

Multiscale modelling of nanoparticle toughening in epoxy: Effects of particle-matrix interface, particle size, and volume fraction

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ABSTRACT

Toughening matrix materials by incorporating rigid nanoparticles has received significant interest for mitigating matrix microcracking in fibre-reinforced polymer-matrix composites, particularly at cryogenic temperatures. Despite recent experimental observations indicating the effectiveness of nanoparticle toughening, a notable gap remains in understanding the effects of nanoparticle size and volume fraction, and particle-matrix interfacial properties, on toughening efficacy. To address this gap, a multiscale model has been developed which employs a high-fidelity micromechanical model to quantify the deformation and energy dissipation caused by the rigid nanoparticles under a triaxial strain state determined from a macroscopic elastoplastic analysis. The interface between the nanoparticle and the matrix is characterized by a cohesive zone model (CZM), revealing a size-dependent phenomenon distinct to nanoparticles, sharply contrasting with micrometre-sized particles. Furthermore, the results reveal, for the first time, an optimum particle size that maximizes the toughening effect for a given particle-matrix combination. The existence of an optimum size is ascribed to the incomplete particle debonding from the matrix as the particle radius approaches the critical separation distance of the CZM. This revelation challenges the prevailing belief that, for a fixed volume fraction of nanoparticles, the enhancement in toughness rises as the particle size decreases as a result of the increase in total particle surface area. The implications for enhancing cryogenic performance are explored.

Nomenclature

English			
	U_e		dissipated energy density for the pure epoxy
b	side length of the unit cell	U_p	dissipated energy density for the particle-toughened epoxy
d	damage variable for the cohesive zone model	U_p^{db}	dissipated energy density due to debonding of nanoparticles
E	Young's modulus of the epoxy matrix	U_p^{pd}	dissipated energy density due to plastic deformation of the matrix surrounding nanoparticles
E'	effective Young's modulus	V_p	particle volume fraction
G_{app}	applied energy release rate	W_a	thermodynamic work of adhesion
G_{cp}	fracture energy for the toughened epoxy	x, y, z	cartesian coordinates

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		Greek	
G_{ce}	fracture energy for the pure epoxy		
G_{int}	interfacial fracture energy	β	proportionality constant
G_{init}	initial value of fracture energy	γ	ratio of interface strength to matrix yield stress
G_{ss}	steady-state value of fracture energy	ΔG	toughness increment due to the presence of nanoparticles
G_{tip}	energy release rate available at the crack tip	ΔT	temperature difference between T_0 and T_c
h	wake height	ΔU	additional energy dissipation due to particle toughening, and $\Delta U = U_p - U_e$
h_p	wake height under an applied driving force	δ, δ_c	interface separation, critical interface separation for the traction law
$G_{app} = G_{cp}$			

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K_{app}	applied stress intensity factor	$\varepsilon_1, \varepsilon_2, \varepsilon_3$	principal strains
R	domain size of the homogeneous continuum crack model	r, θ	polar coordinates
r_p	particle radius	θ_m	angle θ that yields the maximum energy dissipation at a height y from the crack plane
r_Y	Irwin estimate for the plastic zone size	ν	Poisson's ratio of the epoxy matrix
S	penalty stiffness for the traction law	$\bar{\sigma}_1, \bar{\sigma}_2, \bar{\sigma}_3$	average stresses in 1-, 2- and 3-axis directions
T_c, T_o	curing, operating temperatures	σ_{int}	interfacial strength
U	dissipated energy density	σ_Y	tensile yield stress of the epoxy matrix

1. Introduction

The emergence of nanotechnology, particularly nano-sized materials with tailorable surface properties, has spurred significant advances in enhancing the performance of fibre-reinforced polymer-matrix composites under extreme environments by toughening the matrix materials. A number of studies have demonstrated the impressive efficacy of incorporating nanoparticles and/or nano-structured fillers in toughening brittle polymers, such as epoxies [1–7]. The primary focus of the present study is to model and elucidate the mechanisms by which high-stiffness, rigid nanoparticles contribute to the toughening of thermosetting epoxy polymers, because high-stiffness nanoparticles have been shown to be more effective than low-stiffness alternatives, such as rubber toughening, at cryogenic temperatures [1,8]. Furthermore, the use of nanoscale particles has the potential to overcome the problem of fibres filtering out the particles during laminate fabrication [9–12], thereby enabling an effective toughening of the epoxy matrix and mitigating the propensity for matrix cracking at cryogenic temperatures.

Despite extensive studies conducted over the past decade to understand the toughening mechanisms of rigid nanoparticles in epoxies [1,3,4,13–16], the quantitative modelling of the toughening mechanisms of such multi-phase polymers, especially the effects of the nanoparticle-matrix interfacial properties and particle size on the toughening efficacy, remains a significant challenge. Recent experimental findings [1,2,4,6,9,10,13–15] have revealed that the sources of energy dissipation in nanoparticle-toughened epoxies include particle debonding [1,2,4,9], and subsequent plastic void growth around individual particles [4,6,9,10], as well as plastic shear banding between neighbouring particles [1,6,13–15]. Existing theoretical analyses [2,17–22] use a two-step approach involving (i) a continuum analysis to estimate the size of the process zone surrounding a crack tip and (ii) an estimate of the dissipated energy density due to the presence of rigid particles. The estimated energy dissipation relies on various simplifying assumptions, most notably that the stress field is linearly elastic and hydrostatic, and that interactions between neighbouring particles are neglected. Although these existing models offer valuable insights into the mechanisms of nanoparticle toughening, they fall short of accurately predicting the particle size effect.

More recently, the need for more realistic computational models has been recognized [3], based on employing a finite element (FE) analysis to calculate the progression of deformation and energy dissipation within a representative volume element (RVE) under an externally applied load, such as uniaxial tension in Ref. [3]. The present study provides a new multiscale modelling approach that includes several important innovations and enhancements relative to previous work. In particular, the process zone size and the stress state around the growing crack are obtained using an elastoplastic stress analysis of the deformation field around the crack tip, instead of the more commonly used linear elastic analysis. Furthermore, of greater importance, a cohesive zone model (CZM) is employed to characterize the particle-matrix

interface [23] for the modelling of nanoparticle toughening for the first time. This is inspired by recent experimental and theoretical studies demonstrating that continuum mechanics [24–26] and CZM approaches [27–33] can be effectively applied to polymer nanocomposites at scales of a few nanometres. The CZM for the particle-matrix interface introduces a characteristic length into the modelling process, thereby revealing a previously unknown size effect in nanoparticle toughening. This aspect of the model offers substantial new insights into the size effect of rigid particles when toughening polymers at the nanoscale.

The presentation is organized as follows. The multiscale modelling approach is presented in Section 2, where a two-dimensional (2D) plane-strain continuum crack model is coupled with a micromechanical RVE model to determine the additional energy dissipation induced by the presence of rigid nanoparticles compared with the untoughened, pure epoxy. Here the toughening phenomenon is considered to occur within a small-scale process zone around the crack tip, analogous to the condition of small-scale yielding (SSY) in linear elastic fracture mechanics (LEFM). Section 3 outlines key results of the predicted enhancement in fracture energy of a rigid nanoparticle-toughened epoxy. These predictions are compared with experimental observations in Section 4, to reveal the effects of interfacial properties, and of particle size and volume fraction.

2. Multiscale modelling of particle toughening

The aim of the modelling is to predict the fracture energy, G_{cp} , of a material toughened by rigid nanoparticles, assuming the fracture energy of the untoughened material, G_{ce} , is known. For this purpose, it is conventional to consider steady-state cracking. This approach, originally introduced for transformation toughening in ceramics [34], has since been applied to particle toughening [17,18,35], as well as several other toughening mechanisms [19,36,37].

The present work includes two novel features in the extension of the steady-state cracking approach. First, the maximum strains experienced by the RVEs are derived from a macroscale crack model using an elastoplastic stress analysis, as described in Section 2.2, instead of the more commonly employed elastic stress analysis [17,20–22]. Secondly, a micromechanical model for the RVE featuring a CZM for the particle-matrix interface is employed to calculate the additional energy dissipation due to debonding of nanoparticles and the inelastic deformation of the matrix surrounding the nanoparticles, as described in Section 2.3.

2.1. A steady-state crack growth modelling approach

The theoretical idealization of steady-state crack growth considers the geometrical configuration illustrated in Fig. 1(a, b) in which a crack is assumed to grow under a constant crack driving force (or energy release rate), G_{app} , leaving behind a wake of deformed material of height, h , on both sides of the crack plane. It is assumed that there exists a process zone around the crack tip within which the toughening mechanisms are active and energy dissipation occurs. The wake height, h , is assumed to be small compared with all other dimensions, so that the criterion of SSY, i.e. a relatively small-scale process zone, is satisfied. Thus, the crack tip environment can be characterized by a “remote” stress intensity factor K_{app} , which is related to G_{app} by the standard formula, $G_{app} = K_{app}^2/E'$, where $E' = E/(1 - \nu^2)$, and E and ν denote the Young's modulus and the Poisson's ratio, respectively [38].

For the purpose of estimating the toughness increment $\Delta G = G_{cp} - G_{ce}$, it is convenient to assume that crack growth proceeds in accordance with the failure criterion

$$G_{tip} = G_{ce}, \quad (1)$$

where G_{tip} denotes the energy release rate available at the crack tip. This assumption is strictly appropriate only if the wake height for the untoughened material is much smaller than that for the toughened material, which is not the case for particle toughening of epoxy.

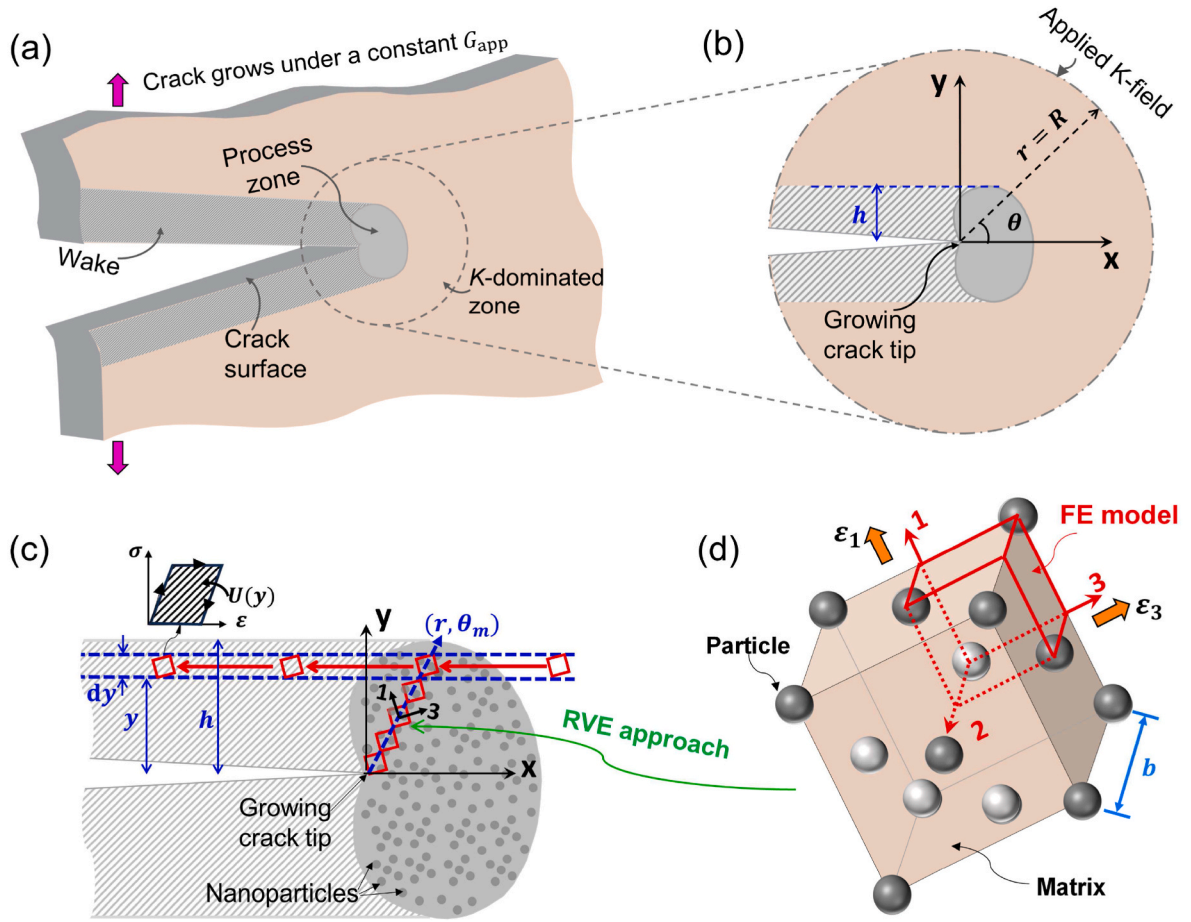


Fig. 1. Schematic depicting the present modelling approach for particle-toughening. (a) A homogeneous, cracked continuum under mode I loading, with the crack growth reaching a steady state. (b) A plane-strain, continuum crack tip model under an applied remote stress intensity factor K_{app} . (c) Discretisation of the radial line $\theta_m = 70^\circ$ for numerical integration of dissipated energy. (d) Model configuration and boundary conditions of the micromechanical RVE model.

Nevertheless, this assumption, which also underpins previous models of epoxy toughening [17–19,35–37], will be adopted here as a pragmatic approximation whose validity will be assessed later, as further discussed in Section 4.4. The toughness increment ΔG can then be estimated as follows,

$$\Delta G = G_{cp} - G_{ce} = 2 \times \int_0^{h_p} [U_p(y) - U_e(y)] dy \quad (2)$$

where $U_p(y)$ and $U_e(y)$ denote, respectively, the dissipated energy density at a height y from the crack plane in the particle toughened epoxy and the pure epoxy, and h_p denotes the wake height under an applied driving force $G_{app} = G_{cp}$. These energy densities can be calculated from the energy dissipation incurred by a material element during a loading-unloading cycle, corresponding to traversing from the front of the crack in Fig. 1(c) to the remote wake [35,37,38]. It will be further assumed, for simplicity, that the unloading is elastic and the endpoint of the load-unload cycle is a state of zero stress, i.e. the possible presence of a residual stress [39,40] and of reverse yielding [39,41] in the wake will be ignored, as in previous theoretical modelling for epoxy [17,18,20–22, 35,37,42,43]; the potential error incurred will be briefly discussed in Section S4 of the Supplementary Material.

It is pertinent to note that under SSY conditions, and for toughening mechanisms triggered by a critical stress criterion, the term ΔG can be expected to be proportional to G_{app} ; confirmation of this proportionality via computational results will be presented in Section 2.4. This proportionality arises because, firstly, the wake height h should scale with K_{app}^2 , by virtue of the inverse square root dependence of stress on

distance from the crack tip that prevails just outside the process zone for SSY. And secondly, because the idealized near-tip geometry in Fig. 1(b) has no intrinsic length scale, the extra dissipated energy density, $\Delta U(y) = U_p(y) - U_e(y)$ must scale with the plastic zone size $r_Y = (K_{app}/\sigma_Y)^2/6\pi$ [38], i.e. ΔU can only depend on the nondimensional parameter y/r_Y . This dependence will also be confirmed computationally in Section 2.4. Denoting the constant of proportionality by β , i.e. with

$$\Delta G = \beta G_{app}, \quad (3)$$

and recalling that $G_{app} = G_{cp}$, then Eq. (2) yields the following fundamental relation for deriving the fracture energy of the toughened material, given that of the untoughened material:

$$G_{cp} = \frac{1}{1 - \beta} G_{ce}. \quad (4)$$

To determine the toughening coefficient β , the multiscale modelling approach in the present work entails two coupled models: (i) a continuum model for the elastoplastic crack-tip strain field and (ii) a micromechanical model to calculate the energy dissipation. For both models, the required stress analysis is performed using the commercial software package ABAQUS 2021 [44]. The flowchart in Fig. 2(a) schematically shows the implementation of the proposed modelling approach.

2.2. The homogeneous continuum model of the crack-tip field

The primary aim of this homogeneous model is to determine the

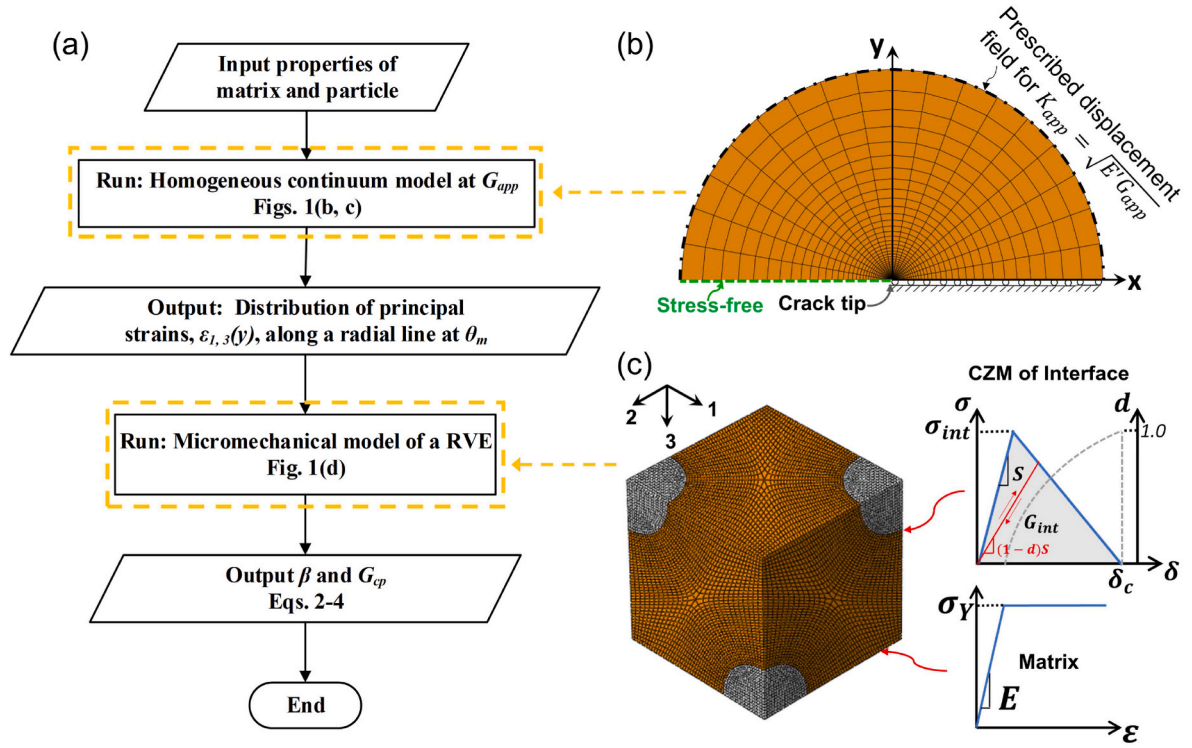


Fig. 2. The implementation of the present model showing: (a) schematically the overall flowchart; (b) the homogeneous continuum crack model and (c) the micromechanical model of the RVE, along with the traction-separation law for the CZM of the particle-matrix interface and the elastic-perfectly-plastic material behaviour for the epoxy matrix.

strain distribution in the crack-tip frontal process zone under a constant crack driving force, G_{app} . To this end, a macroscale crack model is employed to determine the elastic-plastic strain distribution around the crack tip depicted in Fig. 1(b). The FE model represents a circular domain of radius $r = R$, as shown in Fig. 2(b), where the boundary condition along the arc is given by the displacement field corresponding to the crack-tip singularity field with an applied stress intensity factor of K_{app} [38]. The material is assumed to be homogeneous and isotropic, obeying an elastic-perfectly-plastic constitutive relationship with the von Mises yield criterion. The domain size, R , is chosen to ensure that SSY prevails, i.e. $R \gg r_Y$, where r_Y denotes the Irwin estimate for the plastic zone size, r_Y [38]. For typical epoxy polymers, the values of r_Y range from several to tens of micrometres [1–4,17]. The focussed mesh in Fig. 2(b) contains 18 equally spaced angular sectors. Each sector contains 105 elements where their radial sizes are proportional to r . Through a mesh convergence analysis, the smallest element at the crack tip is determined to be approximately $R/100,000$, sufficient to ensure the accuracy of the stresses and strains of the RVE nearest to the crack tip as described in Section 2.3.

While the solution of a steady-state growing crack differs from that of a stationary crack due to the presence of an elastic unloading region and a reversed zone of plastic yielding in the wake behind the tip, the differences between the crack-tip fields ahead of the tip of a stationary crack and a steady-state growing crack are minor, as revealed by Refs. [39,40]. Therefore, calculating the strain distribution ahead of the crack tip of a stationary crack is considered adequate for practical solutions to the steady-state crack growth problem, particularly for improving computational efficiency. A detailed comparison between the solutions for a stationary crack and a steadily growing crack, presented in Section S3 of the Supplementary Material, shows that there is little difference in the strain fields in the frontal process zone ahead of the crack tip.

The FE analysis shows that in the frontal process zone, the principal axes of strain do not coincide with the cartesian axes x, y , as illustrated in Fig. 1(c) where the directions of the in-plane principal strains are

indicated by arrows labelled 1, 3. At a height y above the crack, the principal strain, $\varepsilon_1(x, y)$, reaches its peak magnitude when $x = y/\tan(\theta_m)$, along a radial line inclined at an angle $\theta_m = 70^\circ$. This angle aligns with where the plastic zone size reaches its maximum extent for either a stationary crack [45] or a steadily growing crack [41], as shown in Fig. S1(a) of the Supplementary Material (Further results are presented in Fig. S1(b, c) in the Supplementary Material to show that this choice of θ_m also maximizes the calculated value of the dissipated energy density at a height y from the crack plane.). Along the radial line $\theta_m = 70^\circ$, the distributions of principal strains are given in Figs. S2 (a, b) of the Supplementary Material, which also show that the ratio of the two in-plane principal strains (ε_1 and ε_3) remains approximately constant, $\varepsilon_3/\varepsilon_1 = -0.22$, whereas the out-of-plane principal strain is zero, i.e. $\varepsilon_2 = 0$, by virtue of the plane-strain assumption. Therefore, the strain field along the radial line θ_m can be fully described by a single parameter, viz. the principal strain ε_1 , which greatly simplifies the specification of the applied deformation on the RVE in the next sub-section.

2.3. The micromechanical model of a representative volume element (RVE)

To calculate the dissipated energy densities, we consider next a multi-phase RVE in the form of a cubic unit cell, with spherical particles embedded within a matrix in a face-centred cubic (FCC) array, as shown in Fig. 1(d). This idealization has been shown to provide a practical approximation for a uniform random distribution of particles [3]. The geometry is fixed by specifying the particle radius, r_p , and particle volume fraction V_p , from which one can deduce the side length, b , for the RVE, $b = \sqrt[3]{16\pi r_p^3 / 3V_p}$. For example, in the case of $r_p = 10$ nm and $V_p = 1\%$, then $b = 119$ nm, which is about 1 % of the process zone size. The RVE is oriented such that its sides are aligned with the principal strain directions determined from Section 2.2, as indicated in Fig. 1(c and d). By virtue of the symmetry with respect to all three principal axes, it is

sufficient to construct a micromechanical FE model for only one-eighth of the RVE, as indicated by the red outline in Fig. 1(d).

The FE mesh of the RVE model, which is of the order of nanometres, is developed by choosing millimetres as the dimensional unit and applying a scale factor of 10^{-6} . To capture the stress distribution around nanoparticles, the smallest element in the RVE has been determined, through a mesh sensitivity analysis, to be around 3 nm for the smallest nanoparticles considered in this study ($r_p = 10$ nm). The particle-matrix interface is modelled by a zero-thickness CZM with uncoupled [46,47], bilinear [23,33,44] traction-separation laws as depicted in Fig. 2(c), for the normal and shear deformations across the interface. The final failure of the CZM is governed by the power-law-form criterion with a power-law exponent of 1.0, as explored by Thouless et al. in Refs. [47–50]. Mode-independent cohesive properties (i.e., the interfacial properties in normal and shear modes are equal [48–50]) are assumed in this study. The uncoupled, mode-independent CZM has been applied to a wide variety of different types of interfaces and appears to work well in predicting experimental results [46–50]. This CZM requires two main material properties for the interface, viz. the interfacial strength, σ_{int} , and the interfacial fracture energy, G_{int} . These two properties, in turn, define a critical separation, $\delta_c = 2G_{int}/\sigma_{int}$, beyond which the interface transmits zero load. The traction law in Fig. 2(c) also includes a so-called penalty stiffness, S , characterizing the initial stage of the traction law. However, this penalty stiffness is introduced for computational expediency and it has no physical significance [23,44]. It is conventional to specify $S = 10^{11}$ MPa/mm, which is a sufficiently high value such that it has a negligible influence on subsequent calculations of the dissipated energy. The traction-separation law includes a damage variable, d , with $d = 0$ for no damage, and $d = 1$ for complete separation [23,44]. The matrix phase is assumed to be elastic-perfectly-plastic following the von Mises yield criterion, and the particles are modelled as linear-elastic silica (SiO₂) material. No user-defined material subroutine or user elements are required in the present micromechanical model. The cohesive element and von Mises-type material formulation for the plastic behaviour of the matrix available within ABAQUS version 2021 [44] are used. More information about the implementation of the FE model is given in the Supplementary Material. Thus, the required material properties for the micromechanical model are the particle size, r_p , volume fraction, V_p , interfacial properties, as well as the Young's moduli and Poisson ratios for the particles and the matrix, and the matrix yield stress, σ_Y , which are listed in Tables 1 and 2.

To calculate the dissipated energy at a distance y from the crack plane, the strains applied to the unit cell are increased from zero to the maximum values determined from Section 2.2 (and shown in Fig. S2(a) of the Supplementary Material) at a height y along the radial line $\theta_m = 70^\circ$. The unit cell is then elastically unloaded back to zero stress. This simulates the loading-unloading history of the material element as it progresses from a location ahead of the crack tip, ($x \rightarrow +\infty$) in Fig. 1(c), to a location in the crack wake, ($x \rightarrow -\infty$). Recalling that $\varepsilon_3/\varepsilon_1 = -0.22$ and $\varepsilon_2 = 0$ during the loading process which is then followed by elastic unloading to zero stress, the dissipated energy density $U(y)$ during a loading-unloading cycle can be calculated as:

$$U(y) = \sum_{i=1}^3 \oint \bar{\sigma}_i d\varepsilon_i \quad (5)$$

Table 1
Properties of epoxy [2].

Material property	Value
Young's modulus, E (MPa)	2960
Poisson's ratio, ν	0.3
Yield stress σ_Y (MPa)	88
Fracture energy, G_{ce} (J/m ²)	77
Coefficient of thermal expansion ($^\circ\text{C}^{-1}$)	55×10^{-6}

Table 2
Properties of SiO₂ nanoparticle.

Material property	Value	Ref.
Particle radius, r_p (nm)	10	[2,3]
Elastic modulus (GPa)	70	[3]
Poisson's ratio	0.26	[3]
Coefficient of thermal expansion ($^\circ\text{C}^{-1}$)	0.56×10^{-6}	[3]

where $\bar{\sigma}_1$, $\bar{\sigma}_2$ and $\bar{\sigma}_3$ denote, respectively, the average stresses on the faces normal to the principal axes 1, 2 and 3, and the integrals are taken over a complete loading and unloading cycle. The possible effects of the thin reverse yielding zone and the residual stresses in the wake of the steadily growing crack on the calculated energy dissipation are estimated for the case of pure epoxy; the results are provided in the Supplementary Material, which indicate that the idealization of the elastic, complete unloading as in previous studies [17,18,20–22,35,37,42,43] and the present work should provide a reasonable approximation simplifying the complex toughening analysis of the crack wake.

The integration in Eq. (5) is performed to determine both $U_e(y)$ and $U_p(y)$, and hence $\Delta U(y) = U_p(y) - U_e(y)$, which is then used to compute ΔG via Eq. (2), and hence the proportionality constant $\beta = \Delta G/G_{app}$. The integration rule employed is the centred rectangular rule, so that the first integration point is at the centre of the RVE closest to the crack tip, as indicated in Fig. 1(c).

Two important parameters for the micromechanical model are the interfacial strength and the fracture energy between the particles and the matrix, i.e., σ_{int} and G_{int} . Previous studies [3,6,17,35] have revealed that the onset of plasticity seen in the rigid particle filled epoxies is associated with particle debonding. The interfacial strength is typically less than or equal to the yield stress of the epoxy matrix, i.e., $\sigma_{int} = \gamma\sigma_Y$, with the proportionality factor being denoted as γ . A parametric sensitivity investigation of $\gamma \in [0, 1]$ will be given in Section 4.1. However, for most of the calculations in the present study, it will be assumed that $\gamma = 1$. Indeed, this assumption is generally used in existing theoretical studies, as represented by Lauke [18] and Quaresimin et al. [20–22,51]. Further, the experiments and numerical analysis by Guild et al. [3] strongly support this assumption. Specifically, Table 3 in Ref. [3] shows that the maximum interfacial normal stress just prior to debonding increases as the particle concentration decreases, approaching the yield stress of the epoxy. These results support the proposition that the interfacial strength can indeed reach the matrix's yield stress, particularly at low particle concentrations or with ideal adhesion [3]. Thus, the assumption that $\gamma = 1$ provides a consistent reference point for comparisons to be made in the present study and also provides a practical upper-bound estimate for the debonding initiation criterion.

The thermodynamic work of adhesion, W_a , between the particle material and epoxy provides a conservative estimate for the interfacial fracture energy, G_{int} , as postulated in Refs. [17,18,21,22,52,53]. The value of W_a can be experimentally determined [18,54–57] and some typical values are summarized in Table 3. Accordingly, the baseline value of G_{int} is assumed to be 80 mJ/m², as listed in Table 4. The specified values for σ_{int} and G_{int} , in turn, define a critical separation $\delta_c = 2$ nm. This critical separation constitutes an important characteristic length for the modelling studies, which leads to a size effect for particle toughening, as will be seen below in Section 3.

2.4. The determination of proportionality constant β

It was argued in Section 2.1 that $\Delta G = \beta G_{app}$ because there is no characteristic length for the idealized crack-tip geometry shown in Fig. 1(b). This, in turn, means that the extra dissipated energy density, $\Delta U(y) = U_p(y) - U_e(y)$, depends on the nondimensional distance y/r_Y from the crack plane, where r_Y denotes the Irwin estimate for the plastic zone size, which is proportional to G_{app} , cf. Section 2.2. This dependence

Table 3

Summary of assumed values of G_{int} , experimentally measured values of W_a and MD simulated parameters for the CZM.

Type of interface	Value	Explanation or measurement method	Ref.
Nano-SiO ₂ /Epoxy	240 mJ/m ²	W_a of SiO ₂ /epoxy interface	[17]
Nano-SiO ₂ /Epoxy	10 mJ/m ²	W_a of SiO ₂ /epoxy interface	[22]
Nano-SiO ₂ /Epoxy	10 mJ/m ²	Not given	[21]
Nano-SiO ₂ /Epoxy	10 – 50 mJ/m ²	Not given	[52, 53]
Micro-SiO ₂ /Epoxy	100 mJ/m ²	W_a of SiO ₂ /epoxy interface	[18]
Experimental measurements of W_a of SiO ₂ /epoxy interface:			
SiO ₂ /Epoxy	80 ± 10 mJ/m ²	Three-liquid method	[54, 55]
SiO ₂ /Epoxy	45 – 90 mJ/m ²	Contact mechanics method	[54]
SiO ₂ /Epoxy	82 ± 1 mJ/m ²	Wihelmy Plate method	[56]
SiO ₂ /Epoxy	81 ± 4 mJ/m ²	AFM pull-off method	[56]
SiO ₂ /Epoxy	35 – 48 mJ/m ²	Contact angle method	[57]
CZM parameters obtained by atomistic simulations			
SiO ₂ /Epoxy	$G_{int} = 160$ mJ/m ² $\delta_c = 2.5$ nm	MD simulations	[27]
SiO ₂ /Epoxy	$G_{int} = 20$ mJ/m ² $\delta_c = 2$ nm	MD simulations	[28]
Clay/Epoxy	$G_{int} = 126$ mJ/m ² $\delta_c = 2.5$ nm	MD simulations	[31]
Graphene/Epoxy	$G_{int} = 120$ mJ/m ² $\delta_c = 1$ nm	Van der Waals interactions	[32]
CNT/Epoxy	$G_{int} = 140$ mJ/m ² $\delta_c = 1$ nm	Van der Waals interactions	[32]

Table 4

Baseline CZM parameters for the SiO₂ nanoparticle-epoxy matrix interface.

CZM parameter	Value
Penalty stiffness, S (MPa/mm)	10 ¹¹
Interfacial strength, σ_{int} (MPa)	88
Interfacial fracture energy, G_{int} (mJ/m ²)	80
Critical separation displacement, δ_c (nm)	2

is confirmed by the present results of the multiscale model. Indeed, an example is shown in Fig. 3(a) where the values of ΔU pertinent to five values of G_{app} ranging between $1.0G_{ce}$ and $1.8G_{ce}$ are plotted in terms of the nondimensional coordinate y/r_Y . (The value of G_{ce} is 77 J/m², see Table 1.) Noticeably, all the numerical results lie on the same curve.

It is worth noting that the value of r_Y depends on the yield stress σ_Y , whereas $\Delta U(y)$ depends in addition on the assumed interfacial properties, and hence also on the particle size. Fig. 3(b) shows the results for four different cases: epoxy polymers (i) with 6 vol% and 10 nm SiO₂ nanoparticles, (ii) with 6 vol% and 120 nm SiO₂ nanoparticles, (iii) with 3 vol% and 10 nm SiO₂ nanoparticles, and (iv) with 6 vol% and 10 nm voids wherein the nanoparticles are replaced by the open voids, as shown in Fig. 4. The vertical arrows point to the normalized values of y that correspond to $\Delta U = 0$, indicating the normalized value of zone height, h/r_Y .

Based on the results in Fig. 3(b), the extra energy dissipation due to the presence of rigid nanoparticles, ΔG , can now be computed using Eqs. (2) and (3) at varying values of G_{app} . The results for the four cases are presented in Fig. 3(c). The numerical results, denoted by the symbols, confirm a linear relationship, i.e. $\Delta G = \beta G_{app}$.

3. Results

3.1. Visualisation of progressive deformation

Displacements are applied to the three orthogonal faces of the RVE to produce a triaxial deformation with a strain ratio of $\varepsilon_1 : \varepsilon_2 : \varepsilon_3 = 1 : 0 : -0.22$, as discussed above in Sections 2.2 and 2.3. Fig. 4 shows the progress of deformation within an RVE under an increasing applied strain for three different cases: for case (a) a pure epoxy; case (b) an epoxy with spherical open voids and case (c) a SiO₂ nanoparticle toughened epoxy. For cases (b, c), the void or particle radius is 10 nm and the second-phase volume fraction, V_p , is 6 %. The relevant material properties are listed in Tables 1, 2 and 4. As indicated by the colour-coded contours of von Mises equivalent plastic strain in Fig. 4, the plastic deformation is uniform for the untoughened (i.e. pure) epoxy. By contrast, in the presence of voids or high-stiffness (rigid) particles, plastic deformation in the surrounding matrix is highly non-uniform. When voids are present, plastic yielding in the matrix initiates at the equator of the particle, relative to an axis aligned with the direction of the principal strain ε_1 , whereas for rigid particles yielding initiates about halfway between the equator and poles, as indicated by the location of the maximum equivalent plastic strain in Fig. 4(b and c), as well as by the arrows indicating plastic shear bands and plastic void growth with increasing strain.

Fig. 5 shows the progression of interfacial failure for the nanoparticle toughened epoxy, where for clarity, the particles have been artificially hidden. The normal stress at the interface is maximum at the poles where interface failure initiates, as indicated in Fig. 5, when the normal stress reaches the interfacial strength, σ_{int} . Thereafter, the particles start to separate from the matrix but some load is still transmitted across the interface until the separation, δ , reaches the critical value, δ_c , at which total separation, i.e. debonding, occurs, as indicated in Fig. 5.

3.2. Calculation of energy dissipation from RVE

Since the stresses in the RVE are generally not uniform, it is necessary to define average stresses, $\bar{\sigma}_1$, $\bar{\sigma}_2$ and $\bar{\sigma}_3$, across the RVE faces corresponding to the principal axes 1, 2 and 3. The complete loading-unloading cycles for these average stresses versus the applied strains are presented in Fig. 6(a) for the three cases outlined in Section 3.1. It is observed that although ε_3 is compressive, the corresponding reaction stress $\bar{\sigma}_3$ is tensile, which can be attributed to a Poisson's ratio effect. Thus, the RVE is in a state of triaxial tension in the frontal process zone ahead of the crack tip.

In Fig. 6(a), the open circles mark the onset of epoxy yielding for three cases, indicating that the presence of rigid particles or open voids causes the epoxy to yield at a lower level of applied strain compared to the pure epoxy. By contrast to open voids, which promote yielding, rigid particles lead to the initiation of interface damage prior to yielding, as indicated by the solid green dot in Fig. 6(a). With an increasing applied strain, the interface damage expands, and the interface degrades progressively, with the cohesive elements progressively separating and eventually leading to debonding, as depicted in Fig. 5. Further increases in the applied strain causes complete debonding and void formation, which is marked by the green open square in Fig. 6(a). The extent of plastic void growth and/or shear banding is limited by the maximum strain imposed on the RVE.

The total irreversible energy change of the RVE model can be calculated from the hysteresis exhibited in these loading-unloading curves using Eq. (5). The results are shown in Fig. 6(b) as a function of the maximum strain, ε_1 , in the loading-unloading cycle. While there is an intrinsic energy dissipation, U_e , for the pure epoxy due to plastic yielding at the crack tip, the presence of rigid nanoparticles or open voids in the epoxy matrix leads to additional dissipated energy density, ΔU . The energy balance history outputs from ABAQUS [44] provide a separate quantification of the energy dissipation due to matrix plastic

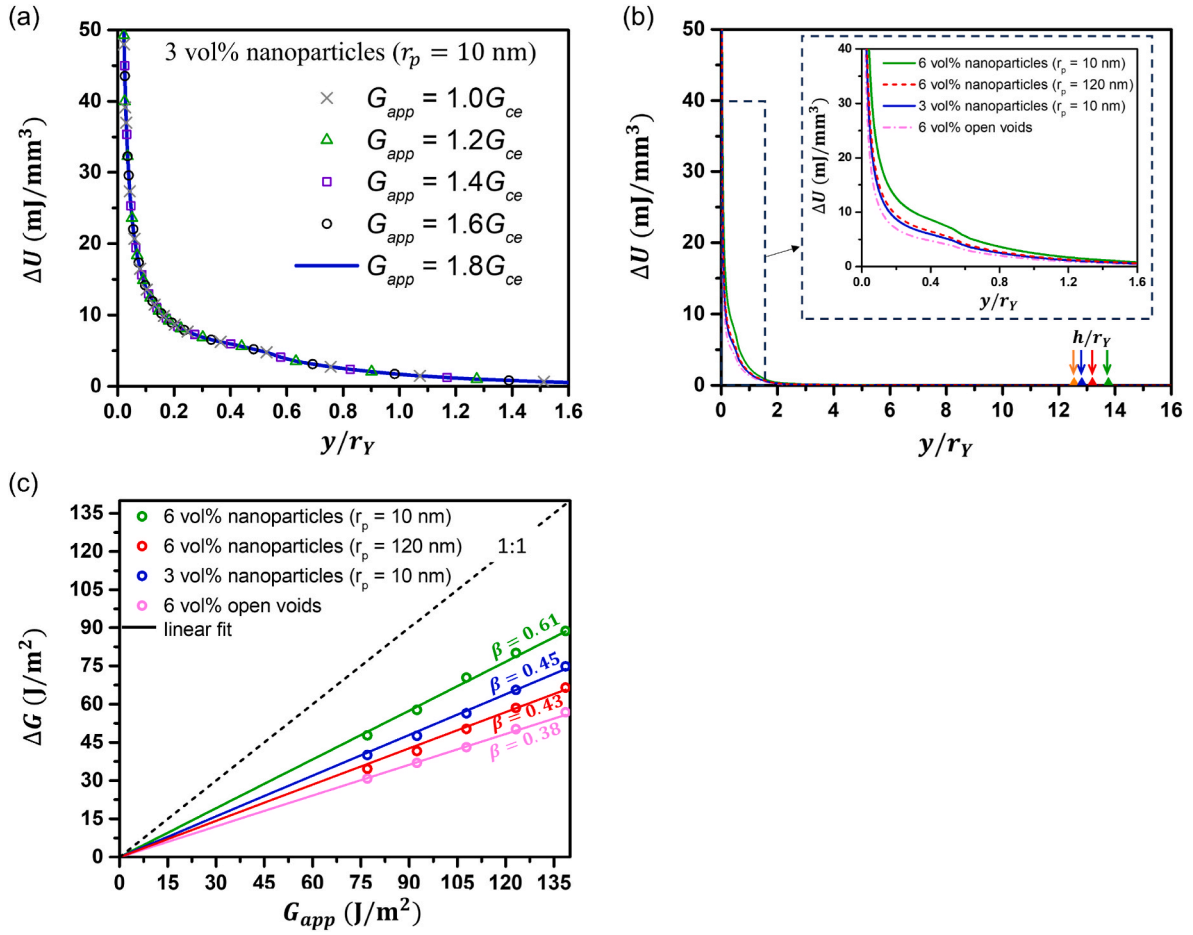


Fig. 3. Calculation of the proportionality constant β . (a) Variation of ΔU with the nondimensional coordinate y/r_Y along $\theta_m = 70^\circ$ for an epoxy with 3 vol% SiO_2 nanoparticles. (b) Variation of ΔU with the nondimensional coordinate y/r_Y along θ_m for different cases, i.e. an epoxy with 6 vol% open voids and an epoxy containing SiO_2 nanoparticles of varying volume fractions and particle radii. Numerical integrations to determine ΔG are performed using the centred rectangular rule. (c) Variation of the calculated ΔG with increasing G_{app} from $1.0G_{ce}$ to $1.8G_{ce}$ for four different toughening systems.

deformation U_p^{pd} , and that due to interfacial failure U_p^{db} . As shown by the green dotted curve in Fig. 6(b), upon the complete debonding of the nanoparticles, the term U_p^{db} reaches its maximum and remains unchanged with further increases in applied strain. This maximum value equals the product of the interfacial fracture energy, G_{int} , times the specific interface area, which is defined as the ratio of the total surface area of the particles in the unit cell ($16\pi r_p^2$) to the volume of the unit cell ($16\pi r_p^3/3V_p$), i.e., $3V_p/r_p$.

Nevertheless, the significant differences in the average stress versus applied strain plots shown in Fig. 6(a) indicate the disparities between the constitutive responses of the pure epoxy and particle-toughened epoxy. The authors acknowledge that the strain distributions from a homogeneous continuum model, which assumes an elastic-perfectly-plastic constitutive law with a Mises material flow rule, may not fully capture the constitutive behaviour of the particle-toughened epoxy. Investigating the effects of nanoparticles and interfacial properties on the constitutive relationship and flow rule of nanocomposites requires rigorous future research. Any interactive analysis with the continuum crack model may require a new concurrent numerical approach to account for the nano-toughening mechanisms associated with the presence of nanoparticles, which is beyond the scope of this work.

3.3. RVE model of different particle sizes

As noted in Section 2.3, the critical separation displacement, δ_c , of the CZM for the particle-matrix interface introduces a characteristic

length into the model, which in turn leads to a dependence of the predicted toughness enhancement on the particle size. By contrast, the model for an epoxy with open voids does not include this characteristic length and consequently the toughness enhancement does not depend on void size, but only on the void volume fraction.

Fig. 7(a) shows average stresses versus applied strains for unit-cell simulations of 6 vol% SiO_2 particle-reinforced epoxy with varying particle sizes, i.e. $r_p = 10, 120$ and 1000 nm, together with the results for an epoxy with an equivalent volume fraction of open voids. (The inclusion of a larger particle size, i.e. $r_p = 1000$ nm, is intended to provide a micrometre-scale benchmark.) As indicated by the black dot in Fig. 7(a), the initiation of interfacial failure between the particle and the epoxy matrix is not influenced by the particle size, as it is governed by a maximum stress criterion. However, the subsequent debonding process is predicted to be dependent on the particle size, as may be seen by the open squares in Fig. 7(a). Specifically, debonding for a larger particle size (i.e. $r_p = 1000$ nm) occurs almost instantaneously upon the interface stress reaching the interface failure initiation threshold, leading to complete debonding. Consequently, after the point of initiation for interface failure, the stress-strain response of the epoxy with the relatively large particles ($r_p = 1000$ nm) closely mirrors that of an epoxy with open voids. By contrast, smaller particles ($r_p = 10$ and 120 nm) exhibit a relatively slow, progressive interfacial failure with increasing strain. This distinction arises from the critical separation displacement $\delta_c = 2$ nm being comparable with the nanoparticle size, around $r_p = 10$ nm, but much smaller than micrometre sized particles with $r_p = 1000$ nm.

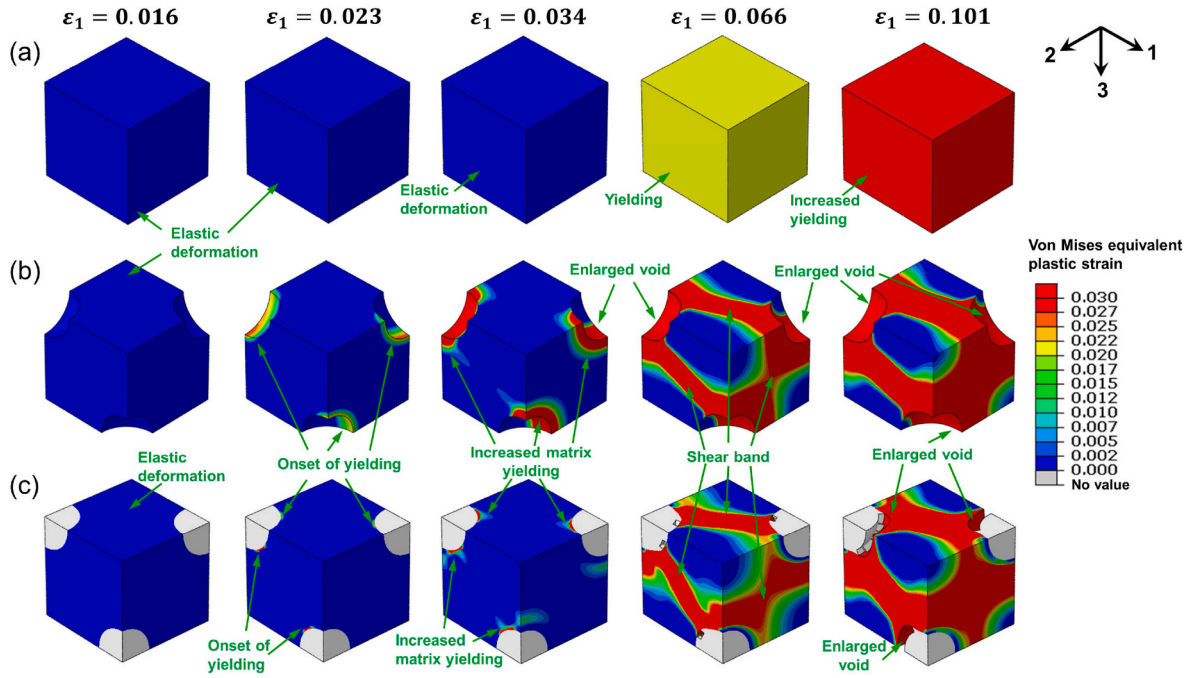


Fig. 4. Contour maps of the von Mises equivalent plastic strain distribution within the unit cell at various applied strain levels for: (a) a pure epoxy, (b) an epoxy with 6 vol% open voids, and (c) an epoxy with 6 vol% nanoparticles ($r_p = 10$ nm). Displacements are applied to the three orthogonal faces of the RVE to induce varying values of principal ε_1 , maintaining a constant triaxial strain ratio of $\varepsilon_1 : \varepsilon_2 : \varepsilon_3 = 1 : 0 : -0.22$.

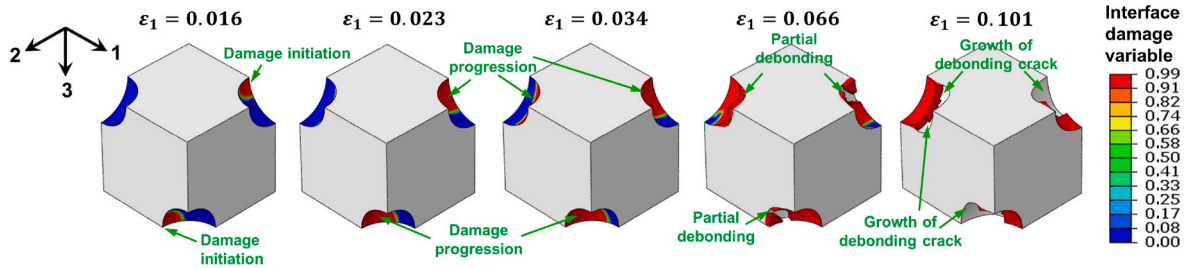


Fig. 5. Contour maps of the damage variable in the CZM for an epoxy containing 6 vol% nanoparticles ($r_p = 10$ nm) at various strains showing the interface damage initiation, progression, and growth of surface debonding. (For clarity, the particles have been artificially hidden). Displacements are applied to the three orthogonal faces of the RVE to induce varying values of principal ε_1 , maintaining a constant triaxial strain ratio of $\varepsilon_1 : \varepsilon_2 : \varepsilon_3 = 1 : 0 : -0.22$.

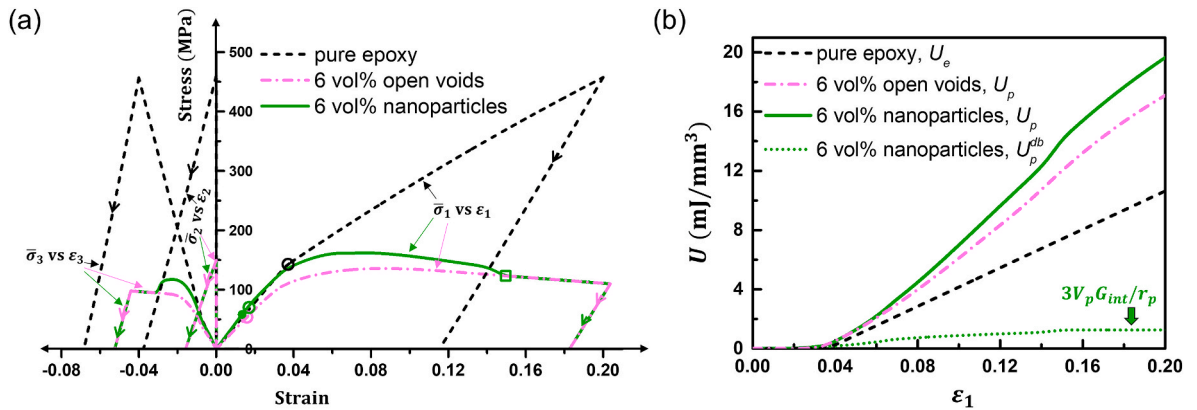


Fig. 6. Determination of the dissipated energy density using the micromechanical RVE model under an applied triaxial strain ratio of $\varepsilon_1 : \varepsilon_2 : \varepsilon_3 = 1 : 0 : -0.22$, followed by elastic, complete unload. (a) Average stress versus strain curves at a distance from the crack plane where $\varepsilon_1 = 0.2$. The open circles indicate the initiation of matrix yielding in the three cases. For the case of '6 vol% nanoparticles', the initiation of interfacial failure and complete debonding are indicated by the solid green dot and green open square, respectively. (b) Variation of the dissipated energy density with ε_1 , where the dissipated energy density due to debonding, U_p^{db} , is also separately shown for the case of '6 vol% nanoparticles'. ($r_p = 10$ nm).

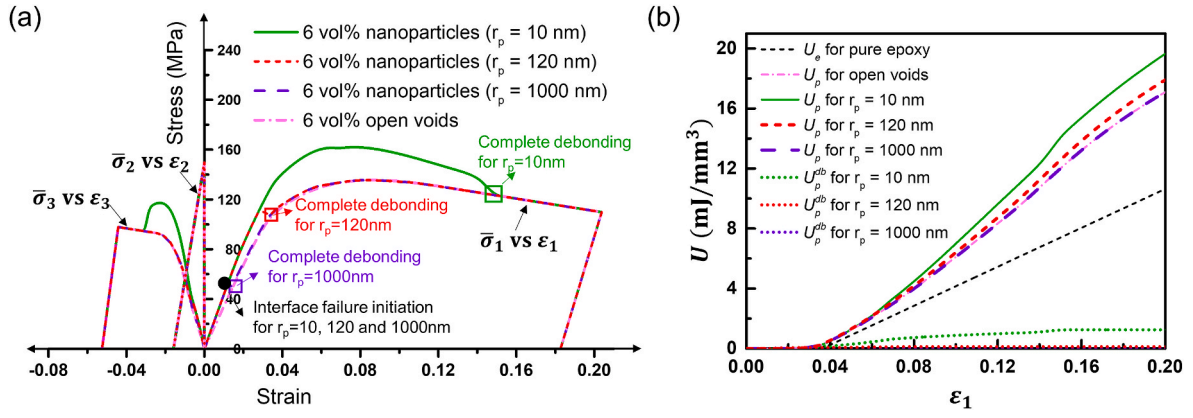


Fig. 7. Micromechanical unit-cell modelling results of the dissipated energy density for different particle radii, under an applied triaxial strain ratio of $\varepsilon_1 : \varepsilon_2 : \varepsilon_3 = 1 : 0 : -0.22$, followed by elastic, complete unload. (a) Average stress versus strain curves, showing that interfacial failure begins at the same applied strains for different nanoparticle sizes. The solid black dots indicate initiation of interfacial failure while the open squares indicate complete debonding. (b) Variation of the dissipated energy density with ε_1 and the dissipated energy density due to debonding, U_p^{db} , for varying particle sizes.

Fig. 7(b) shows the dissipated energy density, U , as a function of the applied strain for an epoxy toughened by rigid SiO_2 particles of varying radii, as well as for the pure and open void-filled epoxy. For the rigid particle toughened epoxy, all the various particle sizes result in an increased energy dissipation compared to the pure epoxy. Notably, large particles ($r_p = 1000$ nm) result in similar values of dissipated energy density to that observed in the case of open voids in the epoxy matrix. It should be noted that the dissipated energy density arising from debonding, U_p^{db} , decreases as the particles increase in size, as shown by

the dotted lines in Fig. 7(b). Indeed, the term U_p^{db} becomes negligible as r_p increases from 10 nm to 1000 nm due to the substantially reduced specific interface area that decreases as r_p increases.

3.4. Comparison with experimental results

The computed values of the normalized fracture energy, G_{cp}/G_{ce} , according to Eq. (4), are compared with the experimental results from SiO_2 nanoparticle toughened epoxies reported in the literature [2,5,13,

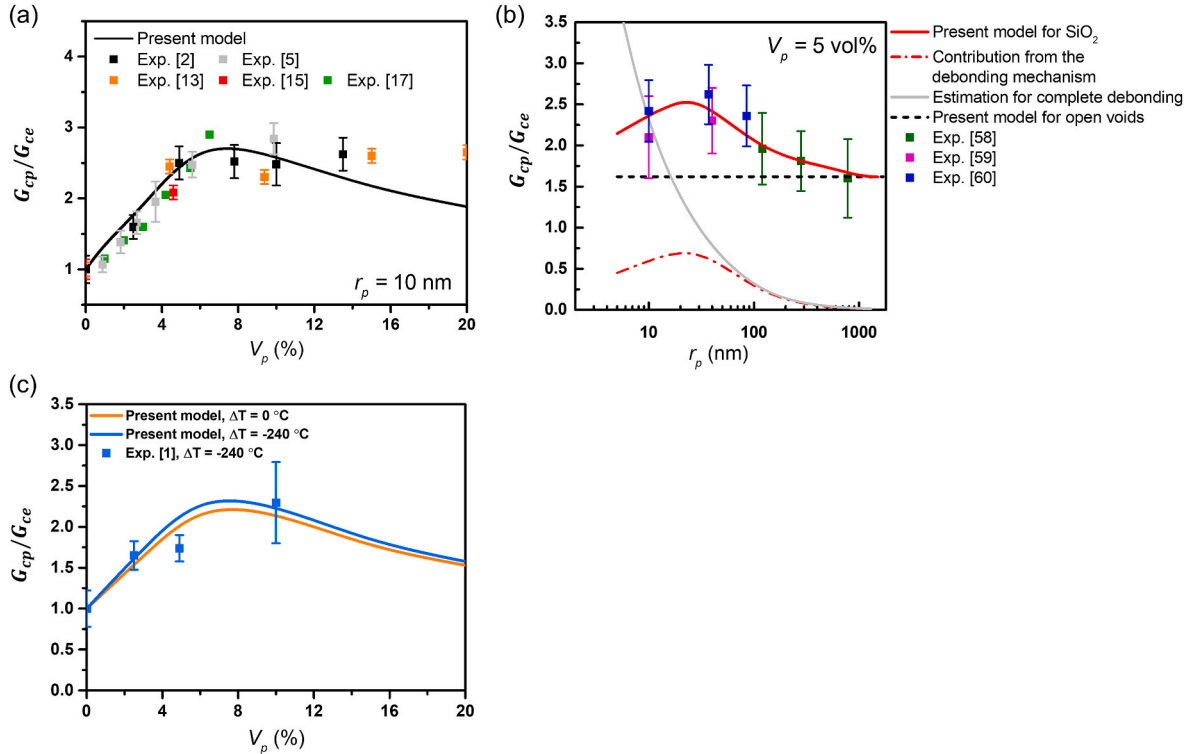


Fig. 8. Comparisons of model predictions and experimental results. (a) Effect of particle volume fraction on the toughening efficiency of SiO_2 nanoparticles. The epoxy polymers have different G_{ce} values but the other matrix properties and curing conditions are similar. (The yield strength σ_Y and Young's modulus E of the pure epoxy in Refs. [2,5,13,15,17] fall within the ranges 79 ± 9 MPa and 3030 ± 170 MPa, respectively, and the curing temperature falls within the range 110 ± 20 °C.) (b) Effect of particle size on the toughening efficiency of SiO_2 nanoparticles. (The solid grey curve represents a surface-area based estimation of the maximum toughening efficacy that might be achieved through solely complete debonding, whereas the dashed red curve shows the predicted contribution by the debonding mechanism to the fracture energy from the present model.) (c) Effect of residual thermal stress at -80 °C on the toughening efficiency of SiO_2 nanoparticles with $r_p = 10$ nm; the curing temperature is 160 °C in Ref. [1], resulting in $\Delta T = -240$ °C.

15,17] in Fig. 8(a), and very good agreement may be seen. These computed values also account for the thermal residual stress due to cooling from the curing temperature to room temperature, as discussed below in Section 3.5. Importantly, the model predicts an optimum volume fraction that will yield the highest toughening for a given particle size. It is worth noting that Eq. (4) indicates the value of β is independent of the fracture energy of the matrix, allowing comparisons with SiO₂-toughening results for different epoxies with varying values of G_{ce} [2,5,13,15,17], when the other matrix properties are similar. (That is, the yield strength σ_Y and Young's modulus E of the pure epoxy in Refs. [2,5,13,15,17] fall within the ranges 79 ± 9 MPa and 3030 ± 170 MPa, respectively.)

Predictions from the model of the effects of particle size are compared with experimental results [58–60] in Fig. 8(b), with the particle sizes ranging from a nano-to micro-scale and a volume fraction of $V_p = 5$ vol%. The model predictions for the open void case, which are size independent, are also included in Fig. 8(b) for comparison. The matrix properties are the same as those reported in Ref. [58]: $G_{ce} = 240$ J/m², $\sigma_Y = 85$ MPa, $\nu = 0.35$ and $E = 3.8$ GPa. The experimental study by Adachi et al. [58] used SiO₂ particles with $r_p = 120, 280$ and 780 nm. Two additional sets of experimental data for smaller size SiO₂ nanoparticles with $r_p = 10, 37, 40$ and 85 nm are taken from Liang et al. [59] and Bray et al. [60] and have been added to Fig. 8(b) for comparison. As can be seen from the red solid curve in Fig. 8(b), the predicted size effect on particle toughening by the present model agrees very well with the experimental results.

3.5. Effect of thermal residual stress

Nano-toughening of the epoxy matrix in fibre-reinforced composites, especially for use in cryogenic environments such as composite vessels for storing liquid hydrogen, has garnered significant attention. In this context, it is therefore important to account for the thermal residual stress, which arises from (i) the temperature difference, ΔT , between the curing temperature, T_c , and the operational temperature, T_o , such as the liquid hydrogen temperature and (ii) the mismatch in the thermal coefficient of expansion (CTE) between the nanoparticles and the epoxy matrix. In these circumstances, Eq. (4) still applies, but with G_{ce} and G_{cp} now denoting the relevant values at T_o , and the proportionality constant being dependent on the material properties at T_o , as well as the thermal stress, which is proportional to ΔT , i.e.:

$$G_{cp}(T_o) = \frac{1}{1 - \beta(T_o, T_c)} G_{ce}(T_o) \quad (6)$$

To investigate the influence of the thermal stress on the proportionality constant $\beta(T_o, T_c)$, which depends on both the curing and operating temperatures, a thermal step is first introduced before applying the displacements in the micromechanical RVE model as described in Section 2.3.

To compare the results from the model with experimental results, we first consider the performance of a SiO₂ nanoparticle toughened epoxy at -80 °C in Ref. [1]. The model uses the matrix properties measured at this operating temperature from Ref. [1]: $G_{ce} = 149$ J/m², $\sigma_Y = 130$ MPa, $\nu = 0.35$ and $E = 3.04$ GPa. The nanoparticle size is $r_p = 10$ nm, with the SiO₂ properties as in Table 2. Values of the CTE for the epoxy matrix and nanoparticles, as in Tables 1 and 2, are applied to the micromechanical RVE model. Interfacial properties are consistently assumed to be $\sigma_{int} = \sigma_Y = 130$ MPa and $G_{int} = W_a = 80$ mJ/m². With a curing temperature of 160 °C, as reported in Ref. [1], then ΔT is -240 °C. To investigate the effect of thermal residual stress, another FE model was conducted where any thermal stress was ignored, i.e. by setting $\Delta T = 0$ °C while keeping all other boundary conditions and material properties unchanged.

Fig. 8(c) shows the modelling results of the normalized fracture energy alongside the experimental data as a function of V_p . The model

predictions with $\Delta T = -240$ °C are again in very good agreement with experimental observations. Compared to the modelling results with $\Delta T = 0$ °C, the presence of thermal residual stress implies a slightly enhanced fracture energy. The reason for this is that, in the case of $\Delta T = -240$ °C, the initial thermal step induces hydrostatic compressive stress at the particle-matrix interface, which was not present in the case of $\Delta T = 0$ °C. The compressive residual stress delays the build-up of the normal tensile stress at the interface, so that the initiation of interfacial failure occurs at a higher strain than the initiation of matrix yielding, in contrast to the case with $\Delta T = 0$ °C, where interfacial failure precedes matrix yielding, as observed in Section 3.2 and Fig. 6(a).

4. Discussion

4.1. Effect of interfacial properties

Determining realistic interfacial properties is experimentally challenging. Consequently, it is worth investigating their effects on the predicted nanoparticle toughening using the computational model that has been developed in the present study. Fig. 9(a) shows the variation of the normalized fracture energy, G_{cp}/G_{ce} as a function of the nondimensional parameters σ_{int}/σ_Y and G_{int}/G_{ce} , for a fixed volume fraction $V_p = 6\%$ of SiO₂ nanoparticles. The value of G_{cp} initially rises with increasing G_{int} but then declines when G_{int}/G_{ce} exceeds 1 %, due to the difficulty in achieving complete debonding for the tougher interface. This results in a maximum toughening at around $G_{int}/G_{ce} = 0.01$ for $\sigma_{int}/\sigma_Y = 1$, which is the value of the interface strength employed for the calculations reported in this study, as noted in Section 2.3.

Assuming $\sigma_{int} = \sigma_Y$, and varying the value of G_{int} , leads to the model predictions shown in Fig. 9(b). In particular, for $G_{int} = W_a = 80$ mJ/m², $G_{cp}/G_{ce} = 2.7$, which is in reasonably good agreement with the experimental result, $G_{cp}/G_{ce} = 2.6$ in Ref. [2]. By varying G_{int} within the range of 50–200 mJ/m², as summarized in Table 3 for typical values of W_a , the present model gives predictions within 12 % of the experimental data in Refs. [2,5,17]. These results corroborate the choice of $G_{int} = 80$ mJ/m², discussed in Section 2.3, as a representative value for the fracture energy of the nano-SiO₂/epoxy interface.

As shown previously by theoretical, computational, and experimental evidence in the literature, continuum mechanics and LEFM remain effective for describing the mechanical behaviour of polymer nanocomposites at the atomic level [24–26], and the CZM approach has been successfully applied at the scale of few nanometres [29–33]. Indeed, the assumed values of $\sigma_{int} = \sigma_Y = 88$ MPa and $G_{int} = W_a = 80$ mJ/m² lead to a critical separation displacement, δ_c , of 2 nm. Molecular dynamics (MD) simulations, increasingly used for atomistic studies of rigid particle-matrix debonding, offer atomic scale inputs for the CZM. Recent MD studies [27,28] attempting to quantify the traction-separation relationship between an epoxy and SiO₂ particles have suggested a critical separation distance of about 2 nm. As summarized in Table 3, this value is also consistent with some recent studies where values as low as 1.0 nm have been used in the CZM for the interface between a polymer matrix and rigid particles, such as clay [29–31], graphene [32] and carbon nanotubes (CNT) [32,33].

4.2. Effect of volume fraction

Fig. 8(a) shows the dependence of the modelling results with $\sigma_{int} = \sigma_Y$ and $G_{int} = 80$ mJ/m² on the value of V_p . The model correctly captures the trend of the available experimental data. At low values of V_p , i.e. below 6%, the model predicts an almost linear rise in the fracture energy with increasing V_p . This increase is attributable to the proportional increase in the specific interface area with the particle volume fraction as given by, for a given r_p , whilst the interactions between adjacent nanoparticles during crack growth remain minor. For higher volume fractions, there is less matrix material that can undergo plastic

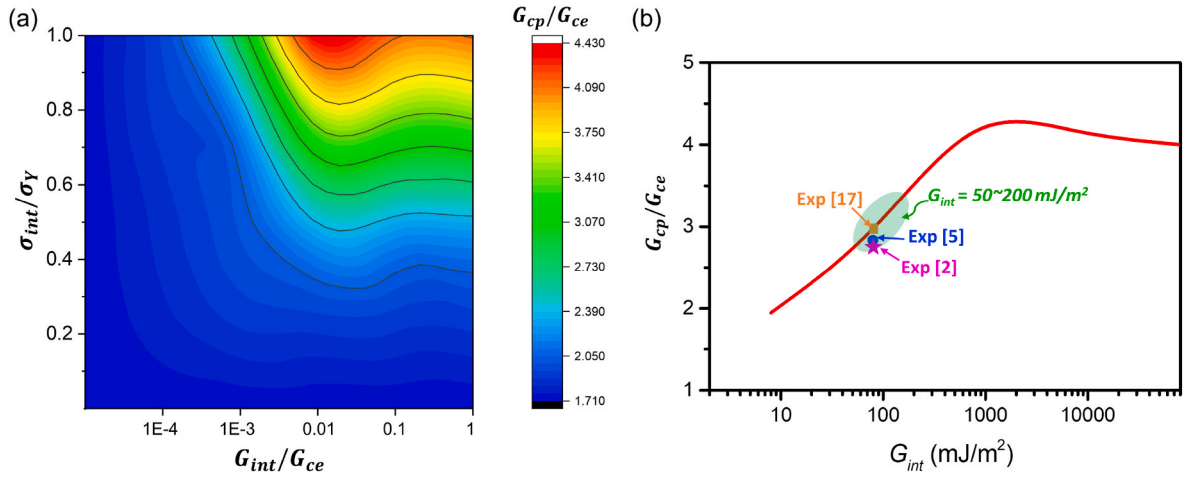


Fig. 9. Parametric investigations of the particle-matrix interfacial properties, i.e. σ_{int} and G_{int} , at $V_p = 6$ vol% and $r_p = 10$ nm. (a) Contour map depicting the effects of interfacial strength and fracture energy on toughening efficiency. (b) Effect of interfacial fracture energy G_{int} on toughening efficiency for the special case of $\sigma_{int} = \sigma_Y = 88$ MPa, with a comparison to experimental results.

deformation and the interparticle distance is reduced, which leads to reduced energy dissipation via shear-band yielding and plastic void growth in the matrix. Consequently, Fig. 8(a) indicates an optimum value of V_p of around 8 vol%.

A similar trend is observed when comparing the present model with experimental data from the authors' previous work [4] for an epoxy containing a different type of nanoparticles, namely cupric oxide (CuO) nanoparticles, as shown in Fig. 10(a). The average radius of the CuO nanoparticles was measured to be $r_p = 135$ nm in Ref. [4], and the interfacial properties are again assumed to be $\sigma_{int} = \sigma_Y$ and $G_{int} = 740$ mJ/m². This last term uses the reported value of W_a for CuO [61], which is significantly higher than that of SiO₂ nanoparticles. The higher fracture energy of the CuO toughened epoxy may be due to its higher interfacial fracture energy, as indicated earlier in Fig. 9(b), and the model predictions align well with the experimental data for a CuO toughened epoxy at relatively low contents (i.e., from 0 to 2.4 vol%) as investigated in Ref. [4]. However, there is a lack of experimental data at higher volume fractions of CuO nanoparticles due to the difficulties in achieving a good dispersion in the experimental studies [4].

Thus, Fig. 10(b) shows a comparison of the present model with two sets of experimental data from Wetzel et al. [62], which investigated an epoxy toughened by either titanium dioxide (TiO₂) or aluminium oxide (Al₂O₃) nanoparticles, with the volume fraction ranging from 0 up to 10

%. The epoxy matrix used in Ref. [62] has a fracture energy of 84 J/m², with $\sigma_Y = 78$ MPa and $E = 2600$ MPa. The rigid metal oxide nanoparticles are spherical, with radii measured to be $r_p = 150$ and 7 nm for TiO₂ and Al₂O₃, respectively [62]. The interfacial properties are again assumed to be $\sigma_{int} = \sigma_Y$, and $G_{int} = 107$ and 125 mJ/m², based on the reported values of W_a for TiO₂ and Al₂O₃, respectively [63]. Using these model parameters, the predictions from the present multiscale model are again found to agree very well with the experimental results for the various rigid particle/epoxy systems covering a wide range of nanoparticle concentrations.

Fig. 10 also shows a comparison of the results from the present model with those from the analytical models proposed by Hsieh et al. [2] and Quaresimin et al. [22] for rigid-particle toughening. Both models show a linear increase in fracture energy with V_p . While they agree reasonably well with experimental observations at low volume fraction range, they fail to predict the tapering-off of the toughening efficiency of nanoparticles as the volume fraction, V_p , increases. This is primarily because these two models do not account for the interactions between neighbouring particles, as acknowledged by the authors [2,22]. By comparison, the present multiscale model gives excellent agreement with the experimental results at both low and high concentration of nanoparticles, as shown in Fig. 10.

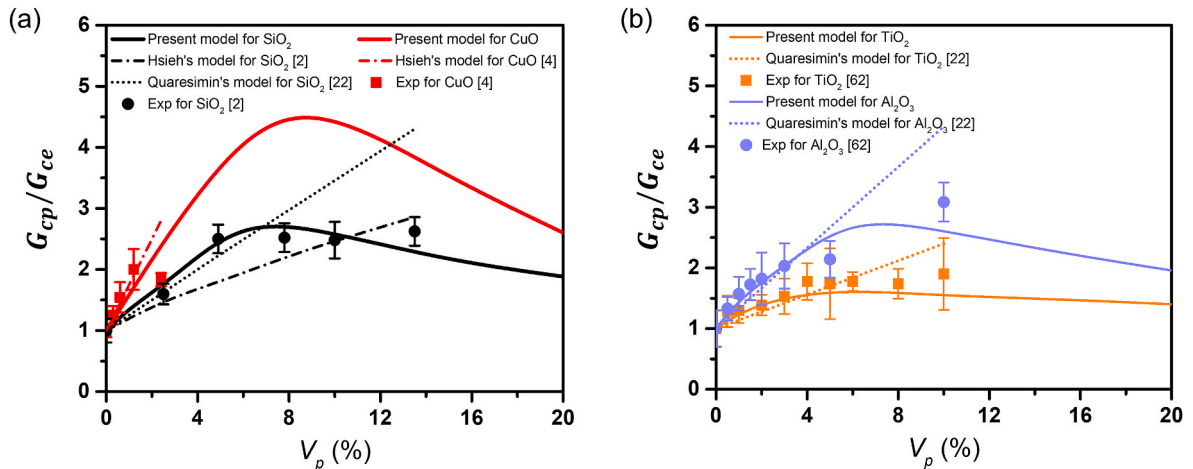


Fig. 10. The effects of volume fraction on the toughening efficiency for different rigid nanoparticles in an epoxy matrix: (a) SiO₂ and CuO nanoparticles and (b) TiO₂ and Al₂O₃ nanoparticles. Both experimental results and predictions from various models are shown.

4.3. Effect of particle size

As noted earlier in Section 3.3, the present model predicts a size effect for nanoparticle toughening and reveals the existence of an optimum particle size that yields the highest toughening effect for a given matrix material. This prediction of the existence of an optimum size explains the mechanism responsible for the experimental observation that the toughness did not increase monotonically as the particle size decreased [58–60]. Furthermore, the model correctly predicts the optimum particle size as shown in Fig. 8(b).

Also included in Fig. 8(b) are the energies released by particle debonding, as discussed in Section 3.2, as a function of the particle radius, r_p . For comparison, the solid grey curve in Fig. 8(b) indicates the predicted value assuming total debonding, which can be seen to increase monotonically for decreasing particle radius. This behaviour is inconsistent with the experimental observations that showed the toughness reached a maximum at a certain particle size. By contrast, the CZM predicts the interface separation does not reach the critical value, δ_c , required for complete debonding, even at the maximum value of applied strain for a given distance from the crack plane. For a given value of applied strain, the interface separation displacement, δ , decreases as the particle size reduces, and hence, for sufficiently small particles (i.e. of radius below 20 nm), no complete debonding can occur. Consequently, as the particle size decreases, this progressive, incomplete interface failure dissipates less energy than would be expected if instantaneous, complete debonding occurred. These energies released during the incomplete debonding are indicated by the red dashed curve in Fig. 8(b).

4.4. Validity of modelling assumptions

The modelling strategy in the present work follows an approach initiated by Evans et al. [35,37] that has also been adopted by several subsequent researchers [1–4,7,17–19,36,60]. This approach generally postulates the toughening mechanisms lead to R-curve behaviour, i.e. to an increasing crack growth resistance with increasing crack extension e.g. [36,64]. The fracture energy increases from an initial value G_{init} , approaching asymptotically a steady-state value G_{ss} . The aim of the modelling is to estimate the increment $G_{ss} - G_{init}$.

In practice, experimental observations on crack growth in toughened epoxies do not always reveal a well-defined R-curve. Nevertheless, the early stages of crack growth still involve a process of crack tip stretching and blunting prior to unstable fracture that is consistent with R-curve behaviour e.g. [62,65,66]. Therefore, the approach in Refs. [35,37] leads to a plausible choice of failure criterion for steady-state cracking, viz. $G_{tip} = G_{init}$. For modelling purposes, it is further conventional to assume that G_{init} can be approximated by G_{ce} , and G_{ss} by G_{cp} , which leads to the failure criterion employed in Section 2.1. This choice of failure criterion requires that the wake height for pure epoxy should be much smaller than that for particle-toughened epoxy, which is not strictly the case in practice, although it can be considered as a pragmatic approximation. This approach has provided several useful insights for materials design, as recorded in previous work [1–4,7,17–19,36,60], and its validity is further confirmed by the good agreement with experimental results presented above.

It is worth noting that from the perspective of continuum mechanics, theoretical considerations suggest that for steady-state crack growth in an elasto-plastic continuum, all of the applied energy release rate G_{app} is expended as plastic dissipation work within the wake, with no energy release being available at the crack tip, i.e. $G_{tip} = 0$. This result, which applies for both pure epoxy and particle-toughened epoxy, precludes the possibility of estimating a toughness increment, because it is not possible to specify a failure criterion. Accordingly, this is not a useful modelling approach from a materials science perspective. Instead, the approach adopted in the present work does provide useful insights for materials

design, albeit relying on agreement with experimental observations to validate the modelling assumptions.

5. Conclusion

A multiscale model of particle toughening of epoxy has been presented in which the enhanced energy dissipation due to the presence of rigid nanoparticles is calculated for an RVE in the form of a cubic unit cell. Two novel features of the model are, first, that the RVE is subjected to a triaxial strain loading and unloading, with the maximum strain and the orientation of the principal strain axes being determined from an elastoplastic stress analysis for a crack in an elastic-perfectly-plastic material. Secondly, the particle-matrix interface is modelled using a CZM, which is a two-parameter model capturing the interfacial strength and an interfacial fracture energy.

This model was employed to calculate the dependence of a nanocomposite's fracture energy on particle volume fraction V_p for a representative particle size $r_p = 10$ nm, as well as the dependence on particle size for a representative volume fraction, $V_p = 5\%$. The results indicate the existence of an optimum volume fraction and an optimum particle size, and these predictions for the first time elucidate the mechanism responsible for the observation that fracture energy reached a maximum and then decreased as the nanoparticle size decreased.

The CZM involves a characteristic length for complete separation, i.e. debonding, which for the case of SiO_2 nanoparticles is found to be $\delta_c = 2$ nm. It has been shown that this characteristic length leads to a size effect for particle toughening, whereby the dissipated energy for micrometre-sized particles can be accurately estimated as the sum of (i) the interfacial energy, and (ii) the plastic deformation energy that would be observed in an epoxy with the same volume fraction of voids. However, for nanoparticles, this sum is shown to overestimate the fracture energy, with the discrepancy increasing with a decreasing particle size. This discrepancy is attributed to the fact that the CZM predicts that nanoparticles do not completely separate from the matrix when their particle size approaches the characteristic separation distance, thus dissipating less energy than the total interface energy.

The model was also employed for a parametric study of the dependence of the predicted fracture energy on the assumed values for the interfacial strength and toughness. The results corroborated the choice of parameters that was used for the predictive calculations. Thus, the present model can be considered to provide a reliable basis for material design, and in particular for assessing the potential benefits of surface functionalization, or other approaches, for tailored interfaces. These fundamental insights into the effects of particle size and interfacial properties, along with our novel multiscale model, open a new avenue for developing advanced toughening strategies to enhance the performance of fibre-reinforced polymer-matrix composites used in storing cryogenic hydrogen, significantly advancing net-zero emission aviation.

CRedit authorship contribution statement

Wenkai Chang: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **L.R. Francis Rose:** Writing – review & editing, Methodology, Conceptualization. **Zhao Sha:** Validation. **Feng Huang:** Software. **Anthony J. Kinloch:** Writing – review & editing, Methodology. **Chun H. Wang:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compscitech.2024.110788>.

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