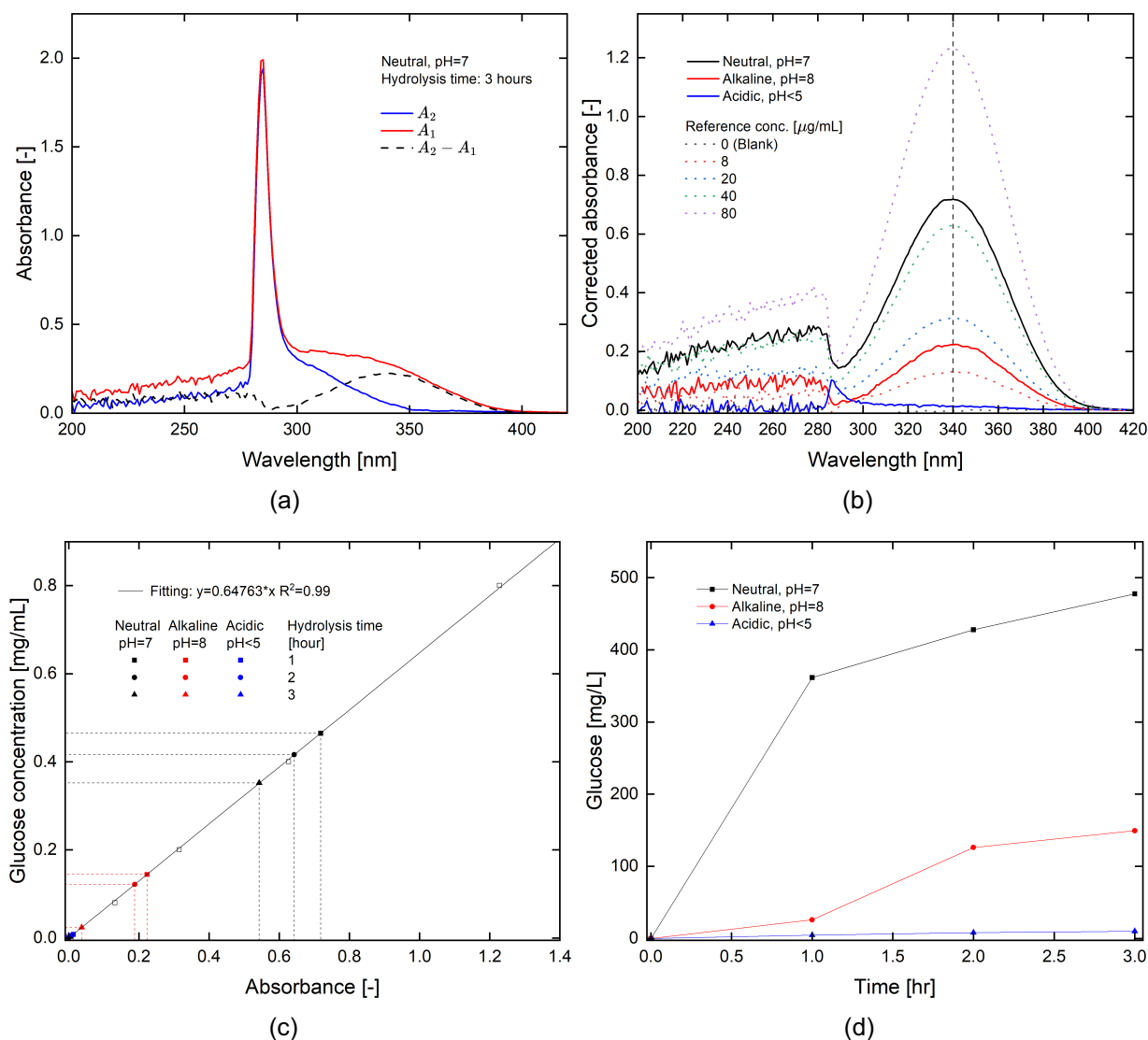


Figure 3.15. Glucose concentration characterisation via UV-Vis spectroscopy after starch hydrogel hydrolysis. (a) Example of original absorbance data before and after assay incubation of a 3-hour hydrolysed solution at neutral pH. A_1 denotes the baseline absorbance before the assay, and A_2 denotes the absorbance after incubation. (b) Corrected absorbance ($A_2 - A_1$) data of the samples and standard D-glucose solutions. (c) Absorbance at 340 nm for the samples and standard D-glucose solutions. The standard curve (solid line), fitted to the standard data (open squares), is used to determine the glucose concentrations of the samples (closed squares). (d) Glucose concentration after hydrolysis at different pH.

3.4 Diffusivity of enzyme in starch hydrogel

3.4.1 Diffusion experiment setup

In [Section 3.3.2](#), the sample size dependence in the enzymatic degradation of the mechanical properties of starch hydrogels was explained by a diffusion-reaction process. Therefore, the enzyme diffusivity in the starch hydrogel was further investigated by a diffusion experiment. A brief summary of the diffusion experiment procedure is as follows. First, α -amylase (introduced in [Section 3.2.2.2](#)) was labelled with a fluorescein isothiocyanate (FITC), as detailed in [Section 3.4.1.1](#). The conjugated FITC- α -amylase was then purified by removing the unconjugated dye using desalting columns, as described in [Section 3.4.1.2](#). The conjugation efficiency was determined by fluorescein to protein (F/P) ratio tests, as described in [Section 3.4.1.3](#), and the enzyme concentration was determined by a bicinchoninic acid (BCA) assay, as described in [Section 3.4.1.4](#).

Flat round samples were prepared within a Petri dish, which was covered by a round glass slide, as shown in [Figure 3.1\(b\)](#) in [Section 3.2.1](#). The conjugated FITC- α -amylase solution was then pipetted outside the perimeter of the sample, as shown in [Figure 3.18](#). The diffusion process was then recorded by a fluorescence microscope, where the colour intensity was quantified as the concentration, and the diffusivity was then calculated by fitting the diffusion profiles with Fick's second law of diffusion, as discussed in [Section 3.4.2](#). The procedure details are described in the following sections.

3.4.1.1 FITC conjugation

FITC (F7250 Isomer I, Sigma-Aldrich) was conjugated to α -amylase (Dhital et al., [2017](#); Edwards et al., [2014](#); The & Feltkamp, [1970](#)). A 1:4 (v/v) ratio of 0.069% (w/v) FITC to 0.5% (w/v) α -amylase was incubated in 0.1 M sodium carbonate-bicarbonate buffer (0.286% (w/v) Na_2CO_3 + 0.756% (w/v) NaHCO_3 pH 9), following the protocol of the manufacturer and Edwards et al., [2014](#). The reaction was allowed to proceed for more than 2 hours at 37°C, whilst mixing using a rotary mixer. As the mixture contains both the conjugated FITC- α -amylase and the unconjugated FITC, the mixture needs to be purified before the diffusion experiment, as described in [Section 3.4.1.2](#).

3.4.1.2 Desalting columns

Unconjugated FITC was removed from the conjugated enzyme solution using desalting chromatography. Specifically, a desalting column (PD-10, Cytiva), 10 cm in height and 1 cm in diameter, packed with a size-exclusion resin (G-25, Sephadex), was used. Within the column, macromolecules are excluded from the pores of the desalting resin and therefore elute earlier than small molecules such as salts or unbound dyes. Following the gravity protocol provided by the manufacturer, the column was first equilibrated with a 0.1 M sodium carbonate-bicarbonate buffer. The conjugated enzyme solution was then applied to the top of the column, and the initial flow-through was discarded. The column was subsequently eluted with the same buffer. Owing to the size difference, the conjugated enzyme eluted first under gravity, enabling its separation from the unconjugated dye. The purified, conjugated enzyme was stored at 4° C in a dark vial to prevent photobleaching.

3.4.1.3 F/P ratio tests

F/P molar ratio tests were performed to determine the ratio of FITC to α -amylase for conjugation. The absorbance of the conjugated enzyme solution was measured at 280 nm and 495 nm using a UV-Vis spectrophotometer (UV-2600i, Shimadzu, Japan), and the results were recorded, as shown in [Figure 3.16](#). Note that the absorbance values at 280 nm were lower than 1.5, and therefore, the samples did not need to be diluted. The F/P molar ratio $f_{F/P}$ is calculated according to the equations provided by the manufacturer of the fluorescein, i.e.,

$$f_{F/P} = \frac{A_{495}}{A_{280} - 0.35A_{495}} \times \frac{M_{\text{enz}} \times E_{280}^{0.1\%}}{389 \times 195} \quad (3.4)$$

where A_{280} and A_{495} are the absorbances at 280 nm and 495 nm, respectively; M_{enz} is the molecular weight of the protein α -amylase, i.e., 51–54 kDa; $E_{280}^{0.1\%}$ is the absorbance at 280 nm of the protein at 0.1% w/v; 389 is the molecular weight of FITC; and 195 is the absorption $E_{280}^{0.1\%}$ of bound FITC at 490 nm at pH 13.0. 0.35 is the correction factor due to the absorbance of FITC at 280 nm. The F/P ratio was found to be 1:2 (v/v). Although it is lower than that suggested (1:1) in the literature (Edwards et al., [2014](#)), it still provided effective conjugation that can be used to calibrate diffusivity.

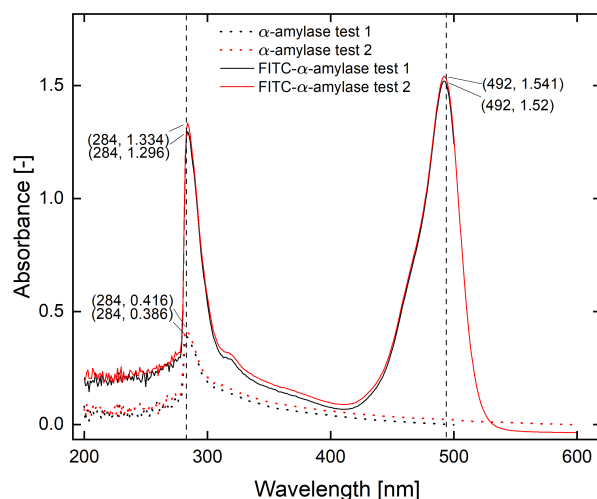


Figure 3.16. Absorbance of the unconjugated and conjugated enzyme solution at 280 nm and 495 nm for F/P ratio calculation.

3.4.1.4 Enzyme concentration test via BCA assay

The eluted fractions were collected and analysed for protein (α -amylase) concentration using a BCA Protein Assay Kit (71285-3, Millipore). According to the protocol provided by the manufacturer, the BCA protein assay is based on the biuret reaction, in which peptide bonds of the protein reduce Cu^{2+} to Cu^{+} under alkaline conditions. The reduced Cu^{+} then forms a purple-coloured complex with BCA, exhibiting strong absorbance at 562 nm proportional to the protein concentration. Following the microscale enhanced assay protocol, 25 μL of each standard or sample was mixed with 200 μL of BCA working reagent in a 96-well microplate and incubated at 60 $^{\circ}\text{C}$ for 15 min. After cooling to room temperature, the absorbance was measured at 562 nm using the spectrophotometer (BMG Labtech Omega microplate reader). A standard curve was generated using 2 mg/mL BSA, and sample protein concentrations were interpolated from the standard curve after blank subtraction, as is shown in Figure 3.17. The dilution ratio after filtration was 2.157, and the enzyme concentration was 0.548 g/L after conjugation and filtration. This concentration was not significantly different in order of magnitude from the initial concentration, indicating that the diffusivity calibrated using the conjugated enzyme is representative.

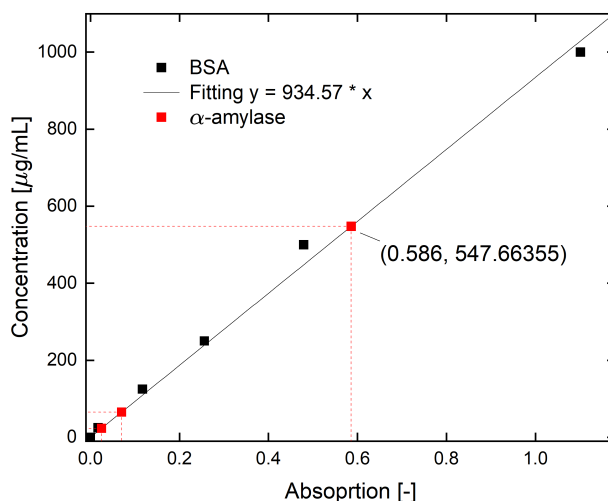


Figure 3.17. Absorbance-concentration relationship of the standard solutions and the conjugated enzyme solution.

3.4.2 Calibration of diffusivity of α -amylase in starch hydrogel

3.4.2.1 Diffusion experiment and data processing

Following the setup in [Section 3.4.1](#), a diffusion experiment was performed on the thin round slice of a starch hydrogel covered with a round glass slide, where the conjugated FITC- α -amylase diffused from the perimeter of the starch hydrogel into the medium. As mentioned in [Section 3.2.1](#), the top and bottom surfaces of the sample were adhered to the glass slide and the Petri dish, respectively, ensuring that the enzyme solution could not diffuse from the top or bottom surfaces. To prevent evaporation of the enzyme solution during the long-term diffusion test, the Petri dish was covered with a glass lid, allowing imaging through it. The schematic representation of the diffusion setup is shown in [Figure 3.18\(a\)](#), and an image of the sample in a Petri dish under the fluorescence microscope at the beginning of the tests is shown in [Figure 3.18\(b\)](#). The diffusion process was then recorded using a fluorescence microscope (SMZ1279, Nikon) at 15-minute intervals for up to 100 hours. The microscope is equipped with a filter cube (P-FL-C GFP-L, Nikon), which transmits blue excitation light (450–490 nm) to excite the labelled enzyme, reflects wavelengths below 500 nm, and allows cyan or green fluorescence around 510 nm to reach the detector. Therefore, the diffusion of the labelled enzyme can be visualised and recorded, and the intensity of the cyan or green colour can be quantified as the concentration. Note that here we assume the enzyme distributes uniformly in the thickness direction, which is reasonable given the in-plane diffusion, with a thickness-to-diameter ratio of <1:10.

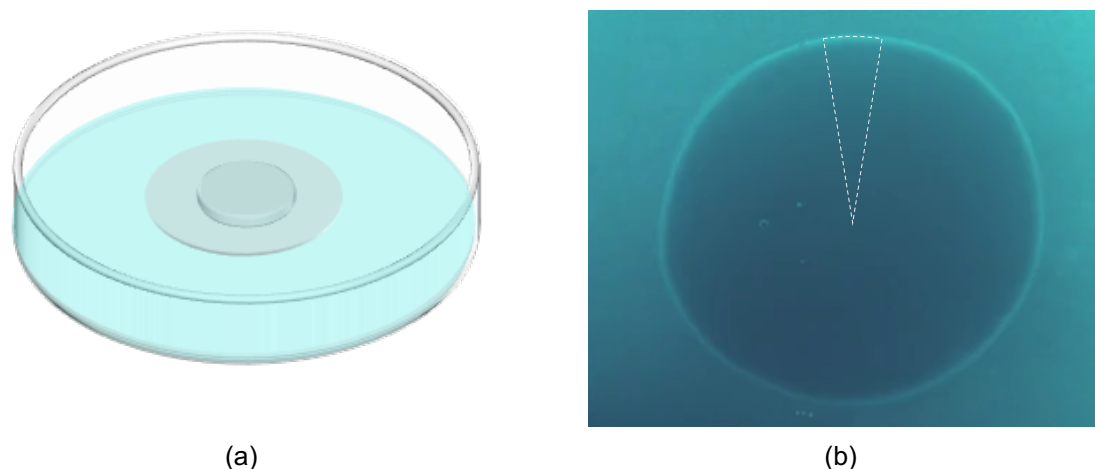


Figure 3.18. Sample for diffusion test. (a) Schematic representation of the diffusion setup. (b) Sample in a Petri dish imaged by a fluorescence microscope, where the white dotted lines represent the region compared in Figure 3.19 at different time intervals.

An example of the diffusion test image is shown in Figure 3.19, where each sector corresponds to the image of the same section of the sample (marked by the dotted lines in Figure 3.18(b)) at different time points. The colour intensity represents the enzyme concentration, and the colour bar shows the range of intensities. The diffusion process can be clearly observed as the lighter colour propagates from the boundary to the centre of the sample over time, indicating an increase in enzyme concentration. The images were processed and analysed in ImageJ to obtain fluorescence intensity profiles (averaged over the same radius at each time point). For example, the diffusion profile, i.e., normalised concentration with respect to the initial concentration versus radius, for two diffusion tests at 24 hours is plotted as dotted lines in Figure 3.20.

Note that due to experimental limitations, the diffusion test was performed at 20°C (ambient temperature) instead of 37°C, which is the incubation temperature for the starch hydrogel hydrolysis test discussed in Section 3.3.1. When we tried to heat the sample to 37°, the Petri dish misted due to a temperature difference between inside and outside, preventing clear imaging. Although temperature changes enzyme activity and therefore influences diffusion, as the concentration gradient mainly drives diffusion, the diffusivity calibrated at 20°C can still provide helpful information about the enzymatic diffusion behaviour in the starch hydrogel at 37°C. The diffusion at 37°C will be considered in future work. In addition, hydrostatic stress may also influence the speed of diffusion, as the stress state of the sample may change during digestion. This effect will also be investigated in future work.

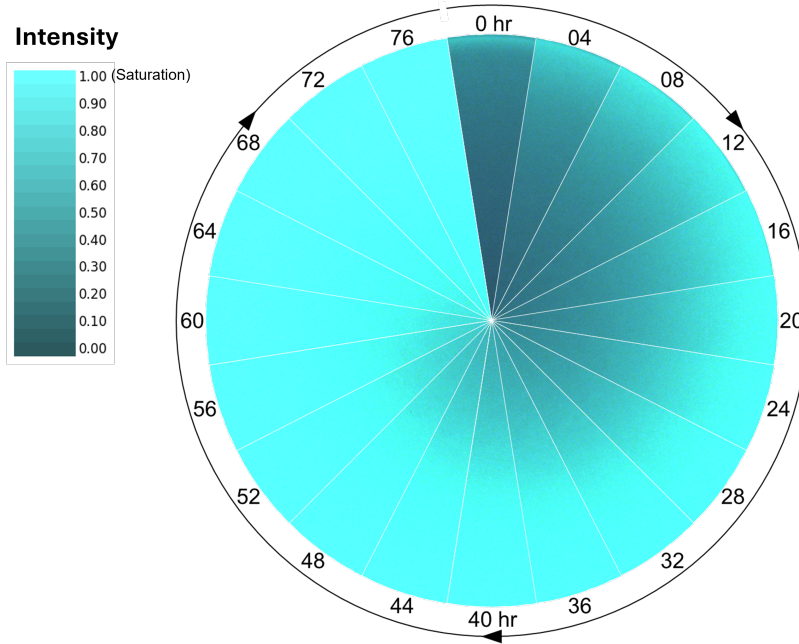


Figure 3.19. Images from the diffusion tests. Each sector in the circle represents the image of the sample of the same section at different time intervals. The colour intensity reflects the enzyme concentration. The colour bar shows the intensity of the colour.

3.4.2.2 Axisymmetric Fickian diffusion model and finite difference discretisation

At each position within the sample, the fluorescence intensity is assumed to be proportional to the local enzyme concentration. The measured intensities are normalised such that the initial state (prior to diffusion) corresponds to zero, and the fully saturated state, defined as the equilibrium concentration matching the external environment, is set to one. We assume that the diffusion of the enzyme within the hydrogel follows Fick's law of diffusion, which assumes that the diffusion flux is proportional to the concentration gradient, i.e.,

$$\mathbf{J} = -D\nabla C, \quad (3.5)$$

where $\mathbf{J}$ is the diffusion flux vector, D is the diffusion coefficient, and C is the concentration. The mass conservation requires that

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J}. \quad (3.6)$$

Combining [Equation 3.5](#) and [Equation 3.6](#), we have

$$\frac{\partial C}{\partial t} = \nabla \cdot [D\nabla C]. \quad (3.7)$$

For a homogeneous and isotropic medium, assuming that D does not vary with time or concentration, the diffusion process can be described by Fick's second law of diffusion, which reads

$$\frac{\partial C}{\partial t} = D \nabla^2 C. \quad (3.8)$$

As the thickness of the sample was far smaller than the diameter, the diffusion was mainly in-plane, and the sample was circular, the diffusion process was approximated by the one-dimensional (1D) axisymmetric form of Equation 3.8, i.e.,

$$\frac{\partial C}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right] \quad (3.9)$$

where r is the radial coordinate.

Owing to the linearity of Fickian diffusion, when the concentration is normalised as

$$C^*(r, t) = \frac{C(r, t)}{C_{\text{eq}}}, \quad (3.10)$$

all 1D axisymmetric diffusion experiments from the outer boundary, even with different equilibrium concentrations, share the same dimensionless boundary and initial conditions. In Equation 3.10, C_{eq} is the equilibrium concentration (concentration after infinite time). The normalised boundary condition is $C(r_0, t) = C_{\text{eq}}$, where r_0 is the radius of the sample, and therefore $C^*(r_0, t) = 1$. The initial condition is $C^*(r, 0) = 0$ for $0 \leq r < r_0$. Consequently, the normalised diffusion equation and its solution are invariant under changes in the equilibrium concentration. This property allows for direct fitting of the experimental data to theoretical diffusion curves.

Equation 3.9 is a parabolic partial differential equation, and its solution can be computed numerically using the finite difference method (FDM). In this method, the spatial and temporal domains are discretised into a grid of nodes, and the derivatives in the diffusion equation are approximated using finite difference operators. The spatial and temporal coordinates are normalised as $R = r/r_0$, $T = Dt/r_0^2$, and therefore Equation 3.9 becomes

$$\frac{\partial C^*}{\partial T} = \frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial C^*}{\partial R} \right) = \frac{\partial^2 C^*}{\partial R^2} + \frac{1}{R} \frac{\partial C^*}{\partial R}. \quad (3.11)$$

In addition, the discretised step sizes are given by $\Delta R = R/n$ and $\Delta T = T/m$, where n and m denote the numbers of spatial and temporal nodes, respectively. The first-order

finite difference, i.e., approximates the first-order time derivative,

$$\frac{dC^*}{dT} \approx \frac{C_{i,j+1}^* - C_{i,j}^*}{\Delta T}, \quad (3.12)$$

where $C_{i,j}^*$ is the normalised concentration at the i -th spatial node and the j -th time step, ΔT is the time step size. Similarly, the first-order spatial derivative yields

$$\frac{dC^*}{dR} \approx \frac{C_{i+1,j}^* - C_{i,j}^*}{\Delta R}. \quad (3.13)$$

The second-order derivative is approximated by the second-order finite difference, e.g.,

$$\frac{d^2 C^*}{dR^2} \approx \frac{\frac{C_{i+1,j}^* - C_{i,j}^*}{\Delta R} - \frac{C_{i,j}^* - C_{i-1,j}^*}{\Delta R}}{\Delta R} = \frac{C_{i+1,j}^* - 2C_{i,j}^* + C_{i-1,j}^*}{[\Delta R]^2}, \quad (3.14)$$

Here, the Crank-Nicolson implicit FDM was adopted, thanks to its stability and accuracy (Crank, 1975). This method approximates $\frac{\partial^2 C^*}{\partial R^2}$ by the average of the finite difference of the j -th and $[j + 1]$ -th time steps, and Equation 3.9 is given by:

$$\frac{C_{i,j+1}^* - C_{i,j}^*}{\Delta T} = \begin{cases} \frac{1}{2[\Delta R]^2} \left[\frac{2i+1}{2i} C_{i+1,j}^* - 2C_{i,j}^* + \frac{2i-1}{2i} C_{i-1,j}^* + \frac{2i+1}{2i} C_{i+1,j+1}^* - 2C_{i,j+1}^* + \frac{2i-1}{2i} C_{i-1,j+1}^* \right], & \text{when } i \neq 0 \text{ and } i \neq n-1, \\ \frac{1}{2[\Delta R]^2} [C_{1,j}^* - C_{0,j}^* + C_{1,j+1}^* - C_{0,j+1}^*], & \text{when } i = 0, \end{cases} \quad (3.15)$$

where $C_{i,j}^*$ is the normalised concentration at the i -th spatial node and the j -th time step. The boundary conditions are:

$$C_{n-1,j}^* = 1 \quad (3.16)$$

The discretisation of 1D axisymmetric diffusion Equation 3.15 and the boundary conditions

Equation 3.16 can be rearranged into a matrix equation:

$$= \begin{bmatrix} 1+2s & -2s & & & & & \\ -\frac{1}{2}s & 2(s+1) & -\frac{3}{2}s & & & & \\ & \ddots & \ddots & \ddots & & & \\ & & -\frac{2i-1}{2i}s & 2(s+1) & -\frac{2i+1}{2i}s & & \\ & 0 & & \ddots & \ddots & \ddots & \\ & & & -\frac{2n-5}{2(n-2)}s & 2(s+1) & -\frac{2n-3}{2(n-2)}s & \\ & & & & 0 & 1 & \end{bmatrix} \begin{bmatrix} C_0^* \\ C_1^* \\ \vdots \\ C_{n-2}^* \\ C_{n-1}^* \end{bmatrix}_{j+1}$$

$$= \begin{bmatrix} 1-2s & 2s & & & & & \\ \frac{1}{2}s & 2(1-s) & \frac{3}{2}s & & & & \\ & \ddots & \ddots & \ddots & & & \\ & & \frac{2i-1}{2i}s & 2(1-s) & \frac{2i+1}{2i}s & & \\ & 0 & & \ddots & \ddots & \ddots & \\ & & & \frac{2n-5}{2(n-2)}s & 2(1-s) & \frac{2n-3}{2(n-2)}s & \\ & & & & 0 & 1 & \end{bmatrix} \begin{bmatrix} C_0^* \\ C_1^* \\ \vdots \\ C_{n-2}^* \\ 1 \end{bmatrix}_j, \quad (3.17)$$

where $s = \Delta T / [\Delta R]^2$. It can be seen that the matrices on both sides of the equation are tridiagonal matrices containing only non-zero elements on the main diagonal and two diagonals immediately above and below it. These matrices can be stored and solved efficiently. The `spsolve` function from the SciPy library in Python was used to solve the sparse linear system Equation 3.17. The numerical solution was computed using 100 spatial nodes and 360000 temporal nodes, which were found to be sufficient for convergence.

By minimising the error between the normalised experimental data and the numerical solutions of the diffusion profile at all time points, the diffusion coefficient was calibrated to $D = 8.6 \times 10^{-5} \text{ mm}^2/\text{s}$. The diffusion profiles at 12 hours and 24 hours obtained by FDM are plotted in a solid line in Figure 3.20(b). It can be seen there are deviations between the experimental data and the numerical solution, which may be due to the non-Fickian diffusion behaviour of the enzyme in the hydrogel, i.e., the diffusion is dependent on the concentration, leading to a steeper slope and faster saturation at higher concentrations, while at lower concentrations the diffusion might be slower, especially at a longer diffusion time, comparing the result at 24 hours to that at 12 hours. However, the overall trend is captured well by the Fickian diffusion model.

The amount of enzyme within the sample can be calculated by integrating the

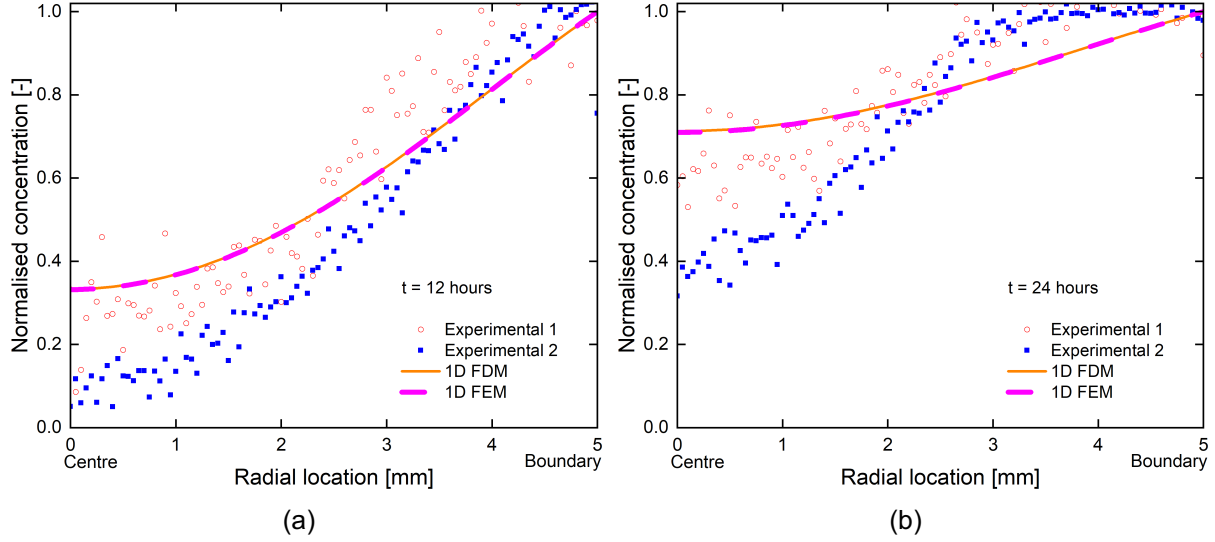


Figure 3.20. Normalised concentration along the radius of the sample for diffusion times of (a) 12 hours, and (b) 24 hours. Comparison between two experimental replicate data and the numerical solution obtained by FDM and FEM.

concentration over the volume of the sample, i.e.,

$$f_{\text{enz}}(t) = \int_A C(r, t) dV = \int_0^{r_0} 2\pi r h C(r, t) dr, \quad (3.18)$$

where h is the sample height. We then define the enzyme saturation ratio as

$$f_{\text{enz}}^*(t) = \frac{f_{\text{enz}}(t)}{f_{\text{enz}}(t \rightarrow \infty)}, \quad (3.19)$$

where

$$f_{\text{enz}}(t \rightarrow \infty) = V C_{\text{eq}} = \pi r_0^2 h C_{\text{eq}} \quad (3.20)$$

is the total amount of enzyme at equilibrium within the sample. The results of the enzyme saturation ratio are illustrated in Figure 3.21, where the experimental data are plotted in dots, and the numerical solution is plotted in a solid line. It can be seen that the enzyme concentration in the sample increases over time, and the experimental data agree well with the numerical solution, confirming that the enzyme diffusion within the starch hydrogel can be effectively described by Fickian diffusion. Note that in Figure 3.20, and Figure 3.21, the FEM result (see details in Section 4.3) is also included in dashed lines for comparison. The FEM results have an excellent agreement with the FDM results.

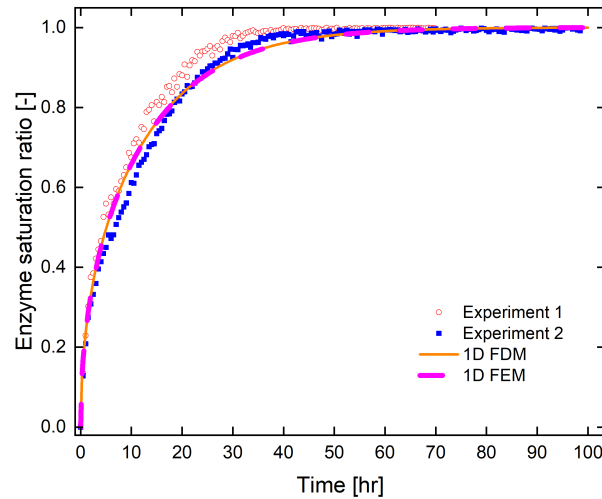


Figure 3.21. Enzyme saturation ratio within the sample over time.

3.5 Conclusion

In this section, the coupled diffusion-reaction-deformation process in starch hydrogels was investigated. First, the mechanical behaviour of the starch hydrogel under various hydrolysis conditions was characterised using cyclic compression tests. It was found that the mechanical properties of the starch hydrogel were affected by enzymatic hydrolysis with α -amylase, with stiffness decreasing and dissipation increasing as the hydrolysis level increased. The hydrolysis level was dependent on specimen size due to the diffusion-reaction process. Increased retrogradation increased the resistance to enzymatic hydrolysis. Acidic hydrolysis was not observed, but the low pH condition deactivated the enzyme, thereby reducing hydrolysis. The enzymatic hydrolysis under SGF conditions was also investigated, and the sugar concentration after hydrolysis was measured to confirm the extent of hydrolysis. Then, the diffusion of fluorescein-labelled α -amylase within the starch hydrogel was monitored using a fluorescence microscope, and the diffusion coefficient was calibrated by fitting the experimental data to a 1D axisymmetric FDM model.

There are several limitations in this study. Firstly, the diffusion and compression tests were not performed at body temperature (37 °C), and the temperature dependence of diffusivity was not considered. Secondly, the Fickian diffusion assumption was adopted. However, the experimental data show deviations from Fickian diffusion behaviour, which affect the accuracy of the simulation. These limitations will be addressed in future work.

Chapter 4

Chemo-mechanical constitutive model for starch hydrogel and numerical implementation for simulation of *in vitro* hydrolysis

4.1 Introduction

In the last chapter, *in vitro* experiments were performed to obtain the mechanical behaviour and measure the degradation of starch hydrogels under enzymatic hydrolysis. The diffusivity of α -amylase in the starch hydrogel was also investigated. As we found that the enzymatic hydrolysis of the starch hydrogel is a diffusion-reaction process, it is necessary to develop a chemo-mechanical constitutive model to describe the coupled diffusion-reaction-deformation behaviour of the starch hydrogel during *in vitro* digestion, which should be incorporated into a numerical framework for simulation.

Various kinetic models have been proposed to describe the enzymatic hydrolysis of starch, including first-order kinetics (Brandam et al., 2003), Michaelis-Menten kinetics (Dhital et al., 2017), models derived from Michaelis-Menten kinetics (Duggleby, 2001; Kusunoki et al., 1982), and other empirical models (Gaouar et al., 1997; Syahariza et al., 2013). A review of these models can be found in Nguyen and Sopade (2018). However, most of these models primarily focus on characterising the hydrolysis rate in well-mixed solutions and predicting the concentration of hydrolysed products over time, while neglecting the transient diffusion of enzymes within the solid.

Furthermore, constitutive modelling of the chemo-mechanical behaviour of starch hydrogels under enzymatic hydrolysis has been scarcely reported. Most available chemo-mechanical constitutive models focused on hydrogels of polymers other than starch. A relevant study is the chemo-mechanical constitutive model developed by Pan et al. (2022), which couples large deformation, swelling, and mass loss of biodegradable synthetic hydrogels to hydrolytic degradation by accounting for the evolving tree-like network topology. Owing to its topology-based formulation, the degradation relationship can be adapted to other hydrolysable polymer networks such as starch hydrogels. Later, they further consider diffusion and reaction in their constitutive model in Pan and Brassart (2023) by decoupling the chain-scission mechanism from the overall reaction kinetics, allowing the degradation mechanism to be identified directly from experimental molecular-weight and mass-loss data. However, their model has not yet been applied to starch-based hydrogels. And the diffusivity was calibrated only from weight changes, which were indirect and may not have been accurate. Additionally, this model was based on hyperelastic behaviour, while viscoelastic behaviour was not included. Nevertheless, their model was a good reference for our model development. The numerical simulation of diffusion-reaction-deformation behaviour during *in vitro* digestion of starch-based systems has also been sparsely reported. Sitaraman et al. (2019) developed a comprehensive CFD computational model for the enzymatic hydrolysis reaction of cellulose in a centrifuge tube, in which fluid dynamics are coupled with dissolved-species transport and chemical reaction. However, the simulation did not account for the mechanical behaviour of the solid.

Therefore, the reaction kinetics of solid starch hydrogels remain to be modelled, and a chemo-mechanical constitutive model describing enzymatic hydrolysis of starch hydrogels has yet to be developed. A numerical simulation of the coupled diffusion-reaction-deformation process during *in vitro* digestion of starch hydrogels has not yet been performed. In this chapter, a chemo-mechanical constitutive model for a starch hydrogel under enzymatic hydrolysis is proposed in [Section 4.2](#). The fundamentals of continuum mechanics are introduced in [Section 4.2.1](#), [Section 4.2.2](#) and [Section 4.2.3](#). The specific energy function is defined in [Section 4.2.4](#). The enzymatic hydrolysis reaction is described by a first-order kinetic model in [Section 4.2.6](#). The mechanical degradation of the hydrogel during hydrolysis is described by the evolution of the network topology, following the approach of Pan et al. (2022). The constitutive model is one-dimensionalised in [Section 4.2.7](#), and calibrated by the mechanical test data from [Chapter 2](#) in [Section 4.2.8](#), and calibrated by the chemo-mechanical test data from [Chapter 3](#) in [Section 4.2.9](#).

The numerical implementation of the constitutive model into a Finite Element (FE) framework is presented in [Section 4.3](#). The introduction of the FE formulation of the constitutive model is introduced in [Section 4.3.1](#). The FE model description is given in [Section 4.3.2](#). The inverse analysis procedure for calibrating the chemical parameters using the experimental data obtained in [Chapter 3](#) is presented in [Section 4.3.3](#). Finally, the simulation of the *in vitro* digestion tests performed in [Chapter 3](#) is presented in [Section 4.3.4](#). The calibrated chemo-mechanical constitutive model parameters are used to simulate the *in vitro* digestion tests in [Section 4.3](#). Note that the detailed operation of tensor calculus will not be explicitly detailed but will follow Chaves (2013).

4.2 Chemo-mechanical constitutive model for starch hydrogel

4.2.1 Kinematics

To describe the finite deformation field of the starch hydrogel, the concept of the deformation gradient tensor $\mathbf{F}$, measuring the change in configuration from the reference state to the current state, is introduced as

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}}, \quad (4.1)$$

where $\mathbf{x}$ is the current position of a material point, and $\mathbf{X}$ is the reference position. The volume change of the material is measured by the Jacobian determinant of the deformation gradient, defined as

$$J = \det(\mathbf{F}). \quad (4.2)$$

The isochoric part of the deformation gradient can be obtained by removing the volumetric change from the deformation gradient as

$$\bar{\mathbf{F}} = J^{-\frac{1}{3}} \mathbf{F}, \quad (4.3)$$

To capture the time-dependent viscoelastic response of an imperfect network of starch hydrogels, the isochoric part of the deformation gradient tensor can be further decomposed multiplicatively as

$$\bar{\mathbf{F}} = \mathbf{F}_{e,j} \mathbf{F}_{v,j}, \quad j = 1, 2, \dots, n \quad (4.4)$$

where $\mathbf{F}_{e,j}$ is the elastic deformation gradient representing the deformation of dangling chains or solvated chain fraction, and $\mathbf{F}_{v,j}$ is the viscous deformation gradient representing the relative motion of these chains to the surrounding medium (Li et al., 2019; Stricher et al., 2015), as discussed in Section 2.5.2. Therefore, Equation 4.4 demonstrates that the combination of the elastic and viscous deformations results in the total deformation, as illustrated in Figure 4.1, and only two of these three deformations are independent. We further denote the maximum historical value of the isochoric deformation gradient over the loading history (Liao et al., 2020a), given by

$$\bar{\mathbf{F}}_{\max} = \max(\bar{\mathbf{F}}). \quad (4.5)$$

Note that the maximum operation is performed independently on each component of the tensor.

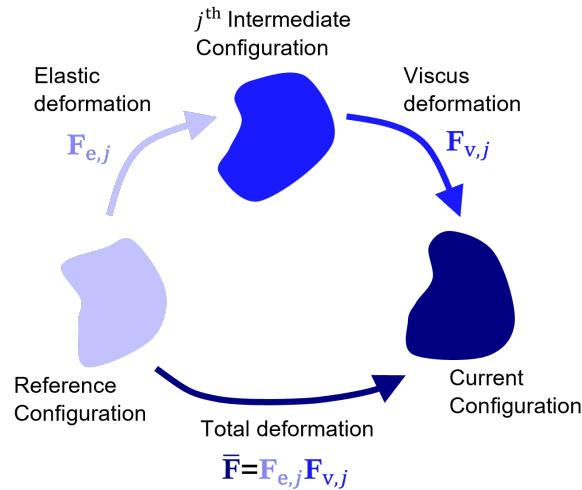


Figure 4.1. Multiplicative decomposition of the isochoric deformation gradient into elastic and inelastic parts (volumetric deformation is not shown).

Furthermore, the total deformation can also be measured by the right Cauchy-Green strain tensor, defined as

$$\mathbf{C} = \mathbf{F}^T \mathbf{F}, \quad (4.6)$$

and according to Equation 4.4, the isochoric deformation can be measured by the isochoric right Cauchy-Green strain tensor, defined as

$$\bar{\mathbf{C}} = \bar{\mathbf{F}}^T \bar{\mathbf{F}} = J^{-\frac{2}{3}} \mathbf{C}. \quad (4.7)$$

Accordingly, the elastic and viscous deformations can be measured by

$$\mathbf{C}_{e,j} = \mathbf{F}_{e,j}^T \mathbf{F}_{e,j} = \mathbf{F}_{v,j}^{-T} \cdot \bar{\mathbf{C}} \cdot \mathbf{F}_{v,j}^{-1}, \quad (4.8)$$

$$\mathbf{C}_{v,j} = \mathbf{F}_{v,j}^T \mathbf{F}_{v,j}, \quad (4.9)$$

respectively, and the maximum historical isochoric deformation is measured by

$$\bar{\mathbf{C}}_{\max} = \bar{\mathbf{F}}_{\max}^T \bar{\mathbf{F}}_{\max}, \quad (4.10)$$

respectively.

4.2.2 Thermodynamics

The existence of a Helmholtz free energy density function, or specific strain energy function, Ψ is assumed for the starch hydrogel material, which is considered a function of the $\bar{\mathbf{C}}$, $\mathbf{C}_{e,j}$ (or $\mathbf{C}_{v,j}$), $\bar{\mathbf{C}}_{\max}$, J introduced in [Section 4.2.1](#) and a chemical internal variable f introduced later in [Section 4.2.5](#). As a standard practice (Hossain & Liao, 2020; Liao et al., 2020b; Yang et al., 2023), the specific strain energy can be decomposed additively into a volumetric contribution and an isochoric contribution, i.e.,

$$\Psi = \Psi(\bar{\mathbf{C}}, \mathbf{C}_{e,j}, \bar{\mathbf{C}}_{\max}, J, f) = \Psi_{\text{vol}}(J) + \tilde{\Psi}_{\text{iso}}(\bar{\mathbf{C}}, \mathbf{C}_{e,j}, \bar{\mathbf{C}}_{\max}, f). \quad (4.11)$$

The isochoric part of the specific strain energy, $\tilde{\Psi}_{\text{iso}}$, can be described by a rheological model. As illustrated in [Figure 4.2](#), we assume that the material is a combination of a hyperelastic branch, a pseudoelastic branch, and two viscoelastic branches in parallel, capturing the hyperelastic, pseudoelastic, and viscoelastic behaviour of the starch hydrogel, respectively. It should be noted that the tilde accent $\tilde{\bullet}$ stands for the component that considers the effect of the chemical internal variable f , while the corresponding variable without the tilde accent stands for that without the impact of f , i.e., the condition before any reaction and degradation occurs. In the viscoelastic branches, $\mathbf{F}_{e,j}$ is represented by the elastic spring and $\mathbf{F}_{v,j}$ is defined by the dashpot. Here, we consider two viscoelastic branches ($j = 1, 2$) to capture the time-dependent response of the starch hydrogel. Accordingly, we further assume that the isochoric part Ψ_{iso} can be additively decomposed into three parts, including an equilibrium part $\tilde{\Psi}^{\text{eq}}$ as a function of $\bar{\mathbf{C}}$, a pseudo-equilibrium part $\tilde{\Psi}^{\text{peq}}$ as a function of $\bar{\mathbf{C}}$ and $\bar{\mathbf{C}}_{\max}$, and non-equilibrium parts $\tilde{\Psi}_j^{\text{neq}}$ as a function of $\mathbf{C}_{e,j}$, and all of them depend on the chemical

internal variable f , i.e.,

$$\tilde{\Psi}_{\text{iso}} = \Psi(\bar{\mathbf{C}}, \mathbf{C}_{e,j}, \bar{\mathbf{C}}_{\text{max}}, f) = \tilde{\Psi}^{\text{eq}}(\bar{\mathbf{C}}, f) + \tilde{\Psi}^{\text{peq}}(\bar{\mathbf{C}}, \bar{\mathbf{C}}_{\text{max}}, f) + \sum_{j=1}^2 \tilde{\Psi}_j^{\text{neq}}(\mathbf{C}_{e,j}, f). \quad (4.12)$$

From the perspective of the micromechanics of the rheology model, the equilibrium part $\tilde{\Psi}^{\text{eq}}$ represents the elastic response of a perfect polymer network. The pseudo-equilibrium part $\tilde{\Psi}^{\text{peq}}$ accounts for the stress-softening behaviour associated with microstructural changes such as crystallite reinforcement and breakage, and therefore depends additionally on the historical maximum strain $\bar{\mathbf{C}}_{\text{max}}$. The non-equilibrium part $\tilde{\Psi}^{\text{neq}}$ captures the time-dependent response arising from network imperfections, such as solvated chain fractions and dangling chains, which contribute to internal friction and viscoelastic dissipation. The ratio of these chains varies during the enzymatic hydrolysis, leading to changes in the equilibrium, pseudo-equilibrium, and non-equilibrium responses of the starch hydrogel.

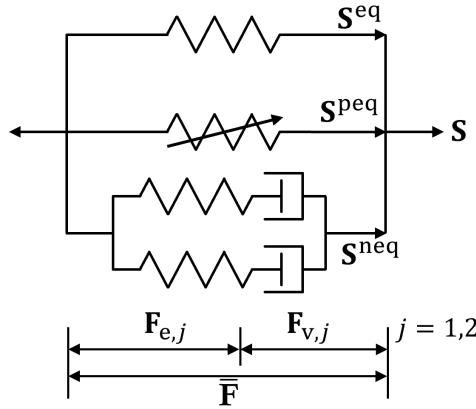


Figure 4.2. The representation of the constitutive model in a rheological framework.

This energy function is supposed to satisfy the second law of thermodynamics, which is given by:

$$\mathbf{S} : \frac{1}{2} \dot{\mathbf{C}} - \dot{\Psi} \geq 0, \quad (4.13)$$

where $\mathbf{S}$ is the second Piola-Kirchhoff stress tensor, which is the energetic conjugate variable of $\mathbf{C}$. Equation 4.13 describes that the mechanical work done on the system is always greater than or equal to the strain energy. Combining Equation 4.12 and Equation 4.13, we have:

$$\left[\mathbf{S} - 2 \frac{\partial \Psi}{\partial \mathbf{C}} \right] : \dot{\mathbf{C}} - 2 \frac{\partial \Psi^{\text{peq}}}{\partial \bar{\mathbf{C}}_{\text{max}}} : \dot{\bar{\mathbf{C}}}_{\text{max}} - \sum_{j=1}^2 2 \mathbf{C}_{e,j} \cdot \frac{\partial \tilde{\Psi}_j^{\text{neq}}}{\partial \mathbf{C}_{e,j}} : \mathbf{d}_{v,j} - \frac{\partial \Psi}{\partial f} \dot{f} \geq 0, \quad (4.14)$$

where

$$\mathbf{d}_{v,j} = \frac{1}{2} [\dot{\mathbf{F}}_{v,j} \mathbf{F}_{v,j}^{-1} + [\dot{\mathbf{F}}_{v,j} \mathbf{F}_{v,j}^{-1}]^T] \quad (4.15)$$

is the viscous deformation rate tensor of the j -th Maxwell element. Following the argumentation by Coleman and Gurtin (1967) and Reese and Govindjee (1998), as $\dot{\mathbf{C}}$ is arbitrary, the formula in the square bracket of the first term in Equation 4.14 should be zero, and we have:

$$\mathbf{S} = 2 \frac{\partial \Psi}{\partial \mathbf{C}}, \quad (4.16)$$

and the remaining terms of the inequality represent the internal dissipation $\mathcal{D}_{\text{int}}$, i.e.,

$$\mathcal{D}_{\text{int}} = -2 \frac{\partial \tilde{\Psi}^{\text{peq}}}{\partial \mathbf{C}_{\text{max}}} : \dot{\mathbf{C}}_{\text{max}} - 2 \sum_{j=1}^2 \mathbf{C}_{e,j} \frac{\partial \tilde{\Psi}^{\text{neq}}}{\partial \mathbf{C}_{e,j}} : \mathbf{d}_{v,j} - \frac{\partial \Psi}{\partial f} \dot{f} \geq 0, \quad (4.17)$$

In a stricter sense, according to physical observation, we can require that each term in the above equation is non-negative (Holzapfel, 2000), i.e.,

$$\mathcal{D}_{\text{int}}^{\text{peq}} = 2 \frac{\partial \tilde{\Psi}^{\text{peq}}}{\partial \mathbf{C}_{\text{max}}} : \dot{\mathbf{C}}_{\text{max}} \leq 0, \quad (4.18)$$

$$\mathcal{D}_{\text{int}}^{\text{neq}} = 2 \mathbf{C}_{e,j} \cdot \frac{\partial \tilde{\Psi}^{\text{neq}}}{\partial \mathbf{C}_{e,j}} : \mathbf{d}_{v,j} \leq 0, \quad j = 1, 2 \quad (4.19)$$

and

$$\mathcal{D}_{\text{int}}^{\text{chem}} = \frac{\partial \Psi}{\partial f} \dot{f} \leq 0, \quad (4.20)$$

representing the internal dissipation for the pseudo-equilibrium, non-equilibrium deformation, and chemical processes, respectively.

4.2.3 Stress

Combining Equation 4.11, Equation 4.12, and Equation 4.16, the second Piola-Kirchhoff stress tensor can be decomposed into parts:

$$\mathbf{S} = \mathbf{S}_{\text{vol}} + \tilde{\mathbf{S}}_{\text{iso}} = \mathbf{S}_{\text{vol}} + \tilde{\mathbf{S}}^{\text{eq}} + \tilde{\mathbf{S}}^{\text{peq}} + \sum_{j=1}^2 \tilde{\mathbf{S}}_j^{\text{neq}}, \quad (4.21)$$

The volumetric stress tensor is given by

$$\mathbf{S}_{\text{vol}} = 2 \frac{\partial \Psi_{\text{vol}}(J)}{\partial \mathbf{C}} = 2 \frac{\partial \Psi_{\text{vol}}(J)}{\partial J} \frac{\partial J}{\partial \mathbf{C}} = -Jp \mathbf{C}^{-1}, \quad (4.22)$$

with the definition of hydrostatic pressure

$$p = -\frac{\partial \Psi_{\text{vol}}(J)}{\partial J}. \quad (4.23)$$

The isochoric stress tensor accounting for chemical reaction is given by

$$\tilde{\mathbf{S}}_{\text{iso}} = 2 \frac{\partial \tilde{\Psi}_{\text{iso}}(\bar{\mathbf{C}}, f)}{\partial \bar{\mathbf{C}}} = 2 \frac{\partial \tilde{\Psi}_{\text{iso}}(\bar{\mathbf{C}}, f)}{\partial \bar{\mathbf{C}}} : \frac{\partial \bar{\mathbf{C}}}{\partial \mathbf{C}} = J^{-2/3} \mathbb{P} : \tilde{\mathbf{S}}, \quad (4.24)$$

where we have introduced a fictitious second Piola-Kirchhoff stress tensor (accounting for chemical reaction) defined as

$$\tilde{\mathbf{S}} = 2 \frac{\partial \tilde{\Psi}_{\text{iso}}(\bar{\mathbf{C}}, f)}{\partial \bar{\mathbf{C}}}, \quad (4.25)$$

and the fourth-order projection tensor

$$\mathbb{P} = J^{\frac{2}{3}} \left(\frac{\partial \bar{\mathbf{C}}}{\partial \mathbf{C}} \right)^{\top} = \mathbb{I} - \frac{1}{3} \mathbf{C}^{-1} \otimes \mathbf{C}, \quad (4.26)$$

where $\mathbb{I}$ is the fourth-order identity tensor. It can be shown that each part of the isochoric stress tensor accounting for chemical reaction is given by

$$\tilde{\mathbf{S}}^{\text{eq}} = J^{-2/3} \mathbb{P} : \tilde{\mathbf{S}}^{\text{eq}}, \quad (4.27)$$

$$\tilde{\mathbf{S}}^{\text{peq}} = J^{-2/3} \mathbb{P} : \tilde{\mathbf{S}}^{\text{peq}}, \quad (4.28)$$

$$\tilde{\mathbf{S}}_j^{\text{neq}} = J^{-2/3} \mathbb{P} : \tilde{\mathbf{S}}_j^{\text{neq}}, \quad (4.29)$$

respectively. Accordingly, the fictitious second Piola-Kirchhoff stress tensors of each part accounting for chemical reaction are

$$\tilde{\mathbf{S}}^{\text{eq}} = 2 \frac{\partial \tilde{\Psi}^{\text{eq}}}{\partial \bar{\mathbf{C}}}, \quad (4.30)$$

$$\tilde{\mathbf{S}}^{\text{peq}} = 2 \frac{\partial \tilde{\Psi}^{\text{peq}}}{\partial \bar{\mathbf{C}}}, \quad (4.31)$$

and

$$\tilde{\mathbf{S}}_j^{\text{neq}} = 2 \frac{\partial \tilde{\Psi}^{\text{neq}}}{\partial \bar{\mathbf{C}}} = 2 \frac{\partial \tilde{\Psi}^{\text{neq}}}{\partial \mathbf{C}_{\text{e},j}} : \frac{\partial \mathbf{C}_{\text{e},j}}{\partial \bar{\mathbf{C}}} = 2 \mathbf{F}_{\text{v},j}^{-1} \frac{\partial \tilde{\Psi}^{\text{neq}}}{\partial \mathbf{C}_{\text{e},j}} \mathbf{F}_{\text{v},j}^{-\top}, \quad j = 1, 2, \quad (4.32)$$

respectively.

4.2.4 Specific form of the specific strain energy functions and the evolution equation

In the previous section, the general framework of a chemo-mechanical hyper-pseudo-viscoelastic constitutive model has been established. To obtain a complete constitutive model, specific forms of the specific strain energy functions must be defined. Here, we first introduce the specific forms of the energy functions for each part in Equation 4.12, decoupling the chemical degradation effect in Section 4.2.4.1, Section 4.2.4.2, and Section 4.2.4.3, and then introduce the degradation effect later in Section 4.2.5.

4.2.4.1 Hyperelasticity

We first consider the strain energy function of a material that is made of a perfect polymer network without chemical degradation, Ψ^{eq} . In this case, neither stress softening nor viscoelasticity is present. Then the material behaves as a hyperelastic material, with the loading and unloading paths coincident and stress and strain in one-to-one correspondence. The material property can then be represented by the energy function and is assumed to be the Yeoh type (Steinmann et al., 2012), given by:

$$\Psi^{\text{eq}} = \Psi_0(\bar{\mathbf{C}}) = \Psi_0(\bar{I}_1) = c_1[\bar{I}_1 - 3] + c_2[\bar{I}_1 - 3]^2 + c_3[\bar{I}_1 - 3]^3, \quad (4.33)$$

where $\bar{I}_1$ is the first strain invariant of the Green strain tensor $\bar{\mathbf{C}}$, i.e.,

$$\bar{I}_1 = \text{tr}(\bar{\mathbf{C}}), \quad (4.34)$$

and c_1 , c_2 , and c_3 (in kPa) are material parameters.

Using Equation 4.30, the fictitious stress tensor of the equilibrium part can be derived as:

$$\bar{\mathbf{S}}^{\text{eq}} = [2c_1 + 4c_2(\bar{I}_1 - 3) + 6c_3(\bar{I}_1 - 3)^2] \mathbf{I}, \quad (4.35)$$

where $\mathbf{I}$ is the second-order identity tensor.

4.2.4.2 Pseudoelasticity

In a polymer network containing crystallites, such as in the starch hydrogel, loading may cause the crystallites to break or be disconnected from the polymer matrix, leading to stress-softening behaviour. This material response is dependent on the maximum

historical strain $\bar{\mathbf{C}}_{\max}$. If $\bar{\mathbf{C}}_{\max}$ varies during the test, the loading path and the unloading path differ, whereas if $\bar{\mathbf{C}}_{\max}$ remains unchanged, the paths remain identical (which can be observed if a third cycle is applied). Therefore, this constitutive relationship is called pseudoelasticity. Following Liao et al. (2020a), Naumann and Ihlemann (2015), and Ogden and Roxburgh (1999), the pseudoelasticity is achieved by scaling the stress response with a softening factor $\eta \in [0, 1]$, which is a function of the historical maximum strain. The corresponding energy function without chemical degradation is given by:

$$\left\{ \begin{array}{l} \Psi^{\text{peq}}(\bar{\mathbf{C}}, \bar{\mathbf{C}}_{\max}) = \int_0^{\Psi_0^{\text{peq}}(\bar{\mathbf{C}})} \eta(\psi, \Psi_{\max}^{\text{peq}}(\bar{\mathbf{C}}_{\max})) d\psi, \end{array} \right. \quad (4.36a)$$

$$\left\{ \begin{array}{l} \eta(\Psi_0^{\text{peq}}(\bar{\mathbf{C}}), \Psi_{\max}^{\text{peq}}(\bar{\mathbf{C}}_{\max})) = 1 - \frac{1}{R} \tanh \left(\frac{\Psi_{\max}^{\text{peq}}(\bar{I}_{1,\max}) - \Psi_0^{\text{peq}}(\bar{I}_1)}{M + \beta \Psi_{\max}^{\text{peq}}(\bar{I}_{1,\max})} \right), \end{array} \right. \quad (4.36b)$$

$$\left\{ \begin{array}{l} \Psi_0^{\text{peq}}(\bar{\mathbf{C}}) = \Psi_0^{\text{peq}}(\bar{I}_1) = c_{p,1}[\bar{I}_1 - 3] + c_{p,2}[\bar{I}_1 - 3]^2 + c_{p,3}[\bar{I}_1 - 3]^3, \end{array} \right. \quad (4.36c)$$

$$\left\{ \begin{array}{l} \Psi_{\max}^{\text{peq}}(\bar{\mathbf{C}}_{\max}) = \Psi_{\max}^{\text{peq}}(\bar{I}_{1,\max}) = \Psi_0^{\text{peq}}(\bar{I}_1 = \bar{I}_{1,\max}), \end{array} \right. \quad (4.36d)$$

Here, $\bar{I}_{1,\max}$ is the historical maximum value of the isochoric first strain invariant $\bar{I}_1$, $M > 0$ (in kJ/m³) is a material parameter with the same dimension as energy density, and $R \in (0, 1]$ and $\beta > 0$ are dimensionless parameters. Ψ_0^{peq} is the energy function of the pseudoelastic part for a perfectly crosslinked network, which takes the same form as Equation 4.33 with different material parameters. $\Psi_{\max}^{\text{peq}}$ is the maximum historical value of Ψ_0^{peq} over the loading history. The definition of the energy function in Equation 4.36 ensures that

$$\Psi^{\text{peq}}(\psi = 0, \Psi_{\max}^{\text{peq}}) = 0, \quad (4.37)$$

which means the specific strain energy of the pseudoelastic part is zero at the initial undeformed state.

Using Equation 4.31, the fictitious second Piola-Kirchhoff stress tensor of the pseudo-equilibrium part can be derived as:

$$\begin{aligned} \bar{\mathbf{S}}^{\text{peq}} &= \frac{\partial \Psi^{\text{peq}}}{\partial \bar{\mathbf{C}}} = \frac{\partial \Psi^{\text{peq}}}{\partial \Psi_0^{\text{peq}}} \frac{\partial \Psi_0^{\text{peq}}(\bar{\mathbf{C}})}{\partial \bar{\mathbf{C}}} \\ &= \eta \bar{\mathbf{S}}_0^{\text{peq}} = \eta [2c_{p,1} + 4c_{p,2}(\bar{I}_1 - 3) + 6c_{p,3}(\bar{I}_1 - 3)^2] \mathbf{I}, \end{aligned} \quad (4.38)$$

where $\bar{\mathbf{S}}_0^{\text{peq}}$ is the fictitious stress tensor of the pseudoelastic part for a perfectly crosslinked network, in the hypothetical state that no damage has occurred.

According to the definition of the $\mathbf{C}_{\max}$, its evolution is given by:

$$\dot{\mathbf{C}}_{\max} = \begin{cases} \dot{\mathbf{C}}, & \text{if } \bar{\mathbf{C}} = \bar{\mathbf{C}}_{\max} \text{ and } \bar{\mathbf{S}} : \dot{\mathbf{C}} > 0, \\ \mathbf{0}, & \text{otherwise,} \end{cases} \quad (4.39)$$

with the initial condition

$$\bar{\mathbf{C}}_{\max}(t = 0) = \mathbf{I}, \quad (4.40)$$

as no pre-stretch exists at the initial state.

Be aware that $\Psi_0^{\text{peq}} \geq 0$ always holds, and according to Equation 4.39, $\dot{\Psi}_{\max}^{\text{peq}} = 2\bar{\mathbf{S}}_0^{\text{peq}}(\bar{I}_{1,\max}) : \dot{\mathbf{C}}_{\max} \geq 0$. Therefore, we have

$$\begin{aligned} & 2 \frac{\partial \Psi^{\text{peq}}}{\partial \bar{\mathbf{C}}_{\max}} : \dot{\mathbf{C}}_{\max} \\ &= 2 \left[\int_0^{\Psi_0^{\text{peq}}(\bar{\mathbf{C}})} \frac{\eta(\psi, \Psi_{\max}^{\text{peq}}(\bar{\mathbf{C}}_{\max}))}{\partial \bar{\mathbf{C}}_{\max}} d\psi \right] : \dot{\mathbf{C}}_{\max} \\ &= - \left[\int_0^{\Psi_0^{\text{peq}}(\bar{\mathbf{C}})} \frac{M + \beta\psi}{R[M + \beta\Psi_{\max}^{\text{peq}}]^2} \cosh^{-2} \left(\frac{\Psi_{\max}^{\text{peq}} - \psi}{M + \beta\Psi_{\max}^{\text{peq}}} \right) d\psi \right] \left[2\bar{\mathbf{S}}_0^{\text{peq}}(\bar{I}_{1,\max}) : \dot{\mathbf{C}}_{\max} \right] \leq 0, \end{aligned} \quad (4.41)$$

which demonstrates that the second law of thermodynamics of the pseudoelasticity Equation 4.18 is satisfied. In Equation 4.41, it can be seen that $\frac{\partial \eta}{\partial \bar{\mathbf{C}}_{\max}} \leq 0$. This can be interpreted straightforwardly, as an increase in the maximum historical strain leads to a decrease in the softening factor η .

4.2.4.3 Viscoelasticity

Imperfections such as solvated chain fraction chains and dangling chains exist in polymers. Their deformation is driven by internal friction with the polymer matrix. As these chains are not tightly attached to the matrix, they can relax and recover to their original state, leading to dissipation or viscoelasticity. Note that viscoelasticity can be modelled in various forms, including the convolution integral form (Goh et al., 2005), differential form (Hossain et al., 2012), and fractional derivative form (Schiessel et al., 1995). In this study, we adopted the differential form, in which the evolution equations for internal variables are incorporated into the constitutive law. To characterise the deformation of microscopic imperfections, two internal variables, $\mathbf{C}_{e,j}$ ($j = 1, 2$), are introduced as a measurement of the deformation of the imperfections of the polymer matrix (such as solvated chain fraction chains and dangling chains), or the spring in the

viscoelastic branch in Figure 4.2. These variables capture different relaxation time scales and are represented by the two parallel spring-dashpot series depicted in Figure 4.2. For simplicity, the energy function of the viscoelastic part without chemical degradation takes the Neo-Hookean form, with only one parameter in each branch, given by:

$$\Psi^{\text{neq}}(\mathbf{C}_{\text{e},j}) = \sum_{j=1}^2 \Psi_{\text{v},j}(\mathbf{C}_{\text{e},j}) = \sum_{j=1}^2 2\mathbf{F}_{\text{v},j}^{-1} \frac{\partial \tilde{\Psi}^{\text{neq}}}{\partial \mathbf{C}_{\text{e},j}} \mathbf{F}_{\text{v},j}^{-\text{T}} = \sum_{j=1}^2 c_{\text{v},j} [I_{1\text{e},j} - 3], \quad (4.42)$$

where $I_{1\text{e},j}$ is the first strain invariant of the non-equilibrium part of the Green strain tensor $\mathbf{C}_{\text{e},j}$ of the j^{th} branch, and $c_{\text{v},j}$ (in kPa) are the material parameters, which can be interpreted as shear moduli of the viscoelastic branches.

Using Equation 4.32, the second Piola-Kirchhoff stress tensor of the non-equilibrium part can be derived as:

$$\bar{\mathbf{S}}_j^{\text{neq}} = 2c_{\text{v},j} \mathbf{C}_{\text{v},j}^{-1}, \quad j = 1, 2, \quad (4.43)$$

where $\bar{\mathbf{S}}_j^{\text{neq}}$ is the fictitious stress tensor of the non-equilibrium part for the j^{th} branch. We further define the intermediate fictitious stress tensor as:

$$\hat{\mathbf{S}}_j^{\text{neq}} = 2 \frac{\partial \Psi^{\text{neq}}}{\partial \mathbf{C}_{\text{e},j}}, \quad j = 1, 2, \quad (4.44)$$

which represents the fictitious stress tensor in the intermediate configuration of the j^{th} viscoelastic branch.

Following Hossain and Liao (2020), Liao et al. (2020b), Shutov et al. (2013), and Yang et al. (2023), the evolution of the viscous deformation can be given as:

$$\mathbf{d}_{\text{v},j} = \frac{1}{2\eta_j} \text{dev} \left(\mathbf{C}_{\text{e},j} \cdot \hat{\mathbf{S}}_j^{\text{neq}} \right), \quad (4.45)$$

where η_j (in Pa.s) is the viscosity of the j^{th} viscoelastic branch, and the operator dev denotes the deviatoric part of a second-order tensor, i.e., $\text{dev}(\bullet) = \bullet - \frac{1}{3} \text{tr}(\bullet) \mathbf{I}$. The deviatoric form is considered here, as the viscous deformation is assumed incompressible. Using the definitions Equation 4.9 and Equation 4.15, the evolution of the viscous deformation is equivalently expressed as:

$$\begin{aligned} \dot{\mathbf{C}}_{\text{v},j} &= \frac{4}{\eta_j} \frac{\partial \Psi_{\text{v},j}}{\partial I_{1\text{e},j}} \left[\text{dev} \left(\bar{\mathbf{C}} : \mathbf{C}_{\text{v},j}^{-1} \right) \cdot \mathbf{C}_{\text{v},j} \right], \\ &= \frac{4}{\tau_j} \left[\bar{\mathbf{C}} - \frac{1}{3} \left[\bar{\mathbf{C}} : \mathbf{C}_{\text{v},j}^{-1} \right] \mathbf{C}_{\text{v},j} \right] \quad j = 1, 2, \end{aligned} \quad (4.46)$$

where

$$\tau_j = \frac{\eta_j}{c_{v,j}} \quad (4.47)$$

(in seconds) is the characteristic relaxation time of the j^{th} viscoelastic branch, indicating the timescale of the branch to relax to equilibrium. The initial condition

$$\mathbf{C}_{v,j}(t = 0) = \mathbf{I}, \quad j = 1, 2, \quad (4.48)$$

is assumed, as the material is stress-free at the initial state, and therefore, no deformation of the viscoelastic branch occurs as well.

Incorporating Equation 4.45 equation into Equation 4.19, and noting the fact that the double dot product between the deviatoric and volumetric parts of an arbitrary tensor satisfies $\text{dev}(\mathbf{A}) : \frac{1}{3} \text{tr}(\mathbf{A}) = 0$, we have:

$$\begin{aligned} 2\mathbf{C}_{e,j} \cdot \frac{\partial \Psi^{\text{neq}}}{\partial \mathbf{C}_{e,j}} : \mathbf{d}_{v,j} &= \mathbf{C}_{e,j} \cdot \hat{\mathbf{S}}_j^{\text{neq}} : \frac{1}{2\eta_j} \text{dev} \left(\mathbf{C}_{e,j} \cdot \hat{\mathbf{S}}_j^{\text{neq}} \right) \\ &= \frac{1}{2\eta_j} \text{dev} \left(\mathbf{C}_{e,j} \cdot \hat{\mathbf{S}}_j^{\text{neq}} \right) : \text{dev} \left(\mathbf{C}_{e,j} \cdot \hat{\mathbf{S}}_j^{\text{neq}} \right) \geq 0, \end{aligned} \quad (4.49)$$

which demonstrates that the second law of thermodynamics of the viscoelasticity Equation 4.19 is satisfied.

4.2.4.4 Incompressibility constraint

In many polymer materials, the volumetric changes during deformation are negligible due to the high bulk modulus compared to the shear modulus. This is especially true for soft materials that undergo large deformations. In this study, the incompressible condition, i.e., $J = 1$, is assumed for the hydrogel. The incompressible condition leads to a hydrostatic pressure p that acts as a Lagrange multiplier in the total strain energy function to enforce the incompressibility constraint instead of obtaining from Equation 4.23. Therefore, Equation 4.11 is replaced by

$$\Psi = \Psi_{\text{iso}} - p(J - 1), \quad (4.50)$$

or

$$\Psi_{\text{vol}} = -p(J - 1). \quad (4.51)$$

In this case, the hydrostatic pressure p serves as a Lagrangian multiplier and can be determined only by applying the equilibrium equations and boundary conditions.

Equation 4.50 shows that the hydrostatic pressure p is workless and does not contribute strain energy (Holzapfel, 2000). Note that the negative sign in front of the pressure term indicates pressure is positive in compression. Using Equation 4.16 and $J = 1$, the second Piola-Kirchhoff stress tensor of the volumetric part for incompressible materials becomes:

$$\mathbf{S}_{\text{vol}} = -pJ\mathbf{C}^{-1} = -p\mathbf{C}^{-1}. \quad (4.52)$$

4.2.5 Degradation of the material properties with the hydrolysis level

In the presence of a chemical reaction, the material properties may change with the reaction level. Chains in the matrix are broken down as the polysaccharide is hydrolysed into sugars that dissolve in water, thereby decreasing the chain and crosslink density and leading to a reduction in the hyperelastic properties. In the meantime, during hydrolysis, the amount of dangling chain or solvated chain fraction increases, resulting in an increase in internal friction and dissipation, and thus the viscoelastic properties. The mechanical properties of the starch hydrogel are thought to depend on the degree of hydrolysis. The substrate ratio, f , defined as the ratio of the remaining substrate mass to the initial substrate mass, is introduced to represent the hydrolysis level, given by:

$$f = \frac{\omega_S}{\omega_{S_0}} = \frac{C_S}{C_{S_0}}, \quad (4.53)$$

where ω_S (w/w) is the mass fraction of the substrate at a certain location of the sample and at a given time for hydrolysis, ω_{S_0} is the initial mass fraction of the substrate, C_S (w/v) is the mass concentration, and C_{S_0} is the initial mass concentration. Equation 4.53 is derived by assuming mass conservation and unchanged total volume. In this study, $\omega_{S_0} = 0.2$ as we used a starch hydrogel of 20% w/w. Knowing that $\rho_{\text{gel}} = 1 \text{ g/cm}^3$ as mentioned in Section 2.2, the initial concentration can be calculated as

$$C_{S_0} = \omega_{S_0}\rho_{\text{gel}} = 0.2 \text{ g/cm}^3. \quad (4.54)$$

f varies from 0 to 1, indicating the degree of hydrolysis, where $f = 1$ represents no hydrolysis, and $f = 0$ represents complete hydrolysis.

Accordingly, the energy functions are updated as follows:

$$\begin{aligned} \Psi_{\text{iso}} &= \tilde{\Psi}^{\text{eq}}(\mathbf{C}, f) + \tilde{\Psi}^{\text{peq}}(\mathbf{C}, \bar{\mathbf{C}}_{\text{max}}, f) + \tilde{\Psi}_e^{\text{neq}}(\mathbf{C}_e, f) \\ &= f[\Psi^{\text{eq}}(\mathbf{C}) + \Psi^{\text{peq}}(\mathbf{C}, \bar{\mathbf{C}}_{\text{max}})] + [1 + m[1 - f]]\Psi_e^{\text{neq}}(\mathbf{C}_e), \end{aligned} \quad (4.55)$$

where $\tilde{\Psi}^{\text{eq}}$, $\tilde{\Psi}^{\text{peq}}$, and $\tilde{\Psi}_e^{\text{neq}}$ are the modified equilibrium, pseudo-equilibrium, and non-equilibrium strain energy density functions dependent on the reaction level. The term $m \in [0, 1]$ represents the portion of the hydrolysis part that is retained in the solid. As hydrolysis proceeds, the material is partially dissolved and extracted from the matrix, leading to a decrease in crosslink density and mass density and providing neither stiffness nor dissipation. It can be seen that as f decreases, i.e., the hydrolysis proceeds, the equilibrium part of the energy function decreases linearly, while the non-equilibrium part increases linearly. Note that in this study, mass loss was not considered, and therefore, $m = 1$ is chosen, and the density remained unchanged. This means it is assumed that hydrolysis only changes the crosslinked polymer network into an imperfect one, with dangling chains and trapped, undissolved chain fractions.

With the consideration of chemical process within the energy functions, the second Piola-Kirchhoff stress tensor Equation 4.21 can be modified as:

$$\tilde{\mathbf{S}} = \tilde{\mathbf{S}}^{\text{eq}} + \tilde{\mathbf{S}}^{\text{peq}} + \sum_{j=1}^2 \tilde{\mathbf{S}}_j^{\text{neq}}, \quad (4.56)$$

$$\begin{cases} \tilde{\mathbf{S}}^{\text{eq}} = f \bar{\mathbf{S}}^{\text{eq}}, \\ \tilde{\mathbf{S}}^{\text{peq}} = f \bar{\mathbf{S}}^{\text{peq}}, \\ \tilde{\mathbf{S}}_j^{\text{neq}} = [1 + m[1 - f]] \bar{\mathbf{S}}_j^{\text{neq}}, \quad j = 1, 2 \end{cases} \quad (4.57a)$$

$$(4.57b)$$

$$(4.57c)$$

Equation 4.20 requires that

$$\frac{\partial \Psi}{\partial f} \dot{f} = [\Psi^{\text{eq}}(\mathbf{C}) + \Psi^{\text{peq}}(\mathbf{C}, \bar{\mathbf{C}}_{\text{max}}) - m \Psi_e^{\text{neq}}(\mathbf{C}_e)] \dot{f} \leq 0. \quad (4.58)$$

The evolution of f is governed by the reaction kinetics, which will be introduced in the next section. During hydrolysis, the substrate concentration continuously decreases, so that $\dot{f} \leq 0$ always holds. Therefore, to satisfy Equation 4.58, the term in the square brackets must be non-negative, i.e.,

$$\Psi^{\text{eq}}(\mathbf{C}) + \Psi^{\text{peq}}(\mathbf{C}, \bar{\mathbf{C}}_{\text{max}}) - m \Psi_e^{\text{neq}}(\mathbf{C}_e) \geq 0. \quad (4.59)$$

This condition indicates that the energy stored in the equilibrium and pseudo-equilibrium parts must be greater than the portion of the energy stored in the non-equilibrium part that is lost due to hydrolysis. In other words, the total energy might be lost but not increased

during the energy conversion from the equilibrium and pseudo-equilibrium parts to the non-equilibrium part.

4.2.6 Reaction Kinetics

The evolution of the substrate concentration during hydrolysis is described by reaction kinetics. In this study, the reaction rate of the enzyme-catalysed hydrolysis was adapted from Michaelis-Menten kinetics (Johnson & Goody, 2011), which is widely used to describe enzyme-catalysed reactions. The derivation of the Michaelis-Menten kinetics is outlined below, starting from the classical enzyme-substrate reaction scheme. The hydrolysis of starch by α -amylase, as illustrated in Figure 4.3, is described by first-order kinetics (Brandam et al., 2003; Sitaraman et al., 2019):

$$\begin{cases} k_{+1}[S][E] = k_{-1}[ES], & (4.60a) \\ \frac{d[P]}{dt} = k_{cat}[ES], & (4.60b) \end{cases}$$

where $[S]$, $[E]$, $[ES]$, and $[P]$ are the concentrations of the substrate, the enzyme, the enzyme-substrate complex, and the product, respectively. k_{+1} and k_{-1} are the forward and backward rate constants for the formation of the enzyme-substrate complex, and k_{cat} is the catalytic rate constant for the formation of the product. Note that we use $[\bullet]$ to delimit a variable representing molar concentration. Equation 4.60 assumes that the substrate is in chemical equilibrium, and the enzyme concentration is significantly less than the substrate concentration (Johnson & Goody, 2011). Consider conservation of the enzyme, i.e.,

$$[E]_0 = [E] + [ES], \quad (4.61)$$

where $[E]_0$ is the initial concentration of the enzyme. Then Equation 4.60a can be rearranged into:

$$[ES] = \frac{[S][E]_0}{\frac{k_{+1}}{k_{-1}} + [S]}, \quad (4.62)$$

and therefore Equation 4.60b can be rewritten as:

$$v = \frac{d[P]}{dt} = -r = \frac{d[S]}{dt} = \frac{k_{cat}[E]_0[S]}{\frac{k_{+1}}{k_{-1}} + [S]} = \frac{r_{\infty}[S]}{K_m + [S]}. \quad (4.63)$$

Here, v is the reaction rate generating product, r is the reaction rate consuming substrate (both in mol/L/s), $K_m = \frac{k_{-1}}{k_{+1}}$ is Michaelis-Menten constant in units of concentration (mol/L), representing the substrate concentration at which the reaction rate is half of the maximum

rate, and the limiting rate r_∞ , defined as

$$r_\infty = k_{\text{cat}}[E]_0, \quad (4.64)$$

represents the reaction rate at saturating substrate concentration for a given enzyme concentration (also in mol/L/s). Based on the above equation, biochemical reactions involving a single substrate, such as the hydrolysis of starch by α -amylase, can be described by Michaelis-Menten kinetics, provided the substrate is in chemical equilibrium and the enzyme concentration is not saturated. When the substrate concentration is lower than K_m , the reaction rate is approximately first-order with respect to the substrate concentration as $v \approx \frac{r_\infty}{K_m}[S]$, while when the substrate concentration is higher than K_m , the reaction rate approaches a maximum value asymptotically and becomes zero-order with respect to the substrate concentration, i.e., a constant $r = r_\infty$.

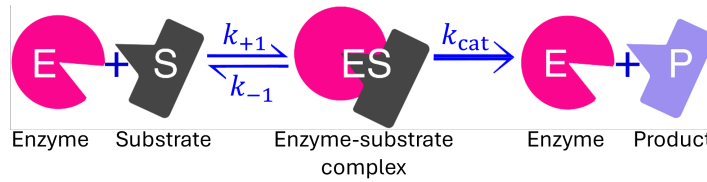


Figure 4.3. Enzymatic hydrolysis: a hydrolysis reaction catalysed by enzymes.

The Michaelis-Menten kinetics simplified the complicated reactions in Equation 4.60 as a single ordinary differential equation Equation 4.63, which is easy to implement and solve numerically. However, if the enzyme is saturated or if it does not distribute evenly in the sample, with some locations having a high concentration, the assumption that the enzyme concentration is significantly less than the substrate concentration may not hold. In such cases, the reaction rate will not increase linearly with increasing enzyme concentration. Therefore, we modify the Michaelis-Menten equation to account for the nonlinear dependence of the reaction rate on enzyme concentration. To incorporate the effect of enzyme concentration on the reaction rate, we define the effective enzyme molar concentration $[\bar{E}]$ as

$$[\bar{E}] = \frac{\bar{C}_{\text{enz}}}{M_{\text{enz}}} \quad (4.65)$$

where $[\bar{E}]$ is the effective enzyme molar concentration (in mol/L), M_{enz} is the molar mass of the enzyme in g/mol mentioned in Section 3.2.2.2, and $\bar{C}_{\text{enz}}$ is the effective enzyme mass concentration (in g/L). "Effective" denotes the enzyme concentration averaged over the

hydrogel, as will be explained later. Then Equation 4.64 is modified as

$$r_{\infty} = k_{\text{cat}}([\bar{\text{E}}]) \cdot [\bar{\text{E}}] = k_{\text{cat}}(\bar{C}_{\text{enz}}) \cdot \frac{\bar{C}_{\text{enz}}}{M_{\text{enz}}}, \quad (4.66)$$

where k_{cat} (the same parameter in Equation 4.66) is the catalytic reaction rate constant in units of /s, representing the rate of the reaction, i.e., the ratio between product generated and enzyme consumed per unit time, when the substrate is sufficient. A similar form still describes the reaction rate of maltose (assumed to be the main final product of hydrolysis) as Equation 4.63, i.e.,

$$\frac{d[\text{M}]}{dt} = r_{\infty}(\bar{C}_{\text{enz}}) \frac{[\text{S}]}{K_{\text{S}} + [\text{S}]} = r_{\infty} \frac{C_{\text{S}}}{\tilde{K}_{\text{S}} + C_{\text{S}}}, \quad (4.67)$$

where C_{S} is the mass concentration (in g/L), and $\tilde{K}_{\text{S}}$ the Michaelis-Menten constant related to the substrate concentration, with the same unit as C_{S} . The r_{∞} is now a function of the effective enzyme concentration $\bar{C}_{\text{enz}}$. Here, we replace the molar concentration in Equation 4.63 with mass concentration because starch is a macromolecule with a varying molar mass. As a result, its degradation should be quantified in terms of mass loss rather than changes in molar concentration. The improvement is that k_{cat} is further assumed to be dependent on the effective enzyme concentration asymptotically, expressed as

$$k_{\text{cat}}(\bar{C}_{\text{enz}}) = k_{\text{cat,max}} \frac{C_{\text{enz}}^0}{\tilde{K}_{\text{enz}} + \bar{C}_{\text{enz}}}, \quad (4.68)$$

where $\tilde{K}_{\text{enz}}$ is the Michaelis-Menten constant related to the enzyme concentration, with the unit of enzyme concentration (g/L). C_{enz}^0 is a reference enzyme concentration constant representing the magnitude of enzyme concentration, and the value of $C_{\text{enz}}^0 = 1.18 \text{ g/L}$ is chosen, the same as the experiment concentration of α -amylase mentioned in Section 3.2.2.2. In addition,

$$k_{\text{cat,max}} = a_{\alpha} M_{\text{enz}} \quad (4.69)$$

is the maximum catalytic reaction rate constant when the enzyme is saturated in a unit of /s, where a_{α} is the specific activity of the enzyme obtained in Section 3.2.2.2 (in units of mol/[g·s]), representing the maximum amount of product generated per second per unit mass of enzyme when the enzyme is saturated. Using Equation 4.66, the increase of the effective enzyme concentration will lead to the reaction rate increase from first order to zero order with respect to the enzyme concentration, similar to the effect of substrate

concentration in Equation 4.63, where the higher concentration of enzyme has been taken into account.

Considering the mass relationship between starch and maltose, the evolution (or the reaction rate) of the substrate concentration C_S can be described as

$$\frac{dC_S}{dt} = -2M_{AGU} \frac{d[M]}{dt}, \quad (4.70)$$

M_{AGU} is the molar mass of anhydroglucose unit (AGU, $C_6H_{10}O_5$) in starch, which is 162.14 g/mol, which is the same as the molar mass of glucose minus the molar mass of water H_2O (180.16-18.02 g/mol). The factor of 2 accounts for the fact that each mole of maltose contains two moles of AGU. The negative sign indicates that the concentration of the substrate, starch, decreases during hydrolysis, while the product, maltose, increases. The initial concentration of the substrate C_S is

$$C_{S_0} = C_S(t = 0) = 0.2 \text{ g/cm}^3, \quad (4.71)$$

as mentioned before. From Equation 4.70, as mass is conserved, it can be seen that

$$\frac{dC_S}{dt} \leq 0 \quad (4.72)$$

always holds, indicating that the substrate concentration continuously decreases during hydrolysis.

In Equation 4.66, the effective enzyme concentration is used instead of the nominal concentration. Because part of the hydrogel volume is occupied by the polymer matrix, the enzyme concentration averaged over the whole hydrogel is lower than the concentration in the pore liquid, given that the equilibrium enzyme concentration within the pores is assumed to be equal to the enzyme concentration in the surrounding fluid (i.e., the boundary concentration). Therefore, the enzyme is effectively diluted within the hydrogel compared to the surrounding liquid phase. The effective enzyme concentration is defined as:

$$\bar{C}_{enz} = \frac{m_{enz}}{V_{gel}} = \frac{V_{liq}}{V_{gel}} \frac{m_{enz}}{V_{liq}} = \phi_l \cdot C_{enz}, \quad (4.73)$$

where

$$\phi_l = \frac{V_{liq}}{V_{gel}} = \frac{m_{gel} - m_s}{\rho_{liq} V_{gel}} = \frac{\rho_{gel} - C_S}{\rho_{liq}} \quad (4.74)$$

is the liquid volume fraction, where m_s , m_{gel} , V_{liq} , and ρ_{liq} are the mass of the substrate, the mass of the hydrogel, the volume, and the density of the liquid phase, respectively.

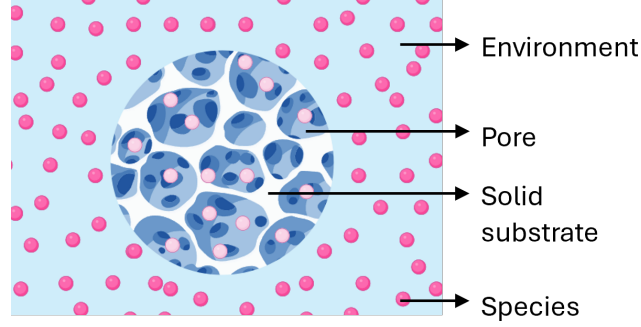


Figure 4.4. Schematics of the volume fraction of the water in the hydrogel.

4.2.7 One-dimensional formulation

Our experiments were performed in a uniaxial compression mode. In order to employ the experimental data in the calibration of the material parameters, 1D expressions of the constitutive law are required. Therefore, the deformation gradient reads:

$$\mathbf{F} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda^{-\frac{1}{2}} & 0 \\ 0 & 0 & \lambda^{-\frac{1}{2}} \end{bmatrix}, \quad (4.75)$$

with the incompressible assumption, i.e.,

$$J = \det \mathbf{F} = 1, \quad \text{or} \quad \bar{\mathbf{F}} = \mathbf{F} \quad (4.76)$$

as the Poisson's ratio is close to 0.5, which was observed during the compression tests, e.g., in [Figure 2.5](#). Furthermore, $\lambda = l/l_0 = \varepsilon + 1$ is the deformation ratio between the deformed length l and the original length l_0 , and ε is the nominal strain. The first strain invariant of $\mathbf{C}$ yields:

$$I_1 = \lambda^2 + 2\lambda^{-1}. \quad (4.77)$$

The maximum historical first strain invariant is then given as:

$$I_{1,\max} = \lambda_{\max}^2 + 2\lambda_{\max}^{-1}, \quad (4.78)$$

which is equivalent to the first strain invariant of $\mathbf{C}_{\max}$, where $\lambda_{\max}$ is the maximum historical deformation ratio. Similar to the total deformation gradient, the deformation gradient of the

viscous part reads:

$$\mathbf{F}_{v,j} = \begin{bmatrix} \lambda_{v,j} & 0 & 0 \\ 0 & \lambda_{v,j}^{-\frac{1}{2}} & 0 \\ 0 & 0 & \lambda_{v,j}^{-\frac{1}{2}} \end{bmatrix}, \quad j = 1, 2 \quad (4.79)$$

where $\lambda_{v,j}$ is the deformation ratio of the viscous part of the j^{th} branch. Multiplicative decomposition of the deformation gradient then yields:

$$\lambda = \lambda_{e,j} \lambda_{v,j}, \quad (4.80)$$

where $\lambda_{e,j}$ is the deformation ratio of the elastic part of the j^{th} branch.

The first Piola-Kirchhoff stress is adopted for the 1D formulation, as nominal stress is obtained from experiments. According to the transformation rule, the first Piola-Kirchhoff stress $\mathbf{P}$ is obtained from the second Piola-Kirchhoff stress $\mathbf{S}$ as:

$$\mathbf{P} = \mathbf{F} \cdot \mathbf{S}. \quad (4.81)$$

Combining this equation, Equation 4.51, and Equation 4.56, we have the first Piola-Kirchhoff stress decomposed form (considering incompressibility and the chemical reaction):

$$\mathbf{P} = -p\mathbf{F}^{-\text{T}} + \tilde{\mathbf{P}}^{\text{eq}} + \tilde{\mathbf{P}}^{\text{peq}} + \sum_{j=1}^2 \tilde{\mathbf{P}}_j^{\text{neq}}, \quad (4.82)$$

where

$$\tilde{\mathbf{P}}^{\text{eq}} = \mathbf{F} \cdot \tilde{\mathbf{S}}^{\text{eq}}, \quad (4.83)$$

$$\tilde{\mathbf{P}}^{\text{peq}} = \mathbf{F} \cdot \tilde{\mathbf{S}}^{\text{peq}}, \quad (4.84)$$

$$\tilde{\mathbf{P}}_j^{\text{neq}} = \mathbf{F} \cdot \tilde{\mathbf{S}}_j^{\text{neq}}, \quad j = 1, 2. \quad (4.85)$$

As is common practice, we assume that each of the three components in Equation 4.83, Equation 4.84, and Equation 4.85 satisfies the boundary conditions independently. This allows the hydrostatic pressure p to be decomposed accordingly, so that each part can be determined individually.

In uniaxial compression, the first Piola-Kirchhoff stress tensor has only one non-zero

component along the loading axis, i.e.,

$$\mathbf{P} = \begin{bmatrix} P & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (4.86)$$

Here, we denote the axial component of the first Piola-Kirchhoff stress as $P = P_{11}$. The lateral surfaces are free of load, and thus,

$$P_{22} = P_{33} = 0, \quad (4.87)$$

which can be used to solve for p as boundary conditions. The decomposition of the axial component of the first Piola-Kirchhoff stress then reads:

$$P = \tilde{P}^{\text{eq}} + \tilde{P}^{\text{peq}} + \sum_{j=1}^2 \tilde{P}_j^{\text{neq}}, \quad (4.88)$$

which is also known as the nominal stress, i.e., force per unit initial cross-sectional area, where

$$\begin{cases} \tilde{P}^{\text{eq}} = \frac{C_S}{C_{S_0}} P^{\text{eq}}, & (4.89a) \end{cases}$$

$$\begin{cases} \tilde{P}^{\text{peq}} = \frac{C_S}{C_{S_0}} P^{\text{peq}}, & (4.89b) \end{cases}$$

$$\begin{cases} \tilde{P}_j^{\text{neq}} = \left[1 + m \left[1 - \frac{C_S}{C_{S_0}} \right] \right] P_j^{\text{neq}}, \quad j = 1, 2, & (4.89c) \end{cases}$$

according to [Equation 4.57](#). Note that in [Equation 4.88](#), for simplicity of expression, the individual hydrostatic pressure contribution mentioned previously has been included in each part of the first Piola-Kirchhoff stress. Therefore, the boundary conditions should be applied to each part to solve for the hydrostatic pressure in each part, i.e.,

$$\tilde{P}_{22}^{\text{eq}} = \tilde{P}_{33}^{\text{eq}} = 0, \quad \tilde{P}_{22}^{\text{peq}} = \tilde{P}_{33}^{\text{peq}} = 0, \quad \tilde{P}_{j,22}^{\text{neq}} = \tilde{P}_{j,33}^{\text{neq}} = 0, \quad j = 1, 2, \quad (4.90)$$

respectively.

Substituting [Equation 4.75](#) into [Equation 4.83](#), and combining [Equation 4.35](#), and using the uniaxial condition, the equilibrium stress in the direction of the loading axis is derived as

$$P^{\text{eq}} = [2c_1 + 4c_2[I_1 - 3] + 6c_3[I_1 - 3]^2] [\lambda - \lambda^{-2}], \quad (4.91)$$

Substituting Equation 4.75 into Equation 4.84, and combining Equation 4.38, and using the uniaxial condition, the pseudo-equilibrium stress in the direction of the loading axis is derived as

$$\begin{cases} P^{\text{peq}} = \eta P_0^{\text{peq}}, & (4.92a) \\ P_0^{\text{peq}} = [2c_{p,1} + 4c_{p,2}[I_1 - 3] + 6c_{p,3}[I_1 - 3]^2] [\lambda - \lambda^{-2}], & (4.92b) \\ \eta = 1 - \frac{1}{R} \tanh \left(\frac{\Psi_0^{\text{peq}}(I_1 = I_{1,\max}) - \Psi_0^{\text{peq}}(I_1)}{M + \beta \Psi_0^{\text{peq}}(I_1 = I_{1,\max})} \right), & (4.92c) \\ \Psi_0^{\text{peq}} = c_{p,1}[I_1 - 3] + c_{p,2}[I_1 - 3]^2 + c_{p,3}[I_1 - 3]^3. & (4.92d) \end{cases}$$

and the evolution of the historical maximum deformation ratio Equation 4.18 becomes:

$$\dot{\lambda}_{\max} = \begin{cases} \dot{\lambda}, & \text{if } \lambda = \lambda_{\max} \text{ and } P\dot{\lambda} > 0, \\ 0, & \text{otherwise.} \end{cases} \quad (4.93)$$

where $\lambda_{\max}$ denotes the historical maximum of the deformation ratio λ . Substituting Equation 4.75 and Equation 4.80 into Equation 4.85, and combining Equation 4.43, and using the uniaxial condition, the non-equilibrium stress in the direction of the loading axis is derived as

$$P^{\text{neq}} = \sum_{j=1}^2 2c_{v,j} \left[\frac{\lambda^2}{\lambda_{v,j}} - \frac{\lambda_{v,j}^2}{\lambda} \right]. \quad (4.94)$$

Using Equation 4.79 and Equation 4.80, the evolution equations of the viscous part, Equation 4.19, become:

$$\dot{\lambda}_{v,j} = \frac{4}{3\tau_j} \left[\frac{\lambda^2}{\lambda_{v,j}} - \frac{\lambda_{v,j}^2}{\lambda} \right], \quad j = 1, 2. \quad (4.95)$$

Combining Equation 4.67, Equation 4.66, Equation 4.68, and Equation 4.73, the evolution of the substrate concentration during hydrolysis reads

$$\dot{c}_S = -2M_{\text{AGU}} a_{\alpha} c_{\text{enz}}^0 \frac{\frac{\rho_{\text{gel}} - c_S}{\rho_{\text{liq}}} c_{\text{enz}}}{\tilde{K}_{\text{enz}} + \frac{\rho_{\text{gel}} - c_S}{\rho_{\text{liq}}} c_{\text{enz}}} \cdot \frac{c_S}{\tilde{K}_S + c_S}. \quad (4.96)$$

Stress-strain relationship, Equation 4.88, Equation 4.89, Equation 4.91, Equation 4.92, Equation 4.94, and evolution equations Equation 4.93, Equation 4.95, Equation 4.96, as well as the initial conditions, constitute the 1D chemo-mechanical constitutive model considering both mechanical response and chemical reaction. Here, mechanical

parameters $c_1, c_2, c_3, c_{p,1}, c_{p,2}, c_{p,3}, c_{v,1}, c_{v,2}, \tau_1, \tau_2, r_s, M, \beta$, and reaction kinetics parameters $\tilde{K}_{enz}$, and $\tilde{K}_S$, are to be calibrated, and $m = 1$ is assumed.

4.2.8 Calibration and validation for cyclic mechanical response of starch hydrogel

The nominal stress-nominal strain data of a multistep loading-unloading compression experiment of the starch hydrogel in [Chapter 2](#) at the benchmark condition in [Figure 2.7](#) were used to calibrate the mechanical material parameters under cyclic loading conditions. Note that the evolution equation of the viscoelastic part, [Equation 4.95](#), an ordinary differential equation, was discretised by the implicit backward Euler scheme and solved by the Newton iteration method (for further details, readers are referred to Hossain et al., [2012](#); Scheffer et al., [2015](#)). By minimising the error of the stress value between the model prediction and the experimental data using the least-squares curve-fitting optimisation algorithm `lsqcurvefit` built-in within the commercial mathematical software MATLAB, the material parameters can be calibrated. Note that in the pure mechanical response calibration, the chemical reaction is not considered, i.e., $c_S = c_{S_0} = \text{const}$ in [Equation 4.89](#). And we here set $c_1, c_2, c_3 = 0$ in [Equation 4.91](#) to neglect the equilibrium part, which implies that the stress softening of the polymer network leads to zero equilibrium stress. The calibrated material parameters are given in [Table 4.1](#).

Table 4.1. Material parameters of the starch hydrogel in the case of pure mechanical response, calibrated by the mechanical tests in [Chapter 2](#).

$c_{p,1}$ [kPa]	$c_{p,2}$ [kPa]	$c_{p,3}$ [kPa]	$c_{v,1}$ [kPa]	τ_1 [s]	$c_{v,2}$ [kPa]	τ_2 [s]	R [kPa]	M [kJ/m ³]	β [-]
1.49e+01	6.00e+01	1.00e+00	1.01e+01	7.92e-05	4.06e+00	3.88e+01	7.70e-01	3.88e-14	2.86e+00

With the data in [Table 4.1](#), we further predict the stress-strain response of the starch hydrogel under a two-cycle loading-unloading test at a maximum strain of 0.2 to compare with the experimental data shown in [Figure 2.6](#), and the comparison is shown in [Figure 4.5\(a\)](#). This study shows that the pseudoelastic-viscoelastic constitutive model captures both the viscoelasticity and stress-softening behaviour of the starch hydrogel under compressive cyclic loading. For example, in [Figure 4.5\(a\)](#), the typical behaviour of the Mullins effect is captured, i.e., the stress level within the strain region smaller than the historical maximum is always smaller than the previous peak stress (stress at the

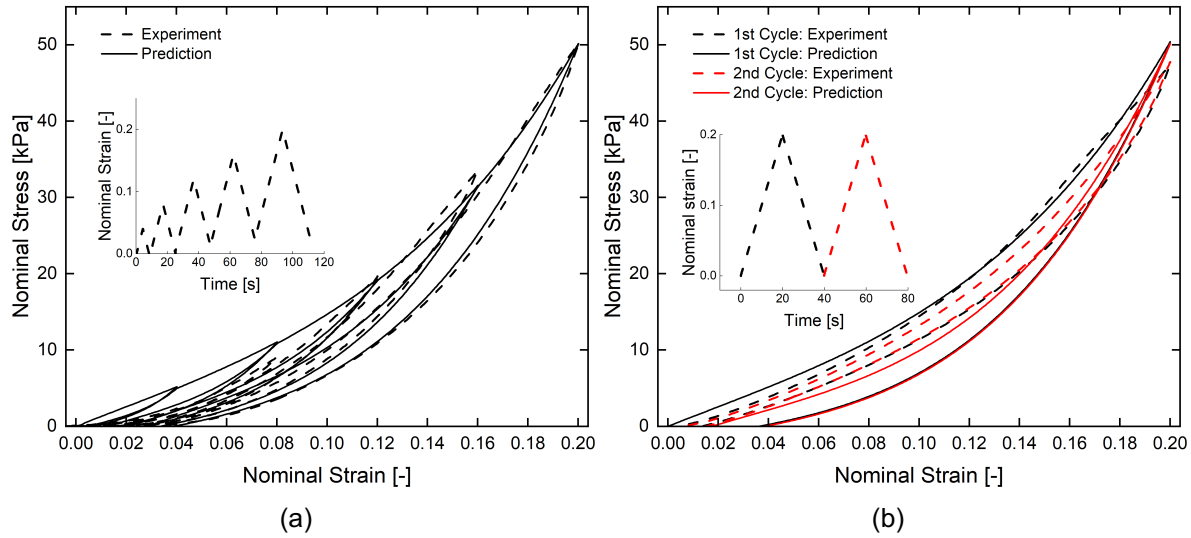


Figure 4.5. Comparison between experimental results and prediction by the constitutive equation of pure mechanical response. (a) Calibration of the pseudoelastic-viscoelastic constitutive model using a multistep loading-unloading test from Figure 2.7, and (b) validation of the pseudoelastic-viscoelastic constitutive model using a two-cycle loading-unloading test in Figure 2.6.

historical maximum strain). If the strain reaches the historical maximum, the stress level returns to its last peak. In Figure 4.5(b), stress decreases in the reloading cycle, and the dissipation changes between the two cycles were captured. Note that stress in the loading path before the strain of 0.1 was overestimated in Figure 4.5(a), while stress in the unloading path was underestimated in Figure 4.5(b) since we only included two non-equilibrium branches. The prediction performed better at larger strains than at lower strains. The discrepancy is attributed to the simplicity of the model and the complexity of the material behaviour. Also, as variations between samples exist, the discrepancy is considered acceptable.

4.2.9 Calibration and validation for chemo-mechanical response of starch hydrogel

The chemo-mechanical response of the starch hydrogel is influenced by both the mechanical properties and the degree of hydrolysis. Therefore, the calibration of the constitutive model for the chemo-mechanical response requires careful consideration of the hydrolysis conditions. Here, we used the nominal stress-nominal strain data of the loading-unloading compression tests of small samples before hydrolysis times in Section 3.3 for calibration of the mechanical material parameters, while the parameters

related to the reaction were calibrated later with the data at various hydrolysis times. Note that the mechanical parameters calibrated here are different from those in [Section 4.2.8](#), as the experiment was performed on a different batch of samples, which could have slightly different mechanical properties. As the experimental data used for calibration include a range of hydrolysis conditions, which represent a more complex scenario than [Section 4.2.8](#), it was found that retaining the equilibrium contribution, i.e., not setting c_1 , c_2 , and c_3 to zero, provides a better description of the mechanical behaviour after significant hydrolysis. The calibrated mechanical parameters are as follows:

Table 4.2. Parameters for mechanical behaviour of starch hydrogel, calibrated by the chemo-mechanical tests in [Chapter 3](#).

Hyperelastic parameters					
c_1 [kPa]		c_2 [kPa]		c_3 [kPa]	
6.74e-06		1.38e-07		2.95e+01	
Pesudoelastic parameters					
$c_{p,1}$ [kPa]	$c_{p,2}$ [kPa]	$c_{p,3}$ [kPa]	R [-]	M [kJ/m³]	β [-]
7.61e+00	2.01e+01	6.20e+00	1.13e+00	4.78e-02	1.51e+00
Viscoelastic parameters					
$c_{v,1}$ [kPa]		τ_1 [s]	$c_{v,2}$ [kPa]		τ_2 [s]
6.59e-01		1.89e+01	1.34e+01		2.27e+00

The simulated curve is illustrated by the black scatter curve in [Figure 4.6\(a\)](#).

Then, the substrate ratio f , defined as the ratio of the substrate concentration to the initial substrate concentration, was estimated by minimising the error between the loading-unloading compression test data and the simulated stress values for the small sample at different hydrolysis times. The data points are represented by the coloured scatter symbols in [Figure 4.6\(b\)](#), with the colour consistent with the hydrolysis time in [Figure 4.6\(a\)](#). Here, we assume that the diffusion is quick enough for the small sample that the enzyme distribution is uniform. This assumption will, in fact, overestimate the reaction level, as diffusion is not instantaneous even in the small sample, and the enzyme concentration is lower in the sample core. Therefore, the calibrated f can be considered as the upper bound of the reaction level, and the calibrated parameters are used as the initial guess for inverse analysis, which will be discussed in [Section 4.3.3](#). Then, the reaction kinetics parameters $\tilde{K}_{enz}$ and $\tilde{K}_S$ in [Equation 4.96](#) can be calibrated by the experimental data of the estimated substrate ratio f at various hydrolysis times.

Note that in Equation 4.96 the specific activity of α -amylase, a_α , is obtained in Section 3.2.2.2. Again, it could vary with temperature, pH, and time as mentioned in Section 3.2.2.2. However, here we take it as a constant representing the activity at a constant condition for simplicity. As we assume the enzyme diffusion is instantaneous in the small sample, the enzyme concentration $c_{\text{enz}} = c_{\text{enz}}^0 = 1.18 \times 10^{-3} \text{ g/cm}^3$ is a constant. The other constants are listed in Table 4.3.

Table 4.3. Constants for chemical degradation of starch hydrogel (α -amylase catalysed). (a) In laboratory units (g, cm, mol, s) and (b) in simulation units (ton, mm, mol, s).

$a_\alpha \left[\frac{\text{mol}}{\text{g} \cdot \text{s}} \right]$	$M_{\text{AGU}} \left[\frac{\text{g}}{\text{mol}} \right]$	$\rho_{\text{gel}} \left[\frac{\text{g}}{\text{cm}^3} \right]$	$\rho_{\text{liq}} \left[\frac{\text{g}}{\text{cm}^3} \right]$	$c_{\text{S0}} \left[\frac{\text{g}}{\text{cm}^3} \right]$	$c_{\text{enz}}^0 \left[\frac{\text{g}}{\text{cm}^3} \right]$	$m [-]$
3.16e-2	1.6214e+2	1.00	1.00	0.20	1.18e-3	1

$a_\alpha \left[\frac{\text{mol}}{\text{ton} \cdot \text{s}} \right]$	$M_{\text{AGU}} \left[\frac{\text{ton}}{\text{mol}} \right]$	$\rho_{\text{gel}} \left[\frac{\text{ton}}{\text{mm}^3} \right]$	$\rho_{\text{liq}} \left[\frac{\text{ton}}{\text{mm}^3} \right]$	$c_{\text{S0}} \left[\frac{\text{ton}}{\text{mm}^3} \right]$	$c_{\text{enz}}^0 \left[\frac{\text{ton}}{\text{mm}^3} \right]$	$m [-]$
3.16e+4	1.6214e-4	1.00e-9	1.00e-9	0.20e-9	1.18e-12	1

Therefore, Equation 4.96 can be simplified as

$$\begin{aligned}
 \dot{c}_{\text{S}} &= -12.1 \times 10^{-3} \frac{\text{g}}{\text{cm}^3 \cdot \text{s}} \frac{1.18 \times 10^{-3} \text{g/cm}^3 - 1.18 \times 10^{-3} c_{\text{S}}}{\tilde{K}'_{\text{enz}} + 1.18 \times 10^{-3} \text{g/cm}^3 - 1.18 \times 10^{-3} c_{\text{S}}} \frac{c_{\text{S}}}{\tilde{K}'_{\text{S}} + c_{\text{S}}} \\
 &= -1.21 \times 10^{-11} \frac{\text{ton}}{\text{mm}^3 \cdot \text{s}} \frac{1.18 \times 10^{-12} \text{ton/mm}^3 - 1.18 \times 10^{-3} c_{\text{S}}}{\tilde{K}'_{\text{enz}} + 1.18 \times 10^{-12} \text{ton/mm}^3 - 1.18 \times 10^{-3} c_{\text{S}}} \frac{c_{\text{S}}}{\tilde{K}'_{\text{S}} + c_{\text{S}}},
 \end{aligned} \tag{4.97}$$

where $\tilde{K}'_{[\bullet]} \left[\frac{\text{g}}{\text{cm}^3} \right] = 10^9 \tilde{K}_{[\bullet]} \left[\frac{\text{ton}}{\text{mm}^3} \right]$ as $1 \frac{\text{g}}{\text{cm}^3} = 10^{-9} \frac{\text{ton}}{\text{mm}^3}$. This equation can be solved by the explicit Runge-Kutta method using ode45 in MATLAB. Then, the reaction kinetics parameters are calibrated and are shown in Table 4.4.

Table 4.4. Parameters for chemical degradation of starch hydrogel catalysed by α -amylase (initial guess, assuming instantaneous diffusion), calibrated by the chemo-mechanical tests in Chapter 3.

$\tilde{K}_{\text{enz}} [\text{ton/mm}^3]$	$\tilde{K}_{\text{S}} [\text{ton/mm}^3]$
8.99e-12	5.23e-9

The initial guess of the reaction kinetics is shown in the black curve in Figure 4.6(b). This curve shows a pattern similar to that observed in the hydrolysis of a starch hydrogel from

various starch sources, including potato starch, in the experimental study of Drechsler and Ferrua (2016), which did not account for diffusion.

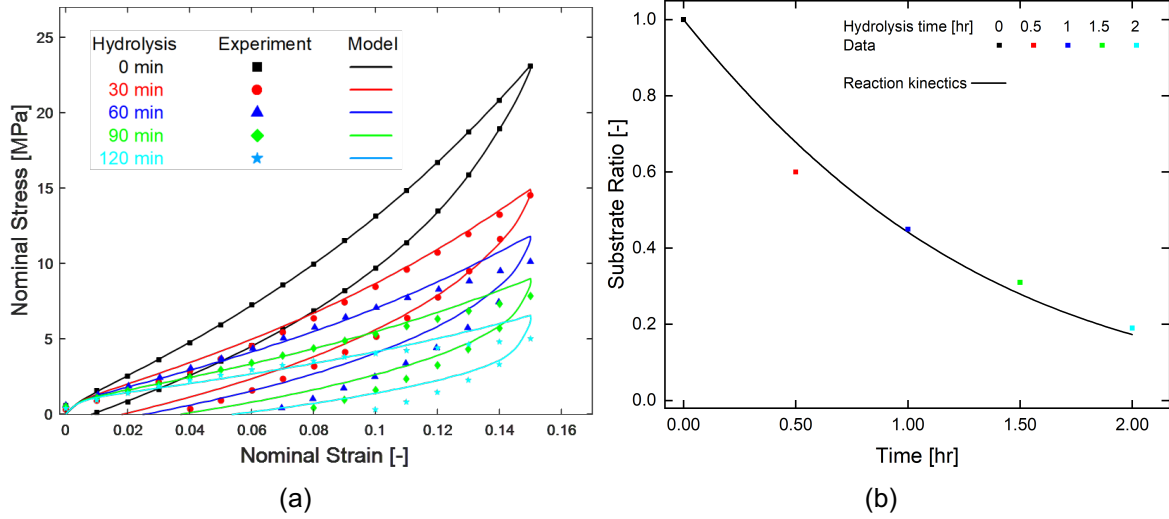


Figure 4.6. Calibration of the constitutive model. (b) Loading-unloading test under different levels of hydrolysis. (a) Substrate ratio of small sample at various hydrolysis times and the initial guess of the reaction kinetics curve (black solid curve).

With the data in Table 4.2 and Table 4.4, the stress-strain response of the starch hydrogel under cyclic loading conditions with different levels of hydrolysis can be predicted. For the problem considering the geometry and diffusion, the constitutive model will need to be implemented into a FE framework. Note that the reaction kinetics parameters could, in principle, be calibrated using liquid state gelatinised starch, as described in Section 3.2.2.2, following a procedure similar to the enzyme activity tests. However, because the substrate in these tests is in a liquid state and may behave differently from the hydrogel, we prefer to calibrate the parameters using solid hydrogels under the same conditions as those used in the mechanical and hydrolysis experiments. However, in a solid state, diffusion and reaction are coupled, and therefore inverse analysis simulation methods are preferred for calibration.

4.3 Finite element simulation for starch hydrogel degradation

In this section, the FE simulation for the diffusion-reaction-deformation process of the starch hydrogel is presented, incorporating the chemomechanical constitutive model developed and calibrated in Section 4.2 using the commercial FE software ABAQUS,

specifically coding with the user material subroutine (UMAT). We aim to simulate the compression test of a large sample under different hydrolysis conditions and, inversely, identify the reaction rate constant k_{cat} using the experimental data. The simulation will validate the constitutive model and the proposed reaction kinetics, and will be applied for digestion simulation in [Chapter 5](#). The brief introduction of the FEM and the implementation of the constitutive model via UMAT is discussed in [Section 4.3.1](#). The details of the model preprocessing and meshing will then be described in [Section 4.3.2](#). The inverse analysis for identifying the reaction rate constant is presented in [Section 4.3.3](#). Finally, the simulation results are discussed in [Section 4.3.4](#).

4.3.1 Finite element implicit formulation

4.3.1.1 Introduction of Finite Element Method

Modelling a diffusion-reaction-deformation process requires solving a coupled system of partial differential equation (PDE) with initial and boundary conditions over a geometrically complex body. Obtaining an exact, analytical solution for such a system is typically impossible. Therefore, numerical methods are employed to find an accurate approximate solution. In the following, the brief introduction of the FEM is presented.

In continuum mechanics, the governing equations comprise the equilibrium, kinematic, and constitutive relations, supplemented by suitable boundary conditions. The strong form of the equilibrium equation in the reference configuration is expressed as:

$$\begin{cases} \nabla_{\mathbf{X}} \cdot \mathbf{P} + b_0 = \mathbf{0} & \text{in } \Omega_0, \\ \mathbf{P} \cdot \mathbf{N} = \bar{\mathbf{P}} & \text{in } \partial\Omega_{t0}, \end{cases} \quad (4.98a)$$

$$(4.98b)$$

where $\mathbf{P}$ is the first Piola-Kirchhoff stress tensor, b_0 the body force per unit reference volume, Ω_0 the reference configuration, $\mathbf{N}$ the outward unit normal on the boundary, and $\bar{\mathbf{P}}$ the prescribed traction on the boundary $\partial\Omega_{t0}$. Kinematic relation varies between small deformation and finite deformation. For the latter, the kinematic relation between the deformation gradient $\mathbf{F}$ and the displacement field $\mathbf{u}$ is given by:

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} = \mathbf{I} + \nabla_{\mathbf{X}} \mathbf{u}, \quad (4.99)$$

where $\mathbf{X}$ and $\mathbf{x}$ denote the position vectors in the reference and current configurations, respectively, and $\nabla_{\mathbf{X}}$ is the gradient operator with respect to the reference coordinates, and $\mathbf{u}$ is the displacement vector. The constitutive equation follows from the strain-energy

density function Ψ as:

$$\mathbf{P} = \frac{\partial \Psi}{\partial \mathbf{F}}, \quad (4.100)$$

where Ψ is the strain energy density function, which is a function of the nominal strain tensor ε for small strain or the deformation gradient $\mathbf{F}$ for finite strain.

The problem can be formulated through a variational principle based on the total potential energy functional:

$$\Pi = \int_{\Omega_0} \Psi \, dV - \int_{\Omega_0} \mathbf{b}_0 \cdot \mathbf{u} \, dV - \int_{\partial\Omega_{t0}} \bar{\mathbf{P}} \cdot \mathbf{u} \, dS, \quad (4.101)$$

The equilibrium configuration corresponds to a stationary point of Π , and noting that the variation operator commutes with the differential and integral operators, it is given by

$$\delta \Pi = \int_V \frac{\partial \Psi}{\partial \mathbf{F}} : \nabla_{\mathbf{X}} \delta \mathbf{u} \, dV - \int_{\Omega_0} \mathbf{b}_0 \cdot \delta \mathbf{u} \, dV - \int_{\partial\Omega_{t0}} \bar{\mathbf{P}} \cdot \delta \mathbf{u} \, dS = 0, \quad (4.102)$$

which is equivalent to the equilibrium equations [Equation 4.98](#) in the weak sense. To see this, substituting [Equation 4.99](#) and [Equation 4.100](#) into [Equation 4.102](#), applying the product rule and the divergence theorem, one obtains:

$$\delta \Pi = - \int_{\Omega_0} [\nabla_{\mathbf{X}} \cdot \mathbf{P} + \mathbf{b}_0] \cdot \delta \mathbf{u} \, dV + \int_{\partial\Omega_{t0}} [\mathbf{P} \cdot \mathbf{N} - \bar{\mathbf{P}}] \cdot \delta \mathbf{u} \, dS = 0, \quad (4.103)$$

which is the weight residual of the equilibrium equations and the natural boundary conditions [Equation 4.98](#), also known as the Principle of Virtual Work. Since the virtual displacement $\delta \mathbf{u}$ is arbitrary, the above condition must hold for all admissible variations, which implies that the integrands vanish and the strong form [Equation 4.98](#) recovers. [Equation 4.102](#) is referred to as the weak form because it only requires the solution to satisfy the governing equations in an integral sense rather than pointwise. Consequently, the displacement field $\mathbf{u}$ only needs to possess first-order continuity (i.e., be sufficiently differentiable for the integrals to be well defined), which allows a broader range of admissible displacement approximations. In contrast, the strong form [Equation 4.98](#) requires a higher degree of smoothness (typically C^1 or C^2 continuity) so that all derivatives exist pointwise.

If the M dimensional displacement field $\mathbf{u}(\mathbf{X})$ is approximated by a finite series of orthogonal basis functions $\mathbf{N}_j(\mathbf{X}) = \{N_{i,j}(\mathbf{X})\}$, $j = 1, 2, \dots, N$ weighted by unknown

coefficients $\delta^j = \{\delta_i^j\}$ in each component direction, we can write

$$u_i \approx u_i^0 + \sum_{j=1}^N N_{i,j} \delta_i^j, \quad i = 1, 2, \dots, M, \text{ (no sum on } i), \quad (4.104)$$

Here $\mathbf{u}^0 = u_i^0$ denotes the prescribed displacement on the essential boundary, and basis functions satisfy $N_j = \mathbf{0}$ on the boundary. The total potential energy functional Π then becomes a function of the unknown coefficients δ_i^j only, and the stationary condition reads

$$\frac{\partial \Pi}{\partial \delta_i^j} = 0, \quad i = 1, 2, \dots, M \quad j = 1, 2, \dots, N. \quad (4.105)$$

This procedure, known as the Ritz method, transforms the continuous variational problem into a finite-dimensional algebraic system.

The orthogonal basis functions can be complicated global functions. Hence, in practice, the FEM is often used, where the body is discretised into small elements. So, equation (4.101) becomes:

$$\Pi = \sum_{e=1}^N \Pi^{[e]} = \sum_{e=1}^N \left[\int_{\Omega_0^{[e]}} \Psi^{[e]} dV - \int_{\Omega_0^{[e]}} \mathbf{b}_0 \cdot \mathbf{u}^{[e]} dV - \int_{\partial \Omega_{t_0}^{[e]}} \bar{\mathbf{P}} \cdot \mathbf{u}^{[e]} dS \right] \quad (4.106)$$

where, N is the number of elements, and the superscript $[e]$ represents the index of the element e , respectively. The stationary condition of $\delta \Pi = 0$ Equation 4.106 yields the weak form of the equilibrium equations for each element:

$$\delta \Pi^{[e]} = \int_{\Omega_0^{[e]}} \mathbf{P}^{[e]} : \nabla_{\mathbf{X}}(\delta \mathbf{u}^{[e]}) dV - \int_{\Omega_0^{[e]}} \mathbf{b}_0 \cdot \delta \mathbf{u}^{[e]} dV - \int_{\partial \Omega_{t_0}^{[e]}} \bar{\mathbf{P}} \cdot \delta \mathbf{u}^{[e]} dS = 0. \quad (4.107)$$

By applying product rule and gauss theorem, and considering the continuity between elements $\mathbf{u}^{[e]} = \mathbf{u}^{[e']}$, and on the essential boundary conditions $\delta \mathbf{u} = 0$, Equation 4.107 is proven to recover the following local balance equations for each element:

$$\begin{cases} \nabla_{\mathbf{X}} \cdot \mathbf{P}^{[e]} + \mathbf{b}_0 = 0 & \text{in } \Omega_0^{[e]}, \\ \mathbf{P}^{[e]} \cdot \mathbf{N}^{[e]} - \bar{\mathbf{P}} = 0 & \text{in } \partial \Omega_{t_0}^{[e]}, \\ \mathbf{P}^{[e]} \cdot \mathbf{N}^{[e]} + \mathbf{P}^{[e']} \cdot \mathbf{N}^{[e']} = 0 & \text{in } \partial \Omega_0^{[ee']}, \end{cases} \quad (4.108a)$$

$$\mathbf{P}^{[e]} \cdot \mathbf{N}^{[e]} - \bar{\mathbf{P}} = 0 \quad \text{in } \partial \Omega_{t_0}^{[e]}, \quad (4.108b)$$

$$\mathbf{P}^{[e]} \cdot \mathbf{N}^{[e]} + \mathbf{P}^{[e']} \cdot \mathbf{N}^{[e']} = 0 \quad \text{in } \partial \Omega_0^{[ee']}, \quad (4.108c)$$

representing the balance within element $\Omega^{[e]}$, on natural boundary $\partial \Omega_{t_0}^{[e]}$ (if exist), and at element interface $\partial \Omega_0^{[ee']}$ between element $[e]$ and $[e']$, respectively.

Within each element, the displacement field is approximated by common simple polynomial basis functions, i.e.,

$$\{\mathbf{u}^{[e]}\}(\mathbf{X}) = [\mathbf{N}](\mathbf{X}) \{\boldsymbol{\delta}^{[e]}\} \quad (4.109)$$

where

- we use $[\bullet]$ to denote matrices and $\{\bullet\}$ to denote vectors.
- $\{\mathbf{u}^{[e]}\}$ is the displacement vector field with m degree of freedom within the element $[e]$,
- $[\mathbf{N}]$ is the shape function matrix of m rows and $m \times n$ columns of elements with n nodes, and
- $\{\boldsymbol{\delta}^{[e]}\} = \{\delta_1^{[e]}, \delta_2^{[e]}, \dots, \delta_{n \times m}^{[e]}\}^T$ is the nodal displacement vector of the element.

Note that we use matrix notation as $[\mathbf{N}]$ could not be expressed in tensor form. The shape function of the corresponding node is chosen such that they satisfy the Kronecker delta property at the nodes, ensuring that $\{\boldsymbol{\delta}^{[e]}\}$ directly correspond to the nodal displacements. Similar to the global Ritz method in Equation 4.105, the stationary condition of each element Equation 4.107 is therefore transformed into the following algebraic system:

$$\frac{\partial \Pi^{[e]}}{\partial \{\boldsymbol{\delta}^{[e]}\}} = 0. \quad (4.110)$$

Combing the Equation 4.109 with kinematic equation Equation 4.99, we have:

$$\delta \{\mathbf{F}^{[e]}\} = \delta[\mathbf{L}] \{\mathbf{u}^{[e]}\} = [\mathbf{B}] \delta \{\boldsymbol{\delta}^{[e]}\}, \quad (4.111)$$

where $[\mathbf{L}]$ is the differential operator and $[\mathbf{B}] = [\mathbf{L}][\mathbf{N}]$ is the geometric matrix. $\{\mathbf{F}^{[e]}\}$ is the Voigt notation vector of the deformation gradient tensor. Then Equation 4.107 (or Equation 4.110) becomes

$$\{\mathbf{R}^{[e]}(\boldsymbol{\delta}^{[e]})\} = \{\mathbf{P}_{\text{int}}^{[e]}\} - \{\mathbf{P}_{\text{ext}}^{[e]}\} = \mathbf{0}, \quad (4.112)$$

where

- $\{\mathbf{R}^{[e]}\}$ is the residual force vector of the element, $\{\mathbf{P}^{[e]}\}$ is the Voigt notation vector of the first Piola-Kirchhoff stress tensor,
- $\{\mathbf{P}_{\text{ext}}^{[e]}\} = \int_{\Omega_0^{[e]}} [\mathbf{N}]^T \{\mathbf{b}_0\} dV + \int_{\partial\Omega_{t_0}^{[e]}} [\mathbf{N}]^T \{\bar{\mathbf{P}}\} dS + \{\mathbf{P}_0^{[e]}\}$ (4.113)
is the applied equivalent external nodal force vector of the element,

- $\{P_0^{[e]}\}$ is the equivalent nodal force vector due to the traction from the neighbouring elements at the element interface, and

- $\{P_{\text{int}}^{[e]}\} = \int_{\Omega_0^{[e]}} [\mathbf{B}]^T \{\mathbf{P}^{[e]}\} dV$ (4.114)

is the internal nodal force vector of the element caused by the material response (deformation) to the applied loads.

Equation 4.112 demonstrates that the equilibrium of each element is achieved when the internal nodal force vector $\{P_{\text{int}}^{[e]}\}$, balances the external nodal force vector $\{P_0^{[e]}\}$, so that the residual force vector $\{R^{[e]}\}$ becomes zero.

In the case of linear elasticity materials, as an example, the kinematic equation can be instead expressed as

$$\{\epsilon^{[e]}\} = [\mathbf{L}] \{u^{[e]}\} = [\mathbf{L}][\mathbf{N}] \{\delta^{[e]}\} = [\mathbf{B}] \{\delta^{[e]}\}, \quad (4.115)$$

where

- $\epsilon^{[e]}$ is the Voigt notation of the strain tensor, and
- $[\mathbf{L}]$ here is the differential operator for small strain.

Then the constitutive relationship is given by

$$\{\sigma^{[e]}\} = [\mathbf{D}] \{\epsilon^{[e]}\} = [\mathbf{D}][\mathbf{B}] \{\delta^{[e]}\}, \quad (4.116)$$

where

- $\{\sigma^{[e]}\}$ is the Voigt notation of the Cauchy stress tensor, and
- $[\mathbf{D}]$ is the material stiffness matrix.

Equation 4.116 can replace $\mathbf{P}^{[e]}$ in Equation 4.112, and the following linear element equilibrium equation is obtained:

$$[\mathbf{K}^{[e]}] \{\delta^{[e]}\} - \{P_{\text{ext}}^{[e]}\} = 0, \quad (4.117)$$

where

- $[\mathbf{K}^{[e]}] = \int_{\Omega_0^{[e]}} [\mathbf{B}]^T [\mathbf{D}] [\mathbf{B}] dV$ (4.118)

is the element stiffness matrix.

Equation 4.117 is linear and can be solved directly by algebraic methods such as Gaussian elimination. With this equation for each element, all elements are then transformed to global coordinates and assembled to form the global system of equations.

As the stiffness matrix involves integration over the element volume, it must be obtained using numerical integration techniques, such as Gaussian quadrature, and then interpolated to the integration points within each element. Also note that tensors in the equilibrium equations are often represented in Voigt notation for computational efficiency.

However, for problems in Equation 4.112, the equation is nonlinear, and thus cannot be solved directly as Equation 4.117. The Newton-Raphson iterative methods are applied to solve the equation (Sharma et al., 2021). We consider an incremental form of Equation 4.112, i.e., for a time increment from t to $t + \Delta t$, we have:

$$\left\{ \mathbf{R}^{[e]} \left(\Delta \boldsymbol{\delta}^{[e]} \right) \right\} = \Delta \left\{ \mathbf{P}_{\text{int}}^{[e]} \right\} - \Delta \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\} \quad (4.119)$$

where

$$\bullet \Delta \left\{ \mathbf{P}_{\text{int}}^{[e]} \right\} = \int_{\Omega_0^{[e]}} [\mathbf{B}]^T \Delta \left\{ \mathbf{P}^{[e]} \left(\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\} \right) \right\} dV \quad (4.120)$$

is the internal nodal force vector increment from t to $t + \Delta t$ according to Equation 4.114,

- $\Delta \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}$ is the external nodal force vector increment from t to $t + \Delta t$,
- $\Delta \left\{ \mathbf{F}^{[e]} \right\}$ is the increment of the deformation gradient tensor Voigt vector form between the time increment from t to $t + \Delta t$, and
- $\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}$ is the nodal displacement vector between the time increment from t to $t + \Delta t$.

We hope to find the increment of the nodal displacement vector $\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}$ that satisfies the equilibrium condition Equation 4.119 with the $\Delta \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}$ given. Applying the Taylor expansion to the residual force vector and neglecting the higher-order terms, we have:

$$\begin{aligned} \left\{ \mathbf{R}^{[e]} \left(\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\} \right) \right\} &= \left\{ \mathbf{R}^{[e]} \left(\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\} = \mathbf{0} \right) \right\} + \frac{\partial \left\{ \mathbf{R}^{[e]} \right\}}{\partial \Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}} \bigg|_{\left\{ \boldsymbol{\delta}^{[e]} \right\}} \Delta \left\{ \boldsymbol{\delta}^{[e]} \right\} \\ &= \left[\mathbf{K}_T^{[e]} \left(\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\} \right) \right] \Delta \left\{ \boldsymbol{\delta}^{[e]} \right\} - \Delta \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}, \end{aligned} \quad (4.121)$$

where

$$\bullet \left[\mathbf{K}_T^{[e]} \right] = \frac{\partial \left\{ \mathbf{R}^{[e]} \right\}}{\partial \Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}} = \int_{\Omega_0^{[e]}} [\mathbf{B}]^T \frac{\partial \Delta \left\{ \mathbf{P}^{[e]} \right\}}{\partial \Delta \left\{ \mathbf{F}^{[e]} \right\}} \frac{\partial \Delta \left\{ \mathbf{F}^{[e]} \right\}}{\partial \Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}} dV = \int_{\Omega_0^{[e]}} [\mathbf{B}]^T [\mathbf{C}^{[e]}] [\mathbf{B}] dV \quad (4.122)$$

is defined as the element tangent stiffness matrix, and

$$\bullet \quad [\mathbb{C}^{[e]}] = \frac{\partial \Delta \{\mathbf{P}^{[e]}\}}{\partial \Delta \{\mathbf{F}^{[e]}\}} = \left[\frac{\partial \mathbf{P}^{[e]}}{\partial \mathbf{F}^{[e]}} \right] = \left[\frac{\partial^2 \Psi^{[e]}}{\partial \mathbf{F}^{[e]} \partial \mathbf{F}^{[e]}} \right] \quad (4.123)$$

is the Voigt notation matrix of the reference material tangent moduli $\mathbb{C}^{[e]}$.

Enforcing Equation 4.121 to be zero to satisfy the equilibrium condition, it becomes an approximation of Equation 4.119 for the nonlinear problem, i.e.,

$$\left[\mathbf{K}_T^{[e]} \right]^{[i]} \Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}^{[i+1]} - \Delta \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}^{[i]} = 0, \quad (4.124)$$

where

- the superscript $[i+1]$ and $[i]$ denote the $i+1^{\text{th}}$ and i^{th} iteration step,
- $\left[\mathbf{K}_T^{[e]} \right]^{[i]}$ is the tangent stiffness matrix at the i^{th} iteration,
- $\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}^{[i+1]} = \left\{ \boldsymbol{\delta}^{[e]} \right\}^{[i+1]} - \left\{ \boldsymbol{\delta}^{[e]} \right\}^{[i]}$ is the increment of the nodal displacement vector at the $i+1^{\text{th}}$ iteration, and
- $\Delta \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}^{[i]} = \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}^{[i]} - \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}^{[i-1]}$ is the increment of the external nodal force vector at the i^{th} iteration. We also denote that
- $\Delta \left\{ \mathbf{P}_{\text{int}}^{[e]} \right\}^{[i+1]} = \left\{ \mathbf{P}_{\text{int}}^{[e]} \right\}^{[i+1]} - \left\{ \mathbf{P}_{\text{int}}^{[e]} \right\}^{[i]}$ is the increment of the internal nodal force vector at the $i+1^{\text{th}}$ iteration.

Equation 4.124 has a similar linear form as Equation 4.117, and therefore can be solved with the information of $\left[\mathbf{K}_T^{[e]} \right]^{[i]}$ and $\left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}^{[i]}$ to obtain $\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}^{[i+1]}$. Then using $\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}^{[i+1]}$, the internal nodal force vector $\Delta \left\{ \mathbf{P}_{\text{int}}^{[e]} \right\}^{[i+1]}$ can be updated by Equation 4.120, and $\left[\mathbf{K}_T^{[e]} \right]^{[i+1]}$ can be updated by Equation 4.122. Using the updated $\Delta \left\{ \boldsymbol{\delta}^{[e]} \right\}^{[i+1]}$, $\Delta \left\{ \mathbf{P}_{\text{int}}^{[e]} \right\}^{[i+1]}$, and $\left[\mathbf{K}_T^{[e]} \right]^{[i+1]}$, the residual force vector $\left\{ \mathbf{R}^{[e]} \right\}^{[i+1]}$ is then evaluated by Equation 4.121. The convergence criterion, i.e.,

$$\|\left\{ \mathbf{R} \right\}\| \leq \epsilon, \quad (4.125)$$

is then evaluated, where ϵ is a prescribed tolerance, and $\|\bullet\|$ is the norm (such as the L^2 norm). If this criterion is not satisfied, the external force at the new iteration is updated by the residual force from the last iteration, i.e.,

$$\Delta \left\{ \mathbf{P}_{\text{ext}}^{[e]} \right\}^{[i+2]} = \left\{ \mathbf{R}^{[e]} \right\}^{[i+1]}, \quad (4.126)$$

and the next iteration begins from Equation 4.124 with updated values. Once the criterion is satisfied, the iteration stops, and $\Delta \delta$ is obtained. This procedure is illustrated

in Figure 4.7. Then the solution at the time increment Δt is obtained, and the next time increment begins, until the solution of the whole nonlinear problem is obtained.

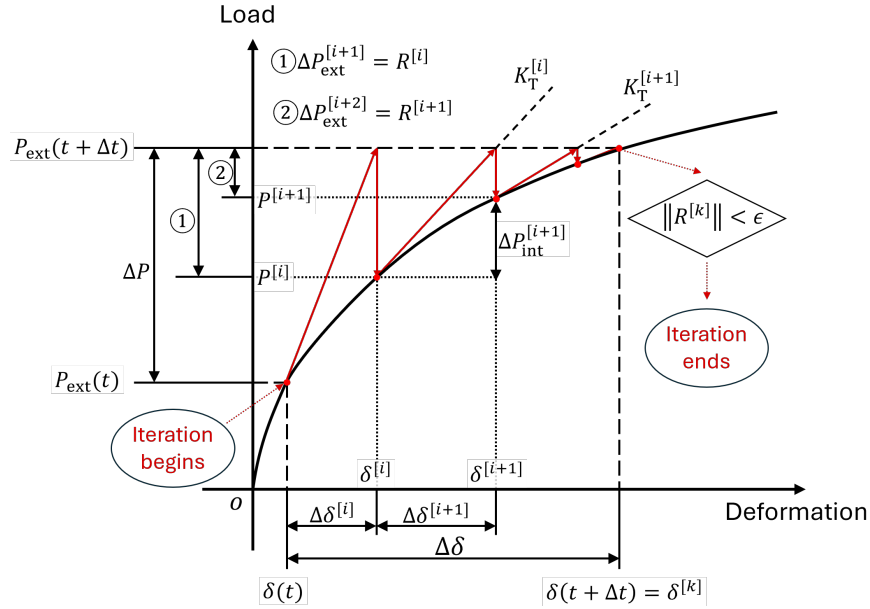


Figure 4.7. Schematic illustration of the Newton-Raphson iterative solution procedure. Note that this illustration is under 1D space, and the superscript $[e]$ is omitted for simplicity.

As Equation 4.121 is an implicit equation that needs to be solved iteratively, the above method is referred to as the implicit FEM. It can be seen that finding the material tangent moduli $\mathbb{C}^{[e]}$ is the key to implementing different constitutive models in the FEM for nonlinear problems. In the following section, the implementation of the chemomechanical constitutive model to the FE analysis tool Abaqus via UMAT will be presented.

4.3.1.2 Implementation of the chemomechanical constitutive model via UMAT

The UMAT in Abaqus/standard provides a flexible interface for implementing customised constitutive models within the FE framework. The subroutine is called at every integration point of every element at each time increment during the analysis. Users need to update the variables, including:

- STATEV, a solution-dependent state variables array with NSTATV components, which stores other variables dependent on the current state or the current values of these variables themselves (solution-dependent), especially the internal state variables defined in the constitutive model,
- DDSDD, a NTENS $\times$ NTENS array variable, which stores the Voigt notation matrix of the fourth-order spatial Jaumann tangent moduli tensor $\mathbb{C}$,

• STRESS, an array variable stores the Voigt notation vector of the second-order Cauchy stress tensor σ , with NTENS components by default or NTENS+3 for hybrid elements, and they can be updated using the variables provided by Abaqus, such as

- TIME(1), the total time at the beginning of the current increment,
- DTIME, the time increment size,
- TEMP, the current temperature at the start of the increment,
- DTEMP, the temperature increment during the current time increment,
- DFGRD0, a 3x3 array variable, which stores the deformation gradient tensor at the beginning of the current time increment,
- DFGRD1, a 3x3 array variable, which stores the deformation gradient tensor at the end of the current time increment.

Here, NTENS is the size of the stress or strain component array, and NSTATV is the number of solution-dependent state variables defined in the UMAT.

The internal variables, $\bar{I}_{1,\max}$, $\mathbf{C}_{v,j}$, and f need to be stored in the solution-dependent variable STATEV at each integration point, and updated at each time increment. Note that $\bar{I}_{1,\max}$ can be updated directly using its definition, while $\mathbf{C}_{v,j}$ and f need to be obtained according to their evolution laws defined in Equation 4.46 and Equation 4.96 by numerical methods. Following Shutov et al. (2013), a backward Euler description of $\dot{\mathbf{C}}_{v,j}$ gives an explicit update formula of $\mathbf{C}_{v,j}$, which avoids numerous iterations within each iteration of the global Newton-Raphson scheme of the FE analysis. Note that the state variables can be initialised via the user subroutine SDVINI. The initial values of these state variables are defined in the input file using the keyword *INITIAL CONDITIONS, TYPE=SOLUTION, USER.

The Cauchy stress tensor can be obtained from the first or second Piola-Kirchhoff stress tensor defined in Section 4.2, using the relation

$$\sigma = J^{-1} \mathbf{P} \cdot \mathbf{F}^T = J^{-1} \mathbf{F} \cdot \mathbf{S} \cdot \mathbf{F}^T. \quad (4.127)$$

The Cauchy stress tensor describes stress response in the current configuration. It should be noted that the stress tensors in Abaqus UMAT are represented in Voigt notation for computational efficiency, with the following ordering:

$$\{\sigma\} = \{\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}, \sigma_{13}, \sigma_{23}\}^T \quad (4.128)$$

for 3D problems, and

$$\{\sigma\} = \{\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}\}^T \quad (4.129)$$

for 2D problems, including plane stress, plane strain and axisymmetric problems.

The spatial Jaumann tangent moduli tensor can be obtained from the reference material tangent moduli $\mathbb{C}$, as described below. Since our constitutive law was developed under the material description with $\mathbf{C}$ and $\mathbf{S}$ as the strain measure and stress measure respectively, the strain energy function Ψ is expressed as a function of $\mathbf{C}$, i.e., $\Psi = \Psi(\mathbf{C})$, instead. Therefore, the variation of the second Piola-Kirchhoff stress tensor can be written as:

$$\delta \mathbf{C} = \frac{1}{2} [(\mathbf{F}^T \nabla_{\mathbf{x}} \delta \mathbf{u})^T + \mathbf{F}^T \nabla_{\mathbf{x}} \delta \mathbf{u}] . \quad (4.130)$$

The differential form of the second Piola-Kirchhoff stress tensor reads:

$$\delta \mathbf{S} = \mathbb{C} : \frac{1}{2} \delta \mathbf{C} \quad (4.131)$$

where

$$\begin{aligned} \mathbb{C} &= \frac{\partial \mathbf{P}}{\partial \mathbf{F}} = \frac{\partial^2 \Psi}{\partial \mathbf{F} \partial \mathbf{F}} \\ &= 2 \frac{\partial \mathbf{S}}{\partial \mathbf{C}} = 4 \frac{\partial \Psi^2}{\partial \mathbf{C} \partial \mathbf{C}} \end{aligned} \quad (4.132)$$

is the referential elasticity tensor (material tangent moduli). Considering the symmetry of the second Piola-Kirchhoff stress tensor and the right Cauchy-Green strain tensor, the fourth-order stiffness matrix actually has only 21 independent variables. Using [Equation 4.131](#) and the Jaumann stress rate definition according to **Holzapfel2000a**; Chaves (2013), we have

$$\delta(J\boldsymbol{\sigma}) = J \left[\mathbb{C} : \delta \mathbf{d} + \delta \mathbf{w} \cdot \boldsymbol{\sigma} - \boldsymbol{\sigma} \cdot \delta \mathbf{w} \right], \quad (4.133)$$

where $\mathbf{d}$ and $\mathbf{w}$ are the spatial rate of deformation tensor and the spin tensor, respectively, defined as

$$\mathbf{d} = \frac{1}{2} \left[\dot{\mathbf{F}} \mathbf{F}^{-1} + [\dot{\mathbf{F}} \mathbf{F}^{-1}]^T \right], \quad (4.134)$$

$$\mathbf{w} = \frac{1}{2} \left[\dot{\mathbf{F}} \mathbf{F}^{-1} - [\dot{\mathbf{F}} \mathbf{F}^{-1}]^T \right]. \quad (4.135)$$

Then the constitutive law in the form of Cauchy stress rate can be obtained as

$$\dot{\boldsymbol{\sigma}} = \mathbb{c} : \mathbf{d}, \quad (4.136)$$

where the spatial Jaumann tangent modulus tensor is expressed as

$$\mathbb{c} = 2\boldsymbol{\sigma} \otimes \mathbf{I} + \frac{1}{J} \left[[\mathbf{F} \otimes \mathbf{F}^T] : \mathbb{C} : [\mathbf{F}^T \otimes \mathbf{F}] \right]. \quad (4.137)$$

For the detailed derivation, please refer to **Holzapfel2000a**; Chaves (2013).

The specific expression of $\mathbb{C}$ must then be obtained. The reference material tangent moduli $\mathbb{C}$, a fourth-order tensor defined in Equation 4.123, needs to be derived for the constitutive model developed in Section 4.2. With Equation 4.11, the referential elasticity tensor $\mathbb{C}$ can therefore be decomposed into an isochoric part $\mathbb{C}_{\text{iso}}$ and a volumetric part $\mathbb{C}_{\text{vol}}$, as follows:

$$\mathbb{C} = \mathbb{C}_{\text{iso}} + \mathbb{C}_{\text{vol}}. \quad (4.138)$$

For the deviatoric part, following Yang et al. (2024a) we have

$$\begin{aligned} \mathbb{C}_{\text{iso}} &= 2 \frac{\partial \mathbf{S}_{\text{iso}}}{\partial \mathbf{C}} \\ &= \mathbb{P} : \bar{\mathbb{C}} : \mathbb{P}^T + \frac{2}{3} J^{-2/3} [\bar{\mathbf{S}} : \mathbf{C}] \tilde{\mathbb{P}} - \frac{2}{3} [\mathbf{C}^{-1} \otimes \mathbf{S}_{\text{iso}} + \mathbf{S}_{\text{iso}} \otimes \mathbf{C}^{-1}] \end{aligned} \quad (4.139)$$

where

$$\bar{\mathbb{C}} = 2J^{-4/3} \frac{\partial \bar{\mathbf{S}}}{\partial \mathbf{C}}, \quad (4.140)$$

$$\tilde{\mathbb{P}} = \mathbf{C}^{-1} \odot \mathbf{C}^{-1} - \frac{1}{3} \mathbf{C}^{-1} \otimes \mathbf{C}^{-1}, \quad (4.141)$$

and the following operators are defined:

$$(\mathbf{A} \odot \mathbf{B})_{ijkl} = -\frac{1}{2} [A_{ik} B_{jl} + A_{il} B_{jk}]. \quad (4.142)$$

According to Equation 4.57c, the isochoric part of the referential elasticity tensor $\mathbb{C}_{\text{iso}}$ considering the chemical effect can be expressed as

$$\mathbb{C}_{\text{iso}} = \tilde{\mathbb{C}}^{\text{eq}} + \tilde{\mathbb{C}}^{\text{peq}} + \sum_{j=1}^2 \tilde{\mathbb{C}}_j^{\text{neq}}, \quad (4.143)$$

$$\left\{ \begin{aligned} \tilde{\mathbb{C}}^{\text{eq}} &= f \mathbb{C}^{\text{eq}}, \end{aligned} \right. \quad (4.144a)$$

$$\left\{ \begin{aligned} \tilde{\mathbb{C}}^{\text{peq}} &= f \mathbb{C}^{\text{peq}}, \end{aligned} \right. \quad (4.144b)$$

$$\left\{ \begin{aligned} \tilde{\mathbb{C}}_j^{\text{neq}} &= [1 + m[1 - f]] \mathbb{C}_j^{\text{neq}}, \quad j = 1, 2 \end{aligned} \right. \quad (4.144c)$$

Here, the expression of $\mathbb{C}^{\text{eq}}$, $\mathbb{C}^{\text{peq}}$, and $\mathbb{C}^{\text{neq}}$ has the same form as Equation 4.139, i.e.,

$$\begin{cases} \mathbb{C}^{\text{eq}} = \mathbb{P} : \bar{\mathbb{C}}^{\text{eq}} : \mathbb{P}^T + \frac{2}{3} J^{-2/3} [\bar{\mathbf{S}}^{\text{eq}} : \mathbf{C}] \tilde{\mathbb{P}} - \frac{2}{3} [\mathbf{C}^{-1} \otimes \mathbf{S}^{\text{eq}} + \mathbf{S}^{\text{eq}} \otimes \mathbf{C}^{-1}] \end{cases} \quad (4.145a)$$

$$\begin{cases} \mathbb{C}^{\text{peq}} = \mathbb{P} : \bar{\mathbb{C}}^{\text{peq}} : \mathbb{P}^T + \frac{2}{3} J^{-2/3} [\bar{\mathbf{S}}^{\text{peq}} : \mathbf{C}] \tilde{\mathbb{P}} - \frac{2}{3} [\mathbf{C}^{-1} \otimes \mathbf{S}^{\text{peq}} + \mathbf{S}^{\text{peq}} \otimes \mathbf{C}^{-1}] \end{cases} \quad (4.145b)$$

$$\begin{cases} \mathbb{C}_j^{\text{neq}} = \mathbb{P} : \bar{\mathbb{C}}_j^{\text{neq}} : \mathbb{P}^T + \frac{2}{3} J^{-2/3} [\bar{\mathbf{S}}_j^{\text{neq}} : \mathbf{C}] \tilde{\mathbb{P}} - \frac{2}{3} [\mathbf{C}^{-1} \otimes \mathbf{S}_j^{\text{neq}} + \mathbf{S}_j^{\text{neq}} \otimes \mathbf{C}^{-1}] \end{cases} \quad j = 1, 2 \quad (4.145c)$$

where

$$\begin{cases} \bar{\mathbb{C}}^{\text{eq}} = 2J^{-4/3} \frac{\partial \bar{\mathbf{S}}^{\text{eq}}}{\partial \mathbf{C}}, \end{cases} \quad (4.146a)$$

$$\begin{cases} \bar{\mathbb{C}}^{\text{peq}} = 2J^{-4/3} \frac{\partial \bar{\mathbf{S}}^{\text{peq}}}{\partial \mathbf{C}}, \end{cases} \quad (4.146b)$$

$$\begin{cases} \bar{\mathbb{C}}_j^{\text{neq}} = 2J^{-4/3} \frac{\partial \bar{\mathbf{S}}_j^{\text{neq}}}{\partial \mathbf{C}} \quad j = 1, 2. \end{cases} \quad (4.146c)$$

Specifically, using Equation 4.35 we have

$$\bar{\mathbb{C}}^{\text{eq}} = 8J^{-4/3} [c_2 + 3c_3[\bar{I}_1 - 3]] \mathbf{I} \otimes \mathbf{I}, \quad (4.147)$$

Using Equation 4.38, we have

$$\bar{\mathbb{C}}^{\text{peq}} = \begin{cases} 8J^{-4/3} \eta [c_{p,2} + 3c_{p,3}[\bar{I}_1 - 3]] \mathbf{I} \otimes \mathbf{I}, & \text{if } \bar{\mathbf{C}} = \bar{\mathbf{C}}_{\text{max}} \text{ and } \mathbf{S} : \dot{\mathbf{C}} > 0, \\ 8J^{-4/3} \eta [c_{p,2} + 3c_{p,3}[\bar{I}_1 - 3]] \mathbf{I} \otimes \mathbf{I} \\ + 2J^{-4/3} \frac{\cosh^{-2} \left(\frac{\Psi_{\text{max}}^{\text{peq}}(\bar{I}_{1,\text{max}}) - \Psi_0^{\text{peq}}(\bar{I}_1)}{M + \beta \Psi_{\text{max}}^{\text{peq}}(\bar{I}_{1,\text{max}})} \right)}{R [M + \beta \Psi_{\text{max}}^{\text{peq}}(\bar{I}_{1,\text{max}})]} \bar{\mathbf{S}}_0^{\text{peq}} \otimes \bar{\mathbf{S}}_0^{\text{peq}}, & \text{otherwise,} \end{cases} \quad (4.148)$$

as

$$\frac{d\bar{I}_{1,\text{max}}}{d\bar{I}_1} = \frac{\dot{\bar{I}}_{1,\text{max}}}{\dot{\bar{I}}_1} = \begin{cases} 1, & \text{if } \bar{\mathbf{C}} = \bar{\mathbf{C}}_{\text{max}} \text{ and } \mathbf{S} : \dot{\mathbf{C}} > 0, \\ 0, & \text{otherwise.} \end{cases} \quad (4.149)$$

And using Equation 4.43,

$$\bar{\mathbb{C}}_j^{\text{neq}} = 4J^{-\frac{4}{3}} c_{v,j} [-\mathbf{C}_{v,j}^{-1} \odot \mathbf{C}_{v,j}^{-1}] : \frac{\partial \mathbf{C}_{v,j}}{\partial \mathbf{C}} \quad j = 1, 2 \quad (4.150)$$

respectively. Here, we denote a time interval as $\Delta t = t^{[i+1]} - t^{[i]}$, where $t^{[i]}$ is the current (i^{th}) time step and $t^{[i+1]}$ is the next ($i + 1^{\text{th}}$) time step, and an explicit Euler forward update formula for $\mathbf{C}_{v,j}$ is used to approximate $\partial \mathbf{C}_{v,j} / \partial \bar{\mathbf{C}}$ combining the evolution

equation Equation 4.46, i.e.,

$$\mathbf{C}_{v,j}^{[i+1]} \approx \mathbf{C}_{v,j}^{[i]} + \Delta t \frac{4}{\tau_j} \left[\bar{\mathbf{C}} - \frac{1}{3} [\bar{\mathbf{C}} : \mathbf{C}_{v,j}^{[i]-1}] \mathbf{C}_{v,j}^{[i]} \right], \quad j = 1, 2, \quad (4.151)$$

and

$$\frac{\partial \mathbf{C}_{v,j}}{\partial \bar{\mathbf{C}}} \approx \frac{\partial \mathbf{C}_{v,j}^{[i+1]}}{\partial \bar{\mathbf{C}}} = \Delta t \frac{4}{\tau_j} \left[\mathbb{I} - \frac{1}{3} \mathbf{C}_{v,j}^{[i]} \otimes \mathbf{C}_{v,j}^{[i]-1} \right], \quad j = 1, 2. \quad (4.152)$$

Note that $\frac{\partial \mathbf{C}_{v,j}}{\partial \bar{\mathbf{C}}}$ is not zero as we take $\mathbf{C}_{v,j}$ as a variable dependent on $\bar{\mathbf{C}}$ and $\mathbf{C}_e$ via Equation 4.4. As only one of $\mathbf{C}_e$ and $\mathbf{C}_{v,j}$ is independent, when finding the derivative, we need to choose one as the dependent variable.

For the volumetric part, note that during the development of the constitutive model, the material is considered incompressible in Section 4.2. However, in incompressible materials, hydrostatic pressure varies without additional displacement, whereas in nearly incompressible materials, even a small additional displacement can cause significant changes in pressure. Therefore, a purely displacement-based solution for an incompressible material suffers from a singularity and, thus, numerical instability. To solve this, a hybrid element is used, which includes an additional degree of freedom to determine the hydrostatic pressure independently. Pressure is coupled to the displacement solution through the constitutive law as a Lagrange multiplier. It is subject to compatibility conditions, known as the hybrid formulation (Simulia, Dassault Systemes, 2012), as it uses both displacement and pressure as primary variables. The detailed formulation of hybrid elements can be found in Bonet et al. (2016) and Simulia, Dassault Systemes (2012). Using Equation 4.132, and Equation 4.156, we have

$$\begin{aligned} \mathbb{C}_{\text{vol}} &= 2 \frac{\partial \mathbf{S}_{\text{vol}}}{\partial \bar{\mathbf{C}}} \\ &= (Jp + J^2 \frac{dp}{dJ}) \mathbf{C}^{-1} \otimes \mathbf{C}^{-1} - 2Jp \mathbf{C}^{-1} \odot \mathbf{C}^{-1} \end{aligned} \quad (4.153)$$

When a hybrid formulation is used, $\hat{J}$ is read from the additional degree of freedom returned by STRESS(NTENS+1) in UMAT, instead of being calculated from the deformation gradient tensor $\mathbf{F}$. Note that $\hat{J}$ is not the actual Jacobian determinant, but an independent variable for computing the hydrostatic pressure. The bulk modulus used in the hybrid element formulation $\hat{K}$, defined as

$$\hat{K} = \hat{J} \frac{\partial^2 \Psi_{\text{vol}}}{\partial \hat{J}^2} = \hat{J} \frac{\partial p}{\partial \hat{J}} \quad (4.154)$$

needs to be assigned to STRESS(NTENS+2) to obtain hydrostatic pressure from $\hat{J}$. If necessary, $\frac{\partial \hat{K}}{\partial \hat{J}} = \hat{J} \frac{\partial^3 \Psi_{\text{vol}}}{\partial \hat{J}^3}$ can also be assigned to STRESS(NTENS+3) for better convergence.

Here, we assume that a specific form of the volumetric energy term $\Psi_{\text{vol}}(\hat{J})$ is given by

$$\Psi_{\text{vol}}(\hat{J}) = \frac{1}{2} \kappa [\hat{J} - 1]^2, \quad (4.155)$$

where κ is the bulk modulus of the material, and $J = \det(\mathbf{F})$ is the Jacobian determinant representing the local volume change. Here, κ is artificially prescribed as a large value to approximate the incompressible condition. Compared to Equation 4.51, Equation 4.155 actually defines the dependence of p on a degree of freedom $\hat{J}$ independent of $\mathbf{F}$. Then the volumetric part of the second Piola-Kirchhoff stress tensor is given by

$$\mathbf{S}_{\text{vol}} = \kappa \hat{J} [\hat{J} - 1] \mathbf{C}^{-1}, \quad (4.156)$$

where

$$p = \frac{\partial \Psi_{\text{vol}}(\hat{J})}{\partial \hat{J}} = \kappa [\hat{J} - 1] \quad (4.157)$$

is the hydrostatic pressure caused by volumetric changes. The bulk modulus used in the hybrid element formulation is

$$\hat{K} = \hat{J} \frac{\partial p}{\partial \hat{J}} = \kappa \hat{J}, \quad (4.158)$$

and its derivative with respect to $\hat{J}$ is

$$\frac{\partial \hat{K}}{\partial \hat{J}} = \frac{\partial}{\partial \hat{J}} \left(\hat{J} \frac{\partial p}{\partial \hat{J}} \right) = \frac{\partial p}{\partial \hat{J}} + \hat{J} \frac{\partial^2 p}{\partial \hat{J}^2} = \kappa + \hat{J} \frac{\partial^2 p}{\partial \hat{J}^2}. \quad (4.159)$$

Finally, the total referential elasticity tensor $\mathbb{C}$ is obtained by substituting Equation 4.143 and Equation 4.153 into Equation 4.138. It should be noted that the numerical approximation of $\mathbb{C}$ is not necessarily exact, as it only influences the gradient of the search direction and convergence rate of the Newton-Raphson iteration, but not the final solution. Therefore, $\mathbb{C}$ (or the inverse of $\mathbb{C}$) can be approximated, and the corresponding iteration method is called the Quasi-Newton method (Simulia, Dassault Systemes, 2012). With a good approximation of $\mathbb{C}$, the convergence rate can be significantly improved.

It should be noted that the fourth-order tangent moduli tensor is represented in Voigt

notation matrix in UMAT for computational efficiency, with the ordering as follows:

$$[\mathbb{C}] = \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1112} & C_{1113} & C_{1123} \\ C_{2211} & C_{2222} & C_{2233} & C_{2212} & C_{2213} & C_{2223} \\ C_{3311} & C_{3322} & C_{3333} & C_{3312} & C_{3313} & C_{3323} \\ C_{1211} & C_{1222} & C_{1233} & C_{1212} & C_{1213} & C_{1223} \\ C_{1311} & C_{1322} & C_{1333} & C_{1312} & C_{1313} & C_{1323} \\ C_{2311} & C_{2322} & C_{2333} & C_{2312} & C_{2313} & C_{2323} \end{bmatrix} \quad (4.160)$$

for 3D problems, and

$$[\mathbb{C}] = \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1112} \\ C_{2211} & C_{2222} & C_{2233} & C_{2212} \\ C_{3311} & C_{3322} & C_{3333} & C_{3312} \\ C_{1211} & C_{1222} & C_{1233} & C_{1212} \end{bmatrix} \quad (4.161)$$

for 2D problems, including plane stress, plane strain and axisymmetric problems.

4.3.1.3 Analogy between heat transfer and diffusion

A special technique is adopted to account for the diffusion-reaction-deformation process in ABAQUS, as the diffusion solver is not coupled with the mechanical model. Bear in mind that the heat transfer equation (Fourier's law) and the mass diffusion equation (Fick's law) have the same form of parabolic PDEs, as shown in Table 4.5. Therefore, one can leverage the fact that the existing heat transfer solver can be used to simulate mass diffusion. In practice, the concentration C is mapped to temperature T , the diffusivity D is mapped to thermal conductivity k , and the mass flux J is mapped to heat flux q . The specific heat capacity ρc_p is set to 1, so that the temperature directly represents the concentration. The analogy is summarised in Table 4.5.

Heat transfer	Fourier's law $\mathbf{q} = -k \nabla (\rho c_p T)$	Temperature $\rho c_p T$	Conductivity k	Heat flux $\mathbf{q}$
Mass diffusion	Fick's law $\mathbf{J} = -D \nabla C$	Concentration C	Diffusivity D	Mass flux $\mathbf{J}$

Table 4.5. Comparison of Heat Transfer and Mass Diffusion

4.3.2 Model geometry and boundary conditions

Simulation of the diffusion test in [Section 3.4](#) was performed first for validation of the diffusivity parameter. The geometry and boundary conditions are illustrated in [Figure 4.8](#), where a cylindrical hydrogel sample with a diameter of 5 mm and a height of 0.1 mm is considered. The height is consistent with [Figure 3.1\(b\)](#) in [Section 3.2.1](#). Taking advantage of the axisymmetry of the sample, the simulation was performed using a 2D axisymmetric model. The left boundary was the axis of axisymmetry, while zero axial displacement was prescribed at the bottom surface. The surface concentration of the enzyme at the right surface is set to be 20% w/w, and the initial concentration of the enzyme is set to be zero inside the sample. The top and bottom surfaces were assigned no diffusion boundary condition (i.e., an insulated boundary condition), consistent with the experiment. The diffusion time for analysis was set to 100 hours, the same as the experiment. The mesh was constructed using structured quadrilateral elements, with 50 elements in the radial direction and 1 in the axial direction. We use a single element along the axial direction, as the height is much smaller than the radius, and the concentration gradient along the axial direction is negligible. The element type was a 4-node axisymmetric thermally coupled quadrilateral element with a hybrid formulation (CAX4HT), and the temperature degree of freedom was treated as a diffusion variable.

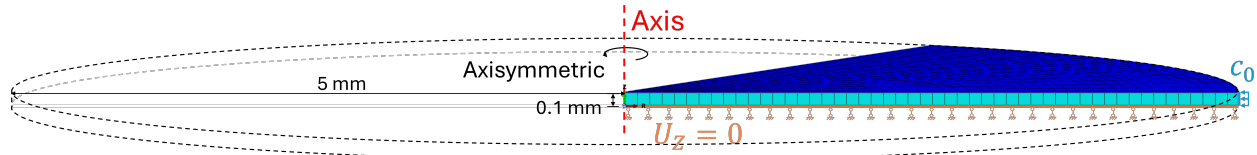


Figure 4.8. The geometry and boundary condition of the Axisymmetric FE simulation for diffusion test. The cyan area represents the simulation mesh.

For the diffusion-reaction-deformation simulation of the compression test after enzymatic hydrolysis in [Section 3.3.2](#), the simulation is performed under the axisymmetric condition as well, where the hydrogel is compressed with continuous cycles. Three different sizes were considered, including 5 mm, 12.5 mm, and 20 mm in diameter, following [Figure 3.1\(a\)](#) in [Section 3.2.1](#), with the same aspect ratio of one between the diameter and height. The model was also performed using 2D axisymmetric elements. Taking advantage of symmetry about the middle cross-section, only half of the model in height was modelled, as illustrated in [Figure 4.9](#). The axial displacement at the bottom surface was constrained, representing a symmetric boundary condition. The top surface was set to move axially under a cyclic load, as in the experiment, at a nominal strain rate of 0.01 /s and a nominal strain of 0.15. The nodes on the top surfaces were constrained to have

the same displacement. Both top and bottom surfaces are free to move tangentially, i.e., friction-free. The left boundary was the axis of axisymmetry. For diffusion, the surface concentration of the enzyme at the outer surface (the top and right surface) is set to be 20% w/w, while the initial concentration of the enzyme is set to be zero inside the sample. The bottom surface was not assigned a boundary condition for diffusion, as it represents the internal symmetric plane of the sample. The diffusion time for analysis was set to be 2 hours, and the compression load was performed after diffusion, which is the same as the *in vitro* experimental setup in Figure 3.4. Note that diffusion and reaction were first simulated in a separate analysis step. As this step does not involve mechanical loading or deformation, a large time increment can be used. In the subsequent analysis step, where compression was applied, the time increment was reduced accordingly. The mesh was constructed using structured quadrilateral elements with 50 elements in the radial and axial directions, with a size bias toward smaller elements near the surfaces. The CAX4HT was also used. For both simulations, the material model developed in Section 4.2 was implemented using UMAT.

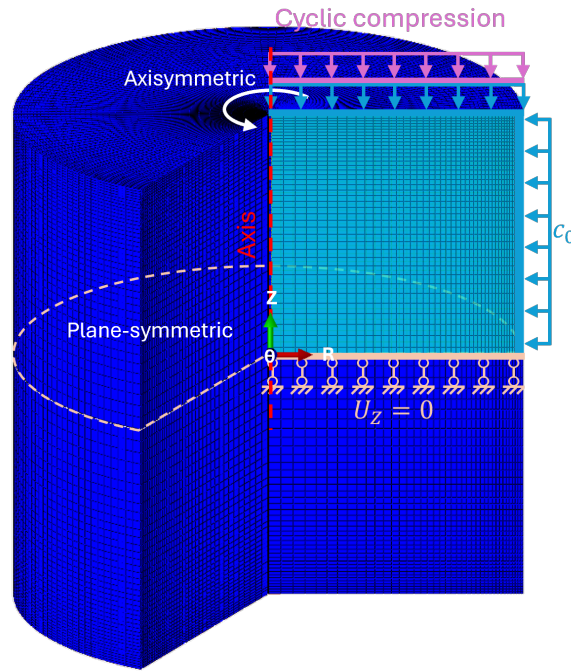


Figure 4.9. The geometry and boundary condition of the Axisymmetric FE simulation for diffusion-reaction-deformation of starch hydrogel.

4.3.2.1 Unit system

In Abaqus, the unit system is not predefined. Therefore, when defining material properties and initial and boundary conditions in Abaqus, the values must be provided in

accordance with the chosen unit system to ensure accurate simulation results. Therefore, it is crucial to maintain consistency in the unit system throughout the simulation. In this study, we adopt the unit system N (ton·mm/s²), mm, s, and K for force, length, time, and temperature, respectively, which is common in engineering practice. The corresponding units for other physical quantities can be derived from these base units, which are summarised in Table 4.6 with the SI unit system presented in the following line and the conversion between the two systems in the last line.

Table 4.6. Abaqus unit systems used in this study versus the SI unit system.

	Length	Area	Volume	Mass	Density	Velocity	Acceleration	Stress
Units in N, mm, s, K	mm	mm ²	mm ³	ton = N · s ² /mm	ton/mm ³ = N · s ² /mm ⁴	mm/s	mm/s ²	MPa = N/mm ²
SI Units	m	m ²	m ³	kg = N · m/s ²	kg/m ³	m/s	m/s ²	Pa = N/m ²
Conversion Equation	1 mm = 10 ⁻³ m	1 mm ² = 10 ⁻⁶ m ²	1 mm ³ = 10 ⁻⁹ m ³	1 ton = 10 ³ kg	1 ton/mm ³ = 10 ¹² kg/m ³	1 mm/s = 10 ⁻³ m/s	1 mm/s ² = 10 ⁻³ m/s ²	1 MPa = 10 ⁶ Pa

	Energy	Power	Diffusion coefficient	Specific heat Capacity	Thermal conductivity	Concentration (mass)	Concentration (molar)	Thermal expansion coefficient
Units in N, mm, s, K	mJ = N·mm	mW = N·mm/s	mm ² /s	mJ/[ton·K] = mm ² /[s ² ·K]	mW/[mm·K]	ton/mm ³	mol/mm ³	1/K
SI Units	J = N·m	W = N·m/s	m ² /s	J/[kg·K]	W/[m·K]	kg/m ³	mol/m ³	1/K
Conversion Equation	1 mJ = 10 ⁻³ J	1 mW = 10 ⁻³ W	1 mm ² /s = 10 ⁻⁶ m ² /s	1 mJ/[ton·K] = 10 ⁻⁶ J/[kg·K]	1 mW/[mm·K] = 1 W/[m·K]	1 ton/mm ³ = 10 ¹² kg/m ³	1 mol/mm ³ = 10 ⁹ mol/m ³	1/K = 1/K

4.3.3 Inverse optimisation of the reaction parameters

Recall that in Section 4.2.9, the parameters of the reaction kinetics were calibrated under the assumption of instantaneous diffusion for the small sample, which overestimates the degree of reaction. To account for the diffusion effect, the PDE of diffusion needs to be solved together with the reaction and deformation using the FEM, and the reaction kinetics parameters are further calibrated by optimising the parameters so that the simulation results of the compression response after diffusion and reaction can match the experimental data. This process is known as inverse analysis. The mechanical parameters in Table 4.2 are directly used in the simulation, while the reaction kinetics parameters, including $\tilde{K}_{enz}$, and $\tilde{K}_S$ in Table 4.4 are used as the initial guess.

The software Isight was used for the analysis, which can be coupled with Abaqus for optimisation. Specifically, the optimisation is illustrated in Figure 4.10. First, the initial

guess of the reaction kinetics parameters is passed from Isight to Abaqus (the left orange parallelogram), and simulations with different conditions, including specimen size and reaction time, are performed by Abaqus (FE solvers in the flowchart). Abaqus (labelled as “FE solver j ” in the flowchart) returns the stress-strain curves to Isight, and the corresponding experimental curves (labelled as “Test data j ” in the flowchart) are also imported. The sum of squared errors (SSE) between the experimental and simulated stresses at the same strain levels, i.e., the objective function, is then computed (data comparison in the flowchart), and the error is evaluated against the convergence criterion:

$$\text{SSE}_j = (\sigma_{\text{FE},j} - \sigma_{\text{Test},j})^2 < \epsilon_j, \quad j = 1, 2, \dots, m, \quad (4.162)$$

where m is the number of experimental conditions considered in the optimisation, as indicated by the pink decision diamond in the flowchart. Here, ϵ_j is the tolerance for condition j , and $\sigma_{\text{FE},j}$ and $\sigma_{\text{Test},j}$ are the stress data sets of simulated and experimental, respectively, for condition j . The stress datasets are vectors containing stress values at different strain levels. The convergence criterion is satisfied when all SSEs across the m conditions fall below the corresponding tolerances. If not, Isight updates the reaction kinetics parameters according to the optimisation algorithm (labelled as “optimiser” in the flowchart), and the new parameters are returned to Abaqus for the next round of iteration. This process continues until convergence is achieved, i.e., the error is below the tolerance provided by the convergence criteria, and the optimised reaction kinetics parameters are then obtained (the right orange parallelogram). Experimental data from three hydrolysis times (30, 60, and 90 minutes) for small samples were used for parameter identification, and the remaining tests (large and medium samples) were used for validation.

When comparing different conditions of experimental data and simulation results, and requiring them to converge simultaneously, this process is known as multi-objective optimisation. In this study, the sequential quadratic programming (SQP), NLPQLP, is adopted as the optimisation algorithm for nonlinear design spaces. According to Isight, this method is gradient-based. It exploits the local area around the initial design point and rapidly finds a local optimum design. The objective and constraint functions can be evaluated simultaneously at predetermined test points along the search direction. In this study, the tolerances for all three conditions were set to be 0.1. The history of the SSEs during the optimisation process is shown in [Figure 4.11](#), which shows that the errors of all experimental conditions generally decreased with iterations until all three conditions

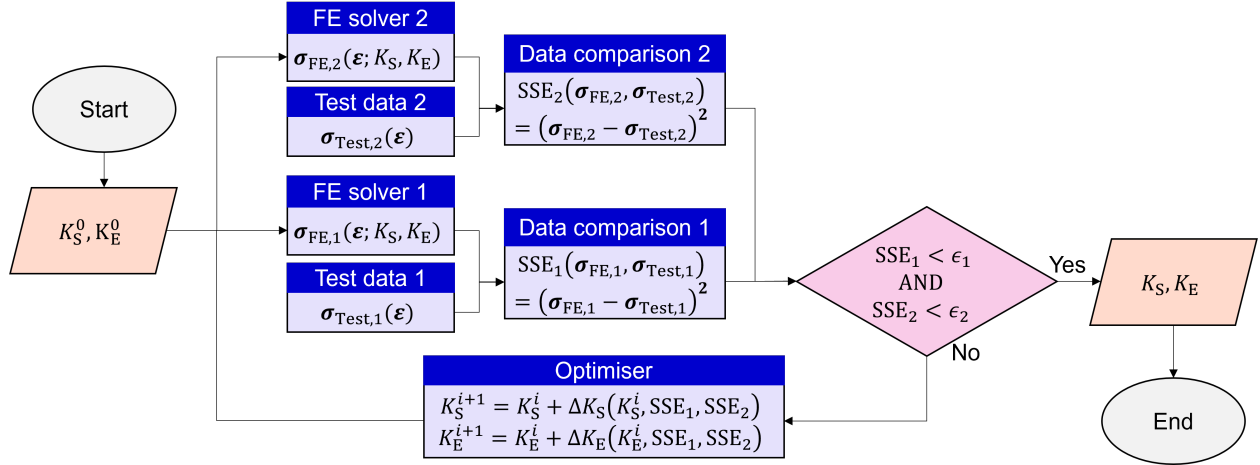


Figure 4.10. Optimisation flowchart for the inverse optimisation process of the enzymatic hydrolysis of starch hydrogel.

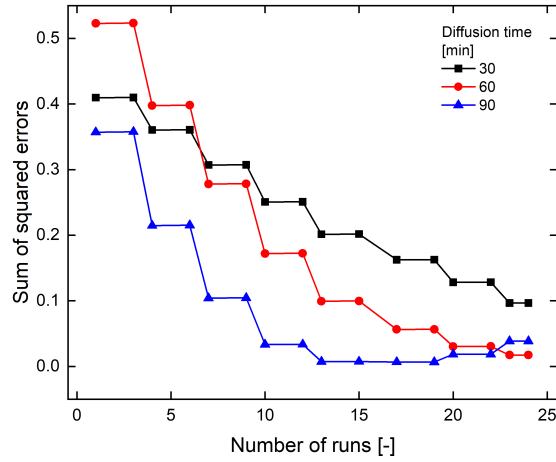


Figure 4.11. Error (sum of squared differences) history of the inverse optimisation process.

converged. The parameters identified are presented in Table 4.7, and the simulation results using the optimised parameters will be presented in the next section.

Table 4.7. Parameters for chemical degradation of starch hydrogel catalysed by α -amylase (optimised by FE inverse analysis).

$\tilde{K}_{enz}$ [ton/mm ³]	$\tilde{K}_S$ [ton/mm ³]
8.99e-12	2.53e-8

Note that the parameters $\tilde{K}_{enz}$, and $\tilde{K}_S$ need to be parameterised in the .inp file. This is done by including the *Parameter keyword and defining the parameter in the name = value format in the following data line. Then these parameters are used in place of input quantities by delimiting them with < > in the *User Material section (or *Material section

if user-defined material is not used), e.g., <K_E> and <K_S>.

4.3.4 Computational results

First, the diffusion simulation result is presented to validate the diffusivity parameter calibrated in [Section 3.4](#). [Figure 4.12](#) shows the comparison of the normalised concentration contour of the specimen between the simulation (left half) and experimental (the right half) results for the diffusion process in starch hydrogel at a time of 12 hours. The pattern of the concentration distribution from the simulation matches the experimental result. Since the specimen is not perfectly circular, the experimental results show some asymmetry, but the ring shape of the concentration contour is observed. Based on the simulation, the concentration profile along the radial direction at times of 12 hours and 24 hours, and the global enzyme ratio, i.e., the ratio of enzyme within the sample over the diffusion process compared to saturation, are extracted, and presented in [Figure 3.20](#) and [Figure 3.21](#) in [Section 3.4.2](#). As mentioned there, the FEM and FDM results match well. Note that to obtain the global enzyme ratio within the sample, [Equation 3.19](#) is discretised and calculated using the numerical integration method over all elements in the sample, i.e.,

$$f_{\text{enz}}^*(t) = \frac{\int_V C(r, t) dV}{V} \approx \frac{\sum_{i=1}^{n_{\text{int}}} C_i V_i}{\sum_{i=1}^{n_{\text{int}}} V_i}, \quad (4.163)$$

where n_{int} is the total number of integration points, C_i and V_i are the local enzyme concentration and the integration point volume of element i , respectively. Specifically, V_i is extracted from the element integration point variable IVOL in Abaqus by post-processing the output database (.odb) file.

Then, the simulation results of the compression test after enzymatic hydrolysis are presented, and compared with the experimental data for validation of the chemomechanical model and the reaction kinetics parameters identified in [Section 4.3.3](#). [Figure 4.13](#) shows a contour plot of the enzyme concentration at time=7200s for the large starch hydrogel sample. It can be seen that the enzyme diffuses from the outer surface to the core of the sample, establishing a concentration gradient. The blue region in the core, which represents a concentration close to zero, occupies a larger area in the larger sample than in the smaller one. This leads to different hydrolysis levels for various sample sizes at the same diffusion time.

As shown in [Figure 4.14](#), with increasing hydrolysis, the mechanical properties decrease,

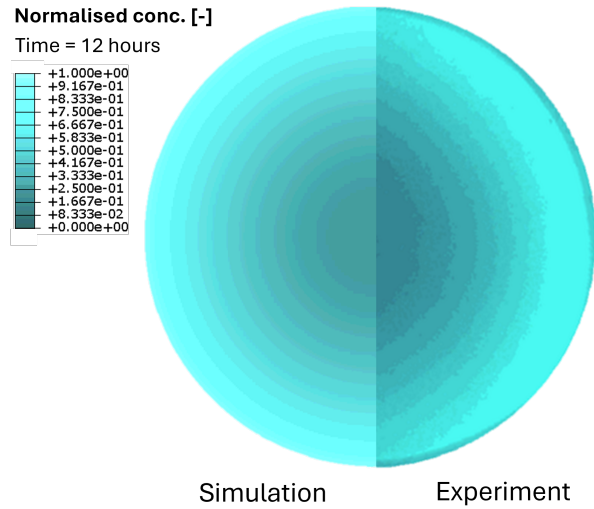


Figure 4.12. Comparison of simulation and experimental results for the diffusion process in starch hydrogel at a time of 12 hours.

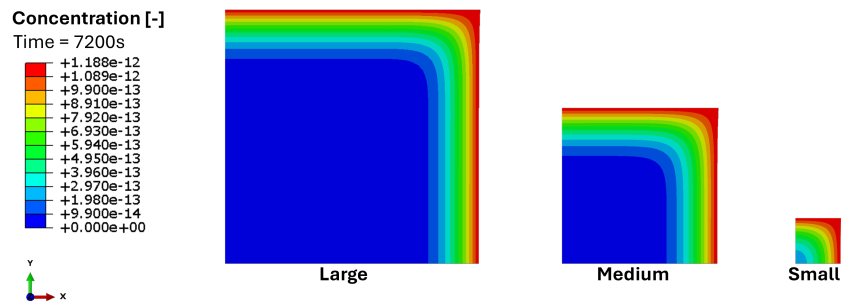


Figure 4.13. The contour of concentration for simulation of the diffusion process at time=7200s on the starch hydrogel.

and the stress-strain curve of the starch hydrogel shows lower stress. Both the simulation and experimental results show a decrease in stress with increasing hydrolysis time for all three sample sizes. For smaller samples, both the simulation and experimental results show a greater decrease in stress compared to the larger samples, as the smaller samples have a higher hydrolysis level due to the diffusion effect. Note that the trend of the simulation results matches well with the experimental data. Generally, the simulation stress level falls within the error bands of the experimental results. However, some discrepancies remain. For example, both the large and medium samples show higher stress levels than the experimental results, while the small sample at hydrolysis times of 30 and 60 minutes shows lower stress levels than the experimental results. This may be due to the assumptions made in the model, such as the assumption of Fickian diffusion, which has shown an error in capturing diffusion behaviour in [Figure 3.20](#), and the assumption that the loss fraction of substance $m = 1$ in [Equation 4.55](#). Further improvements can be made in future studies to enhance the accuracy of the model.

To further illustrate the hydrolysis level within the sample during the diffusion-reaction process, the global properties of an entire sample are extracted from the simulation results. [Figure 4.15\(a\)](#) shows the global enzyme ratio over the diffusion, which is calculated following [Equation 4.163](#), and smaller samples show a faster increase of the enzyme ratio. The Global substrate ratio, i.e., the ratio of unhydrolysed starch remaining within the sample over time during diffusion-reaction, is calculated by:

$$f_S^*(t) = \frac{\int_V C_S(r, t) dV}{\int_V C_{S_0} dV} \approx \frac{\sum_{i=1}^{n_{\text{int}}} C_{S,i}(t) V_i}{C_{S_0} \sum_{i=1}^{n_{\text{int}}} V_i}. \quad (4.164)$$

where $C_{S,i}(t)$ is the local starch concentration at time t at integration point i , C_{S_0} is the initial starch concentration, and V_i is the volume of the integration point i (IVOL in Abaqus). The results are presented in [Figure 4.15\(b\)](#), where the results for the large, medium, and small samples are plotted in red, blue, and green, respectively. It can be seen that for all three sample sizes, the amount of enzyme in the sample increases with time, while the amount of starch remaining decreases, as expected. For larger samples, the global enzyme ratio increases more slowly, and starch degradation is slower as well due to the longer diffusion path. The reaction kinetics of [Equation 4.96](#) under a homogeneous enzyme distribution condition are also recalculated using the optimised parameters in [Table 4.7](#), and are plotted in a black solid curve in [Figure 4.15\(b\)](#). The decrease rate of the substrate ratio is found to be faster than that of the initial guess

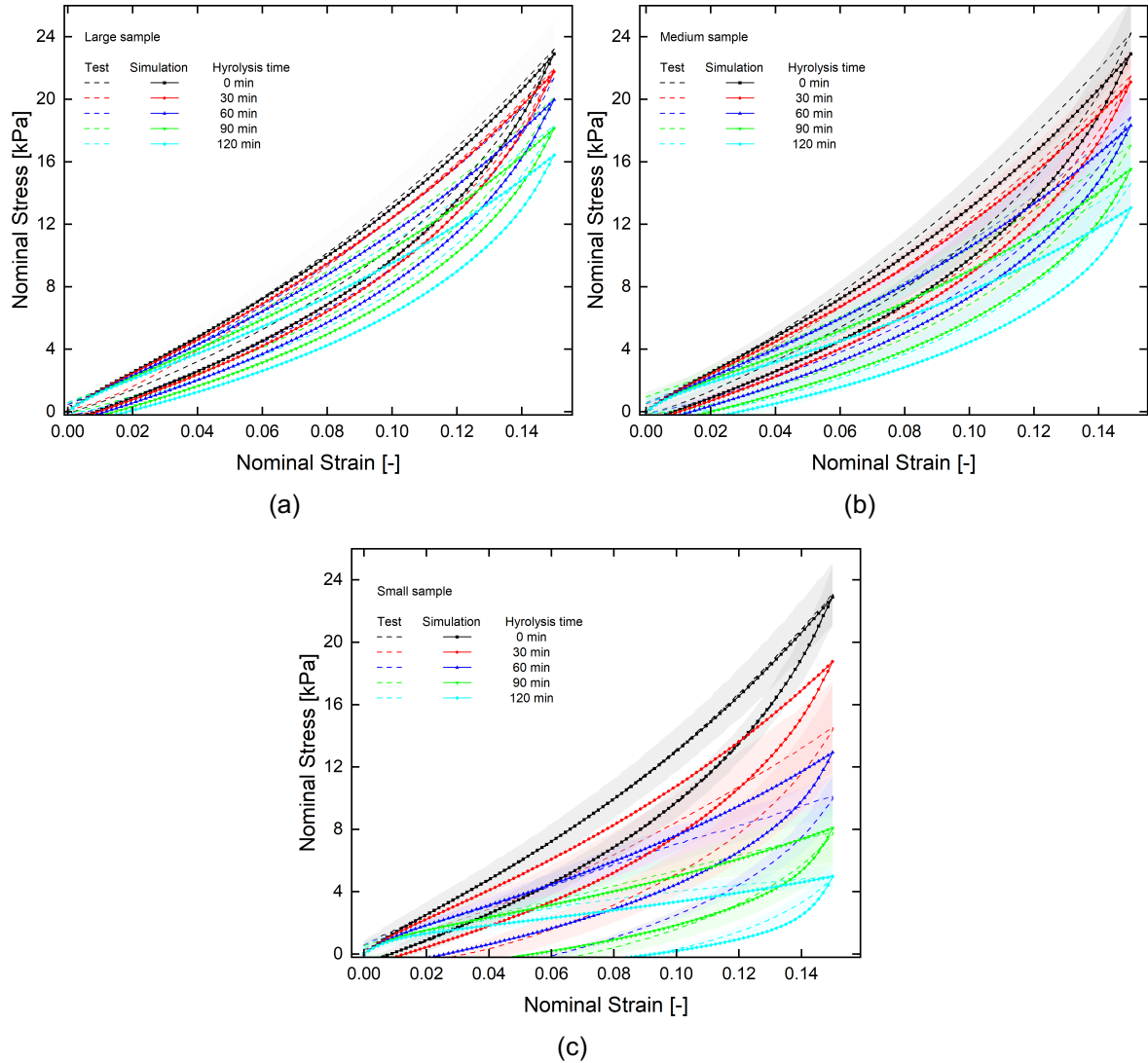


Figure 4.14. Comparing simulation (solid lines with symbol) and experiments (dashed lines with error band) of stress-strain curve of compression tests on specimens under varying hydrolysis time. (a) Large sample. (b) Medium sample. (c) Small sample.

plotted in the black dashed curve (copied from Figure 4.6(b)). Note that the substrate was found almost fully hydrolysed after two hours, as shown by the black solid curve in Figure 4.15(b), which is consistent with the digestion physiology findings (Bellmann et al., 2016). It can also be seen that the substrate starch ratio of the small sample (green curves) deviates from the reaction kinetics curve. This is because the reaction kinetics curve assumes instantaneous enzyme diffusion and homogeneous reaction within the sample, whereas in Figure 4.15(a) the enzyme diffusion in the small sample (green curves) approached 1 gradually. It did not reach 1 at 2 hours of diffusion, which is significantly different from the assumption of instantaneous diffusion. It demonstrates the necessity of considering the diffusion-reaction coupling in the model and performing an inverse analysis to obtain the material parameters.

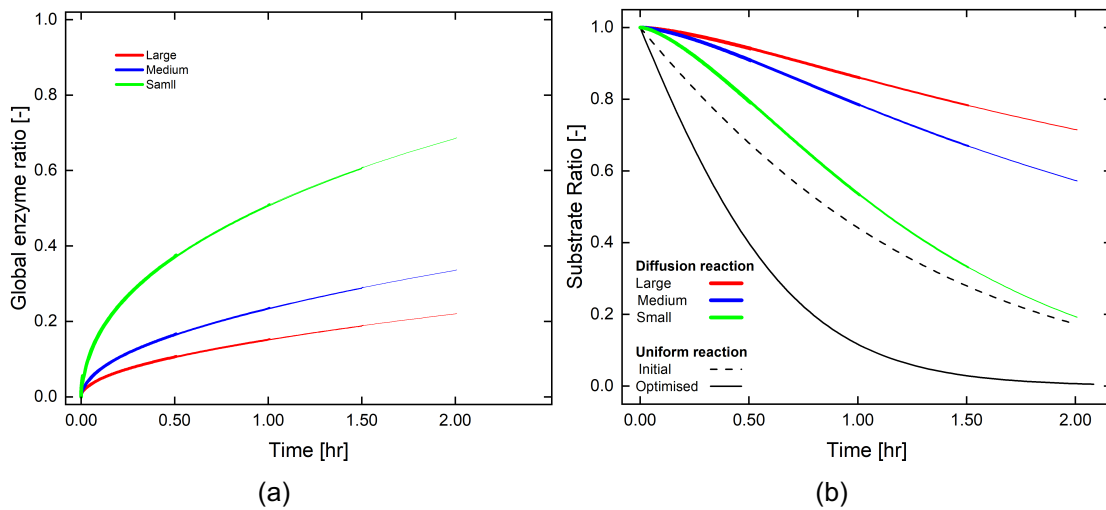


Figure 4.15. (a) The global ratio of enzyme within the specimen. (b) The substrate ratio (the ratio of starch remaining within the sample).

Finally, the contours of strain in Figure 4.16 and stress in Figure 4.17 within the sample during compression after diffusion-reaction are presented to illustrate the mechanical response. Due to diffusion and reaction, the mechanical properties are not homogeneous within the sample, and therefore, the contours of stress and strain are not uniform. It can be seen that for all samples, the strain in both the axial direction Figure 4.16(a) and lateral direction Figure 4.16(b) are larger near the top outer surface compared to the core region, as the outer surface has a higher hydrolysis level. Therefore, a lower stiffness (softer), and this is more obvious for the smaller sample, as the smaller sample has stronger hydrolysis. The shear strain Figure 4.16(c) concentrates near the top (right) corner, but the concentration is more significant for the larger sample, as the gradient of the hydrolysis level. Thus, the stiffness is stronger for

the larger sample.

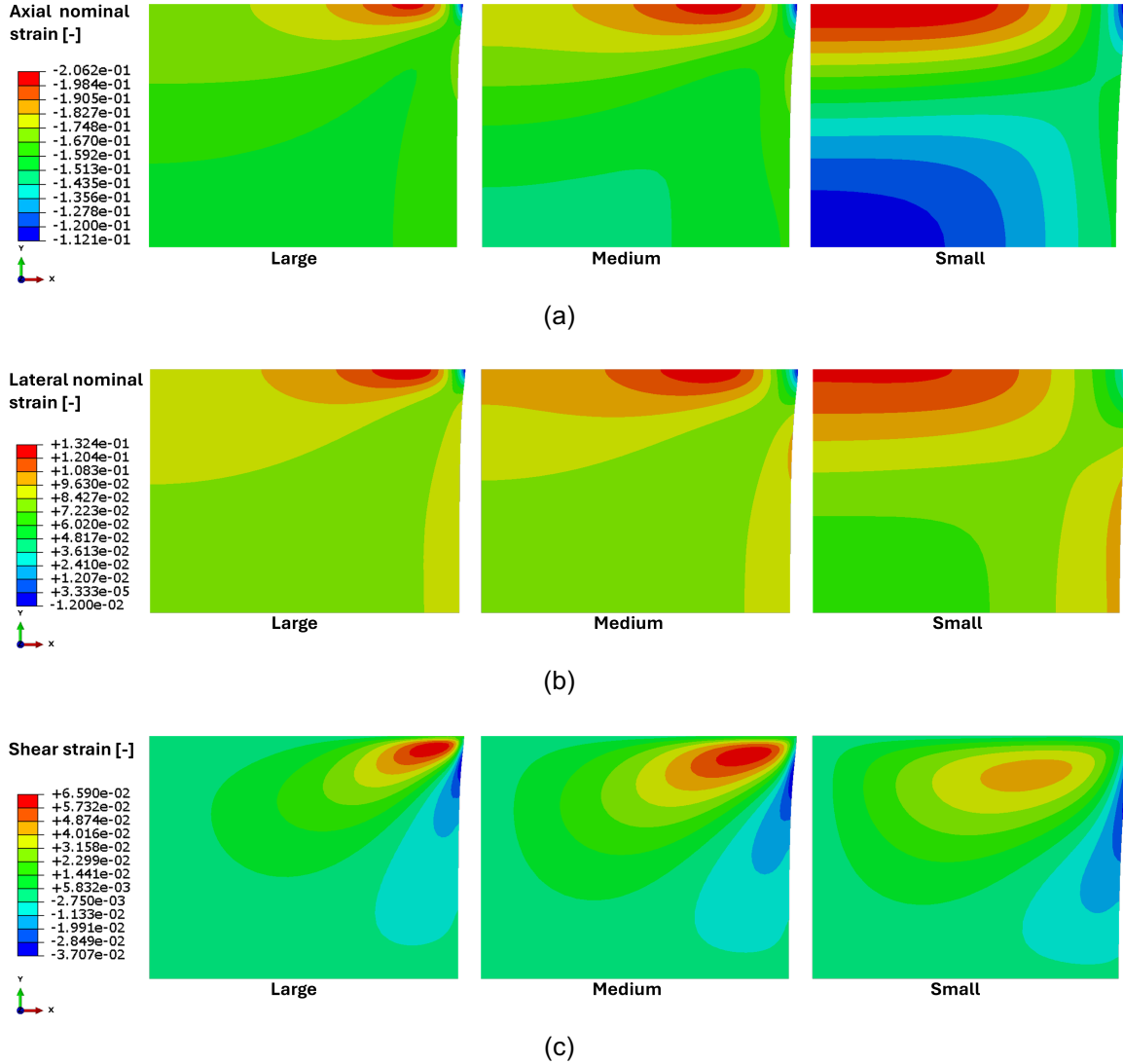


Figure 4.16. The contour of strain for simulation of compression after diffusion and reaction on the starch hydrogel at a time of 2 hours. (a) Axial strain. (b) Lateral strain. (c) Shear strain.

Meanwhile, both the Mises stress (Figure 4.17(a)) and pressure (Figure 4.17(b)) contours are more uniform for the smaller sample than the larger sample, again due to a more uniform hydrolysis level for the smaller sample. The maximum Mises stress is located below the top surface but away from the centre, as shown by the red region in Figure 4.17(a). This distribution arises from the competing effects of stress concentration caused by the stiffness gradient and the reduction of stiffness due to hydrolysis. In contrast, the maximum pressure Figure 4.17(b) is near the centre region at the top surface, as the volumetric strain is more significant there. The pattern of Mises stress

provides information about the internal stress distribution and potential failure points within the material.

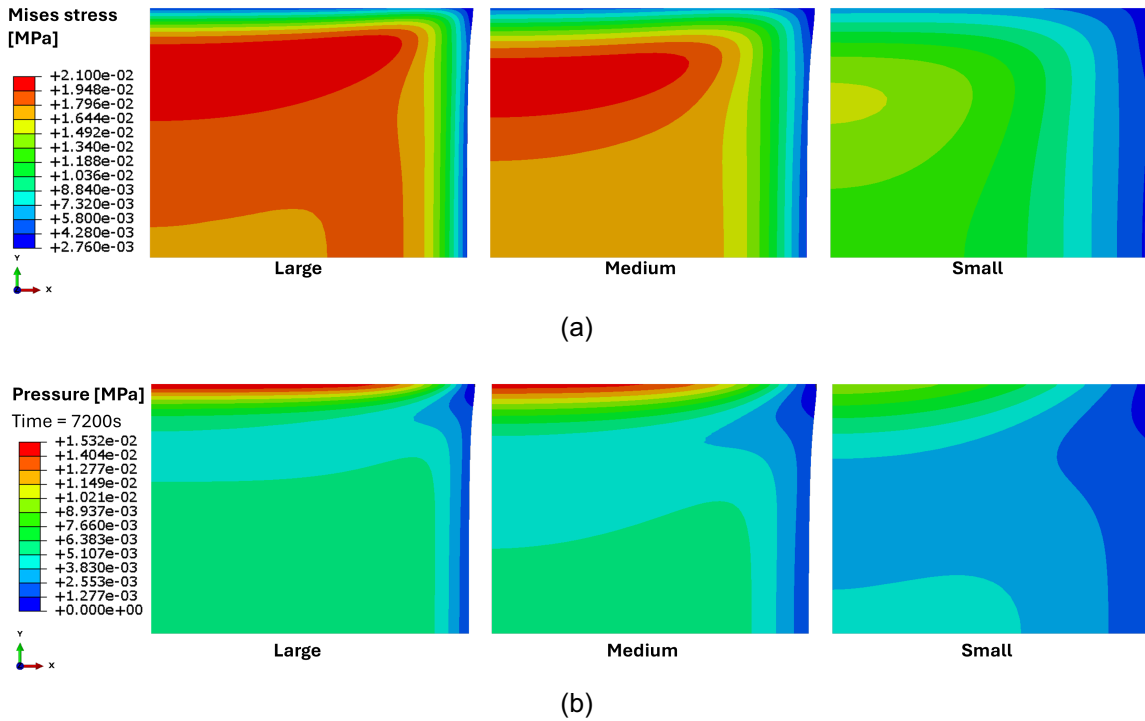


Figure 4.17. Stress contour during compression after diffusion and reaction for a hydrolysis time of 2 hours. (a) Mises stress. (b) Pressure.

4.4 Conclusions

Using the diffusivity and diffusion-reaction-deformation experimental data obtained from [Chapter 3](#), a chemomechanical pseudo-hyper-viscoelastic constitutive model is proposed to describe the mechanical behaviour of starch hydrogel under enzymatic hydrolysis. By introducing the substrate ratio, which represents the fraction of substrate remaining after hydrolysis, the model captures the evolution of material stiffness. As the substrate ratio decreases and polymer chains in the matrix break, the stiffness of the (pseudo-)equilibrium part scales down. In contrast, the viscoelastic contribution scales up because the number of dangling chains and solvated chain fraction increases, enhancing internal dissipation. The reaction kinetics of enzymatic hydrolysis were modelled using a modified Michaelis-Menten equation to account for the concentrations of both enzyme and substrate.

The constitutive model was implemented in Abaqus via the UMAT subroutine to simulate cyclic compression tests following enzymatic hydrolysis. Because diffusion plays an

important role in hydrolysis, a diffusion-reaction-deformation coupled simulation framework was established using the analogy between heat transfer and mass diffusion in Abaqus. An inverse optimisation process was performed to identify the reaction kinetics parameters by matching the simulation results with experimental data. The simulation captured the effect of sample size on hydrolysis level and mechanical properties. As the diffusion was not instantaneous, mechanical property degradation varied across the sample, leading to non-uniform stress and strain distributions during compression.

The model predicted the hydrolysis level of the starch hydrogel under different hydrolysis conditions. Using this model, simulations of *in vivo* digestion can be performed to predict the breakdown of the starch hydrogel in the human gastrointestinal tract. Furthermore, as starch hydrogel is used not only in food products but also in pharmaceutical applications as a drug delivery vehicle, understanding its breakdown behaviour during digestion helps design a drug delivery system with a tailored release profile.

Note that the current model has some limitations. For example, the second law of thermodynamics for the reaction, expressed in [Equation 4.59](#), is satisfied only by manually imposing parameter constraints in the energy function [Equation 4.55](#) during calibration. The imposed constraints are not physical and are not guaranteed to hold unconditionally, which could limit the generality and applicability of the model. This could be remedied by developing a micromechanical constitutive model that statistically accounts for the change in chain density due to hydrolysis, thereby satisfying thermodynamic principles. In addition, the mass loss and density change in the constitutive model are not yet accounted for, as we set $m = 1$, which is inconsistent with the idea that mechanical degradation due to hydrolysis depends on the mass loss fraction. Moreover, the reaction kinetics assume that the only product is maltose, whereas the actual starch hydrolysis, as shown in [Figure 1.9](#), is a more complex process. Therefore, a more realistic kinetic model for mechanical degradation will be considered. Furthermore, the damage-to-failure transition of the hydrogel during compression was not accounted for in the constitutive model, which may limit the simulation to a relatively small deformation range, whereas the hydrogel breaks down under large deformation during digestion. Future work can address these limitations to improve the model further.

Chapter 5

Gastric digestion of starch hydrogel

5.1 Introduction

In [Chapter 2](#) and [Chapter 3](#), we have investigated the mechanical and chemical properties of starch hydrogels experimentally, and then developed constitutive models in [Section 4.3](#) to describe their mechanical properties with various preparation conditions as well as their chemo-mechanical behaviour under hydrolysis. The material parameters were calibrated using experimental data. The calibrated chemo-mechanical constitutive model was implemented into the FEM software Abaqus to reproduce uniaxial compression experiments on starch hydrogel specimens after enzymatic degradation. The good agreement between the experimental data, the solution of the constitutive model in 1D form, and the numerical simulation results of the *in vitro* test validated the constitutive model implementation. In this chapter, we extend the simulations from uniaxial compression of homogeneous cylindrical hydrogel specimens to the more complex *in vivo* digestion process, which involves mechanical breakdown of the food bolus by peristaltic waves of the geometrically complex stomach wall, along with interactions with gastric fluid.

In [Section 1.4](#), we discussed approaches for studying human carbohydrate digestion, including *in vivo*, *in vitro*, and *in silico* methods, and we reviewed *in silico* models of the oral, gastric, and intestinal phases. As this chapter focuses on gastric digestion, we highlight the most relevant gastric *in silico* studies. Early computational studies primarily focused on the fluid gastric contents and their mixing and transport. Pal et al. ([2004](#)) developed a 2D lattice Boltzmann model to simulate motion, pressure and mixing of gastric fluids caused by peristaltic waves. The stomach geometry was obtained from MRI. It was

treated not as a deformable solid but as a prescribed moving boundary with no-slip conditions, constraining the fluid velocity at the wall to match the prescribed wall motion. Ferrua and Singh (2010) extended the study of Pal et al. (2004) into 3D using ANSYS. The gastric contents were modelled as incompressible Newtonian fluids with varying viscosities. The stomach geometry was generated from a 2D anatomical profile by stacking cross-sectional circles along the lesser and greater curvatures to create a three-dimensional shape. Radial displacements of the wall along the centreline were imposed to represent peristaltic waves, based on physiological data according to Pal et al. (2004). The wall is also treated as a moving boundary, so no fluid-solid interaction is involved. Harrison et al. (2018) developed an SPH model of gastric mixing and emptying of fluid contents. While the stomach geometry was reconstructed from MRI data following Ferrua and Singh (2010), the surface nodes of the wall mesh were converted into boundary SPH particles, repositioned at each time step according to wall deformation, and interacted directly with the gastric fluid SPH particles. Skamniotis et al. (2020) developed a Coupled Eulerian-Lagrangian (CEL) Finite Element (FE) model in Abaqus to investigate the deformation and fracture behaviour of a biscuit bolus. The bolus was represented as a soft solid, with mechanical behaviour captured by a viscoplastic damage model calibrated through uniaxial compression, shear rheometry, cylindrical cutting, and wire-cutting tests. The stomach geometry was simplified from the J-shaped configuration described by Ferrua and Singh (2010) to an axisymmetric wedge shape. Although the stomach wall was modelled as a hyperelastic deformable Lagrangian structure, motility was still imposed by prescribing peristaltic wall displacements against the straight centreline. The interaction between the Lagrangian wall and Eulerian contents was handled using the immersed boundary method within the CEL framework. Kuhar et al. (2022) constructed a three-dimensional CFD model via ViCar3D using the immersed boundary method on an anatomically realistic stomach reconstructed from medical imaging data. The gastric contents were modelled as a Newtonian fluid containing protein, with enzymatic hydrolysis represented by coupled diffusion-convection-reaction equations for pepsin. The stomach wall was treated as a no-slip immersed boundary, and peristaltic waves were imposed as radial contractions along the centreline. The fundic and pyloric boundaries switched between zero velocity and zero pressure gradient to control inflow and outflow, while mass-flux boundaries were used to simulate gastric secretion. Li and Jin (2021) developed a CFD model in OpenFOAM using the finite volume method and reconstructed the stomach geometry following Ferrua and Singh (2010). Gastric contents were treated as incompressible Newtonian mixtures. To account for wrinkles in the stomach wall, an outer layer adjacent

to the wall was modelled as a porous medium using Darcy's law. At the same time, gastric juice secretion was imposed as a mass source in an inner layer governed by diffusion-convection-reaction. Gastric motility was represented by prescribed antral waves, terminal antral collapse, and tonic contraction, with a PID controller regulating stomach mass. Ghosh et al. (2025) applied the SPH method to simulate deformation and mechanical breakdown of solid beads within a fluid medium by a realistic stomach geometry. Solid beads were modelled with elastic-plastic and elastic-brittle constitutive laws and interacted with the fluid digesta and prescribed antral contraction waves, including terminal antral contractions, providing one of the first *in silico* demonstrations of coupled fluid-structure-fracture behaviour in gastric digestion. Their results consistently demonstrated the role of bolus kinematics driven by peristaltic waves in gastric digestion. Low-viscosity meals were shown to generate retropulsion jets and eddies that enhanced mixing, whereas high-viscosity meals suppressed these flow structures and relied more on pressure-driven transport (Ferrua & Singh, 2010; Kuhar et al., 2022; Pal et al., 2004). Retropulsion and indentation were found to promote bolus fragmentation, while hydrostatic pressure near the pylorus facilitated agglomeration, together shaping the surface-to-volume ratio and thereby governing the rates of emptying and hydrolysis (Skamniotis et al., 2020).

Apart from prescribing wall motion, several studies have attempted to model stomach contraction physiologically. Brandstaeter et al. (2018) developed a FE electromechanical model of the gastric wall, in which electrical activity in interstitial cells of Cajal (ICC) generated active strains in an anisotropic hyperelastic tissue model that incorporated the fibre orientations of the circumferential and longitudinal muscle layers. In this way, physiologically realistic peristaltic contractions were driven by electrical signals rather than imposed as boundary conditions. Building on this work, Klemm et al. (2020) incorporated calcium dynamics to drive active-stress generation, extending the framework into an electro-chemo-mechanical constitutive model of the stomach. Acharya et al. (2022) further introduced a multi-physics FE model of active gastric peristalsis and bolus emptying based on the IBAMR open-source code. Gastric contents were treated as Newtonian fluids with varying density and viscosity, and the fully coupled fluid-solid interaction between the solid gastric wall and the fluid gastric contents was handled using the immersed boundary method. This model successfully reproduced retropulsive jets, bolus mixing, and gravity-driven emptying, while also highlighting limitations, including idealised geometry, the omission of oblique muscle fibres, and simplified fluid rheology. More comprehensive reviews of stomach digestion modelling were provided by Brandstaeter et al. (2019), Palmada et al. (2023), and Liu et al. (2024).

These *in silico* studies have contributed significantly to the mechanism of gastric digestion, yet several limitations remain. Most models considered gastric contents as incompressible Newtonian fluids, which cannot capture the mechanical behaviour of solid food, except for the study of Ghosh et al. (2025) and Skamniotis et al. (2020). Electromechanical models of the gastric wall can reproduce peristaltic contractions, but typically neglect interactions with gastric contents, apart from the study of Acharya et al. (2022), and are computationally demanding. In addition, many of them construct stomach geometries from simplified two-dimensional profiles that do not reflect the anatomical complexity of the organ, except in the study by Kuhar et al. (2022).

Alongside *in silico* modelling, *in vitro* experiments provide an alternative to *in vivo* studies and serve as complementary approaches to *in silico* modelling, allowing mutual validation between the two methods. Guerra et al. (2012) reviewed the development of gastric and small intestinal *in vitro* models. These range from static mono-compartmental systems, which apply fixed pH, enzyme, and temperature conditions for simple digestion studies, to dynamic mono-compartmental setups that incorporate time-dependent processes, and to more sophisticated bi- and multi-compartmental simulators such as the TIM system (Minekus et al., 1995), which simulate sequential digestive phases with controlled motility, secretion, and absorption. These approaches successfully reproduced biochemical environments and aspects of transit dynamics, but did not capture the anatomical structure of the stomach and realistic peristaltic waves. To address this gap, more recent simulators have introduced anatomy-inspired and motility-driven designs. Kong and Singh (2010) developed the Human Gastric Simulator (HGS), an *in vitro* stomach model driven by rollers, belts, pulleys, and a motor. The system was capable of reproducing continuous peristaltic contractions, gastric secretion, and gastric emptying, enabling more physiologically relevant mechanical breakdown and physicochemical transformations of solid foods during gastric digestion. Bellmann et al. (2016) developed the TIMagc system with flexible silicone rubber compartments representing the gastric body, antrum, and pyloric sphincter, where contractions were generated by pressure applied through surrounding water jackets. Dang et al. (2021) proposed the SoGut system, composed of four anatomically inspired segments with circular pneumatic chambers that were pneumatically actuated in sequence to generate tunable radial contractions. Hashem et al. (2023) further advanced the SoGut design into the SoRSS system, a fully anatomical silicone stomach actuated by 95 bellow-driven soft pneumatic actuators, enabling continuous peristaltic waves with physiologically accurate occlusion ratios and pressure profiles. In this chapter, the dynamic gastric simulator developed by Bellmann et al. (2016) is employed, owing to its availability

through our collaborators, for comparison with the proposed *in silico* digestion model.

The objective of this chapter is to establish an *in silico* framework for studying gastric digestion and gastric emptying in a three-dimensional stomach geometry, addressing the gap in most existing models, which treat gastric contents as simple Newtonian fluids and fail to capture the behaviour of solid hydrogels. To balance physiological authenticity and computational efficiency, the electromechanical behaviour of the gastric wall is not considered here. Instead, peristaltic waves are prescribed as boundary conditions in a generalised form. Parallel *in vitro* experiments using a dynamic stomach simulator are conducted to validate the proposed model. With both methods, we overcome the ethical and practical limitations of *in vivo* studies.

This chapter is structured as follows. First, we introduce the fluid-solid interaction methods, namely the Coupled Eulerian-Lagrangian (CEL) approach and the immersed boundary method. Next, we describe the FE *in silico* digestion model, including a simplified stomach geometry as well as the implementation of peristaltic waves along a straight line. Then, we simulate the anatomically realistic stomach geometries and the peristaltic waves along a curved path. For comparison, the simulations are followed by dynamic *in vitro* digestion experiments using a stomach simulator. Finally, we conclude with a summary of the main findings and an outlook on future work. The Abaqus subroutines for this chapter are provided in [Section A.1](#).

5.2 Coupled Eulerian-Lagrangian finite element method for fluid-solid interaction simulation

In gastric digestion, the stomach wall undergoes hyperelastic deformation without damage, whereas the starch hydrogel undergoes substantial deformation and eventually breaks down. In addition, gastric fluid fills the stomach lumen, further complicating fluid-solid interactions. To capture these effects, the Coupled Eulerian-Lagrangian (CEL) method is adopted, in which the stomach wall is modelled as a Lagrangian region, and the starch hydrogel and gastric fluid are represented as Eulerian regions. The advantage is that even though fluid is modelled in the Eulerian region, both regions are modelled using the explicit FE method.

In general, the Eulerian FE formulation follows a two-step procedure. First, a Lagrangian calculation is performed, during which the mesh deforms with the material. The solution is then remapped onto the original undeformed mesh, as illustrated in [Figure 5.1](#).

Specifically, following Benson (1992), Benson and Okazawa (2004), and Zhang et al. (2018), in the Lagrangian description, the governing equations track the condition of a material point as it moves through space and time. In contrast, in the Eulerian description, the equations describe the condition at a fixed spatial point that different materials may occupy over time. Accordingly, the time derivative of a material point, denoted by $\frac{D}{Dt}$, is used in the Lagrangian description, while the partial derivative, denoted by $\frac{\partial}{\partial t}$, is used in the Eulerian description. Their relationship is expressed in continuum mechanics as:

$$\frac{D(\bullet)}{Dt} = \frac{\partial(\bullet)}{\partial t} + \mathbf{v} \cdot (\nabla \bullet), \quad (5.1)$$

where $\mathbf{v}$ is the material velocity and ∇ is the gradient operator. Here, $\bullet$ represents any field variable. The Lagrangian description is therefore suitable for modelling materials that deform with the mesh, whereas the Eulerian description is more appropriate for materials whose deformation is better represented without mesh distortion.

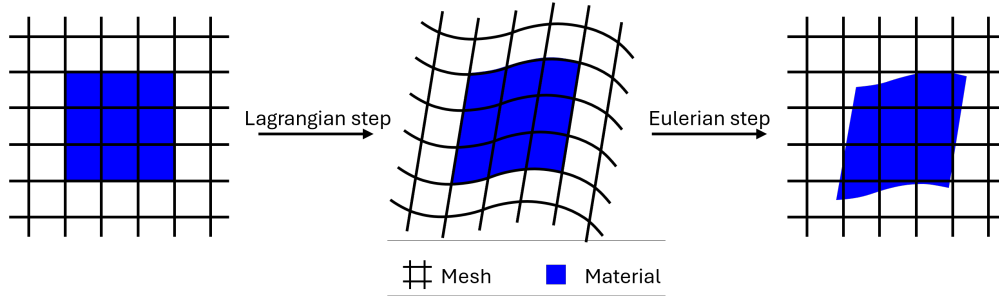


Figure 5.1. Two-step algorithm of the Eulerian FE formulation.

The conservation equations of mass, momentum, and energy in the Lagrangian description can be written as:

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0, \quad (5.2)$$

$$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{b}, \quad (5.3)$$

$$\frac{De}{Dt} = \boldsymbol{\sigma} : \mathbf{d}, \quad (5.4)$$

respectively, where ρ is the density, $\mathbf{v}$ is the velocity, $\boldsymbol{\sigma}$ is the Cauchy stress tensor, $\mathbf{b}$ is the body force per unit mass, e is the internal energy density, and $\mathbf{d}$ is the deformation rate tensor (defined in Equation 4.134). By applying Equation 5.1 to Equation 5.2 - Equation 5.4, the conservation equations of mass, momentum, and energy in the

Eulerian description can be expressed as:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (5.5)$$

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{b}, \quad (5.6)$$

$$\frac{\partial e}{\partial t} + \nabla \cdot (e \mathbf{v}) = \boldsymbol{\sigma} : \mathbf{d}, \quad (5.7)$$

where $\otimes$ denotes the tensor product. The Eulerian form of the conservation equations can be written in the general form as:

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \Phi(\phi, \mathbf{v}) = \mathbf{S}, \quad (5.8)$$

where ϕ is a generic scalar or vector field variable (e.g., density, momentum, or energy), Φ the corresponding flux, and $\mathbf{S}$ the local source terms. Following Benson (1992), Equation 5.8 can be updated in time using an operator split. Over each time step, the equation is decomposed into two subproblems:

$$\begin{cases} \frac{\partial \phi}{\partial t} = \mathbf{S}, & (5.9a) \\ \frac{\partial \phi}{\partial t} + \nabla \cdot \Phi = 0. & (5.9b) \end{cases}$$

The two subproblems are solved sequentially. Equation 5.9a is solved first, which accounts for local physics such as constitutive updates, body forces, stress work, and heat sources. This is called the Lagrangian step because the computational grid is conceptually moved with the material, eliminating relative advection. As a result, the advection terms in Equation 5.8 vanish, yielding Equation 5.9a. Using the result of the Lagrangian step as initial data, we then solve Equation 5.9b, known as the Eulerian step, which performs conservative transport/remap on a fixed grid by evaluating the flux divergence. In this phase, the meshes are stationary, and material flows through the elements. Using the result of the Lagrangian step as the initial state, Equation 5.9b is then solved on a remapped fixed grid, which is known as the Eulerian step. In this phase, the mesh remains stationary while material flows through elements. With sufficiently small time steps, subject to stability constraints, the operator split yields a solution that converges to that of the original equation Equation 5.8. It should be noted that this operator splitting into Lagrangian and Eulerian steps is a numerical strategy applied only in Eulerian analysis.

As materials flow in the Eulerian region, tracking the Eulerian boundary becomes essential when considering contact either between different Eulerian materials or between Eulerian materials and Lagrangian structures. This is achieved by computing the material volume fraction in each element, referred to as the Eulerian Volume Fraction (EVF). The interface is then approximately reconstructed from the EVF data, represented as planar facets according to the algorithm implemented in Abaqus. Consequently, a finer mesh resolution is required to achieve more accurate interface reconstruction. The interaction between the Eulerian and Lagrangian regions is handled by the immersed boundary method Benson and Okazawa (2004) and Simulia, Dassault Systemes (2012). In this approach, the Lagrangian region occupies void elements (i.e., elements without material) within the Eulerian mesh. When materials flow into these void elements, contact is detected, and the algorithm applies a penalty method to push the Eulerian material out of the Lagrangian region, thereby preventing two materials from occupying the same space simultaneously. In practice, the penalty method allows a small amount of penetration, which is corrected by restoring forces, and the contact state is updated at each time increment to capture the dynamic interaction between Eulerian materials and Lagrangian structures. It is worth noting that Abaqus provides an enhanced contact algorithm to improve the accuracy of contact detection and response, particularly in cases involving large deformations or complex geometries, where fluid leakage may otherwise occur through the Lagrangian structure. This improvement is achieved by applying adaptive mesh refinement to the Lagrangian step of the Eulerian analysis, enabling local mesh refinement in regions of contact to capture interface behaviour better. The feature is activated by including the `*ADAPTIVE MESH REFINEMENT` keyword in the `.inp` file (input file).

5.3 Explicit finite element analysis and constitutive model VUMAT implementation

As mentioned earlier, the CEL method in Abaqus is applicable for explicit analyses. Unlike implicit analyses, which use the Newmark method and require solving coupled nonlinear equations iteratively, explicit analyses employ the central difference method, advancing the solution directly without iteration. Therefore, the explicit method does not suffer from convergence issues. However, the stability explicit analysis is conditionally guaranteed,

and to obtain valid results, the following stability conditions must be satisfied:

$$\Delta t < \frac{l_c}{c} = l_c \left(\sqrt{\frac{E}{\rho}} \right)^{-1}, \quad (5.10)$$

$$\Delta t < l_c^2 \frac{\rho c_{\text{eff}}}{2k_{\text{eff}}}, \quad (5.11)$$

where l_c is the characteristic length (the smallest element dimension in the mesh), c is the speed of sound in the material, E is the material's tangential modulus, ρ is the material's density, c_{eff} is the effective specific heat capacity, and k_{eff} is the effective thermal conductivity. Equation 5.10 is the stability condition for purely mechanical problems, while Equation 5.11 is the additional stability condition for analysis involving heat conduction. Note that as we did not consider thermal conduction or mass diffusion in this chapter, only Equation 5.10 is relevant here. According to Equation 5.10, time steps are often necessary for refined meshes or materials with high stiffness. In our future work, if diffusion is included, using the analogy between heat transfer and diffusion, Equation 5.11 is applicable, where k_{eff} is replaced by the effective diffusivity.

Since the explicit solver does not require an iterative solution, the stress can be updated directly without the tangent stiffness tensors discussed in Section 4.3.1.2. Consequently, the user only needs to return the Cauchy stress and the state variables to the solver. Several differences between VUMAT and UMAT in naming conventions should be noted. In VUMAT, the variables `stressOld` and `stateOld` represent the Cauchy stress and state variables at the beginning of the increment, provided by the program. The variables `stressNew` and `stateNew` correspond to the Cauchy stress and state variables at the end of the increment and must be returned to the solver. Another important difference is the ordering of tensor components in vector notation. In VUMAT, the stress components are ordered as

$$\{\boldsymbol{\sigma}\} = \{\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}, \sigma_{23}, \sigma_{13}\}^T, \quad (5.12)$$

for three-dimensional problems, where the last two shear components differ from UMAT. For two-dimensional problems, the ordering remains

$$\{\boldsymbol{\sigma}\} = \{\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}\}^T, \quad (5.13)$$

which is consistent with UMAT. In addition, if the strain tensor is used as input, VUMAT provides the tensorial strain components ε_{ij} for $i \neq j$, whereas UMAT provides the engineering shear strains $\gamma_{ij} = 2\varepsilon_{ij}$ for $i \neq j$. Unlike UMAT, which is called once per

material point, VUMAT is called for a block of material points at a time. Therefore, explicit loops over the number of material points in the block, given by `nblock`, must be implemented inside the VUMAT routine.

5.4 Finite element simulation for gastric digestion in a simplified stomach geometry

In this section, the gastric digestion process is modelled using a simplified stomach geometry. The focus is on the mathematical description of stomach geometry and the peristaltic waves acting on the stomach wall.

5.4.1 Initial geometry of the simplified stomach and its mathematical description

A simplified stomach geometry at $t = 0$ (initial stage) is adopted to reduce model complexity and computational cost, providing initial validation of the approach. The geometry follows the model proposed by Skamniotis et al. (2020), reconstructed from a bisected stomach profile as described by Ferrua and Singh (2010). In their study, a wedge-shaped axisymmetric model of the stomach wall was used. Here, to further simplify the model and reduce computational cost, we adopt a plane-strain model as a preliminary approach. As shown in Figure 5.2, the stomach is simplified to a geometry generated by revolution around a straight centreline (x -axis), ranging from $x = 0$ to $x = x_l = 265$ mm. For further simplification, the region inside the dashed-line box (from $x = x_1 = 210$ mm to $x = x_l = 265$ mm, highlighted by the yellow curve) is considered. Note that even though the geometry is axisymmetric, the CEL method is only applicable for three-dimensional modelling. Therefore, instead of using an axisymmetric or plane strain model, a pseudo-plane strain model is adopted, as shown in Figure 5.3, where the thickness of the model is reduced to one element along the z -axis. The model is meshed with C3D8R elements in 3D space, but only one element is used along the z -axis, with plane strain boundary conditions applied on the two surfaces at $z = 0$ and $z = 1$ mm. In this way, the x -axis represents the stomach centreline, with the x -coordinate of each element assigned accordingly to its location along the centreline, while the y -coordinate denotes the distance of each element from the centreline.

The initial shape of the stomach wall needs to be described mathematically before applying the peristaltic wave. The original distance from the centreline is denoted as $y_0 = y(t =$

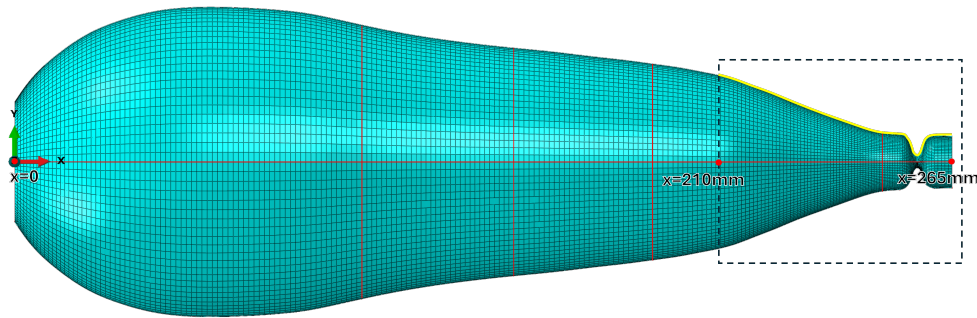
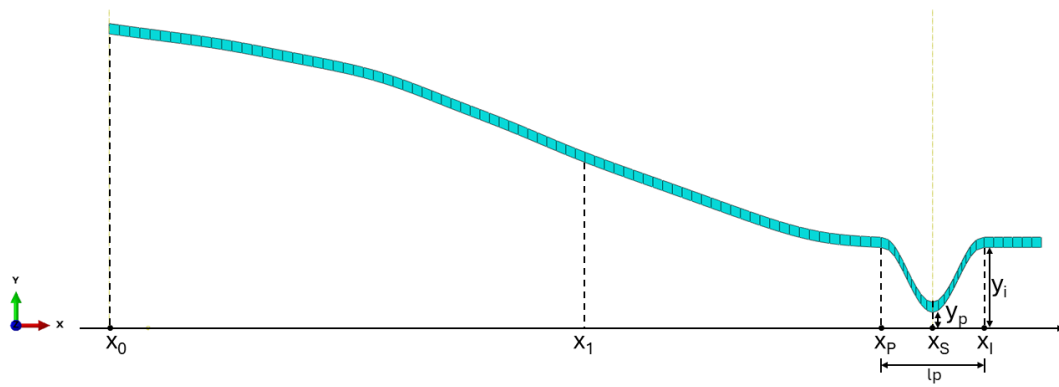
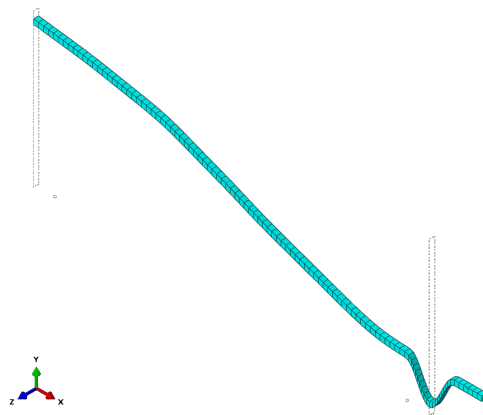


Figure 5.2. Straightened stomach geometry at $t = 0$ modified from a bisected stomach profile.



(a)



(b)

Figure 5.3. Simplified pseudo-plane strain geometry of the stomach wall at time $t = 0$: (a) front view, (b) isometric view, showing a pseudo-plane strain model with thickness.

0), corresponding to the initial y -coordinate of each element in the pseudo-plane strain model. A straightforward way to obtain y_0 is to approximate the stomach wall profile as a polynomial function of the centreline coordinate x :

$$y_0(x) = k_{y1}x^5 + k_{y2}x^4 + k_{y3}x^3 + k_{y4}x^2 + k_{y5}x + k_{y6}, \quad x_0 < x < x_p, \quad (5.14)$$

where the dimensionless coefficients k_{yi} are determined by curve fitting to the stomach wall contour and are listed in Table 5.1, $x = x_0 = 210$ mm denotes the left boundary of the region of interest, and $x = x_p = 255$ mm is the centreline coordinate at the left end of the pylorus in this study.

Table 5.1. Polynomial coefficients used to describe the stomach wall profile according to Skamniotis et al. (2020).

	k_{y1} [mm ⁻⁴]	k_{y2} [mm ⁻³]	k_{y3} [mm ⁻²]	k_{y4} [mm ⁻¹]	k_{y5} [-]	k_{y6} [mm]
$x_0 < x < x_1$	5.12e-10	-4.83e-7	1.56e-4	-2.18e-2	1.16	2.89e+1
$x_1 < x < x_p$	0	3.23e-5	-3.10e-2	1.11e+1	-1.78e+3	1.07e+5

The pylorus is assumed to open and close dynamically. The pylorus extends from x_p to $x_i = x_p + l_p$, with its midpoint at $x_s = \frac{1}{2}(x_p + x_i)$. The slope at these three points is set to zero to ensure a smooth transition. To describe the pyloric shape under these conditions, a Lagrangian interpolation basis function is employed:

$$y_0 = y_i - (y_i - y_p) \cdot l_x^{n_1}(x), \quad x_p < x < x_i, \quad (5.15)$$

$$l_x^{n_1}(x) = \left(\frac{(x - x_p)(x_i - x)}{(\frac{1}{2}l_p)^2} \right)^{n_1}. \quad (5.16)$$

where at the start ($x = x_p = 255$ mm) and end ($x = x_i = 265$ mm) of the pylorus, the exponential term becomes zero and thus $y_0 = y_i$, while at the midpoint $x = x_s = 260$ mm, it becomes one and thus $y_0 = y_p$. The first derivative of $l_x^{n_1}(x)$ with respect to x is

$$\frac{dl_x^{n_1}}{dx} = 8l_x^{n_1-1} \frac{x_s - x}{l_p}, \quad (5.17)$$

which turns to zero at x_p , x_s , and x_i , ensuring smooth transitions at these locations. The parameter $n_1 = 2.5$ controls the sharpness of the function near the symmetric point, while $l_p = 10$ mm denotes the pyloric length.

5.4.2 Peristaltic wave in the pseudo-plane strain model

The peristaltic wave is applied to the stomach wall elements as a function of the centreline coordinate x , the distance from the centreline y , and time t . Following the approach of Drechsler and Ferrua (2016) and Kuhar et al. (2022), and based on Skamniotis et al. (2020), the displacement is assumed proportional to the initial distance from the centreline y_0 . Therefore, it is defined as

$$\Delta y = \Delta y(x, y_0, t) = \lambda(x, t)y_0, \quad (5.18)$$

where Δy is the displacement of the element in the y -direction, x the centreline coordinate, y_0 the original distance from the centreline, t time, and $\lambda(x, t)$ the contraction ratio. The stomach wall motility is represented by the summation of two components: the propagating peristaltic waves and the opening-closing motion of the pylorus.

The peristaltic wave is represented as a sequence of individual wavelets propagating along the stomach centreline. Therefore, the contraction ratio λ is decomposed multiplicatively into a spatially varying amplitude $\lambda_{\max}(x)$ and a spatial-temporal propagation function $h(x, t) \in [0, 1]$:

$$\lambda(x, t) = \lambda_{\max}(x) \cdot h(x, t). \quad (5.19)$$

The contraction ratio amplitude $\lambda_{\max}(x)$ is assumed to increase linearly from x_0 to $x_2 = 257.5$ mm, a location near the pylorus, and then decrease linearly to zero at the pyloric centre x_s , and is expressed as

$$\lambda_{\max}(x) = \begin{cases} \lambda_0 + (\lambda_1 - \lambda_0) \frac{x-x_0}{x_2-x_0}, & x_0 < x < x_2 \\ \lambda_1 + (\lambda_2 - \lambda_1) \frac{x-x_2}{x_s-x_2}, & x_2 < x < x_s \\ 0, & x > x_s \end{cases} \quad (5.20)$$

where the parameters were chosen to produce sufficiently large contractions, as listed in Table 5.2 and illustrated in Figure 5.4, which does show a wave propagation along the x -axis with time.

Table 5.2. Parameters of the contraction ratio amplitude $\lambda_{\max}(x)$.

λ_0 [-]	λ_1 [-]	λ_2 [-]
0.4	0.9	0.0

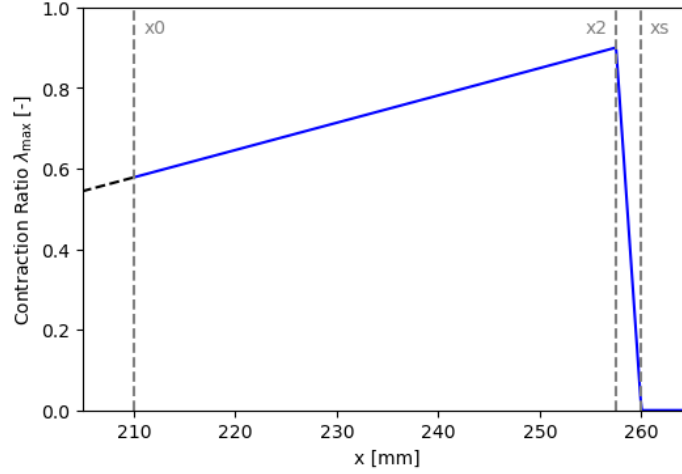


Figure 5.4. Contraction ratio amplitude $\lambda_{\max}(x)$ along the stomach centreline. The curve beyond x_0 is plotted in a black dotted line, whereas the curve of interest after x_0 is plotted in a blue solid line.

The propagation function $h(x, t) \in [0, 1]$ defines the spatio-temporal evolution of the wavelets. Each wavelet is described by an interpolation basis function, with the wave back (the left end of a wavelet) $x = x_b$, propagating from x_0 to x_s . Defining the wave back as the origin of a local coordinate system along the x -axis, the local coordinate of a point on the wave is

$$\xi(t) = x - x_b(t). \quad (5.21)$$

The wavelet shape is given by

$$h(\xi) = \begin{cases} \left(\frac{\xi(l_w - \xi)}{(\frac{1}{2}l_w)^2} \right)^{n_2}, & 0 < \xi < l_w \\ 0, & \text{otherwise} \end{cases} \quad (5.22)$$

where l_w is the wavelet length and $n_2 = 5$ is a positive integer controlling the sharpness of the wavelet. Similar to Equation 5.16, both the values and the derivatives of Equation 5.22 at $\xi = 0$ and $\xi = l_w$ vanish, while the value peaks at $\xi = \frac{1}{2}l_w$ and the derivative also vanishes. Here, the wavelet length is further assumed to decrease linearly with the global coordinate x :

$$l_w = l_{w0} + (l_{wf} - l_{w0}) \frac{x - x_0}{x_s - x_0}, \quad (5.23)$$

where $l_{w0} = 30$ mm is the initial length at $x = x_0$ and $l_{wf} = 10$ mm is the final length at the right end of the stomach. Each wavelet is assumed to travel at a constant speed $c_w = 25$

mm/s, with constant spacing between consecutive wavelets:

$$x_b(t) = x_0 + c_w \cdot t_{\text{step}} - d_k \quad (5.24)$$

where c_w is the wave speed, t_{step} is the time interval between wavelets and d_k is the offset between the first and the k^{th} wavelet. Here $d_k = (2k + 1)l_{w0}$ is adopted. The evolution of $h(x - x_b(t))$ is illustrated in Figure 5.5. The wave back $x_b(t)$ propagates from left to right at speed c_w , while the wavelet length l_w decreases along the global coordinate, leading to slightly asymmetric wavelets. As shown in Figure 5.5(c), $\xi = 0$ corresponds to the wave back, $\xi = l_w$ to the wave front, and $\xi = \frac{1}{2}l_w$ to the wavelet peak. It can also be seen in Figure 5.5(e) that the second wavelet has an offset of d_1 to the first wavelet.

Combining Equation 5.18 to Equation 5.24, the contraction displacement Δy is expressed as

$$\Delta y_c(x, y_0, t) = \begin{cases} \lambda_{\max}(x) \cdot h(x - x_b(t)) \cdot y_0, & x_0 < x_b + l_w \text{ and } x_b < x_s. \\ 0, & \text{otherwise} \end{cases} \quad (5.25)$$

Here, the conditions mean that only wavelets within the specified range are considered in the calculation. It should be noted that the wave pattern is defined in an idealised form, since the primary aim here is to demonstrate the simulation methodology. A more realistic wave pattern could be constructed from medical data to improve model fidelity in future investigations of gastric digestion.

5.4.3 Antrum contraction in the pseudo-plane strain model

The pylorus is controlled to open and close by changing the original distance from the centreline y_0 of the elements in the pyloric region. The additional displacement is defined as

$$\Delta y_p = \lambda_p(t) y_0 \left(\frac{x(l_p - x)}{(\frac{1}{2}l_p)^2} \right)^{n_p}, \quad x_p < x < x_i \quad (5.26)$$

where $\lambda_p(t)$ is the time-dependent contraction ratio of the pylorus, controlling the opening and closing motion, and $n_p = 10$ is the exponent controlling spatial sharpness of pyloric contraction. Equation 5.26 ensures that the contraction is zero at the pyloric entrance x_p and exit x_i , and gradually increases from both ends towards the midpoint x_s . The temporal

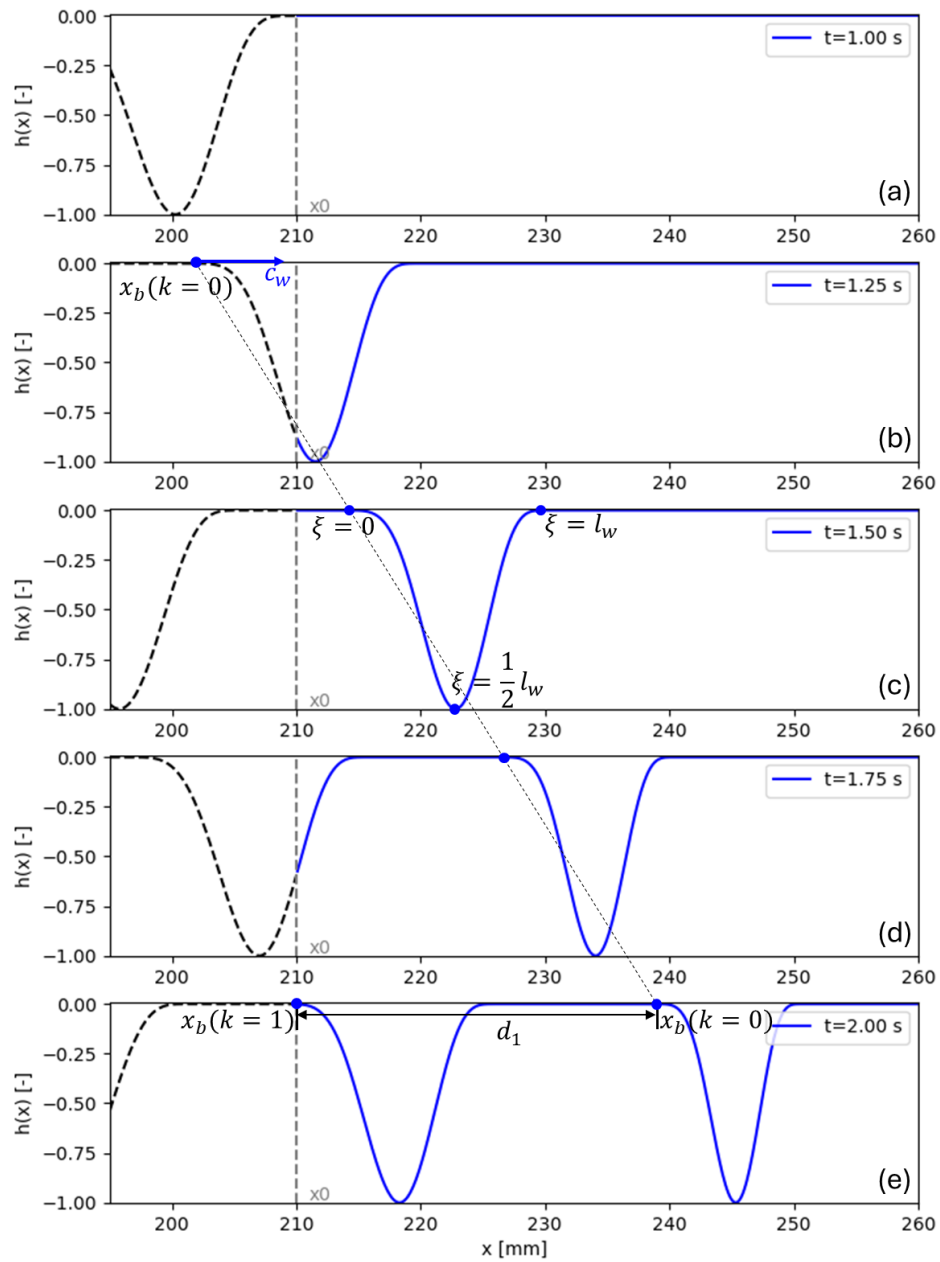


Figure 5.5. Temporal evolution of the wave propagation function $h(\xi(t))$. (a) $t = 0$ s, (b) $t = 0.5$ s, (c) $t = 1$ s, (d) $t = 1.5$ s, (e) $t = 2$ s. The curve beyond x_0 is plotted in a black dotted line (not modelled), whereas the curve of interest after x_0 is plotted in a blue solid line.

variation of $\lambda_p(t)$ is defined as

$$\lambda_p(t) = \begin{cases} \frac{t}{t_p}, & t_0 < t < t_p \\ 0, & t \geq t_p \end{cases} \quad (5.27)$$

to simulate the linear closure of the pylorus. Here, $t_0 = 0$ s is the initial time of pylorus contraction, and $t_p = 0.1$ s represents the time taken for the pylorus to close fully, and it is also an arbitrary parameter for the simulation.

The total contraction displacement Δy of the elements in the pyloric region is given by the superposition of the peristaltic wave contribution and the pyloric contraction, i.e.

$$\Delta y = \Delta y_c + \Delta y_p. \quad (5.28)$$

The peristaltic wave and pyloric contraction are implemented in Abaqus using the user displacement subroutine for explicit solver (VDISP), which allows for user-defined displacement boundary conditions to be applied to the stomach wall elements. For the pseudo-plane strain model, the pylorus was set to close at $t = 0$ s to avoid the direct emptying of the stomach contents, owing to the limitation of the oversimplified geometry.

5.4.4 Description of the pseudo-plane strain gastric digestion model setup

The interaction between gastric fluid, starch hydrogel, and the stomach wall is modelled using the Coupled Eulerian-Lagrangian (CEL) method mentioned in [Section 5.2](#). As mentioned earlier, the entire model is constructed in a pseudo-plane strain configuration, where only one element is used along the z -axis, and plane strain boundary conditions are applied to the two surfaces at $z = 0$ and $z = 1$ mm (planes 1 and 2 in [Figure 5.7\(a\)](#)). The stomach wall is enclosed by the Eulerian region, while the gastric fluid and starch hydrogel are both represented as Eulerian materials, with their discrete fields generated from the reference geometry. Free outflow and no inflow boundary conditions are applied to planes 5 and 6, and a symmetry boundary condition is imposed on plane 3. Gravity is applied in the x -direction to the Eulerian region. Two simulation cases, with and without gastric fluid, are performed and compared, as shown in [Figure 5.7\(b\)](#).

The stomach wall was modelled as a Neo-Hookean hyperelastic material. Since it primarily served as a deformable solid boundary, the detailed stress-strain response was not critical to the simulation outcomes. Therefore, the material parameters, though not

physically representative, were selected to allow large deformations, with sufficiently high density and low modulus adopted to ensure numerical stability and computational efficiency. Here, the density was set as $\rho_w = 1.0 \times 10^{-5} \text{ ton/mm}^3$, the shear modulus $C_{10} = 5 \times 10^{-6} \text{ MPa}$, and the compressibility parameter $D_1 = 1 \times 10^{-1} \text{ MPa}^{-1}$. The stomach wall was discretised with a thickness of 1 mm and a mesh size of approximately 2 mm, resulting in 5,280 elements. Note that these parameters are not representative of real stomach tissue but were chosen to enable large deformations during the simulation. Currently, the realistic mechanical properties of the stomach wall lead to numerical instability and aborted simulations due to excessive element distortion. Future work could focus on improving the model stability to incorporate more accurate stomach wall properties.

The starch hydrogel was modelled as an elastic-plastic material using the properties of the crushed-reformed hydrogel, with an elastic Young's modulus of $E_s = 45 \text{ kPa}$ and a Poisson's ratio of $\nu_s = 0.49$. The evolution of yield stress followed an isotropic hardening rule extracted from experimental data from [Section 2.9](#), as shown in [Figure 5.6](#), and was input into Abaqus as a tabulated function. The hydrogel density was set as $\rho_s = 1.07 \times 10^{-9} \text{ ton/mm}^3$. The gastric fluid was modelled as an incompressible Newtonian fluid, either through an equation of state (EOS) or an idealised pseudo elastic-plastic formulation, where elastic deformation is set to be negligible, and the yield stress is sufficiently small. The idea behind this pseudo-elastic-plastic approach is to exploit the plastic flow behaviour to approximate the flow characteristics of water, acknowledging that water itself is not an elastic-plastic material. The fluid density was set to $\rho_l = 1.0 \times 10^{-9} \text{ ton/mm}^3$. For the EOS approach, Mie-Grüneisen (linear $U_s - U_p$) equations of state (Simulia, Dassault Systemes, [2012](#)) were adopted with parameters $c_0 = 1 \times 10^5$, $s = 0$, $\Gamma_0 = 0$, and a dynamic viscosity of $0.1 \text{ Pa}\cdot\text{s}$. For the elastic-plastic approach, the parameters were Young's modulus $1 \times 10^{-4} \text{ MPa}$, Poisson's ratio $\nu_l = 0.49999$ (nearly incompressible), and yield stress $1 \times 10^{-6} \text{ MPa}$. General contact was used with a friction coefficient of 0.1. In this case, contact between the fluid, the starch hydrogel, and the stomach wall, and their self-contact, were considered. The stomach wall was discretised with 4-node reduced integration shell elements (S4R), while the starch hydrogel and gastric fluid were discretised with 8-node linear Eulerian brick elements (EC3D8R) with hourglass control. Both the EOS and the pseudo elastic-plastic approaches produced comparable flow patterns. However, the elastic-plastic formulation required significantly less computational time. Therefore, this method was adopted in the subsequent simulations.

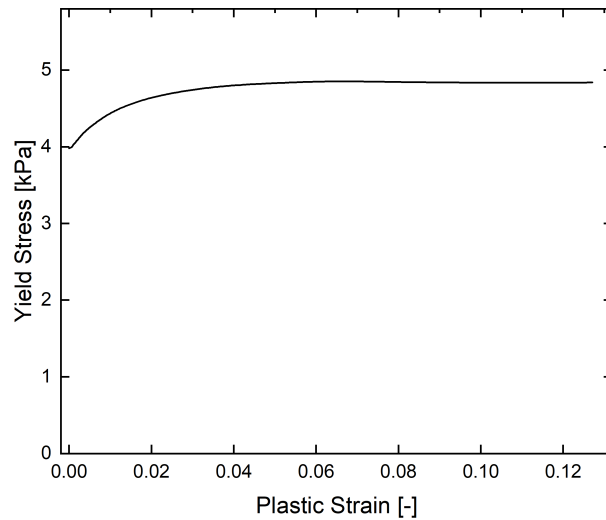


Figure 5.6. Yield stress of the starch hydrogel as a function of plastic strain, fitted to experimental data from [Section 2.9](#).

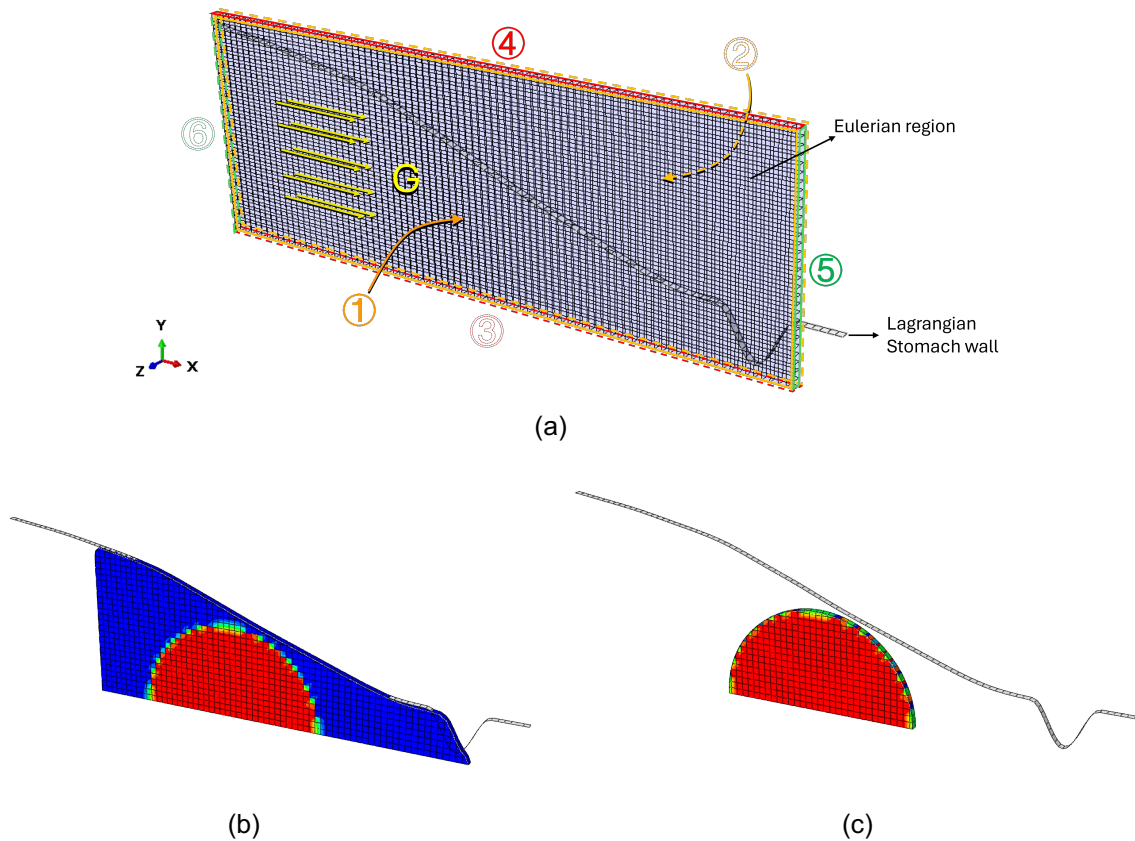


Figure 5.7. (a) Simplified stomach geometry constructed in CAE. (b) Model with gastric fluid, where the red region represents starch hydrogel and the blue region gastric fluid. (c) Model without gastric fluid.

5.4.5 Results for the pseudo-plane strain model

Figure 5.8 illustrates the breakdown of starch hydrogel boluses in the pseudo-plane strain model from $t = 0$ s to $t = 2.2$ s. The left column corresponds to the case without gastric fluid, while the right column shows the case with gastric fluid. In both cases, the pylorus was closed at $t_p = 0.1$ s (see Equation 5.27), in order to prevent immediate outflow of gastric contents under gravity along the x -direction, given the simplified geometry. The breakdown patterns of the hydrogel boluses differ between the two cases. Without gastric fluid, the bolus deforms into a long, thin shape under retropulsion. In contrast, with gastric fluid, which is more physiologically relevant, the bolus interacts strongly with the fluid, is broken down into multiple smaller, rounder fragments, and is pushed back rather than reaching the pyloric region. The fragmentation and mixing might increase the surface area of the hydrogel exposed to enzymatic action, potentially enhancing chemical degradation and disintegration of starch during enzymatic hydrolysis. It should be noted that between $t = 1.4$ s and $t = 1.8$ s, fluid leakage through the stomach wall was observed. This occurred under large deformations of the Lagrangian region, reflecting a limitation of the CEL method. Therefore, in the subsequent simulations (Section 5.5), the gastric fluid is not considered.

The average and maximum pressures within the stomach are shown in Figure 5.9(a) and Figure 5.9(b), respectively. Here, the average pressure is calculated by the weighted average of the pressure field over the Eulerian element of the bolus or fluid, i.e.,

$$\bar{p} = \frac{\sum_i p_i f_i}{\sum_i f_i}, \quad (5.29)$$

where p_i and f_i are the pressure and effective volume fraction of the material (either bolus or fluid) i^{th} Eulerian element, respectively. The maximum pressure is the peak value among all Eulerian elements. In the meantime, the maximum pressure is defined as

$$p_{\max} = \max(p_i H(f_i)) \quad (5.30)$$

where $H(f_i)$ is the Heaviside step function, which equals 1 when $f_i > 0$ and 0 when $f_i = 0$, ensuring that only elements containing the material of interest are considered. The pressure data were calculated by processing the .odb file using Python scripts. The average pressure reflects the overall field of each material, while the maximum pressure is a localised peak value near the interaction location of materials and the stomach wall.

Within the first peristaltic wave ($0 < t < 2$ s), the "with-fluid" case shows pressure peaks

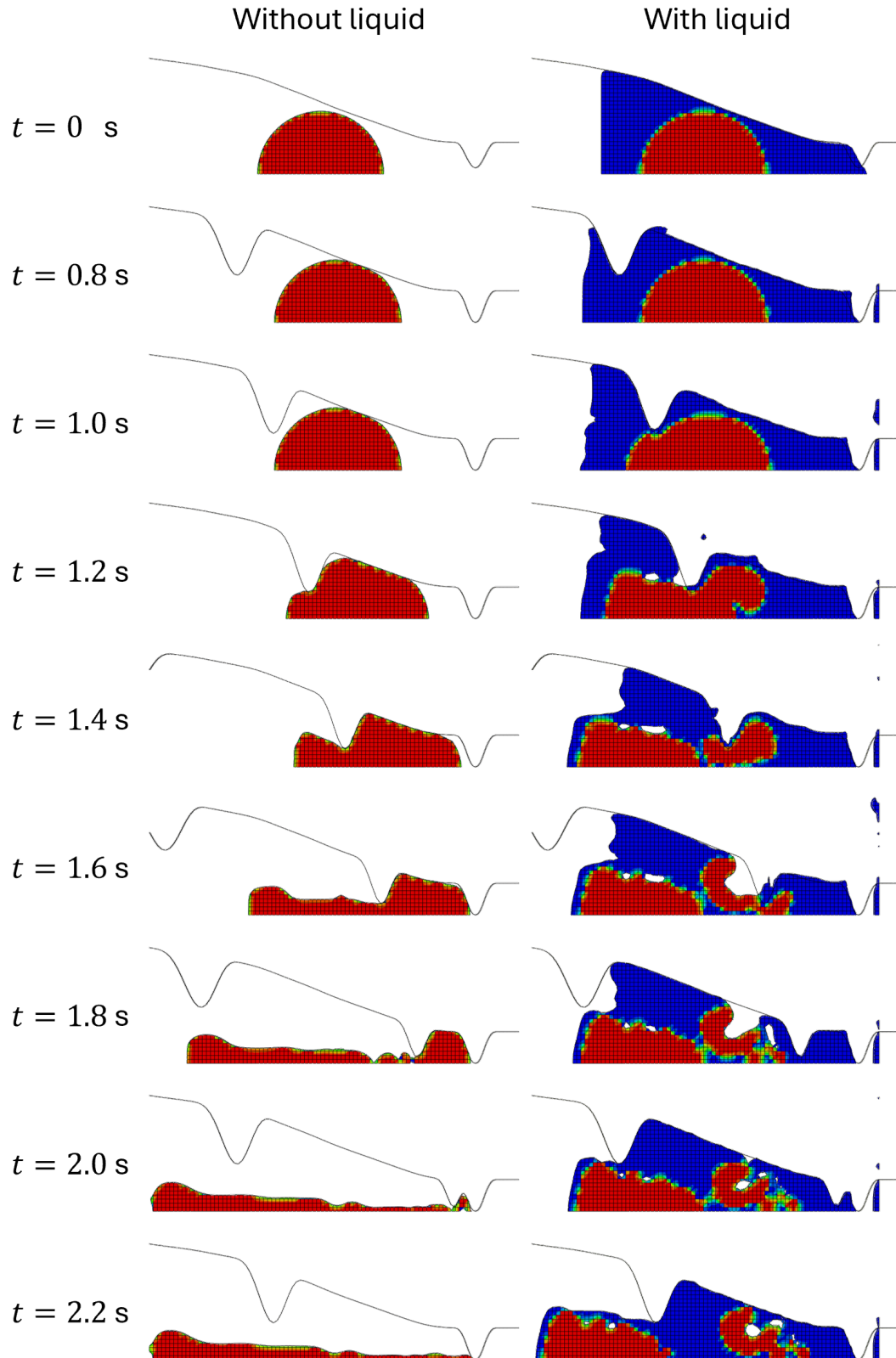


Figure 5.8. Peristaltic wave in the pseudo-plane strain model.

of the bolus at around 8 kPa in average pressure and 40 kPa in maximum pressure, whereas the "without-fluid" case reaches 15 kPa and 50 kPa, respectively. In the first wave, the average pressure of the bolus is smaller than that of the fluid, as the fluid cushions the bolus in the "with-fluid" case. From the second wave onwards, mixing leads the bolus to interact more strongly with the wall, reversing this trend, where the average pressure of the bolus becomes higher than that of the fluid. Without fluid, bolus-wall contact occurs mainly during the first wave, after which the pressure drops quickly. This means that the existence of fluid provides a more sustained pressure environment and a smoother breakdown of the bolus. The presence of fluid thus enhances pressure generation under peristalsis. In subsequent waves, the average pressure of the bolus in the "with-fluid" bolus remains 6 to 10 kPa, while it drops below 2 kPa in the "without-fluid" case. Maximum pressure oscillates between 20 and 40 kPa in the "with-fluid" case, while the "without-fluid" case shows only brief peaks at wave arrival. These trends indicate that peristalsis in the presence of fluid sustains content loading over longer durations, which is consistent with the enhanced mixing and fragmentation of the hydrogel bolus observed in [Figure 5.8](#). In the "without-fluid" case, subsequent waves contribute little additional breakdown after the first wave. Note that Bellmann et al. (2016) reported that *in vivo* gastric pressure waves, measured using the SmartPill, can reach peak values of 250–300 mmHg (33–40 kPa), which is comparable to the peak pressures at a specific location obtained in [Figure 5.9\(b\)](#). By contrast, the pressures measured in the proximal antrum of the TIMagc simulator typically range from 2 to 18 mmHg (0.3–2.4 kPa). These values may be interpreted as representing an average intragastric pressure, similar to the simulated average pressures in [Figure 5.9\(a\)](#), which reached a peak of approximately 13 kPa and oscillated between 2 and 6 kPa. One limitation should be noted: the horizontal symmetric boundary restricts the bolus from rotating out of the horizontal symmetry plane. In reality, three-dimensional rotation would further promote mixing and breakdown, and therefore, the present pressure histories may underestimate rotational contributions to mechanical disintegration.

5.5 Finite element simulation for peristalsis in an anatomically realistic stomach geometry

This section introduces the implementation of peristaltic waves in an anatomically realistic stomach geometry. Since this geometry has an irregular vessel-like shape, the peristaltic wave must be described as a function of the curvilinear coordinate system

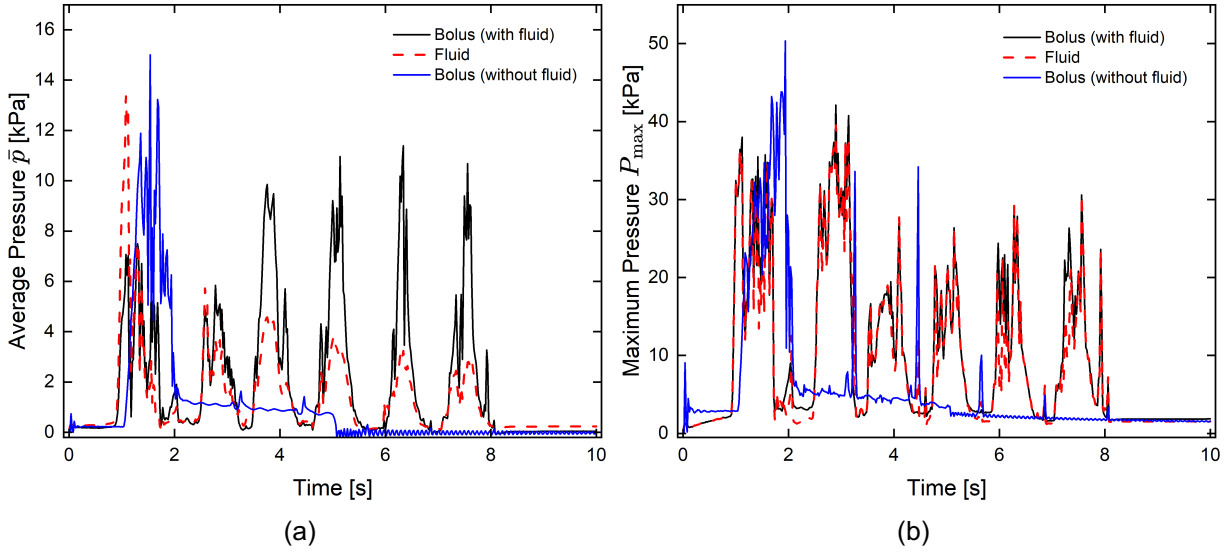


Figure 5.9. (a) Average pressure in the stomach. (b) Maximum pressure in the stomach.

defined along the stomach centreline, which therefore needs to be obtained first. In addition, the corresponding coordinate transformation must be taken into account.

5.5.1 Anatomically realistic stomach geometry

The anatomically realistic stomach geometry was reconstructed using two approaches. The first approach, following Ferrua and Singh (2010) and Skamniotis et al. (2020), generated a 3D shell geometry from a 2D bisected stomach image obtained from MedlinePlus (2024), as shown in Figure 5.10(a). From this image, points along the stomach perimeter were selected. For each cross-section, a pair of points (white circles with red outlines) was identified, one on the lesser curvature and one on the greater curvature (yellow dashed curves). The centre point (white crosses with red outline) was then defined as the midpoint of this pair. The set of these centre points formed a 2D centreline (yellow solid curve). Their coordinates, together with the corresponding perimeter points at varying distances r (white dashed lines), were extracted using ImageJ. By revolving circles (in yellow) of the corresponding radius r around the centreline to pass through the corresponding perimeter points, a series of circular cross-sections was generated, from which the 3D stomach shell surface was constructed using the function loft with guide curves (the lesser and greater curvatures) by the SOLIDWORKS software. The final geometry imported into Abaqus is shown in Figure 5.10(b), where the centreline is highlighted in red.

An alternative approach is to reconstruct the 3D stomach geometry directly from Computed

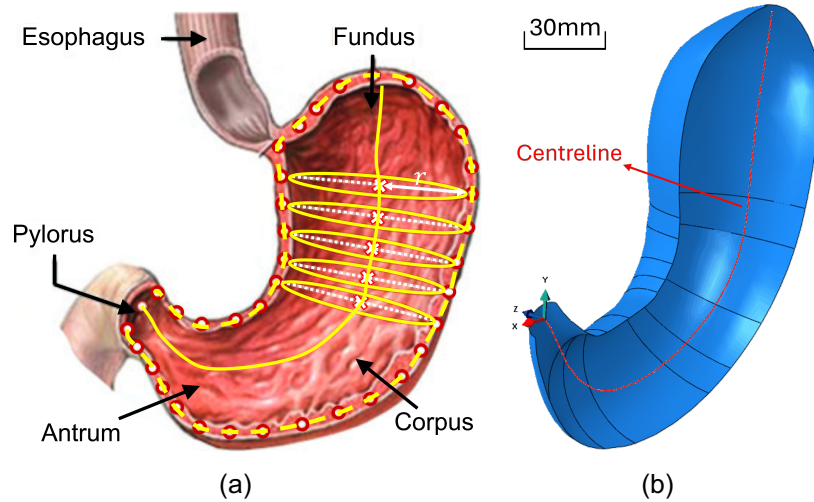


Figure 5.10. (a) Schematic of the anatomically realistic stomach geometry (MedlinePlus, 2024). (b) CAE model of the anatomically realistic stomach geometry.

Tomography (CT) scans of a real human stomach, for example, from the Virtual Population Library database (Gosselin et al., 2014), as shown in Figure 5.11. Its centreline in red was generated using the Voronoi diagram method discussed later in Section 5.5.3. In this study, however, we adopt the geometry shown in Figure 5.10(b), which provides a smoother surface and is thus potentially more stable computationally as an initial study.

Since it is difficult to obtain a direct mathematical description of the surface for anatomically realistic stomach geometries, a more practical approach is adopted, namely, extracting the nodal coordinates directly from the FE model, as described in the following section Section 5.5.2.

5.5.2 Obtaining nodal coordinates

This section describes the methodology to obtain the nodal IDs (nodal numbers) and coordinates of the anatomically realistic stomach geometry in Figure 5.10(b) required for applying the peristaltic wave boundary condition. The coordinates can be obtained from the .inp file or the .dat file. In Abaqus, geometries such as the stomach wall and the food bolus are created as individual parts in local coordinates, and then each part is repositioned and assembled into the global system.

The element coordinates in the .inp file are always local to the part, with transformations defined separately. When the “Do not use parts and assemblies in .inp files” is turned off,

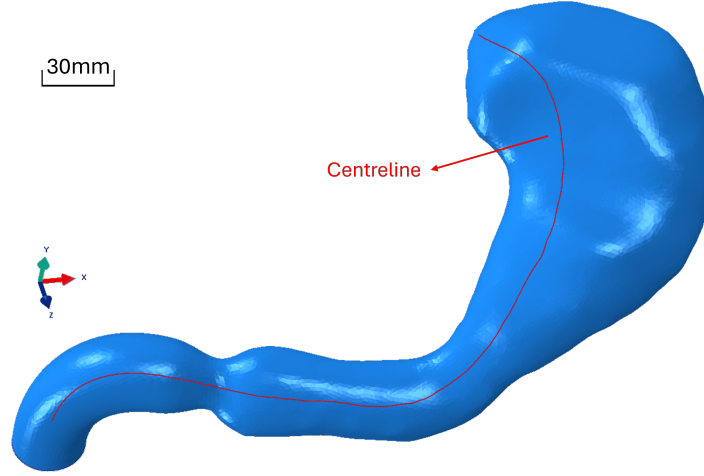


Figure 5.11. CAE model of the anatomically realistic stomach geometry reconstructed from CT data (Gosselin et al., 2014). The centreline is highlighted in red.

the part/instance structure in the `.inp` file is maintained, and the IDs are local to the part. The nodal information is listed below the `*Node` keyword in the `*Part` or `*Instance` section. The transformation information is given in the `*Instance` section, where the first data line gives the components of translation t , and the second line provides the coordinates of the lower point a and upper point b of the rotation axis, together with the angle of rotation θ in degrees. The unit vector along the rotation axis is $k = \frac{b-a}{|b-a|}$, as is shown in Figure 5.12(a). Following the Rodrigues' rotation formula:

$$v_{\text{global}} = v_{\text{local}} \cos \theta + (k \times v_{\text{local}}) \sin \theta + k(k \cdot v_{\text{local}})(1 - \cos \theta) + t, \quad (5.31)$$

where v_{local} is the local coordinate vector, v_{global} is the transformed global coordinate vector, θ is the rotation angle, and t is the translation vector.

When parts and assemblies are not used in the `.inp` file ("Do not use parts and assemblies in `.inp` files" is turned on), the nodal information is listed under the `*Node` keyword in the `*System` section with global nodal IDs. The first data line specifies the global coordinates of the local origin a and a point b on the local x -axis, while the second data line gives the coordinates of a point c in the local x - y plane (including any point on the local y -axis). These three points define the direction cosines between the local and global axes, which are elements of the rotation matrix $\mathbf{R}$. The nodal coordinates are then mapped into the global system rotated by $\mathbf{R}$ and translated by t , as illustrated in Figure 5.12(b), via the following equation:

$$v_{\text{global}} = \mathbf{R} \cdot v_{\text{local}} + t. \quad (5.32)$$

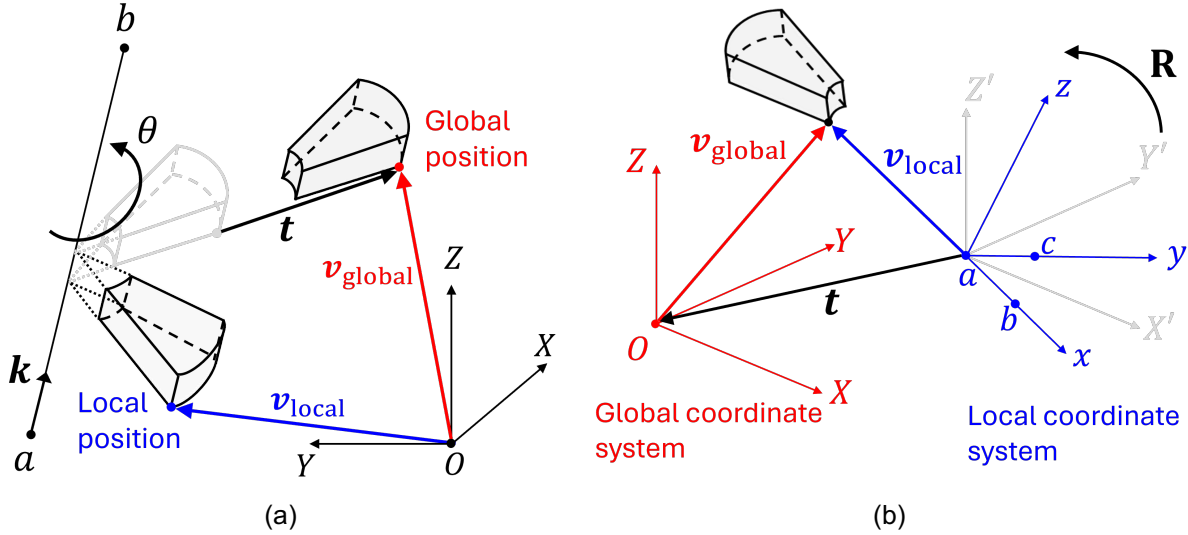


Figure 5.12. Schematic representation of the coordinate transformation of an element. (a) using parts and assemblies in the `.inp` file; (b) without using parts and assemblies in the `.inp` file.

If the data need to be obtained from the `.dat` file, the global coordinates with global nodal IDs can be directly retrieved when the `*Preprint, Model=Yes` option is used in the `.inp` file. The nodal information is listed under the `NODE DEFINITIONS` section, where the first column is the global nodal ID, and the following three columns are the global x , y , and z coordinates, respectively. More information can be found in Simulia, Dassault Systemes (2012). In this study, we obtained the nodal information from the `.inp` file without using parts and assemblies (using Equation 5.32), as this involves fewer steps, although it requires more lines of code than obtaining it from the `.dat` file.

5.5.3 Obtaining the centreline information of the stomach

With the global coordinates of the geometry obtained, the next step is to extract the stomach centreline, which is required to apply the peristaltic wave as a boundary condition. The centreline provides a natural curvilinear coordinate system for vessel-like geometries such as blood vessels, intestines, and the stomach, and thus serves as a convenient reference for defining the propagation of peristaltic waves.

Since the definition of a centreline for a vessel-like geometry is not unique, we follow the method of Antiga (2002), in which the centreline of a geometry is defined as the locus of the centres of its maximum inscribed spheres, yielding a path that locally maximises the distance from the vessel boundary. As the stomach is a complex vessel-like geometry

without an analytical description, we adopt a numerical approximation using the VMTK Python package, which computes the centreline using an approach based on the Voronoi diagram. Specifically, a Delaunay tessellation is first performed on the stomach geometry, discretising it into tetrahedral elements whose vertices are sampled from the surface of the geometry. Each Delaunay tetrahedron is circumscribed by a sphere, known as a Voronoi sphere, which by definition contains no sampling points other than its own tessellation vertices. Connecting the circumcentres of adjacent tetrahedra that share a face forms an edge of the Voronoi diagram, as illustrated in [Figure 5.13](#).

The embedded portion of the Voronoi diagram lying entirely within the stomach geometry of [Figure 5.10\(b\)](#) is shown in [Figure 5.14\(a\)](#), where the contour represents the radius of the Voronoi sphere, with red indicating larger spheres and blue indicating smaller ones. It appears noisy and contains many branches, which reflect the presence of small Voronoi spheres generated from flat Delaunay tetrahedral elements constructed among neighbouring vertices. A stable subset of the Voronoi vertices, known as the poles and defined as the farthest Voronoi vertices from the surface associated with each tessellation vertex, is then extracted, as the poles are found to converge to the centreline (Antiga, 2002), as shown in [Figure 5.14\(b\)](#). For further details on the theory, the reader is referred to Antiga (2002).

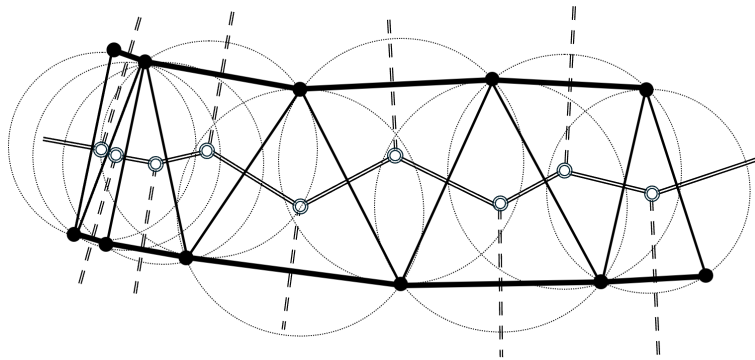


Figure 5.13. 2D illustration of Delaunay tessellation and Voronoi diagram of a tube geometry. Delaunay tessellation (thick and thin solid lines) of a 2D point set (solid dots), discretised boundary (thick solid line), Voronoi diagram (solid and dash double lines), embedded Voronoi diagram (solid double lines), Voronoi vertices (double solid line empty dots), and circumscribed circles (dotted line circle) are shown (Antiga, 2002).

Using VMTK, the stomach centreline is extracted and imported into Abaqus as a line object. By combining this line with the stomach geometry, the nodal coordinates of the centreline can be obtained following the procedure in [Section 5.5.2](#). The centreline then serves as the reference for defining the curvilinear coordinate system, where the

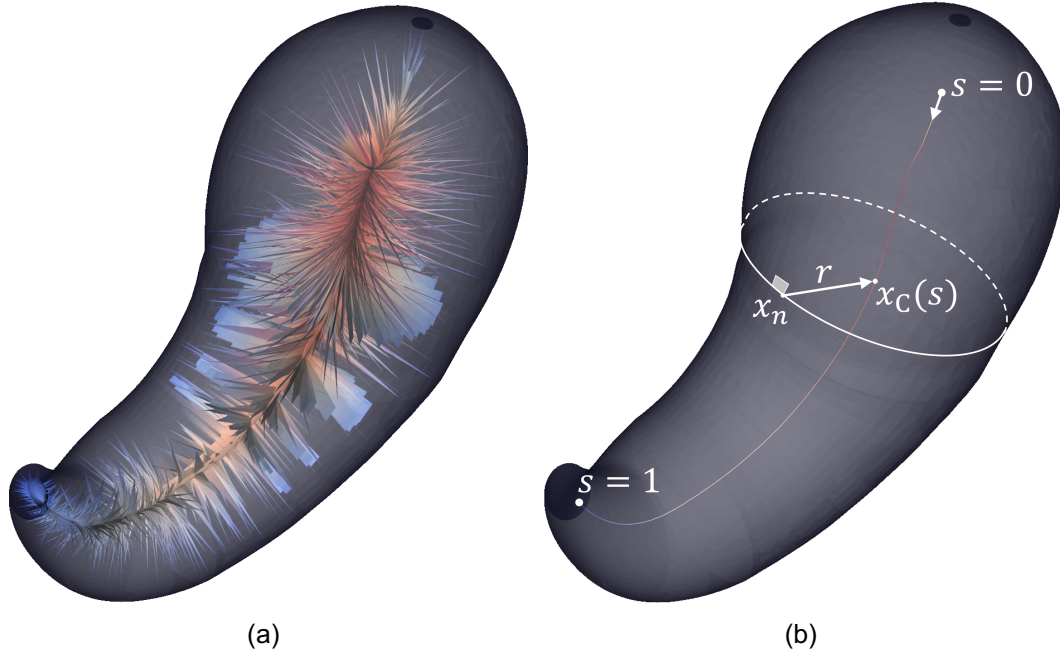


Figure 5.14. (a) Embedded Voronoi diagram constructed from the Delaunay tessellation of the stomach geometry. (b) Centreline extracted from the stomach geometry using VMTK. Colours from red (large) to blue (small) map the radius of the Voronoi sphere.

curvilinear coordinate s is introduced as the normalised arc length along the centreline, ranging from 0 to 1 from the starting point to any point of interest. A continuous representation of the centreline is obtained by B-spline interpolation, using the `splprep` function to generate the B-spline representation and `splev` to evaluate the spline, both from the `scipy.interpolate` package. In this way, the `splev` function is used to map the curvilinear coordinate s to global Cartesian coordinates along the centreline. Next, the curvilinear coordinate s is assigned to each surface node of the stomach by locating the nearest point on the centreline. This is achieved by minimising the distance between the node position x_n and the spline-defined centreline $x_c(s)$ with respect to s . This is conducted by the `minimize_scalar` function from the `scipy.optimize` package. Once the optimal curvilinear coordinate $s = s(x_n)$ is found, the corresponding Cartesian coordinates $x_c(s)$ are obtained from `splev`, and the radius vector of the node,

$$\mathbf{r} = [r_x, r_y, r_z] = \mathbf{x}_c(s) - \mathbf{x}_n, \quad (5.33)$$

can be calculated, as illustrated in Figure 5.14(b). Finally, the nodal information is exported to `.txt` files in the format `(node_ID, s, r_x, r_y, r_z)`, which are subsequently read by the Abaqus subroutine user external database subroutine for explicit solver (VEXTERNALDB)

as arrays. A mapping between the global IDs and the local IDs (array indices) of the stomach wall nodes is also created to exchange information between the VEXTERNALDB and VDISP subroutines.

5.5.4 Applying peristaltic waves in the anatomically realistic stomach geometry

Unlike the pseudo-plane strain model described in [Section 5.4.1](#), the geometry of the stomach is irregular. Therefore, the nodal coordinates of the geometry are obtained directly from the `.inp` file, while the curvilinear coordinate system is derived from the centreline information introduced in [Section 5.5.3](#). This is implemented using the VEXTERNALDB subroutine in Abaqus, which allows for reading an external database. To ensure the subroutine is executed only once at the start of the analysis, the condition statement (`l0p .eq. j_int_StartAnalysis`) is applied, where `l0p` is a flag variable returned from Abaqus indicating the phase of the analysis. This procedure is general and can be applied to any stomach geometry, provided that both the nodal and centreline information are available.

With the nodal information of the stomach wall and the centreline, the peristaltic wave is applied as a boundary condition at the nodes, analogous to the pseudo-plane strain model in [Section 5.4.2](#). Here, the dependence on the x -coordinate is replaced by the curvilinear coordinate s along the centreline, and the y -displacement is replaced by the radial displacement Δr of the nodes:

$$\Delta r = \lambda(s, t) \cdot r_0 = \lambda_{\max}(s) \cdot h(s - s_b(t)) \cdot r_0, \quad (5.34)$$

where r_0 is the initial radius vector of the node, and

$$s_b(t) = s_0 + c_w \cdot t_{\text{step}} - d_k \quad (5.35)$$

is the curvilinear coordinate of the wave back. The wave shape function $h(\cdot)$ remains the same as in [Equation 5.22](#), while the wavelet length varies with the curvilinear coordinate s :

$$l_w(s) = l_{w0} + (l_{wf} - l_{w0}) \frac{s - s_0}{s_s - s_0}. \quad (5.36)$$

Following the above methodology, the peristaltic wave can be applied to the nodes on the stomach wall of the anatomically realistic geometry. An example of a single wavelet propagating from 0 to 8 s (the first of three wavelets) is shown in [Figure 5.15](#). Note that

in the current model, the pylorus was open throughout the simulation to allow the bolus to exit the stomach. More physiologically accurate modelling of pyloric opening and closure could be incorporated into future work.

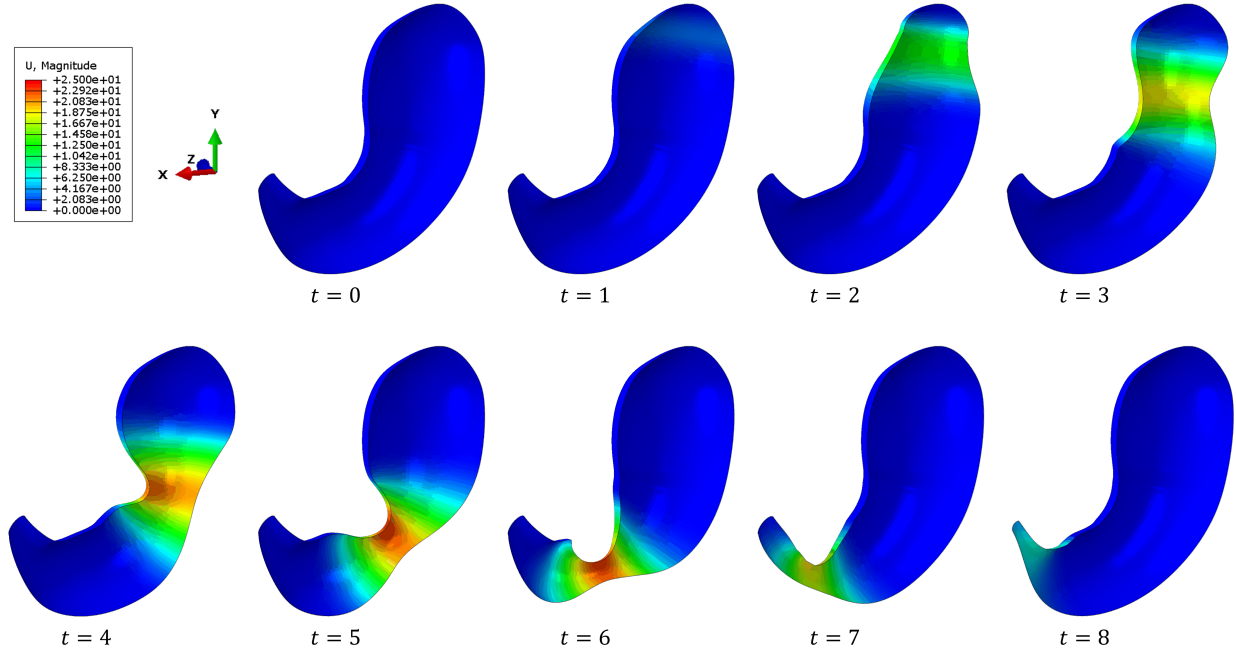


Figure 5.15. The first of three peristaltic waves in the anatomically realistic stomach geometry, with only the stomach wall shown. The contour represents the radial displacement magnitude of the stomach wall (in mm).

5.5.5 Description of the anatomically realistic gastric digestion model setup

Similar to [Section 5.4.4](#), the CEL method is used to simulate the interaction between peristaltic waves of the stomach wall and the food bolus. The stomach wall was also modelled as a Neo-Hookean hyperelastic material with the same parameters as in [Section 5.4.4](#) to allow large deformations, and S4R elements with hourglass control were used. For the starch hydrogel bolus, two types of material behaviour are considered. The first is a pseudo-viscoelastic model defined through a VUMAT subroutine, adapted from the constitutive model in [Section 4.2](#), with pre-assigned degradation levels of 0 and 0.6 to represent different stages of hydrolysis in a simplified manner. The second is an elastic-plastic model calibrated from experimental data on crushed-reformed hydrogel, with parameters the same as those in [Section 5.4.4](#). The bolus is represented in the Eulerian region using EC3D8R elements with hourglass control.

The meshes of both the Eulerian and Lagrangian regions are shown in Figure 5.16(a), where the Eulerian region ($210 \text{ mm} \times 125 \text{ mm} \times 46 \text{ mm}$) fully encloses the Lagrangian region. The hydrogel material is assigned as a discrete field created from a reference sphere of diameter 50 mm using the volume fraction tool, as illustrated in Figure 5.16(b). We use such a large diameter to amplify the interaction between the bolus and the stomach wall, which is not physiologically representative. We did not apply a larger amplitude peristaltic wave, as it could cause computational instability and computation abortion. General contact is defined between the stomach wall and the bolus and their self-contact with a friction coefficient of 0.9 , following Skamniotis et al. (2020). Gravity is applied to the bolus in the negative y -direction. Exploiting symmetry, only half of the stomach and bolus are modelled, as shown in Figure 5.16, with symmetry boundary conditions imposed on the blue X - Y symmetric plane for both the Lagrangian wall (black edges) and the Eulerian domain (blue surface), i.e., constraining the displacement in z direction. Gastric fluid is not included in the simulations.

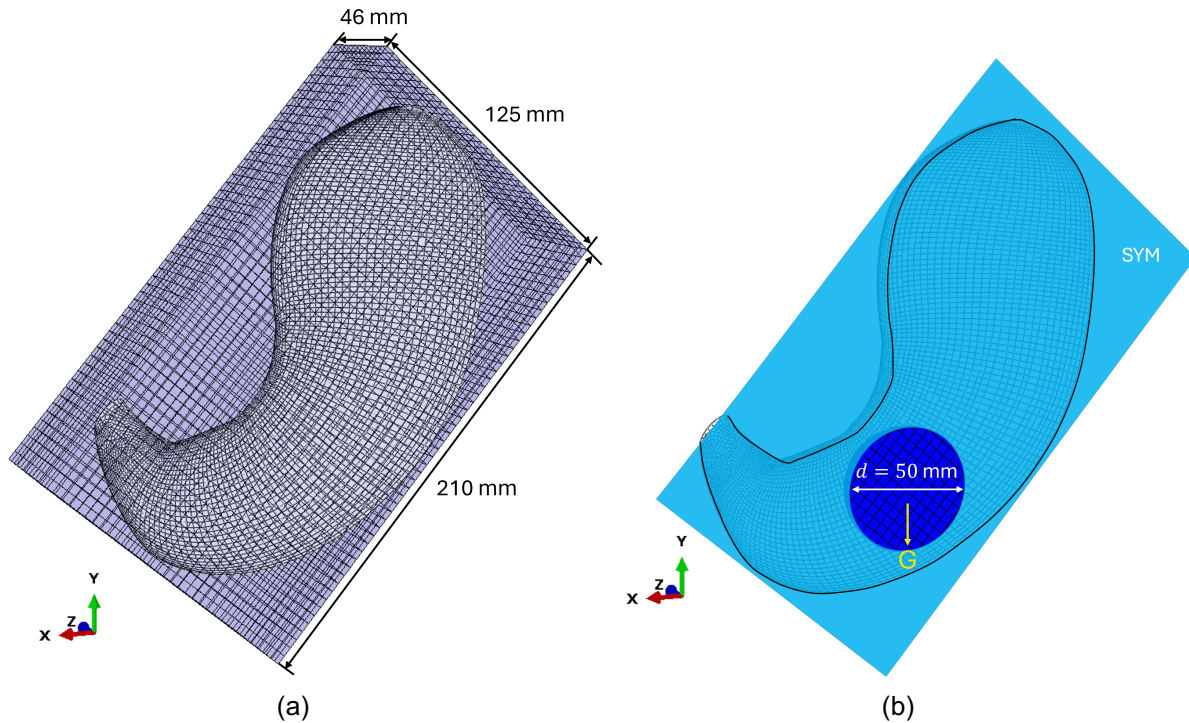


Figure 5.16. (a) CAE model of the anatomically realistic stomach geometry with meshes. (b) Boundary conditions applied to the CAE model.

5.5.6 Summary of the methodology for modelling the peristaltic wave in anatomically realistic stomach geometry

The overall procedure for modelling peristaltic waves in an anatomically realistic stomach geometry can be summarised as follows:

1. Construct the stomach geometry.
2. Read the nodal IDs and coordinates of the stomach wall from the `.inp` file, and transform from the local to the global coordinate system.
3. Extract the stomach centreline using the VMTK Python package and import it into Abaqus together with the stomach geometry.
4. Define the curvilinear coordinate s as the normalised arc length along the centreline, and assign s to each stomach wall node by locating its nearest point on the centreline.
5. Compute the radius vector r of each stomach wall node relative to the centreline.
6. Export the nodal information (global node ID, curvilinear coordinate s , and radius vector r) to a `.txt` file.
7. Use the VEXTERNALDB subroutine in Abaqus to read the exported file and establish a mapping between local and global node IDs.
8. Apply the peristaltic wave as a boundary condition via the VDISP subroutine, using the curvilinear coordinate system along the centreline. The radial displacement is computed according to [Equation 5.34](#).
9. Model the hydrogel bolus in the Eulerian region and the stomach wall in the Lagrangian region using the CEL method, with the Eulerian region enclosing the Lagrangian region.
10. Define general contact between the stomach wall and the hydrogel bolus (interaction resolved by the immersed boundary method), and apply gravity to the bolus in the negative y -direction.
11. Impose symmetry boundary conditions on the X - Y symmetric plane for both the stomach wall and the Eulerian region.

5.5.7 Results for realistic stomach geometry

[Figure 5.17](#), [Figure 5.18](#), and [Figure 5.19](#) illustrate the interaction between the hydrogel bolus and the stomach wall at 5–8 s, 12–16 s, and 20–24 s, corresponding to the first (also shown in [Figure 5.15](#)), second, and third wavelets, respectively. The contours show the Eulerian volume-averaged pressure (SVAVG, Pressure) distribution. In each case,

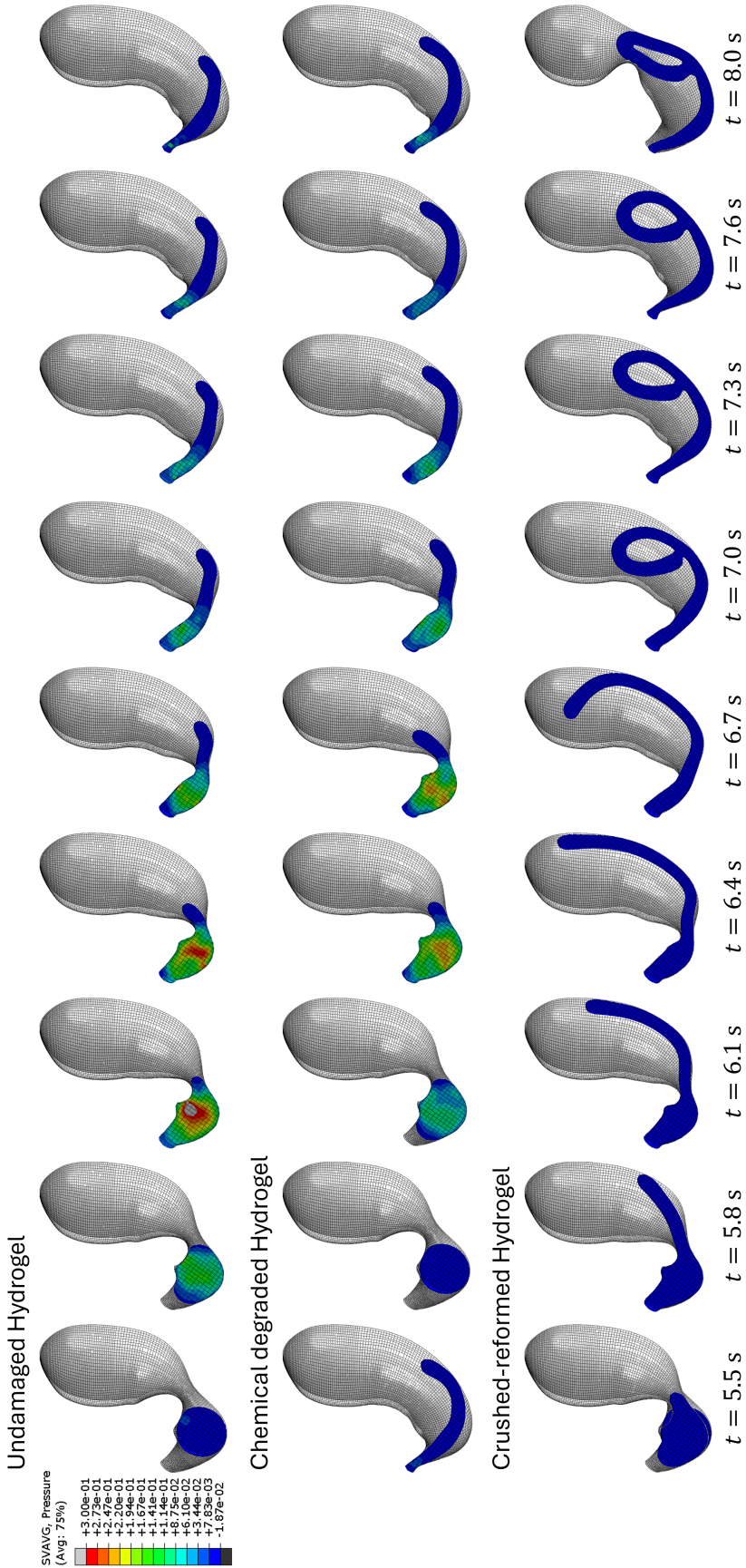
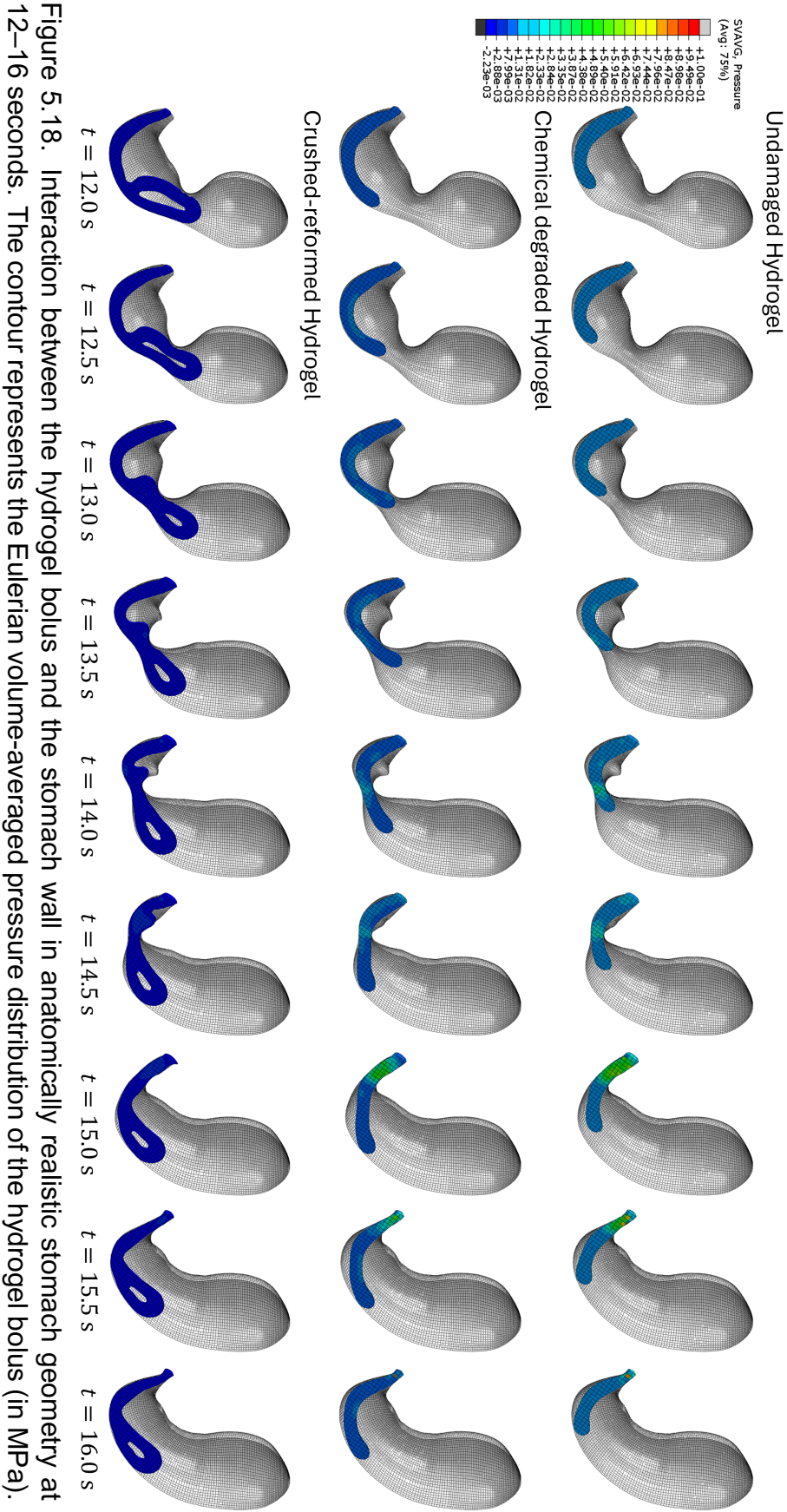


Figure 5.17. Interaction between the hydrogel bolus and the stomach wall in anatomically realistic stomach geometry at 5–8 seconds. The contour represents the Eulerian volume-averaged pressure distribution of the hydrogel bolus (in MPa).



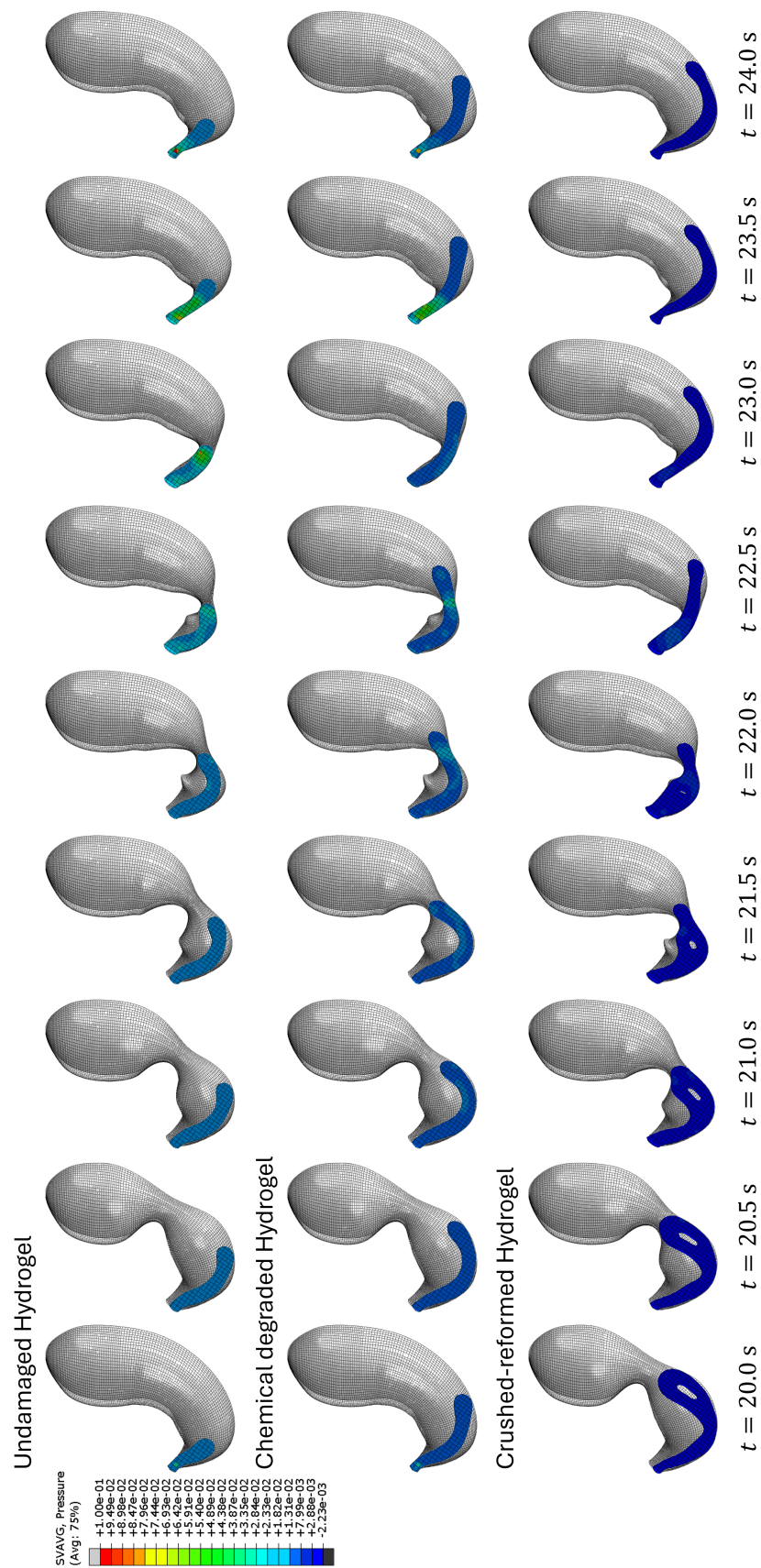


Figure 5.19. Interaction between the hydrogel bolus and the stomach wall in anatomically realistic stomach geometry at 20–24 seconds. The contour represents the Eulerian volume-averaged pressure distribution of the hydrogel bolus (in MPa).

the behaviour of undegraded, partially chemically degraded, and crushed-reformed hydrogels is compared. During the first wavelet, all boluses undergo substantial deformation, with pressure peaking near the bolus centre and remaining low at both ends towards the pylorus and the corpus. This pressure gradient drives simultaneous propulsion and retropulsion, pushing part of the bolus towards the pylorus while the rest is forced backwards into the corpus. The undegraded hydrogel deforms the least, followed by the degraded hydrogel, while the crushed-reformed hydrogel shows the most significant deformation, consistent with their decreasing stiffness. For the crushed-reformed hydrogel, pronounced self-contact and mixing are observed. The bolus is elongated into a thin tube with a larger surface area than in the other two cases, then buckles and folds onto itself, and subsequently merges and mixes further when acted upon by the next wavelet. The mixing likely enhances the exposure of the hydrogel to enzymatic action, potentially increasing the rate of chemical degradation and disintegration of starch, similar to the inclusion of gastric fluid as mentioned in [Section 5.4.5](#). In all cases, a portion of the bolus was pushed through the pylorus following deformation, since the pylorus remained open throughout the simulation. However, in reality, pyloric opening and closure occur periodically and are regulated by neural and hormonal mechanisms, which were not considered in the present model.

[Figure 5.20\(a\)](#) and [Figure 5.20\(b\)](#) show the average and maximum pressures in the stomach during digestion, respectively. The average pressure decreases significantly between the first and the second wavelet. During the first wavelet, the average pressure reaches peaks of approximately 180 kPa for the undegraded hydrogel, 150 kPa for the chemically degraded hydrogel, and 10 kPa for the crushed-reformed hydrogel. The maximum pressure exhibits a similar trend, with peaks of about 380 kPa, 360 kPa, and 25 kPa for the undegraded, chemically degraded, and crushed-reformed hydrogels, respectively. The reduction in pressure with increasing degradation level is attributed to the lower stiffness of the hydrogel bolus, which provides less resistance to peristaltic loading. The second and third wavelets produce substantially lower pressures than the first wavelet because the bolus is already highly deformed after the initial loading. Moreover, due to the nature of the CEL method, once the material has flowed significantly, it is less likely to recover its undeformed shape. It should also be noted that the damage and failure behaviour of the hydrogel was not included in the model. As a result, the predicted pressures for the undegraded and chemically degraded hydrogels are unrealistically high. In reality, such hydrogels would fracture and fragment under these loads, leading to lower pressures and a more effective digestion process. Note that the pressure responses were unrealistically high compared to physiological

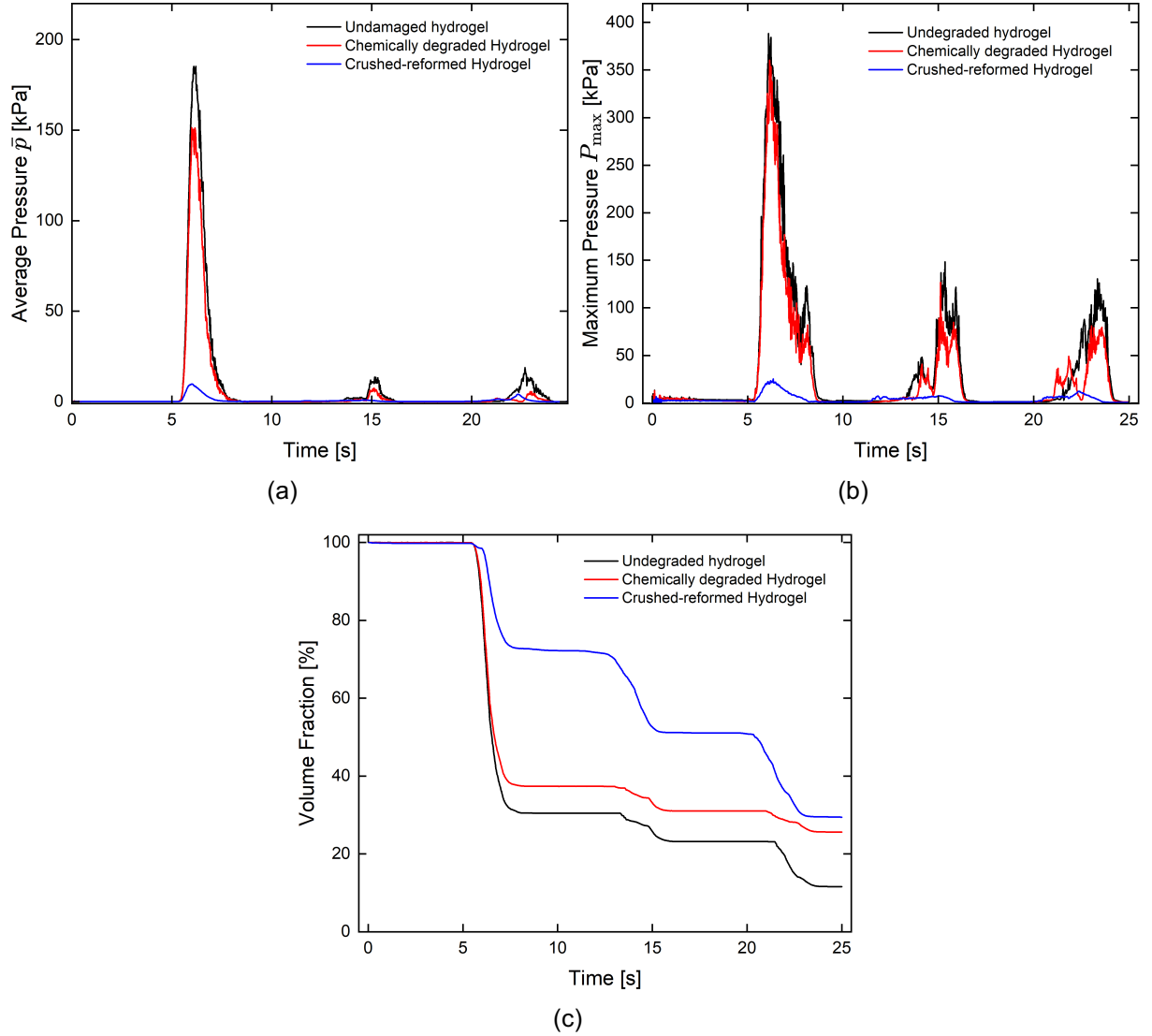


Figure 5.20. (a) Average pressure in the stomach during digestion. (b) Maximum pressure in the stomach during digestion. (c) Volume fraction of the hydrogel bolus remaining in the stomach.

measurements (Bellmann et al., 2016), are higher than the results of the anatomical model in Section 5.4.5. This is due to the omission of the damage and failure behaviour of the hydrogel, along with the enforced large deformation of the stomach wall, which leads to an overestimation of the deformation resistance of the bolus and thus the pressure.

Figure 5.20(c) shows the hydrogel volume fraction remaining in the stomach during digestion. With each peristaltic wavelet, a portion of the bolus is propelled through the pylorus, resulting in a gradual decline in volume fraction. Interestingly, the stiffer hydrogels (undegraded and chemically degraded) emptied from the stomach more rapidly but underwent less fragmentation. This suggests that although these boluses were transported out more quickly, their digestion was less effective, which may reduce the rate and extent of nutrient release and absorption. It should be noted, however, that the observation of softer boluses emptying more slowly than stiffer ones contradicts both the experimental findings and *in vivo* behaviour. This discrepancy arises again from current model limitations, particularly the absence of damage and failure mechanisms in the hydrogel material model. Without these mechanisms, the stomach wall's prescribed motion imposes non-physical deformation and pressure on the bolus, artificially pushing the stiffer hydrogels out of the stomach.

Note that, as mentioned earlier, the parameters of the stomach wall were selected to allow large deformations, and the shear and volumetric moduli were set empirically to avoid excessive element distortion and numerical instability. However, when the fluid was included, the wall did not establish contact with the fluid, and leakage occurred through the wall. As discussed by Skamniotis et al. (2020), a reasonable ratio of bulk modulus to shear modulus is crucial for achieving reliable results. If this ratio is too high (greater than 100), numerical instabilities or oscillatory solutions may occur, whereas if the ratio is too low, the contact stiffness may become insufficient, leading to contact penetration or leakage. Therefore, the stomach wall parameters need to be further calibrated in future work to represent physiological conditions better while maintaining numerical stability and adequate contact stiffness.

5.6 Dynamic *in vitro* digestion

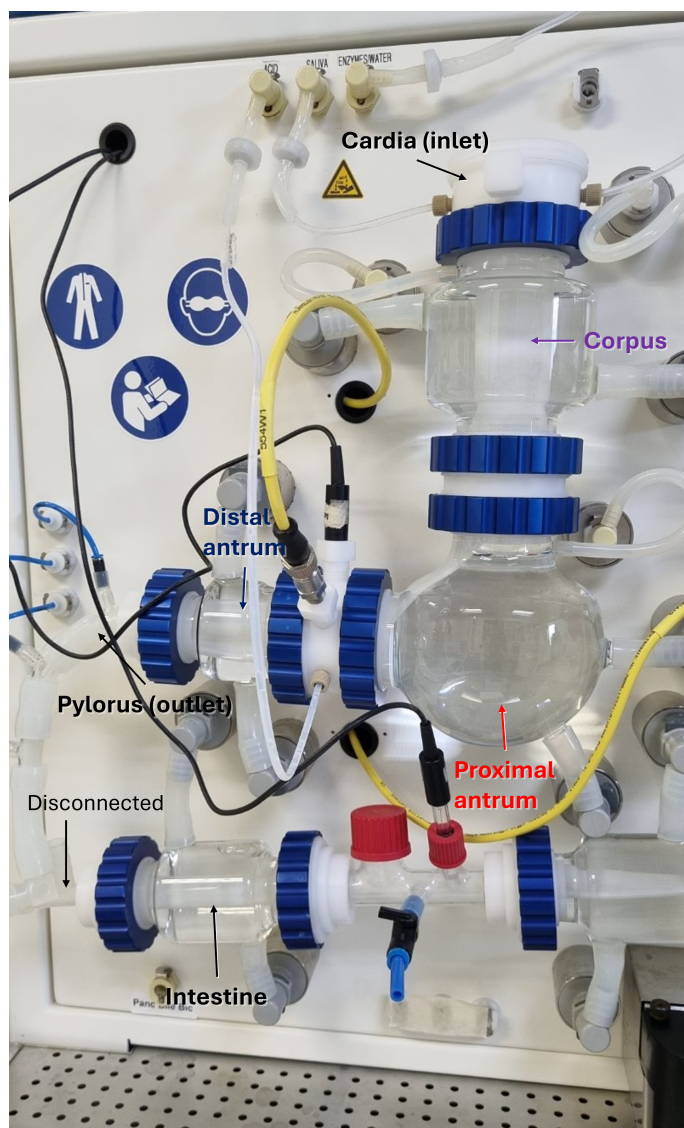
5.6.1 Experimental setup

The dynamic *in vitro* digestion experiments were performed using the TIMagc simulator (Bellmann et al., 2016), with the assistance of Dr Chaiwut Gamonpilas (National Method and Technology, Thailand). The TIMagc device is shown in Figure 5.21, and its internal compartments, comprising the corpus, proximal antrum, and distal antrum, are illustrated in Figure 5.21(a). The inlet to the corpus and the outlet of the distal antrum correspond to the cardia and pylorus, respectively. Each compartment consists of a silicone rubber sleeve enclosed by a glass chamber. The volume of each sleeve is regulated by water pressure applied in the gap between the sleeve and the surrounding glass chamber, with the pressure being controlled by water inlet and outlet via a pneumatic pumping system. In this way, the cyclic inflation and deflation of the silicone sleeves generated peristaltic waves within the compartments, reproducing physiological peristaltic motion. Although the TIMagc system also includes intestinal compartments, they were disconnected to isolate gastric digestion. Accordingly, the pylorus served as the outlet through which digesta was collected, as shown in Figure 5.21(b).

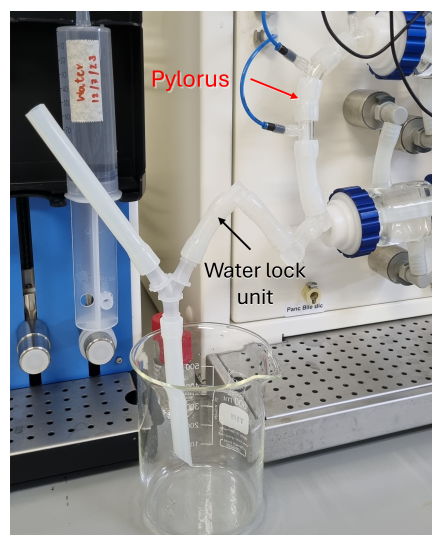
Starch hydrogel was used as the model food bolus. Samples were prepared at a concentration of 20% w/w and moulded into cylinders of 20 mm in height and 20 mm in diameter, then retrograded for 48 hours following the same procedure as the standard samples described in Section 2.2. It is noted that the experiment was conducted in a laboratory in Thailand, where the ambient temperature was approximately 30°C. A “pharma-fasted” pianoroll was used to prescribe the gastric emptying motility in the fasted state (Bellmann et al., 2016). According to Elashoff et al. (1982), in the fasted state, the fraction of ingesta remaining in the stomach, $f(t)$, can be described by the Elashoff equation:

$$f(t) = 2^{-\left[\frac{t}{t_{1/2}}\right]^\beta}, \quad (5.37)$$

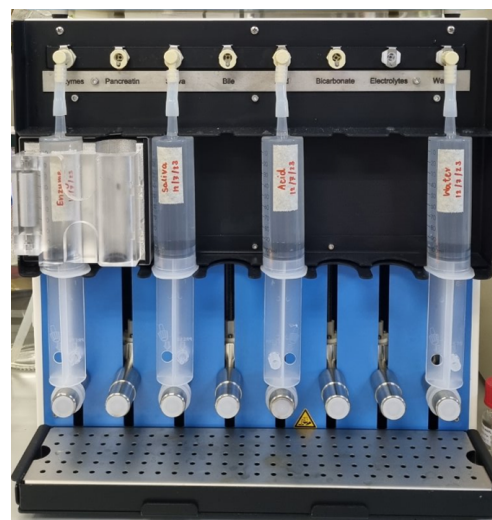
where the emptying half-time was set to $t_{1/2} = 15$ min and the shape parameter to $\beta = 1$, resulting in the emptying profile shown in Figure 5.22. By controlling the ratio of the gastric volume (total volume of the three compartments) at a given time to the initial gastric volume (equal to the ingesta volume), following the Elashoff equation, the desired pattern of the emptying profile can be achieved. While emptying is ongoing, peristalsis is simultaneously generated by coordinating volume between the compartments in short, frequent cycles, producing propulsion and retropulsion that mix and mechanically break down the gastric



(a)



(b)



(c)

Figure 5.21. TIMagc simulator: (a) compartments, (b) water lock unit, (c) solutions.

contents.

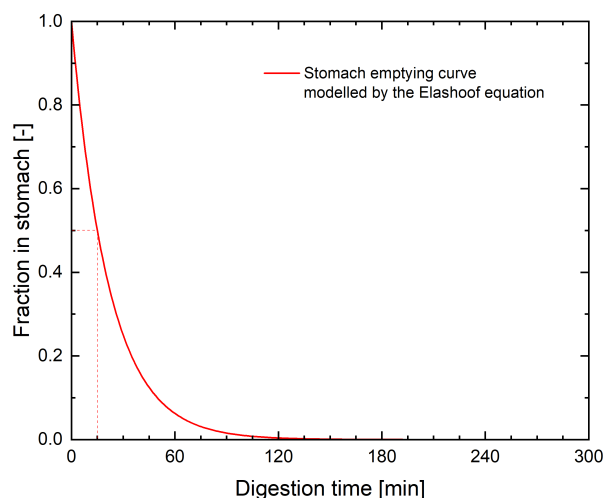


Figure 5.22. Emptying profile model used in the TIMagc simulator.

The simulated meal (ingesta), consisting of 270 mL of deionised water together with one starch hydrogel sample, was introduced through the corpus inlet (cardia). Digestion was then simulated through the combined action of peristaltic contractions and gastric secretion on the sample. Each experiment ran for one hour under the prescribed pianoroll following Bellmann et al. (2016). The pyloric valve was opened by a pump once the intragastric pressure reached 0.1 bar (10 kPa), allowing digesta to exit the stomach compartment. Samples were collected from the pylorus outlet every 10 minutes. The collected digesta were subsequently dried in an oven, and the dry mass was measured to quantify the extent of hydrogel breakdown.

Four different modes of dynamic *in vitro* digestion of simulated secretion fluids were investigated, including:

1. Water mode: DI water.
2. Acid mode: 1 M HCl.
3. Enzyme mode: simulated digestion fluid (SDF) without added acid.
4. Acid and enzyme mode: SDF supplemented with 1 M HCl.

The composition of the SDF, composed of gastric electrolyte secretion (GES) and enzymes, following the INFOGEST protocol (Brodkorb et al., 2019), is provided in Table 5.3.

Table 5.3. Composition of gastric enzyme solutions.

Solution	Ingredient	Amount [g]	Margin [$\pm$ g]
GES 10x conc.	Deionised water	966.0	2.0
	NaCl	80.0	0.6
	KCl	17.0	0.2
	CaCl ₂ ·2H ₂ O	1.6	0.1
SDF	GES 1x conc.	298.9	2.0
	Acetate buffer	3.0	0.1
	Pepsine	1440k unit	–
	Lipase	6k unit	–
	α -amylase	42k unit	–

Simulated secretion fluids were delivered into the compartments using the syringes shown in [Figure 5.21\(c\)](#), and the injection, again prescribed by the pianoroll, was controlled by the system motors.

5.6.2 Dynamic *in vitro* digestion results

During the dynamic *in vitro* digestion, the intragastric pH was continuously monitored using a pH probe. As shown in [Figure 5.23](#), the pH initially increased due to the intake of neutral water and subsequently decreased as acid was secreted. The pH then stabilised after approximately 10 to 15 minutes. For the acid mode and the acid+enzyme mode, the target pH was set to 2.0. In the water mode, all injected secretion fluids were deionised water, and the gastric pH stabilised between 6 and 7. In the enzyme mode, the pH stabilised at a lower value than in the water mode, because the GES introduced (see [Table 5.3](#)) had an intrinsic pH of approximately 4.75.

The intragastric pressure was also monitored. As shown in [Figure 5.24](#), the pressure oscillated between approximately 5 and 10 kPa, with an average value of around 8 kPa. Since the pressure was recorded at 1-minute intervals, while the motility pattern repeats multiple times per minute, the sampling frequency may not capture short peak pressures of up to 10 kPa, at which the pylorus opens to allow digesta to empty from the stomach compartment.

Photos of the dynamic *in vitro* digestion process are shown in [Figure 5.25](#), illustrating one inflation-deflation cycle of the sleeves. The sequence begins at $t = t_{de}$, when the sleeve

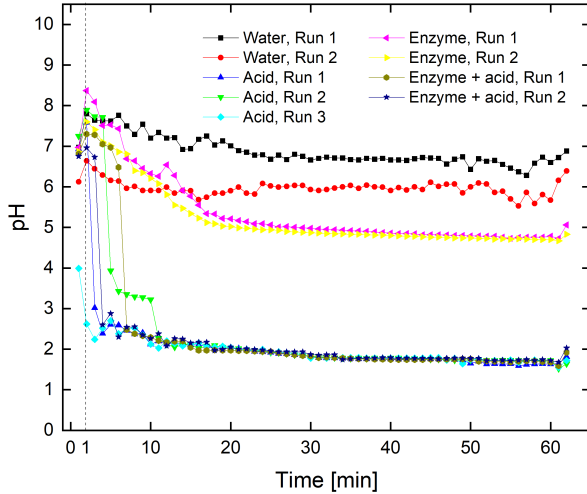


Figure 5.23. Profile of pH control in the TIMagc simulator.

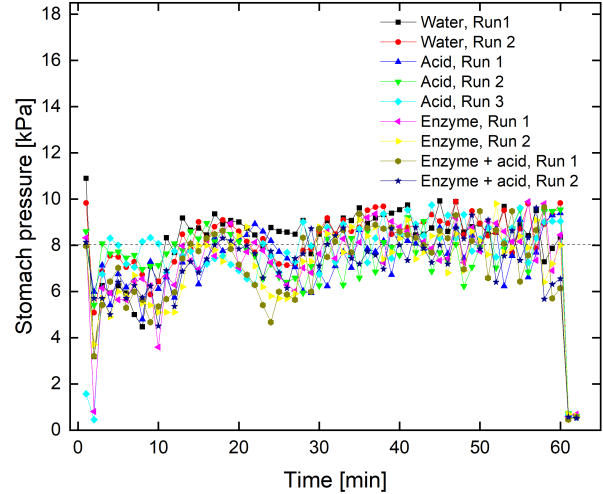


Figure 5.24. Profile of pressure control in the TIMagc simulator.

of the proximal antrum (purple label) is in a deflated state (Figure 5.25(a)). Over the subsequent 30 seconds (from Figure 5.25(b) to Figure 5.25(d)), this sleeve progressively inflates. In contrast, the sleeve of the distal antrum (blue label) is deflated at $t = t_{de}$ (Figure 5.25(a)), inflates in Figure 5.25(b) and Figure 5.25(c), and then deflates again in Figure 5.25(d). Meanwhile, the sleeve surrounding the hydrogel sample (green label) also undergoes cyclic changes during this period. This coordinated sequence of inflation and deflation across the compartments controls the total volume of the compartments and, at the same time, produces the peristaltic wave responsible for the propulsion and retropulsion of the gastric contents (green label).

The digesta collected from the TIMagc simulator at different time intervals are shown in Figure 5.26, Figure 5.27, Figure 5.28 and Figure 5.29, under the water mode, acid mode, enzyme mode, and enzyme + acid mode, respectively. It can be observed from the photos that, as digestion time increased, the amount of digesta collected generally increased, indicating progressive breakdown of the hydrogel sample. Little digesta was collected in the acid mode, as shown in Figure 5.27, and the hydrogel sample remained largely intact in the stomach, as evidenced by the residual material. When acid was combined with the enzyme, as shown in Figure 5.29, more digesta was recovered, indicating that enzymatic hydrolysis occurred. In this condition, the digesta also showed greater particle disintegration, characterised by a higher number of particles and smaller particle sizes, particularly toward the end of the digestion experiment. Compared with the enzyme mode in Figure 5.28, the amount of the collected digesta in the enzyme + acid mode was smaller, reflecting the partial deactivation of the enzyme under the

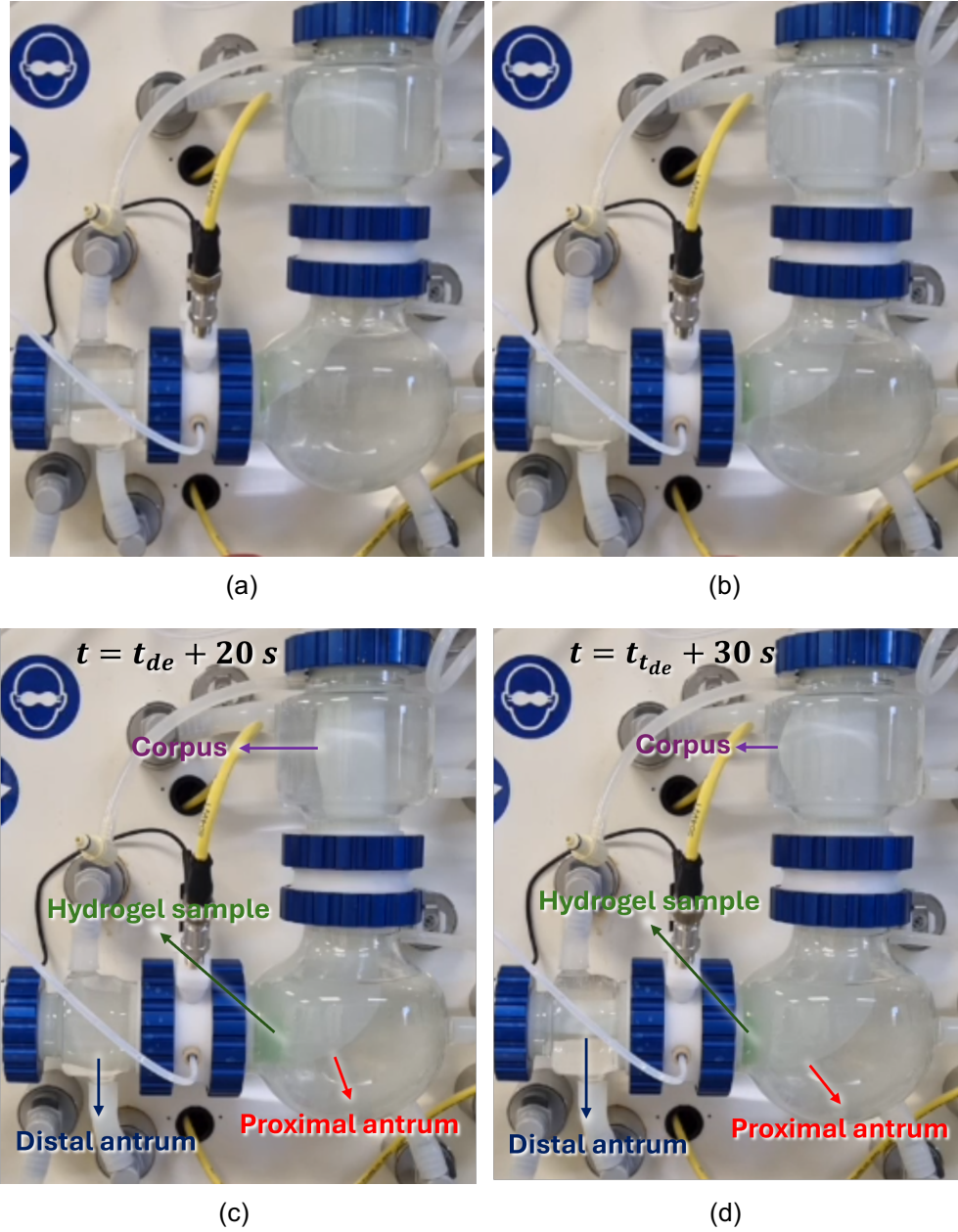


Figure 5.25. Photos of the inflation-deflation cycle of the sleeves during the dynamic *in vitro* digestion simulation. The four photos were taken within 30 seconds, starting from $t = t_{de}$. (a) $t = t_{de}$, (b) $t = t_{de} + 10s$, (c) $t = t_{de} + 20s$, (d) $t = t_{de} + 30s$.

low-pH conditions. Physiologically, because the gastric environment was maintained at a low pH, enzyme activity was limited, and the hydrolysis was less effective than in more favourable conditions, e.g., in the intestinal phase. Surprisingly, a considerable amount of digesta was obtained in the water mode, as shown in Figure 5.26. This was attributed to the mechanical disintegration of the hydrogel driven by gastric motility, together with the inherent variability and uncertainty of dynamic *in vitro* digestion experiments.

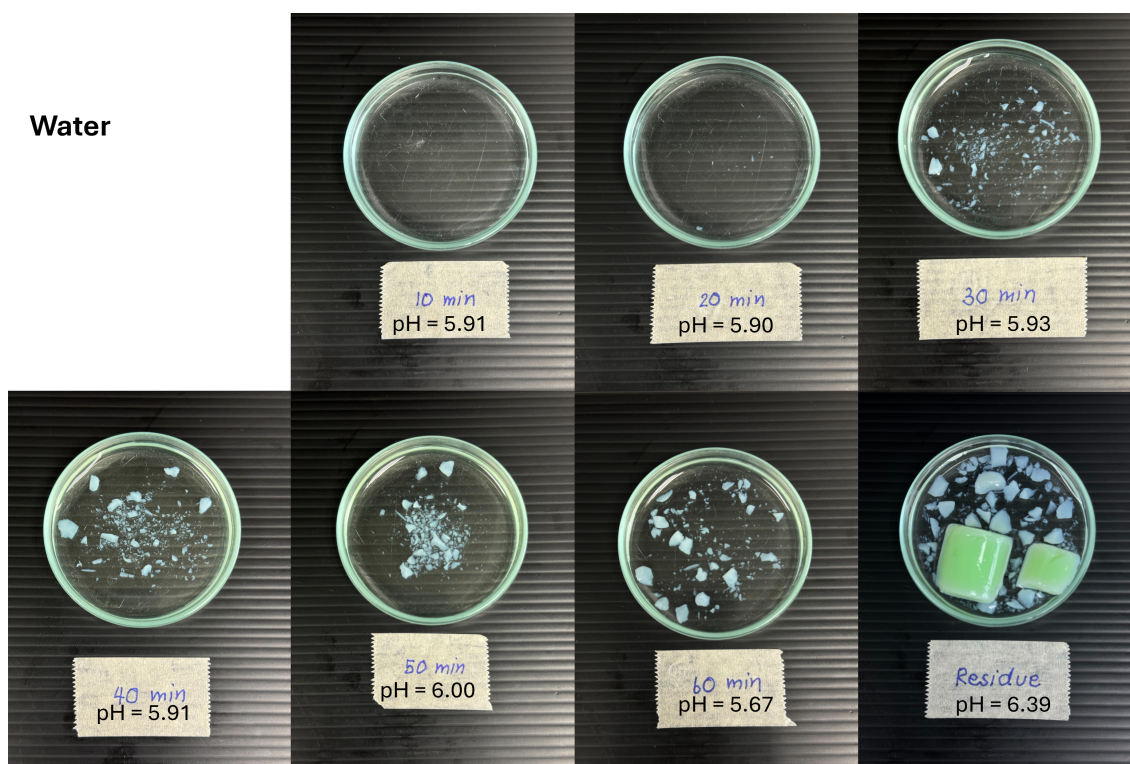


Figure 5.26. Digesta collected under water conditions at different time intervals.

To obtain a quantitative analysis of digestion under different modes, the digesta dry mass ratio was obtained, calculated as the dry mass of the collected digesta divided by the initial dry mass of the starch hydrogel sample. The results are summarised in Figure 5.30, in which Figure 5.30(a) shows the dry mass ratio across different modes, and Figure 5.30(b) shows the dry mass ratio with respect to digesta collection time. The residual content remaining in the stomach compartment after 60 minutes was also measured by rinsing the chamber with water and drying the collected material.

Note that, owing to the natural variability of biomaterials and the complexity of digestion behaviour, the experiments exhibit considerable scatter, as shown by the error bars in Figure 5.30. Such variability is common in dynamic *in vitro* digestion studies. Nevertheless, the overall trends remain clear. From Figure 5.30(a), the enzyme mode (third group) left the smallest amount of residual material in the stomach after 60

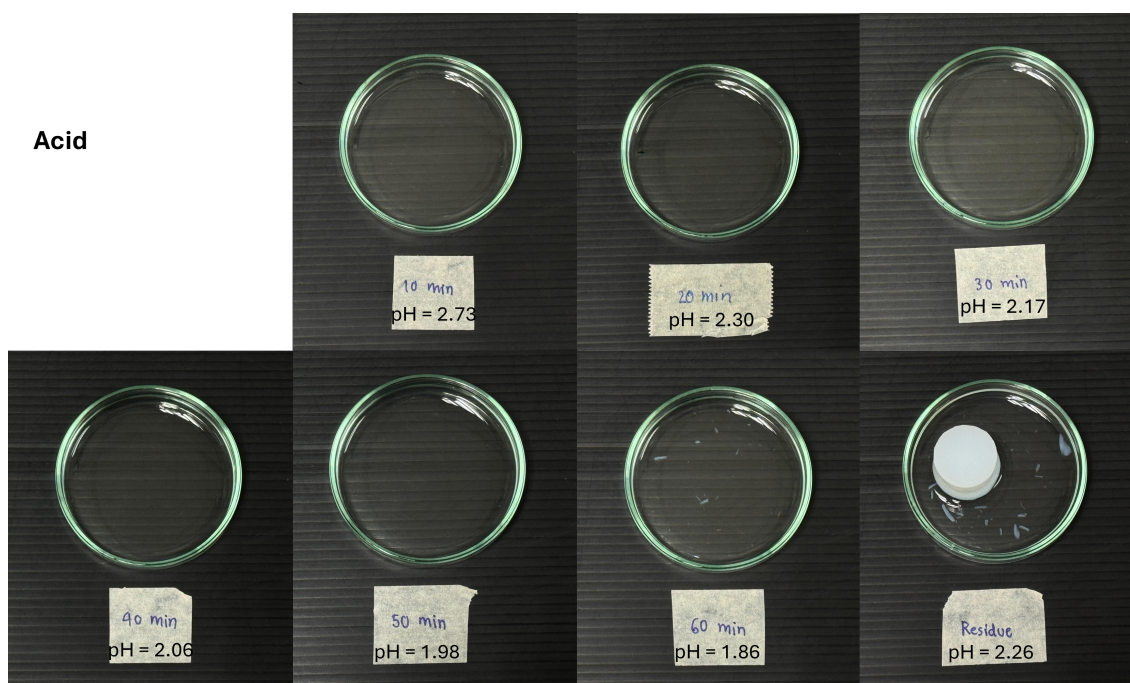


Figure 5.27. Digesta collected under acid conditions at different time intervals.

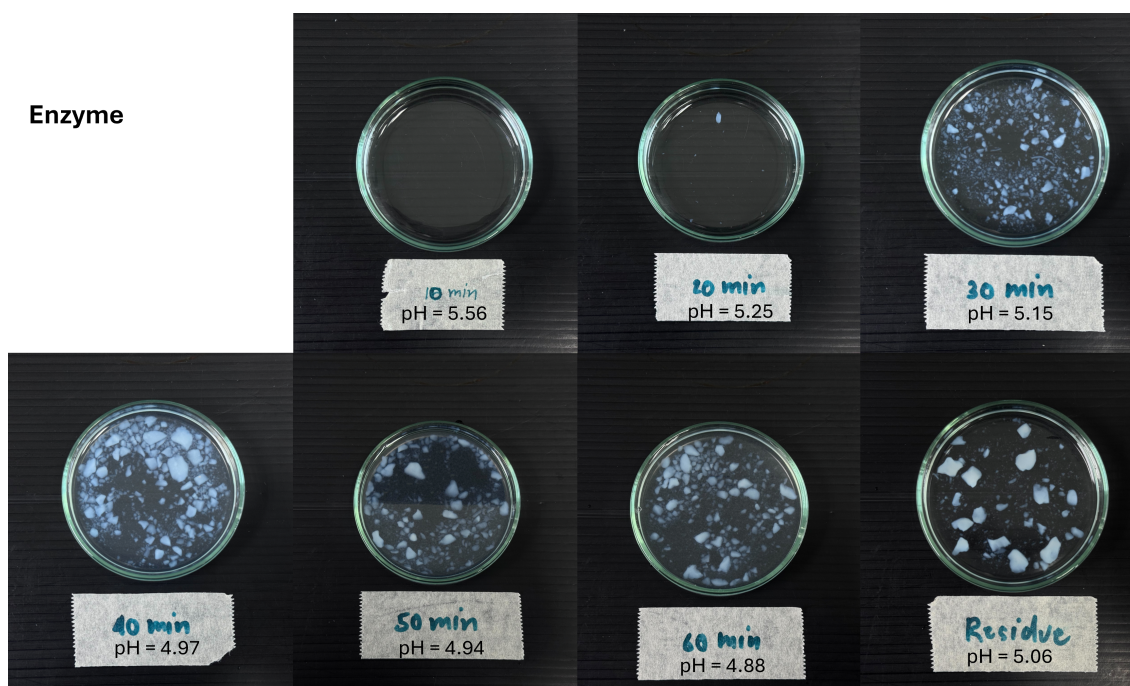


Figure 5.28. Digesta under enzyme conditions at different time intervals.

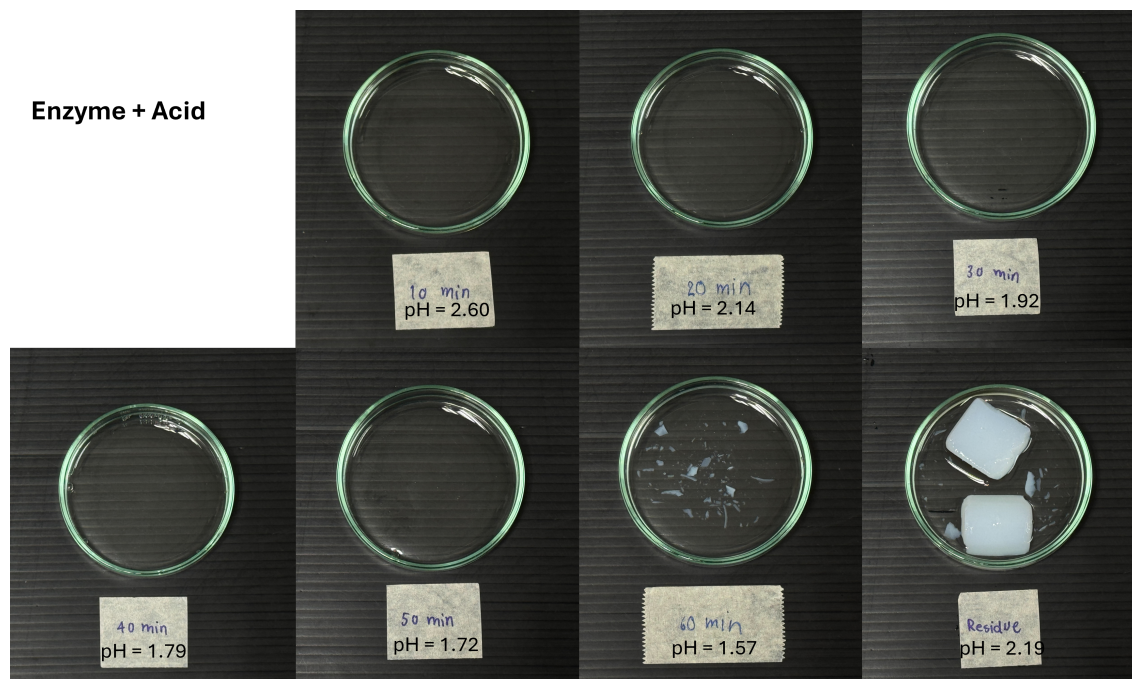


Figure 5.29. Digesta under enzyme and acid conditions at different time intervals.

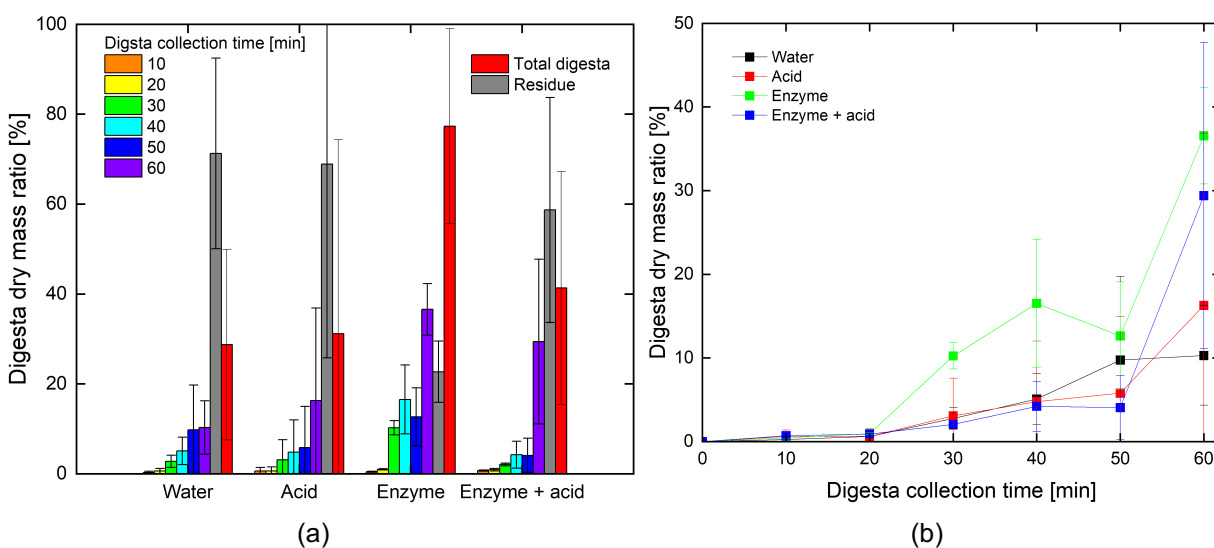


Figure 5.30. (a) Digesta dry mass ratio at different conditions. (b) Digesta dry mass ratio at different collection times.

minutes. Approximately 80% of the hydrogel mass (red bar) was disintegrated and emptied, with only about 20% (grey bar) remaining. In contrast, the other modes left comparable residual masses, typically between 60% and 70%, corresponding to 30–40% emptying. Suppose the digesta obtained in the enzyme mode is assumed to result from both mechanical breakdown and enzymatic hydrolysis, while the water mode reflects predominantly mechanical disintegration. In that case, the relative contributions can be estimated from the emptied dried mass ratio. The enzyme mode produced about 80% digesta, whereas the water mode produced roughly 30%, giving an approximate ratio of chemical to mechanical contributions of about 1:1 to 5:3. It should be noted that the enzyme was not operating at its optimal activity under these conditions; therefore, the chemical contribution may be higher under physiological gastric conditions. [Figure 5.30\(b\)](#) shows that the digesta dry mass ratio generally increased with digestion time for all modes. The enzyme mode (green curve) consistently yielded the highest dry mass ratio at each time point, highlighting the critical role of enzymatic hydrolysis in the breakdown of the starch hydrogel. The other three modes produced similar amounts of digesta up to around 40 minutes. Beyond this point, the acid mode (red curve) and the water mode (black curve) produced less digesta than the acid+enzyme mode (blue curve), which exhibited a marked increase by 60 minutes. Notably, both the water and acid modes still produced, on average, around 10% digesta at 50 and 60 minutes. This indicates that acidic conditions alone have a limited effect on starch hydrogel digestion, whereas mechanical breakdown driven by gastric motility can play a noticeable role. Overall, these *in vitro* observations align with the findings presented in [Chapter 3](#), providing further evidence of the relative contributions of mechanical breakdown, acidic hydrolysis, and enzymatic hydrolysis to the digestion of the starch hydrogel.

5.7 Discussion and conclusion

In this chapter, we performed *in silico* modelling of the gastric digestion of starch hydrogels using the CEL FE method in Abaqus. We first modelled a simplified configuration, in which the stomach and the hydrogel bolus were represented using a pseudo-plane-strain model. The peristaltic wave was prescribed as a boundary condition on the Lagrangian stomach wall, where the nodal displacements were computed from the x -coordinate and the local wall radius based on the analytical description of the wall geometry. The hydrogel bolus was modelled within the Eulerian region, and simulations were performed both with and without gastric fluid to evaluate the influence of solid-fluid interaction. The model was then extended to an anatomically realistic stomach geometry.

Peristaltic waves were applied along a curvilinear coordinate system defined by the centreline of the stomach. The nodal coordinates of the stomach wall were extracted directly from the `.inp` file, and the centreline was generated using the VMTK toolkit with B-spline interpolation. Each wall node was assigned a local curvilinear coordinate and a corresponding radial vector, enabling the peristaltic wave to be imposed as a radial displacement field dependent on s and r . The hydrogel bolus was again represented in the Eulerian domain, with general contact enforcing its interaction with the stomach wall. Finally, dynamic *in vitro* digestion experiments were conducted using the TIMagc simulator. In these experiments, starch hydrogels were exposed to various simulated gastric secretions, including water-only, acid, enzyme, and enzyme + acid conditions, and subject to peristaltic deformation generated by cyclic inflation and deflation of silicone sleeves driven by water pressure. Together, the computational and experimental approaches offer complementary insight into the digestion behaviour of starch hydrogels.

The simulations revealed the coupled roles of mechanical breakdown and enzymatic hydrolysis. In the pseudo-plane-strain model, the presence of gastric fluid altered the deformation pattern of the bolus, leading to pronounced fragmentation that increased the available surface area and enhanced mixing. The simulations showed that the presence of gastric fluid and softer hydrogel materials promoted bolus fragmentation and mixing under peristaltic waves. Similar trends have been reported in the literature, where bolus viscosity was found to influence its breakdown mode. For example, low-viscosity meals tended to generate retropulsive jets and mixing, whereas high-viscosity meals relied more on pressure-driven breakdown and mixing Ferrua and Singh (2010). These findings suggest that peristaltic waves act synergistically with enzymatic hydrolysis during digestion, consistent with the conclusion that mechanical forces are crucial for gastric breakdown. In the anatomically realistic geometry, the material stiffness governed the hydrogel response to peristaltic loading. Under this preliminary modelling setup, the results indicated that undegraded hydrogels, being stiffer, resisted deformation and retropulsion, and were propelled out of the stomach more rapidly. In contrast, degraded or crushed-reformed hydrogels, with substantially reduced stiffness, deformed extensively and remained in the stomach for longer durations, which presented a discrepancy from the subsequent *in vitro* tests and *in vivo* observations. Nevertheless, the results clearly demonstrate that the mechanical properties of the bolus play a significant role in gastric emptying behaviour. When comparing undegraded and chemically degraded hydrogels, the softer degraded hydrogels underwent greater deformation under peristaltic waves. Their increased deformability promoted self-contact, fragmentation, and mixing, which, in turn, facilitated enzymatic access and

accelerated breakdown, showing that enzymatic activity amplified these mechanically driven effects, consistent with the findings of the subsequent *in vitro* experiments.

The dynamic *in vitro* experiments proved these trends. Starch hydrogel produced measurable digesta even in the absence of enzymes, confirming that gastric motility alone can initiate mechanical disintegration. The addition of enzymes markedly increased the rate and extent of digestion, whereas acidic conditions alone produced only limited effects. Based on the digesta dry mass ratios, enzymatic hydrolysis contributed approximately 1 to 1.67 times more to breakdown than mechanical disintegration under the tested conditions, with the relative contribution expected to be even higher under optimal physiological enzyme activity. Overall, these observations highlight the interplay between mechanical forces, hydrogel material properties, and biochemical activity in governing the digestion behaviour of starch hydrogels. The dynamic *in vitro* experiments further supported this view, showing that peristaltic motion plays a key role in mechanical disintegration, while enzymatic hydrolysis subsequently accelerates overall digestion. Both simulations and experiments demonstrate that mechanical forces are essential for initiating digestion, but that gastric fluid and enzymes enhance efficiency and completeness. The material properties of the hydrogel determine the mode of breakdown and the rate of gastric emptying.

Despite the findings gained above, the current study has several limitations. First, the *in silico* model relies on several assumptions and simplifications regarding the hydrogel and gastric fluid properties, boundary conditions, and stomach geometry, any of which may compromise accuracy. For example, in the pseudo-plane-strain model, the pylorus was modelled as constantly closed, and therefore, the emptying was not represented. Meanwhile, in the anatomically realistic model, it was kept permanently open, resulting in a faster emptying rate for stiffer materials, which is inconsistent with experimental observations. In addition, hydrolysis was prescribed rather than coupled to mechanical deformation. As a consequence, the hydrogel behaviour before degradation, after degradation, and after fragmentation was represented as separate cases, without capturing the transitions between these states. Moreover, the omission of damage and fracture, together with the prescribed stomach wall motion that imposes deformation on the hydrogel regardless of its stiffness, led to unrealistically high stress responses. These factors likely contributed to the discrepancies between the simulation results and the experimental observations. Some simulations were also conducted without gastric fluid to improve numerical stability, which, however, reduces physiological realism due to limitations of the CEL method, where leakage of fluid from solid boundaries may occur.

Regarding the dynamic *in vitro* experimental validation, it did not perfectly replicate the numerical conditions, for example, pH, enzyme concentration, temperature, or food composition. In particular, there is a discrepancy in the characteristic digestion timescales. In the simulations, the stable time increment is on the order of 10^{-3} s, according to [Equation 5.10](#) and [Equation 5.11](#). As a result, simulating 24 s of digestion required approximately half an hour of computation using 32 CPUs (AMD Ryzen Threadripper PRO 5975WX). By contrast, the *in vitro* experiments lasted 60 minutes, and typical *in vivo* gastric digestion occurs over 2 to 4 hours (Banks et al., [2025](#); Bellmann et al., [2016](#)). This mismatch arises from computational constraints on feasible simulation times. Bridging this gap will likely require multiscale modelling strategies or improved numerical efficiency, enabling simulated digestion dynamics to more closely approach experimental and physiological timescales.

To address these limitations, several directions should be considered in future work. First, within the *in silico* framework, the development of advanced constitutive models that capture mechanical degradation (damage) and fracture in hydrogels is essential. This could be achieved using continuum damage mechanics or phase-field formulations implemented through a UEL subroutine in Abaqus. Incorporating hydrogel microstructure and polymer chain physics will further enable a more realistic representation of chemo-mechanical coupling during enzymatic degradation. More sophisticated fluid-solid interaction techniques are required to improve the accuracy of flow and contact mechanics and to reduce leakage artefacts. Boundary conditions should also be refined, including physiologically realistic pyloric opening and closing. Ideally, the stomach wall would be represented as an electromechanically driven system rather than as prescribed peristaltic displacements (Brandstaeter et al., [2018](#)), allowing the simulation of anatomically realistic peristaltic waves and pyloric contractions governed by neural and hormonal feedback. In addition, simulating the dynamic *in vitro* digestion apparatus itself would enable closer alignment between numerical and experimental conditions, while further experimental validation would improve the robustness of the predictions. Finally, extending the model to explore a broader range of *in vivo* conditions—including pH, enzyme concentration, temperature, food composition, and inter-individual variability in gastric anatomy and physiology—would enhance its applicability to physiological and clinical contexts.

Chapter 6

Conclusions and Future Work

This thesis addresses the limited understanding of how the material properties of starch hydrogels govern their gastric digestion behaviour. Starch digestion is inherently a coupled mechanical-chemical process involving enzyme diffusion, polymer network degradation, and large-deformation mechanics. Highly processed starch-based foods often exhibit rapid breakdown and gastric emptying, posing challenges for glucose homeostasis. To bridge this knowledge gap, comprehensive *in vitro* experiments were performed to characterise the chemo-mechanical behaviour of starch hydrogels, and an *in silico* framework was developed to simulate their coupled diffusion-reaction-deformation behaviour during digestion, informed and validated by experimental results.

The mechanical behaviour of starch hydrogels prepared under different conditions, including gelatinisation, retrogradation, and water content, was systematically characterised. Microscopy, thermal analysis, and a suite of mechanical tests (compression, tension, rheology, and wire-cutting) were conducted to quantify the influence of these factors on stiffness, viscoelasticity, and fracture behaviour. A mechanistic interpretation is proposed in which gelatinisation forms a polymer matrix, while retrogradation generates crystallites that act as reinforcing fillers. Water content modulates the mechanical response by influencing these structural changes and by plasticising the network. Increased gelatinisation and retrogradation both led to stiffer hydrogels with enhanced energy dissipation, with retrogradation promoting more brittle fracture behaviour. Mechanical tests further showed that starch hydrogels are weaker in tension and shear than in compression, and exhibit rate-dependent fracture consistent with their viscoelastic nature. Overall, these results demonstrate that processing conditions can be used to tailor the mechanical properties of starch hydrogels and, consequently, their digestive behaviour.

The degradation of starch hydrogel mechanical properties during enzymatic hydrolysis was investigated using uniaxial compression tests. Stiffness and strength decreased with increasing hydrolysis time, with more pronounced degradation under neutral pH conditions, consistent with polymer network cleavage by α -amylase. Smaller samples exhibited greater degradation, attributed to a higher effective enzyme volume fraction during diffusion. Complementary diffusion experiments quantified enzyme diffusivity, providing the key reaction-diffusion parameters for subsequent modelling.

A coupled chemo-mechanical hyper-pseudo-viscoelastic constitutive model was developed based on the experimental findings. The gelatinised polymer network was represented as a hyperelastic matrix, while network imperfections accounted for the time-dependent viscoelastic response. Retrogradation-induced crystallites were modelled as reinforcing fillers with pseudoelastic damage. Enzymatic hydrolysis was described as a first-order reaction reducing crosslink density and increasing network imperfections. The model was able to capture the coupled chemo-mechanical behaviour of starch hydrogels during enzymatic hydrolysis.

The constitutive model was implemented within the FEM framework via user-defined subroutines and inversely calibrated and validated against *in vitro* experiments of coupled diffusion-reaction-deformation processes. Simulations indicated that diffusion generates a non-uniform enzyme concentration field, leading to spatially heterogeneous degradation and the observed size dependence of hydrogel's mechanical behaviour. The constitutive model was implemented within a fluid-structure interaction framework using the CEL method to simulate gastric peristalsis in both simplified and anatomically realistic stomach geometries. In the simplified model, fluid motion was incorporated, and simulations indicated that gastric fluid enhanced bolus deformation, fragmentation, and mixing, thereby increasing the available surface area. In the anatomically realistic model, fluid motion was not explicitly considered. Instead, different degrees of prior material degradation were used to represent stages of enzymatic hydrolysis. These simulations showed that increased degradation led to greater bolus deformability and altered transport and emptying behaviour under peristaltic loading. The proposed simulation framework therefore offers an intuitive and quantitative tool for visualising digestion mechanisms that are otherwise difficult to access experimentally. Complementary dynamic *in vitro* experiments were conducted using a gastric simulator to replicate stomach conditions. Although some discrepancies between *in vitro* and *in vivo* environments were observed, both approaches indicate that increasing deformability of the bolus due to enzymatic hydrolysis promotes fragmentation and breakdown.

Despite the advances presented in this thesis, several limitations remain that could be addressed in future work. Experimentally, although the roles of amylose and amylopectin in determining mechanical and digestive properties were acknowledged, this thesis focused on wheat starch with a fixed amylose content. Future work could examine starches with a broader range of amylose-to-amylopectin ratios to clarify their individual contributions. In diffusion experiments, enzyme diffusivity was measured under alkaline conditions at room temperature, and the current diffusion model assumes a constant diffusivity that remains unchanged during hydrogel degradation. Future studies should explore enzyme diffusion under physiologically relevant conditions (acidic pH, body temperature) and incorporate degradation-dependent diffusivity. Regarding the constitutive framework, mass loss and shrinkage during enzymatic hydrolysis were not explicitly modelled, which may influence predictions. The energy functions and reaction kinetics employed were phenomenological rather than micromechanical, limiting direct links to microstructure. Future developments could incorporate mass transport, volume change, and polymer chain statistics to enhance predictive capability. For the gastric digestion simulation, several physiological aspects were simplified. The current CEL framework did not include full FSI coupling in three-dimensional simulations. Hydrogel failure behaviour and the transition from an intact sample to a bolus state were handled separately rather than unified within one simulation pipeline. Future work should aim to integrate full FSI, failure mechanics and bolus formation into a unified simulation environment to better represent *in vivo* digestion. Finally, more extensive validation against dynamic *in vitro* and *in vivo* digestion data, closely matched to simulation conditions, will be performed to further validate and refine the numerical framework.

Overall, this thesis establishes a robust foundation for modelling the chemo-mechanical response of starch hydrogels during gastric digestion. The combined experimental and numerical approach provides valuable insights into the interplay of enzymatic degradation, mechanical behaviour, and digestive conditions. With further refinement and extension, the proposed framework offers significant potential to inform the rational design of starch-based foods, hydrogels, and drug-delivery systems with tailored digestive properties.

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Appendices

A.1 Subroutines for gastric digestion simulation

```
1  !=====!  
2  !      Module to store node data from VEXTERNALDB to be used in VDISP  
3  !=====!  
4      module node_data  
5          implicit none  
6          integer nNodes  
7          real(kind=8) :: S_centerline  
8          integer, allocatable :: node_id(:)  
9          real(kind=8), allocatable :: Natural_coord(:)  
10         real(kind=8), allocatable :: Radius_vec(:, :)  
11         integer, allocatable :: global_to_local(:)  
12     end module node_data  
13 !=====!  
14  
15  
16 !!=====!  
17 !!=====!  
18 !!      Mathematical utilities used in ABAQUS subroutines  
19 !!=====!  
20 !!=====!  
21     MODULE MODULE_MATHS  
22     IMPLICIT NONE  
23  
24     !!-----!  
25     !! Global parameters  
26     !!-----!  
27     REAL(KIND=8), PARAMETER :: ZERO=0.D0, ONE=1.D0, TWO=2.D0,  
28     + THREE=3.D0, FOUR=4.D0, FIVE=5.D0, SIX=6.D0,  
29     + SEVEN=7.D0, EIGHT=8.D0, NINE=9.D0, HALF=1.D0/2.D0,  
30     + THIRD=1.D0/3.D0, TWOTHIRDS=2.D0/3.D0,  
31     + FOURTHIRDS=4.D0/3.D0, FIVETHIRDS=5.D0/3.D0
```



```

32     REAL(KIND=8), PARAMETER :: IDEN(3,3)= reshape(
33 + (/ ONE, ZERO, ZERO,
34 +     ZERO, ONE, ZERO,
35 +     ZERO, ZERO, ONE /),
36 + (/ 3, 3 /) )
37     CHARACTER*256 :: FILENAME=''
38     INTEGER :: NCALL=0 , DWRITE=10000
39     !-----!
40     !   Material Parameters
41     !-----!
42     REAL(KIND=8), PARAMETER ::
43     !-----!
44     ! Hyperelastic parameters
45     !-----!
46 + a                                = 6.7451D-09 ,
47 + b                                = 1.3808D-10 ,
48 + c                                = 2.9515D-02 ,
49     ! bulk modulus
50 + K_bulk                          = 2.D0          ,
51     !-----!
52     ! Viscoelastic parameters
53     !-----!
54 + c3_NeoHook                      = 6.5864D-04 ,
55 + TAU3_NeoHook                    = 1.8864D+01 ,
56 + c4_NeoHook                      = 1.3407D-02 ,
57 + TAU4_NeoHook                    = 2.2744D+00 ,
58     !-----!
59     ! Pseudoelastic parameters
60     !-----!
61 + cs1_soften                      = 7.6098D-03 ,
62 + cs2_soften                      = 2.0047D-02 ,
63 + cs3_soften                      = 6.1987D-03 ,
64 + R_soften                        = 1.1299D+00 ,
65 + M1_soften                      = 4.7823D-05 ,
66 + M2_soften                      = 1.5106D+00 ,
67     !-----!
68     ! Diffusion parameters
69     !-----!
70 + cond                            = 8.6D-5        ,
71 + specHeat                        = 1.D9          ,
72     !-----!
73     ! Enzymatic reaction parameters
74     !-----!

```

```

75 + r_enz_ini           = 1.0817D+01 ,
76 + Ke                 = 7.6200D-08 ,
77 + Ks                 = 1.7501D-01 ,
78 + Conc_starch_ini    = 0.2D+00
79
80 CONTAINS
81
82 ! -----!
83 ! Functions
84 ! -----!
85
86 ! =====!
87 FUNCTION DET_TEN2_(A) RESULT(DET)
88 ! -----!
89     IMPLICIT NONE
90     REAL(KIND=8), INTENT(IN) :: A(3,3)
91     REAL(KIND=8) :: DET
92     DET =
93 +     A(1,1)*A(2,2)*A(3,3)+A(1,2)*A(2,3)*A(3,1)+A(1,3)*A(2,1)*A(3,2)
94 +     -A(3,1)*A(2,2)*A(1,3)-A(3,2)*A(2,3)*A(1,1)-A(3,3)*A(2,1)*A(1,2)
95 END FUNCTION DET_TEN2_
96 ! -----!
97
98 ! =====!
99 FUNCTION TR_TEN2_(A) RESULT(TRACE)
100 ! -----!
101     IMPLICIT NONE
102     REAL(KIND=8), INTENT(IN) :: A(3,3)
103     REAL(KIND=8) :: TRACE
104     TRACE = A(1,1)+A(2,2)+A(3,3)
105 END FUNCTION TR_TEN2_
106 ! -----!
107
108 ! =====!
109 FUNCTION NORM_TEN2_(A) RESULT(NORM)
110 ! -----!
111     IMPLICIT NONE
112     REAL(KIND=8), INTENT(IN) :: A(3,3)
113     REAL(KIND=8) :: NORM
114     NORM = SQRT(SUM(A**2))
115 END FUNCTION NORM_TEN2_
116 ! -----!
117

```

```

118      !=====!
119      FUNCTION TRANS_TEN2_(A) RESULT(TRANS)
120      !-----!
121      IMPLICIT NONE
122      REAL(KIND=8), INTENT(IN) :: A(3,3)
123      REAL(KIND=8) :: TRANS(3,3)
124      INTEGER :: I,J
125      DO I = 1, 3
126          TRANS(I, I) = A(I, I)
127      END DO
128      DO I = 1, 2
129          DO J = I + 1, 3
130              TRANS(I, J) = A(J, I)
131              TRANS(J, I) = A(I, J)
132          END DO
133      END DO
134      END FUNCTION TRANS_TEN2_
135      !-----!
136
137      !=====!
138      FUNCTION COFAC_TEN2_(A) RESULT(COFAC)
139      !-----!
140      IMPLICIT NONE
141      REAL(KIND=8), INTENT(IN) :: A(3,3)
142      REAL(KIND=8) :: COFAC(3,3)
143      COFAC(1,1) =  A(2,2)*A(3,3) - A(3,2)*A(2,3)
144      COFAC(1,2) = -(A(2,1)*A(3,3) - A(3,1)*A(2,3))
145      COFAC(1,3) =  A(2,1)*A(3,2) - A(3,1)*A(2,2)
146      COFAC(2,1) = -(A(1,2)*A(3,3) - A(3,2)*A(1,3))
147      COFAC(2,2) =  A(1,1)*A(3,3) - A(3,1)*A(1,3)
148      COFAC(2,3) = -(A(1,1)*A(3,2) - A(3,1)*A(1,2))
149      COFAC(3,1) =  A(1,2)*A(2,3) - A(2,2)*A(1,3)
150      COFAC(3,2) = -(A(1,1)*A(2,3) - A(2,1)*A(1,3))
151      COFAC(3,3) =  A(1,1)*A(2,2) - A(2,1)*A(1,2)
152      END FUNCTION COFAC_TEN2_
153      !-----!
154
155      !=====!
156      FUNCTION INV_TEN2_(A) RESULT(INV)
157      !-----!
158      IMPLICIT NONE
159      REAL(KIND=8), INTENT(IN) :: A(3,3)
160      REAL(KIND=8) :: DET, COFAC(3,3)

```

```

161     REAL(KIND=8) :: INV(3,3)
162     INTEGER :: I,J
163     DET = DET_TEN2_(A)
164     IF ((DET .LT. 1.0D-10) .AND. (NCALL .GT. 1)) THEN
165         WRITE(6,*) 'FUNCTION INV_TEN2_ ERROR'
166         WRITE(6,*) 'NCALL = ', NCALL
167         WRITE(6,*) 'DET = ', DET
168     END IF
169     COFAC = COFAC_TEN2_(A)
170     DO I = 1,3
171         DO J = 1,3
172             INV(I,J) = COFAC(J,I)/DET
173         ENDDO
174     ENDDO
175     END FUNCTION INV_TEN2_
176     !-----!
177
178     !=====!
179     FUNCTION DBLCTRC_42_(TEN, MAT) RESULT(MATOUT)
180     !-----!
181     IMPLICIT NONE
182     REAL(KIND=8), INTENT(IN) :: TEN(3,3,3,3), MAT(3,3)
183     REAL(KIND=8) :: MATOUT(3,3)
184     INTEGER :: I, J, K, L
185     REAL(KIND=8) :: SUM
186     DO I = 1, 3
187         DO J = 1, 3
188             SUM = ZERO
189             DO K = 1, 3
190                 DO L = 1, 3
191                     SUM = SUM + TEN(I,J,K,L) * MAT(K,L)
192                 ENDDO
193             ENDDO
194             MATOUT(I,J) = SUM
195         ENDDO
196     ENDDO
197     END FUNCTION DBLCTRC_42_
198     !-----!
199
200     !=====!
201     FUNCTION PROGTEN_(IDEN, C_INV, C_1) RESULT(PPROJ)
202     !-----!
203     IMPLICIT NONE

```

```

204     REAL(KIND=8), INTENT(IN) :: IDEN(3, 3), C_INV(3, 3), C_1(3, 3)
205     REAL(KIND=8) :: PPROJ(3, 3, 3, 3)
206     INTEGER :: I, J, K, L
207     PPROJ = ZERO
208     DO I = 1, 3
209         DO J = 1, 3
210             DO K = 1, 3
211                 DO L = 1, 3
212                     PPROJ(I,J,K,L) =
213 +                     HALF*((IDEN(I,K)*IDEN(J,L))+ (IDEN(I,L)*IDEN(J,K)))
214 +                     - THIRD*(C_INV(I,J)*C_1(K,L))
215                 ENDDO
216             ENDDO
217         ENDDO
218     ENDDO
219 END FUNCTION PROGTE_
220 ! -----!
221
222 ! =====!
223 FUNCTION V_VecToMat_TEN2_(Vec, NTENS) RESULT(Mat)
224 ! -----!
225     IMPLICIT NONE
226     INTEGER, INTENT(IN) :: NTENS
227     REAL(KIND=8), INTENT(IN) :: Vec(NTENS)
228     REAL(KIND=8) :: Mat(3,3)
229     SELECT CASE (NTENS)
230     CASE (6)
231         Mat(1,1) = Vec(1)
232         Mat(2,2) = Vec(2)
233         Mat(3,3) = Vec(3)
234         Mat(1,2) = Vec(4)
235         Mat(2,1) = Vec(4)
236         Mat(2,3) = Vec(5)
237         Mat(3,2) = Vec(5)
238         Mat(3,1) = Vec(6)
239         Mat(1,3) = Vec(6)
240     CASE (4)
241         Mat(1,1) = Vec(1)
242         Mat(2,2) = Vec(2)
243         Mat(3,3) = Vec(3)
244         Mat(1,2) = Vec(4)
245         Mat(2,1) = Vec(4)
246         Mat(2,3) = ZERO

```

```

247     Mat(3,2) = ZERO
248     Mat(1,3) = ZERO
249     Mat(3,1) = ZERO
250     CASE DEFAULT
251         WRITE(6,*) 'FUNCTION V_VecToMat_TEN2_ ERROR'
252         WRITE(6,*) 'NTENS = ', NTENS
253         WRITE(6,*) 'Should be 4 or 6'
254         CALL XPLB_ABQERR(-2,'NTENS incorrect! See .log',0,ZERO,' ')
255         CALL XPLB_EXIT
256     END SELECT
257 END FUNCTION V_VecToMat_TEN2_
258 !-----!
259
260 !=====!
261 FUNCTION V_NonsymVecToMat_TEN2_(Vec, NTENS) RESULT(Mat)
262 !-----!
263     IMPLICIT NONE
264     INTEGER, INTENT(IN) :: NTENS
265     REAL(KIND=8), INTENT(IN) :: Vec(NTENS)
266     REAL(KIND=8) Mat(3,3)
267     SELECT CASE (NTENS)
268     CASE (9)
269         Mat(1,1) = Vec(1)
270         Mat(2,2) = Vec(2)
271         Mat(3,3) = Vec(3)
272         Mat(1,2) = Vec(4)
273         Mat(2,3) = Vec(5)
274         Mat(3,1) = Vec(6)
275         Mat(2,1) = Vec(7)
276         Mat(3,2) = Vec(8)
277         Mat(1,3) = Vec(9)
278     CASE (5)
279         Mat(1,1) = Vec(1)
280         Mat(2,2) = Vec(2)
281         Mat(3,3) = Vec(3)
282         Mat(1,2) = Vec(4)
283         Mat(2,1) = Vec(5)
284         Mat(2,3) = ZERO
285         Mat(3,2) = ZERO
286         Mat(1,3) = ZERO
287         Mat(3,1) = ZERO
288     CASE DEFAULT
289         WRITE(6,*) 'FUNCTION V_NonsymVecToMat_TEN2_ ERROR'

```

```

290      WRITE(6,*) 'NTENS = ', NTENS
291      WRITE(6,*) 'Should be 5 or 9'
292      CALL XPLB_ABQERR(-2,'NTENS incorrect! See .log',0,ZERO,' ')
293      CALL XPLB_EXIT
294  END SELECT
295  END FUNCTION V_NonsymVecToMat_TEN2_
296  !-----!
297
298  !=====!
299  FUNCTION V_MatToVec_TEN2_(Mat, NTENS) RESULT(Vec)
300  !-----!
301  IMPLICIT NONE
302  INTEGER, INTENT(IN) :: NTENS
303  REAL(KIND=8), INTENT(IN) :: Mat(3,3)
304  REAL(KIND=8) :: Vec(NTENS)
305  SELECT CASE (NTENS)
306  CASE (6)
307      Vec(1) = Mat(1,1)
308      Vec(2) = Mat(2,2)
309      Vec(3) = Mat(3,3)
310      Vec(4) = Mat(1,2)
311      Vec(5) = Mat(2,3)
312      Vec(6) = Mat(3,1)
313  CASE (4)
314      Vec(1) = Mat(1,1)
315      Vec(2) = Mat(2,2)
316      Vec(3) = Mat(3,3)
317      Vec(4) = Mat(1,2)
318  CASE DEFAULT
319      WRITE(6,*) 'FUNCTION V_MatToVec_TEN2_ ERROR'
320      WRITE(6,*) 'NTENS = ', NTENS
321      WRITE(6,*) 'Should be 4 or 6'
322      CALL XPLB_ABQERR(-2,'NTENS incorrect! See .log',0,ZERO,' ')
323      CALL XPLB_EXIT
324  END SELECT
325  END FUNCTION V_MatToVec_TEN2_
326  !-----!
327
328  !=====!
329  FUNCTION V_TenToMat_TEN2_(Ten, NTENS) RESULT(Mat)
330  !-----!
331  IMPLICIT NONE
332  INTEGER, INTENT(IN) :: NTENS

```

```

333     REAL(KIND=8), INTENT(IN) :: Ten(3,3,3,3)
334     REAL(KIND=8) :: Mat(NTENS,NTENS)
335     IF (NTENS.EQ.6) THEN
336         Mat(1,1) = Ten(1,1,1,1)
337         Mat(1,2) = Ten(1,1,2,2)
338         Mat(1,3) = Ten(1,1,3,3)
339         Mat(1,4) = Ten(1,1,1,2)
340         Mat(1,5) = Ten(1,1,2,3)
341         Mat(1,6) = Ten(1,1,3,1)
342         Mat(2,1) = Ten(2,2,1,1)
343         Mat(2,2) = Ten(2,2,2,2)
344         Mat(2,3) = Ten(2,2,3,3)
345         Mat(2,4) = Ten(2,2,1,2)
346         Mat(2,5) = Ten(2,2,2,3)
347         Mat(2,6) = Ten(2,2,3,1)
348         Mat(3,1) = Ten(3,3,1,1)
349         Mat(3,2) = Ten(3,3,2,2)
350         Mat(3,3) = Ten(3,3,3,3)
351         Mat(3,4) = Ten(3,3,1,2)
352         Mat(3,5) = Ten(3,3,2,3)
353         Mat(3,6) = Ten(3,3,3,1)
354         Mat(4,1) = Ten(1,2,1,1)
355         Mat(4,2) = Ten(1,2,2,2)
356         Mat(4,3) = Ten(1,2,3,3)
357         Mat(4,4) = Ten(1,2,1,2)
358         Mat(4,5) = Ten(1,2,2,3)
359         Mat(4,6) = Ten(1,2,3,1)
360         Mat(5,1) = Ten(2,3,1,1)
361         Mat(5,2) = Ten(2,3,2,2)
362         Mat(5,3) = Ten(2,3,3,3)
363         Mat(5,4) = Ten(2,3,1,2)
364         Mat(5,5) = Ten(2,3,2,3)
365         Mat(5,6) = Ten(2,3,3,1)
366         Mat(6,1) = Ten(3,1,1,1)
367         Mat(6,2) = Ten(3,1,2,2)
368         Mat(6,3) = Ten(3,1,3,3)
369         Mat(6,4) = Ten(3,1,1,2)
370         Mat(6,5) = Ten(3,1,2,3)
371         Mat(6,6) = Ten(3,1,3,1)
372     ELSE IF (NTENS.EQ.4) THEN
373         Mat(1,1) = Ten(1,1,1,1)
374         Mat(1,2) = Ten(1,1,2,2)
375         Mat(1,3) = Ten(1,1,3,3)

```



```

376      Mat(1,4) = Ten(1,1,1,2)
377      Mat(2,1) = Ten(2,2,1,1)
378      Mat(2,2) = Ten(2,2,2,2)
379      Mat(2,3) = Ten(2,2,3,3)
380      Mat(2,4) = Ten(2,2,1,2)
381      Mat(3,1) = Ten(3,3,1,1)
382      Mat(3,2) = Ten(3,3,2,2)
383      Mat(3,3) = Ten(3,3,3,3)
384      Mat(3,4) = Ten(3,3,1,2)
385      Mat(4,1) = Ten(1,2,1,1)
386      Mat(4,2) = Ten(1,2,2,2)
387      Mat(4,3) = Ten(1,2,3,3)
388      Mat(4,4) = Ten(1,2,1,2)
389      ELSE
390          WRITE(6,*) 'FUNCTION V_TenToMat_TEN2_ ERROR'
391          WRITE(6,*) 'NTENS = ', NTENS
392          WRITE(6,*) 'Should be 4 or 6'
393          CALL XPLB_ABQERR(-2,'NTENS incorrect! See .log',0,ZERO,' ')
394          CALL XPLB_EXIT
395      END IF
396  END FUNCTION V_TenToMat_TEN2_
397  !-----!
398
399
400  !-----!
401  ! Subroutines
402  !-----!
403
404  !=====!
405  SUBROUTINE Write_VoigtVec(UNIT, Vec, NTENS)
406  !-----!
407      IMPLICIT NONE
408      INTEGER, INTENT(IN) :: NTENS
409      INTEGER, INTENT(IN) :: UNIT
410      REAL(KIND=8), INTENT(IN) :: Vec(NTENS)
411      INTEGER :: I
412      WRITE(UNIT, '(6(E12.4,1x))') (Vec(I), I = 1, NTENS)
413  END SUBROUTINE Write_VoigtVec
414  !-----!
415
416  !=====!
417  SUBROUTINE Write_Mat(UNIT, Mat)
418  !-----!

```

```

419     IMPLICIT NONE
420     INTEGER, INTENT(IN) :: UNIT
421     REAL(KIND=8), INTENT(IN) :: Mat(3,3)
422     INTEGER :: I, J
423     DO I = 1, 3
424         WRITE(UNIT, '(3(E12.4,1x))') (Mat(I, J), J = 1, 3)
425     END DO
426 END SUBROUTINE Write_Mat
427 !-----!
428
429 !=====!
430 SUBROUTINE Write_V_Ten4Voigt(UNIT, Ten_4)
431 !-----!
432     IMPLICIT NONE
433     INTEGER, INTENT(IN) :: UNIT
434     REAL(KIND=8), INTENT(IN) :: Ten_4(3,3,3,3)
435     WRITE(UNIT, '(9(E12.2,1x))')
436 + Ten_4(1,1,1,1), Ten_4(1,1,2,2), Ten_4(1,1,3,3),
437 + Ten_4(1,1,1,2), Ten_4(1,1,2,3), Ten_4(1,1,3,1),
438 + Ten_4(1,1,2,1), Ten_4(1,1,3,2), Ten_4(1,1,1,3)
439     WRITE(UNIT, '(9(E12.2,1x))')
440 + Ten_4(2,2,1,1), Ten_4(2,2,2,2), Ten_4(2,2,3,3),
441 + Ten_4(2,2,1,2), Ten_4(2,2,2,3), Ten_4(2,2,3,1),
442 + Ten_4(2,2,2,1), Ten_4(2,2,3,2), Ten_4(2,2,1,3)
443     WRITE(UNIT, '(9(E12.2,1x))')
444 + Ten_4(3,3,1,1), Ten_4(3,3,2,2), Ten_4(3,3,3,3),
445 + Ten_4(3,3,1,2), Ten_4(3,3,2,3), Ten_4(3,3,3,1),
446 + Ten_4(3,3,2,1), Ten_4(3,3,3,2), Ten_4(3,3,1,3)
447     WRITE(UNIT, '(9(E12.2,1x))')
448 + Ten_4(1,2,1,1), Ten_4(1,2,2,2), Ten_4(1,2,3,3),
449 + Ten_4(1,2,1,2), Ten_4(1,2,2,3), Ten_4(1,2,3,1),
450 + Ten_4(1,2,2,1), Ten_4(1,2,3,2), Ten_4(1,2,1,3)
451     WRITE(UNIT, '(9(E12.2,1x))')
452 + Ten_4(2,3,1,1), Ten_4(2,3,2,2), Ten_4(2,3,3,3),
453 + Ten_4(2,3,1,2), Ten_4(2,3,2,3), Ten_4(2,3,3,1),
454 + Ten_4(2,3,2,1), Ten_4(2,3,3,2), Ten_4(2,3,1,3)
455     WRITE(UNIT, '(9(E12.2,1x))')
456 + Ten_4(3,1,1,1), Ten_4(3,1,2,2), Ten_4(3,1,3,3),
457 + Ten_4(3,1,1,2), Ten_4(3,1,2,3), Ten_4(3,1,3,1),
458 + Ten_4(3,1,2,1), Ten_4(3,1,3,2), Ten_4(3,1,1,3)
459     WRITE(UNIT, '(9(E12.2,1x))')
460 + Ten_4(2,1,1,1), Ten_4(2,1,2,2), Ten_4(2,1,3,3),
461 + Ten_4(2,1,1,2), Ten_4(2,1,2,3), Ten_4(2,1,3,1),

```

```

462 + Ten_4(2,1,2,1), Ten_4(2,1,3,2), Ten_4(2,1,1,3)
463 WRITE(UNIT, '(9(E12.2,1x))')
464 + Ten_4(3,2,1,1), Ten_4(3,2,2,2), Ten_4(3,2,3,3),
465 + Ten_4(3,2,1,2), Ten_4(3,2,2,3), Ten_4(3,2,3,1),
466 + Ten_4(3,2,2,1), Ten_4(3,2,3,2), Ten_4(3,2,1,3)
467 WRITE(UNIT, '(9(E12.2,1x))')
468 + Ten_4(1,3,1,1), Ten_4(1,3,2,2), Ten_4(1,3,3,3),
469 + Ten_4(1,3,1,2), Ten_4(1,3,2,3), Ten_4(1,3,3,1),
470 + Ten_4(1,3,2,1), Ten_4(1,3,3,2), Ten_4(1,3,1,3)
471 END SUBROUTINE Write_V_Ten4Voigt
472 !-----!
473 !!=====
474 !!=====
475 END MODULE MODULE_MATHS
476 !!=====
477 !!=====
478
479
480
481
482 !!=====
483 !!=====
484 !! STATE VARIABLE INITIALISATION SUBROUTINE
485 !!=====
486 !!=====
487 SUBROUTINE VSDVINI(
488 ! Read only -
489 + nblock, jElem, nIntPt, nLayer, nSectPt,
490 + ndim, nstatev, cmname, coordMp, charLength,
491 ! Write only (modifiable) -
492 + stateIni )
493 !-----!
494 ! Declaration
495 !-----!
496 USE MODULE_MATHS
497 include 'vaba_param.inc'
498 ! Read only arguments
499 INTEGER, INTENT(IN) :: nblock, jElem(nblock), nIntPt, nLayer,
500 + nSectPt, ndim, nStateV
501 REAL(KIND=8), INTENT(IN) ::
502 + charLength(nblock), coordMp(nblock,ndim)
503 CHARACTER*80, INTENT(IN) :: cMName
504 ! Write only arguments

```

```

505     REAL(KIND=8), INTENT(OUT) :: stateIni(nblock,nStateV)
506     ! Local variables
507     INTEGER km, ntens
508     !-----!
509     ! Initialisation
510     !-----!
511     ntens = ndim * 2
512     DO km = 1,nblock
513         ! Viscoelastic internal variables
514         stateIni(km,ntens*0+1:ntens*1) = V_MatToVec_TEN2_(Iden,ntens)
515         stateIni(km,ntens*1+1:ntens*2) = V_MatToVec_TEN2_(Iden,ntens)
516         ! Pseudoelasticity internal variables
517         stateIni(km,ntens*2+1)          = ONE
518         stateIni(km,ntens*2+2)          = THREE
519         ! Reaction parameters
520         stateIni(km,ntens*2+3)          = ONE
521         stateIni(km,ntens*2+4)          = ZERO
522         stateIni(km,ntens*2+5)          = r_enz_ini
523         ! First Piola-Kirchhoff stress tensor
524         stateIni(km,ntens*2+6)          = ZERO
525         stateIni(km,ntens*2+7)          = ZERO
526         stateIni(km,ntens*2+8)          = ZERO
527     END DO
528     !!=====
529     !!=====
530     END SUBROUTINE VSDVINI
531     !!=====
532     !!=====
533
534
535
536
537     !!=====
538     !!=====
539     !!    VUMAT MATERIAL SUBROUTINE
540     !!=====
541     !!=====
542     SUBROUTINE VUMAT(
543         ! Read only (unmodifiable)variables -
544         + nblock, ndir, nshr, nstatev, nfieldv, nprops, jInfoArray,
545         + stepTime, totalTime, dtArray, cmname, coordMp, charLength,
546         + props, density, strainInc, relSpinInc,
547         + tempOld, stretchOld, defgradOld, fieldOld,

```

```

548 + stressOld, stateOld, enerInternOld, enerInelasOld,
549 + tempNew, stretchNew, defgradNew, fieldNew,
550 ! Write only (modifiable) variables -
551 + stressNew, stateNew, enerInternNew, enerInelasNew )
552 !!-----!
553 !! Variables dDeclaration
554 !!-----!
555 USE MODULE_MATHS
556 INCLUDE 'vaba_param.inc'
557 !-----!
558 ! Abaqus/Explicit variables
559 INTEGER, INTENT(IN) :: nblock,ndir,nshr,nstatev,nfieldv,nprops,
560 + jInfoArray(*)
561 REAL(KIND=8), INTENT(IN) :: stepTime, totalTime,
562 + dtArray(2*(nblock)+1), density(nblock), coordMp(nblock,*),
563 + charLength(nblock), props(nprops),
564 + strainInc(nblock,ndir+nshr), relSpinInc(nblock,nshr),
565 + tempOld(nblock), stretchOld(nblock,ndir+nshr),
566 + defgradOld(nblock,ndir+nshr+nshr),
567 + fieldOld(nblock,nfieldv), stressOld(nblock,ndir+nshr),
568 + stateOld(nblock,nstatev),
569 + tempNew(nblock),
570 + stretchNew(nblock,ndir+nshr),
571 + defgradNew(nblock,ndir+nshr+nshr),
572 + fieldNew(nblock,nfieldv)
573 CHARACTER*80, INTENT(IN) :: cmname
574 REAL(KIND=8), INTENT(OUT) :: stressNew(nblock,ndir+nshr),
575 + stateNew(nblock,nstatev)
576 !-----!
577 ! User-defined variables
578 INTEGER km, ntens, ntens_nsym
579 REAL(KIND=8) DT,
580 + detF,
581 + I1_bar,I2_bar,
582 + I1_bar_mx_0,I1_bar_mx,
583 + ZETA_0,ZETA,
584 + p_hydro
585 REAL(KIND=8), DIMENSION(3,3)::
586 + F_1,U_1,R_1,
587 + F_bar,F_bar_inv,
588 + C_1,C_inv,C_bar,
589 + Cv3_0,Cv4_0,
590 + Cv3,Cv4,

```

```

591 + S_bar ,
592 + S_bar_EQ ,
593 + S_bar_NEQ_v3,S_bar_NEQ_v4 ,
594 + S_bar_NEQ_s ,
595 + S_iso, S_vol, S_1, Sigma, Sigma_tilde
596 REAL(KIND=8), DIMENSION(3,3,3,3)::
597 + PProj
598   ! Chemical reaction variables
599 REAL(KIND=8) r_enz ,
600 + frac_starchOld, frac_starchNew,
601 + Conc_starch ,
602 + Conc_enz , Conc_enz_eff
603
604 !!-----!
605 !!   Constants Assignment
606 !!-----!
607 NCALL = NCALL + 1
608 ntens      = ndir+nshr
609 ntens_nsym = ndir+nshr+nshr
610 DT         = dtArray(1)
611
612 !!-----!
613 !!   LOOP OVER NBLOCKS OF ELEMENTS
614 !!-----!
615 DO km = 1,nblock
616   !!=====
617   !! Passed in variables
618   !! Inherit state/internal variables at the beginning of time step
619   !!=====
620 F_1   = V_NonsymVecToMat_TEN2_(
621 +      defgradNew(km,1:ntens_nsym),ntens_nsym)
622 U_1   = V_VecToMat_TEN2_(stretchNew(km,1:ntens),ntens)
623 Cv3_0 = V_VecToMat_TEN2_(stateOld(km,ntens*0+1:ntens*1),ntens)
624 Cv4_0 = V_VecToMat_TEN2_(stateOld(km,ntens*1+1:ntens*2),ntens)
625 ZETA_0      = stateOld(km, ntens*2+1)
626 I1_bar_mx_0 = stateOld(km, ntens*2+2)
627 frac_starchOld = stateOld(km, ntens*2+3)
628 Conc_enz      = ZERO !tempNew(km)
629
630   !!=====
631   !!   Calculate kinematic variables
632   !!=====
633 detF      = DET_TEN2_(F_1)

```

```

634      F_bar      = detF**(-third)    * F_1
635      F_bar_inv  = detF**(-third)*INV_TEN2_(F_1)
636      R_1        = MATMUL(F_1,INV_TEN2_(U_1))
637
638      C_1        = MATMUL(TRANS_TEN2_(F_1),F_1)
639      C_inv      = INV_TEN2_(C_1)
640      C_bar      = detF**(-two/three) * C_1
641      I1_bar     = TR_TEN2_(C_bar)
642      I2_bar     = detF**(-four/three)
643      +          * TR_TEN2_(C_inv) * (detF**two)
644      I1_bar_mx  = MAX(I1_bar_mx_0,I1_bar)
645
646      IF (detF < 1D-10) THEN
647          WRITE(6,*) 'detF too small! km=', km
648          WRITE(6,*) 'NCALL= ', NCALL
649          WRITE(6,*) 'defgradNew(km,:)=', defgradNew(km,:)
650          WRITE(6,*) 'F_1= ', F_1
651      END IF
652
653      !!=====
654      !! Update the degree of reaction
655      !!=====
656      Conc_starch = frac_starchOld * Conc_starch_ini
657
658      Conc_enz_eff = Conc_enz * (1-Conc_starch)
659      r_enz = r_enz_ini*Conc_enz_eff / (Ke + Conc_enz_eff)
660
661      Conc_starch = Conc_starch -
662      +          r_enz * Conc_starch / ( Ks + Conc_starch ) * DT
663      frac_starchNew = Conc_starch / Conc_starch_ini
664      IF (frac_starchNew .LT. ZERO) THEN
665          frac_starchNew = ZERO
666          WRITE(*,*) 'frac_starch=0 !'
667      END IF
668
669      !!=====
670      !! Fictitious stress tensor:
671      !!=====
672      ! Calculate Variables for Hyperelastic part (EQ)
673      !-----
674      CALL Modular_Carroll(
675      +      a,b,c,
676      +      I1_bar,I2_bar,
```

```

677 +   C_bar ,
678 +   S_bar_EQ
679 + )
680 !=====
681 ! Calculate Variables for ISO_NEQ_v part
682 !-----
683 CALL Modular_NEQ_v_NeoHook(
684 +   c3_NeoHook,TAU3_NeoHook,
685 +   DT,
686 +   C_bar,Cv3_0,
687 +   Cv3,S_bar_NEQ_v3
688 + )
689 !-----
690 CALL Modular_NEQ_v_NeoHook(
691 +   c4_NeoHook,TAU4_NeoHook,
692 +   DT,
693 +   C_bar,Cv4_0,
694 +   Cv4,S_bar_NEQ_v4
695 + )
696 !=====
697 CALL Modular_NEQ_s(
698 +   cs1_soften,cs2_soften,
699 +   R_soften,M1_soften,M2_soften,
700 +   I1_bar,I1_bar_mx,ZETA_0,
701 +   ZETA,
702 +   S_bar_NEQ_s
703 + )
704
705 !!=====
706 !! Total Fictitious stress tensor:
707 !!=====
708 S_bar = frac_starchNew * S_bar_EQ
709 +      + (TWO - frac_starchNew) * S_bar_NEQ_v3
710 +      + (TWO - frac_starchNew) * S_bar_NEQ_v4
711 +      + frac_starchNew * S_bar_NEQ_s
712
713 !=====
714 ! Isochoric part of the second Piola stress tensor
715 PProj = PROGTEN_(Iden,C_inv,C_1)
716 S_iso = detF**(-TWOHIRDS) * DBLCTRC_42_(PProj,S_bar)
717
718 !=====
719 ! Volumetric part of the 2nd Piolar-Kirchoff stress tensor

```



```

720      ! Compressible material:
721      p_hydro = K_bulk*(detF - ONE)
722      ! Volumetric part of second Piola stress
723      S_vol = detF*p_hydro*C_inv
724
725      !=====
726      !   Second Piola stress tensor
727      S_1 = S_iso + S_vol
728
729      !=====
730      !   Cauchy Stress tensor
731      Sigma = detF**(-ONE)*MATMUL(MATMUL(F_1,S_1),TRANS_TEN2_(F_1))
732
733      ! Cauchy stress tensor in corotational coordinate system
734      Sigma_tilde = MATMUL(TRANS_TEN2_(R_1),MATMUL(Sigma,R_1))
735
736      !!=====
737      !!       Abaqus/Explicit Returns stressNew, stateNew
738      !!       stress, state variables under Voigt notation
739      !!=====
740      !-----!
741      ! Return Abaqus/Explicit the Cauchy stress
742      stressNew(km,:) = V_MatToVec_TEN2_(Sigma_tilde, ntens)
743      !-----!
744      ! Update state variables at the end of the increment
745      ! The viscoelasticity Green-Lagrange strain tensor Cv_0
746      stateNew(km,ntens*0+1:ntens*1) = V_MatToVec_TEN2_(Cv3,ntens)
747      stateNew(km,ntens*1+1:ntens*2) = V_MatToVec_TEN2_(Cv4,ntens)
748      ! The softening fraction and equivalent strain invariant
749      stateNew(km,ntens*2+1) = ZETA
750      stateNew(km,ntens*2+2) = I1_bar_mx
751      ! Chemical reaction variables
752      stateNew(km,ntens*2+3) = frac_starchNew
753      stateNew(km,ntens*2+4) = Conc_enz_eff
754      stateNew(km,ntens*2+5) = r_enz
755      ! Return variables for validation purpose
756      stateNew(km,ntens*2+6) = Sigma(1,1)/F_1(1,1)
757      stateNew(km,ntens*2+7) = Sigma(2,2)/F_1(2,2)
758      stateNew(km,ntens*2+8) = Sigma(3,3)/F_1(3,3)
759
760      END DO
761
762      !!=====

```

```

763  !!      SUROUTINES FOR VUMAT
764  !!=====
765  !-----!
766  !      ELEMENT RESPONSES SUBROUTINES
767  !      Hyperelasticity Carroll, Viscoelastic NeoHook 1, NeoHook 2,
768  !      Pseudoelasticity (Stress softening)
769  !-----!
770
771  CONTAINS
772
773  !=====
774  ! Calculate the Equilirium Carroll type element (Hyperelasticity)
775  !=====
776  SUBROUTINE Modular_Carroll(
777  + a,b,c,
778  + I1_bar,I2_bar,
779  + C_bar,
780  + S_bar_Carroll
781  + )
782  !-----!
783  ! Argument declaration
784  !-----!
785  REAL(KIND=8)
786  ! Parameters
787  + a,b,c,
788  ! Variables to be read
789  + I1_bar,I2_bar,
790  + C_bar(3,3),
791  ! Variables to be updated
792  + S_bar_Carroll(3,3)
793  !-----!
794  ! Fictitious stress of the Carroll type element
795  !-----!
796  S_bar_Carroll =
797  + (TWO*a + EIGHT*b*I1_bar**THREE) * Iden +
798  + c * (I1_bar*Iden-C_bar) * I2_bar**(-HALF)
799  END SUBROUTINE Modular_Carroll
800  !=====
801
802
803  !=====
804  ! Calculate the Nonequilirium viscoelsticity NeoHookean element
805  !=====

```

```

806     SUBROUTINE Modular_NEQ_v_NeoHook(
807     + nonlinearNH_c,nonlinearNH_TAU,
808     + DT,
809     + C_bar,Cv_0,
810     + Cv,S_bar_NeoHook_v
811     + )
812     !-----!
813     !   Argument declaration
814     !-----!
815     REAL(KIND=8)
816     ! Parameters
817     + nonlinearNH_c,nonlinearNH_TAU,
818     ! Variables to be read
819     + DT,
820     + C_bar(3,3),Cv_0(3,3),
821     ! Variables to be updated
822     + Cv(3,3),S_bar_NeoHook_v(3,3),
823     ! Local variables
824     + detCvEBM,
825     + Cv_inv(3,3),CvEBM(3,3)
826
827     INTEGER :: K1,K2
828     !-----!
829     ! Viscoelasticity Green-Lagrange strain tensor
830     DO K1=1, 3
831         DO K2=1, 3
832             CvEBM(K1,K2)=Cv_0(K1,K2)
833         +         +FOUR*DT/nonlinearNH_TAU*C_bar(K1,K2)
834         END DO
835     END DO
836     detCvEBM = DET_TEN2_(CvEBM)
837     DO K1=1, 3
838         DO K2=1, 3
839             Cv(K1,K2)=detCvEBM**(-THIRD)*CvEBM(K1,K2)
840         END DO
841     END DO
842     !-----!
843     ! Fictitious stress of the NeoHookean viscoelasticity element
844     !-----!
845     Cv_inv = INV_TEN2_(Cv)
846     S_bar_NeoHook_v = TWO*nonlinearNH_c*Cv_inv
847     END SUBROUTINE Modular_NEQ_v_NeoHook
848     ! =====!

```

```

849
850
851      !=====
852      ! Calculate the Nonequilibrium softening element (Pseudoelasticity)
853      !=====
854      SUBROUTINE Modular_NEQ_s(
855      + cs1_soften,cs2_soften,
856      + R_soften,M1_soften,M2_soften,
857      + I1_bar,I1_bar_mx,ZETA_0,
858      + ZETA,
859      + S_bar_NEQ_s
860      + )
861      !-----!
862      !Argument declaration
863      !-----!
864      REAL(KIND=8)
865      ! Parameters
866      + cs1_soften,cs2_soften,
867      + R_soften,M1_soften,M2_soften,
868      ! Variables to be read
869      + I1_bar, I1_bar_mx, ZETA_0,
870      ! Variables to be updated
871      + ZETA,
872      + S_bar_NEQ_s(3,3),
873      ! Local variables
874      + S_bar_NEQ_s_ini(3,3)
875      !-----!
876      ! Softening factor
877      !-----!
878      ZETA = ONE - ONE/R_soften*
879      + TANH( ( ( cs1_soften*(I1_bar_mx-THREE)
880      +          + cs2_soften*(I1_bar_mx-THREE)**TWO
881      +          + cs3_soften*(I1_bar_mx-THREE)**THREE)
882      +        - ( cs1_soften*(I1_bar-THREE)
883      +          + cs2_soften*(I1_bar-THREE)**TWO
884      +          + cs3_soften*(I1_bar-THREE)**THREE))
885      +      / ( M1_soften+M2_soften*
886      +          ( cs1_soften*(I1_bar_mx-THREE)
887      +          + cs2_soften*(I1_bar_mx-THREE)**TWO
888      +          + cs3_soften*(I1_bar_mx-THREE)**THREE)) )
889      !-----!
890      ! the fictitious stress of the softening part
891      !-----!

```

```

892     S_bar_NEQ_s_ini = ( TWO*cs1_soften
893 +                     + FOUR*cs2_soften*(I1_bar-THREE)
894 +                     + SIX*cs3_soften*(I1_bar-THREE)**TWO) * Iden
895     S_bar_NEQ_s = ZETA_0*S_bar_NEQ_s_ini
896     END SUBROUTINE Modular_NEQ_s
897     !=====
898
899     !!=====
900     !!=====
901     END SUBROUTINE VUMAT
902     !!=====
903     !!=====
904
905
906
907     !=====
908     !      User subroutine VEXTERNALDB to obtain external data
909     !=====
910     subroutine vexternaldb(lOp, i_Array, niArray, r_Array, nrArray)
911     !=====
912     use node_data
913     include 'vaba_param.inc'
914     integer, parameter :: j_int_StartAnalysis = 0
915     character(len=256) :: outdir, filename, jobname, message
916
917     call vgetoutdir( outdir, lenoutdir )
918     call vgetjobname( jobname, lenjobname )
919
920     !===== Read file at the start of the analysis =====
921     if (lOp .eq. j_int_StartAnalysis) then
922         unit = 99
923         filename =
924 + outdir(1:lenoutdir)//'/'//jobname(1:lenjobname)
925 + //'_NaturalCoord_DistanceVec.txt'
926         open(unit=unit, file=filename, status='old', action='read',
927 + iostat=ios)
928         if (ios .ne. 0) then
929             message = 'VEXTERNALDB Error: Cannot open file %S!, ios=%I'
930             end if
931             !---- Read the first line to get the number of nodes ----!
932             read(unit, *, iostat=ios) nNodes
933             !----- Allocate arrays based on the number of nodes -----!
934             allocate(node_id(nNodes))

```

```

935     allocate(Natural_coord(nNodes))
936     allocate(Radius_vec(3,nNodes))
937     !- Read the second line to get the centerline total length-!
938     read(unit, *, iostat=ios) S_centerline
939     !---- Read the file line by line from the second line ----!
940     max_node_id = 0
941     do i = 1, nNodes
942         read(unit, *, iostat=ios)
943 +         node_id(i), Natural_coord(i), Radius_vec(:,i)
944         if (node_id(i) > max_node_id) max_node_id = node_id(i)
945     end do
946     close(unit)
947
948     !- Create a mapping from global node ID to local node ID -!
949     allocate(global_to_local(max_node_id))
950     global_to_local(:) = 0
951     do i=1, nNodes
952         global_to_local(node_id(i)) = i
953     end do
954     end if
955
956     !=====
957     end subroutine vexternaldb
958     !=====
959
960
961
962     !=====!
963     ! User subroutine VDISP to prescribe boundary conditions
964     ! for 3D peristaltic wave
965     !=====!
966     subroutine vdisp(
967         ! Read only -
968 + nblock,nDof,nCoord,kstep,kinc,stepTime,totalTime,dtNext,dt,
969 + cbname,jBCType,jDof,jNodeUid,amp,coordNp,u,v,a,rf,rmass,rotaryI,
970         ! Write only -
971 + rval )
972     !=====!
973     use node_data
974     use MODULE_MATHS
975     include 'vaba_param.inc'
976     !----- Abaqus parameters -----!
977     integer :: nblock, nDof, nCoord, kstep, kinc

```

```

978     dimension jDof(nDof), jNodeUid(nblock), coordNp(nCoord, nblock),
979 +   amp(nblock), u(nDof,nblock), v(nDof,nblock), !a(nDof,nblock),
980 +   rf(nDof,nblock), rmass(nblock), rotaryI(3,3,nblock),
981 +   rval(nDof,nblock)
982     character(len=80) cbname
983     !----- User defined parameters -----!
984     real(kind=8), parameter ::
985 +   s0      = -0.1d0,
986 +   s1      = 20.d0 /270.d0,
987 +   s2      = 200.d0/270.d0,
988 +   sS      = 420.d0 /270.d0,
989 +   l_wv_0  = 155.d0  /270.d0,
990 +   l_wv_f  = 155.d0  /270.d0,
991 +   v_wv    = 40.d0   /270.d0,
992 +   nSpace_wv = 2.d0,
993 +   n_sharp = 5.d0
994     integer, parameter :: n_wv = 5
995     !----- Local variables -----!
996     real(kind=8)
997 +   t_step,
998 +   s_k,
999 +   s_t,
1000 +   ratio_con_wv,
1001 +   ratio_con_t,
1002 +   l_wv_k,
1003 +   front,
1004 +   back
1005     real(kind=8), dimension(3) ::
1006 +   X_k,
1007 +   R_k0,
1008 +   dr_wv,
1009 +   dr_sph
1010     integer :: k, count,
1011 +   global_id,
1012 +   local_id
1013     !=====
1014
1015     rval = zero
1016     t_step = stepTime
1017
1018     do k=1, nblock
1019
1020     !===== Retrieve Node local ID =====

```

```

1021     global_id = jNodeUid(k)
1022     ! Optimized lookup of local_id
1023     if (global_id > size(global_to_local)) cycle
1024     local_id = global_to_local(global_id)
1025     if (local_id == 0) cycle
1026     !===== Nodal coords, Natural coord & Radius vector =====
1027     X_k(:) = coordNp(:,k)
1028     s_k = Natural_coord(local_id)
1029     R_k0(:) = Radius_vec(:,local_id)
1030
1031     !===== contraction ratio =====
1032     if (s_k .le. s1) then
1033         ratio_con_wv = 0.3d0 * s_k/s1
1034     else if (s_k .le. s2) then
1035         ratio_con_wv = 0.3d0 + (0.8d0-0.3d0)*(s_k-s1)/(s2-s1)
1036     else if (s_k .le. sS) then
1037         ratio_con_wv = 0.8d0 + (zero-0.8d0)*(s_k-s2)/(sS-s2)
1038     else
1039         ratio_con_wv = zero
1040     end if
1041
1042     !===== peristaltic waves =====
1043     l_wv_k = l_wv_0 + (l_wv_f-l_wv_0)*(s_k-s0)/(sS-s0)
1044     ratio_con_t = zero
1045     do count = 0 , n_wv
1046         front = s1 + v_wv*t_step - nSpace_wv*count*l_wv_0
1047         back = s1 + v_wv*t_step - (nSpace_wv*count+1)*l_wv_0
1048         if (s_k .le. front .and. s_k .ge. back) then
1049             s_t = s_k - back
1050             ratio_con_t = ratio_con_wv
1051 +             * (s_t*(l_wv_k-s_t)/((half*l_wv_k)**two))*n_sharp
1052             if (ratio_con_t .lt. zero) then
1053                 ratio_con_t = zero
1054             end if
1055         end if
1056     end do
1057     dr_wv = ratio_con_t * R_k0
1058
1059     !===== sphincter static contraction =====
1060     dr_sph = zero
1061     !===== total contraction =====
1062     rval(:,k) = dr_wv + dr_sph
1063 end do

```



```
1064 !=====
1065         end subroutine vdisp
1066 !=====
```