

GAS-POLYMER INTERACTION AT HIGH PRESSURES

by

Salman Zakaria

A dissertation submitted to the University of London for the degree of
Doctor of Philosophy

**Department of Chemical Engineering and Chemical Technology
Imperial College of Science Technology and Medicine
London SW7 2BY, United Kingdom**

December 1989

To my late father
and
to my mother

P r e f a c e

This dissertation is a description of the work carried out in the Department of Chemical Engineering and Chemical Technology at Imperial College, London between October 1986 and October 1989. Except where acknowledged, the material presented is the original work of the author and includes nothing which is the outcome of work done in collaboration and no part of it has been submitted for a degree at any other University.

I am deeply indebted to Dr Brain J. Briscoe for his moral and technical support throughout the course of this work. His help and guidance has been invaluable. I would like to thank him for this friendly help and encouragement. The technical assistance provided by other members of the Department, particularly S. Roach, R. Wood and L. Moulder is also gratefully acknowledged.

I would like to thank all my fellow members of the Particle Technology and Interface Science group namely, D. Liatsis, M. B. Khan, F. Motamedi, M. Kamyab, B. Chaudhary, D. Williams, K. Galvin, R. Shaoran and I. Blazquez for their cooperation during the study period. I am also thankful to J. E. Burberry for her care and dedication in the typing of this dissertation.

The scholarship grant by the Ministry of Science and Technology, Pakistan, under which this work was carried out is gratefully acknowledged.

Salman Zakaria

December 1989.

ABSTRACT

The thesis describes mainly an experimental study of the interactions of selected gases with a number of elastomers at high ambient pneumatic pressures of up to 27 MPa. The gases studied were nitrogen and carbon dioxide interacting with a silicone elastomer, a nitrile rubber and a PTFE. Certain polymers were also filled with glass spheres of a range of characterised interfacial qualities. Significantly large quantities of gases were absorbed by these polymers when they were exposed to high pressures. The influence of the absorbed gases on the physical and the mechanical properties of the polymeric matrix depended upon the nature of the gas and the ambient pressure. Basically, two types of studies have been undertaken; equilibrium and transient. The equilibrium studies were focused upon the measurement of the amount of the gas absorbed, the sorptive swelling of the test specimens and the changes in the moduli of the specimens at various high pressure conditions. The thermodynamic state of the gas in the polymer-gas mixture was also evaluated. When the surrounding gas pressure was rapidly released the saturated specimen was no longer in equilibrium with the ambient gas. It was observed that at a certain stage during such transient conditions the polymeric specimens were unable to withstand the negative hydrostatic stress exerted by the absorbed high pressure gas and fractured internally. The pressures and the volumetric strains at which the cracks were nucleated in the specimens have been determined for a range of systems. The consequent inflation of the specimens as the cracks grow under the applied negative stress have also been monitored. The peculiar crack patterns which were observed in the damaged specimens have also been investigated. It has been shown that the polymer-filler interfacial quality strongly affects the crack nucleation, the crack orientation, the crack number and the average crack size. These results have been interpreted using a hydrostatic stress

model and a satisfactory account of the data is obtained using this approach.

Overall the thesis demonstrates that the introduction of gases into polymers at high pressure and the subsequent removal of these gases provokes pronounced internal stresses in the polymer solution. The presence of internal interfaces with rigid impermeable filler particles significantly modifies these stress fields and generally suppress the damage caused by gaseous solutes.

LIST OF CONTENTS

	PAGE
Preface	3
Abstract	4
List of Contents	6
List of Figures	12
List of Tables	20
List of Plates	21
List of Symbols	22
 CHAPTER 1:	
Introduction	27
 CHAPTER 2:	
Literature Review: Gases and Polymers	
2.1: Introduction	33
2.2: Mechanism of gas absorption and diffusion in polymers	34
2.2.1: Summary	37
2.3: Effects of penetrant type on absorption and diffusion	37
2.3.1: Summary	39
2.4: Effects of filler particles on gas absorption and diffusion through polymers	40
2.4.1: Summary	45
2.5: Effects of polymer nature on gas absorption and diffusion	46
2.5.1: Summary	48
2.6: Dilation of polymers in high pressure gas ambient	48
2.6.1: Experimental techniques to measure sorptive dilation	54
2.6.2: Summary	57

2.7:	Plasticisation of polymers by absorbed gases	57
2.7.1:	Summary	60
2.8:	Effects of rapid gas pressure release from the ambient of saturated polymers	60
2.8.1:	Summary	65

CHAPTER 3: Literature review: Rupture and Mechanical Properties of Polymeric Systems

3.1:	Introduction	66
3.2:	Internal rupture of elastomers under triaxial stresses	67
3.2.1:	Summary	71
3.3:	Mechanical properties of filled polymers	72
3.3.1:	Summary	74
3.4:	Fracture in polymers containing filler particles	74
3.4.1:	Summary	79
3.5:	Bulk dilation of filled elastomers under tension	79
3.5.1:	Summary	81
3.6:	Elastic behaviour of bonded rubber layers	83
3.6.1:	Summary	84

CHAPTER 4: Experimental Methods, Materials and Procedures

4.1:	Introduction	87
4.2:	Polymeric materials	87
4.3:	Sample preparation	87
4.3.1:	Silicone elastomer	87
4.3.2:	Nitrile rubber	88

4.3.3:	PTFE	88
4.3.4:	Low speed cutting wheel	89
4.4:	Fillers	89
4.4.1:	Interfacial characterisation	90
4.5:	Gases	92
4.6:	High pressure equipment	92
4.6.1:	The gas booster pump	92
4.6.2:	The intermediate gas receiver	96
4.6.3:	The main pressure vessel	96
4.7:	Gas mass sorption probe	98
4.7.1:	Principle of the technique	98
4.7.2:	The vibrating beam	98
4.7.3:	Operation of the vibrating reed as a mass sorption sensor	100
4.7.4:	Analysis of the experimental data	102
4.7.4.1:	Calibration: entrained mass due to change in ambient density	102
4.7.4.2:	Calibration: entrained mass due to change in compression area	103
4.7.4.3:	Mass of gas absorbed	104
4.8:	Ultrasonic technique	106
4.8.1:	General discussion	106
4.8.2:	Mode-1	107
4.8.3:	Mode-2	107
4.8.4:	Instrumentation	112
4.8.4.1:	Ultrasonic transducers	112
4.8.4.2:	Pulser receiver unit	115
4.8.4.3:	Data acquisition systems	115
4.8.5:	Operation	116

4.8.5.1:	Mode-1	118
4.8.5.2:	Mode-2	118
4.8.6:	Data analysis	119
4.8.6.1:	Mode-1	124
4.8.6.2:	Mode-2	125
4.9:	Optical observations	125
4.9.1:	Optical microscope	125
4.9.1:	Scanning electron microscope	125
4.9.3:	Image analyser	126
4.10:	Measurement of mechanical properties	126
4.10.1:	Mechanical testing machine	126
4.10.1.2:	Specimen shape for various experiments	126
	Uniaxial tensile test	126
	Diametric compression	126
	Uniaxial compression of bonded rubber disks	126
4.10.2:	Dynamic mechanical testing machine	128
4.10.3:	Hydrostatic compression	128
 CHAPTER 5: Solubility of High Pressure Gases in Silicone Elastomer Systems		
5.1:	Introduction	130
5.2:	Nitrogen gas sorption	130
5.2.1:	Sorption in filled systems	131
5.2.2:	Dynamic measurements of nitrogen gas sorption	137
5.3:	Carbon dioxide gas sorption	141
5.3.1:	Effects of filler particles on gas sorption	146
5.3.2:	Dynamic measurements of carbon dioxide gas sorption	149
5.4:	Conclusions	151

CHAPTER 6: Volumetric Strain in Polymers under the Influence of Pneumatic Gas and Hydrostatic Pressures

6.1:	Introduction	152
6.2:	Compressibility of polymeric specimens under hydrostatic pressure	154
6.3:	Volumetric strain of specimens under gas pressure	162
6.3.1:	High pressure nitrogen gas environment	162
6.3.1.1:	Effect of filler particle addition on sorptive dilation	167
6.3.1.2:	Density changes	171
6.3.2:	High pressure carbon dioxide gas environment	174
6.3.2.1:	Role of matrix-filler interfaces on sorptive dilation	177
6.3.2.2:	Changes in specimen density	179
6.3.2.3:	Partial molar volume of absorbed carbon dioxide gas	181
6.3.2.4:	Carbon dioxide gas induced dilation of other polymeric systems	189
6.4:	Polymer inflation during rapid gas decompression	191
6.4.1:	Specimen inflation during nitrogen gas decompression	191
6.4.1.1:	Effects of filler particles on specimen inflation	195
6.4.2:	Specimen inflation during carbon dioxide gas decompression	196
6.4.2.1:	Effect of matrix-filler interfacial quality on the inflation characteristics	196
6.5:	Conclusions	204

CHAPTER 7: Monitoring Ultrasonic properties of materials under Pneumatic pressures

7.1:	Introduction	206
7.2:	Material properties under nitrogen gas pressure	207

7.2.1:	Changes in ultrasonic velocity	207
7.2.2:	Specimen moduli under nitrogen gas pressure	212
7.2.3:	Crack detection during nitrogen gas decompression	215
7.2.3.1:	Acoustic emission technique for crack detection	219
7.3:	Material properties in high pressure carbon dioxide gas environment	221
7.3.1:	Ultrasonic velocity changes in certain fluids	221
7.3.2:	Ultrasonic velocity changes in silicone elastomer	223
7.3.3:	Moduli changes under carbon dioxide gas pressure	227
7.3.4:	Crack detection during carbon dioxide gas decompression	227
7.4:	Conclusions	230
 CHAPTER 8: Gas Induced Damage in Elastomeric Composites		
8.1:	Introduction	232
8.2:	Visual inspection	233
8.3:	Optical methods	237
8.3.1:	Effects of ambient gas on internal rupture	240
8.3.2:	Microscopic study of the internal rupture	245
8.4:	Mechanical properties of the damaged specimens	254
8.4.1:	Diametric compression	254
8.4.2:	Cyclic diametric compression	263
8.4.3:	Dynamic mechanical testing	263
8.5:	Conclusions	268
 CHAPTER 9: Conclusions		
	Appendix	277
	References	279

LIST OF FIGURES

CHAPTER 2	PAGE
2.1: Schematic representation of gas sorption into filled systems; E, experimental; R, polymer; F, filler (Clark-Monks & Ellis, 1973).	42
2.2: Schematic representation of elastomer inflation during gas decompression; (a), sponginess; (b), large internal cracks; (c), no visible change (Ender, 1986).	63
 CHAPTER 3	
3.1: Schematic representation of; (a), an unstrained composite specimen; (b), stressed composite leading to dewetting of the filler particle; (c), stressed composite leading to matrix cavitation.	76
3.2: Schematic representation of stress-strain curve for a composite specimen exhibiting filler particle dewetting.	82
3.3: Schematic representation of normal and shear stress distribution across the diameter of a circular rubber sheet bonded between rigid plates (Tobolsky and Mark, 1971).	85
 CHAPTER 4	
4.1: Schematic representation of the blister test apparatus (Briscoe and Panesar, 1988).	91
4.2: Interfacial fracture energy for the various interfaces as a function of crack velocity.	93
4.3: Schematic representation of the pressure vessel assembly.	94
4.4: Schematic diagram of the vibrating reed.	99
4.5: Diagrammatic representation of the vibrating reed instrumentation.	101

4.6:	Change in a/b ratio as a function of specimen compression area (Liatsis, 1985).	105
4.7:	Schematic diagram of the ultrasonic technique mode-1.	108
4.8:	Schematic representation of the ultrasonic mode-2 arrangement; (a), with a commercial transducer; (b), with a transducer made in author's laboratory.	110
4.9:	Schematic representation of a typical commercial ultrasonic transducer.	113
4.10:	Diagrammatic representation of the ultrasonic data acquisition system.	117
4.11:	Change in the ultrasonic velocity for distilled water as a function of N ₂ pressure, 20°C.	120
4.12:	Change in the ultrasonic velocity for distilled water as a function of N ₂ depressurisation.	121
4.13:	Course of phase change for reflected sound waves; (a), wave travelling from sonically hard to a sonically soft material; (b), Wave travelling from sonically soft to a hard material.	122
4.14:	A typical ultrasonic signal showing the first and the second reflection.	123
4.15:	A typical autocorrelogram shown as a function of time lag parameter given in units of sampling time.	123
4.16:	A typical dumbbell shaped specimen all dimensions are in mm and 't', the specimen thickness equals 3 mm.	127
4.17:	The calibration curve of the mercury porosimeter used for measuring volumetric strain of polymers under pure hydrostatic pressure.	129

CHAPTER 5

5.1:	Percentage mass uptake for the various silicone elastomer specimens as a function of N ₂ gas pressure, 20°C.	132
5.2:	Percentage mass uptake for the various silicone elastomer specimens as a function of N ₂ gas density, 20°C.	133
5.3:	Percentage mass uptake on pure polymer basis for the various 20% filled silicone elastomer specimens as a function of N ₂ gas pressure, 20°C.	134
5.4:	Normalised N ₂ gas mass uptake for the unfilled silicone elastomer specimen as a function of square root of time.	138
5.5:	Normalised N ₂ gas mass uptake for a 20% (w/w) glass filled silicone elastomer specimen as a function of square root of time.	139
5.6:	Theoretical mass uptake curves against square root of time for diffusion. Numbers on the curves represent diffusion coefficient in cm ² ·sec ⁻¹ (Liatsis, 1989).	140
5.7:	Percentage entrained mass due to dilation for the various silicone elastomer specimens as a function of CO ₂ gas pressure, 42°C.	142
5.8:	Percentage mass uptake for the various silicone elastomer specimens as a function of CO ₂ gas pressure, 42°C. Data from Fleming and Koros (1986) are also shown.	143
5.9:	Percentage mass uptake for the various silicone elastomer specimens as a function of ambient CO ₂ gas density, 42°C.	145
5.10:	Percentage mass uptake on pure polymer basis for the various silicone elastomer specimens as a function of CO ₂ gas pressure, 42°C.	147
5.11:	Glass beads in a swollen polymer, (a) nonswollen state, (b) halos around glass spheres (Oberth, 1967).	148

5.12:	Normalised CO ₂ gas uptake for the silicone elastomer as a function of square root of time.	150
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CHAPTER 6

6.1:	Percentage volumetric compression for the unfilled silicone elastomer specimen as a function of hydrostatic pressurisation and depressurisation in the mercury porosimeter.	156
6.2:	Percentage volumetric compression for the various 20% filled silicone elastomer specimens as a function of hydrostatic pressure in the mercury porosimeter. Data for the unfilled specimen are also shown.	158
6.3:	Percentage volumetric compression on the basis of polymer volume fraction for the various 20% filled silicone elastomer specimens as a function of hydrostatic pressure in the mercury porosimeter. Data for the unfilled specimen are also shown.	159
6.4:	Percentage volumetric compression for the various polymeric specimens as a function of hydrostatic pressure in the mercury porosimeter.	160
6.5:	Percentage linear dilation for the unfilled silicone elastomer as a function of N ₂ gas pressure, 20°C.	163
6.6:	Percentage linear compression for the various polymeric specimens as a function of N ₂ gas pressure, 20°C.	165
6.7:	Percentage linear dilation for the various 20% filled silicone elastomer specimens as a function of N ₂ gas pressure, 20°C. Data for the unfilled specimen are also shown.	168
6.8:	Applied mechanical stress for the various disc type specimens as a function of linear strain, data for the cylindrical unconstrained specimens are also shown	170

6.9:	Percentage linear strain for the various disc type specimens as a function of N ₂ gas pressure, 20°C.	172
6.10:	Percentage change in density for the various specimens as a function of N ₂ gas pressure, 20°C.	173
6.11:	Percentage linear dilation for the various silicone elastomer specimens as a function of CO ₂ gas pressure, 42°C. Swelling data for a silicone elastomer reported by Fleming and Koros (1986) are also plotted.	175
6.12:	Percentage swelling for the unfilled silicone elastomer in cyclohexane solvent as a function of time, room temperature (20°C).	178
6.13:	Percentage change in density for the various silicone elastomer specimens as a function of CO ₂ gas pressure.	180
6.14:	Percentage change in volume for the various silicone elastomer specimens as a function of the absorbed CO ₂ concentration.	182
6.15:	Partial molar volume for the absorbed CO ₂ in the various silicone elastomer specimens as a function of ambient CO ₂ gas pressure.	184
6.16:	Plots of ultrasonic signals transmitted through the unfilled silicone elastomer specimen under CO ₂ gas pressure at; a, 0.1 MPa ; b, 10 MPa; c, 12 MPa.	187
6.17:	Percentage linear dilation for the nitrile rubber and the PTFE as a function of CO ₂ gas pressure.	190
6.18:	Percentage linear inflation for the various silicone elastomer specimens as a function of ambient high pressure N ₂ gas decompression.	192
6.19:	Typical N ₂ gas decompression profile as a function of time.	193

6.20: Typical profile of the pressure vessel temperature as a function of time during N ₂ gas depressurisation.	194
6.21: Percentage linear inflation for the various silicone elastomer specimens as a function of ambient high pressure CO ₂ gas decompression.	197
6.22: Typical CO ₂ gas decompression profile as a function of time.	198
6.23: Typical profile of the pressure vessel temperature as a function of time during CO ₂ gas depressurisation.	199
6.24: Percentage linear inflation for the various silicone elastomer specimens during CO ₂ gas decompression as a function of time.	201
6.25: Percentage linear inflation for the nitrile rubber specimen as a function of CO ₂ gas depressurisation.	203

CHAPTER 7

7.1: Ultrasonic signal transit time for a round trip through the length of the silicone elastomer specimen, 20°C and 0.1 MPa.	208
7.2: Ultrasonic velocity for the various prestrained unfilled silicone elastomer specimens as a function of N ₂ gas pressure, 20°C.	209
7.3: Ultrasonic velocity for the distilled water as a function of pressure, 20°C.	211
7.4: Percentage change in the modulus of the unfilled silicone elastomer specimen as a function of N ₂ gas pressure.	213
7.5: Percentage change in the modulus for the unfilled silicone elastomer specimen as a function of the specimen density change in high pressure N ₂ gas ambient.	214

7.6:	Change in ultrasonic signal attenuation for the silicone elastomer specimen during ambient high pressure N ₂ gas decompression. The specimen inflation under similar conditions is also shown.	217
7.7:	Acoustic emission event counts for the silicone elastomer specimen during ambient high pressure N ₂ gas decompression. The specimen inflation under similar conditions is also shown.	220
7.8:	Velocity of sound in the distilled water as a function of CO ₂ gas pressure.	222
7.9:	Percentage change in ultrasonic velocity for the silicone fluid (400 cp), as a function of CO ₂ gas pressure, 42°C.	224
7.10:	Percentage change in ultrasonic velocity for the unfilled silicone elastomer specimen as a function of CO ₂ gas pressure, 42°C.	225
7.11:	Percentage change in the modulus for the unfilled silicone elastomer specimen as a function of CO ₂ gas pressure.	228
7.12:	Change in ultrasonic signal attenuation for the unfilled silicone elastomer specimen as a function of ambient high pressure CO ₂ gas decompression.	229

CHAPTER 8

8.1:	Silicone elastomer specimen filled with 20% (w/w) carbon black; (a), cured at 20°C; (b), cured at 100°C.	234
8.2:	Appearance of the silicone elastomer specimen at various stages of the explosive decompression experiment; (a), before the experiment; (b), 20 min after the experiment, (c), 24 hours after the experiment.	235
8.3:	Cross section of the CO ₂ gas damaged specimens; (a), unfilled; (b), untreated filler; (c), release agent treated filler; (d), silated filler; (e), primered filler.	238

8.4:	Cross section of the N ₂ gas damage specimen; (a), unfilled; (b), filled (0.5%).	241
8.5:	Lateral depth of the N ₂ gas induced internal rupture (saturation time 15 min).	243
8.6:	Typical ring cracks in the cross section of CO ₂ gas damaged nitrile rubber.	246
8.7:	Internal crack initiated from a release agent coated filler particle.	247
8.8:	Interfacial rupture of an internal untreated interface.	248
8.9:	Crack arrested at a strong internal interface.	250
8.10:	SEM micrograph of internal interfaces treated with the adhesion promoter; (a), cohesive rupture of the matrix; (b), broken glass bead in the crack path.	252
8.11:	Model silicone elastomer-glass interfaces; (a), interfacial failure for the weak interface; (b), Cohesive failure for the strong interface.	253
8.12a:	Stress as a function of diametric strain for the various CO ₂ gas damaged silicone elastomer specimens.	255
8.12b:	Stress as a function of diametric strain for the various N ₂ gas damaged silicone elastomer specimens.	256
8.13:	Cross section of a cylindrical specimen. The rectangle ABCD is the shape assumed for the rubber carrying the load (Lindley, 1966).	257
8.14:	Normalised stress as a function of diametric strain for the various CO ₂ gas damaged silicone elastomer specimens.	258
8.15:	Surface of internal cracks for the silicone elastomer; (a), N ₂ gas damaged; (b), CO ₂ gas damaged.	262

8.16a: The force requirement for 30% diametric strain for the various N ₂ gas damaged silicone elastomer specimens as a function of cyclic loading.	265
8.16b: The force requirement for 30% diametric strain for the various CO ₂ gas damaged silicone elastomer specimens as a function of cyclic loading.	266
8.17: Loss tangent for the various CO ₂ gas damaged silicone elastomer specimens	267

LIST OF TABLES

Chapter 2	PAGES
2.1: Solubility and diffusivity in silicone elastomer; atmospheric pressure, 27°C.	47
Chapter 5	
5.1: Solubility of high pressure N ₂ gas and CO ₂ gas in the silicone elastomer and its composites.	136
Chapter 6	
6.1: Measured mechanical properties of the various polymeric specimen.	161
6.2: Dimensional response of the various specimens to hydrostatic pressure and N ₂ gas pressure.	166
6.3: Partial Molar Volume of CO ₂ in various liquids at 25°C; atmospheric pressure (Horiuti, 1931)	185

Chapter 8

8.1:	Optical assessment of damage in the various silicone elastomer specimens after CO ₂ gas decompression.	244
8.2:	Normalised stress at 20% diametric strain.	260
8.3:	Interfacial fracture energy at a crack velocity of 0.2 m/s.	261

LIST OF PLATES

CHAPTER 4	PAGE
4.1: The high pressure equipment exhibiting the booster pump, the gas receiver and the pressure vessel enclosed in the heat exchanger. Some of the electronic instrumentation is also shown.	95
4.2: The ultrasonic mode-1 experimental arrangement attached to the pressure vessel cap.	109
4.3: The ultrasonic mode-2 experimental arrangement.	111
4.4: The electronic instrumentation involved in the ultrasonic technique.	113

LIST OF SYMBOLS

Chapter 2

Latin

- D Diffusion coefficient
- D_0 Arrhenius constant for temperature dependence of diffusion coefficient
- E_D Activation energy for diffusion
- G Shear modulus
- P Pressure
- r Void radius
- R Gas constant
- S Solubility coefficient
- S_f Solubility coefficient of a gas for the filler particles in a composite specimen
- S_0 Arrhenius constant for temperature dependence of solubility coefficient
- S_r Solubility coefficient of a gas for the polymer fraction in a composite specimen
- S_{vac} Solubility coefficient of a gas for the filler voids
- T Temperature
- T_b Boiling temperature
- T_c Critical temperature
- V_f Volume fraction of the filler particles in a composite specimen
- V_r Volume fraction of the polymer in a composite specimen
- V_{vac} Volume fraction of the filler voids in a composite specimen

Greek

- γ Surface energy of rubber
- ΔH Heat of solution
- λ Extension ratio

- ρ_g Density of gas
- ρ_{liq} Density of liquid
- σ_g Solubility parameter of gas
- σ_{liq} Solubility parameter of liquid

Chapter 3

Latin

- a Radius of the specimen
- d Radial distance
- e Compressive strain
- E Young's modulus of a specimen
- E_o Young's modulus of an unfilled specimen
- G Shear modulus
- G_a Bond fracture energy
- h Specimen thickness
- K Numerical constant
- P Hydrostatic inflation pressure
- P_c Critical pressure
- r Radius of filler particle
- S' Cracking stress
- s Stress concentration factor
- t Shear stress
- V_f Volume fraction

Greek

- ϵ_b Strain to break
- λ Extension ratio
- σ_1 Homogeneous compressive stress
- σ_2 Stress due to interfacial constraints

- σ' Critical stress
- σ_a Dewetting stress
- σ_b Breaking stress
- σ_r Radial stress
- σ_θ Tangential stress
- σ_z Axial stress
- ν Poission's ratio

Chapter 4

Latin

- a Numerical constant
- a_c Debond radius at rupture conditions
- A_c Specimen compression area
- b Numerical constant
- c Ratio of specimen mass to beam mass
- E Young's modulus
- F Frequency of vibration at higher pressures
- F_0 Frequency of vibration at atmospheric conditions
- F_r Gas flow rate
- h Thickness of elastomer layer
- H_c Blister height at rupture conditions
- J Coefficient of transmission of sound waves
- k Thickness of displaced gas
- K Radius of gyration
- l Length of specimen
- l_r Length of rod
- L Longitudinal modulus
- M_{Ac} Entrained mass due to change in specimen compression area
- M_{Al} Entrained mass for aluminium sample

M_{el}	Apparent mass of polymeric sample
$\dot{P}_c$	Critical pressure
R	Coefficient of reflection of sound waves
t_c	Time at rupture
T	Period of vibration
V	Velocity of sound
V_l	Longitudinal velocity
z	Auxiliary variable, dimensionless
Z	Acoustic impedance

Greek

Γ	Debond fracture energy
Δm	Added mass
ρ	Density
ρ_s	Density of the beam material
τ	Transit time
ν	Poisson's ratio

Chapter 6

Latin

B	Bulk modulus
C	Concentration of absorbed gas in the polymer
E	Young's modulus
g	Molar volume of gas at STP
l_s	Linear strain
V	Final specimen volume
V_o	Original specimen volume
V_p	Partial molar volume of absorbed gas
R	Coefficient of reflection of sound waves

Z Acoustic impedance

Greek

ν Poisson's ratio

Chapter 7

Latin

L Longitudinal modulus

V Longitudinal velocity

Greek

ρ Density

Chapter 8

Latin

b Width of load bearing sides

d Diameter of cylindrical specimen

ϵ Specimen strain

Greek

θ Angle formed at the specimen axis corresponding to the width of the load bearing side

CHAPTER ONE

INTRODUCTION

Organic polymers are employed in many technologically important areas and the applications may expose the polymers to very hostile and demanding gaseous environments. For example, polymers are being currently used as membranes for gas separation at elevated pressures and temperatures. They are also applied as coatings on metal surfaces to protect the metal against the effects of corrosive ambients. The high elasticity of certain polymers, particularly elastomers, also makes them uniquely suitable for seals and hoses in high pressure service environments. As such organic polymers may be exposed to gases under high pressures for prolonged periods. These situations occur in gas transportation pipelines, gas compressors, valve seatings and separation units. In the nuclear industry, the gas cooled reactors and auxiliaries have a number of penetrations, many of which have demountable sealing plugs made out of elastomeric materials. It is well known that when high pressure gases and polymers are in contact significant quantities of the gases are absorbed by the latter. A number of studies have been conducted and reported in this area.

The high pressure ambient gas will have two potentially opposing effects on the polymeric system. The first, is the hydrostatic pressure effect which resembles the compressive stress exerted by an impenetrable fluid media, for example mercury. The polymer will tend to contract. The second is caused because the gas is able to penetrate into the material. The presence of sufficient amounts of the penetrant reduces the hydrostatic compressive effects. There may in fact be a considerable dilation of the polymer as a result. These situations may not pose potentially significant problems in sealing applications or in membranes as long as

isobaric conditions prevail. However, if a rapid reduction of the ambient pneumatic pressure occurs the polymer's coherence may be destroyed. The gas dissolved in the material under the high pressure is no longer in equilibrium with the ambient when the pressure is removed. A pressure gradient between the interior of the polymer and its periphery is thus created. The specimen behaves somewhat like a pressure vessel with high pressure gas inside. The polymeric material is unable to withstand the large negative hydrostatic stresses. Bubbles are nucleated and expand resulting in the internal rupture of the polymeric matrix. This type of damage is sometimes termed as 'explosive decompression rupture'. It resembles cavitation in simple liquids.

Conventionally, the effects of high pressure gas decompression on a polymer are investigated by exposing the polymer to the gas in a pressure vessel and inspecting the sample after the pressure cycle is completed. Thus, it is only possible by these means to detect the permanent damage and the changes in the polymer at the end of the experiment. Generally, the changes produced in the tensile strength, the Young's modulus and the hardness, as obtained from measurements before and after the pressurisation, are compared. Then on the basis of the visual inspection and the degradation of some of these mechanical properties speculations are made regarding the interaction of the gas with the polymer. This kind of research has been carried out by the research and development departments of several industries with an interest in this problem. The main objective has been to evaluate the behaviour of different commercial polymeric compounds and to rank these materials according to their decompression resistance. Typical examples of such research or testing studies are those conducted by Eudes *et al* (1967), Schremp and Roberson (1973), Kosmala (1984) and Cox (1985). Several different commercial elastomers have now been ranked according to their resistance to gas decompression induced damage. The process engineers have used this type of information to facilitate the selection of the most appropriate material for a given

application.

A number of other studies have been conducted to detect changes in the physical dimensions of polymeric specimens under gas pressure. These measurements were made through a window in the pressure vessel (Kamiya *et al*, 1988; Fleming and Koros, 1986). The behaviours were primarily examined to describe the anomalous gas sorption isotherms for the materials tested.

The major theme of the current study has been to investigate the influence of different high pressure gases on polymeric materials in situ and to determine the response of these systems as the high pressure gas ambients were rapidly reduced in pressure. The study has been restricted to a rather narrow selection of organic polymers and composites. These include silicone elastomer and its composites, a carbon filled nitrile rubber and a PTFE. The effects of the filler particle addition in certain polymers with various matrix-filler interfacial qualities have also been examined in this study. Nitrogen (N₂) and carbon dioxide (CO₂) gases were selected as the pneumatic pressure media. The areas of interest reported in this thesis include the gas solubility measurements at high pressures, the volumetric strains induced by the various high pressure environments, the effects of the high pressure gases on the specimen modulus, the nucleation of internal cracks in the specimens during the explosive decompressions and the extent of inflation during these transient conditions. Finally, after the completion of the pressure cycle the extent, the pattern and the nature of the damage has been examined and is described. The degradation of certain mechanical properties has also been investigated.

Central to this whole experimental study is the specific adaptation of an ultrasonic pulse-echo technique for use in high pneumatic pressure environments. The technique basically employs piezoelectric transducers that transmits and receives compression waves propagated through the polymeric specimens under pressure and during decompression. The changes in the signal transmission

characteristics, in conjunction with the results obtained by using other techniques, have provided an insight into the behaviour of the polymeric systems in various high pressure gas environments. The physical state of the gas absorbed by the system has been considered in certain cases. The internal cracks in the specimens that were usually observed after the experiments were completed have been detected with the ultrasonic technique as they nucleate during the rapid release of the ambient gas pressures. The same technique has also been employed in a different manner to determine the gas induced sorptive dilation of the specimens and their inflation during the pressure reductions.

The thesis is presented in nine chapters. The current Chapter provides a general introduction to the theme of the study undertaken. The Chapter 2 and 3, are in the form of literature review Chapters which consider the basic concepts and precedents associated with this work. The former principally deals with the interaction of gases with polymers. The available literature is described including the established gas absorption mechanisms with special emphasis on the effects of penetrant type, polymer structure and the presence of filler particles in polymeric absorbents. The sorptive dilation and the plasticisation observed by other researchers is surveyed along with their respective experimental techniques. Finally, the rather limited literature in the field of the so-called 'explosive decompression' is reviewed. Chapter 3 is a review of the fracture behaviour of polymers under hydrostatic tension and of the effects of filler particles on the mechanical and the fracture properties of such systems. The information gleaned from these chapters is found to be useful in understanding and interpreting the experimental results which are presented later.

In Chapter 4 the details of the materials and the experimental techniques employed are provided. In addition, this Chapter includes sections describing the experimental procedures. The fracture energy curves for the model interface systems are included. The calibration curves for some of the experimental

techniques used in this study are also provided.

Chapters 5, 6 and 7 report and discuss the experimental results obtained for the interaction of the high pressure gases with the polymers. Chapter 5 deals with the gas sorption in the polymeric systems. N_2 and CO_2 gas mass uptake data at high pressures are reported. For the composite systems the gaseous uptake is presented as such and also on the basis of the polymer fraction in the specimens. The variations in the gas sorption data are interpreted according to the matrix-filler interfacial quality. The results provided in this Chapter are discussed in the later Chapters of the Thesis. The measured volumetric strains of the polymeric specimens under the hydrostatic and the pneumatic pressures are presented in Chapter 6. The effects of the high pressure N_2 and CO_2 gases are discussed separately. The influences of the filler particles with different interfacial qualities are also presented. The amount of the CO_2 gas absorbed in the silicone elastomer system is significantly higher and correspondingly the sorptive dilation is also larger than for the nitrile rubber system. The magnitude of the swelling resembles that induced by a liquid solvent at ambient pressure. The partial molar volume of the absorbed CO_2 gas in the silicone elastomer has been calculated. In the high pressure CO_2 gas environment the deterioration of the ultrasonic signals which travel through the silicone elastomer specimen is interpreted as an evidence for gas domain formation. This supposition is consistent with the partial molar volume data. The inflation of the various polymeric specimens during the rapid decompression of the ambient gas to the atmospheric pressure is also described in this Chapter.

Chapter 7 deals with the changes in the ultrasonic properties of the various materials under the pneumatic pressures. The observed variations in the velocity of the ultrasound are indicative of the changes in the specimen modulus. The values of the moduli were computed with the help of the gas sorption and the dilation data

which were reported in the previous two Chapters. In addition, results are presented indicating the changes in the ultrasonic signal attenuation during the decompressions. The generation of the acoustic emission signals under similar conditions have also been reported. These data detect the initiation and development of the cracks in the specimens. The results are also compared with the inflation data for similar specimens given in Chapter 6.

In the penultimate chapter (Chapter 8) the damage induced in the various polymeric specimens during the explosive decompressions is presented. The damage instigated by the different gases are clearly distinguishable. The size, the pattern and the extent of the internal lacerations are described and compared. The cohesive and adhesive nature of the cracks are identified and related to the matrix-filler interface qualities determined previously. The relative degradation in the stiffness of the ruptured specimens are quantified by performing certain mechanical tests. A correlation is found between the observed extent of the damage and the degradation in the mechanical properties.

The thesis concludes with Chapter 9, which summaries the major findings of the research study.

CHAPTER TWO

LITERATURE REVIEW: GASES AND POLYMERS

2.1 INTRODUCTION

In this Chapter a review of the published work dealing with the interaction of various high pressure gases with polymers is presented. Generally, polymeric materials are able to absorb significant amounts of gases, especially at high ambient pressures. Overall, the amount of a gas absorbed in a polymer has been found to depend on the gas type, the ambient gas pressure, the ambient temperature and the nature of the polymeric system. The large quantity of the absorbed gas may induce dilation of the specimen and also influence the mechanical properties of the polymer.

The main purpose of this review Chapter is to provide a background in which the data from the subsequent chapters may be interpreted and compared with previous studies. The Chapter is divided into several sections. It begins with a description of the basic principles and mechanisms of gas absorption and the associated diffusion processes. The effects of polymer type, the presence of inclusions in the specimen and the type of penetrant gas are also reviewed. Then, the subjects of sorptive dilation and mechanical properties of polymer-gas solutions are discussed. The response of the saturated polymers to the rapid release of the ambient gas pressures has also been described in light of the available literature. Some of the publications considered here deal with more than one of the above subjects, therefore, it is common for a description of these communications to appear under different section headings.

2.2 MECHANISM OF GAS ABSORPTION AND DIFFUSION IN POLYMERS

The mechanisms of gas absorption and diffusion have been frequently discussed in terms of the structural characteristics of the polymeric matrix and the molecular dimensions of the gas. It is proposed by Meares (1954) that a polymer bulk structure below its glass transition temperature (T_G) contains a number of 'holes', that are essentially regions of low density in the matrix and the dissolved gas molecules are accommodated in these regions. Above the transition temperature the increased mobility of the polymeric chains results in an equilibrium distribution of the 'holes' in the bulk of the polymer and the dissolving gas molecules have to create their own space by separating the inter-chain molecular contacts. Stannett and Williams (1965) argue that perhaps the number of the so-called 'holes' do not change substantially above the T_G of the polymer. In fact the size of the 'holes', which depends upon the amplitude of the segmental oscillations, increases. If the penetrant molecules are small, the change in solubility with temperature will not be exhibited, since, the probability of the penetrant molecules encountering the 'holes' remains almost the same. However, with larger molecules, the 'hole' dimension becomes important. Large penetrant molecules are accommodated more easily at higher temperatures and an increase in the amount of the gas absorbed will occur. Stannett and Williams (1965) and Meares (1954) have observed this effect while studying the oxygen gas absorption in polyvinyl acetate above and below the T_G .

With the viewpoint of explaining gas sorption in rubbers van Amerongen (1964) proposed that the so-called 'holes' covered a whole spectrum of sizes and are continuously being formed and destroyed. At a given temperature, there is a definite size distribution and a state of equilibrium exists. In respect of gas solubility, a rubbery polymer was regarded equivalent to an organic liquid. Several other researchers have agreed with this analogy (Fleming and Koros, 1986;

Southern, 1985; Hirose *et al*, 1986; George, 1984). The experimental results for CO₂ absorption in a silicone elastomer and a fluorocarbon rubber obtained by George (1984) closely followed the results obtained by Shair and Prausnitz (1961) for CO₂ gas absorption in organic liquids. It was proposed that due to this similarity in the results the gas-plus-liquid model can be applied to gas-plus-elastomer solutions. The experimental results in the low pressure range obtained in the present study also agree with this proposed correspondence.

The extent of gas sorption at atmospheric and moderate pressures generally follows Henry's law. Recent studies by Koros and Fleming (1985) have shown that the absorption of CO₂ gas in a butyl rubber follows Henry's law until a pressure of ca. 2 MPa at 35°C. The solubility coefficient of $6.25 \times 10^{-6} \text{ m}^3(\text{STP}) \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$, is in good agreement with the values presented earlier by van Amerongen (1964, p.1101) at atmospheric conditions. Similarly, the CO₂ gas sorption in a silicone elastomer at 35°C also obeyed Henry's law up to 2 MPa (Fleming and Koros, 1986). However, in the higher pressure range, from 2 MPa to 6 MPa, the sorption isotherm showed a positive deviation from Henry's law. The causes for such a behaviour will be discussed in a later section of this Chapter.

In polymers, below their T_G , the sorption of a gas is often explained by a dual-mode sorption theory (Stannett, 1978). It elaborates the earlier concept of the so-called 'holes' as discussed by Meares (1954, 1958). According to this theory two concurrent modes of penetrant sorption are operative. In one mode, penetrant uptake occurs in a 'dissolved' state. This behaviour is like gas sorption in rubbery polymers and can be described by Henry's law. In the second mode, gas sorption is viewed as uptake into molecular scale 'berths' or microvoids that are present due to the non-equilibrium nature of glassy polymers; they are often referred to as Langmuir sites of absorption. These microvoids have been described as being due to the restrictions on the molecular segment motion at temperatures below the T_G . The chain relaxation is comparatively slow and the trapped free volume may be

immobilised over relatively long periods of time. They have also been termed as 'frozen microvoids' in the matrix (Koros and Paul, 1978).

The solubility of a penetrant gas is related to the temperature and the heat of solution by an Arrhenius-type relation:

$$S = S_0 \exp (-\Delta H/RT) \quad (2.1)$$

where 'S' is the solubility coefficient, ' ΔH ' is the heat of solution, 'R' is the gas constant and 'T' is the absolute temperature. With gases, for which the heat of solution is negative, the solubility will decrease with an increase in the temperature and *vice versa*. However, a small increase in the solubility above the T_G of a glassy polymer may occur even if the heat of solution is negative. The solubility of more volatile gases like helium (He), hydrogen (H_2) and N_2 increases with an increase in the temperature, while that of less volatile gases like CO_2 it decreases with a temperature increase (van Amerongen, 1964, 1950).

Gases are compressible, therefore their solubility is also pressure dependent and it is possible to significantly augment the solubility by increasing the gas pressure. This topic is discussed later in some detail.

Meares (1954) and van Amerongen (1950, 1964) have proposed that the diffusion of gases in polymers above and below the T_G proceeds by the movement of the penetrant molecules into the 'holes' created by the movement of the polymer chains. The rate of diffusion depends on the concentration of these 'holes' which are of a sufficient size to accommodate the diffusing molecules. The smaller molecules will therefore diffuse faster than the larger ones since the smaller cavities will occur more frequently. It is expected that for the small molecules little disturbance of the medium is required, while the diffusion of the larger molecules involves larger zones of activation. The movement of the chains also requires an energy to overcome the intermolecular (van der Waals) forces (Meares, 1954). Hence, the activation energy and the temperature are related to the diffusion coefficient by the following Arrhenius-type equation:

$$D = D_0 \exp (-E_D/RT) \quad (2.2)$$

where 'D' is the diffusion coefficient, 'D₀' is the pre-exponential factor, 'E_D' is the activation energy, 'R' is the gas constant and 'T' is the absolute temperature. Generally, the greater the energy of activation for a system, the slower will be the diffusion. An increase in the temperature will increase the diffusion rate.

The activation energy has been related to the temperature dependence of polymer viscosity by van Amerongen (1950), although the movements of the polymer segments in this case are not of the same size as in viscous fluids (Meares, 1954). Thus, the higher the viscosity, the higher will be the activation energy, resulting in a lower diffusion rate.

2.2.1 Summary

It has been proposed that the gas absorbed in polymers resides in the available 'free volume'. In sorption terms, elastomers are analogous to organic liquids and at low to moderate pressures Henry's law is followed. However, glassy polymers are non-equilibrium in nature and the penetrant molecules are also accommodated into the molecular scale voids present in the system. This is referred to as Langmuir sorption. An increase in the system temperature will increase the penetrant diffusion rate and affect the sorption capacity of the polymer. It has been observed that with increasing temperature the solubility of volatile gases (He, H₂ and N₂) increases whilst that of less volatile gases (CO₂, NH₃) decreases.

2.3 EFFECTS OF PENETRANT TYPE ON ABSORPTION AND DIFFUSION

The nature of the penetrant gases have a strong influence on the solubility and the diffusivity through polymers. The solubility increases with gases of higher

critical temperature or higher boiling point. Thus, it can be said that, the easier for a gas to condense, the more soluble it is. The solubility as a function of critical temperature (T_c) and boiling temperature (T_b) has been described by the following linear relations (van Amerongen, 1950):

$$\log S = -2.1 + 0.0074 T_c \quad (2.3)$$

$$\log S = -2.1 + 0.0123 T_b \quad (2.4)$$

These equations were based on the assumption that solubility is synonymous with condensation followed by mixing in the polymers (Barrer and Chio, 1965). The easily condensable gases like CO_2 , SO_2 and NH_3 were found to be more soluble than the permanent gases (van Amerongen, 1964; Southern, 1985). The solubility of CO_2 gas was found to be 20 times that of N_2 gas in natural rubber and 50 times that in nitrile rubber (Eudes *et al*, 1968). Similarly, the more soluble a gas in water or any other liquid, the more soluble it is in polymers (van Amerongen, 1964; Stannett, 1978). This point also supports the analogy between rubbers and organic liquids, except that rubbers are crosslinked and cannot flow. It might be contemplated that the smaller gas molecules merely fill the vacant spaces between the larger polymer molecules. This is certainly not the case with liquids, as the volumes are additive. Similarly, it is not the case for highly soluble gases and polymers (Southern, 1985). This is also explained by the data obtained by the expressions (2.3) and (2.4) given above. van Amerongen (1964, p. 1103) found that for the gases with boiling point higher than CO_2 , the volume of the dissolved gas was larger than the volume of the rubber involved. This positively indicates that the process of gas sorption is not just the 'filling up' of the vacant spaces in the polymer. The presence of the penetrant molecules can cause plasticisation and expansion of the matrix. This process will be further elaborated in a later section of the Chapter.

The size of the penetrant gas molecules also shows its effect on the solubility and the diffusivity through polymers (Stannett and Williams, 1965). The

CO₂ gas molecules are larger than those of many other permanent gases and its solubility is high. Similarly, the pentane molecules are even larger and their solubility is also greater (Southern, 1985).

The diffusivity of gases in polymers decrease with an increase in the penetrant molecular size (van Amerongen, 1950, 1964; McBride, 1979). The smaller molecules diffuse faster; for example, the diffusion of He gas is faster than CO₂ gas. However, the solubility comparison is reversed (Micheals and Park, 1959). The activation energy for gas diffusion is related to the cohesive energy of the elastomers and the chain stiffness of the glassy polymers. For the elastomers it is proportional to the diameter of the penetrant molecule and for the latter to the square of the diameter (Stannett and Williams, 1965).

There is a general rule for mixing of liquids, that is, like mixes with like. It is also true for gas solubility in polymers (van Amerongen, 1950, 1964; Southern, 1985). This point has been experimentally demonstrated by van Amerongen, (1950) while studying the sorption of non-polar He, N₂, O₂ and polar CO₂ gases in a mixture of a non-polar butadiene rubber and a polar acrylonitrile rubber. It was observed that as the quantity of the polar acrylonitrile increased in the mixture the solubility of the non-polar gases was reduced.

2.3.1 Summary

The penetrant gases that are easy to condense are more soluble in polymers than the permanent gases. Similarly, the gases with larger molecules are absorbed more significantly. However, the diffusion rate decreases with the penetrant size. The polar penetrant gases were found to be more readily soluble in the polar polymers than in the non-polar materials and *vice versa*. The absorbed gas molecules do not merely fill up the vacant spaces in the polymer, they may also induce dilation of the system.

2.4 EFFECTS OF FILLER PARTICLES ON GAS ABSORPTION AND DIFFUSION THROUGH POLYMERS

Polymer compounds may contain a considerable amount of fillers. These fillers may be non-reinforcing or reinforcing to a varying degree. The particles may be spherical or non-spherical. Hence, depending upon the filler type and its interaction with the matrix, the fillers show a considerable influence on the solubility and the diffusivity of the penetrant gases. Generally, the solubility of gases in filled systems depends upon three factors (Van Amerongen, 1964; Melikhova *et al*, 1959):

- (a) The solubility in the rubber phase;
- (b) Gas adsorption by the filler surfaces not wetted by the polymer;
- (c) The filling up of gas pockets or vacuoles in the porous fillers.

It was therefore proposed that the term sorption rather than solubility should be used for such systems, regardless of the sorption mechanism. The sorption constant of a gas in a filled system may be higher or lower than the solubility in the unfilled polymer. The concept of 'normal sorption' was introduced by Melikhova *et al* (1959). It denotes the amount of the gas dissolved in the polymer fraction of the filled system.

Clark-Monks and Ellis (1973) have described seven different situations for sorption that might occur in filled polymeric systems; these are illustrated in Figure 2.1.

1. When the adhesion between the filler and the polymer matrix is zero, they absorb the penetrant independently and the total sorption can be obtained by adding the two according to the volume fraction of each component, Figure 2.1-a.
2. If the adhesion between the filler surface and the polymer matrix is strong, absorption of the penetrant only occurs by the polymer, Figure 2.1-b.
3. If there is a strong matrix-filler interaction the penetrant sorption can be even

less than that which might occur in the pure polymer. Such a situation is attributed to a reduced sorption in the polymeric layers near the filler surfaces, Figure 2.1-c.

4. The strong polymer-filler bonds restrict penetrant sorption in the layers near the filler surfaces. However, above a critical penetrant pressure all the polymer fraction in the specimen begins to contribute in the absorption process, Figure 2.1-d.

5. The strong interaction between the polymeric matrix and the filler is only effective at low pressures. Above a certain critical pressure both the filler and the polymer contribute to the sorption process, Figure 2.1-e.

6. This case is similar to the above (case 5); however, a transition is observed in the sorption process relative to the pressure over which the filler gradually begins to participate in the sorption process, Figure 2.1-f.

7. Here the total sorption in the composite is greater than the cumulative absorption by the polymer and the filler, Figure 2.1-g.

Most of the experimentally determined sorption behaviours for various filled systems will fit any one of the seven models presented above. In the present study, situations similar to the cases 3 and 7 have been observed.

Melikhova *et al* (1959) found that N₂ gas sorption in several rubbers with 20% channel black decreased by 30 to 50% of the normal sorption. In the case of butadiene-acrylonitrile copolymer the decrease in the N₂ gas sorption was of the order of 75%. Kwei and Kumin (1964) used a vapour sorption method to investigate polymer-filler interactions, at temperatures above and below the T_G of the polymeric matrix. They observed that the titanium dioxide filled polyvinyl acetate absorbed less acetone vapours than the unfilled polymer. However, at higher vapour pressures the sorption isotherm for the filled system corresponded to the isotherm for the unfilled polymer. A typical example of the case-4 sorption model given above. A noticeable decrease in chloroform vapour sorption was also observed in a copper phthalocyanine filled epoxy (Kwei and Kumin, 1964).

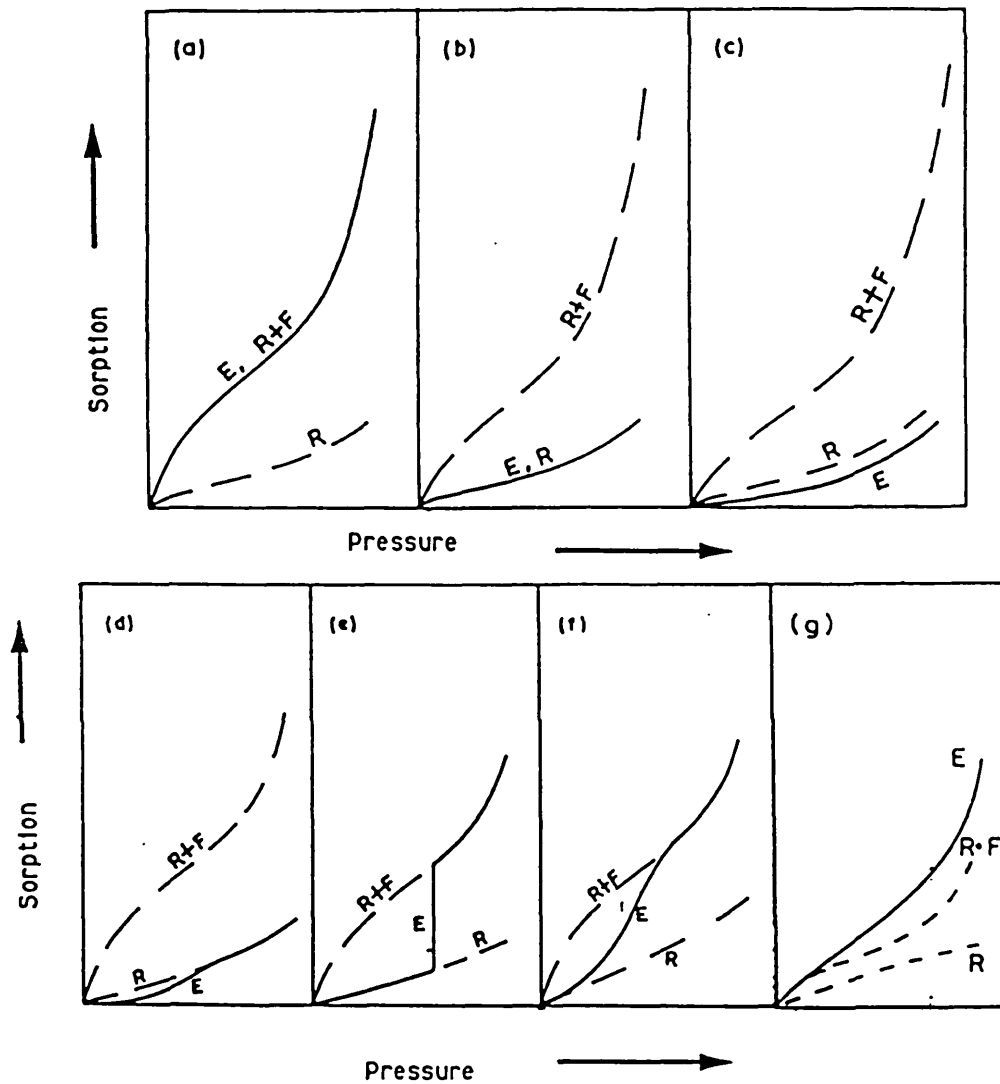


Figure 2.1: Schematic representation of gas sorption into filled systems; E, experimental; R, polymer; F, filler (Clark-Monks & Ellis, 1973).

At low vapour pressures the decrease in the sorption was proportional to the amount of the filler incorporated. The adsorption of the polymer chains on the filler surfaces was thought to have reduced the possible configurations of the polymer molecules. It was implied that the properties of the adsorbed polymer layers were different from that of the unfilled polymer. However, weakening of the polymer-filler interaction may occur due to the possible competitive adsorption of the absorbed molecules on the filler surfaces. Carpenter and Twiss (1940) have also described a reduction in the gas absorption which they considered to result from the polymer adsorption on the filler surfaces. They suggested that this effect may be interpreted as removing a fraction of the polymer from the phase that was likely to contribute in the sorption process. Barrer *et al* (1960) investigated the effects of high surface area silica fillers on the solubility and the diffusivity of C4 and C5 hydrocarbon vapours in a silicone elastomer. The solubilities were discussed in terms of two simplified models. In the first model, the filler and the polymer phases act independently as sorbents and the solubility is given as;

$$S = S_r V_r + S_f V_f \quad (2.5)$$

where 'S' is the solubility, 'V' is the volume fraction and the subscripts 'r' and 'f' refer to the polymer and the filler respectively. In the second model the filler is regarded as completely wetted by the polymer and it does not adsorb the vapours, therefore the total solubility is given as:

$$S = V_r S_r \quad (2.6)$$

The experimental results obtained by these researchers were consistent with the second model.

Fillers like aluminium oxide, barium sulphate and carbon black, when incorporated in natural rubber have been shown to cause an increase in gas sorption (van Amerongen, 1955, 1964). The reason given for such a trend was, that the filler particles were only partially wetted by the polymer. In the case of the carbon black filler the small cavities and capillaries were not filled with the polymer and

were able to take up the gas molecules. As the surface area of the filler increased the sorption of the gas also increased. In this case, the total solubility was given by the following relation:

$$S = V_r S_r + V_f S_f + V_{vac} S_{vac} \quad (2.7)$$

The subscript 'vac' refers to filler voids.

Tanioka *et al* (1982) have also observed an increased CO₂ gas sorption in natural rubbers which was proportional to the carbon black content. At higher concentrations, the carbon black seemed to form aggregates which also contributed to the increased gas sorption. Previously, Carpenter and Twiss (1940) had also attributed the increase in the gas sorption to the adsorption by the carbon filler. The sorption isotherms for the carbon black filled natural rubbers were neither Langmuir nor Henry's type (Tanioka *et al*, 1982). The slope of the isotherms decreased with the increased penetrant pressure and then became constant. The sorption isotherm for the carbon black powder was Langmuir type and tended to saturate with the increasing pressure. On the other hand, the sorption isotherm for the natural rubber was linear and followed Henry's law. Hence, the different sorption behaviours for the natural rubber and the carbon black contributed to the anomalous isotherm for their composite.

The diffusivity of penetrant molecules in polymers is also affected by the presence of filler particles. The impermeable fillers behave like geometric obstructions in the path of the gas passing through the polymer. Lengthening of the diffusion path occurs as the diffusing molecules have to pass 'around' the filler particles (van Amerongen, 1955, 1964; Melikhova *et al*, 1959; Barrer *et al*, 1962). A decrease in the molecular chain flexibility of the polymer due to the interaction with the filler surfaces may also contribute to the decreased diffusivity. A high modulus phase in the vicinity of the filler particles may be formed which has a longer relaxation time than the ordinary polymer (Melikhova *et al*, 1959; Tanioka *et al*, 1982). A part of the penetrant gas may also be adsorbed on the filler surfaces

and be rendered unable to take part in the diffusion process (van Amerongen, 1955, 1964; Most, 1970).

Melikhova *et al* (1959) has reported that increasing the filler content above a certain limit would result in an increase in the diffusion coefficient. This phenomenon would normally occur due to improper wetting of the filler particles. Rapid transport of the penetrant molecules can then occur along the surfaces of the interconnected filler particles; this process is termed as short circuit diffusion. Tanioka *et al* (1982) have suggested that by decreasing the aggregation of polymer molecules, the diffusion rate can be increased. The addition of filler particles can help in the breaking up of the aggregates and this consequently would lead to a higher diffusivity.

2.4.1 Summary

In a filled polymeric system gas sorption and diffusion are affected by the nature of the filler particles and the matrix-filler interaction. In the systems where the fillers are not completely wetted by the polymer, an increase in the gas sorption has been observed. On the other hand, a strong polymer-filler interface results in a decrease in the penetrant uptake. However, weakening of the interaction may occur due to the competitive adsorption of the absorption molecules on the filler surface. Seven possible situations for sorption in filled systems have been proposed. Generally, the experimentally determined sorption behaviours fit any one of these models. The impermeable fillers act as geometric obstructions and lead to lengthening of the diffusion path. However, increasing the filler content above a certain limit can result in short circuit diffusion along the surfaces of the interconnected filler particles.

2.5 EFFECTS OF POLYMER NATURE ON GAS ABSORPTION AND DIFFUSION

It has been mentioned in an earlier section, that the modes of gas absorption in glassy and rubbery polymers are qualitatively different. The sorption and transport of gas molecules have been used as a probe to obtain information and insights into polymer structure and the mobility of polymer chains. Micheals & Parker (1959) and Micheals & Bixler (1961) have studied the effects of amorphous and crystalline polymer structures on the absorption and transport behaviours of non-condensable gases. The crystallinity present in the polymer was regarded as an impermeable filler particles in the amorphous matrix. It was proposed that the crystalline component of the polyethylene does not take part in the gas sorption and it may also reduce the chain segment mobility in the interstitial amorphous phase. As a result, the penetrant diffusion was more difficult (Klein and Briscoe, 1976). The crystallites also contribute towards increasing the tortuosity of the diffusion path (Micheals and Park, 1959; Micheals and Bixler, 1961). Similarly, the hard segments in a polyurethane were also considered to act as filler particles and restrain the motion of the soft segment chains. These segments were impenetrable towards the penetrant molecules, therefore, increase the length of the diffusion path (McBridge, 1979).

The polydimethyl siloxane polymer, mostly used in this study, has a very high degree of chain mobility. This is reflected by an easy diffusion of penetrant molecules through the polymer (Barrer *et al*, 1962; Warrick *et al*, 1979; Polmanteer, 1982). This polymer has a wide range of solubilities for various gases. The solubility and the diffusivity values for different gases at atmospheric pressure, taken from Warrick *et al* (1979, p. 478), are given in Table 2.1. The solubility of hydrocarbon vapours like butane and pentane in silicone elastomer was found to be similar to that in natural rubber but the diffusion rate was an order of magnitude

<u>GAS</u>	<u>DIFFUSIVITY</u> (cm ² /s x 10 ⁶)	<u>SOLUBILITY</u> (cm ³ (STP)/cm ³ ·atm)
He	60.0	0.045
H ₂	43.0	0.12
CH ₄	12.7	0.57
N ₂	15.0	0.15
O ₂	16.0	0.31
Ar	14.0	0.33
CO ₂	11.0	2.20
C ₄ H ₁₀	~5.0	15.0

Table 2.1: Solubility and diffusivity in silicone elastomer, atmospheric pressure, ca. 27°C.

higher (Barrer *et al*, 1962). The degree of crosslinking seemed to have little effect on the solubility, at low concentrations at least. Silicone elastomers have a very low activation energy for diffusion, about 4 kcal/mole. This low value indicates that in gas diffusion the movement of only a small number of chain segments is involved. This is probably an outcome of the greater chain flexibility and lower 'internal' viscosity. Clustering of penetrant molecules can occur in silicone elastomers. This process is more prominent at high penetrant concentrations. The gaseous aggregates formed can reduce the chain mobility and a decrease in the diffusivity may occur (Warrick *et al* , 1979).

2.5.1 Summary

The studies of gas sorption and transport in polymers may reveal some information about their structure. In a given polymer system the presence of crystallinity can reduce the sorption and the diffusion capabilities as compared to the state where the system is amorphous. Silicone elastomers have high degree of chain mobility and the gas diffusivity is higher. The gas solubility in these materials is also higher and clustering of the penetrant molecules may also occur at high gas concentrations.

2.6 DILATION OF POLYMERS IN HIGH PRESSURE GAS AMBIENT

A liquid solvent for an uncrosslinked polymer will swell the crosslinked polymer. The dilation of polymers by liquid solvents have been extensively studied (Treloar, 1975). Similarly, when polymers are exposed to gases at high pressures, swelling of the matrix may occur. The extent of the swelling depends upon the swelling potential of the gas and the elastic properties of the polymer. Gas induced

volumetric swelling in rubbers of the order of 50% has been reported by Ender (1986). Gases like H_2S , SO_2 and CO_2 which have relatively high solubilities in polymers, are strong swelling agents at higher pressures (Griffiths, 1985; Ender, 1986; Eudes *et al*, 1968; Liau and McHugh, 1985). Most of the recently reported gas induced swelling studies have been conducted with CO_2 gas under a pressure of ca. 6 MPa and at a temperature of 35°C. The critical temperature of CO_2 is 31.4°C.

Eudes *et al* (1968) reported the findings of their investigations in a search for a suitable elastomeric material that could be used in CO_2 gas cooled nuclear reactors as pipeline plugs. The original plugs were found to swell by 8 to 10% in the CO_2 gas atmosphere at 6 MPa and gave a spongy appearance to the polymer. It was found that the softer materials had a much greater tendency to dilate than the harder materials. Another study by George (1984) for silicone and fluorocarbon elastomers, in similar applications, showed that the swelling was proportional to the amount of the CO_2 gas absorbed and which, in turn, varied linearly with the CO_2 gas pressure. An increase in temperature decreased the amount of CO_2 gas absorbed and correspondingly the extent of the swelling also reduced. It was observed that at 100°C and at a CO_2 gas pressure of 4 MPa the volumetric swelling in the silicone elastomer was ca. 4%. However, the swelling reduced to ca. 3% at a higher temperature of 140°C at a similar pressure. This indicates that all the gas absorbed in the elastomer contributes in the swelling process. The effects of elastomer hardness on the extent of the gas sorption and the swelling were similar to those found by Eudes *et al* (1968).

Ender (1986) has measured the swelling of various nitrile rubbers and fluorocarbon elastomers in different high pressure gas environments in the pressure range of up to 28 MPa at 100°C. The gases used were H_2S , CO_2 , CH_4 and C_2H_6 . The fluoro-elastomers with different hardness and moduli exhibited similar swelling; ca. 18% linear expansion in the CO_2 gas ambient. The behaviour of the

nitrile rubbers was, however, specific to the individual elastomer and the extent of the dilation was lower than that for the fluoro elastomers. In one case, a nitrile rubber specimen was slightly compressed over the pressure range. This was attributed to the presence of voids in the matrix. Liatsis (1989) has also reported compression in polyurethane specimens under a CO₂ gas pressure of ca. 20 MPa. The urethane specimens had a large number of voids entrapped in the matrix. It was suggested that the hydrostatic component of the gas pressure collapsed the voids and resulted in this particular trend.

It has been found that H₂S is the most effective swelling agent for ethylenepropylene polymer (EPDM). It induced a linear swelling of ca. 18% at 28 MPa and 100°C (Ender, 1986). This was followed by C₂H₆, CO₂ and CH₄ gas which induced 6%, 4% and 3.5% linear swelling respectively. Ender (1986) has considered that these gases acted as solvents for the polymers. This opinion was based on the fact that the compression of gases to a super-critical state, i.e. to a pressure above its critical pressure at a temperature above its critical temperature, gives them a positive solvent power normally not possessed at low pressures (Czubryt *et al*, 1970). Super-critical CO₂ has been used to extract impurities from polymers and other solids. The solvent density controls the solubility in the super-critical phase. A small change in pressure near the critical point can vary the solvent power over a wide range (Liau and McHugh, 1985; King, Eissler and Friedrich, 1988). The solubility parameter is a function of the density and is given as (Czubryt *et al*, 1970):

$$\sigma_g = \sigma_{Liq} [\rho_g / \rho_{Liq}] \quad (2.8)$$

where ' σ ' is the solubility parameter and ' ρ ' is the density, and the subscripts 'g' and 'Liq' are for the gas and the liquid phases. The densities of gases with high critical temperature, like CO₂, NH₃ and H₂S at high pressures, are in the range of 0.3 to 0.9 times the equivalent liquid density. Czubryt *et al* (1970) have shown that the solubility of organic compounds peak in the CO₂ at the pressures at which the

solubility parameter of the gas equals that of the solute. The elastomers are crosslinked and insoluble, therefore it was proposed by Ender (1986) that a swelling maximum would be expected at these conditions.

Liau and McHugh (1985) investigated the dilation of polymethyl methacrylate (PMMA) in He gas and super-critical CO₂. No dilation was observed in the He environment of up to ca. 25 MPa at ca. 58°C. However, the polymer was swollen by around 10% in the CO₂ ambient under similar conditions. The dilation was initially linear and then increased more slowly until it reached a limiting value at higher pressures. The CO₂ sorption in the polymer also followed a similar pattern. It was proposed that under pressure the CO₂, which possesses liquid-like density, was solubilised in the PMMA in large amounts. This process led to the significant swelling of the matrix. At still higher pressures the CO₂ absorption reached a saturation point since further increase in the pressure had very little effect on the CO₂ properties. Hence, a plateau in the PMMA swelling as a function of pressure was observed.

Anomalous high pressure sorption isotherms are observed for certain polymeric systems. In the case of glassy polymers they were concave to the pressure axis in the low pressure range and change to convex or to a straight line at higher pressures. For rubbery polymers, they sometimes change from the usual straight line to a convex curve at higher pressures. These aforementioned behaviours cannot be explained on the basis of ordinary sorption models. For example such trends have been associated with depression in glass transition temperatures and plasticisations leading to a dilation of the polymer matrices. In addition, for the commonly used methods of determining gas sorption isotherms, the dilation of the polymeric specimens needs to be considered in making accurate measurements. The gravimetric method requires a correction for the buoyance change and in the barometric method, specimen dilation necessitates a correction in the void volume of the vessel containing the polymeric sample. The void volume is

used in the material balance calculations to determine the gas sorption. Similarly, the vibrating reed mass sorption sensor used in this study needs to be calibrated for the increases in the entrained mass associated with specimen swelling. A number of researchers have conducted sorptive dilation studies (Fleming and Koros, 1986; Koros and Fleming, 1985; Hirose *et al*, 1986; Sefcik, 1986 a, b; Wissinger and Paulatis, 1987; Kamiya *et al*, 1988 a, b). A range of different polymers with CO₂ gas in the pressure range of up to 10 MPa at 35°C have been investigated.

The gas absorbed in a polymer occupies some volume which is generally termed as the partial molar volume (PMV). In low density polyethylene (LDPE) at temperatures above its T_G the sorptive dilation has been found to be proportional to the gas concentration (Hirose *et al*, 1986). Every CO₂ gas molecule sorbed contributed equally to the volume expansion. For this polymer the dilation was anisotropic and the average linear sorptive dilation coefficient per unit pressure at 35°C was measured as $1.7 \times 10^{-9} \text{ Pa}^{-1}$.

In a silicone elastomer-CO₂ system the sorptive dilation was also proportional to the amount of CO₂ absorbed (Fleming and Koros, 1986, Koros and Fleming, 1985). It was observed that for the CO₂ gas pressures above 2 MPa the sorption isotherm did not follow Henry's law model and became convex to the pressure axis. The dilation isotherm also followed a similar trend. The departure from linearity was attributed to the high concentration of the sorbed penetrant. At the CO₂ gas pressure of ca. 6 MPa the isotropic linear dilation was measured as ca. 9.0%. The CO₂ concentration in the elastomer at this pressure was measured as ca. $140 \text{ m}^3(\text{STP}) \cdot \text{m}^{-3}(\text{poly})$. The partial molar volume of the CO₂ in the silicone elastomer-CO₂ mixture was determined as $46.2 \text{ cm}^3 \cdot \text{mole}^{-1}$. Similarly, in a LPDE the PMV has been computed as $44.5 \text{ cm}^3 \cdot \text{mole}^{-1}$ (Hirose *et al*, 1986). These values for the two polymers above their T_G are in reasonable agreement with the PMV values reported for certain organic solvents; they range between 43 to 48 cc/mole (Horiuti, 1931). This agreement indicates that the rubbery polymers are

equilibrium solids and their interaction with CO₂ is very similar to that of CO₂ with low molecular weight liquids (Fleming and Koros, 1986; Hirose *et al*, 1986).

In glassy polymers where gas sorption is described by the so-called dual-mode sorption model, it has been suggested that only a fraction of the total sorption is associated with actual chain separation and may hence cause dilation. The gas sorbed in the microvoids or the 'holes' in glassy polymers does not contribute to sorptive dilation (Fleming and Koros, 1986). However, Kamiya *et al* (1988 a, b) are of the opinion that the microvoids which are smaller than the volume of a penetrant gas molecule will contribute to matrix dilation. Sefcik (1986 a, b) does not agree with both and argues that the measured dilations cannot arise from the contributions of a fraction of the total sorbed molecules. Much seems to be a matter of semantics in this area.

In certain glassy polymers, such as polyethylene terephthalate (PET), polyvinyl benzoate (PVB) and polymethyl methacrylate (PMMA) the slope of the CO₂ gas induced dilation isotherms start to increase rapidly at a certain high pressure. This has been linked to the occurrence of the glass transition (Sefcik, 1986b; Wissinger and Paulatis, 1987; Kamiya *et al*, 1988 a, b). The knowledge of these behaviours have helped explaining the anomalous CO₂ gas sorption isotherms for these polymers. The sorption isotherms for PET, PVB and PMMA were typically concave to the pressure axis in the lower pressure regions and became linear in the higher pressure regions. The dilation versus penetrant concentration curves also exhibited an inflection point which divided the curves into two parts. The inflection points were attributed to the isothermal glass transitions induced by the increasing CO₂ concentrations; the systems were plasticised. However, the dilation isotherm for PMMA presented by Liau and McHugh (1985) did not follow the above-mentioned behaviour. Wissinger and Paulatis (1987) have attributed this anomaly to the differences in the experimental techniques used by different groups.

Another distinct type of CO₂ sorption isotherm was observed for

polycarbonate (Wissinger and Paulatis, 1987). In the low pressure region, it was concave (up to 7 MPa) and at higher pressures it almost levelled off and seemed to reach a maximum. The swelling isotherm also showed a similar trend. It was suggested that the levelling off of the dilation isotherm was due to the absence of the CO₂ induced glass transition in the pressure range investigated. The gas solubility exhibited a maximum before the glass transition. The solubility maximum with increasing gas pressure occurred owing to the hydrostatic effects which reduced the polymer free volume and hence the gas solubility.

The dilation of polymers by the sorption of other high pressure gases such as He, N₂ and Ar have either not been observed or are very slight. Sefcik (1986b) have measured the dilation of polystyrene in He gas up to a pressure of ca. 2 MPa at various temperatures. The specimen thickness only increased slightly in the experiment conducted at ca. 35°C. At higher temperatures the specimen seemed unaffected and in certain cases it was actually compressed. No swelling of PMMA was observed in He gas up to ca. 24 MPa at 58°C (Liau and McHugh, 1985). Similarly, high pressure N₂ gas did not dilate LPDE (Kamiya *et al*, 1986). PTFE and HDPE have been reported to compress under N₂ gas pressures of up to ca. 25 MPa (Briscoe and Mahgerefteh, 1984a). The probable cause of such behaviours is the relatively low solubility of these gases in the polymers.

2.6.1 Experimental Techniques to Measure Sorptive Dilation

Several techniques for measuring the sorptive dilation of polymers by high pressure gases have been described in the literature. The basic principle of these techniques is obviously to determine the swelling by measuring the change in one or more dimensions of the polymeric sample. The most common method involves the use of a cathetometer to measure the dimensional changes in the X or Y directions of the specimen through a window in the pressure vessel (Fleming and

Koros, 1986; Liau and McHugh, 1985; Hirose *et al*, 1986; Wissinger and Paulatis, 1986; Kamiya *et al*, 1988a). This technique has only been used up to a pressure of ca. 10 MPa due to the limitations of the experimental apparatus. The test samples were in the form of rectangular films or cylindrical rods. The changes in the length and the width were compared to examine the isotropic behaviour of the specimens. The gas pressure was incrementally increased and the changes in the dimensions were measured after the sorption equilibrium had been reached. Displacement callipers have also been used to measure the sorptive dilation by CO₂ up to ca. 6 MPa (Eudes *et al*, 1968).

A method based on optical interferometry was developed by Sefcik (1986a) to measure sorptive dilation in thin films. This technique has been applied up to a pneumatic pressure of 2 MPa. A thin polymer film was cast on a quartz window of a pressure cell. A UV-visible light was used as a probe. The information obtained was the product of the refractive index and the film thickness; optical thickness. The refractive index of the film under gas pressure was not known, therefore an estimated value was used to obtain the film thickness. Sefcik (1986a), however, does not recommend using this technique generally, because of the uncertainty in determining the refractive index of the film under pressure.

Buckley *et al* (1962) used an optical method which involved interposing the polymer sample dipped in a solvent, in the path of a light beam. The amount of light intercepted by the specimen was measured. As the sample swelled, a greater portion of the light was obstructed and hence with the necessary calibration, specimen swelling was determined.

Liatsis (1989) has measured the strain produced in a steel beam due to the CO₂ gas induced dimensional change in a block of a polymer specimen. The beam had a strain gauge attached to it. One end of the beam was rigidly clamped and the free end was in contact with the specimen. The changes in the strain gauge resistance with the increasing pressure were translated into the dimensional changes

of the specimen. The strain gauge characteristics were not found to be affected by the high pressure ambient. Moffat and Weale (1955) have directly attached a strain gauge to a block of coal to determine sorptive dilation in a high pressure methane environment.

The technique developed by Briscoe and Mahgerefteh (1984a) involved monitoring the changes in the capacitance between two metallic plates. The cylindrical specimen was attached to one of the plates in the capacitance cell. This method has been successfully used up to a pressure of 54 MPa but it is only suitable for hard polymers. Briscoe *et al* (1986) have employed the same basic concept by using a series of capacitance leaves located around a cylindrical test piece. Only certain sample diameters could be used and relatively large diametric swellings were detected.

A linear variable differential transformer (LVDT) was used by Ender (1986) to record dimensional changes in a polymeric specimen subjected to various high pressure gases. The coil of the LVDT was placed outside the pressure vessel over a metallic tube. The transducer tracked the position of the LVDT core on top of a follower rod inside the tube. The foot of the follower rod was placed on the specimen. The method operated successfully up to a pneumatic pressure of 28 MPa and 100°C.

A thermal mechanical analyser (TMA) that measured movements of a probe in the vertical direction using a LVDT have also been used by Machin and Rogers (1970) to measure polymer swelling in liquid solvents.

George (1984) also employed a linear voltage displacement transducer to measure the separation of two steel plates between which a test specimen was sandwiched. The whole assembly was placed inside a pressure vessel. The maximum working pressure was ca. 4 MPa. Briscoe *et al* (1986) have also employed a spring-loaded potentiometer to measure the dimensional changes of cylindrical elastomer specimens over a complete pressure cycles, i.e. pressurisation

and depressurisation.

2.6.2 Summary

The gas molecules absorbed in a polymer occupy a certain partial molar volume in the new mixture. The highly soluble gases, specially the super-critical gases, can induce significant swelling of the polymeric matrix. The supercritical gases act like liquid solvents and can dissolve organic solids. Therefore, they are also able to induce large swellings in crosslinked polymers. Generally the shape of the dilation isotherms mimics the sorption isotherms. The extent of the sorptive dilation depends upon the swelling potential of the gas and the elastic properties of the polymer. The knowledge of the gas sorption induced dilation is necessary for accurate determination of the mass uptake and explaining the various anomalous sorption isotherms. A number of direct and indirect methods have been employed to measure the sorptive dilation of polymers. Usually the changes in the linear dimensions have been measured. The cathetometer, the LVDT and the capacitance cell have been the most successful instruments for this purpose.

2.7 PLASTICISATION OF POLYMERS BY ABSORBED GASES

The plasticisation of polymers by high pressure CO₂ gas has been reported by several researchers (Sefcik, 1986b; Wissinger and Paulatis, 1987; Kamiya *et al*, 1988 a,b). The change in the shape of the dilational isotherm and the corresponding increase in the slope of the elongation versus gas concentration curve for glassy polymers was interpreted as the plasticisation of the polymers by the sorbed gas. The relatively small gas molecules, when sufficiently absorbed in a polymeric matrix, increase the mobility of the polymer chains. They also cause the matrix to expand allowing the chain segments to move more freely, thus lowering

the glass transition temperature. The high pressure gas will also affect the molecular motion in an opposing way. The hydrostatic component of the pneumatic pressure decreases the free volume of the polymer, hence, reducing the segmental mobility. Jones Parry and Tabor (1974) have observed that the shear modulus of various polymers increases under N₂ and He gas pressure. These two gases are relatively insoluble in polymers. A larger increase in the modulus was detected for plasticised PVC and polypropylene which have glass transition temperatures of 18°C and 2°C respectively. The application of a N₂ gas pressure of about 136 MPa shifted the transition temperatures upwards. The onset of the glassy state was suggested as a cause for the large increase in the shear modulus.

Systematic studies have been conducted using different methods to investigate the plasticisation and the opposing effects of various high pressure gases on polymers. Assink (1974) has reported the use of a NMR (nuclear magnetic resonance) technique for this purpose. the spin-lattice and the spin-spin relaxation times were measured. The interactions of He, N₂ and Ar gases with a silicone elastomer have been investigated up to a pressure of ca. 207 MPa. It was observed that the He gas acted only as a hydrostatic pressurising medium and thus restricted the molecular chain motions. The molecular relaxations exhibited at lower temperatures were shifted to higher temperatures. However, the Ar gas which was more soluble in the silicone elastomer, increased the distance between adjacent chains. Only a small pressure dependence by the polymer relaxation was exhibited when the N₂ gas was used as the pressurising media.

Wang *et al* (1982) have employed an ultrasonic technique to study the plasticisation of polystyrene (PS) by CO₂ gas up to a pressure of ca. 100 MPa. The ultrasonic wave velocity was measured after an equilibrium had been reached under a certain CO₂ gas pressure. It was shown that the modulus of the PS specimen initially decreased with an increase in the CO₂ gas pressure (up to ca. 20 MPa) and then gradually increased again with the further pressurisations. This was

an indication that at higher pressures the hydrostatic effect of the ambient gas tends to suppress the plasticisation effect of the dissolved gas. The free volume decreases under hydrostatic pressure and stiffening of the polymer matrix occurs. It has been noted that in this study the sorptive dilation of the PS specimen was not considered. PS dilates by ca. 4% linearly under a CO₂ gas pressure of ca. 7 MPa (Wissinger and Paulatis, 1987). Creep testing of polystyrene (PS) specimens have also been performed in the high pressure CO₂ gas ambients (Wang *et al*, 1982). The compliance of the specimen increased with CO₂ gas pressure. Hence, the results obtained by the ultrasonic and the creep methods exhibited a similar trend. When the effects of the plasticisation and the hydrostatic pressure on the T_G were separated it was revealed that the CO₂ gas was a severe plasticiser for the PS over the whole pressure range (0-100 MPa).

Hojo and Findley (1973) have investigated the creep behaviour of polycarbonate (PC) in the presence of different high pressure gases such as He, N₂, O₂, CO₂, air and Freon-22 up to a pressure of ca. 20 MPa. The maximum gas induced strain in the tubular specimens was observed with Freon-22, followed by CO₂. The effects of the other gases on the polymer volume were less significant. The absolute stiffness of the PC in the presence of the various gases was given in the following order: He (greatest stiffness), N₂, air, O₂, CO₂ and Freon-22. When the Freon-22 pressure was released after the creep test a thin layer of clouded PC was left on the specimen surface. It was associated with the plasticisation effects of the Freon-22 which reduced the strength of the material by craze formation.

A decrease in the T_G of a polymer in the presence of an absorbed gas is an indication of plasticisation. Chiou *et al* (1985) have used a differential scanning calorimeter (DSC) to determine the extent of this effect. They studied the plasticisation effects of CO₂ gas in a pressure range of 0-2.5 MPa on polyvinylidene fluoride (PVF₂), PMMA and their blends, PVC, PET, PS and PC. It was observed that in all the cases the T_G decreased with the increased

concentration of the absorbed CO₂. However, they have also reported a certain degree of gas induced crystallisation in the PVF₂ and the PET.

2.7.1 Summary

Certain high pressure gases that are absorbed in significant quantities in polymers increase the mobility of the chain segments. Hence, they cause plasticisation of the polymeric matrix. The CO₂ absorption is a typical example. However, an opposing effect is also exerted by the hydrostatic component of the gas pressure. When the latter effect is dominant, it results in an increase in the specimen moduli. Several experimental methods have been employed to study these effects. Generally CO₂ and Freon-22 act as plasticisers, whilst, He and N₂ introduce the opposite effect.

2.8 EFFECTS OF RAPID GAS PRESSURE RELEASE FROM THE AMBIENT OF SATURATED POLYMERS

It has been mentioned earlier in this chapter that polymers; especially elastomers, can absorb certain high pressure gases in significantly large quantities. The absorbed gases can cause swelling and plasticisation of the polymeric matrix. In this section a review will be presented for the studies conducted to examine the effects of rapid gas depressurisation from the ambients of the saturated polymers. The ambient gas pressures have ranged from 4 MPa to 70 MPa and the decompression times from as low as 10 seconds to up to 15 minutes. On a sudden pressure reduction, the polymer originally saturated with the gas, is no longer in equilibrium. An internal hydrostatic pressure is generated in the polymer as the dissolved gas escapes slowly relative to the rate of the ambient pressure reduction. If the internal pressure is high enough cavitation or crack initiation from preexisting

voids in the matrix may result (Gent and Tompkins, 1969a; George, 1984; Schremp and Roberson, 1973; Southern, 1985; Cox, 1985). This phenomenon can be explained further by considering it analogous to the boiling out of the volatile dissolved phase from a solution. Eudes *et al* (1968), Kosmala (1984), Potts (1985), Cook (1985), Briscoe *et al* (1986) and Liatsis (1989) have all observed internal lacerations and surface blisters in the elastomeric specimens after the rapid depressurisations of the equilibrated high pressure ambients. In the literature, this phenomenon has often been referred to as 'explosive decompression damage'.

Gent and Tompkins (1969 a, b) have conducted experimental and theoretical studies for the gas desorption induced bubble nucleation and growth in elastomers. The gases used were CO₂, N₂ and Ar. As the rubbers are usually crosslinked the formation of visible bubbles indicates localised fracture. It was assumed that the bubbles or fractures initiate from preexisting voids in the matrix and the pressure, 'P', required to inflate a bubble was given by:

$$P = \frac{G}{2} \left(5 - \frac{4}{\lambda} - \frac{1}{\lambda^4} \right) + \frac{2\gamma}{r} \quad (2.9)$$

where 'G' is the shear modulus of the elastomer, ' λ ' is the extension ratio of the bubble radius, ' γ ' is the surface energy of the rubber and 'r' is the radius of the void. The value of 'P' is computed to be very large for a small initial void radius in the range of 1-10Å. When the initial radius is of the order of 10⁻⁴ mm the 'P' acquires a lower limit of 5 G/2. It was assumed that the voids of this size or greater already exist in elastomers due to a number of reasons and in this case the surface energy term may be neglected. When a pneumatic pressure is applied the gas dissolves in the polymer and eventually fills the voids with a pressure equal to the ambient. On a sudden release of the external gas pressure, the pressure inside the voids results in their inflation. The experimental results were in fair agreement with this theory. A number of other interesting features were also observed. For the comparatively less soluble gases like N₂ and Ar a considerably higher initial

pressure was necessary and the size of bubbles formed with these gases were small. The total number of the bubbles that appeared were a function of the initial gas pressure. At higher pressures even the smaller sized voids could be activated and a larger number of bubbles were observed after the pressure release cycle was completed.

Customarily, the effects of explosive decompression that are permanent or those which last for sufficiently long time after the decompression experiment have been investigated. However, Ender (1986) used a LVDT to measure the inflation of elastomers during the rapid decompressions and recently Briscoe *et al* (1986) have employed a spring-loaded sliding potentiometer for the same purpose. Eudes *et al* (1968) have reportedly made the dimensional measurements with the help of displacement callipers. It was observed that usually a specimen would begin to inflate when the ambient pressure was considerably below the starting pressure. In certain cases a linear inflation of more than 100% was observed. The extent of the inflation depends upon the degree of the gas solubility in the polymer, the diffusion coefficient and the elastic properties of the polymer (Eudes *et al*, 1968; Wolcott and Strazmickas, 1985). The rate of the ambient gas depressurisation also influences the degree of the inflation. Briscoe *et al* (1986) have depressurised polyurethane specimens saturated with CO₂ gas at 6 MPa in 20 seconds, 50 minutes and 30 hours and observed the maximum linear expansion of the order of 100%, 20% and 0% respectively.

The inflation behaviour of various polymers can be classified into three main categories, Figure 2.2 (Ender, 1986). In the first category, the inflation persists for several hours or days after the decompression is complete and the specimen becomes "spongy" in nature, Figure 2.2-a. Sometimes the inflation is in the shape of a large spike, Figure 2.2-b. This type of behaviour has been seen with silicone elastomers when a CO₂ gas ambient at 6 MPa was rapidly depressurised (Eudes *et al*, 1968). It was linked with the mechanical fragility of the polymer during the

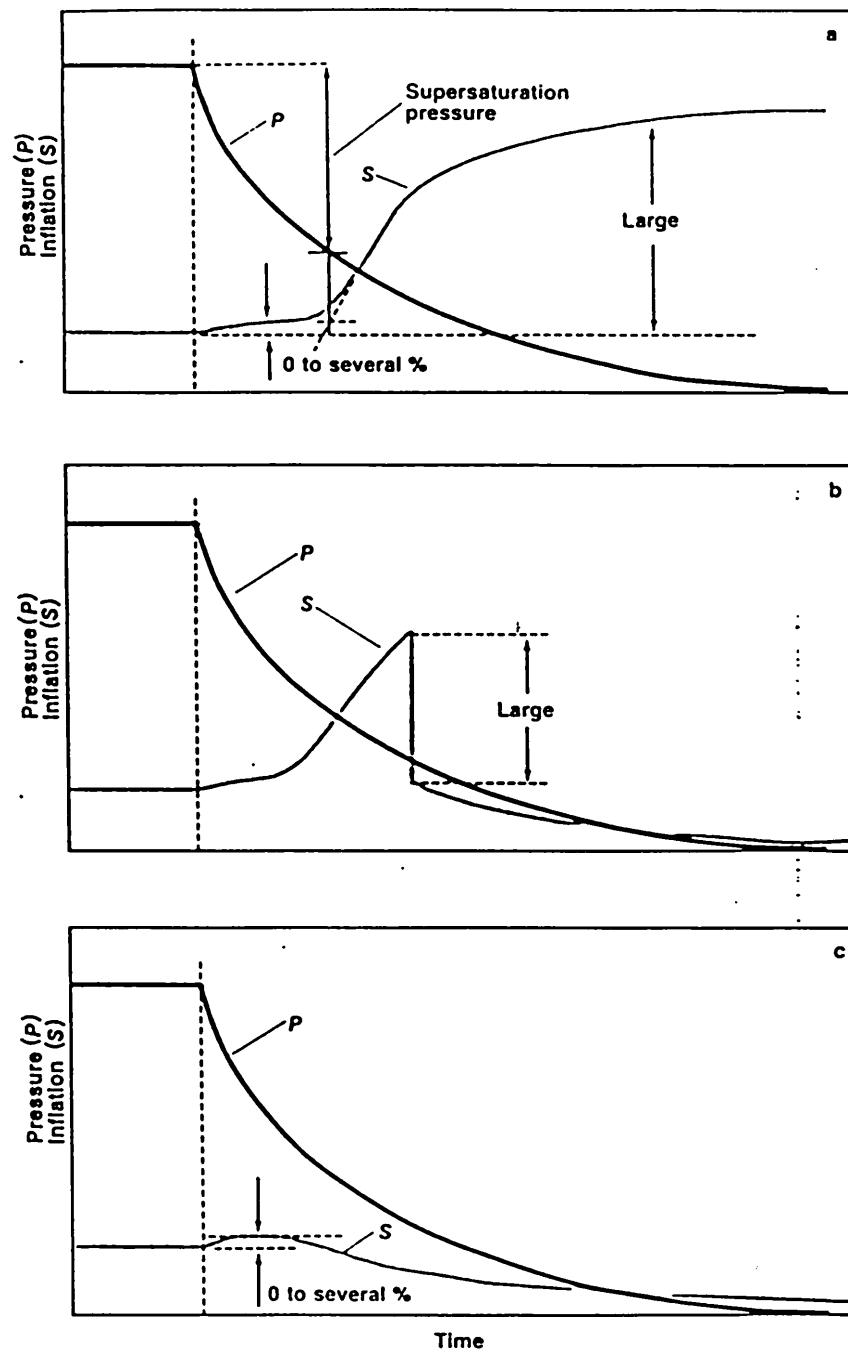


Figure 2.2: Schematic representation of elastomer inflation during gas decompression; (a), sponginess; (b), large internal cracks; (c), no visible change (Ender, 1986).

decompression. Large cracks were produced in the specimen that promoted rapid deflation by venting off the absorbed gas in short circuit diffusion paths. Inflation spikes have also been detected in the present study involving CO₂ gas and a silicone elastomer (Chapter 6). In the third category no detectable inflation is produced during explosive decompression, Figure 2.2-c. A similar behaviour was observed for the N₂ gas-nitrile rubber system in this study (Chapter 6).

The extent of degradation caused by the explosive decompression has been assessed by measuring certain mechanical properties at the end of the decompression cycle. Visual examination of the damaged specimens have also been made to produce an initial rating for commercial elastomers. The loss in the specimen hardness, modulus, tensile strength and elongation to break have been monitored (Potts, 1985; Cook, 1985; Cox, 1985; George, 1984). Potts (1985) has tested several elastomers and concluded that the specimens with an initial high tensile strength, modulus and hardness were generally more resistant to the explosive decompression damage. A similar criterion was proposed by Cook (1985). High loadings of small sized fillers with reactive surfaces in an elastomer also produced a material more resistant to this type of damage (Potts, 1985; Cox, 1985).

Griffiths (1985) has identified that special rubber compoundings, in which the formation of gaseous by-products during the vulcanisations had been reduced and other nucleating agents effectively eliminated, were not damaged by the explosive decompression. This observation is consistent with the theory proposed by Gent and Tompkins (1969b).

Wolcott and Strazmickas (1985) have examined explosively decompressed specimens under a microscope. The pressurising medium was CO₂ gas. Various observations were made ranging from no detectable damage in certain specimens to total destruction of the others, with surface blisters and surface cracks. The severely damaged specimens broke into pieces when bent. Cox (1985) has

observed longitudinal splits normal to the pressure gradient in the cross-section of gas damaged specimens. Large circular cracks along the circumference of the cylindrical specimens have also been reported by Liatsis (1989) and George (1984). The study conducted by Briscoe *et al* (1986) revealed that the internal cracks were very well defined. They usually formed surfaces of the same shape as the specimens but of smaller dimensions. For example, cracks within a cubic specimen formed smaller cubes. It was proposed that these cracks are produced due to the generation of internal pressure gradients across the specimens.

The type of gas saturated in the polymer matrix has a significant influence on the explosive decompression damage. Cracks were always detected in the cases of CO₂ and Ar, while N₂ was unable to rupture polyurethane and nitrile rubbers (Weston, 1983; Briscoe *et al*, 1986). However, N₂ gas is known to readily produce cracks in silicone elastomers (see Chapter 8).

2.8.1 Summary

On a sudden release in the ambient pneumatic pressure, a polymer saturated with the gas is no longer in equilibrium. A negative hydrostatic pressure is generated in the polymer. This process may lead to the rupture of the polymeric matrix and significant inflation of the specimen may occur. The cracks initiate from preexisting voids. The extent of the damage and the inflation depends upon the amount of the gas initially absorbed and the elastic modulus of the polymer. The type of the gas absorbed also influences the scale of the rupture. A number of experimental techniques have been used to determine the extent of the specimen inflation during the decompression process and the degree of the degradation ultimately produced.

CHAPTER THREE

LITERATURE REVIEW: RUPTURE AND MECHANICAL PROPERTIES OF POLYMERIC SYSTEMS

3.1 INTRODUCTION

One of the important properties of elastomers is their ability to undergo large deformations and return to their original shape. In uniaxial tension they can be strained by more than 100% of the original length without affecting the elastic response. The addition of filler particles in elastomers can improve some of the elastic mechanical properties even further. It is this capability to accommodate reversible strains which makes these materials useful for the construction of seals. In the present context their failure modes probably arise from the generation of hydrostatic tensile fields.

In material testing, hydrostatic compression and hydrostatic tension possess a unique characteristic of symmetry. The hydrostatic compression field can be easily applied to materials. However, the state of hydrostatic tension cannot be generated readily. Also, there is a great deal of difference in the manner in which materials respond fracture-wise to these two stress environments. Before rupture can occur it is necessary to have an energy release mechanism so that the stored energy can be expended to create new surfaces. Therefore, fracture does not occur in pure hydrostatic compression (Lindsey, 1967). Furthermore, the fracture initiation in a hydrostatic tensile field, or even in uniaxial tension, occurs from some microscopic flaw or hole already present in the material (Gent and Lindley, 1959a; Lindsey, 1967; Greensmith, 1964; Smith, 1974).

In this Chapter a review of the published literature will be presented that deals with the fracture of unfilled and filled polymers, specially in the hydrostatic

tensile fields. The general effects of rigid filler addition on the mechanical properties of a polymeric matrix will also be presented.

3.2 INTERNAL RUPTURE OF ELASTOMERS UNDER TRIAXIAL STRESSES

A peculiar horizontal region was observed (in the tensile stress-strain curve) by Yertzley (1939) while testing adhesive bonds formed between a neoprene rubber and metallic discs. It was concluded that this discontinuity was a result of the internal rupture in the rubber and was referred to as a yield point. The location of this point depended upon the modulus of the rubber and also on the thickness of the specimen. A detailed experimental and theoretical treatment of this uniaxial rupture process was later presented by Gent and Lindley (1959a). They had encountered a similar phenomenon in the course of experimentally determining tensile strength of short rubber cylinders bonded between plane metallic end pieces. The aspect ratio defined as the 'thickness/diameter' ratio of the test specimens were in the range of 0.28 to 0.49. The appearance of the internal cracks was also detected visually in a transparent rubber. The size, the number and the disposition of the cracks was found to be very dependent upon the thickness of the test piece. In thinner samples, a large number of small cracks were found uniformly distributed in the cross section but ceasing in the neighbourhood of the free surface. As the thickness of the test piece increased the average crack size became larger and the number decreased, until only one or two large cracks were found to occur in the centre of the specimen. The cracking stress, 'S'', was linearly dependent on the Young's modulus, 'E', of the rubber. An empirical relation between the two parameters was given as:

$$S' = 0.55E + 0.5 \text{ kg/cm}^2 \quad (3.1)$$

The conventional tensile strengths of the rubbers were found to have little

correlation with the observed values of the cracking stress. The test piece ultimately failed at a value of the applied stress many times larger than the cracking stress. When the steel plates between which the thin elastomeric specimen was strongly bonded were pulled apart in a direction perpendicular to the face of the plates the test piece was strained linearly but was also restricted from contracting diametrically. The amount of this restraint was a function of the specimen aspect ratio. If the test specimen was sufficiently thin it was assumed that although the specimen was strained in the linear direction, an effective negative hydrostatic pressure was generated in the material. The theoretical value of the critical hydrostatic pressure, ' P_c ', necessary to produce internal rupture was given as (Gent and Lindley, 1959a):

$$- P_c = 5 E/6 \quad (3.2)$$

where 'E' is the Young's modulus. This prediction was found to be in fairly good agreement with the experimental results.

A similar technique was employed by Lindsey (1967) to generate hydrostatic tension in a thin, transparent polyurethane specimen. The rigid grips were also made of a clear material. Hence, with this arrangement the crack initiation and propagation in the specimen interior were readily photographed. It was assumed that in the short cylindrical specimen the strain was only in the axial direction and negligibly small in other directions. Under these conditions the stress fields became (Lindsey, 1967):

$$\sigma_r = \sigma_\theta = [\nu/(1-\nu)] \sigma_z \quad (3.3)$$

where ' σ ' is the stress and the subscripts 'r', ' θ ' and 'z' are the cylindrical coordinates. For rubbers with Poisson's ratio, ' ν ', equal to half, the stress in all three coordinates becomes equal. The triaxial stress state approaches the hydrostatic condition. It was observed that in hydrostatic tension, elastomers exhibited only 2-3% of the ultimate rupture strain observed in conventional uniaxial tension. As the number of stress axes increased the ultimate stress also increased

while the ultimate strain decreased. The state of hydrostatic tension is a limiting case and provides a maximum in the stress that a material can withstand, as well as a minimum in the strain at which fracture may be produced. The experimental results observed by Lindsey (1967) showed that the critical hydrostatic tensile stress at which the material fractured was 2.5 to 3 times the ultimate strength in uniaxial tension. It was also proposed that the fracture nucleated from a point of weakness in the material. The observed fracture was a circular, planar crack that enlarged in the radial directions. Initially, the rate of the crack growth was slow but after reaching a critical size the growth became very fast. This was indicated on the fractured surface by a dark centre with smooth mirror like surface around it. A similar crack propagation behaviour has been reported by Halpin (1965) and Smith (1974).

An equivalent mode of internally rupturing elastomers involves inflating the preexisting voids in the matrices by pressurised fluids. The voids may be present due to the air entrapped in the crosslinked rubbers during the initial mixing of the reactants. Appreciably large holes may be retained in the materials without much size reduction due to diffusion. It has been proposed that voids of $10\text{\AA}$ or so in radius cannot be avoided in elastomeric solids (Gent and Tompkins, 1969b).

Rubber blocks have been swollen to equilibrium in a suitable solvent and then rapidly heated to vaporise the dissolved liquid (Denecour & Gent, 1968). Bubbles of the vapour appeared in the rubber interior and grew rapidly until bursting occurred. The inflation pressure, 'P', for a small spherical void in a large block of rubber was given as:

$$P = G/2 (5 - 4\lambda^{-1} - \lambda^{-4}) \quad (3.4)$$

where 'G' is the shear modulus of the swollen rubber and ' λ ' is the ratio of the hole radius in the deformed state (at 'P') to that in the undeformed state ('P' gauge equal to zero). This expression is similar to that given by Gent and Tompkins (1969a) for the inflation of a small hole in a rubber matrix with pressurised gas (see Chapter

2). The predicted inflation pressure attains an asymptotic value of $5G/2$ with increasing initial hole size. Hence, the critical inflation pressure, ' P_c ' was proposed as being:

$$P_c = 5G/2 \quad (3.5)$$

Denecour and Gent (1968), also observed that in certain highly crosslinked swollen rubbers the cracks appeared in the outer regions of the specimens rather than as internal cavities. It was implied that this was due to the fact that these materials had extremely low extensibility. The rapidly deswollen outer regions were in a state of tensile strain which made them more susceptible to the surface bubble/crack formation. A similar technique of bubble formation and one that resembles the method used in this study for the internal rupture of elastomers involves the use of a high pressure gas (Gent and Tompkins 1969a). A gas was dissolved in an elastomeric matrix under sufficiently high pressure. When the ambient pressure was released, the high pressure gas present within the elastomer inflated the initially dormant cavities in the material. More details of this method have been given in the previous Chapter.

It seems worthwhile to mention here that the foaming of plastics also involves a process in which gas bubbles are produced in the matrix and allowed to expand under controlled conditions. The source of the gas is usually a low-boiling liquid, a chemical blowing agent or a high pressure gas dissolved in the molten polymers (Chanda and Roy 1987).

The critical value of internal gas pressure for bubble formation in elastomers ($5G/2$) and the critical value of negative hydrostatic pressure required to internally rupture an elastomer in a triaxial stress field ($5E/6$) coincide numerically with each other. The shear modulus and the Young's modulus of a material are related to one another by the following relation:

$$E = 2 G(1 + \nu) \quad (3.6)$$

where ' ν ' is the Poisson's ratio. For elastomers ' ν ' is very nearly equal to 0.5,

therefore the Young's modulus is almost three times the shear modulus. Hence, the values of critical pressure given in the two cases are equal.

Gent and Hindi (1988) have described a phenomenon known as 'blowout'. It arises from the generation of sufficient quantities of volatile products in elastomers at higher temperatures. An internal pressure is developed which is able to expand the preexisting internal cavities. The temperatures at which the 'blowout' occurs also depends upon the modulus of the test specimens. It has been observed that the specimens with lower moduli ruptured at lower temperatures and the higher moduli materials appeared to withstand higher temperatures before the 'blowout' occurred. For the hard materials a higher internal pressure was necessary to cause the expansion of the internal cavities. It was concluded that the 'blowout' process was not a simple chemical decomposition of the elastomer since extensive chemical degradation requires much higher temperatures than those observed when the 'blowout' process was detected.

3.2.1 Summary

Polymers undergo internal rupture when subjected to triaxial stress fields. These stress fields have been generated by stretching a thin bonded layer of rubber. The state of hydrostatic tension provides a maximum in the stress that a material can withstand and a minimum in the strain at which fracture occurs. Various theoretical and experimental studies have been conducted to evaluate the response of polymeric materials to such stress fields. It has been concluded that the cracks nucleate from preexisting voids in the matrix and the critical stress is proportional to the modulus of the material. The internal rupture has also been produced by inflating the voids with a pressurised gas or vapour. The inflation pressure was again found to depend upon the specimen modulus and had a value similar to that required for the rupture under pure triaxial stresses.

3.3 MECHANICAL PROPERTIES OF FILLED POLYMERS

The mechanical properties of polymers are often improved by the addition of filler particles. The degree of reinforcement provided by the filler particles depends on a number of variables, for example, the filler particle size, the filler concentration and the degree of bonding between the polymer and the filler particles. Relatively, the elastic modulus, the yield stress and the yield strain of a composite increases with a decrease in the filler size (Alter, 1965; Mitsuishi *et al*, 1985; Nielsen, 1967). For mineral fillers the strength of the composite has been related to the reciprocal of the filler diameter (Alter, 1965). However, the ultimate strength of the specimens filled with spherical filler particles has been demonstrated to be inversely proportional to the square root of the filler diameter (Leidner and Woodham, 1974).

The presence of rigid filler particles increases the modulus of the specimen (Nielsen, 1967; Sahu and Broutman, 1972; Smith, 1959; Guth, 1945; Mitsuishi *et al*, 1985). The polymer chains may become adsorbed or adhere to the filler surface and hence the surface restricts the molecular mobility. The increase in the modulus has been argued to be proportional to the number of polymer-filler attachments, which in turn is proportional to the filler surface area (Alter, 1965; Kraus, 1978, pp. 339-364; Mitsuishi *et al*, 1985). Guth (1945) has proposed an expression relating the modulus of filled rubbers to the filler concentration:

$$E = E_o (1 + 2.5 V_f + 14.1 V_f^2) \quad (3.7)$$

where 'E' and 'E_o' are the moduli of the filled and unfilled specimens respectively and 'V_f' is the filler volume fraction in the polymer. The increase in the modulus was attributed to the fact that the rigid filler particles can carry a major portion of the applied load, hence, enabling the composite to withstand higher stresses before the breaking stress of the matrix is reached (Oberth, 1967). However, the yield stress and the yield strain of a filled system decreases with increasing filler content

(Smith, 1959; Mitsuishi *et al*, 1985). The tensile strength of a material may also decrease but this is not always the case (Nielsen, 1967). The tensile strength of styrene-butadiene rubber was found to increase with an increase in carbon black concentration (Kraus, 1978, pp. 339-364). Similarly, Dreyfuss *et al* (1980) have shown that the tensile strength of polybutadiene rubber increases with the addition of glass fillers which were strongly bonded to the polymeric matrix. In contrast, the specimen with weakly bonded glass beads had a lower breaking stress. The breaking elongation of the composite specimens with strong and weak interfaces was however, lower relative to the unfilled polymer. In an epoxy resin system the tensile strength was detected to decrease with the addition of particulate glass filler. The maximum reduction was for the system containing the filler particles treated with a mould release agent (Sahu and Broutman, 1972).

Nielsen (1967) has presented several simple relations to predict the stress-strain properties of various specimens as a function of filler concentration. In the case of perfect matrix-filler adhesion, the strain to break, ' ϵ_b ', for the filled system relative to that for the unfilled polymer was given as:

$$\epsilon_{b \text{ (filled)}} / \epsilon_{b \text{ (unfilled)}} = 1 - V_f^{1/3} \quad (3.8)$$

where ' V_f ' is the volume fraction of the filler. In the system with poor adhesion between the filler particles and the polymer, it was assumed that the inclusions do not carry any load. The relative strength was then predicted by the following relationship:

$$\sigma_{b \text{ (filled)}} / \sigma_{b \text{ (unfilled)}} = (1 - V_f^{2/3}) s \quad (3.9)$$

where ' σ_b ' is the stress to break and ' s ' is the stress concentration factor; it has a value of 1.0 if there is no stress concentration.

Lewis and Nielsen (1970) have measured the dynamic mechanical properties of an epoxy matrix filled with glass beads. It was observed that the shear modulus of the filled system increased and the damping decreased. Kraus (1978, pp. 339-64) also observed an increase in the shear modulus of a butyl rubber when it

was filled with a carbon black.

3.3.1 Summary

The addition of filler particles in a polymer improves the mechanical properties of the system. The degree of reinforcement depends upon the filler size and concentration. The moduli always increase with the filler addition, whilst, the tensile strength may increase or decrease depending upon the degree of bonding between the polymer and the filler. Simple relations have been presented relating the stress-strain properties of composite specimens as a function of filler concentrations.

3.4 FRACTURE IN POLYMERS CONTAINING FILLER PARTICLES

It has been discussed previously that a strong bond between the filler particles and the polymeric matrix leads to higher tensile strengths and comparatively stiffer components. The filler particles with the weak bonds do not increase the tensile strength appreciably. The higher strength does not necessarily result from the inhibition of fracture initiation. It may arise from the so-called crack "blunting" mechanism. The dispersed filler particles not only increase the capacity for energy dissipation but they may also deflect the growing cracks or cause the cracks to bifurcate (Smith, 1974). When a composite specimen is under tension the surfaces of the inclusions can act as stress concentration sites and can cause internal rupture of the system (Leidner and Woodham, 1974). In this section, the significance of polymer-filler interface quality on the matrix fracture processes will be reviewed.

The stretching of an elastomer containing rigid fillers above a certain limit may cause vacuole formation around the filler particles. This phenomenon is

generally referred to as 'dewetting'. It is attributed to the detachment of the weakly bonded polymer from the surfaces of the filler particles (Gent and Park, 1984). On the other hand, when an elastomer is strongly bonded to the rigid inclusions the interfacial detachment is resisted and a cohesive fracture in the matrix is produced. It can be said that in this case the cohesive strength of the binding matrix is less than the adhesive strength of the filler-matrix interface bond (Farris, 1964; Gent and Park, 1984). A fracture process of this type is termed as cavitation. Cavitation has been regarded as an elastic expansion of a preexisting void, too small to be readily detected, followed by its growth as a running crack when the maximum extent of the material elongation is exceeded. The growth of the void stops when it becomes large enough to alleviate the excess tensile strain (Cho *et al*, 1987). A schematic representation of the dewetting and the cavitation processes is given in Figure 3.1.

A mechanism for matrix cavitation and filler particle dewetting in a filled elastomeric matrix under tension has been put forward by Oberth and Bruenner (1965). In the system studied the adhesive bonds between the filler particles and the matrix were stronger than the cohesive strength of the matrix. It was observed that, prior to the separation of the elastomeric binder from the filler, a small cavity was formed near the polymer-filler interface in the binder phase. The hole was produced at the point of maximum stress concentration around the filler where an effective triaxial stress was generated. The tensile stress was dissipated by the tearing of the polymer phase. This mechanism was later endorsed by Oberth (1967), Lindsey and Murch (1973) and Gent (1984). The critical stress, ' σ' ', which produced this type of cavity was given as:

$$\sigma' = (E + P)/2 \quad (3.10)$$

where 'E' is the Young's modulus and 'P' is the external pressure on the system. This expression is similar to that given by Gent and Lindley (1959a) for the internal rupture of elastomers in triaxial tension. On further straining the cavity near the filler particle reaches the surface of the inclusion and may tear the thin layer

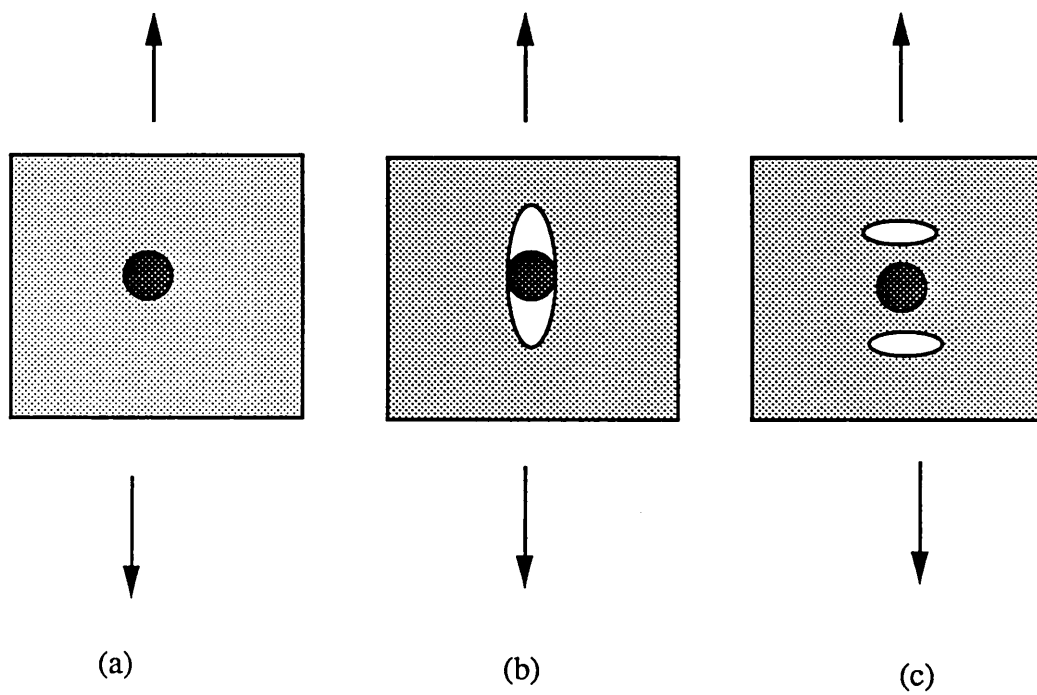


Figure 3.1: Schematic representation of; (a), an unstrained composite;
(b), stressed composite leading to dewetting of the filler particle;
(c), stressed composite leading to matrix cavitation.

of polymer separating the two. This phenomena has been referred to as 'blanching'. The adhesion between the matrix and the filler becomes important after the specimen has passed the critical stress. A weaker interface will facilitate 'blanching', while a stronger interface will hinder the crack cavity propagation to the filler surface.

The cession of the adhesive bond between the filler and the matrix can lead to dewetting (Lindsey and Murch, 1973). Gent (1980) has presented a theoretical model for the detachment of an elastic matrix weakly bonded to a rigid circular inclusion. It was assumed that the detachment initiates from a small, initially debonded, area on the spherical inclusion. The minimum stress for dewetting, ' σ_a ', was given as:

$$\sigma_a^2 = 4 \pi G_a E / 3r \quad (3.11)$$

where ' G_a ' is the bond fracture energy, ' E ' is the Young's modulus and ' r ' is the radius of the filler bead. However, it was suggested that when the adhesion between the filler and the matrix is high a mechanism similar to that presented by Oberth and Breunner (1965) will be followed. A criterion was also put forward to distinguish between cavitation and dewetting. It was proposed that adhesive detachment will occur if:

$$G_a / r < 3 E / 16 \quad (3.12)$$

Gent and Park (1984) have conducted an experimental study to confirm the debonding model proposed by Gent (1980). It was observed that the dewetting stresses decrease with an increase in the Young's modulus, in contrast to the cavitation stresses that increase with the modulus of the matrix. It was proposed that since the bond fracture energy between an elastomer and a rigid surface decreases with modulus, the net effect is a reduction in the dewetting stresses for harder materials. It was also found that the debonding stress increased as the size of the inclusions decreased approximately in accordance to a negative half power of the filler diameter.

As a constituent model of a particulate composite, an elastomeric matrix with two glass beads have been stretched along the bead diameter axis (Gent and Park, 1984). It was found that a stress somewhat lower than that necessary to cause a void to appear near an isolated inclusion was sufficient to incite cavity growth near the poles of the two beads. This indicated that significant triaxial stresses were developed at these points. On further straining a second cavity was observed midway between the two inclusions. A similar phenomenon had occurred in thin elastomer layers bonded between rigid plates and placed under tension. When the second crack emerged out from the vicinity of the inclusions, it grew catastrophically and led to specimen splitting. The growth rate of the cavity at right angles to the applied stress depended on the distance between the two inclusions. In the case when the gap was large the crack growth was rapid. A number of other studies have been carried out using simple models to further elucidate the mechanism of matrix cracking in filled systems. Cho and Gent (1988) studied crack formation in layers of transparent silicone elastomer rigidly bonded between two steel spheres and steel rods of diameters in the range of 6 mm to 50 mm. When these steel ends were pulled apart axially the elastomeric matrix ruptured at the middle in a way similar to that observed by Gent and Park (1984). It was concluded that when the rubber thickness was more than 5% of the end piece diameter the stress required to ensure rupture was $5E/6$ which is similar to that required to dilate a preexisting void in an elastomeric matrix. However, for thinner layers, substantially higher stresses were required.

Crack initiation in systems containing rigid inclusions other than spherical has been considered by Cho *et al* (1987). Matrix cavitation occurred near the flat end surface of a rigid rod embedded in a silicone elastomer. The specimen was under tension in the direction of the rod axis. The damage mechanism was typical of that discussed above, i.e. growth of a void near the inclusion surface and on further straining the cavity approaching the inclusion surface. However, a

difference was observed while comparing crack initiation near short rods or discs and near spherical inclusions. In the latter case, the critical stress increased with a decrease in the size, while for the discs of same diameter and varying heights the critical stress remained constant. This was because the volume of the material under the dilational stresses decreased with the size of the spherical inclusion whilst it remained constant for the discs.

Another method which has been adopted for debonding filler particles from a polymeric matrix involves swelling the filled system in an appropriate solvent (Oberth, 1967). It was observed that a polyurethane matrix expanded through the uptake of a solvent and as the glass filler particles did not swell, the matrix broke loose. However, the fillers that were strongly bonded with the matrix did not dewet and the swelling was restrained. A similar phenomena is described in the current study

3.4.1 Summary

In a composite specimen the filler particles act as stress concentration sites. Under stress, the weak matrix-filler interfaces dewet, while, matrix cavitation occurs if the interfacial bonds are strong. The cavitation initiates from small preexisting voids near the interfaces. Theoretical expressions, confirmed by experimental studies, have been presented to predict the occurrence of these processes. Model studies have shown that the cavitation stresses depend upon the polymer modulus and the distances between the filler particles.

3.5 BULK DILATION OF FILLED ELASTOMERS UNDER TENSION

Bulk dilation of filled elastomeric systems upon uniaxial stretching has been

reported by several researchers. Schipped (1920) observed that when natural rubber specimens filled with a pigment were uniaxially stretched their specific gravity decreased. The increase in the volume was greater for the systems containing larger concentrations of the pigment. A similar behaviour was observed by Depew & Easley (1934) and Jones & Yiengst (1940) for several other pigmented elastomers. Specially constructed dilatometers have been used to measure the volume increase on stretching (Smith, 1959; Farris, 1964; Sekhar and Van Der Hoff, 1971). Oberth (1967) demonstrated that the dilation of a composite specimen was caused by vacuole formation around the filler particles and it was directly proportional to the volume fraction of the inclusions. However, strong links between the filler particles and the matrix significantly reduced the composite dilation. Sekhar and Van Der Hoff (1971) have proposed that the internal cavities formed in stretched rubbers are initially devoid of air and vacuum exists inside. The air dissolved in the matrix diffuses into these pockets and caused positive hysteresis while unloading. These points were elaborately demonstrated by comparing the dilation of various natural rubber composites saturated with different gases. It was observed that the specimen with absorbed gas exhibited greater dilation on straining than a similar sample stretched in vacuum. The additional dilation was attributed to gas diffusion into the cavities. Similarly, a specimen initially dilated under vacuum was compressed when a pneumatic pressure was suddenly applied but it extended again as the gas diffused into the cavities. This type of behaviour was much less pronounced in an unfilled specimen. It was, therefore, implied that in the unfilled specimens the cavities developed were actually an expansion of tiny gas pockets present in the raw material or included during sample preparation. This conclusion is in agreement with the proposed existence of trapped air pockets in crosslinked elastomers (Gent and Tompkins, 1969a).

Several researchers have proposed that the irregular stress-strain curves reported for filled specimens are due to the formation of internal voids and cavities

(Smith, 1959; Oberth and Breunner, 1965; Oberth, 1967; Lindsey and Murch, 1973; Lepie and Adicoff, 1974; Markin and Williams, 1974). These stress-strain curves had several distinct regions, Figure 3.2. In the initial region the stress increased with the strain but later its increase was markedly lowered. It was this second region where rapid filler dewetting occurred. Further increases in the strain only stretched the binder and enlarged the vacuoles. Markin and Williams (1974) have also employed a number of other different techniques to investigate dewetting and cavitation in stretched elastomeric composites. The Poisson's ratio of various filled specimens was measured. It was observed that for the samples with weakly bonded fillers the decrease in specimen width on linear elongation was greater than for the systems with strong matrix-filler bonds. Hence, the measured Poisson's ratio of the specimen was higher in the former case than in the latter. A photographic study was also undertaken by the same authors. It indicated that interfacial cracks were produced at the poor interfaces, while matrix phase fracture was predominant in the specimen with strong interfaces.

Lipe and Adicoff (1975) have attempted to measure microstructural damage in particulate composites by measuring the difference in the stress-strain curves obtained from the successive straining of a specimen. It was observed that on every subsequent stretching a lower stress was required for the same strain. It was argued that the energy difference between two successive stress-strain curves was too large to be simply due to adhesive void formation. Secondly, the debonding energy was suggested to be recoverable since the specimen volume decreased to the original after removing the stress. It was concluded therefore that along with adhesive debondings, scission of molecular chains was also occurring.

3.5.1 Summary

Bulk dilation of filled polymers has been observed on stretching. It is

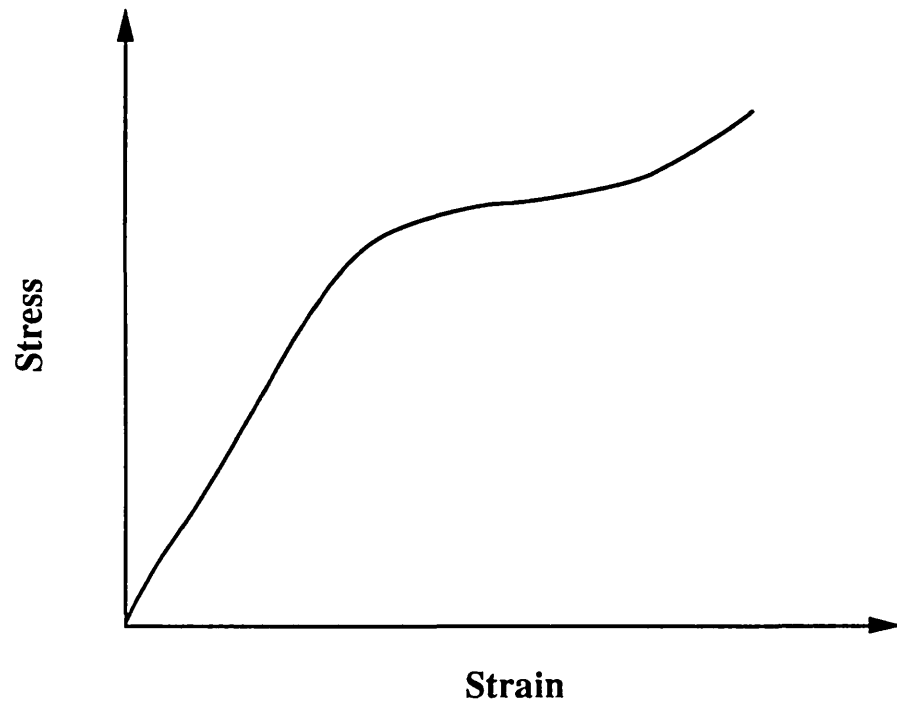


Figure 3.2: Schematic representation of stress-strain curve for a composite specimen, exhibiting filler dewetting.

caused by vacuole formation around the filler particles. The internal cavities are initially in a state of vacuum, however, additional dilation is caused by gas diffusion through the matrix into the voids. This behaviour is much less pronounced in unfilled systems. The irregular stress-strain curves for the filled specimens also indicate internal cavity formation which cause the detected specimen dilation. It has been proposed that matrix rupture also occurs along with the filler dewetting.

3.6 ELASTIC BEHAVIOUR OF BONDED RUBBER LAYERS

The stress-strain behaviour of a thin layer of rubber bonded between rigid surfaces provides an insight into the phenomenon of stiffness and reinforcement in particle-filled composites. Rubbers are usually assumed to be linearly elastic for relatively large strains. However, thin rubber layers bonded between rigid ends do not exhibit this linearity when strained. Gent (1956) observed, while compressing flat pads of different shapes and thicknesses (aspect ratio in the range ca. 0.2 to 0.1), that the stress-strain curves were convex to the strain axis. The overall deformation, it was argued, consisted of two terms; an homogeneous compression, as between perfectly lubricated plates and a shear deformation sufficient to restore points in the bonded planes to their original positions in these planes. Since the rubber specimens were virtually incompressible and the volume between the planes was to be conserved during deformation, an outward bulging of the initially plane sides occurred. The interfacial restrictions on flow produced a hydrostatic pressure in the interior of the rubber (Gent and Lindley, 1959b; Gent *et al*, 1974; Gent and Meinecke, 1970). The overall compressive stress may thus be resolved into two components; the first component, ' σ_1 ', due to the homogeneous compression of the specimen was given as (Gent *et al*, 1974):

$$\sigma_1 = K E e \quad (3.13)$$

where 'E' is Young's modulus of the rubber, 'e' is the fractional compressive strain and 'K' is a numerical factor, equal to unity for rubber specimen that can undergo unrestricted lateral expansion and equal to 1.33 for the test piece prevented from expanding in the lateral direction. The second component ' σ_2 ' is due to the hydrostatic pressure, 'P', which arises from the restraints at the bonded surfaces and was given as:

$$P = \sigma_2 = E e (a^2/h^2) (1 - d^2/a^2) \quad (3.14)$$

where 'a' is the radius of the test piece, 'h' is the thickness and 'd' is the radial distance at which the stress acts. It is clear from this expression that in thinner layers of larger radius, the hydrostatic pressure generated in the interior would be greater. Also for a given thickness the maximum pressure would be generated at the centre (d=0). The shear stress 't' acting at the bonded surface was given as:

$$t = E e d / h \quad (3.15)$$

These stress distributions are schematically represented in Figure 3.3.

When a thin bonded layer of rubber is subjected to tensile loading a state of triaxial tension (negative hydrostatic pressure) is set up in the central region of the test specimen (Gent, 1978, pp. 419-452). The tensile stress is approximately equal to the hydrostatic pressure generated when a similar specimen is compressed. The behaviour of rubbers in the triaxial tensile field so generated has already been discussed (section 3.2).

3.6.1 Summary

The stiffness and reinforcement of filled polymeric specimens have been studied with the help of model rubber layers bonded between rigid platens. It has been observed that the stress-strain behaviour of the rubber layers was not linear in this situation. This is mainly due to the interfacial constraints imposed by the

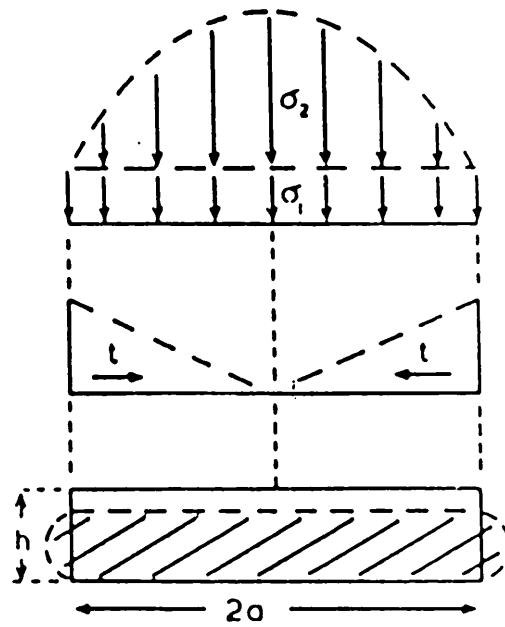


Figure 3.3: Schematic representation of normal and shear stress distribution across the diameter of a circular rubber sheet bonded between rigid plates (Tobolsky and Mark, 1971).

bonded ends. During the uniaxial compression of such pads a hydrostatic pressure, proportional to the specimen height, is generated in the rubber interior. Similarly, if the thin bonded layer is stretched a negative hydrostatic pressure is produced in the interior of the elastomer.

C H A P T E R F O U R

EXPERIMENTAL METHOD, MATERIALS AND PROCEDURES

4.1 Introduction

This Chapter describes the materials studied in this thesis, the high pressure equipment used and the experimental techniques employed. The description of the ultrasonic technique used for measuring volumetric strains and certain mechanical properties of the specimens under high pneumatic pressures is given in detail. Various subsidiary techniques employed in this study are also described.

4.2 Polymeric Materials

The polymeric system mainly investigated in this study was a silicone elastomer, polydimethyl siloxane (Dow Corning, Sylgard-184). This particular system was chosen due to its transparency and colourless nature. A similar silicone elastomer has been extensively studied by Gent and coworkers (1984, 1987, 1988). A nitrile rubber (BP, Sunbury on Thames, UK) and a polytetrafluoroethylene (ICI, Preston, UK) were also investigated.

4.3 Sample Preparation

4.3.1 Silicone Elastomer

The silicone elastomer was prepared by thoroughly mixing the liquid silicone pre-polymer (Sylgard S-184) with the curing agent (Sylgard C-184) in a ratio 10 parts of the pre-polymer to 1 part of the curing agent, by weight. The

surface modified fillers were added to the mixture to prepare the various filled specimens. The filler quantities added were 0.5% and 20% by weight of the mixed elastomer. The lower filler concentration produced a silicone elastomer specimen which remained relatively transparent. A large quantity of air was entrapped in the pre-polymer during mixing. The mixtures were exposed to a vacuum of ca. 1.32×10^2 Pa (30 torr) for ca. 45 minutes to ensure the production of a void-free specimen. The vacuum was released several times initially to break the bubbles that were formed. The liquid pre-polymer, free from trapped air, was cast into various moulds to make the test specimens for different experiments. The clear elastomer and the specimens with lower filler concentrations were allowed to cure at room temperature for 7 days to attain their full mechanical properties. The highly filled specimens were cured by heating in an oven to avoid settling of the filler particles. The cure temperature was ca. 65°C for ca. 4 hours.

4.3.2. Nitrile Rubber

The carbon filled uncured nitrile rubber was obtained in the form of 2 mm thick sheets. The cylindrical specimens were made by rolling the uncured sheet material. The rolls were preheated in an oven at ca. 100°C for ca. 45 minutes before being placed in special preheated moulds at ca. 150°C. A temperature controlled hydraulic press was used to compress the specimen to a pressure of ca. 15 MPa for ca. 30 minutes. Uniform cylinders with no visible signs of the rolled sheet structure were obtained by this means.

4.3.3. PTFE

The PTFE specimens were machined to size from a large diameter rod obtained from a commercial source (ICI).

4.3.4 Low Speed Cutting Wheel

A Bulher low speed diamond cutting wheel was used to cut thin cross-sections, ca. 1 mm, of the specimens damaged during the rapid gas decompressions. The specimens had been cast in an epoxy resin to facilitate this cutting process.

4.4 Fillers

Glass ballotines of particle size ca. 60 microns were used as filler in the silicone elastomer. Various chemical surface modifications of the glass filler were undertaken to increase and to reduce the interfacial adhesion. The glass beads were thoroughly washed first with acetone to remove any oil or grease. They were then dried in an oven at a temperature of ca. 150°C for ca. 1 hour.

The interfacial bonding between the glass filler particles and the silicone elastomer was improved by treating the clean glass beads with a 10% w/w solution of dichlorodimethyl-silane in a dichloromethane solvent (Luckham, 1986). The beads were dipped in the silating solution for ca. 30 minutes and latter removed and dried in an oven for ca. 3 hours at a temperature of ca. 100°C. The other chemical treatment used for improving the adhesion was a commercial adhesion promoter (Dow Corning, 92-023 Primer) specifically formulated for this purpose. The primer was sprayed on the filler particles in a rotatory mixer (Dascal Mixer II) so that it was applied uniformly to the filler surface. The filler particles were allowed to air dry for ca. 90 minutes in the rotating mixer.

In order to decrease the adhesion between the filler particles and the silicone elastomer a 5% w/w solution of a silicone resin (GE silicones, SR350) in toluene was sprayed on the clean particles in a way similar to that used to apply the commercial primer.

The surface treatments described above were also applied to smooth glass plates to provide specimens for various other experiments including model matrix-filler adhesion studies involving a blister test.

4.4.1 Interface Characterisation

The blister test experiments were performed to quantify the effects of the surface chemical treatments on the silicone elastomer-glass interface quality. A schematic diagram of the apparatus is shown in Figure 4.1. The instrumented apparatus had been developed previously in the author's laboratory by Briscoe and Panesar (1986). Circular discs of the silicone elastomer ca. 3 mm thick, ca. 100 mm diameter were cast on the chemically modified glass substrates with a 5 mm diameter plugged hole at the centre of the glass substrate. The plug was then removed and the hole served as a port to admit pressurised N₂ gas. During the blister test the gas pressure was measured by a transducer and recorded on a microcomputer. A blister was formed in the elastomer layer by the gas. At a particular maximum pressure, 'P_c', the interface between the elastomer and the glass ruptured. The height of the blister was measured by a displacement transducer and was also recorded on the microcomputer. The debond fracture energy was computed by the following relationship (Briscoe and Panesar, 1988):

$$\Gamma = [P_c^4 a_c^4 / 576 (1-\nu)^2 E h]^{\frac{1}{3}} \quad (4.1)$$

where 'Γ' is the fracture energy, 'P_c' is the critical pressure, 'a_c' is the debond radius, 'E' is the Young's modulus, 'ν' is the Poisson's ratio and 'h' is the thickness of the elastomer disc.

Assuming that the blister was a spherical cap, the crack velocity was given by the following relationship (Panesar, 1986):

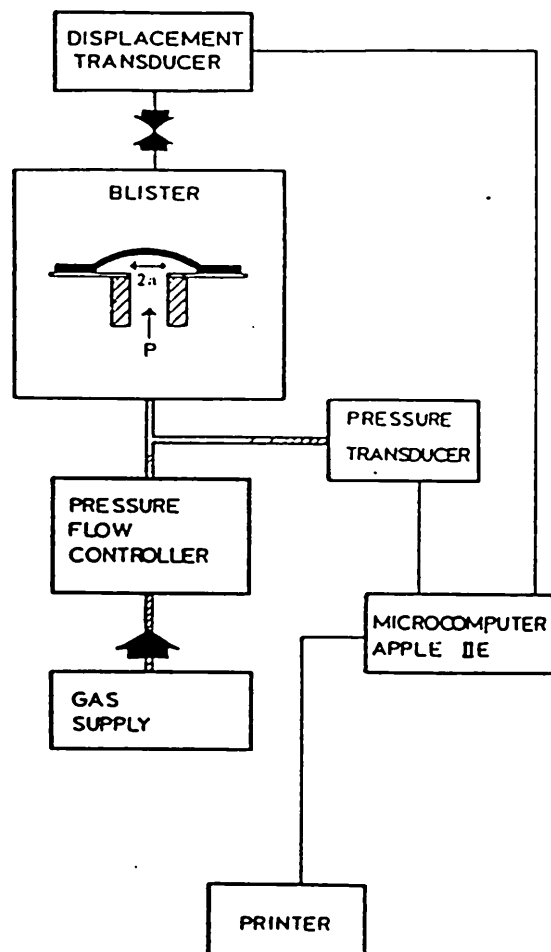


Figure 4.1: Schematic representation of the blister test apparatus (Briscoe and Panesar, 1988).

$$\left(\frac{da}{dt}\right)_c = \frac{P_c F_r t_c \left(\frac{d 1/P}{dt}\right)_c}{\pi a_c H_c} \quad (4.2)$$

The subscript, 'c', refers to the value of parameters at the chosen rupture conditions, 'a' is the corresponding debond radius, 't' is the time, 'P' is the pressure, 'F_r' is the gas flow rate and 'H' is the corresponding blister height, where as the term;

$$\left(\frac{d 1/P}{dt}\right)_c$$

is obtained from the slope of the pressure-time profile immediately proceeding the chosen rupture condition. The fracture energies as a function of the crack velocities for the various interfaces are given in Figure 4.2.

4.5 Gases

The gases used were carbon dioxide (CO₂) and nitrogen (N₂). They were supplied by BOC in conventional cylinders and were used as such.

4.6 High Pressure Equipment

The high pressure equipment essentially consisted of the high pressure chamber, the intermediate gas receiver and the gas booster pump. A schematic layout of the high pressure equipment is shown in Figure 4.3, Plate 4.1 is a photograph of the high pressure equipment.

4.6.1. Gas Booster Pump

The pressure vessel was charged up by a reciprocating commercial gas booster pump (Charles Madam, Altrincham). The gas supply to the pump came from a conventional high pressure gas cylinder fitted with a regulator. The booster

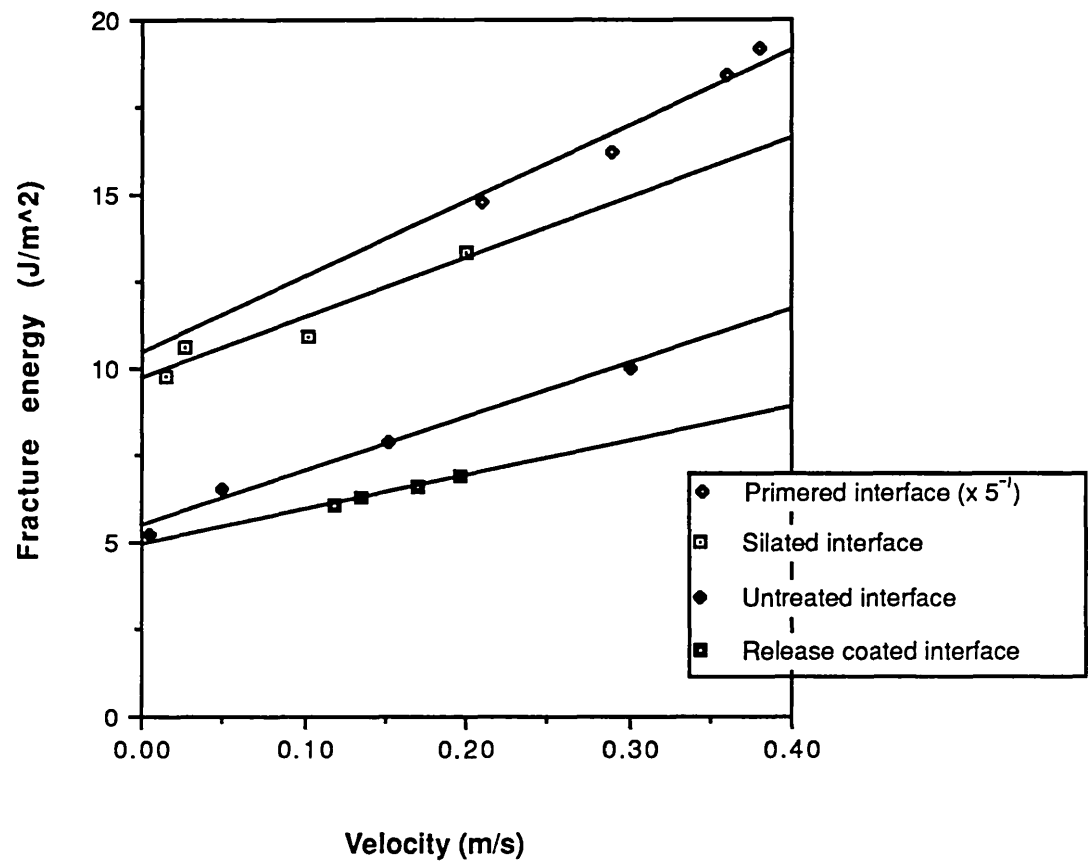


Figure 4.2: Interfacial fracture energy for the various interfaces as a function of crack velocity.

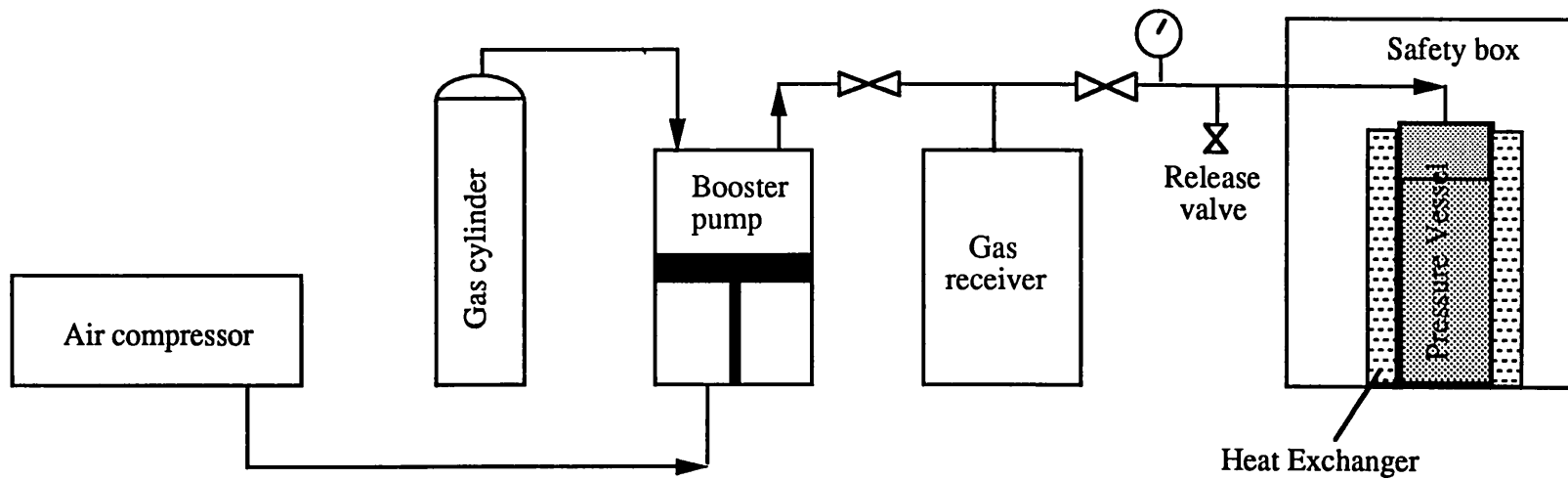


Figure 4.3: Schematic representation of the pressure vessel assembly.

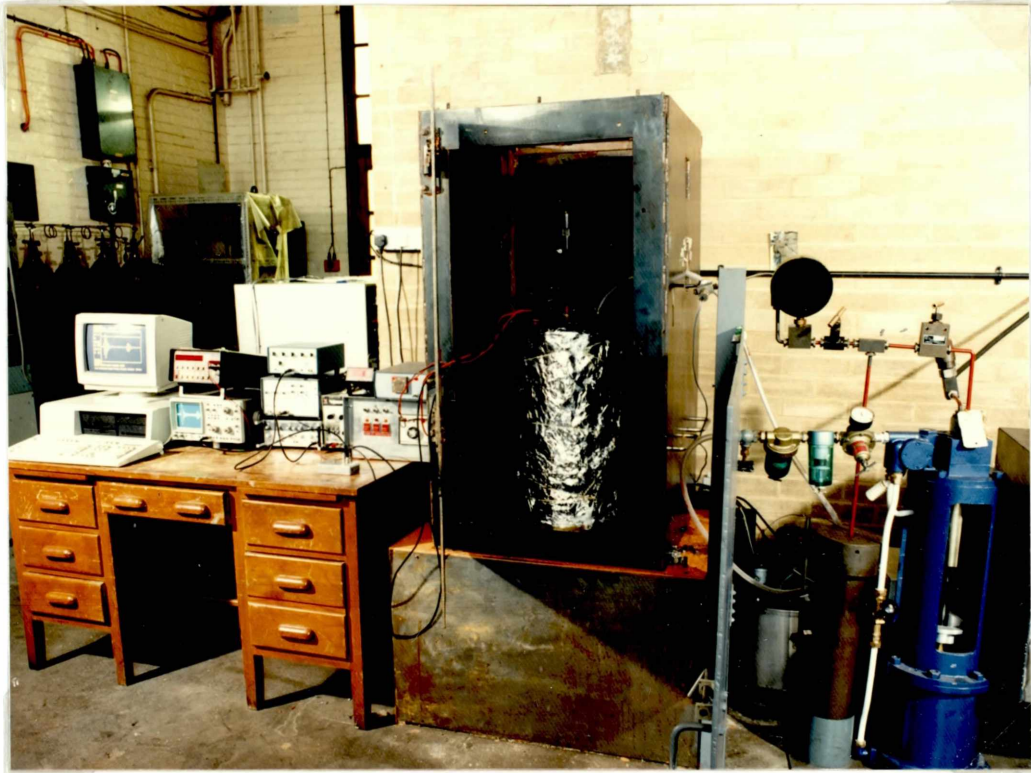


Plate 4.1: The high pressure equipment exhibiting the booster pump, the gas receiver and the pressure vessel enclosed in the heat exchanger. Some of the electronic instrumentation is also shown.

pump was driven by pressurised air (ca. 1 MPa), supplied by a 2.6 KW, 1450 RPM hydrovane compressor (Whittaker Hall, Manchester) with a 0.52m³ compressed air reservoir. The air flow to the pump passed through water and oil separators and was regulated by a pressure regulator. The gas booster pump had a compression ratio of 85 : 1 and could pump the gas up to a pressure of 55 MPa. An important feature of this system was its ability to maintain isobaric conditions. A simple adjustment to the driving air pressure regulator allowed a balanced condition to be maintained (± 0.5 MPa).

4.6.2 The Intermediate Gas Receiver

The intermediate gas receiver, five times the volume of the main pressure vessel, was connected between the gas booster pump and the pressure vessel via a stop valve. It acted as a pressure stabiliser or buffer and ensured that small leaks in the pressure vessel did not lead to a rapid drop in the pressure when the two vessels were interconnected. It also dampened the pressure fluctuations during pressure buildup by the reciprocating gas booster pump. The vessel was constructed from mild steel with a safe working pressure of ca. 135 MPa.

4.6.3 The Main Pressure Vessel

The pressure vessel was designed and fabricated by Billingham (1969). It was constructed from Vibrac 45; EN26, a high tensile steel. The dimensions of the main chamber were 610 mm length with an O.D. of 127 mm and an I.D. of 50.8 mm. The two mushroom shaped caps were secured to the body of the vessel by six high tensile bolts on each cap. Six insulated electrical connections made from 'Invar' ran through the top cap for driving and recovering electrical signals from the various transducers which were incorporated in the pressure vessel. A central 3

mm hole was used to admit the high pressure gas supply. Rubber seals (O.D. 50.8 mm, I.D. 41.2 mm and 5.4 mm thick) between bronze anti-extrusion rings were used to seal the mushroom caps and the pressure vessel. The pressure vessel had a safe working pressure of ca. 258 MPa and a safe working temperature range of -20°C to 150°C.

The high pressure gas was supplied through Madan stock high pressure tubing made from an alloy steel with an O.D. of 9.52 mm and an I.D. of 3.17 mm. The gas pressure in the vessel was measured by both a conventional steel tube Budenburg pressure gauge (0-10,000 psi) and a pressure transducer (Maywood Instruments). The pressure transducer was supplied with a DC voltage of 10 volts (Solartron, Power supply unit AS 1410). It could measure pressures up to ca. 68 MPa with an accuracy of ca. 0.03 MPa. The output from the transducer was a DC voltage proportional to the pressure ranging from 0 to 200 mv. A digital multimeter (Keithly 195A) capable of storing 100 reading at variable time intervals was used to record these data.

A 3 mm needle valve situated between the pressure vessel and the gas receiver was used to release the high pressure gas. During this throttling process the gas temperature decreased due to the Joule-Thompson effect. Release of CO₂ resulted in the formation of ice on the valve. This prevented the free and fast escape of the gas. The problem was overcome by heating the needle valve with a commercial fan heater.

The temperature in the pressure vessel was controlled by means of an external heat exchanger which enveloped its whole body. The heat exchanger was separated from the pressure vessel by its inner wall which was in close proximity to the vessel. The exchanger was filled with a heating oil (Thermia Oil, Shell). A temperature of up to ca. 150°C could be achieved by a ca. 1 kW electric heater. A platinum resistance temperature controller was used to maintain a constant ambient temperature ($\pm 0.5^\circ\text{C}$). An electrical fuse fitted in series with the electrical heater

was used as a safety measure to prevent over-heating of the oil. The heat exchanger was wrapped with mineral wool to reduce heat losses.

Cooling of the pressure vessel could also be achieved by circulating a pre-cooled water-ethylene glycol mixture through a coil which was wound around the inner wall of the heat exchanger. The coolant temperature was lowered by the use of a 0.6 kW thermostatically controlled cryostat.

4.7 Gas Mass Sorption Probe

4.7.1 Principle of the Technique

The technique used to determine the mass of the gas absorbed in a polymeric specimen involved the measurement of the first harmonic frequency of a slender steel beam rigidly clamped at one end. The polymeric specimen was attached at the free end. At high ambient pressures this technique relates the changes in the resonance frequency to the effective mass change induced in the elastomeric specimen. This vibrating beam technique was developed by Briscoe and Mahgerefteh (1984b) and later modified and improved by Liatsis (1985,1989) in the author's laboratory.

4.7.2 The Vibrating Beam

The vibrating beam was made from a 1 mm thick sheet of a magnetic stainless steel. The other dimensions of the beam are given in Figure 4.4. The beam was clamped onto a heavy base which, in turn, was fastened to the pressure vessel top cap. The heavy base was necessary to suppress the effects of external random vibrations. A rectangular elastomeric specimen (28 x 8 x 8 mm) was attached to the free end of the beam with two small screws (12 BA). A strain gauge (Showa Measuring Instruments Co. Ltd.) was attached to the beam near the

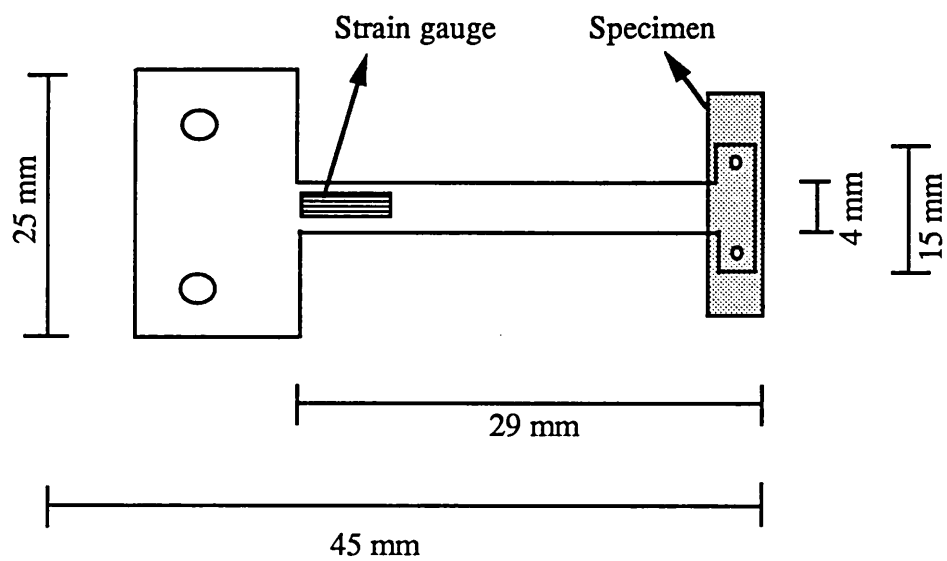


Figure 4.4: Schematic diagram of the vibrating reed.

clamped end by a special adhesive (NP-50, Tokyo Sokki Kenkyojo Co. Ltd.).

The device operated in a close-loop mode. The reed was mechanically excited by a magnetic flux generated by a solenoid. The solenoid was driven by a suitable alternating current. The frequency of induced oscillations was measured by the strain gauge attached to the beam. The variations of the gauge resistance were a measure of the vibration amplitude. The strain gauge was balanced by a 120 ohm resistance and connected to a carrier frequency bridge (Philips PR 9308). The output signal was a sine wave with an amplitude of up to 1 volt. This signal went to a timer-counter (Philips PM 6671) and its frequency (period) was measured. The signal amplitude was measured by a digital multimeter (Keithly 195A). The signal was also fed to an oscilloscope (Schlumberger 5021) for visually monitoring the quality of the beam vibrations.

The close loop operation of the device was obtained by inputting the transducer signal into an amplifier (Dim wideband power amplifier, WPA 301A) via a DC filter. The amplified signal was fed to the solenoid. The amplifier gain was adjusted so that the amplitude of the signal from the frequency bridge was constant ca. 0.4 volts, corresponding to a displacement of ca. 0.5 mm. Higher gains overheated the electromagnetic coil which ultimately resulted in a short circuit of the coil. A schematic diagram of the vibrating reed device is given in Figure 4.5.

4.7.3 Operation of the Vibrating Reed as a Mass Sorption Sensor

The vibrating reed probe, along with the elastomeric specimen, was placed in the pressure vessel. The pressure of the ambient gas was then raised in steps of ca. 4-5 M Pa. The stability of the output signal improved significantly when the pressure increased even slightly above the atmospheric. However, the amplitude of vibrations decreased at higher ambient gas pressures due to the increase in the

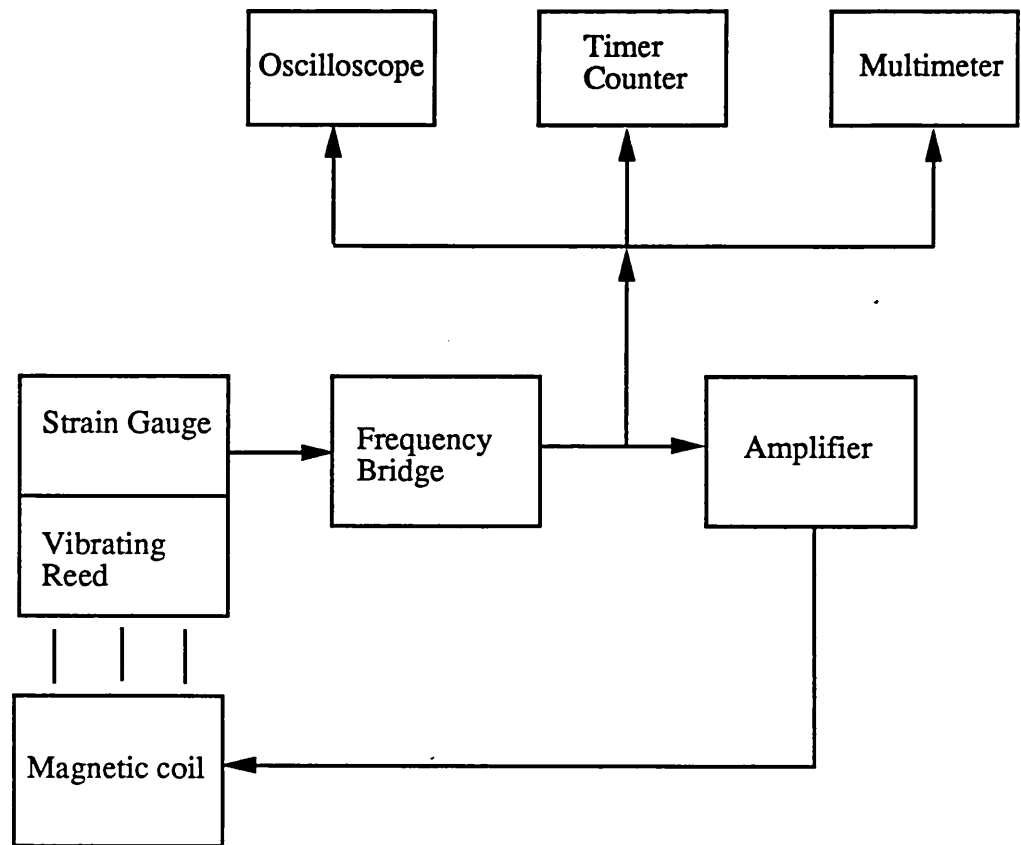


Figure 4.5: Diagrammatic representation of the vibrating reed instrumentation

viscous losses in the gaseous media. The viscosity of N₂ gas increases by ca. 40% at a pressure of ca. 25 MPa and ca. 20°C, relative to the atmospheric value (Gracki, 1969). Similarly, the viscosity of CO₂ increases by ca. 500% at a pressure of ca 31 MPa and 42°C (Diller and Ball, 1985). These viscous effects were sometimes so significant that the vibrations were completely damped. It was then necessary to adjust the driving power and rebalance the carrier frequency bridge to compensate for the viscous effects.

The operation of the vibrating reed to obtain dynamic and equilibrium mass sorption measurements requires a rapid increase in the ambient gas pressure. The changes in the period of vibration were measured at frequent intervals until the change in its value with time was not significant and a quasi-equilibrium condition had been obtained (ca. 45 minutes). During these measurements care was taken to maintain a constant amplitude of vibration and a constant ambient pressure.

4.7.4 Analysis of the Experimental Data

The resonant frequency of the vibrating beam was found to be sensitive not only to the increase in specimen mass due to gas sorption, but also to an increase in the ambient gas density (Briscoe and Mahgerefteh, 1984b) and to the change, if any, in the area of the specimen normal to the plane of vibration called the compression area (Liatsis, 1985). Therefore, the necessary precursors to determine the amount of ambient gas actually absorbed by the polymeric specimen warrants calibration of the vibrating reed device with a non-absorbing specimen.

4.7.4.1 Calibration: Entrained mass due to change in ambient density

In the calibration experiment the polymeric specimen was replaced with an inert aluminium (Al) sample of the similar geometry. The resonant frequency of the vibrating beam to which the Al sample was attached, changed at high pressures

although obviously no gas was absorbed by aluminium (Briscoe and Mahgerefteh, 1984b). This was equivalent to the behaviour of a vibrating beam with a heavier rest mass in vacuum (Mahgerefteh, 1984). The difference between the value of virtual mass and the real mass is called the 'added mass' and corresponds to the mass of the entrained gas (Birkhoff, 1950). It is effectively the product of the gas volume displaced and the gas density. The 'added mass' (Δm) has been shown to a good approximation by the following relation (Liatsis, 1985):

$$\Delta m = k A_c \rho \quad (4.3)$$

where ' ρ ' is the density of gas, ' A_c ' is the specimen area normal to the plane of vibration and ' k ' is the thickness of the gas displaced during vibration.

4.7.4.2 Calibration: Entrained mass due to change in compression area

The area of the rectangular specimen normal to the direction of vibration is referred to as the 'compression area' in such experiments. It has been shown (Briscoe and Mahgerefteh, 1984b) that a change in the 'compression area' effects the sensitivity of the vibrating reed device. Liatsis (1985) has given an empirical relation between the frequency drop, ' F_0/F ' (frequency of vibration at atmospheric condition/frequency of vibration at higher pressures) and the gas density, ' ρ ', at higher pressures:

$$F_0/F = 1 + a \cdot \rho \quad (4.4)$$

where ' a ' is constant. It has also been shown that the frequency drop, ' F_0/F ', and the added mass, ' Δm ', can be accurately approximated by a straight line of the form:

$$F_0/F = 1 + b \Delta m \quad (4.5)$$

where ' b ' is a constant. Combining these two equations, (4.4) and (4.5) gives:

$$\frac{a}{b} = \frac{\Delta m}{\rho} \quad (4.6)$$

The added mass (Δm) is proportional to the compression area and the density of ambient gas equation (4.3). Replacing ' Δm ' in equation (4.3) by equation (4.6) will give the relation:

$$a/b = k \cdot A_c \quad (4.7)$$

A plot of the ratio ' a/b ' and the compression area, Figure 4.6, gives a straight line of slope $k = 9.103 \text{E-}3 \text{ cm}^3/\text{mm}^2 = 9.103 \text{ mm}$. The values of the ratio ' a/b ' were determined for various compression areas by using equation (4.7) and the contribution to the entrained mass due to the change in compression area was thus calculated using equation (4.6).

4.7.4.3 Mass of Gas Absorbed

The period of oscillations of a thin rod (or beam) clamped at one end and having a rest mass attached at the free end is given by (Prescott, 1924),

$$T = \frac{2\pi}{K} \cdot \left(\frac{l_r}{Z}\right)^2 \cdot \left(\frac{\rho_s}{E}\right)^{\frac{1}{2}} \quad (4.8)$$

where ' T ' is the period of vibration, ' K ' is the radius of gyration of a section of the rod (or beam) about the axis through its centre of gravity perpendicular to the plane of motion, ' l_r ' is the rod length, ' ρ_s ' is the density of the tine and ' E ' is the Young's modulus. The variable ' z ' satisfies the equation:

$$\frac{1 + \cos h z \cdot \cos z}{\cos h z \cdot \sin z - \sin h z \cdot \cos z} = c \cdot z \quad (4.9)$$

where ' c ' is the ratio of the rest mass attached at the free end to the mass of the rod.

The period of the vibrating beam is proportion to the term $1/z^2$ (equation 4.8), the variable, ' z ', depends on the ratio, ' c ', and therefore on the rest mass in a way dictated by equation (4.9). When the ambient pressure is increased from P_1 to P_2 the period of vibrations at resonance change from ' T_1 ' to ' T_2 '. If all the other variables in equation (4.8) remain constant, then:

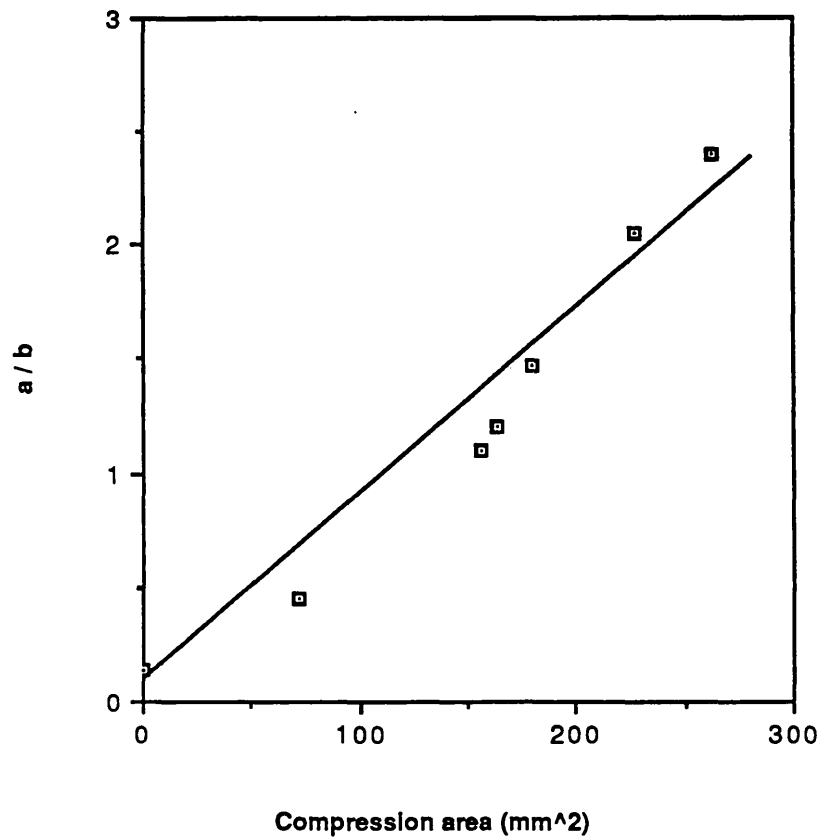


Figure 4.6: Change in a/b ratio as a function of specimen compression area (Liatsis, 1985).

$$\frac{T_1}{T_2} = z_2^2/z_1^2 \quad (4.10)$$

The virtual mass changes from 'M₁' to 'M₂' and consequently the ratio 'c' changes from 'c₁' to 'c₂'. If the initial value of 'c₁' is known, then equation (4.9) gives the value of 'z₁'. The final value of 'z₂' can then be determined from equation (4.10). Substituting the value of 'z₂' in equation (4.9) then gives the value of 'c₂' and hence the final value of 'M₂'. These computations have been performed with the help of the software developed by Liatsis (1985).

The value of mass so obtained at P₂ also includes the contributions of the entrained gas mass due the changes in ambient gas density and the specimen compression area (if applicable). Hence, the gas mass actually absorbed by the specimen at equilibrium in a pressure step (P₁ to P₂) is:

$$\Delta m = (M_{el}^2 - M_{Al}^2 - M_{Ac}^2) - (M_{el}^1 - M_{Al}^1 - M_{Ac}^1) \quad (4.11)$$

The superscript 1 and 2 refer to the initial and final conditions and M_{el} is the mass of the specimen, M_{Al} is the entrained mass due to ambient density change and M_{Ac} is the entrained mass due to the change in the specimen compression area.

The development and operation of this vibrating reed device to measure gas sorption in polymers has been discussed in more detail by Briscoe and Mahgerefteh (1984b) and Liatsis (1985, 1989).

4.8 Ultrasonic Technique

4.8.1 General discussion

The physical and mechanical properties of polymeric materials are effected by high pressure ambient gases. An ultrasonic pulse-echo method (Breazeale *et al*, 1981, pp. 85-89) has been used to study these effects. It involves the transmission of a short duration ultrasonic signal through a homogeneous medium and the receiving of its reflection from the opposite face of the specimen. In this technique the transit time of the signal to traverse through the specimen length and the

attenuation of the signal were determined to study the effects of the ambient gas pressure and later its rapid decompression. The first experimental configuration used, later described as mode-1, was suitable for rubbers through which the ultrasonic signals can easily be transmitted. The second configuration, mode-2, was employed for highly filled and more dissipative systems through which the transmission of the ultrasonic signals was difficult.

4.8.2 Mode -1

Figure 4.7 and Plate 4.2 show the mode-1 experimental setup. Two ultrasonic transducers were used. They were mounted on a brass frame consisting of four circular discs held together by three long 2 BA studs. The elastomeric specimens used in the experiments were cylindrical, ca. 25 mm diameter and ca. 15 mm long. Care was taken while cutting the specimens so that the two opposite faces were smooth and parallel. The unconstrained specimen (A-1, Figure 4.7) was placed on one of the transducers. The second transducer was directly loaded on to the other specimen by one of the circular discs in the brass frame (A-2, Figure 4.7) and strained by ca. 10%. A thin layer of a liquid acoustic couplant (Ultragel II, Diagnostic Sonar, UK) was applied between the specimens and the transducers which ensured a uniform contact between the two. The pre-strained specimen was a reference in the experiment, since it was assumed that in this case no linear dimensional changes occurred. With the help of this arrangement the velocity of sound in the material and the dilation of the elastomeric specimen were computed under pressure.

4.8.3 Mode-2

The mode-2 experimental arrangement involved the use of only one ultrasonic transducer; Figure 4.8 and Plate 4.3 The transducer was held partially dipped in a liquid inside a small container placed on the upper plane surface of the

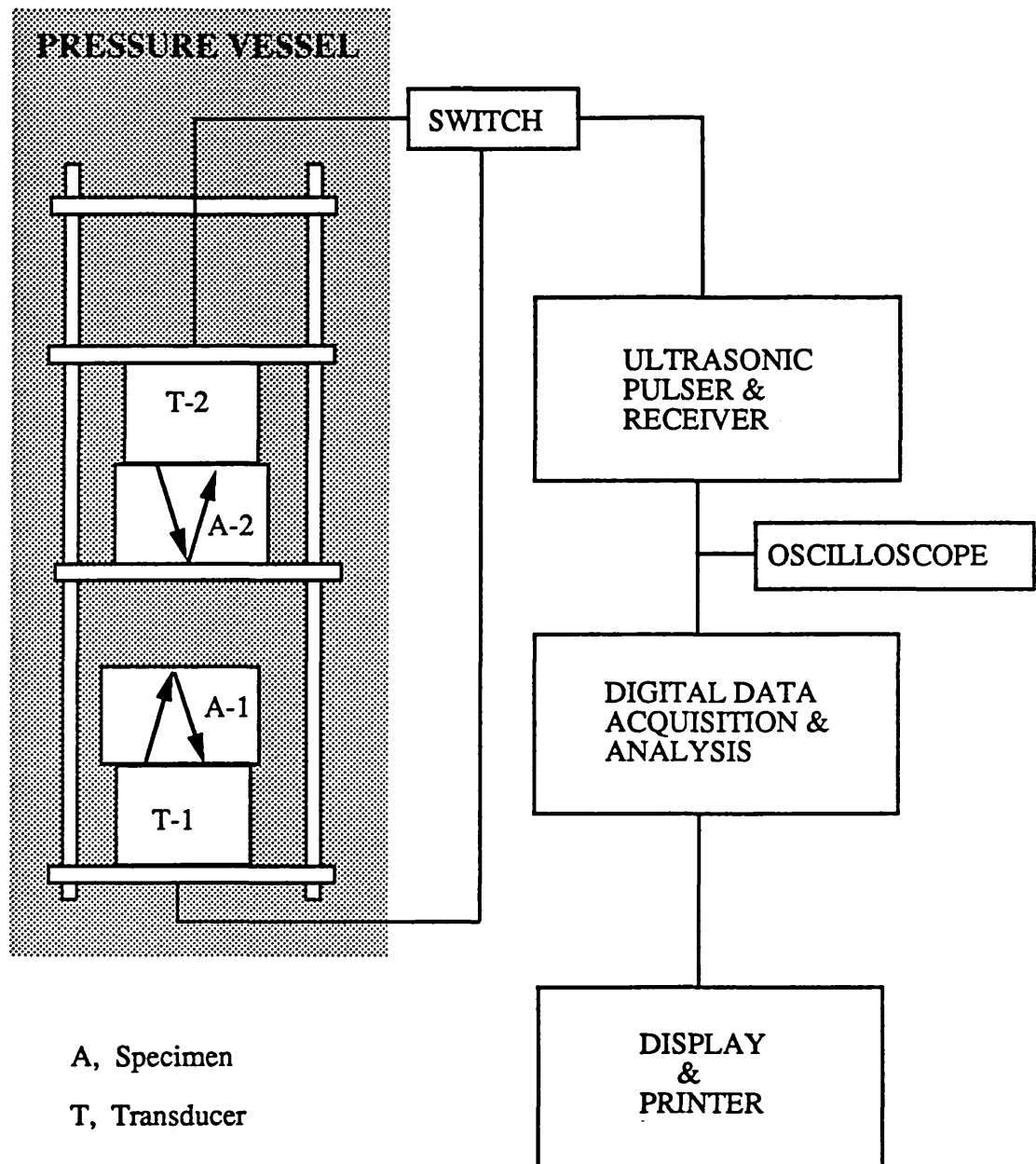


Figure 4.7: Schematic diagram of the ultrasonic technique mode-1

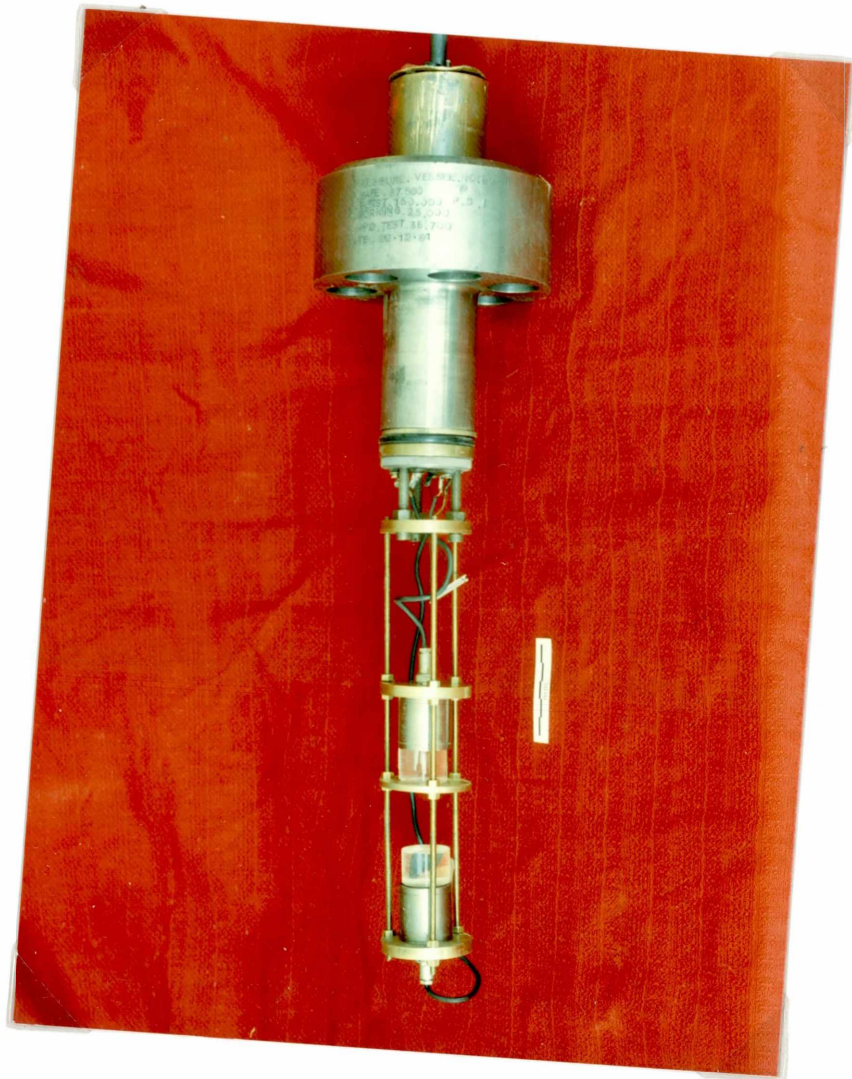
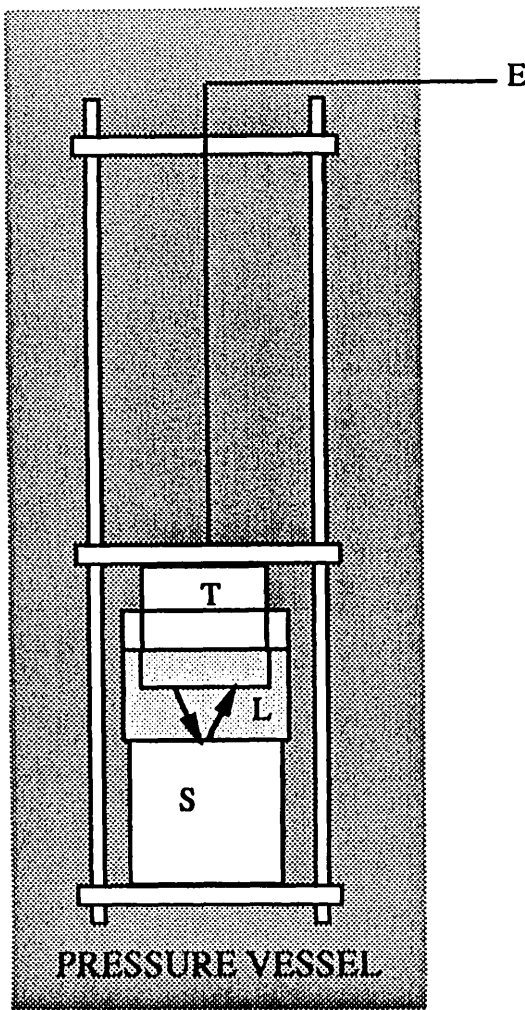
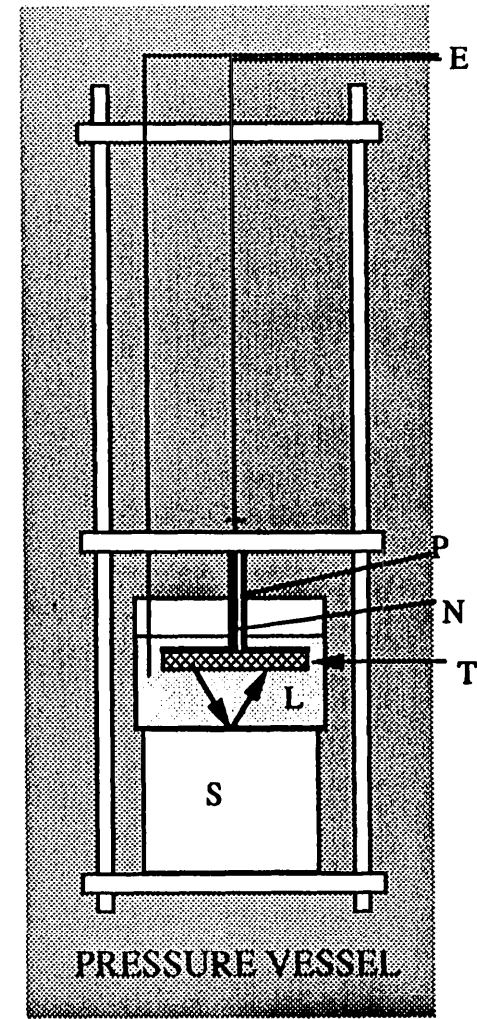


Plate 4.2: The ultrasonic mode-1 experimental arrangement attached to the pressure vessel cap.



(a)

T, Piezoelectric Transducer
 L, Signal transmitting fluid
 S, Polymeric specimen
 N, Stud bolt
 P, Insulation
 E, Electrical connection



(b)

Figure 4.8: Schematic representation of the ultrasonic mode-2 arrangement; (a) with a commercial transducer; (b), with a transducer made in author's laboratory

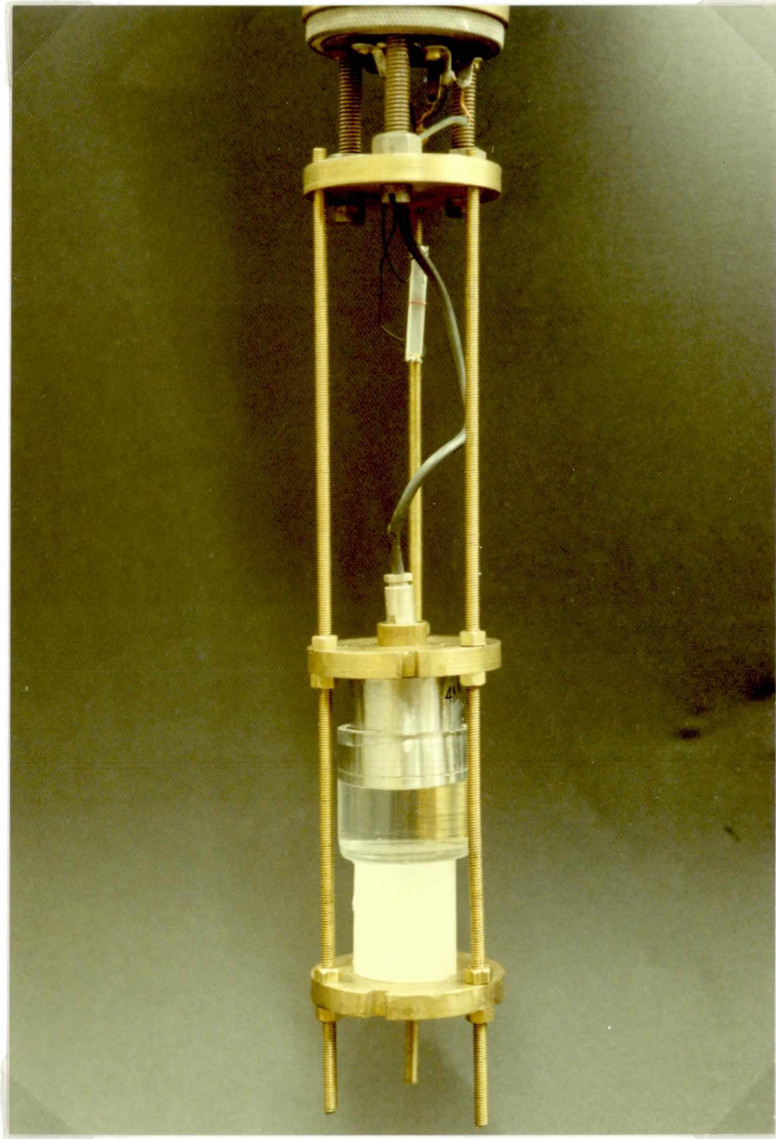


Plate 4.3: The ultrasonic mode-2 experimental arrangement.

specimen. The liquid was the signal transmitting medium. The ultrasonic signals from the transducer travelled through the liquid and were reflected back from the base of the liquid container. If the elastomeric specimen contracted or expanded during the pressure cycle, the distance travelled by the signal increased or decreased respectively in direct proportion. This arrangement operated as a simple and effective displacement transducer. It was found suitable for studying the dilational behaviour of highly attenuating specimens. The formation of acoustically dispersive internal cracks in the specimen during the rapid gas decompression did not affect the ability of this arrangement to detect the dimensional changes over the whole pressure cycle.

4.8.4 Instrumentation

A general pictorial view of the electronic instrumentation involved in the ultrasonic techniques is given in Plate 4.4.

4.8.4.1 Ultrasonic Transducers

The instrumentation involved essentially consisted of piezoelectric transducers, a pulse generator, an amplifier and an oscilloscope. The contact type, compression wave transducers, of ca. 1 MHz resonant frequency were built in stainless steel casings by Rolls Royce Mateval (England). The transducer diameter was ca. 28 mm. These transducers could be used as signal transmitters and receivers. Small holes of ca. 1 mm diameter were drilled in their casings near the back non-active faces so that the ambient pressures were balanced inside the casing cavity. Most transducers of this type are constructed with a polymeric damping component which encapsulates the 'back face' surface of the piezoelectric crystal. The 'front surface' of the crystal is flush with a ceramic wear plate; Figure 4.9. The electrical connections on either side of the crystal are made by an electrical conducting glue. The backing polymer and the glue used for electrical connections are quite vulnerable to certain gases at high pressures and to their rapid

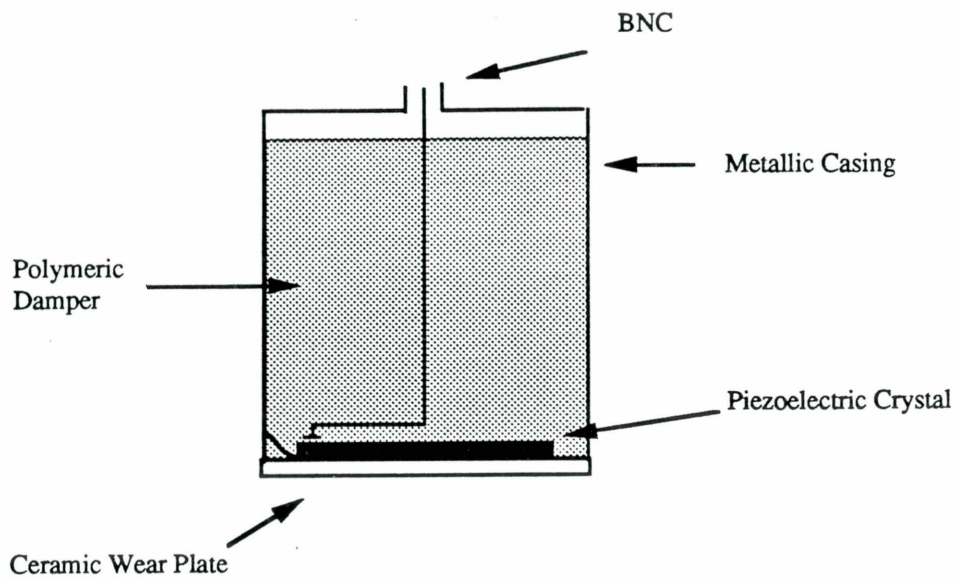


Figure 4.9 : Schematic representation of a typical commercial ultrasonic transducer.

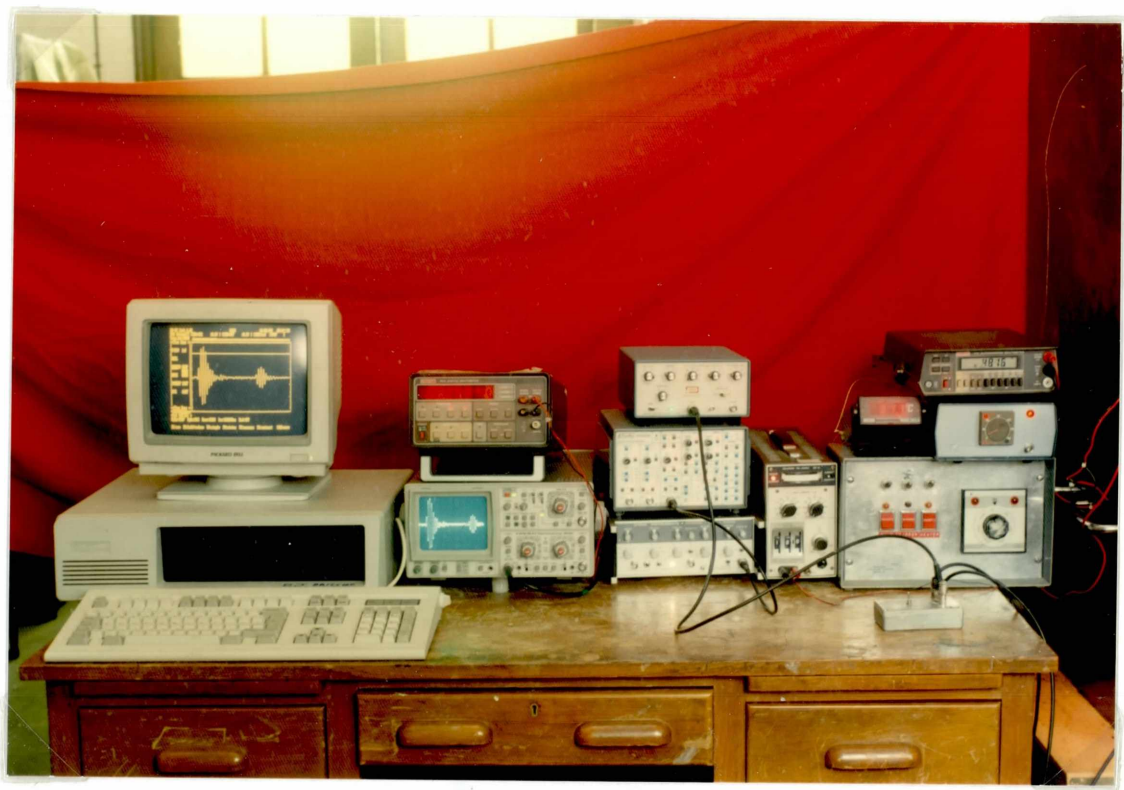


Plate 4.4: The electronic instrumentation involved in the ultrasonic technique.

decompressions; they suffer explosive decompression failure. This is particularly so for CO₂ gas. However, the N₂ gas pressures of up to ca. 30 MPa and the rapid decompressions does not seem to have any detrimental effects on the commercial transducers described.

The problem of not being able to use these commercial transducers in the high pressure CO₂ environments was resolved by manufacturing simple transducers during the course of this work. These units consisted of a silver-coated piezoelectric crystal disc, ca. 10 mm in diameter, ca. 1 mm thick and with 1 MHz resonant frequency (Unilator Matrock, UK). Both sides of the crystal were silver coated. On one side a thin electrical wire was soldered near the edge which acted as one electrode. On the other side, a 12 BA, ca. 25 mm long stud was soldered. The stud was carefully screwed at the centre of a circular disc in the transducer frame and was used as the other electrode. These simple transducers were used in the mode-2 experimental arrangement. The performance of these transducers was not affected by the CO₂ pressures of up to 25 MPa and its rapid decompressions down to the atmospheric condition. When mercury was used as the ultrasonic signal transmitting medium instead of water (see later) a number of problems occurred. Firstly, because it is an electric conductor. The electrodes on either side of the piezoelectric crystal were short circuited. Secondly, the mercury removed the silver coatings on the sides of the crystal. The electrode wires soldered on the silvered surfaces were detached once the transducer was dipped in mercury. These difficulties were overcome by applying a thin layer of paint (Japlac, International Paint, UK) on the stud side of the transducer. The stud holding the piezoelectric crystal in position served as one electrode and the mercury in which the crystal was dipped became the other electrode. A thin layer of the acoustic couplant was applied on the front face of the piezoelectric crystal. The transducer was submerged in the mercury, ca. 5 mm. The dimensional changes in the elastomeric specimens over the whole CO₂ pressure cycles were then amenable to measurements.

4.8.4.2 Pulser receiver unit

The piezoelectric crystal in the transducer was excited by a short large-amplitude electrical pulse from a pulser-receiver unit (Panmatrics Inc., model 5052 PRX 75). In mode-1 the electric pulses were alternated between the two transducers by a three-way switch. Multiple echoes were obtained because the first wave reflected back from the opposite face, transmitted only a small portion of its energy to the probe. It was reflected again and passed through the specimen a second time and so on. The pulse repetition frequency of the pulser-receiver unit was chosen as 250 Hz. The time interval between the two electrical pulses (4×10^{-3} sec) was long enough for the back wall echoes (reflections) amplitude to reach zero. The reflections received by the transducer were converted into electrical signals and transferred to the amplifier section of the pulser-receiver unit. They were amplified and transferred to the oscilloscope for display and to the digital data acquisition system for storage and subsequent data analysis.

4.8.4.3 Data acquisition systems

The digital data acquisition system used initially was a software driven, wave acquisition and generation board (WAAG, Markenrich Corp.) in conjunction with an IBM-XT compatible computer (Digitask, Business System, Ltd). The board had an 'on-board' memory of 16 kilobytes. The data sampling frequency was variable and ranged from 2 KHz to 20 MHz. The selected sampling frequency was 20 MHz. The software driving the data acquisition system configured the computer and the WAAG memory in such a way that a maximum of 40 sets of 1400 data points could be recorded. The time interval between each acquisition set, the number of total acquisitions, the number of data points in each acquisition and the data sampling frequency could be varied. The WAAG board was triggered by the synchronising signal from the pulser-receiver unit. This acquisition system was quite suitable for the current work, specially while making the transient

measurements during the rapid decompressions.

The precision of the measurements were further improved later by putting together another data acquisition system; Figure 4.10. A digital storage adaptor (Thurlby, DSA 524) with a digital memory of 4 kilobytes was used. The selectable data sampling frequency range of the adaptor was from 1 KHz to 2 GHz. At the higher sampling rates (50 MHz to 2 GHz), the data was acquired by equivalent sampling procedure. This system was only suitable for repetitive signals since it took 4-5 seconds to capture an event. The sampling rates usually used in this study were 100 MHz and 200 MHz depending upon the length of the specimens. The storage adaptor was triggered externally by a signal from a pulse generator (Lyon Instruments, 112A). A suitable delay in the trigger signal was introduced by the pulse generator, such that only the first and the second reflections of the input pulse were captured by the storage adaptor. The captured signals were displayed on an oscilloscope. A software package (DS-PC Link, Version 2.0) was used which enabled an IBM-compatible PC to act as a display device for the storage adaptor and it also provided complete control of the adaptor from the PC. The additional facility provided by the software was that the display could be stored on the computer hard disk.

4.8.5 Operation

The frame mounted with the ultrasonic transducer(s) and the elastomeric specimen(s) arranged in either of the experimental set-ups (mode-1 or mode-2) was secured to the pressure vessel cap and placed in the high pressure chamber. The ambient gas pressure was increased in steps (ca. 3-5 MPa). The ultrasonic signals were continuously transmitted after a step pressure increment. The signals were recorded after a quasi-equilibrium condition had been achieved, ca. 45 minutes. The experiments with the N₂ gas were preformed at ca. 20°C and with the CO₂ gas at a

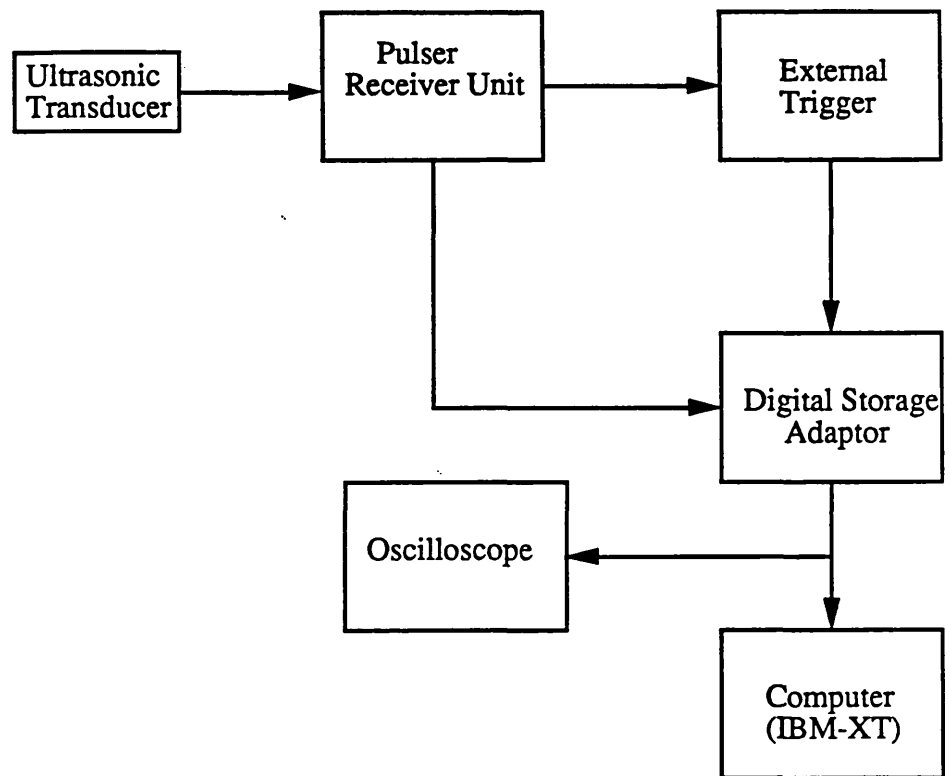


Figure 4.10 : Diagrammatic representation of the ultrasonic data acquisition system.

temperature of ca. 42°C.

4.8.5.1 Mode-1

The transmission of the ultrasonic signals was alternated between the two specimens and recorded at the appropriate conditions. During the decompressions of the ambient gas pressure, the ultrasonic signals were continuously transmitted through the unconstrained specimen to detect the initiation of internal cracks in the specimen. The data acquisitions were made at an interval of ca. 5 seconds and recorded for subsequent analysis.

4.8.5.2 Mode-2

Distilled water was chosen as the signal transmitting medium in the small container placed over the specimen surface. Its acoustic properties are well known (Urlick, 1967) and have also been studied extensively under hydrostatic pressures (Wilson, 1958, 1959). The water provided a uniform path for the transmission of ultrasonic signals. The problem of air entrapment in the bulk and at the transducer liquid interface, associated with more viscous liquids like silicone fluid, did not occur. The acoustic length of the water in the container (ca. 15 mm) was adjusted relative to the anticipated inflation of the specimen during the rapid release of the ambient gas pressure in a given experiment. The diameter of the container was ca. 3 mm larger than the commercial transducer.

The experiments with CO₂ were performed with the transducer made in the author's laboratory. Another experimental difficulty with CO₂ was the significant solubility of this gas in water, ca. 6% by weight at ca. 21 MPa and 45°C (Perry and Chilton, 1983, 3-96). When the ambient gas pressure was rapidly reduced, the gas in the water desorbed resulting in the formation of bubbles that scattered the ultrasonic signals travelling through the water. Consequently, the inflation of the specimen could not be followed. A liquid medium was required whose signal

transmitting properties were least effected by the CO₂ pressure cycle. Mercury was found to be a useful medium.

The variations in sound velocity for the distilled water under the N₂ gas pressures are given in Figure 4.11. The transient variations during the N₂ gas decompression are shown in Figure 4.12. It has been observed that with the available level of detection, the acoustic properties of the mercury did not change under the CO₂ gas pressures of up to ca. 23 MPa and during the transient depressurisation. The two figures (4.11 & 4.12) serve as the necessary calibration for the mode-2 experiments.

4.8.6 Data Analysis

The propagation of an acoustic wave through a medium is disrupted when it meets an interface. A part of the wave is reflected and a part is transmitted into the other material. The coefficient of reflection, 'R' ($= (Z_2 - Z_1) / (Z_2 + Z_1)$), and the coefficient of transmission, 'J' ($= (2Z_2) / (Z_2 + Z_1)$), depend upon the acoustic impedances, 'Z' ($= \rho \cdot V$), of the two materials. The phase of the reflected and the transmitted waves are determined by the signs of 'R' and 'J' respectively; Figure 4.13.

A typical plot of a sampled ultrasonic signal is shown in Figure 4.14. It includes the first and the second reflections of the input signal from the opposite face of the specimen. The analysis of the stored pulse-echo data required the selection of an array with the two consecutive back wall echoes. If the reflections were out of phase with respect to each other, correction was made to bring the two into phase. These selections were autocorrelated and the time-lag between the two maximas of relative uniformity were measured. A typical autocorrelogram is shown in Figure 4.15. In the pulse-echo technique a signal travels through the specimen length twice before it returns back to the transducer. The time-lag is thus

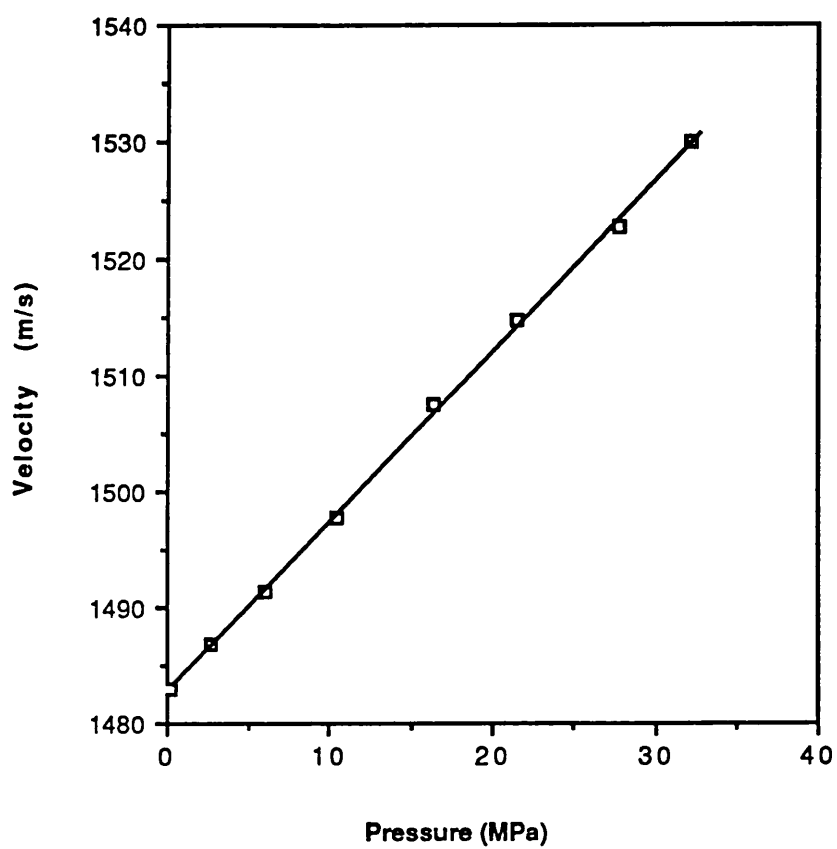


Figure 4.11: Change in the ultrasonic velocity for distilled water as a function of N_2 pressure, 20°C.

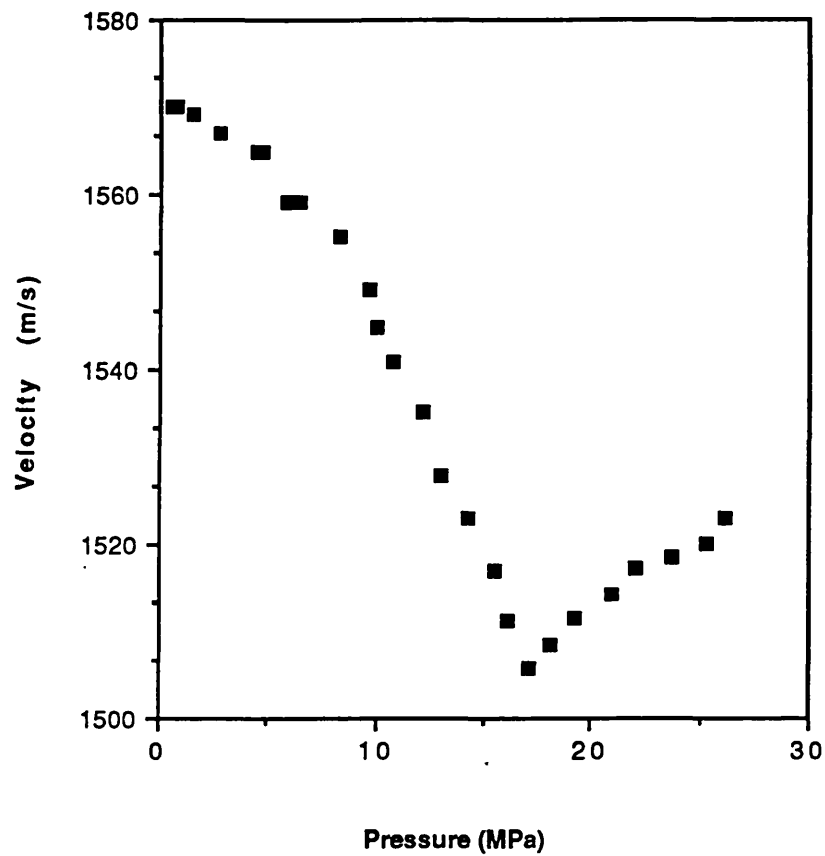


Figure 4.12: Change in the ultrasonic velocity for distilled water as a function of N_2 depressurisation.

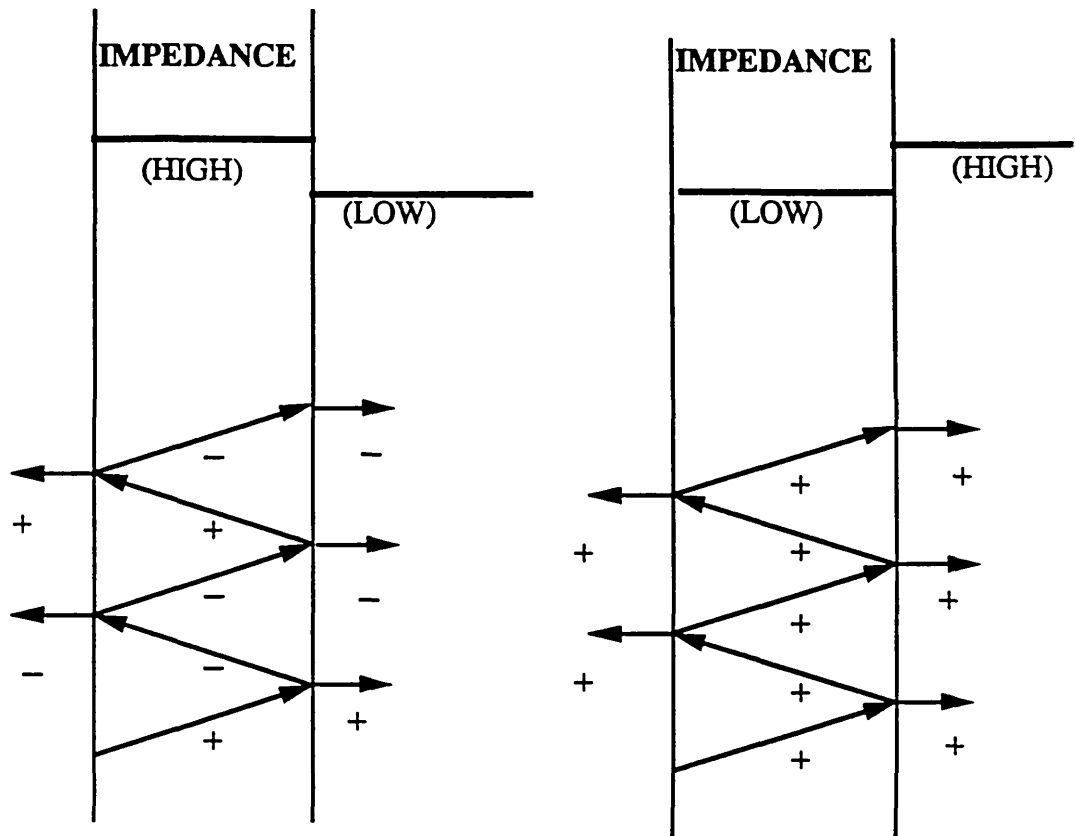


Figure 4.13: Course of phase change for reflected sound waves; (a), wave travelling from sonically hard to a sonically soft material; (b), wave travelling from sonically soft to a hard material.

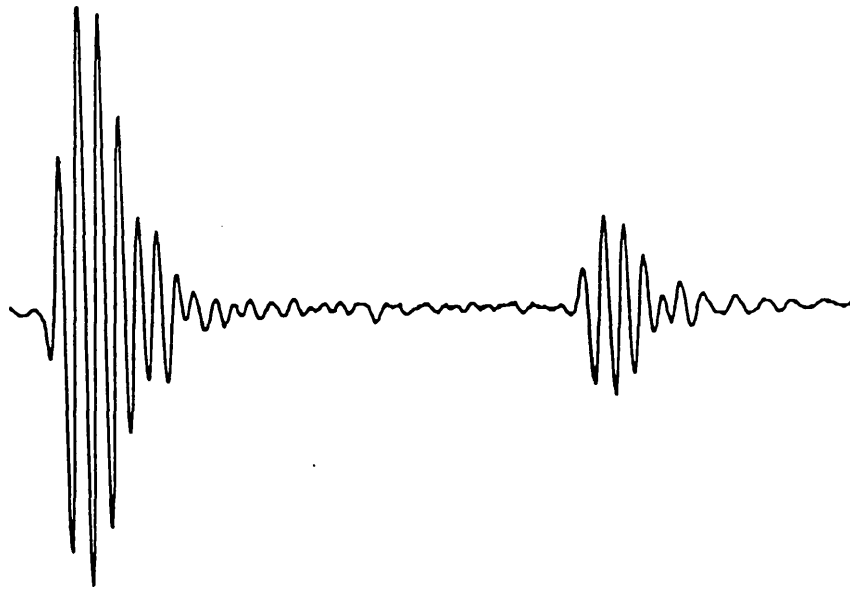


Figure 4.14: A typical ultrasonic signal showing the first and the second reflection.

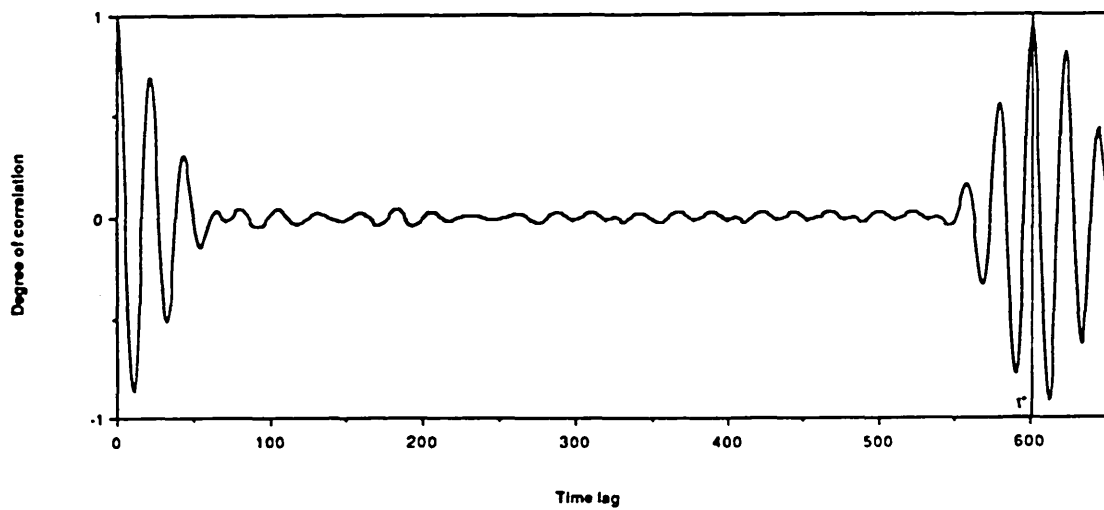


Figure 4.15: A typical autocorrelogram shown as a function of time lag parameter given in units of sampling time, $0-t^*$ is the time lag.

twice the time a signal takes to traverse the specimen length. The velocity of sound 'V' in the material is given by:

$$V = 2 l/\tau \quad (4.12)$$

where 'l' is the specimen length and 'τ' is the transit time. Typically, 'l' was of the order of ca. 15×10^{-3} m. The error of measurement was of the order of $\pm 0.18\%$ at a sampling frequency of 20 MHz. The precision of the measurements were significantly improved while using the digital storage adaptor at a sampling frequency of 100 MHz. The error of measurement was reduced to ca. $\pm 0.035\%$.

4.8.6.1 Mode-1

The initial thickness of the specimen was known and the measurement of the signal transit time at the start of the experiment gave the velocity of sound in the material. The change in the transit time observed following a pressure step was a consequence of the combined effects of the changes in the specimen's modulus, density and dimensions. For the pre-strained specimen, this change was assumed to result only from the variations in the specimen modulus and density. The transit times of the ultrasonic signal at various pressures for this specimen were measured and used to calculate the sound velocities as described in the above section. The signal lapse time for the unconstrained specimen and the reference values of the sound velocity were employed to evaluate its dimensions at various pressures.

The elastic behaviour of solids can be determined by measuring ultrasonic wave velocity. The velocity of sound, the density and the modulus of a material are related by the expression (Vary, 1980, p. 164):

$$L = V_1^2 \cdot \rho \quad (4.13)$$

where 'L' is the longitudinal modulus, 'V₁' is the longitudinal velocity and 'ρ' is the density. Hence, if the changes in the specimen density and sound velocity at various pneumatic pressures are known the moduli may be computed.

The formation and development of the internal cracks in a specimen during

the rapid ambient pressure release were also monitored using this experimental arrangement. The ultrasonic data were collected by the WAAG data acquisition system at regular intervals, while the ambient gas pressure was being reduced. Subsequently, Fast Fourier Transform (FFT) of the two consecutive back wall echoes in each data set were performed. The amplitudes of the 1 MHz frequency components in the spectrums were compared to determine the attenuation of the transmitted signal. The creation of substantially large cracks or voids provided effective scattering centres and true attenuation of the signals occurred.

4.8.6.2 Mode-2

In this mode the signal transit times during the equilibrium and the transient pressure conditions were effected by the changes in the ultrasonic velocity in the signal transmitting medium and the dimensional strains of the specimen. With the help of the velocity calibration factors (Figure 4.11& 4.12) the linear strains in the specimen were computed.

4.9 Optical Observations

4.9.1 Optical Microscope

The matrix-filler interfaces of the damaged specimens were studied using an Olympus optical microscope (BH2), fitted with a Cannon T-90 camera. The microscope was used in the transmission mode.

4.9.2 Scanning Electron Microscope

A Jeol, T200A scanning electron microscope was also used to study the matrix-filler interfaces of the damaged specimens. The samples were coated with a thin layer of gold to make them electrically conductive.

4.9.3 Image Analyser

The number of cracks and the percentage crack area in the cross-sections of the damaged specimens were measured using an Optomax image analyser (Analytical Measuring Systems).

4.10 Measurement of Mechanical Properties

4.10.1 Mechanical Testing Machine

The stress-strain properties of the various elastomeric specimens under study were obtained using a mechanical testing machine (Instron 1122). The cross-head speed employed in all the experiments was 50 mm/min.

4.10.1.2 Specimen Shape for Various Experiments

Uniaxial tensile test

The Young's modulus of the various specimens were determined using a 3 mm thick standard (ISO/DIS 527, Type A) dumb bell shaped specimen; Figure 4.16.

Diametric compression

Cylindrical specimens, diameter 25 mm, length 25 mm, were used in the diametric compression experiments to determine the 'softening' of the various explosively decompressed specimens.

Uniaxial compression of bonded rubber disks

Discs of the silicone elastomer, diameter 25 mm, bonded between two rigid glass plates were uniaxially compressed. The aspect ratios (thickness/ diameter)

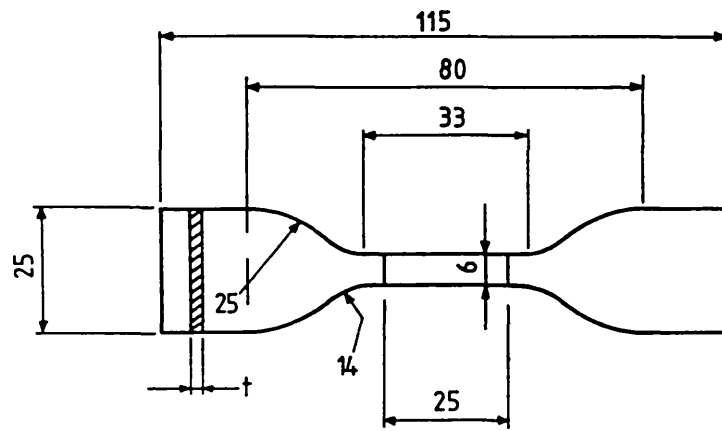


Figure 4.16: A typical dumbbell shaped specimen, all dimensions are in mm and 't', the specimen thickness equals 3 mm.

of the specimens were in the range of ca. 0.09 to 0.2. These experiments were undertaken to observe the effects of the interfacial constraints on the stress-strain behaviours of the specimens

4.10.2 Dynamic Mechanical Testing Machine

The dynamic mechanical behaviours of the various specimens were studied using Polymer Laboratories, DMTA. The dimensions of the specimens used were: 5 mm wide, 15 mm long and 3 mm thick. The storage modulus and the loss modulus (shear mode) were measured as a function of temperature between 25°C to 80°C, at a constant frequency of 5 Hz and an amplitude of 250 μm .

4.10.3 Hydrostatic Compression

A mercury porosimeter (Carlo Erba Instrumentazione, Series 800) was used to determine the compressibility of the various polymeric specimens. A hydrostatic pressure of up to 100 MPa of mercury was applied. The dilatometer containing a void free specimen was filled with mercury under vacuum to avoid any air entrapment. The mercury pressure was gradually increased and the changes in the volume were recorded. A separate experiment was also performed with only mercury in the dilatometer to obtain the necessary correction term; Figure 4.17.

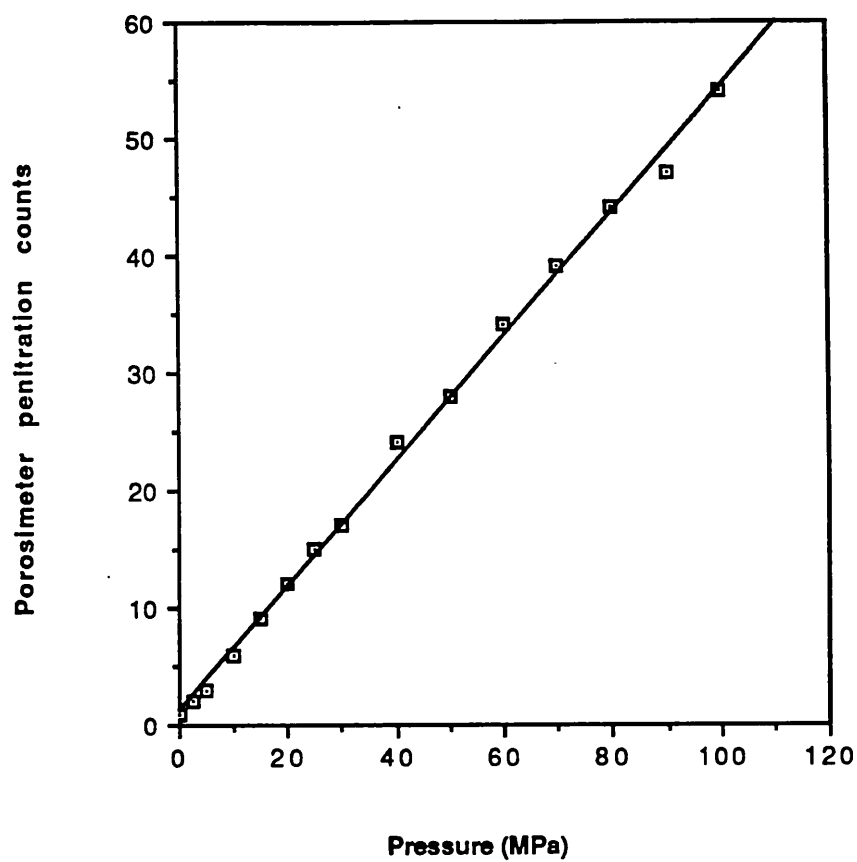


Figure 4.17: The calibration curve of the mercury porosimeter used for measuring volumetric strain of polymers under pure hydrostatic pressure.

CHAPTER FIVE

SOLUBILITY OF HIGH PRESSURE GASES IN SILICONE ELASTOMER SYSTEMS

5.1 INTRODUCTION

In this Chapter the experimental results for the sorption of high pressure N₂ gas and CO₂ gas in the silicone elastomer systems, described in Chapter 4, are presented and discussed. The gas uptake was measured using the vibrating reed technique which is also described in Chapter 4 of this thesis. A special correction of the measured data was necessary due to the extensive sorptive dilation of the elastomeric test specimens. The magnitude of this correction was very significant especially in the CO₂ gas environment. A significant difference in the amounts of the N₂ gas and the CO₂ gas absorption in the specimens of a similar type is observed. The sorption data for the composite specimens is also described. The extent of the sorption in these systems is shown to be a function of the polymer-filler interfacial quality.

5.2 NITROGEN GAS SORPTION

The sorption measurements of the high pressure N₂ gas in the silicone elastomer and its composites with 20% (w/w) glass filler were made at room temperature (20°C). The maximum ambient gas pressure adopted was ca. 27 MPa. The original data from the vibrating reed probe were obtained in the form of the period of the oscillations as a function of the pressure. These data were converted into mass uptake data using the various calibrations and the analysis described in

Chapter 4. The apparent mass sorption values were corrected for the 'added mass' associated with the increase in the ambient gas density. The N_2 gas pressure was increased in relatively small increments and the changes in the periods of the oscillations were continuously monitored and recorded until a constant period (equilibrium mass sorption) was obtained. It was assumed that at this stage the test specimen was saturated with the high pressure gas. Generally, the time allowed between the measurement phases of two successive pressure steps was ca. 45 minutes. The quasi-equilibrium gas mass uptake values as a function of the ambient gas pressure are given in Figure 5.1. The observed increase, in the mass of the unfilled specimen, at the maximum pressure of ca. 27 MPa is ca. 22% w/w. The sorption data for the filled specimens are also shown in the same figure; the extent of the gas sorptions, based on the total specimen mass, are less than that obtained for the unfilled polymer. The mass uptake isotherms also exhibit a tendency to curve towards the pressure axis. This is particularly noticeable for the filled system with the strong internal interfaces.

The sorption data have also been plotted against the N_2 gas density; Figure 5.2. The shape of the curves remain similar to that observed with the pressure variable. The experimental temperature (20°C) is considerably higher than the critical temperature of N_2 gas (-147°C). In the pressure range studied an almost linear relationship exists between the N_2 gas density and the corresponding pressure.

5.2.1 Sorption in Filled Systems

The 'normalised' amounts of the absorbed N_2 gas in the composite systems are shown in Figure 5.3. The sorption isotherm for the unfilled specimen is also given in the same figure for comparison purposes. It is observed that the quantities of the absorbed N_2 gas in the polymer fractions of the systems with the weak

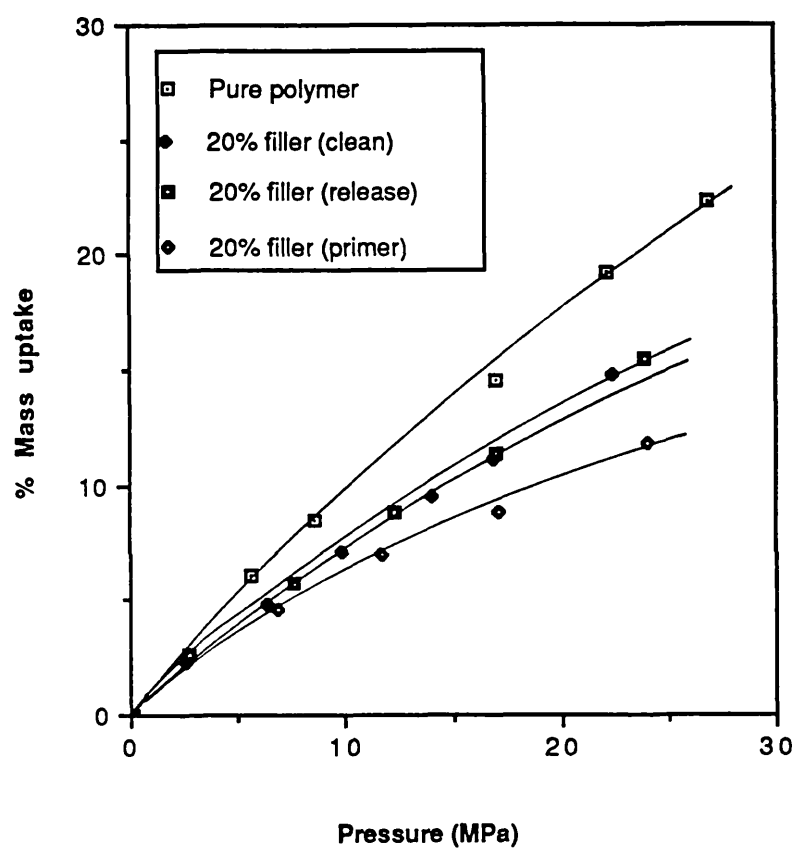


Figure 5.1: Percentage mass uptake for the various silicone elastomer specimens as a function of N_2 gas pressure, 20°C.

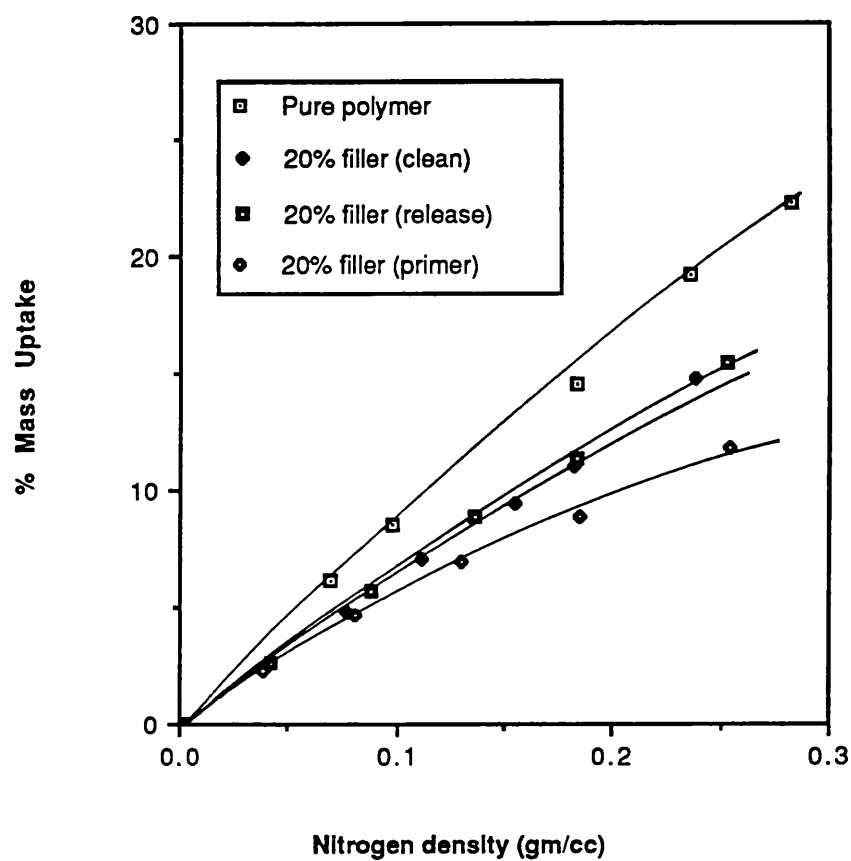


Figure 5.2: Percentage mass uptake for the various silicone elastomer specimens as a function of N_2 gas density, 20°C.

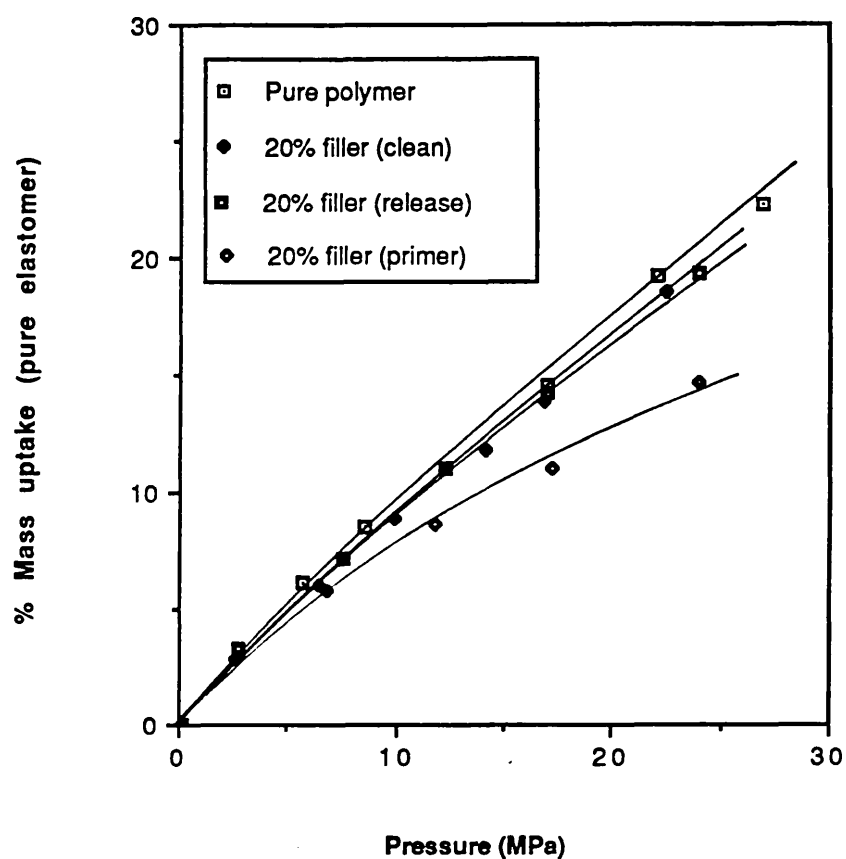


Figure 5.3: Percentage mass uptake on pure polymer basis for the various 20% filled silicone elastomer specimens as a function of N_2 gas pressure, 20°C.

internal interfaces remain lower than that in the unfilled specimen. However, the differences are not very significant. In the system where the filler particles were treated with the commercial adhesion promoter and the matrix-filler interfacial bonds were strong the decrease in the penetrant uptake, on the same basis, is significant. This behaviour resembles the 'case-3' situation as described by Clark-Monks and Ellis (1973). It appears that a portion of the polymer fraction is unable to absorb the high pressure gas. Similar trends have been observed by Melikhova *et al* (1959) and Kewei & Kumins (1964) for channel black filled rubbers and titanium oxide filled polyvinyl acetate, respectively. A 'filler sphere of influence' concept in composite specimens has been proposed by Clark-Monks and Ellis (1973). This effect is interpreted as being due to the layers of polymer which strongly adhered to the filler surfaces and are effectively removed from the sorption process.

The slope of a straight line fitted through the sorption data points may be used to obtain the solubility parameter of the high pressure N₂ gas in these elastomeric systems. The calculated values are listed in Table 5.1. A first order estimate of the solubility coefficient for the unfilled system is ca. $7.3 \times 10^{-6} \text{m}^3(\text{STP}) \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$. The reported values in the literature (Lomax, 1985; Warrick *et al*, 1978), at atmospheric pressure, are of the order of ca. $1.5 \times 10^{-6} \text{m}^3(\text{STP}) \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$. An increase of approximately 5 times with pressure is thus observed. Liatsis (1989), in a similar study involving nitrile rubbers, found that the N₂ gas solubility increased by more than ten times at high pressures as compared to that at atmospheric conditions. This implies that the N₂ gas solubility coefficient at elevated pressures is therefore higher than at atmospheric conditions. It has been noted that in absolute terms the N₂ gas sorption in the silicone elastomer, under similar conditions, is 2.5 times than in nitrile rubber and about 18 times more than that in PTFE (Briscoe and Mahgerefteh, 1984b). The differences are an indication of the higher sorptive capacity of the silicone elastomer system.

Specimen	Nitrogen ambient (0-20MPa) (m ³ (STP)/m ³ xPa)	Carbon dioxide ambient (0-5MPa) (m ³ (STP)/m ³ xPa)
Unfilled	7.3x10 ⁻⁶	25.4x10 ⁻⁶
Composite with 20% clean filler particles	6.0x10 ⁻⁶	~23.5x10 ⁻⁶
Composite with 20% release agent treated filler particles	5.8x10 ⁻⁶	~23.5x10 ⁻⁶
Composite with 20% primed filler particles	4.4x10 ⁻⁶	16.4x10 ⁻⁶

Table 5.1: Solubility of high pressure nitrogen gas and carbon dioxide gas in the silicone elastomer and its composites.

5.2.2 Dynamic Measurements of N₂ Gas Sorption

As mentioned earlier, the dynamic measurements of the N₂ gas sorption following an increasing pressure step have also been made. The experimental conditions following a pressure ramp were unstable. Therefore, the measurements at times less than 1 minute after the application of every pressure step are not presented. The sorbed mass at various times during each pressure step, normalised by the extrapolated total mass sorbed in the step, have been plotted against the square root of time. These transient data for the unfilled system are shown in Figure 5.4. There was no significant difference in the sorption curves for the various filled systems; Figure 5.5 is a typical representation. The characteristics of the two figures (5.4 and 5.5) are quite similar; the sorption is relatively slow. An interesting general observation is that all the curves in each data set do not fall on one master curve. This indicates that the diffusion coefficient is a function of the ambient pressure. The initial (lower pressure) sorption curve is always higher than the subsequent ones. A first order estimate for the value of the diffusion coefficient has been made by comparing the experimentally measured mass curves with those generated theoretically. The necessary theoretical curves were developed by Liatsis (1989) for specimens of a geometry similar to that used in this study. Typical mass uptake profiles are shown in Figure 5.6. A Fickian diffusion of a gas into a cylinder with constant diffusion coefficient was assumed (Crank, 1973, p.175). It is realised that the form of the experimental curves is different to the theoretical predictions. Nevertheless, a crude assessment of the diffusion coefficient may be made. In the unfilled system the estimated diffusion coefficient for the first step is ca. $3.0 \times 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1}$. This value is approximately 3 times the value in the subsequent pressure intervals. Similarly, for the filled systems the estimated diffusion coefficients for the initial step is ca. $2.0 \times 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1}$. The difference between the values for the first (low pressure) and the subsequent steps (high

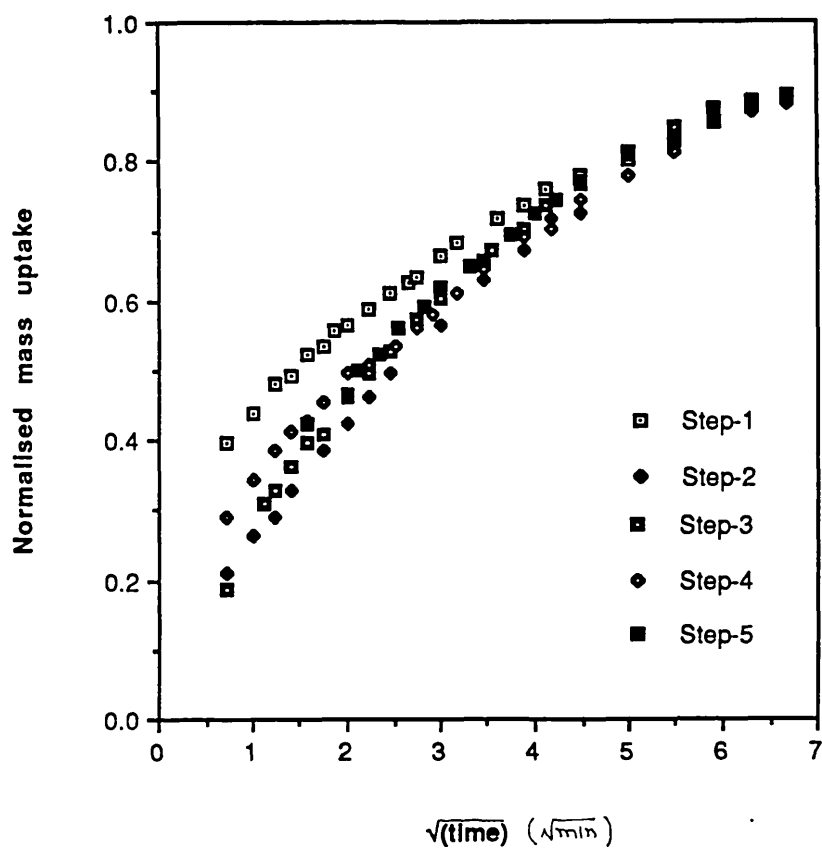


Figure 5.4: Normalised N_2 gas mass uptake for the unfilled silicone elastomer specimen as a function of square root of time.

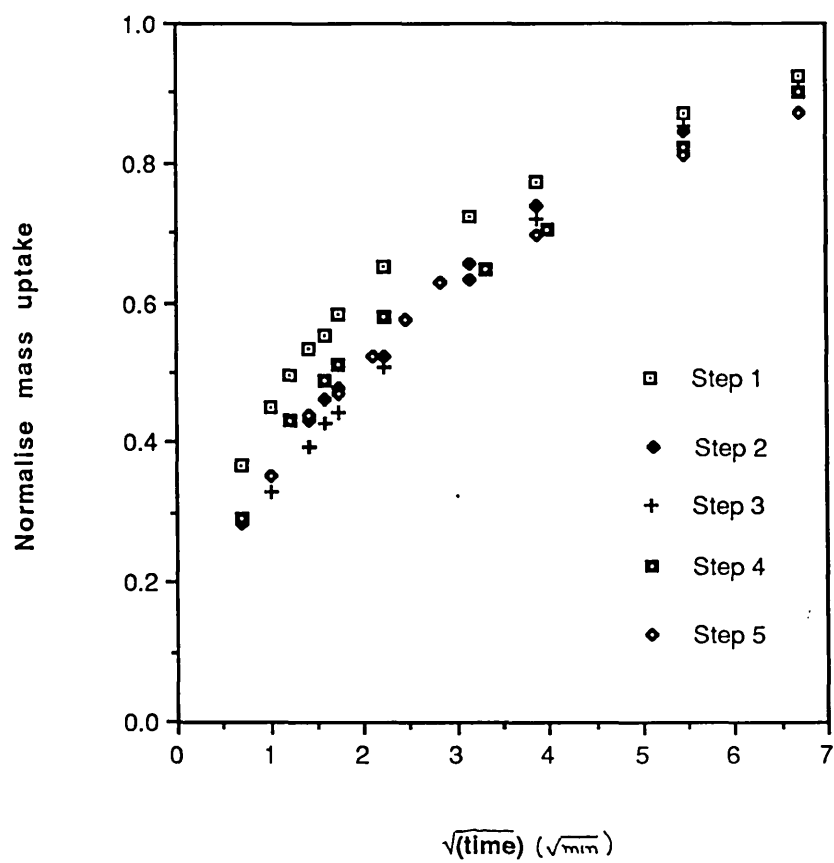


Figure 5.5: Normalised N_2 gas mass uptake for a 20% (w/w) glass filled silicone elastomer specimen as a function of square root of time.

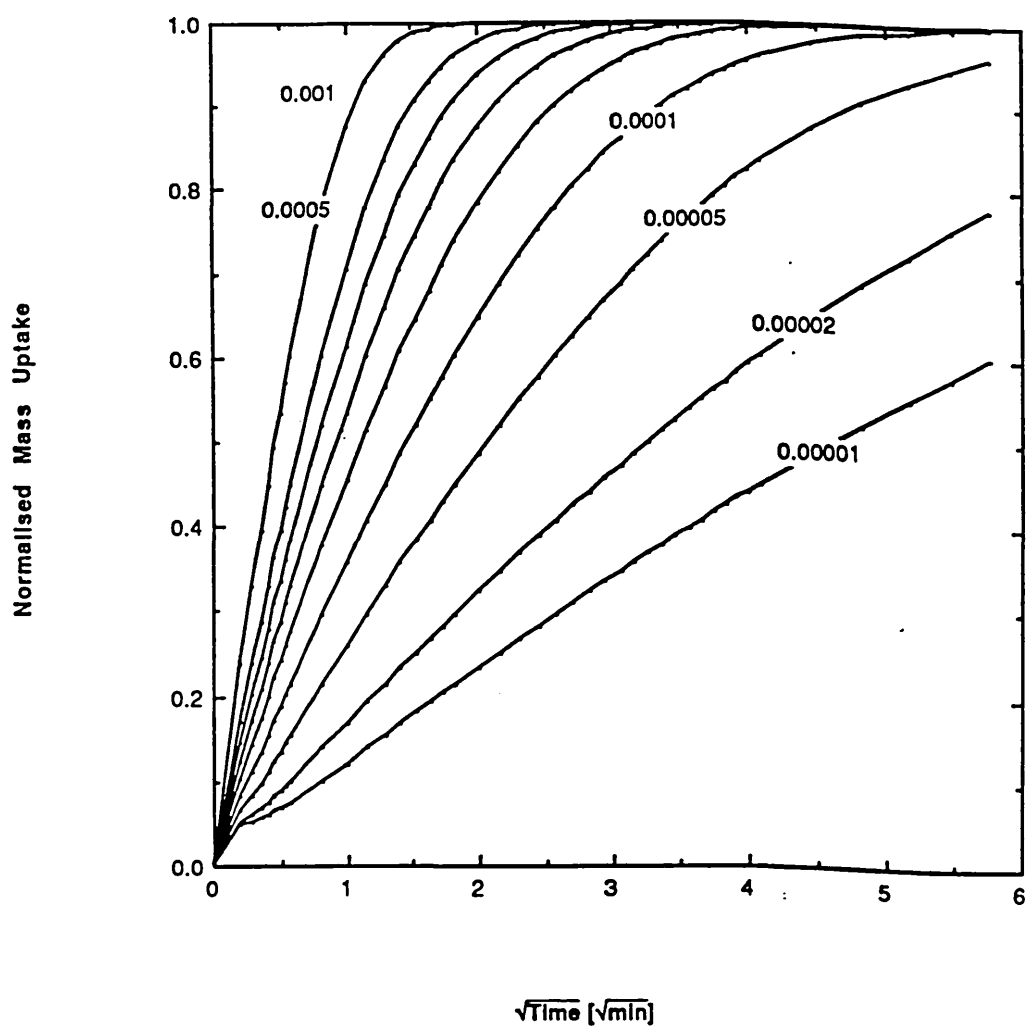


Figure 5.6: Theoretical mass uptake curves against square root of time for diffusion. Numbers on the curves represent diffusion coefficient in $\text{cm}^2\cdot\text{sec}^{-1}$ (Liatsis, 1989).

pressure) is approximately a factor of two.

5.3 CARBON DIOXIDE GAS SORPTION

The high pressure CO₂ gas sorption in the silicone elastomer and its composites was measured up to a pressure of ca. 22 MPa. The temperature was maintained at 42°C. The experimental procedures were the same as those employed in the case of N₂ gas. However, the final mass uptake values were also corrected for the sorptive dilation (see Chapter 6) of the specimens. This is the first time that it has been necessary to introduce this type of correction with this technique. The additional increase in the 'entrained mass' due to the increase in the specimen compression areas were taken into account (Chapter 4, Section 4.7.4.2). The computed values of the entrained masses as a function of the ambient gas pressure for the various specimens are given in Figure 5.7. The value of this pseudo mass may be as high as ca. 55% of the original specimen weight. It is a significant correction. If this factor was not accounted for, it would have led to gross over-estimation of the actual absorbed mass (up to 55%). The corrected or true quasi-equilibrium CO₂ gas mass uptake values for the different samples are given in Figure 5.8. Each data point represents the percentage change in mass ca. 45 minutes after the introduction of an increasing pressure step. Some interesting features emerge for this figure. First, in the unfilled specimen the mass uptake at a pressure of ca. 22 MPa is ca. 145% (w/w). This amount of sorption is ca. 7 times more than the N₂ gas uptake in a similar system and at the same pressure. This observation confirms the notion that easily condensable gases and those more soluble in water are also highly soluble in polymers (van Amerongen, 1958, 1964; Stannett, 1978; Southern, 1985). Similarly, the proposal put forward by Stannett and Williams (1965) stating that, the larger the penetrant gas molecule the greater the solubility, also seems to be confirmed.

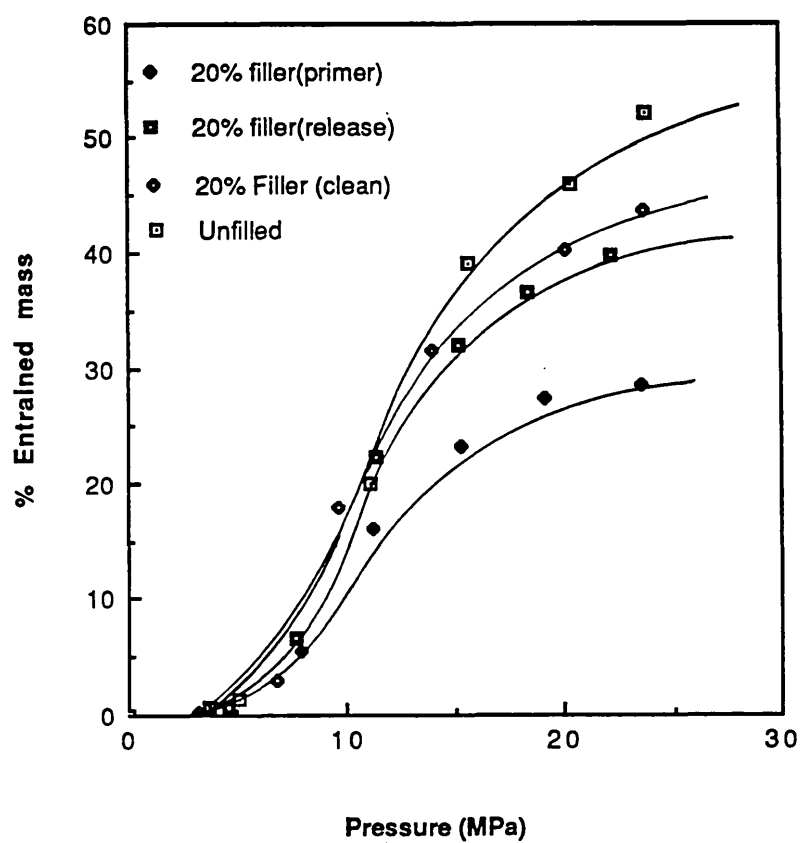


Figure 5.7: Percentage entrained mass due to dilation for the various silicone elastomer specimens as a function of CO₂ gas pressure, 42°C.

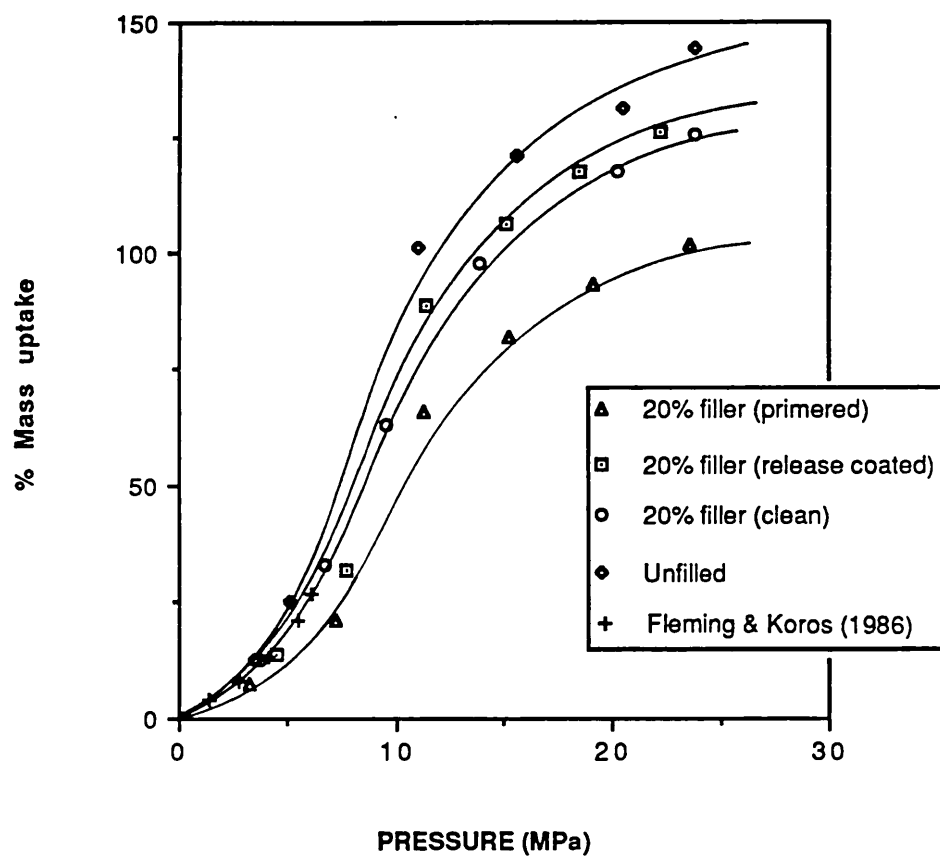


Figure 5.8: Percentage mass uptake for the various silicone elastomer specimens as a function of CO₂ gas pressure, 42°C. Data from Fleming & Koros (1986) are also shown

The shape of the CO₂ gas mass sorption isotherm for the unfilled specimen is not quite linear over the whole pressure range. It is only so in the low pressure range, up to a pressure of ca. 4 MPa. On further increases in the penetrant pressure the sorption isotherm rises substantially. A similar behaviour has been reported by Fleming and Koros (1986) for CO₂ gas sorption in an unfilled silicone elastomer. Their reported data (using a different technique) up to a pressure of ca. 6 MPa, are also plotted in Figure 5.8. A reasonable agreement is observed between the two sets of data. It has been noted that in the pressure region ca. 5-12 MPa, the CO₂ gas density shows a rapid increase with pressure (Angus *et al*, 1976). Hence, in these conditions the CO₂ becomes supercritical and this results in significant dilation of the elastomeric matrix (Chapter 6). This transition seems to facilitate a pronounced increase in the gas sorption. At pressures above ca. 12 MPa, it is observed that the sorption curve becomes concave to the pressure axis. It may be supposed that this effect is due to the saturation of the specimen with the ambient supercritical gas. However, the CO₂ gas density versus pressure (0.1-22 MPa) curve also has a similar shape. The CO₂ gas sorption data as a function of the ambient gas density are given in Figure 5.9. A linear relationship is expected. Nevertheless, when the data are interpolated, ignoring the origin, the sharp increase in the solubility is found to be less apparent (Figure 5.9). The curve only exhibits a relatively small convex curvature with respect to the density axis. This indicates that the CO₂ gas mass uptake is more closely related to the penetrant density than to its pressure. A linear relationship between high pressure gas sorption and ambient gas density has been reported by other researchers (Briscoe and Mahgerefteh, 1984b; Briscoe *et al*, 1986). The convex shape of the isotherm with respect to the x-axis in Figure 5.9, suggests an increase in the sorptive capability of the unfilled silicone elastomer due to the significant dilation of the specimen (Chapter 6). A similar behaviour is observed for the various filled samples.

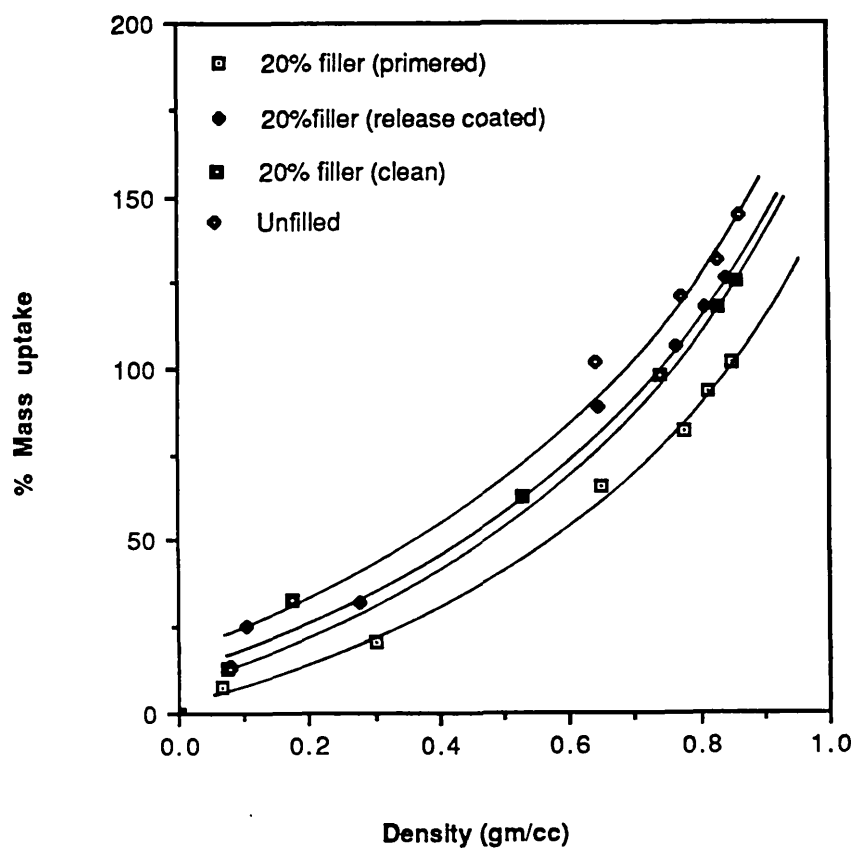


Figure 5.9: Percentage mass uptake for the various silicone elastomer specimens as a function of CO₂ gas density, 42°C.

5.3.1 Effects of Filler Particles on Gas Sorption

Generally, the composite systems with 20% (w/w) glass fillers of various interface qualities follow the trends exhibited by the unfilled elastomer; Figure 5.8. The effects of the various types of internal interfaces can be elucidated more clearly by presenting the equilibrium mass uptake data on the basis of the polymer fraction present in each specimen; Figure 5.10. The data for the unfilled system is also plotted for comparison purposes. It is observed that the gas sorption in the systems with the weak matrix-filler bonds is actually higher than that detected for the unfilled matrix, whilst for the composite system with the strong internal interfaces the amount of the penetrant uptake on the same basis is lower. These two situations are typical examples of 'case 7' and 'case 3' of gas sorption behaviour, respectively, as proposed by Clark-Monks and Ellis (1973). In the former situation, it appears that the large amount of the absorbed CO₂ corrupts and weakens the polymer-filler interfaces and the 'excess' amount of the sorbate possibly resides at these interfacial locations. The strong interfaces remain unaffected and their inhibiting 'sphere of influence' remains operative. Such a situation has been pictorially represented by Oberth (1964) for a solvent-particulate composite system; Figure 5.11. It is seen that the penetrant solvent is able to detach the matrix from the weaker interfaces whilst the strong bonds remain intact. However, it is not necessary that the decrease in the sorptive ability is only invoked by the formation of a modified layer of the polymer around the filler particles, as suggested by the classical literature. This phenomenon can also be rationalised by considering the stress fields generated by the internal interfaces in the composite specimens that inhibit unrestrained sorptive dilation (see later, Chapter 6).

The slope of the sorption isotherm for the unfilled silicone elastomer in the low pressure region (0-5 MPa) gives a solubility coefficient of ca. $25.0 \times 10^{-6} \text{m}^3(\text{STP}) \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$. This value is in reasonable agreement with a value

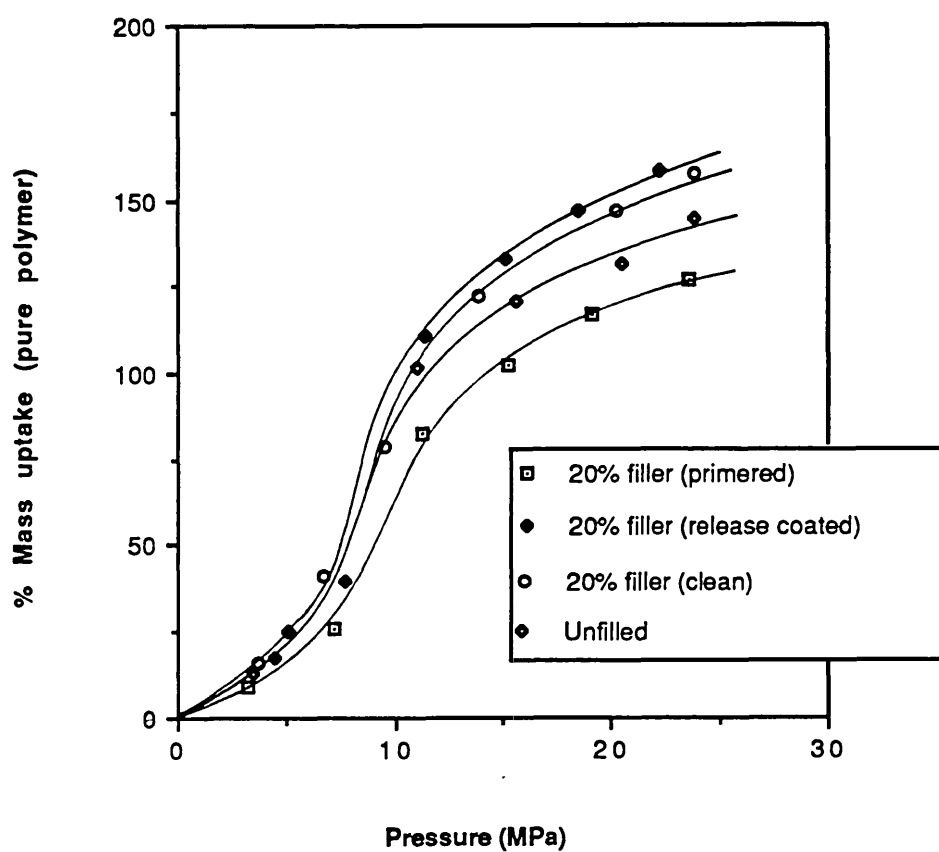


Figure 5.10: Percentage mass uptake on pure polymer basis for the various silicone elastomer specimens as a function of CO₂ gas pressure, 42°C.

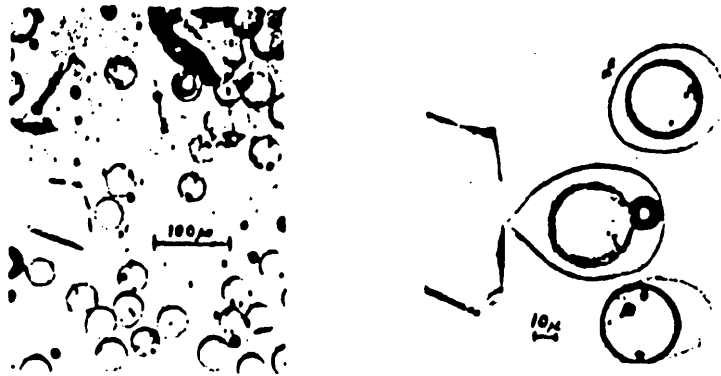


Figure 5.11: Glass beads in a swollen polymer, (a) nonswollen state, (b) halos around glass spheres (Oberth, 1967).

of $22.0 \times 10^{-6} \text{m}^3(\text{STP}) \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$ for this material at atmospheric conditions (Lomax, 1985; Warrick *et al*, 1979). It also agrees closely with the solubility coefficient of ca. $23.0 \times 10^{-6} \text{m}^3(\text{STP}) \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$ calculated from the sorption data presented by Fleming and Koros (1986) for pressures of up to ca. 6 MPa. The sorption coefficients for the filled systems are given in Table 5.1.

5.3.3 Dynamic Measurements of CO₂ Gas Sorption

The dynamic measurements for the high pressure CO₂ gas sorption in the elastomeric specimens have also been made. However, the transient sorptive dilation data were not available and the necessary important corrections could not be made. A typical uncorrected normalised data set as a function of square root of time is presented in Figure 5.12. These data should not be over interpreted. However, the diffusion process is clearly quite slow and again there is evidence that the diffusion coefficient is a function of the ambient pressure.

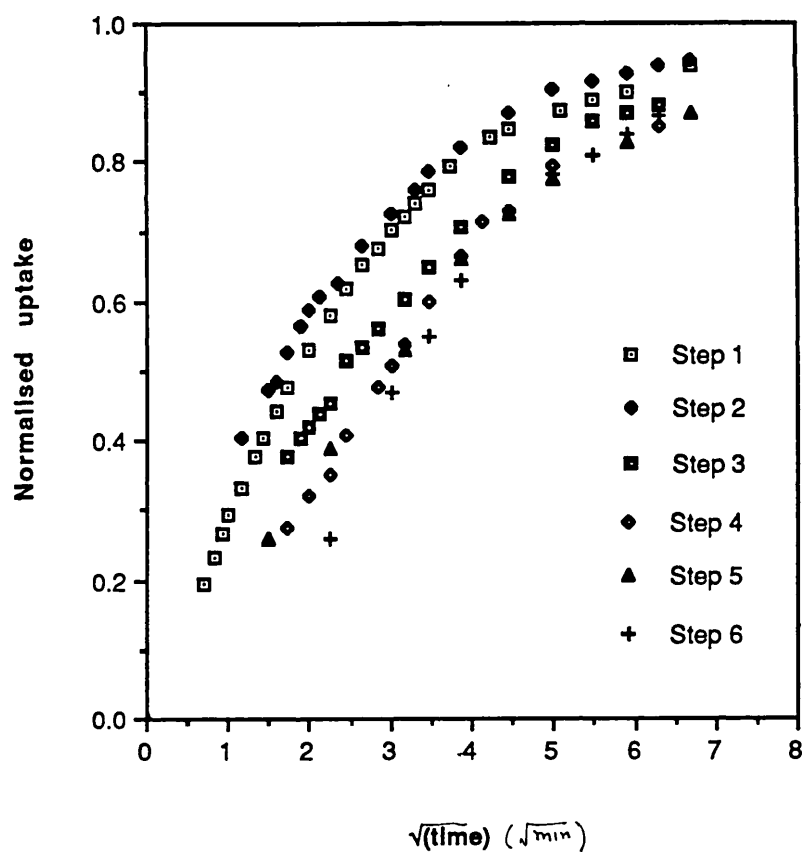


Figure 5.12: Normalised CO₂ gas uptake for the silicone elastomer as a function of square root of time.

5.4 CONCLUSIONS

The silicone elastomer systems have the capability of absorbing significantly large quantities of ambient high pressure gases. In the case of the N_2 gas the sorption isotherms were almost linear functions of the ambient gas pressure. For the CO_2 gas the shapes of the isotherms were similar to the density-pressure profile of the gas. Hence, the high pressure CO_2 gas sorption was almost proportional to the ambient gas density. The amount of mass uptake was a strong function of the penetrant type. The high pressure CO_2 gas, which was near its critical temperature, was ca. 7 times more sorptive than the high pressure N_2 gas. Corrections to the mass uptake data associated with the significant CO_2 gas induced dilation were necessary. Without this type of corrections errors as high as ca. 55% could be introduced in the sorption results.

In the composite specimens with weak matrix-filler interactions a large quantity of the absorbed CO_2 gas was apparently able to penetrate the interfaces. The amounts of gas uptake, on the basis of pure elastomer, were higher than that for the unfilled specimen. However, this behaviour was not observed in the N_2 gas sorption. The stronger internal interfaces inhibit the sorption processes and the gas uptakes (CO_2 and N_2) on the basis of pure polymer fraction were lower than that in the unfilled specimen.

CHAPTER SIX

VOLUMETRIC STRAIN IN ORGANIC POLYMERS UNDER THE INFLUENCE OF PNEUMATIC GAS AND HYDROSTATIC PRESSURES

6.1 INTRODUCTION

In the previous Chapter it has been shown that organic polymers can absorb significant amounts of gases in high pressure pneumatic environments. The extent of the gas sorption was found to depend on the gas type, the ambient pressure of the gas medium and the nature of the polymeric system.

The gas was absorbed under the action of a pneumatic stress and thus there is a special interest in the dimensional state of the specimen. It is natural to consider that polymeric materials will be compressed under such pressures. However, with a significant amount of gas present within the polymer a volume increase may also be anticipated. Thus, the direction of the volume change cannot be predicted *a priori*. An experimental study has been undertaken to ascertain whether the pneumatic pressurisation entails an expansion or a contraction of the matrix in various gas media. The present Chapter describes the results obtained using a technique designed and developed for this purpose. The method involves the use of ultrasonic transducers. The apparatus and procedures have been explained in Chapter 4. It should, however, be noted that linear dimensional changes are measured and that isotropic volume changes are therefore assumed. The volumetric strain is estimated by using the following relation:

$$\frac{V}{V_o} = (1 + l_s)^3 \quad (6.1)$$

where 'V' is the final volume, 'V_o' is the original volume and 'l_s' is the measured

linear strain in one chosen direction. It is an unanswered question as to whether the assumption of isotropic linear strain is valid for the present work. The available literature indicates that this is a reasonable assumption for the equilibrium conditions at least. Most other workers have adopted this assumption. Significant complications in the experimental methods would be necessary to confirm this assumption and hence have not been attempted in this study. The following comment indicates the likely quality of the isotropic assumption. For the so called equilibrium data the assumption seems reasonable for the unfilled systems and for the dilute filled systems. The local strains are most likely homogeneous in length scales, much smaller than the sample size, the filler size is only ca. 0.24% of the smallest sample dimension. The situation with the volumetric changes computed during gas depressurisation are less apparent. Here the swelling stress gradient will be different axially to those generated radially at longer times. The hydrostatic component is however probably uniform providing that no major stress relaxation phenomena occurs with the time scale of the decompression cycle. For the moment these questions can only be answered by further elaboration of the experimental method and the examination of additional data which directly addresses this problem. In this work it is assumed that the isotropic behaviour prevails and any departures from this condition are negligible compared with the errors of the present method. It must however be noted that whilst volumetric strains are quoted in this work they have been derived by measuring the linear strains in the axial direction of the short cylinders. The data for the hydrostatic compression in mercury are of course volumetric data.

These volume data are of considerable importance in developing a better understanding of the interaction between gases and polymers. These measurements were made after quasi-equilibrium conditions had been attained following a pneumatic pressure ramp. The results so obtained have also been correlated with the corresponding gas mass sorption results described earlier in Chapter 5.

A comparative study was also carried out to compare the effects produced in polymers by permeable and impermeable pressure transmitting fluids. A high pressure mercury porosimeter was used for this purpose.

The ultrasonic technique adopted to measure the dimensions under gas pressure was also successfully employed to monitor the specimen inflation during the rapid decompression of the ambient gas. The results of this study are also presented and described in this Chapter.

The Chapter first presents the effects of the pure hydrostatic pressures on the various polymeric specimens. Then, the computed volumetric strains observed under the pneumatic pressures are described. Finally, the inflation of the various specimens during the rapid pressure reductions are reported.

6.2 COMPRESSIBILITY OF POLYMERIC SPECIMENS UNDER HYDROSTATIC PRESSURE

The volumetric dimensional changes produced in the various test specimens under pure hydrostatic pressures were investigated using a mercury porosimeter. The instrument was capable of generating pressures of more than 120 MPa. The experimental technique basically involves confining the test specimen in mercury and monitoring the volume change of the system following the application of hydrostatic pressure. The compressibility of mercury was evaluated separately as a necessary calibration (Chapter 4). Unlike certain other liquids, mercury acts as an inert pressure medium and a pure hydrostatic stress is applied without the complexities of environmental solvation. It has been generally reported that sufficiently long exposures to a hydraulic oil for example leads to a significant re-expansion of certain compressed specimens (Mahgerefteh, 1984). The compressibility of the unfilled silicone elastomer, its composites with 20% (w/w) glass beads of various matrix-filler interface qualities, the PTFE specimen and the

nitrile rubber were assessed. The compressibility is expressed as the ratio of the volume change to the reference volume at 0.1 MPa and room temperature (20°C).

A few comments on the phenomena and interpretation of the influence of pressure on polymers is appropriate at this stage. According to Bueche (1962), cited in Wei and Cuculo (1980), the compressibility consists of two parts. One resulting from 'squeezing out' of the free volume in the sample and the second results from 'reduction' in the equilibrium separation between the polymer chains. Hence, the application of hydrostatic pressure causes a rearrangement of the molecular segments to a more compactly packed form. In certain cases this process may favour crystallisation, which is essentially the removal of the free volume at certain sites. Hence, the pressure effects may be considered to be the inverse of the effects of temperature. For example, with the application of sufficiently large pressures an upward shift in the glass transition temperatures of polymeric specimens has been reported (Zoller, 1978). Similarly, there are the corresponding effects in the density and certain mechanical properties such as the modulus.

Figure 6.1 shows the compressive volumetric strain in the unfilled silicone elastomer specimen for both the hydrostatic (mercury) pressurisation and the depressurisation. It is observed that the volumetric strain is almost linear up to ca. 50 MPa. A decrease in the slope occurs as the pressure is increased further. The overall volumetric compression of the specimen is ca. 6.5% for a pressure of ca. 100 MPa. During depressurisation a positive hysteresis is observed. The hysteresis indicates that either the volume relaxation including the free volumes and/or the chain relaxation may be relatively slow or indeed irreversible. 'Permanent' densification of PTFE specimens has been reported by Mahgerefteh (1984). The time dependence of the measured contractions was not detected in the present experiments since the pressurisation process was relatively slow. The final pressure of ca. 100 MPa was developed in approximately 2 hours and the depressurisation was completed within ca. 15 minutes. No systematic attempt was

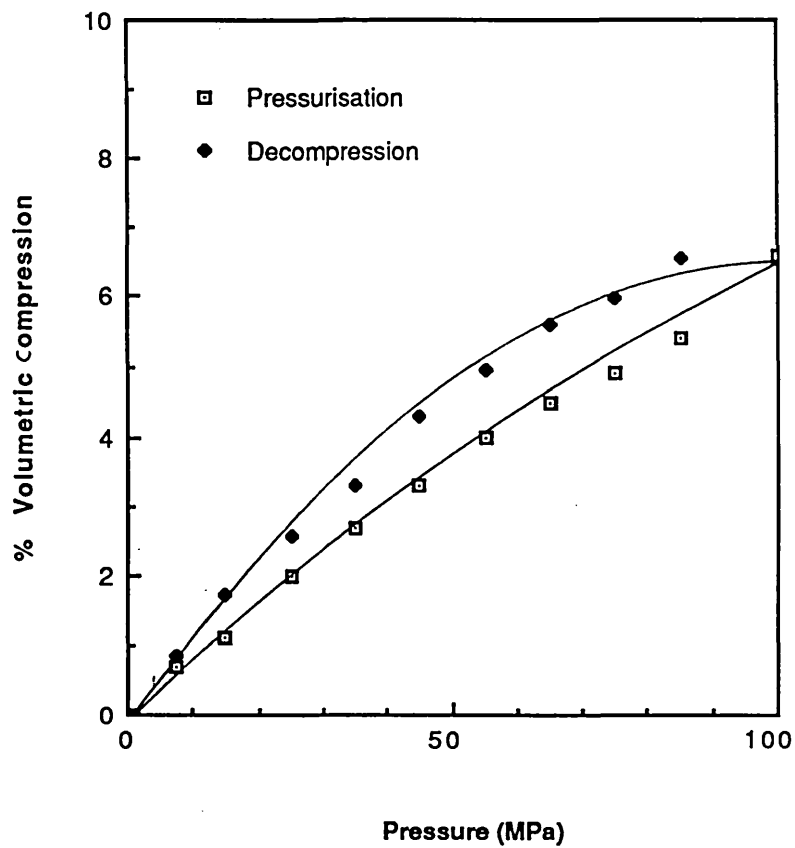


Figure 6.1: Percentage volumetric compression for the unfilled silicone elastomer specimen as a function of hydrostatic pressurisation and depressurisation in the mercury porosimeter.

made to investigate the time response of the volumetric changes.

Figure 6.2 shows the effects of filler addition on the compressibility of the same silicone elastomer described previously in Figure 6.1. It is observed that the incorporation of the filler particles results in a decrease in the compressibility. However, no clear distinction is perceived on the basis of the various matrix-filler interfacial qualities. The compressibilities of these filled systems, in terms of pure polymer fraction, are given in Figure 6.3. It is noted that the compressibilities incurred by the polymer fractions are lower for the filled systems than that for the unfilled sample.

The compressibilities of the unfilled silicone elastomer, the nitrile rubber and the PTFE specimens are given in Figure 6.4. The silicone elastomer specimen is found to be the most compressible. The reason for this behaviour is probably the high degree of the molecular chain mobility (Polmanteer, 1981) and the unusually high free volume content. A free volume value which is five times greater than some other elastomeric systems has been reported (Ziegel and Eirich, 1970) for silicone elastomers. These characteristics will also contribute to the ability of this system to absorb large quantities of gases (Chapter 5) and consequently lead to a greater sorptive dilation (see later).

The curves for the nitrile rubber and the PTFE are linear and indicate a volumetric compressibility of ca. 4.5% and 2% respectively at 100 MPa. The bulk modulus, 'B', of the specimens can be computed from the compressibility versus pressure curves and are listed in Table 6.1. Other properties of the specimens are also listed in the same table. The Poisson's ratio ' ν ' of the various specimens were computed from the following relation:

$$E = 3B(1-2\nu) \quad (6.2)$$

where 'E' is the Young's modulus and 'B' is the bulk modulus. The Young's modulus of different specimens were measured from the tensile experiments conducted on an Instron mechanical testing machine. The value for PTFE has been

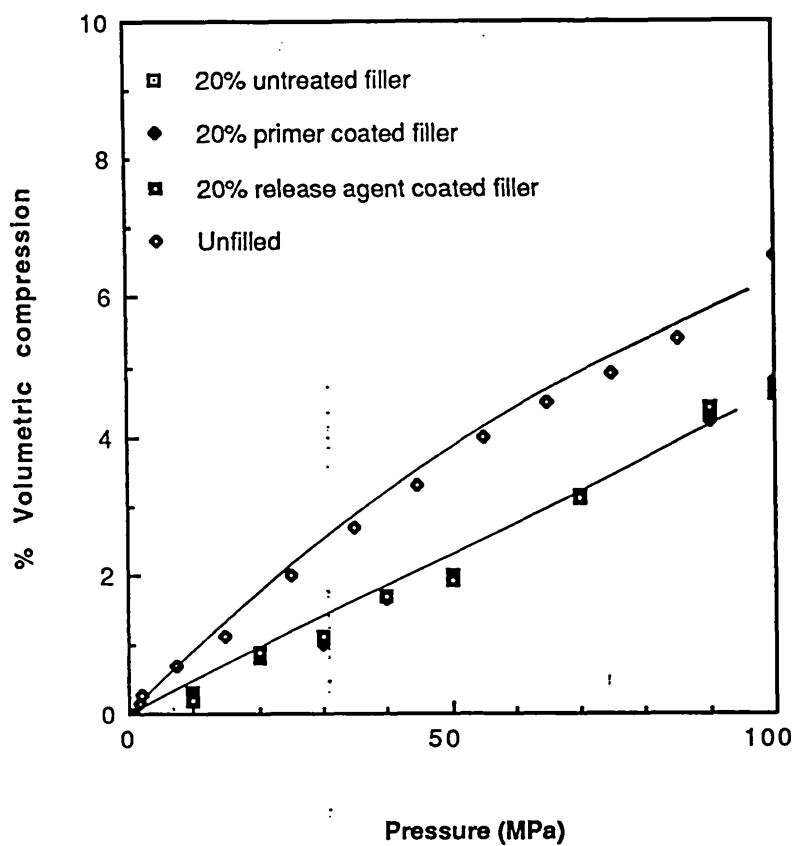


Figure 6.2: Percentage volumetric compression for the various 20% filled silicone elastomer specimens as a function of hydrostatic pressure in the mercury porosimeter. Data for the unfilled specimen are also shown.

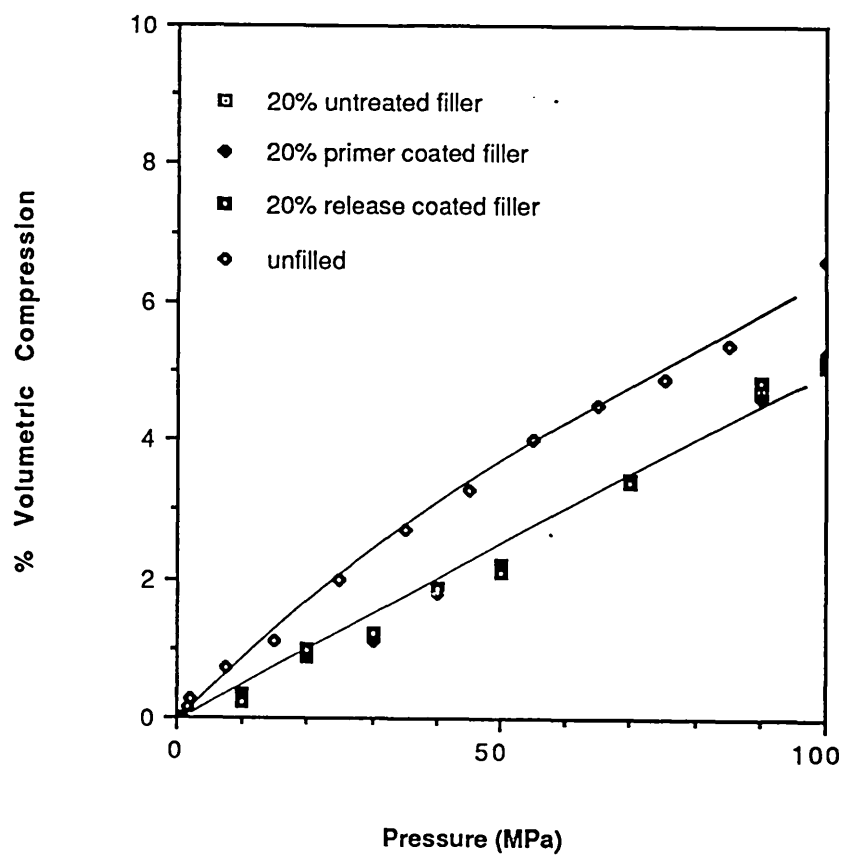


Figure 6.3: Percentage volumetric compression on the basis of polymer volume fraction for the various 20% filled silicone elastomer specimens as a function of hydrostatic pressure in the mercury porosimeter. Data for the unfilled specimen are also shown.

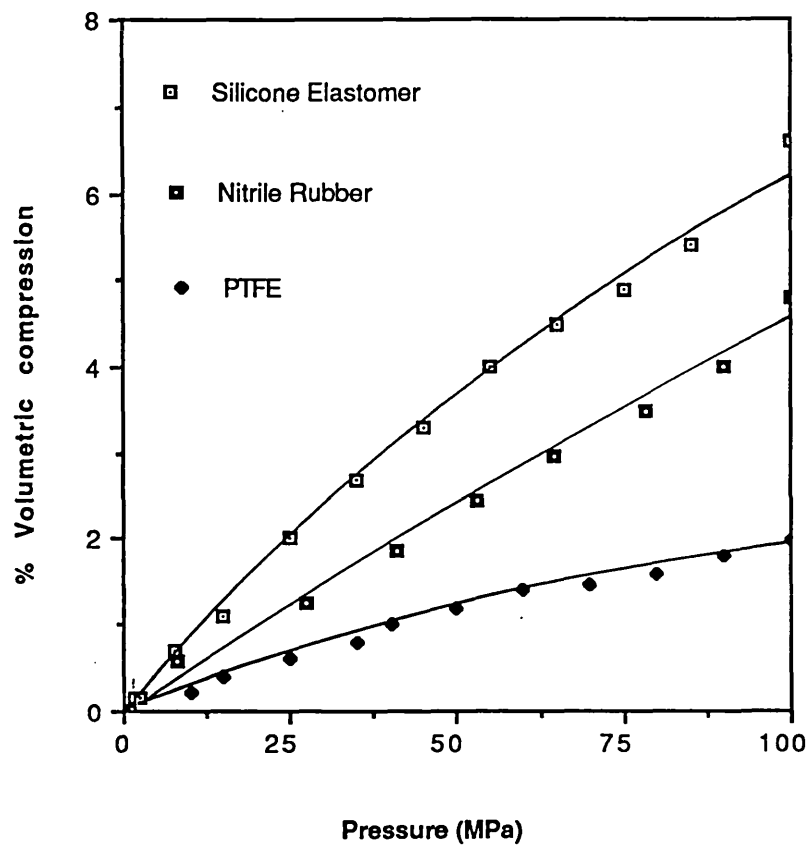


Figure 6.4: Percentage volumetric compression for the various polymeric specimens as a function of hydrostatic pressure in the mercury porosimeter.

SPECIMEN	Density (Kg/m ³)	Bulk Modulus (MPa)	Young's Modulus (MPa)	Poisson's Ratio
Silicone Elastomer (Unfilled)	1023	1335	1.4	0.4998
Silicone Elastomer Composite (20% glass filler)	1152	2100	2.2	0.4998
Nitrile Rubber	1200	2200	8.8	0.4993
PTFE	2180	4350	390	0.4850

Table 6.1: Measured mechanical properties of the various polymeric specimens.

taken from the literature (Rodrigeuz, 1985).

6.3 VOLUMETRIC STRAIN OF SPECIMENS UNDER GAS PRESSURE

6.3.1 High Pressure N₂ Gas Environment

In this section the effects of N₂ gas pressure on the physical dimensions of the various polymeric specimens will be presented and discussed. The experimental temperature was maintained at 20°C. In the case of the unfilled silicone elastomer specimen the dimensional changes were computed using both the direct (mode-1) and the indirect (mode-2) ultrasonic methods. However, for the silicone elastomer composites with 20% (w/w) glass filler, the carbon filled nitrile rubber and the PTFE specimens, the mode-2 method was used. In the mode-1 configuration significant attenuation of the ultrasonic signals occurred in the latter cases.

Figure 6.5 shows the response of the unfilled silicone elastomer specimen. It is apparent from the figure that, in the initial stages of the experiment, the specimen contracts up to a pressure of ca. 6 MPa. The further increases in the gas pressure induces a dilation of the sample. The specimen is seen to experience ca. 1.5% linear dilation at a pressure of ca. 27 MPa. In order to reaffirm the initial contraction followed by the expansion, the experiment was repeated a number of times. The results obtained were similar. It is believed that the specimen dilation is produced by the gas that is absorbed in the elastomeric matrix. Generally, for a given gas, the greater the amount absorbed the larger would be the extent of dilation. The origins of initial contraction are not fully understood. Sehkar and Van Der Hoff (1971) have reported a similar trend for the specimens with internal voids. It was observed that with the application of a sudden gas pressure there is

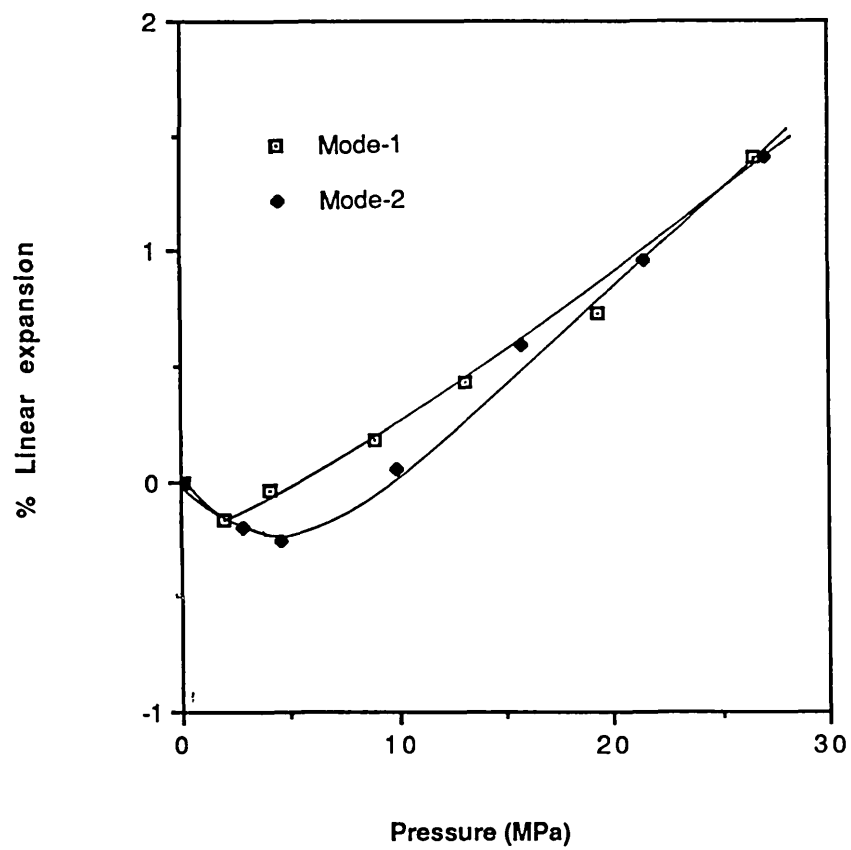


Figure 6.5: Percentage linear dilation for the unfilled silicone elastomer as a function of N_2 gas pressure, 20°C.

an initial contraction followed by an expansion. They associated the contraction with the collapse of voids present in the specimen. Ender (1986) and Liatsis (1989) have also reported the contraction of certain elastomeric specimens under pneumatic pressures and argued it to be the result of collapsed air pockets present in the matrices. It is also possible that the contraction is associated with the processes responsible for the contraction observed for this polymer in mercury. Hence, it is useful to make a comparison between the initial negative slope in Figure 6.5 (N_2 gas pressure) and the specimen compression, in a similar pressure range, under the mercury hydrostatic pressure; Figure 6.1. It is observed that the slope produced by the gas medium is ca. 0.18 while that induced by the pure hydrostatic pressure is significantly less, ca. 0.1. The converse was anticipated and it is therefore apparent that, during the initial stages, the role of the pneumatic pressurisation medium is quite complex. The external compressive stress exerted by the gas will compress the matrix. At the same time, the gas absorbed in the matrix will induce dilation and act against the effect produced by the compressive stress. However, the gas stress appears to facilitate the compression and assist the polymer chain segments to acquire a more closely packed arrangement. As more gas is absorbed and the chain segments have readjusted, the internal swelling pressure becomes dominant and the system now shows a priority to expand. The implication is that the data cited for the mercury medium may not correspond to the equilibrium conditions. For the gas medium the absorbed species appear to 'lubricate' the volumetric contractions.

Figure 6.6 gives the extent of the compression in the nitrile rubber and the PTFE specimens under the N_2 gas pressures. The overall slopes of these curves and those for the corresponding mercury hydrostatic pressure medium are given in Table 6.2. It appears that for the nitrile system, the presence of gas inside the specimen counteracts the effects of external pressure to some extent. If the measured pure hydrostatic component of the nitrile rubber compression is deducted from the curve in Figure 6.6, a dilation of the nitrile specimen will be observed.

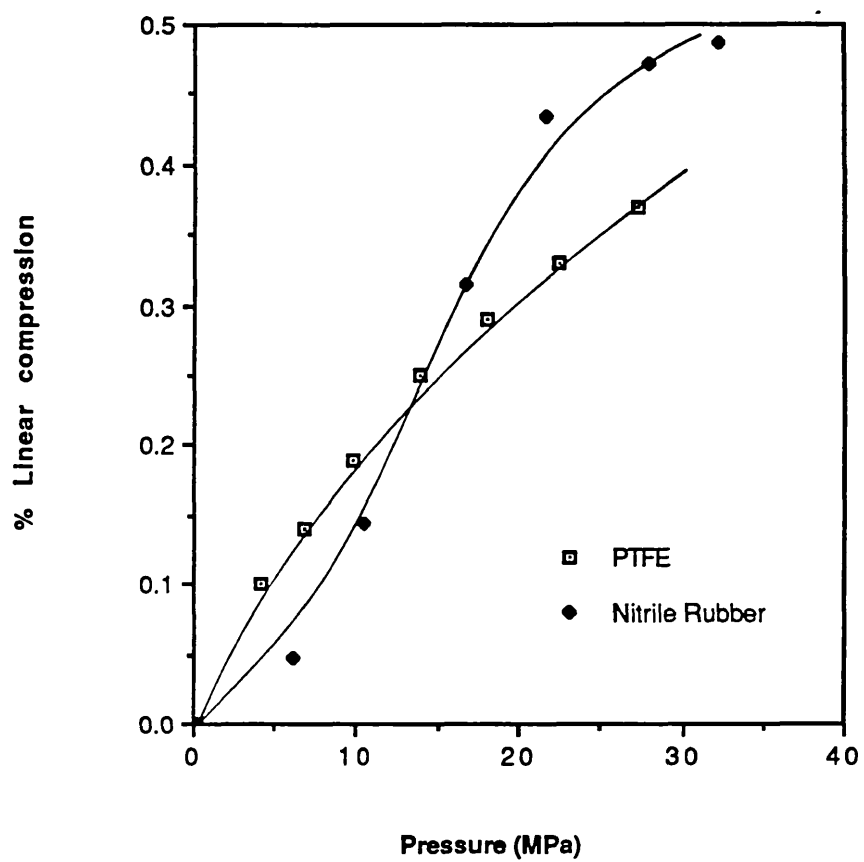


Figure 6.6: Percentage linear compression for the various polymeric specimens as a function of N₂ gas pressure, 20°C.

SPECIMEN	MERCURY (volumetric compression/MPa)	NITROGEN PRESSURE (volumetric compression/MPa)
Unfilled Silicone Elastomer	-0.072	+0.17
20% filled silicone Elastomer	-0.048	+0.05
Nitrile Rubber	-0.047	-0.045
PTFE	-0.023	-0.0411

Table 6.2: Dimensional response of the various specimens to hydrostatic pressure and to nitrogen gas pressure.

However, for the PTFE specimen the N₂ gas pressure appears to have induced a larger compression. This behaviour finds consistency with the results reported by Briscoe and Mahgerefteh (1984a) for PTFE using a different experimental technique.

The relative N₂ gas solubilities at ca. 20°C for the three main systems are: silicone elastomer (1.0) > nitrile rubber (0.4) > PTFE (0.07). The bracketed quantities are the relative mass based solubility parameters. The solubility data for nitrile rubber and PTFE were taken from Briscoe and Liatsis (1989) and Briscoe and Mahgerefteh (1984b) respectively. Considering these ratios and the dimensional responses of the systems, given in Figures 6.5 and 6.6, it may be concluded that when sufficiently large amounts of the gas are absorbed, the polymeric matrices have a propensity to swell even when triaxial compressive stresses are being imposed by the high pressure pneumatic ambient.

6.3.1.1 Effects of Filler Particle Addition on Sorptive Dilation

The dilational responses of the silicone elastomer composites with 20% glass filler are given in Figure 6.7. The curves follow the same trend as those observed for the unfilled system but the magnitudes of the contraction and the swelling phases are less. The relatively small compressions detected at the beginning of the experiments are followed by only a ca. 0.5% linear expansion. No influence of the matrix-filler interfacial quality has been detected. The same figure shows the data for the virgin silicone elastomer.

It has been mentioned earlier (Chapter 5) that the 'normalised' amounts of the N₂ gas absorbed in the composite specimens is less than that observed for the unfilled elastomer. This suggests that the matrix-filler bonds remain unaffected by the imbibed gas. The interfaces would appear to restrain the matrix dilation in the regions around the filler particles. This would then lead to a constraint on the natural dilation processes.

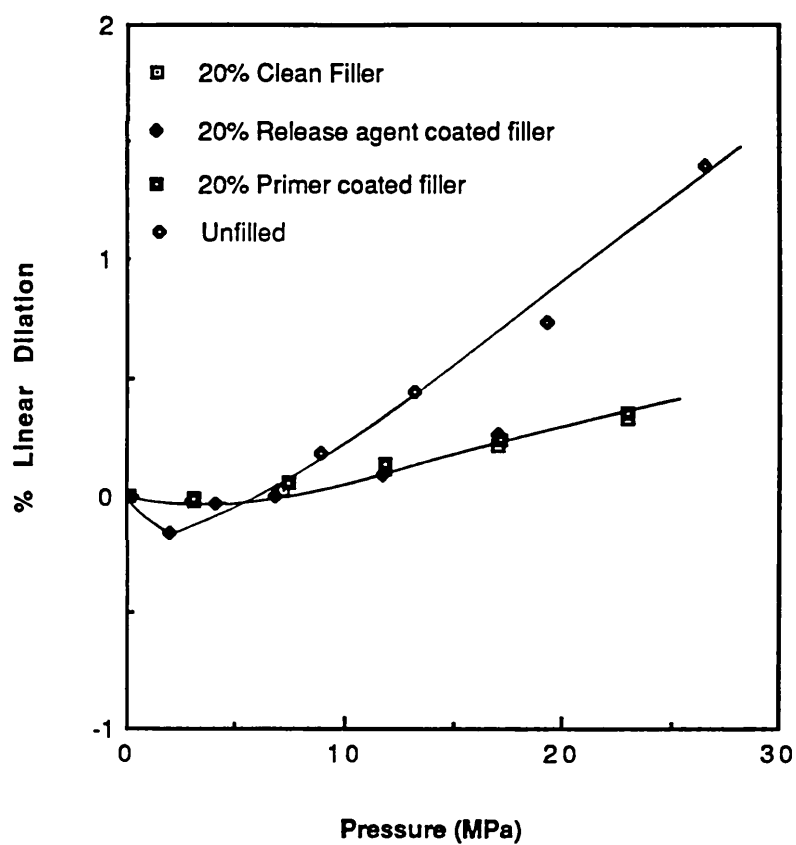


Figure 6.7: Percentage linear dilatation for the various 20% filled silicone elastomer specimens as a function of N₂ gas pressure, 20°C. Data for the unfilled specimen are also shown.

The experimental evidence cited earlier for the nitrile rubber and the PTFE samples indicates that the extent of the gas induced dilation of the polymers may be correlated with their tensile moduli. Generally, the higher is the modulus the lesser is the net dilation. The relative swellings of the unfilled silicone elastomer and its composite with 20% (w/w) glass filler are consistent with this trend. The Young's modulus of the virgin elastomer is ca. 1.4 MPa and that for its composites is ca. 2.2 MPa (Table 6.1).

In order to investigate how the filler particles influence the N₂ gas induced sorptive dilation, a simple model system was chosen. It consisted of a thin layer of the silicone elastomer bonded between two rigid glass discs. The basic idea was that the interfaces so formed will restrain the dilation of the elastomer. A comparable phenomenon is observed in unidirectional mechanical deformation. The sorptive dilation characteristics are correlated with the apparent mechanical properties of the polymeric specimens (see later). The situation in the composite specimens is, however, more complex with a large number of filler particles distributed in the matrix. Gent and Hwang (1988) have used a similar model system to study the role of interfaces in the particulate reinforcement of elastomeric matrices.

The compressive stiffness of the various aspect ratio (thickness/diameter) elastomer discs were measured on a tensometer, the data are shown in Figure 6.8. It is observed that the samples with lower aspect ratios are stiffer. In the same figure the compressive stress-strain behaviours of the unfilled cylindrical specimen and that of a 20% (w/w) glass filled sample are also shown. In the specimen with 20% (w/w) filler particles of radii 30×10^{-6} m, the mean distance between the particles is estimated as 20×10^{-6} m and the effective polymer layer aspect ratio within the composite was therefore ca. 0.67.

The thin bonded disc specimens of similar effective geometry were also subjected to N₂ gas pressurisations and the axial dimensional changes were

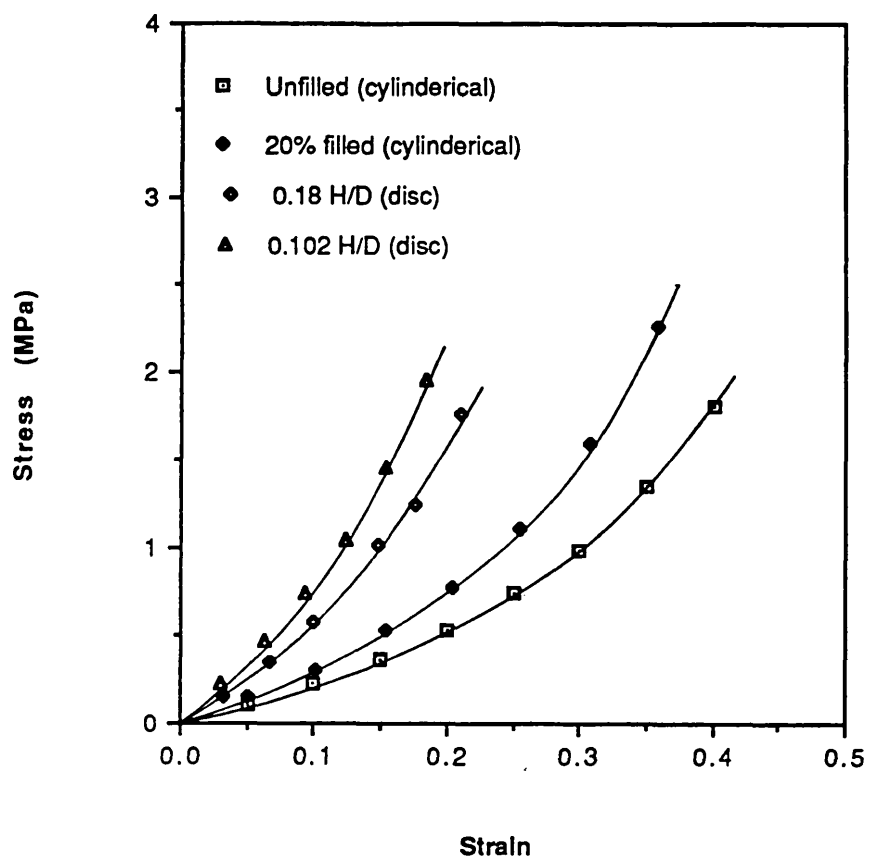


Figure 6.8: Applied mechanical stress for the various disc type specimens as a function of linear strain, data for the cylindrical unconstrained specimens are also shown.

determined. The ultrasonic signals obtained from these test specimens were complicated because of the multiple reflections from the various interfaces. However, by a careful study and enhancement of the echo pattern resolution, it was possible to identify the appropriate echoes and hence the required dimensional measurements were obtained. Figure 6.9 shows the percentage linear dimensional changes as a function of the ambient N_2 gas pressure. The response of the specimen with clean untreated interfaces is typical of that observed for the unfilled cylindrical silicone elastomer specimen (mentioned previously). However, the thin discs that were strongly bonded to the rigid end pieces did not dilate to the same extent. The test piece with an aspect ratio of ca. 0.09 only expanded linearly by ca. 0.5%, while the specimen with an H/D ratio of ca. 0.191 dilated by ca. 1.2%. It is also observed that for the strong interface systems the initial stages of the pneumatic pressurisation results in specimen contraction. The thinner specimen is seen to remain in a compressed state up to relatively higher pressures (ca. 15 MPa) than the one with an H/D ratio of ca. 0.191. The cause of this effect is certainly the interfacial constraints which are more pronounced when the specimen is thinner. The effects of the interfacial restraints and the H/D ratio are also clearly demonstrated in the experiments conducted on the tensiometer, Figure 6.8.

6.3.1.2 Density Changes

Figure 6.10 shows the computed density changes for the silicone elastomer, the nitrile rubber and the PTFE as a function of the gas pressure. The necessary mass sorption data for the silicone elastomer are given in Chapter 5. The data for the nitrile rubber and the PTFE were obtained from Briscoe and Liatsis (1989) and Briscoe and Mahgerefteh (1984b) respectively. Initially, the densities increase rapidly through the combined effects of the volume reduction and the gas mass uptake. The trend of these curves indicate that at a certain point at high gas pressures the densities will assume constant values. Further sorption of the gas

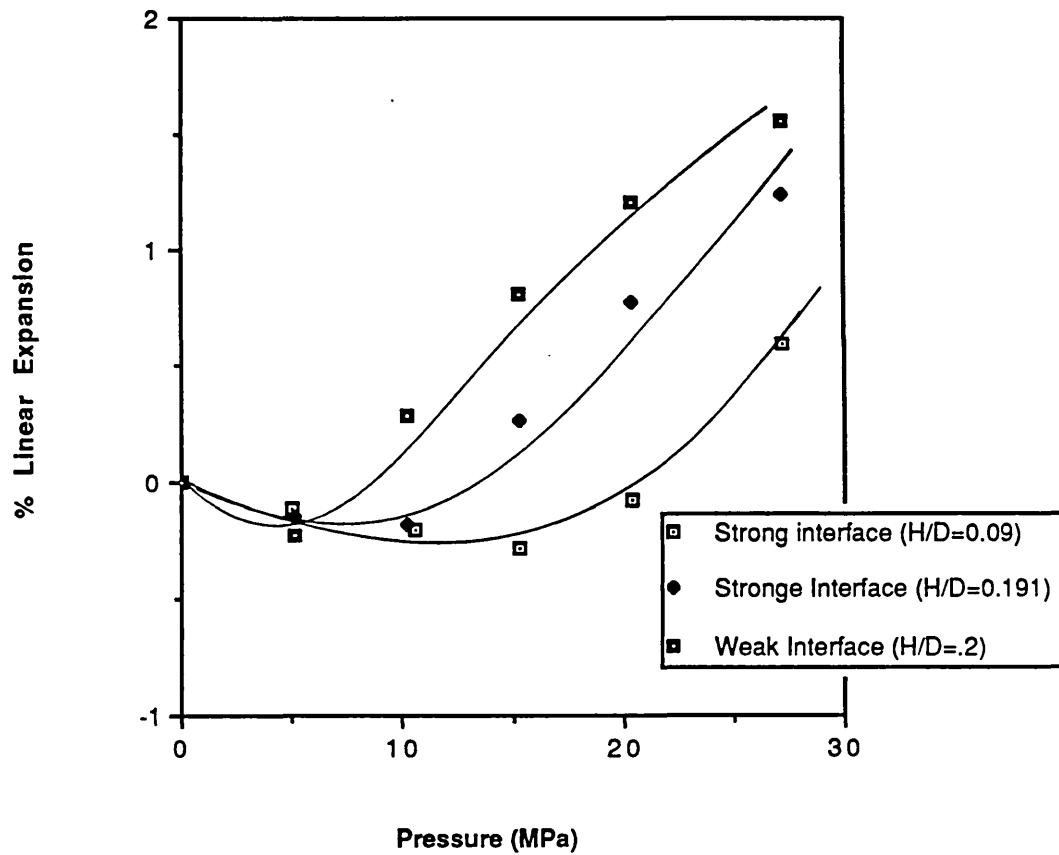


Figure 6.9: Percentage linear strain for the various disc type specimens as a function of N₂ gas pressure, 20°C.

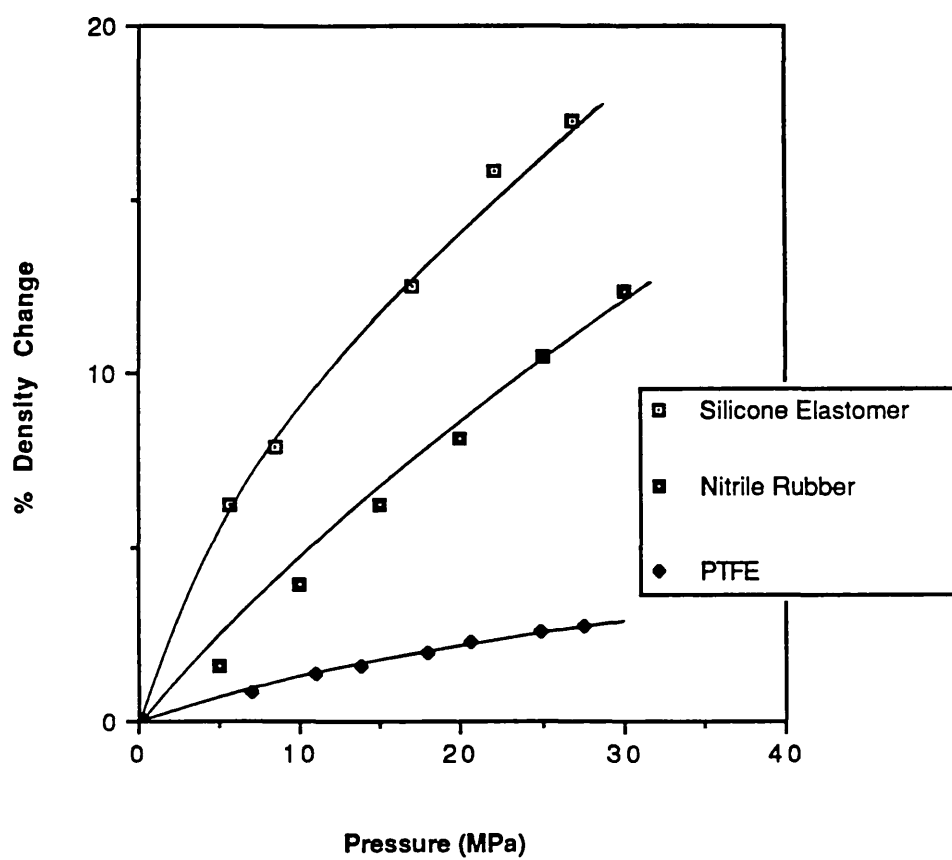


Figure 6.10: Percentage change in density for the various specimens as a function of N₂ gas pressure, 20°C.

would be restricted by the pneumatic hydrostatic stresses acting on the specimens and *vice versa*. It can be concluded that the compressive stress is a force opposing gas absorption since it inhibits the matrix from swelling and hence reduces the mass sorption for a given sample.

6.3.2 High Pressure CO₂ Gas Environment

The measurement of the CO₂ gas induced dilations at high pressures (ca. 23 MPa and ca. 42°C) involved modifying the ultrasonic technique used previously in the N₂ gas environments. The experimental difficulties associated with CO₂ gas have been described previously (Chapter 4). Only the modified mode-2 arrangement was used. In this section, the measured dimensional strains for the various polymeric specimens will be presented and discussed.

The isothermal swelling data are shown in Figure 6.11, as the percentage change in linear dilation of the cylindrical elastomeric specimens pressurised to up to ca. 23 MPa. Each measurement was taken after ca. 45 minutes of an increasing pressure step when the system had reached a quasi-equilibrium state. For the unfilled silicone elastomer specimen a linear axial dimensional increase of ca. 21% is observed. It is realised that in the N₂ gas environment, the dilation under similar pressures was much less, ca. 1.5%. The marked difference in the response of the same elastomer in the two environments becomes clear when we consider the amounts of the gases absorbed by the system (Chapter 5). The amount of CO₂ gas imbibed by the unfilled silicone elastomer was ca. 140% (mass/mass) at a pressure of 23 MPa while with N₂ gas the mass change was only ca. 20%. Generally, the gas absorption is associated with actual separation of the chain segments to accommodate the penetrant. This will cause volumetric swelling of the specimen. Hence, it can be assumed that the molecules of the absorbed gas contributes towards the volume change and greater the quantity absorbed, greater is the

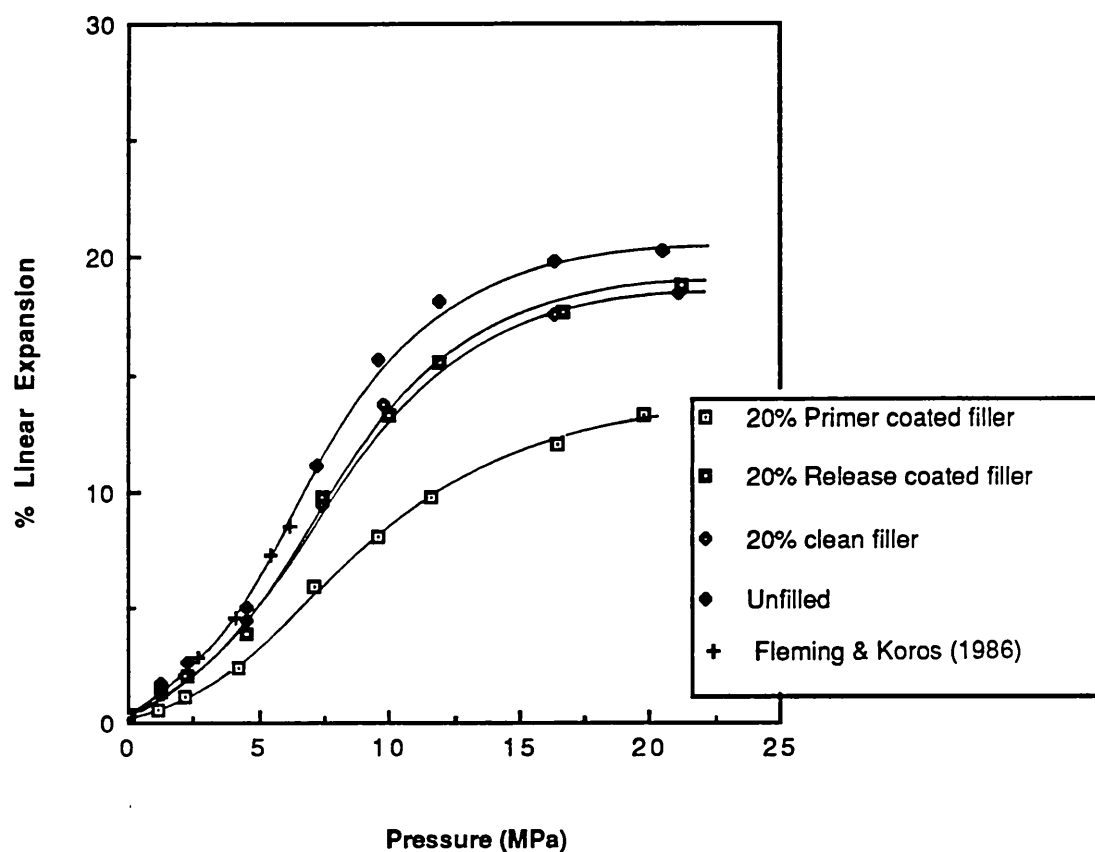


Figure 6.11: Percentage linear dilation for the various silicone elastomer specimens as a function of CO_2 gas pressure, 42°C . Swelling data for a silicone elastomer reported by Fleming and Koros (1986) are also plotted.

specimen swelling. It is notable that the dilation isotherm mimics the shape of the CO₂ gas sorption isotherm.

It is also observed that for the unfilled silicone elastomer specimen the dilation curve in Figure 6.11 is linear in the low pressure range up to a pressure of ca. 4 MPa. At higher pressures the dilation becomes convex to the pressure axis. However, at pressures above ca. 11 MPa, the hydrostatic pressure effects start to dominate and the rate of swelling decreases very significantly. The volume appears to attain a limiting value at higher pressures. The measured dimensional change between 11 MPa and 21 MPa is approximately 4%. In the relatively low pressure range (up to 6 MPa) Fleming and Koros (1986) have also measured CO₂ gas induced swelling of a silicone elastomer. The results obtained by these researchers are included in Figure 6.11. A reasonably good agreement with their data is seen over this range. In the pressure interval between ca. 5 MPa and 11 MPa the unfilled silicone elastomer specimen dilated rapidly by more than 11%. Similar trends in the CO₂ gas induced dilation of PMMA and polystyrene have been reported by Wissinger and Paulaitis (1987). Ender (1986) has observed ca. 18% linear swelling for various fluoroelastomers up to a CO₂ gas pressure of ca. 27 MPa. It was observed that the slope of the dilation curve began to decrease at pressures above ca. 15 MPa. Liau and McHaugh (1985), Wissinger and Paulaitis (1987) and Kamiya *et al* (1988) have also observed the asymptotic trend in the CO₂ gas induced dilation isotherms for PMMA, polycarbonate and polyvinyl benzonate respectively. This effect was attributed to the presence of a maximum in the gas solubility with increasing pressure arising from the free volume effects.

The swelling is equivalent in some respects to a three dimensional stretching of the system. In a mechanically generated volumetric dilating strain, elastomers are known to internally rupture at low volumetric strains, typically 3-5% (Lindsey, 1967). However, it is believed that the CO₂ gas dilated test specimens do not rupture even when linearly swollen by ca. 21%. The magnitude of the CO₂ gas

induced dilation of the silicone elastomer resembles the swelling induced by a liquid solvent. It was found that cyclohexane solvent causes the elastomer to swell volumetrically by ca. 145% (ca. 45% linearly); Figure 6.12. Internal cracking of the clear swollen elastomer was not detected in this process.

High pressure CO₂ gas has also been considered to act as a solvent for certain organic solids. Scholsky (1987) has reported that the solubility of naphthalene in CO₂ gas rises with an increase in the gas pressure. Similarly, Czubryt *et al* (1970) observed that the solubility of certain commercial organic waxes in compressed CO₂ gas reached a maximum and then started to decrease with further increases in the gas density.

At pressures higher than 5 MPa and temperatures above 31°C the compressed CO₂ gas is above its critical point and becomes a supercritical fluid. This new phase exhibits properties common to both gases and liquids (Gidding *et al*, 1968). Eisenbach (1984), cited in Scholsky (1987), regarded this phase as the fourth state of matter. In supercritical fluids the solubility is a strong positive function of the pressure particularly above the critical pressure. In this state the mean distance between the molecules decrease and it possesses a liquid-like density. Gidding *et al* (1968), while working with a supercritical fluid (NH₃), found that one of the rubber 'O' ring gaskets in the pressure vessel actually disappeared by dissolving in the fluid and only a small residue was left behind.

6.3.2.1 Role of Matrix-Filler Interfaces on Sorptive Dilation

The effects of the filler particles on the sorptive dilation of the silicone elastomer are also shown in Figure 6.11. The weight ratio between the filler particles and the elastomer was 2:8 (ca. 1:9 volumetric ratio). It will be realised that the general shape of the dilation curve remains the same when compared with the virgin elastomer. However, the glass filler particles appear to suppress the overall gas induced dilation of the elastomer. This effect is even more pronounced in the

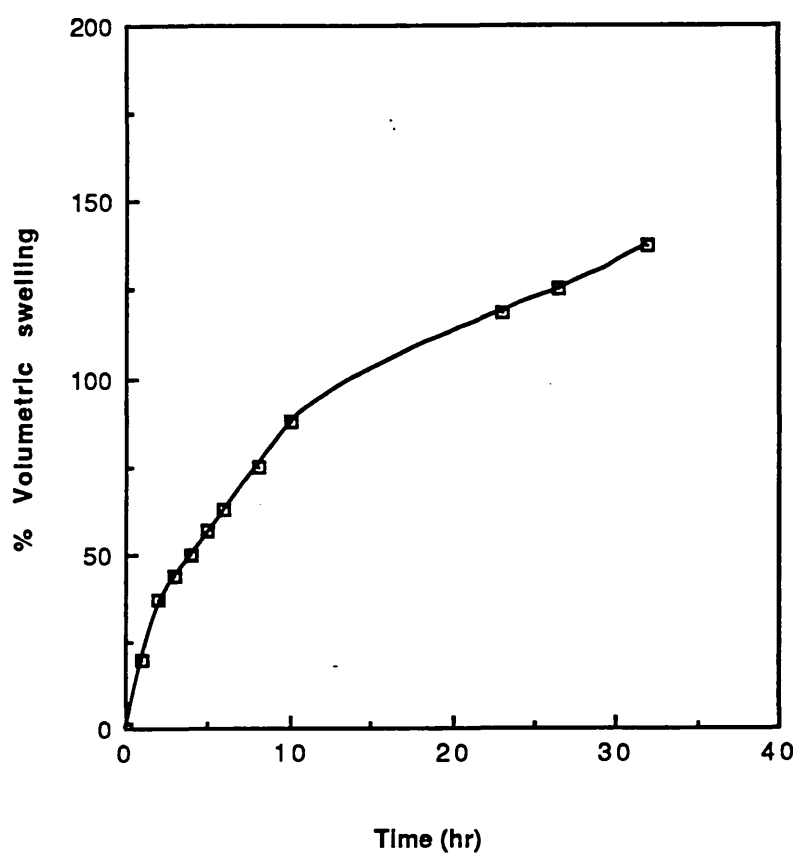


Figure 6.12: Percentage swelling for the unfilled silicone elastomer in cyclohexane solvent as a function of time, room temperature (20°C).

case when the internal interfaces between the elastomer and the filler particles are strong. The strong interfaces are not corrupted by the absorbed gas and hence they restrict swelling in the regions around the filler particles. This then leads to an overall reduction in the network dilation. In the systems with the weak and the unmodified matrix-filler interfaces, the swelling, in terms of the elastomer volume fraction, approximates the dilation of the virgin test specimen. The extensive volumetric swelling may cause the formation of vacuoles around the weakly bonded filler particles. Hence, a fraction of the sorbed gas would then reside at these interfacial sites. Secondly, the short distances between the filler particles in the composite specimens would also make the swelling process more complex, especially when the particle size is small (ca. 60×10^{-6} m). Eckstein and Dreyfuss (1982) have observed that in a filled elastomer with particle size below 100×10^{-6} m, the (liquid) solvent induced swelling was less than that for the unfilled rubber. Fedors and Laudel (1966), cited in Eckstein and Dreyfuss (1982), also concluded that the swelling ratio decreases with the filler concentration. It is not necessary that complete halos are formed around the filler particles. A fraction of the filler particle surface may still remain bonded with the matrix, acting as an anchor, and hindering the dilation of the matrix. Oberth (1967) has observed distorted halos around glass spheres in swollen polyurethanes. It is reasonable to postulate that for these reasons, the CO₂ gas induced matrix swelling in the filled systems will not necessarily be directly proportional to the amount of the gas sorbed.

6.3.2.2 Changes in Specimen Density

Figure 6.13 shows the percentage change in the density of the various silicone elastomer specimens as a function of the CO₂ gas pressure. The data shown in the figure are derived from the data given earlier in Figure 6.11 and Figure 5.8 (Chapter 5). The curves for the various specimens are 'S' shaped and significantly different to those found in the N₂ gas environments; Figure 6.10. At

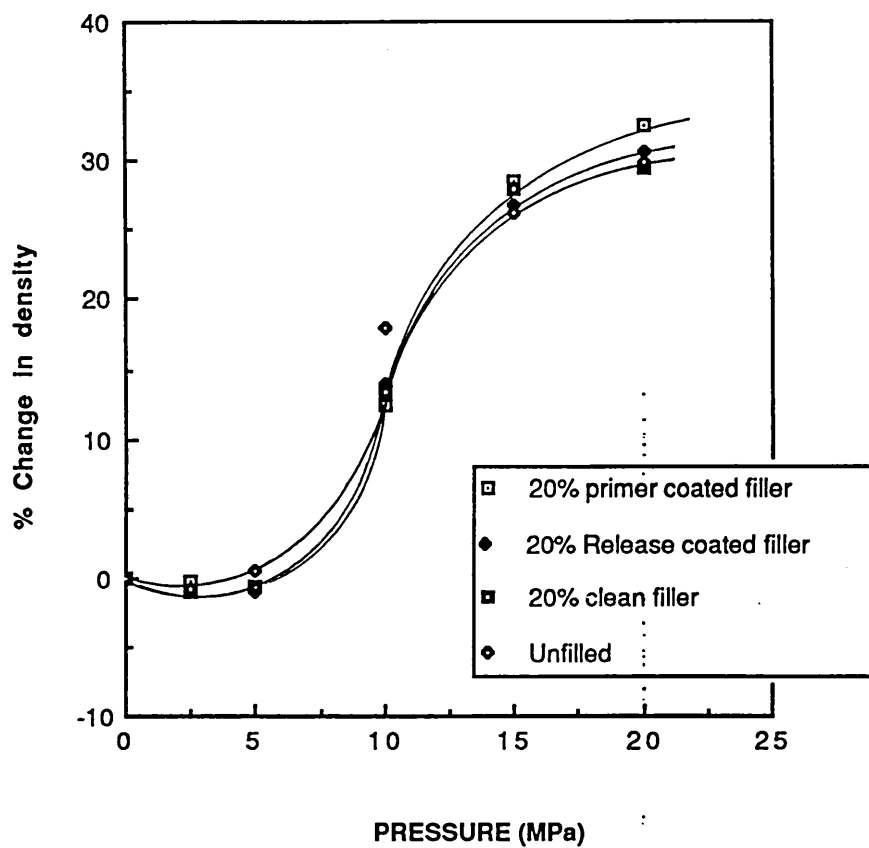


Figure 6.13: Percentage change in density for the various silicone elastomer specimens as a function of CO₂ gas pressure.

lower pressures there is a slight decrease in the density. However, above a pressure of approximately 5 MPa, a sharp rise in the density occurs. At higher pressures the increase in the density is less rapid. A very clear distinction between the density changes of the various specimens is not apparent. However, it appears that at higher pressures the maximum density change occurs for the composite specimen with the strong internal interfaces. All the filled systems do however initially show an increase in the density which is at a lower rate than that of the unfilled system.

6.3.2.3 Partial Molar Volume of Absorbed CO₂ Gas

The dilation data for the various silicone elastomer systems given in Figure 6.11 are replotted in Figure 6.14 as a function of the gas concentration. The concentration is given as the volume of the sorbed gas at standard conditions (0°C and 0.1 MPa) per unit volume of the penetrant free specimen. It can be seen from the figure that during the initial stages of the experiments the sorptive dilations rise very rapidly in a linear fashion and then concave towards the concentration axis. This behaviour imply that the gas induced dilational effects are strong up to a certain point. Additivity applies to the volumes of the absorbed gas and the elastomeric specimen, since the partial molar volumes of the gas in the solutions remain constant in this region (see later). However, as the hydrostatic component of the ambient gas pressures begin to dominate, the sorbed fluid will transform into a more dense phase and the expansion effects decrease. In order to elucidate the state of the absorbed CO₂ gas in the silicone elastomer specimens the partial molar volume (PMV) of the penetrant, ' V_p ', in the test samples has been determined. The volume occupied by ' n ' moles of the penetrant in a volume ' V ' of the polymer is the partial molar volume ' V_p ' and is expressed in cm³·mole⁻¹. It is computed by (Kamiya et al, 1988);

$$V_p = g [(\partial V/V_o)/\partial C] \quad (6.3)$$

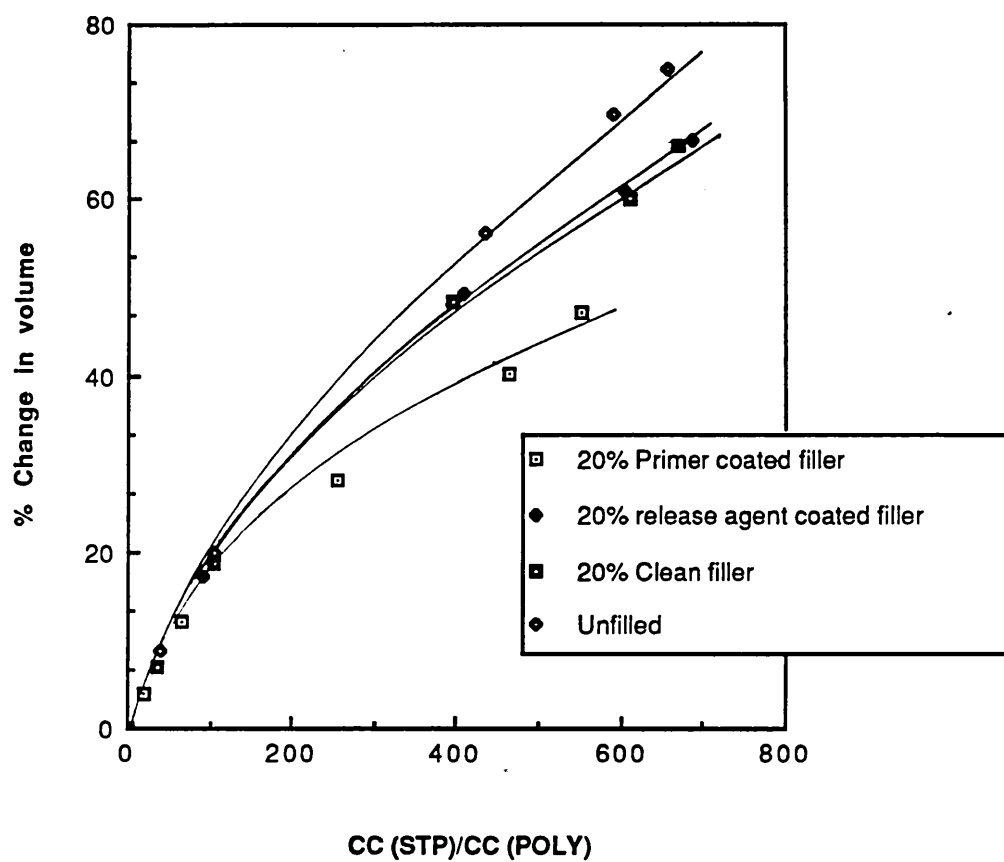


Figure 6.14: Percentage change in volume for the various silicone elastomer specimens as a function of the absorbed CO₂ concentration.

where ' V_o ' is the specific volume of the penetrant free polymer, ' C ' is the concentration of the absorbed gas in the polymer and ' g ' denotes the molar volume of the penetrant gas at standard temperature and pressure (STP), i.e. 0°C and 0.1 MPa; $22.4 \times 10^3 \text{ cm}^3(\text{STP}) \cdot \text{mole}^{-1}$. The values of the partial molar volumes are essentially the slopes of the dilation versus concentration curves given in Figure 6.14. The calculated values for the silicone elastomer and its composites as a function of CO₂ gas pressure are shown in Figure 6.15. The partial molar volumes seem to have an almost constant value for pressures of up to ca. 5 MPa, corresponding to a CO₂ gas concentration of up to ca. $100 \text{ cm}^3(\text{STP}) \cdot \text{cm}^{-3}(\text{poly})$. Its value for the unfilled specimen averages at about $46 \text{ cm}^3 \cdot \text{mole}^{-1}$ in this range. This value is slightly lower, ca. $44 \text{ cm}^3 \cdot \text{mole}^{-1}$, in the case of the composites with the weak and the untreated matrix-filler interfaces. In the case of the composite with strong internal interfaces the PMV has an average value of ca. $42 \text{ cm}^3 \cdot \text{mole}^{-1}$ at low pressures. These measured values are in reasonable agreement with the PMV of CO₂ gas at infinite dilution in some organic solvents at atmospheric pressure; the reported values are in the range of $43\text{--}48 \text{ cm}^3 \cdot \text{mole}^{-1}$; Table 6.3 (Horiuti, 1931). Fleming and Koros (1986) have determined a value of $46.2 \text{ cm}^3 \cdot \text{mole}^{-1}$ for CO₂ gas in a silicone elastomer at 35°C and in a pressure range of 0-5 MPa. A similar value of ca. $44.5 \text{ cm}^3 \cdot \text{mole}^{-1}$ was reported by Hirose *et al* (1986) for CO₂ gas dissolved in LPDE over the same pressure range and at temperatures of up to 55°C. The behaviour of dissolved CO₂ gas in different rubbery polymers and in low molecular weight liquid media appear to be very similar at these pressures. The sorptive equivalence between rubbers and solvent liquids, proposed by van Amerongen (1964), seems to be valid.

It is also observed in Figure 6.15 that as the ambient CO₂ gas pressure increases further there is a substantial drop in the measured value of the CO₂ partial molar volumes. It attains a value of ca. $29 \text{ cm}^3 \cdot \text{mole}^{-1}$ for the unfilled specimen and an average value of ca. $25 \text{ cm}^3 \cdot \text{mole}^{-1}$ for the 20% glass filled silicone

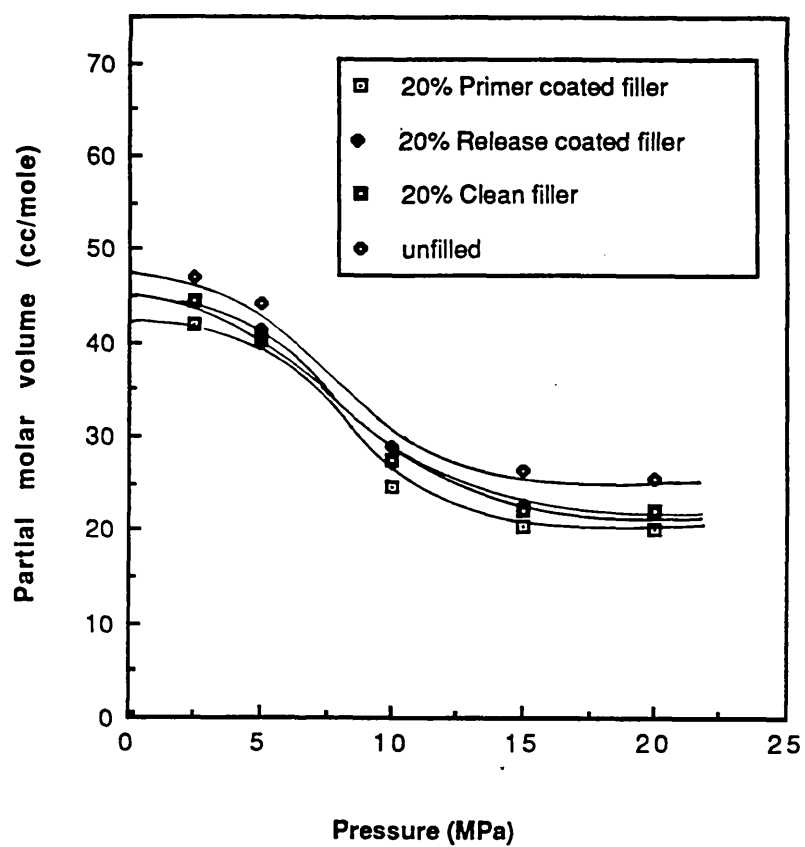


Figure 6.15: Partial molar volume of the absorbed CO_2 in the various silicone elastomer specimens as a function of ambient CO_2 gas pressure.

<u>Medium</u>	<u>Partial Molar Volume</u> (cm³·mole⁻¹)
carbon tetrachloride	48.2
chlorobenzene	44.6
benzene	47.9
acetone	44.7
methyl acetate	44.5
methanol	43.0

Table 6.3: Partial Molar Volume of CO₂ in various liquids at 25°C, atmospheric pressure (Horiuti, 1931).

elastomer specimens. Additional increases in the pressure does not induce significant decreases in partial molar volumes beyond 12 MPa. The molar volume of solid CO₂ is 28 cm³·mole⁻¹. The large drop in the partial molar volumes in the specimens corresponds to the CO₂ gas becoming supercritical and undergoing a rapid density increase. A decreasing trend in the CO₂ partial molar volume with increasing pressure has been reported previously for polycarbonate and polystyrene (Sefcik, 1986 a, b). It is probable that during the transition from 5 to 10 MPa, transformation or clustering of the absorbed CO₂ gas occurs. This proposition has been examined by studying the transmission of ultrasonic signals through the unfilled silicone elastomer specimen. In this experimental arrangement a 10 mm diameter piezoelectric crystal was cast into the test specimen. A strong contact between the crystal and the silicone elastomer was ensured by applying a thin layer of the commercial adhesion promoter mentioned previously in Chapter 4. The experimental arrangement (mode-1) is also described in that Chapter. Essentially, when the crystal is pulsed by a short duration electrical potential the ultrasound propagates to the opposite free boundary and is reflected as a tensile wave. At the supported boundary (crystal-elastomer) it is reflected as a compressive wave. The signal is sensed by the transducer when the ultrasound returns to the piezoelectric crystal. The plots of the ultrasonic signals at 0.1 MPa (ambient pressure), ca. 10 MPa and ca. 12 MPa are shown in Figures 16.6 a, b and c respectively. A comparison of the signals at 0.1 MPa and ca. 5 MPa showed that there was no detectable effect of pressure on the signal shape. However, on increasing the CO₂ gas pressure further, scattering of the signal occurs which is similar in form to the signal scatter detected after the nucleation and growth of internal lacerations (Chapter 7). Similar signals were also observed for the particle glass filled elastomers at atmospheric pressure. It has been demonstrated before, using a cyclohexane solvent, that the unfilled silicone elastomer can swell volumetrically by more than 135% without developing any cracks. Therefore, it is reasonable to

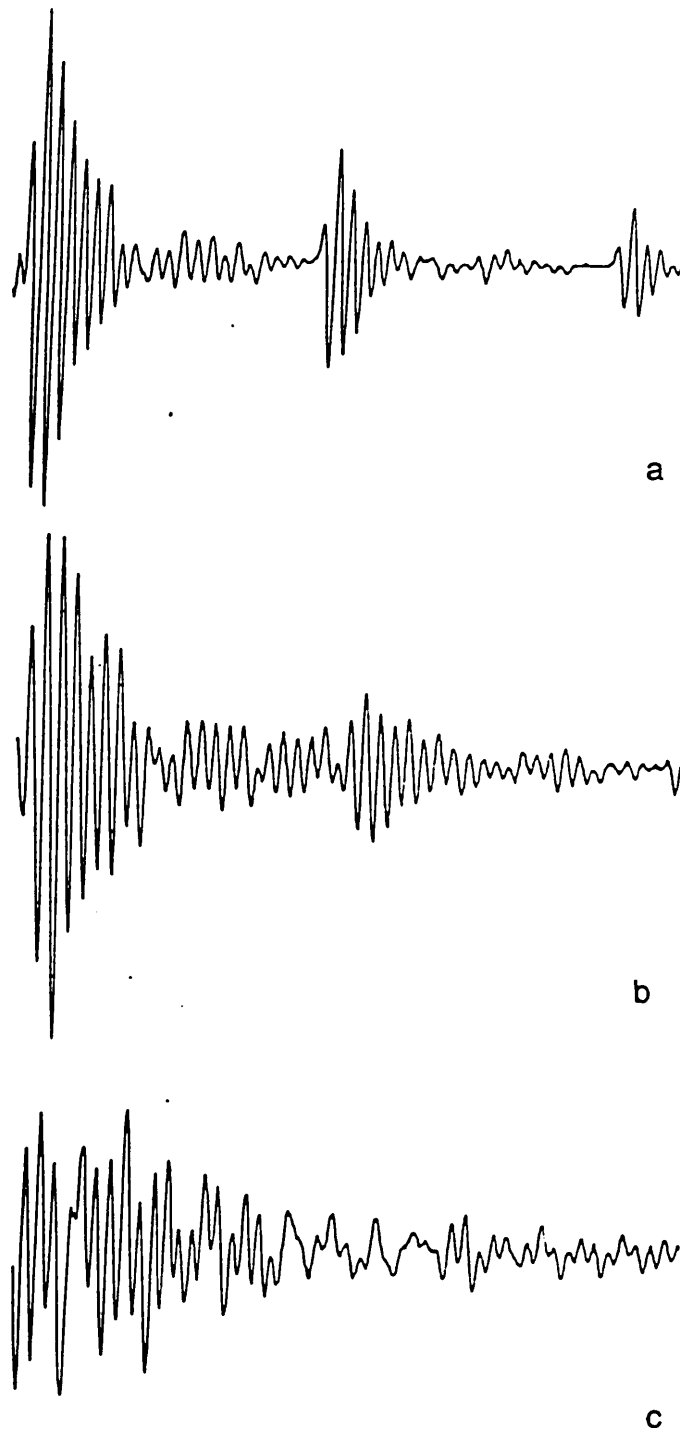


Figure 6.16: Plots of ultrasonic signals transmitted through the unfilled silicone elastomer specimen under CO_2 gas pressure at; a, 0.1 MPa ; b, 10 MPa; c, 12 MPa.

suppose that the scattering of the ultrasonic signals under pressure (>10 MPa) is not due to the formation of internal cracks. It is possible that such scattering zones may be created by the interfaces formed due to the clustering or pockets of the CO_2 in the elastomer. The density of CO_2 at 12 MPa is ca. $650 \text{ Kg}\cdot\text{m}^{-3}$ and the sound velocity is ca. $255 \text{ m}\cdot\text{sec}^{-1}$ (Angus *et al*, 1976). Hence the acoustic impedance, Z_2 , (density $\times$ velocity of sound) is ca. $1.66 \times 10^5 \text{ N}\cdot\text{s}\cdot\text{m}^{-3}$. The comparable value for the silicone phase, Z_1 , is ca. $9.6 \times 10^5 \text{ N}\cdot\text{s}\cdot\text{m}^{-3}$. The difference in the acoustic impedances is significant, ca. $8.0 \times 10^5 \text{ N}\cdot\text{s}\cdot\text{m}^{-3}$ and hence, the coefficient of reflection, $R = (Z_2 - Z_1 / Z_2 + Z_1)$, at these boundaries is ca. 70%. Glass has an acoustic impedance of ca. $128 \times 10^5 \text{ N}\cdot\text{s}\cdot\text{m}^{-3}$ (Kinsler and Frey, 1967). Thus the coefficient of reflection, R , at a silicone elastomer-glass interface would be ca. 85%; comparable with the value computed for a distinct supercritical CO_2 -silicone elastomer interface. It is of course a moot point whether such a CO_2 -silicone elastomer interface would provide a step function in the acoustic impedance. A gradual transition in the property may occur and hence suppress the severity of the acoustic reflections.

Further evidence of the proposed clustering phenomenon comes from the observation that the quality of the distorted signal exhibited an improvement with an increase in the experimental temperature while keeping the pressure constant. Clustering of water and methanol in a silicone elastomer at higher penetrant concentrations have been reported by Barrie and Michin (1969). A similar phenomenon with water was witnessed by Southern and Thomas (1979). Internal rupture of the specimen was not observed and deterioration in the tensile strength of the specimen after slow drying was not detected. The clustering was attributed to the predominance of water-water interactions at higher concentrations. The chain segments in an elastomer are in a state of rapid motion such that the system develops an internal pressure with a vector sum equal to zero. When the elastomer is deformed, as in swelling, the vector sum is changed such that an extra

non-equilibrium pressure is exerted by the more freely moving molecular chain segments on the penetrant. This type of process may also facilitate the phase transformation and the clustering of the absorbed CO₂ gas.

It is likely that the partial molar volume computed is actually lower than the absolute value. The main reason for this opinion is that it was assumed that all of the increase in elastomer volume was due to the sorbed CO₂ gas. Factually, some of the volume occupied by the guest CO₂ molecules would come from the space formerly occupied by the host polymer; its free volume. As mentioned earlier, silicone elastomers are known to have higher than 'normal' amounts of free volume. Ziegel and Eirich (1970) estimated a free volume element of $0.15 \times 10^{-9} \text{ m}^3$ for this elastomer, while for polyurethane and polyethyl methacrylate it was $0.022 \times 10^{-9} \text{ m}^3$ and $0.026 \times 10^{-9} \text{ m}^3$ respectively. Hence, the silicone elastomer will itself contribute more space for the absorbed CO₂ gas than most other polymers.

6.3.2.4 CO₂ Gas Induced Dilation of Other Polymeric Systems

The dimensional changes of the nitrile rubber and the PTFE specimens when subjected to CO₂ gas pressurisations are shown in Figure 6.17. Both these polymers exhibit dilation. However, the extent of the expansion is considerably less than that observed for the silicone elastomer and its composites under similar conditions. The linear dilation for the nitrile rubber specimen at a pressure of ca. 23 MPa is ca. 1.75%, whilst the PTFE sample only dilated by 0.2%. Ender (1986) has measured CO₂ gas induced swelling of various commercial nitrile rubbers. The detected responses range from a small compression in certain cases to expansion of varying degrees in others. The maximum linear swelling detected amongst this class of polymer was ca. 8% for a pressure of 30 MPa. The tensile moduli of the nitrile rubber and the PTFE are greater than that of the silicone elastomer specimens (Table 6.1). It is generally recognised that stiffer materials are more difficult to swell. It may be recalled that the response of these polymer systems to the high

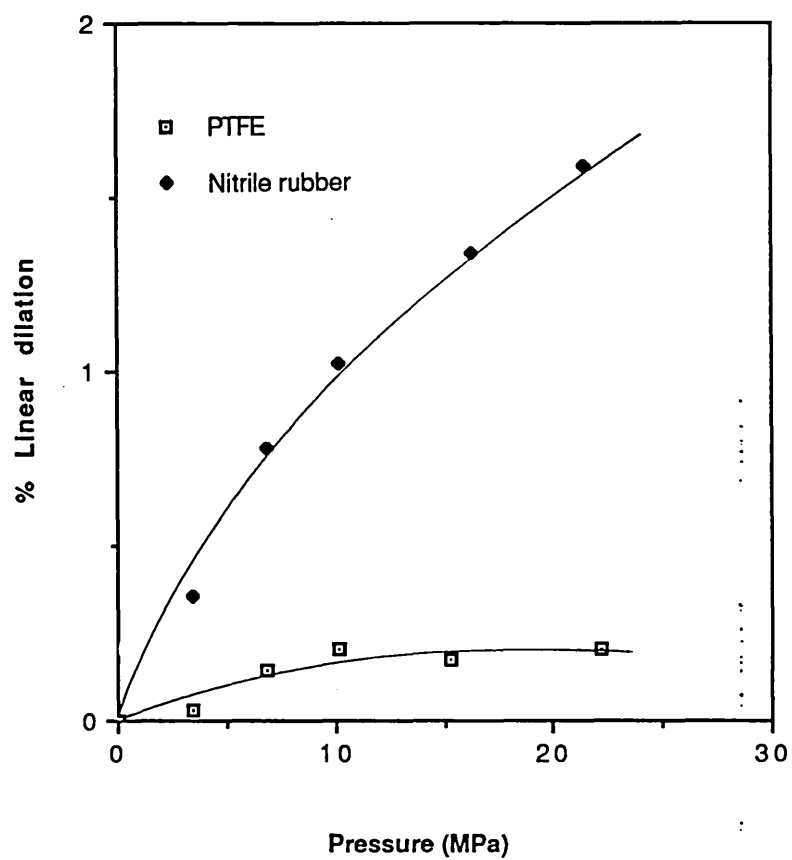


Figure 6.17: Percentage linear dilation for the nitrile rubber and the PTFE as a function of CO₂ gas pressure.

pressure N₂ gas environments was a small compression.

6.4 POLYMER INFLATION DURING RAPID GAS DECOMPRESSION

Internal cracks have been detected in the various elastomeric specimens after the completion of the pneumatic pressure cycles (Chapter 8). They are most certainly produced during the rapid decompressions of the ambient high pressure gases (Chapter 7). Under these conditions, a saturated test specimen behaves like a pressure vessel with high pressure gas trapped in its interior. The gas originally dissolved in the sample under higher pressure is no longer confined when the surrounding pressure is reduced and there is an excess burden of the gas pressure in the polymer. The gas will, of course, begin to diffuse out of the polymer but nevertheless a stage will be reached when the internal hydrostatic stress, or rather the stress fields, reach a critical level and the polymer is ruptured. The actual process is probably much more complex, but to a first order it is reasonable to suppose that the polymer will rupture when it has accumulated a critical level of volumetric strain during the decompression process. Therefore, the volume changes of the specimen whilst the gas pressure is being released are of considerable interest. The ultrasonic mode-2 technique has been employed for this purpose.

6.4.1 Specimen Inflation during N₂ Gas Decompression

The inflations produced in the various silicone elastomer specimens during the N₂ gas depressurisations are given in Figure 6.18. Typically the pressures were reduced from ca. 23 MPa to the atmospheric in ca. 5 minutes; Figure 6.19. The decompression processes were largely adiabatic and the temperature profile in the pressure vessel is exemplified in Figure 6.20. It is observed that the unfilled

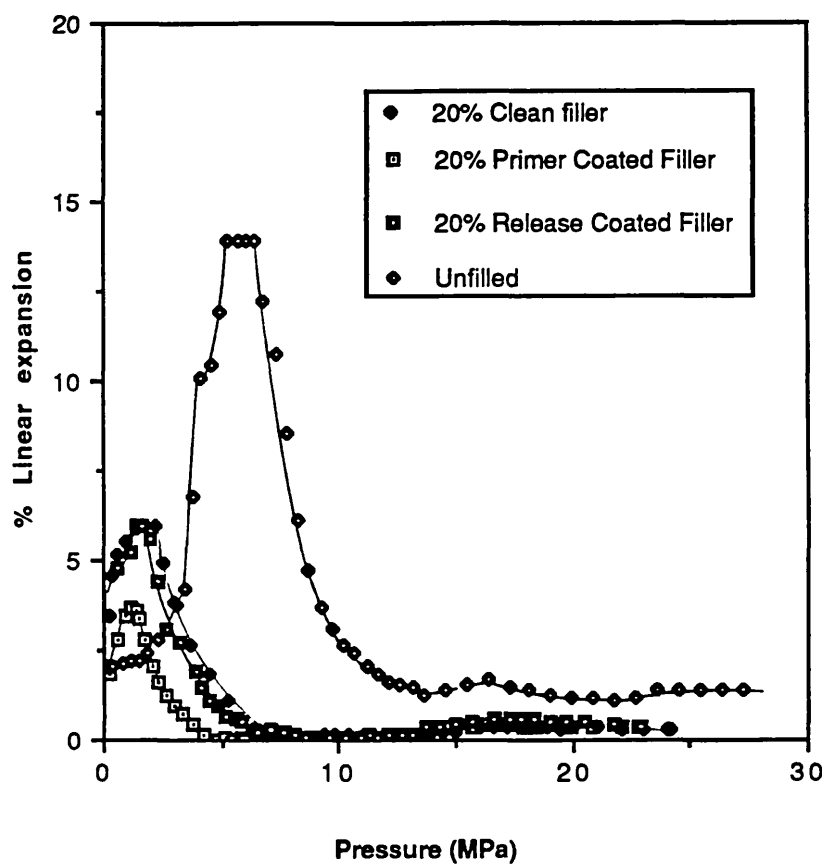


Figure 6.18: Percentage linear inflation for the various silicone elastomer specimens as a function of ambient high pressure N_2 gas decompression.

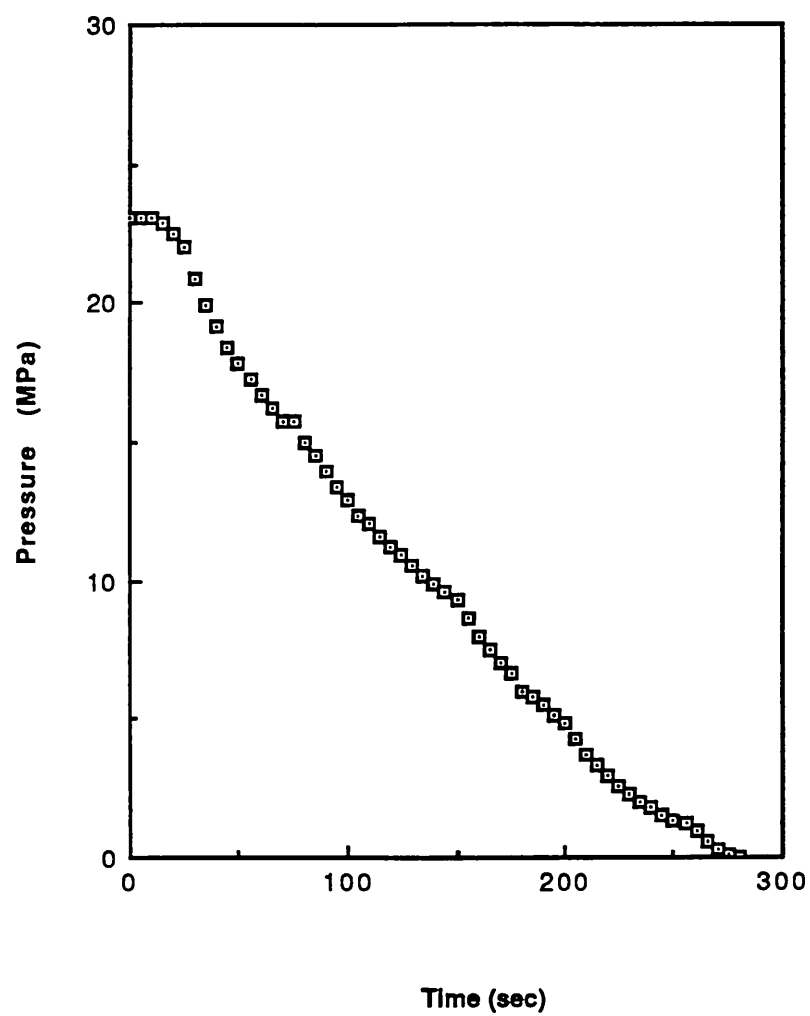


Figure 6.19: Typical N₂ gas decompression profile as a function of time.

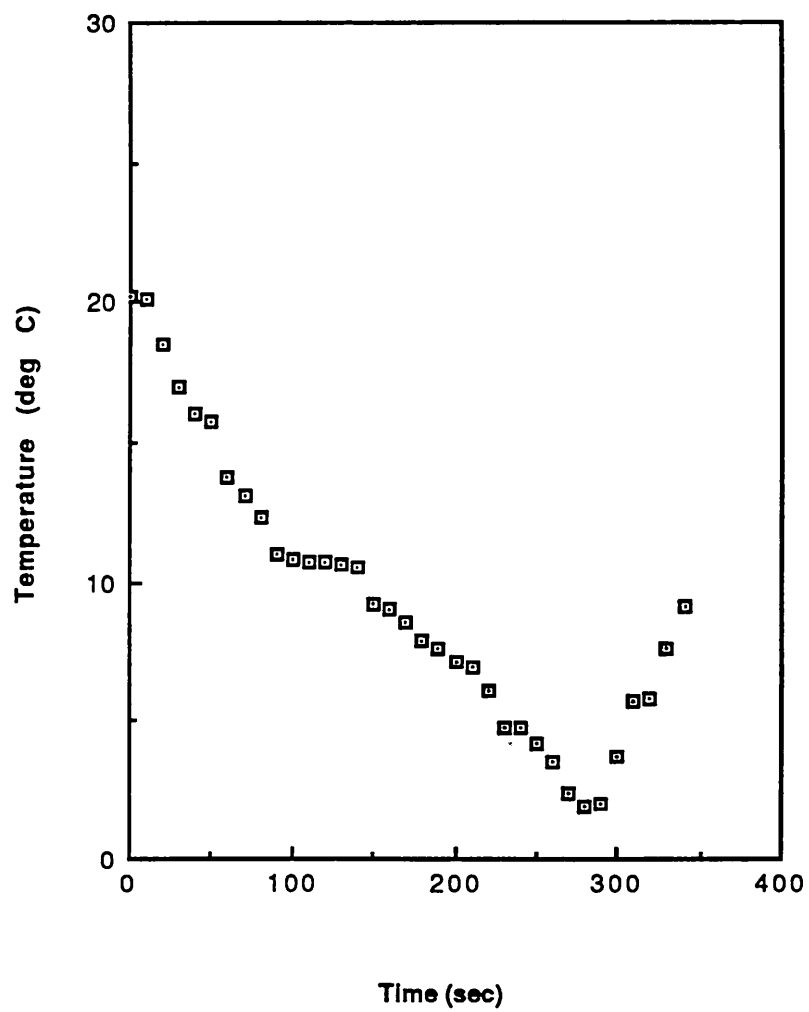


Figure 6.20: Typical profile of the pressure vessel temperature as a function of time during N₂ gas depressurisation.

silicone elastomer specimen gradually begins to expand at a first critical pressure of ca. 16 MPa. The available evidence suggests that it is here that the initial internal cracks are formed (Chapter 7). The data are not sufficiently precise to accurately measure the volumetric strain at the first critical pressure but it is estimated as about 4-6% volumetric expansion from the original volume of the sample. The maximum linear inflation of ca. 14% for the unfilled specimen occurs at a second critical pressure of ca. 7 MPa. At this stage there is a plateau in the curve. It is proposed that the internal cracks or bubbles in the specimen would have sufficiently developed by this point and adequate surface area had been generated to desorb the gas, by short circuit diffusion paths, at a rate equivalent to the ambient gas depressurisation. As the pressure gradient between the polymer interior and the surroundings, and also within the matrix, decreases and the elastic recovery properties of the fractured elastomer regain dominance the specimen reverts to its original size. Towards the end of the experiment the test piece is seen to have almost returned to its initial size.

6.4.1.1 Effects of Filler Particles on Specimen Inflation

The addition of 20% (w/w) glass filler decreases the two critical inflation pressures. In other words, the filled specimens are probably able to withstand larger pressure gradients between the specimen interior and the ambient before the initial rupture and the catastrophic inflation occurs (Figure 6.18).

For the specimens with the weak internal interfaces, that is the ones with the release agent coated fillers and that with the unmodified particles, the first sign of detectable inflation was exhibited at ca. 7 MPa. However, the amounts of N₂ gas absorbed in these specimens on the basis of elastomer weight fraction were close to that in the unfilled system. These composite specimens reached the maximum inflation of ca. 6.5% at ca. 2 MPa and then started to deflate. The sample with the strong internal interfaces was able to resist inflation up to a decreasing

pressure of ca. 5 MPa and then it only inflated by 4.0%. This test specimen also underwent the lowest extent of inflation.

The nitrile rubber and the PTFE test specimens did not exhibit any detectable inflation during the N₂ gas decompression processes. It has been noted earlier, that these polymeric materials are stiffer and also absorb less gas.

6.4.2 Specimen Inflation during CO₂ Gas Decompression

The inflations suffered by the various silicone elastomer specimens during the rapid release of the high pressure CO₂ gas ambients are presented in Figure 6.21. The decompression processes were completed in ca. 6 minutes. Figure 6.22, shows a typical CO₂ gas decompression profile. Figure 6.23 gives the temperature profile of the interior of the pressure vessel during this process. It is seen from Figure 6.21 that as the decompression commences, there is a slight increase in the swelling of the already dilated specimens. This is probably due to the sudden reduction in the external hydrostatic loading. Before the specimens actually inflate in a gross way it is observed that they exhibit a small contraction. On the whole the sorptive dilation is maintained although the specimens are losing gas. This is an indication that there may be a negative hydrostatic stress acting on the samples. In this set of experiments it is noted that the filled samples begin to inflate at a higher critical pressure, whilst the unfilled system inflates at the end of the decompression ramp at ca. 1.5 MPa. It may be that the CO₂ gas desorption is more rapid in the unfilled sample.

6.4.2.1 Effect of Matrix-Filler Interfacial Quality on The Inflation Characteristics

A trend is noted in respect of the initial critical inflation pressures for the filled specimens; Figure 6.21. It is higher for the systems with the weak internal

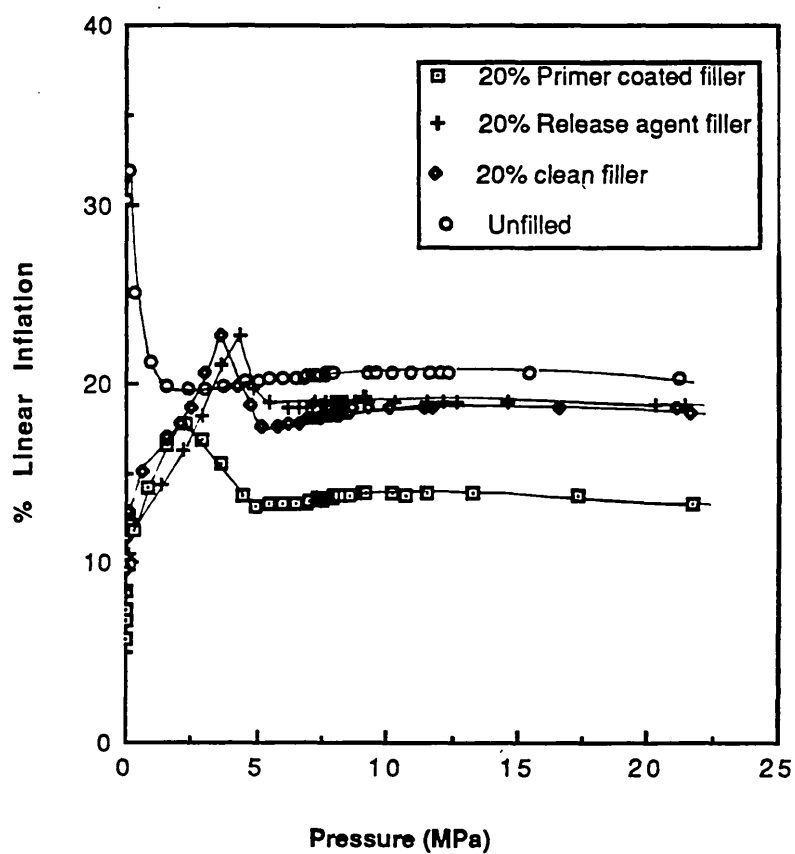


Figure 6.21: Percentage linear inflation for the various silicone elastomer specimens as a function of ambient high pressure CO₂ gas decompression.

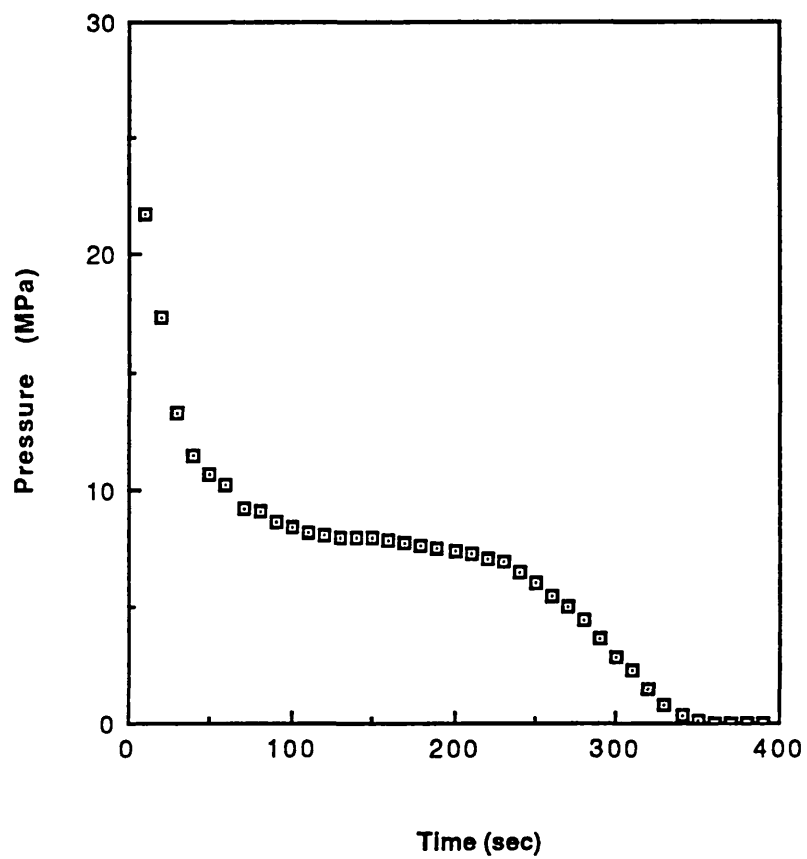


Figure 6.22: Typical CO₂ gas decompression profile as a function of time.

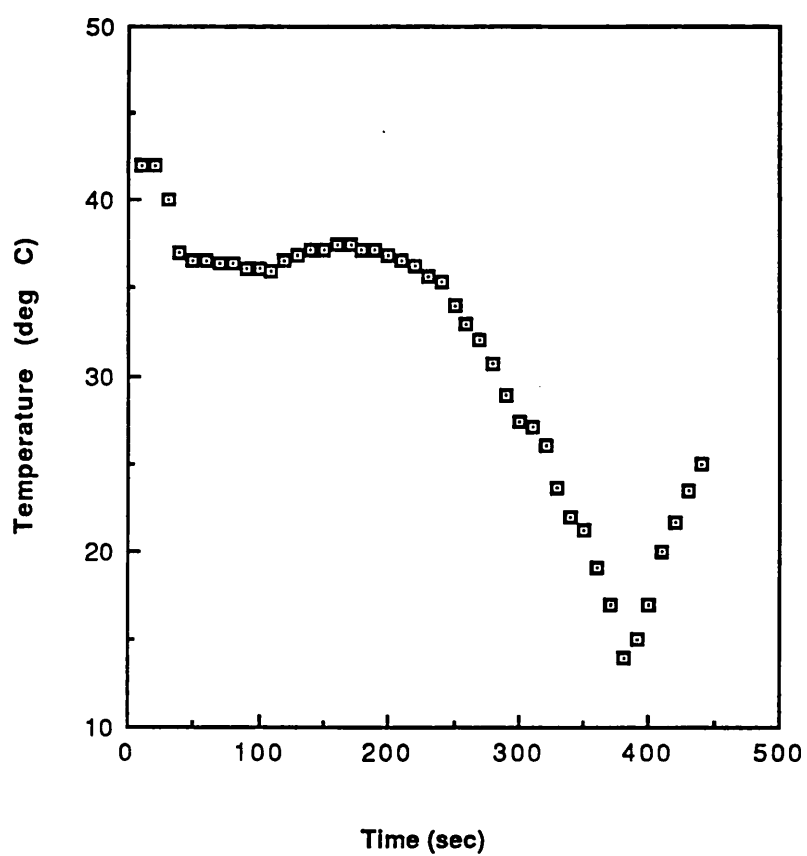


Figure 6.23: Typical profile of the pressure vessel temperature as a function of time during CO₂ gas depressurisation.

interfaces and has a lower value when the matrix-filler bondings are robust. The rate of inflation is also lower in the latter case, indicating an inherent resistance to the internal pressure. In the specimen with the release agent coated fillers the blowing process initiates at ca. 6.25 MPa and for the test piece with untreated fillers it starts at ca. 5.25 MPa. The maximum inflation levels of ca. 23% are reached at ca. 4.5 MPa and ca. 3.5 MPa respectively. In the composite with the strong internal interfaces, the rapid and pronounced expansion starts at ca. 4.5 MPa and it attains the maximum of ca. 17.5% by ca. 2 MPa. It is noted that the unfilled specimen suffers a significantly larger inflation of ca. 14% relative to its initial swollen state. The inflation commences when the ambient CO₂ gas pressure is reduced to ca. 1.5 MPa.

The inflation data in Figure 6.21 are again shown in Figure 6.24 as a function of the lapsed decompression time. In this figure the deflation behaviour of the specimens can be observed with more clarity. The inflation curves rise and fall more rapidly and do not exhibit the small plateau found during the N₂ gas depressurisations. Sharp expansion-contraction 'spikes' were observed, specially with the virgin silicone elastomer, on the oscilloscope screen during the course of the experiment. However, these could not be recorded efficiently because of the large time intervals (ca. 10 seconds) between each data acquisition. A single spike probably represents the rupture of a large gas bubble in the specimen which allows the trapped gas to escape. These spikes were not observed during the N₂ depressurisations. The CO₂ gas induced damage, as mentioned in Chapter 8, is in the form of large internal cracks while with N₂ gas the individual crack sizes are smaller and the specimens appear to have foamed. Another important difference in the response of the specimens is the extent of the overall inflation during the decompression of these gaseous environments (N₂ and CO₂). With the CO₂ gas, the specimens were dilated significantly under pressure and then inflated even further during the depressurisations. Hence, the overall inflation experienced

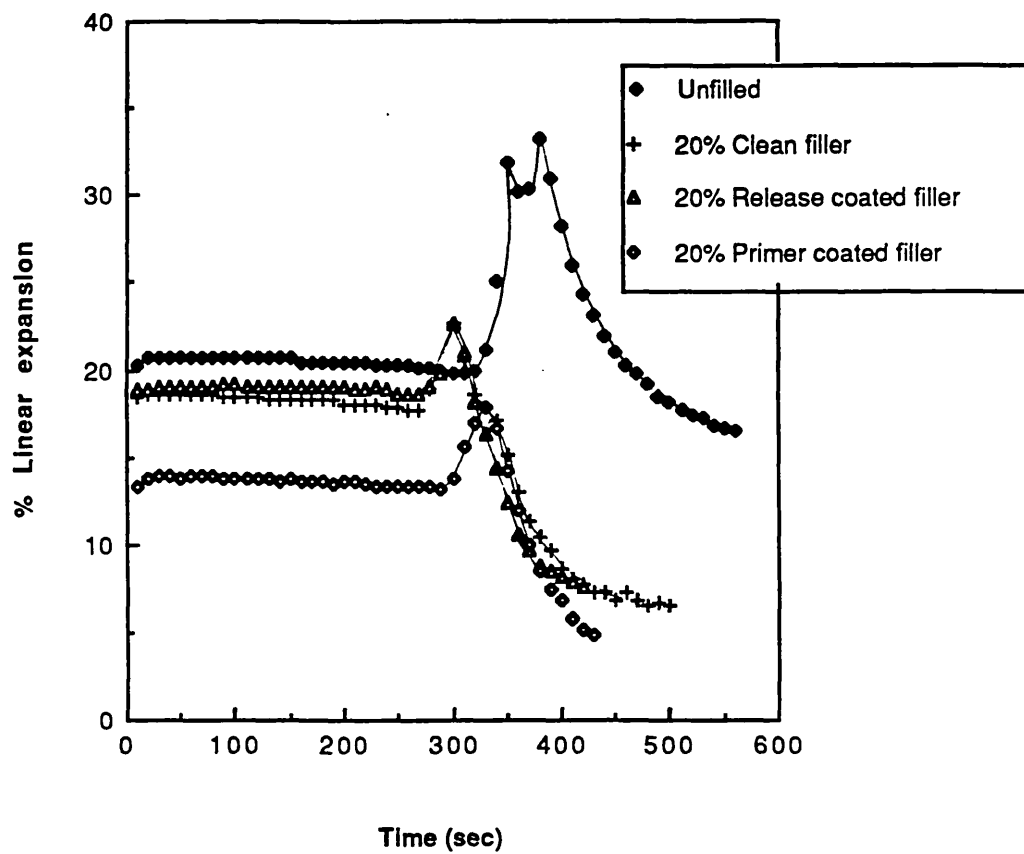


Figure 6.24: Percentage linear inflation for the various silicone elastomer specimens during CO₂ gas decompression as a function of time.

by the specimens, with reference to the original dimensions, is significantly more than that incurred by similar test pieces during the N₂ decompressions. However, in both cases the specimens quickly regained their original dimensions and there was no 'sponginess' by the time the pressure vessel was opened and the specimens were inspected. Liatsis (1989) has also reported a large (more than 100%) CO₂ gas induced inflation in polyurethane rubbers that lasted for a much longer period of time after the decompression cycle.

Figure 6.25 indicates the extent of the inflation suffered by the nitrile rubber specimen during the CO₂ gas blowdown. The inflation commences when the decreasing ambient pressure is at ca. 5 MPa and reaches the maximum of ca. 9% at ca. 1 MPa. The deflation of this specimen is even faster. No inflation was detected in the case of the PTFE specimen.

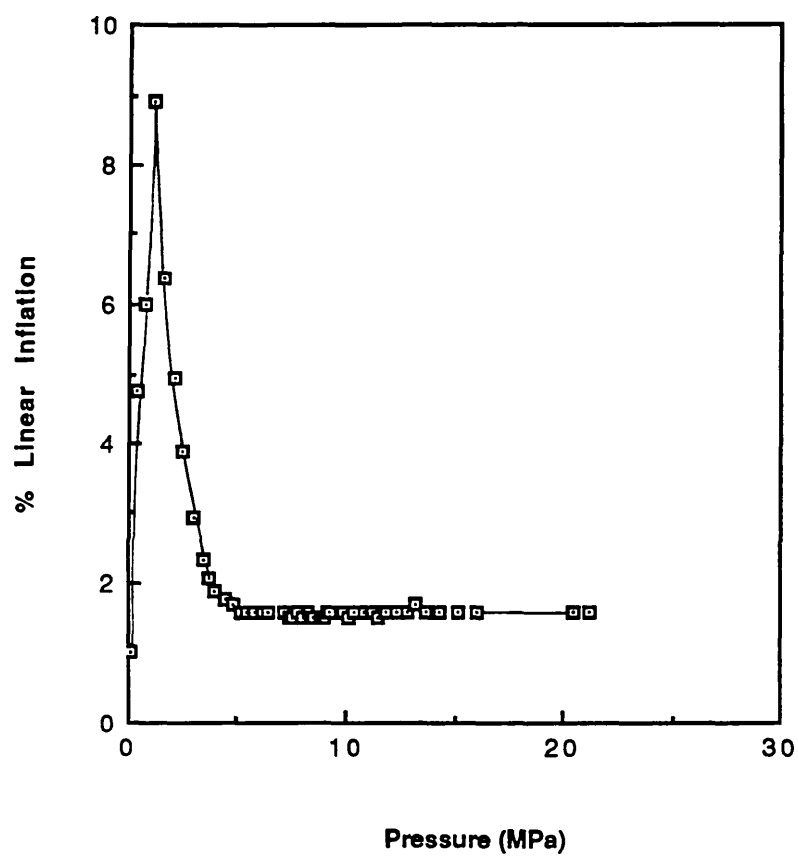


Figure 6.25: Percentage linear inflation for the nitrile rubber specimen as a function of CO₂ gas depressurisation.

6.5 CONCLUSIONS

The changes in the linear dimensions of the various polymeric materials, when subjected to pressures by the permeable and the impermeable media, have been described. Compression of the specimens occurred when the hydrostatic pressure was exerted by mercury. A volumetric compression, ca. 6.5%, was observed in the unfilled silicone elastomer. The polymer compression was reduced after the addition of the filler particles. The permeable pneumatic pressures caused swelling of the specimens. The extent of the dilation depended on the swelling potential of the penetrant gas and the elastic properties of the polymer. Stiffer polymers which experienced less compression under the mercury pressure were also found to be more resistant to the gas induced dilation. Markedly different gas-polymer interactions were observed with N_2 gas and CO_2 gas. In the N_2 gas, the sorptive dilation of the silicone elastomer was only 4.5% volumetric, whilst, in the high pressure CO_2 gas environment the elastomer was swollen volumetrically by more than 70% at a similar pressure. It is concluded that under a pneumatic pressure if less gas enters the matrix the triaxial compressive stresses experienced by the polymer are greater. The net result could then resemble the effects produced by a purely hydrostatic environment. The high pressure CO_2 gas acted like a solvent and was able to produce significant swelling in the various specimens. Even the stiffer polymers exhibited a certain degree of dilation.

The addition of the filler particles appeared to suppress the extent of the dilation. This effect was especially pronounced when the matrix-filler bondings were strong.

At pressures below the CO_2 gas critical pressure the partial molar volume of the absorbed CO_2 gas in the silicone elastomer was constant. It was similar to the values reported for CO_2 gas in certain organic solvents. This fact verified the notion that at low pressures the gas sorption behaviours of rubbery polymers and of

simple viscous liquids are similar. However, a substantial decrease in the computed partial molar volume occurred when the CO₂ gas pressure was raised above its critical point. Clusters or pockets of high density CO₂ seem to have formed in the silicone elastomer.

During the rapid release of the pneumatic pressures, inflation of the saturated specimens occurred. The inflation started when the ambient pressure had dropped considerably and a critical pressure difference between the specimen interior and the surrounding had established. The addition of filler particles into a matrix, especially those which form strong bonds with the matrix, enabled the specimen to withstand a greater pressure difference before the rupture occurred. In the CO₂ gas decompression experiment short duration expansion-contraction 'spikes' in the virgin silicone elastomer inflation curve were observed. These spikes indicated the rupture of large gas bubbles in the matrix. In the N₂ gas decompression process such spikes were not observed; the inflation curve exhibited a small plateau. The inflation pressures generated in the latter case were not sufficient to produce expansion in the nitrile rubber and the PTFE specimens. The PTFE specimen remained unaffected even during the rapid decompression of the CO₂ gas ambient. The various inflated specimens reverted to the original sizes after most of the gas had resorbed.

CHAPTER SEVEN

MONITORING ULTRASONIC PROPERTIES OF MATERIALS UNDER PNEUMATIC PRESSURES

7.1 INTRODUCTION

This Chapter describes the ultrasonic properties of the various materials under static and transient pneumatic pressures. These properties have been evaluated by the ultrasonic method (mode-1) which operates in the pulse-echo mode. In this mode, ultrasonic signals are transmitted through a medium and are reflected back from the opposing sample boundary. The properties of the longitudinal waves that travel through the silicone elastomer have been used to compute the modulus changes under different pneumatic pressure environments. The elastomeric specimens were pre-strained and it was assumed that the changes in the transit times under pressure were not due to any linear dimensional changes. The same waves were also used to detect the crack initiation and growth under the transient pressure conditions. In this case the specimens were not dimensionally restrained and were allowed to undergo volumetric expansions. Hence, the speed of wave propagation and the signal attenuation in the materials were the primary measured quantities.

In Chapter 6 the effects of pure hydrostatic pressure were observed to be significantly different from those produced by the pressuring environments that were soluble in the materials. An hydrostatic pressure would tend to decrease the available free volume. However, the effects of high pressure ambient gases are more complex and mainly depend upon the type of gas-polymer interaction.

The generation of internal cracks during the N₂ gas decompression process

has also been studied with the acoustic emission technique. The experimental results of this study are also presented.

7.2 MATERIAL PROPERTIES UNDER NITROGEN GAS PRESSURE

7.2.1 Changes in Ultrasonic Velocity

The sound or ultrasonic velocity is a characteristic of the material. Ultrasonic waves have been previously employed to study the physical properties of polymers (Wada, 1956; Kono, 1960; Maeda, 1955). The transit times of the longitudinal compression waves through various lengths of the unfilled silicone elastomer, at 20°C and 0.1 MPa are given in Figure 7.1. The transit time is required by the pulse to make a 'round trip' through the specimen. Therefore, the velocity of sound in the material is simply twice the gradient of the line in Figure 7.1. A value of 1052 m·s⁻¹ has been estimated. Hartman and Tanznski (1974) have also measured the velocity of longitudinal waves through a polydimethyl siloxane. Their estimate of 1020 m·s⁻¹ is in reasonable agreement with the value obtained in this study.

The application of the N₂ gas pressure on the silicone elastomer test specimen results in an increase in the velocity of sound in the material; Figure 7.2. The specimen was pressurised in steps of about 3.5-4.5 MPa and allowed to equilibrate. The changes in the signal transit time were in fact taken after 45 minutes of a pressure ramp. The experimental temperature was ca. 20°C. The initial thickness of the specimen is known and the sample was restrained from sorptive dilation in the direction of wave propagation. The velocity increases are therefore attributed to the combined effects of the changes in the specimen modulus and density. It is assumed here that the modest pre-strain, which is within the

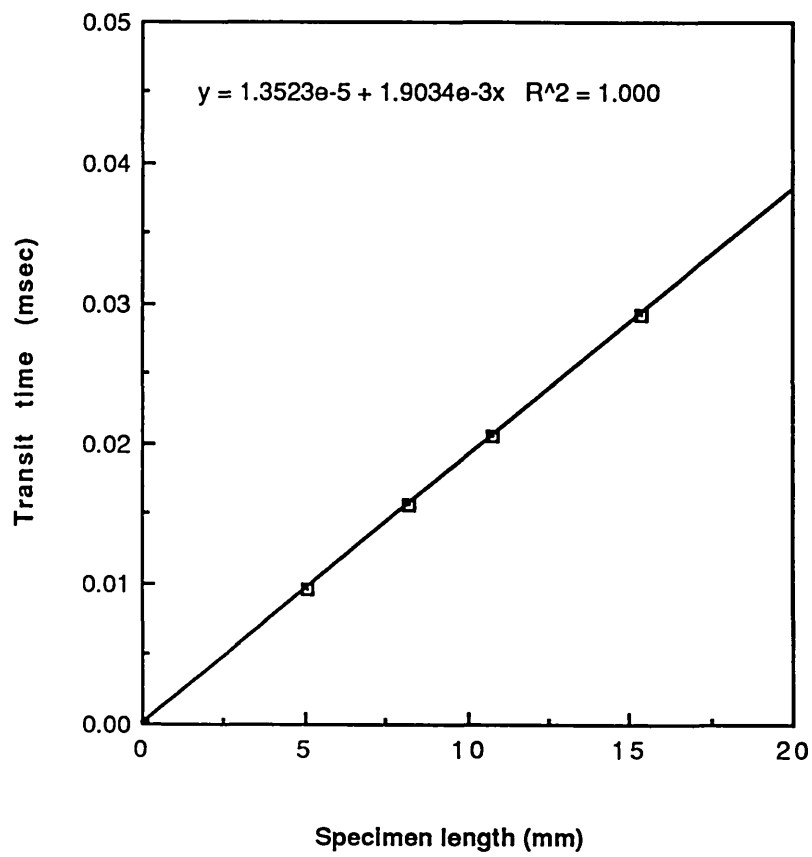


Figure 7.1: Ultrasonic signal transit time for a round trip through the length of the silicone elastomer specimen, 20°C and 0.1 MPa.

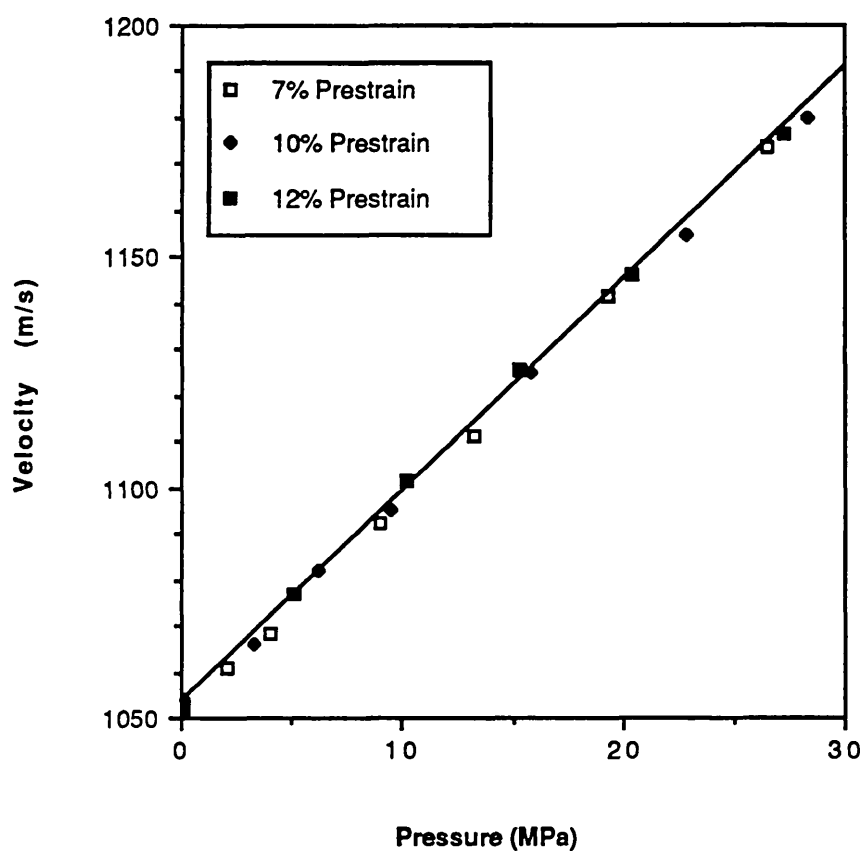


Figure 7.2: Ultrasonic velocity for the various prestrained unfilled silicone elastomer specimens as a function of N_2 gas pressure, 20°C.

linear stress-strain response of the elastomer, does not produce a modulus-gas pressure (or density-gas pressure) characteristic which is significantly different to that of an unstrained sample. It is believed that the changes in the density and the modulus arise from gas sorption in the specimen and the relative compression of the same by the pneumatic stress. The confinement of a test piece in a way that restricts its volumetric changes under pneumatic stresses will influence the extent of gas mass absorption and thus the modulus. However, the linearly strained specimen whose height to diameter ratio was of the order of ca. 0.6 and whose interfaces with the plates (transducer face and confinement plate) were not bonded and were able to expand diametrically, will suffer no significant additional effective hydrostatic stresses for a modest pre-strain. Hence, it is considered appropriate to assume that the effects produced in the pre-strained specimen are comparable to those in the unconstrained test piece. This supposition is also substantiated by the observations that the changes in the signal velocities at given gas pressures for different sizes of the silicone elastomer specimens, strained to various extents, were numerically similar within experimental error. In Figure 7.2 the velocity increases for the specimens pre-strained by ca. 6%, 10% and 12% are plotted. The measured values for the three specimens lie on the same line and a velocity increase of ca. 12% is observed for a pressure of 27 MPa.

It has been mentioned previously, in the experimental section of the thesis, that the velocity of sound in water also increases with increasing N_2 gas pressure. A comparison is made here with the increase in velocity caused by the application of pure hydrostatic pressure; Figure 7.3. The velocity data for water under triaxial stresses are taken from Wilson (1959). It is realised that the velocity of sound is more sensitive to pure hydrostatic pressure than to a numerically equivalent N_2 gas pressure. This difference is obviously associated with the gas absorption in the water. A similar trend is seen with polymers. Under these conditions the density increase of the water will most certainly be higher as compared with the application

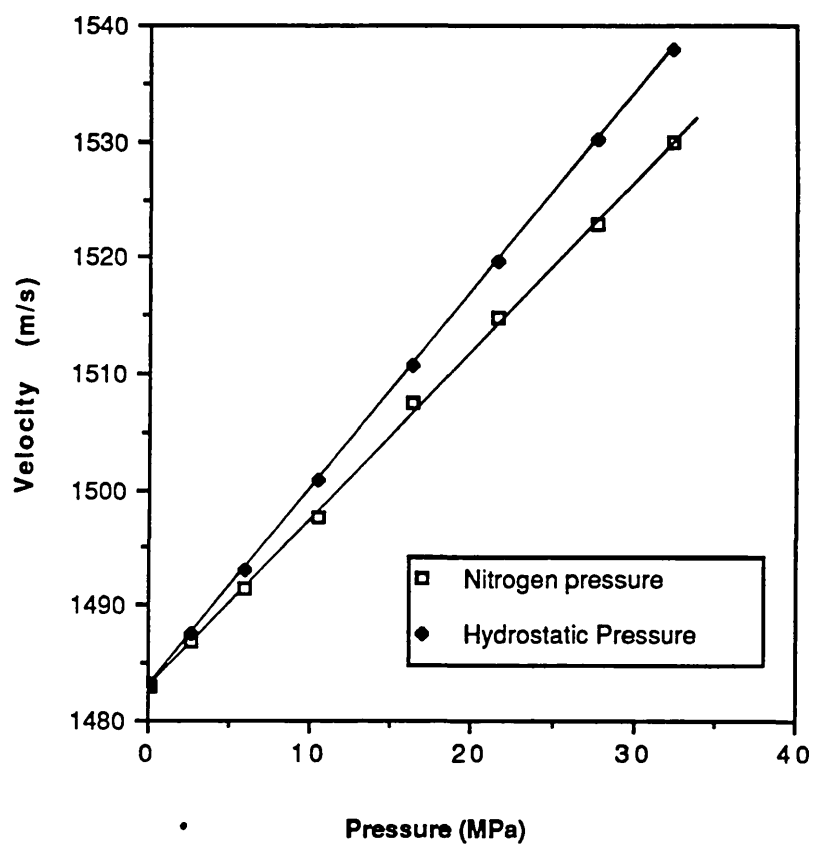


Figure 7.3: Ultrasonic velocity for the distilled water as a function of pressure, 20°C.

of a simple triaxial stress.

7.2.2 Specimen Moduli Under Nitrogen Gas Pressure

It has been mentioned earlier that the elastic behaviour of materials can be determined by measuring the ultrasonic wave velocity. The velocities of the longitudinal waves transmitted through the silicone elastomer under the various N₂ gas pressures have been measured. The longitudinal modulus, 'L', of the specimen can be computed by using the following relationship (Vary, 1980, p. 164):

$$L = \rho V^2 \quad (7.1)$$

where 'ρ' is the density of the material in kg·m⁻³ and 'V' is the velocity of sound in the material in m·s⁻¹.

The changes in the density of the silicone elastomer under the N₂ gas pressure have been described in Chapter 6. Hence, the modulus of the test specimen at various pressures may be computed by using the relation given above. The changes in the modulus with respect to the N₂ gas pressure are shown in Figure 7.4. An increase of ca. 45% in the value for a pressure of ca. 27 MPa is noted. The modulus appears to change more rapidly than the specimen density and an increase in the sound velocity through the material is observed. It has been proposed that modulus and density of materials are interrelated (Vary, 1980, pp. 164-5). The modulus-density relationship for the silicone elastomer may be examined in more detail from Figure 7.5. It is realised that the modulus of the elastomer increases with an increase in its density. However, the relation given above (7.1) indicates an inverse dependence of density on velocity relative to the modulus. Hence, it cannot be assumed always that the modulus itself is a function of density as suggested by Figure 7.5.

The application of a pure hydrostatic pressure will reduce the available free

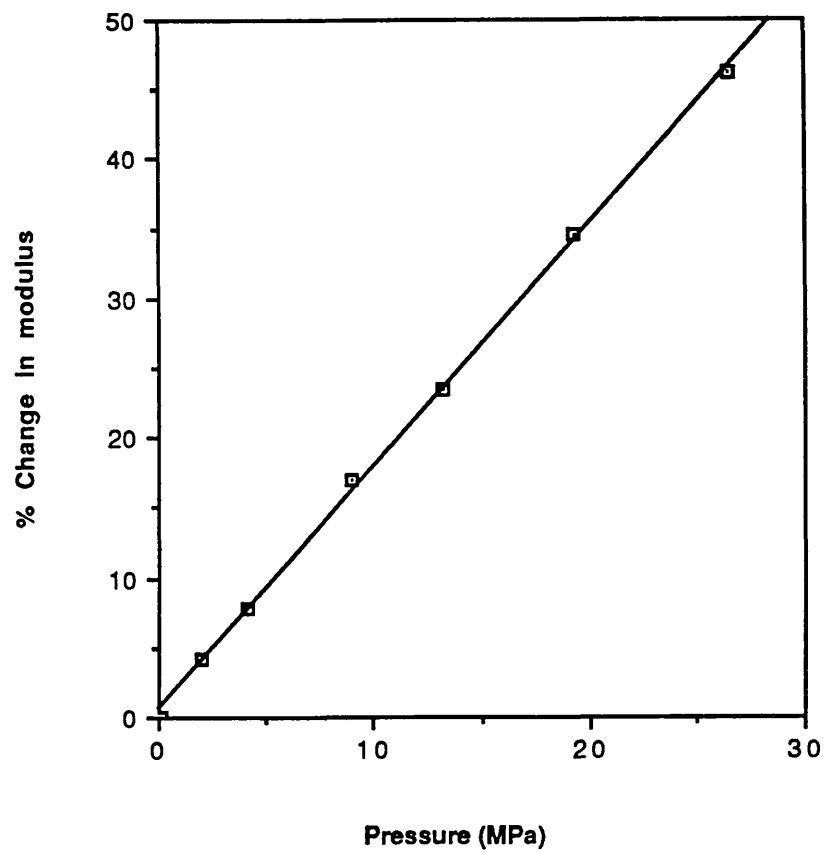


Figure 7.4: Percentage change in the modulus of the unfilled silicone elastomer specimen as a function of N_2 gas pressure.

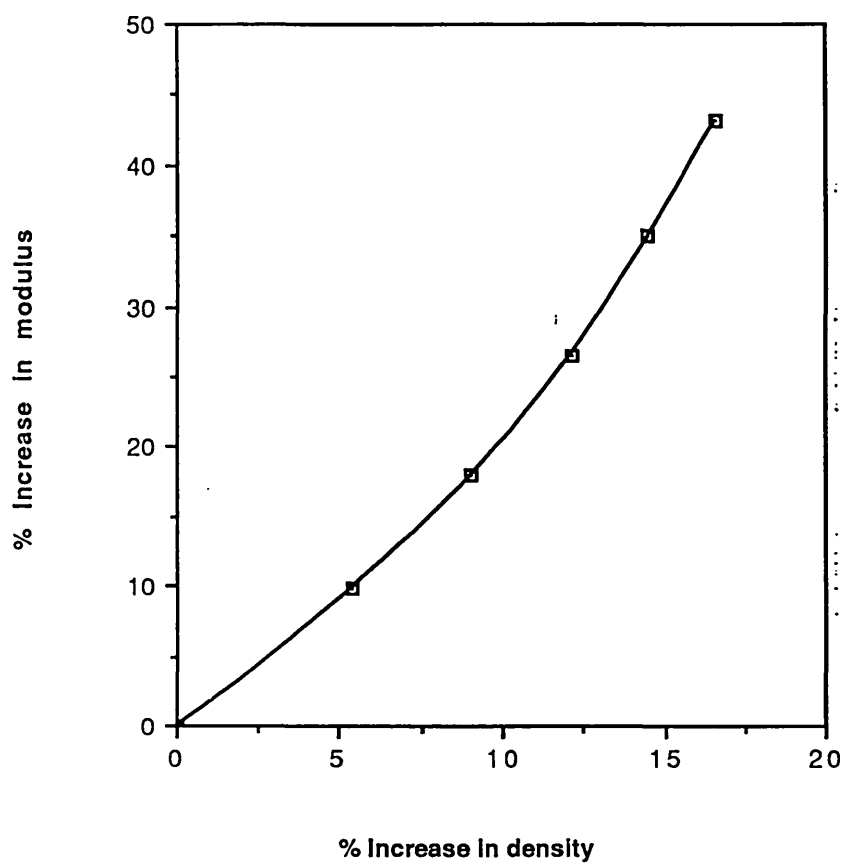


Figure 7.5: Percentage change in the modulus for the unfilled silicone elastomer specimen as a function of the specimen density change in high pressure N_2 gas ambient.

volume and hinder the microscopic movements required to accommodate macroscopic strains. Consequently, this will have a significant effect on the mechanical properties of polymers. Paterson (1964) found that rubbers including, silicone elastomers, undergo large increases in elastic modulus when subjected to significantly high hydrostatic pressures. Similarly, a number of other researchers have reported increases in moduli for various other polymeric systems (Mears *et al*, 1969; Rabinowitz *et al*, 1970; Jones-Parry and Tabor, 1974). It appears that in the application of the N₂ gas pressure, the hydrostatic component of the pressure is dominant over the dilational or plasticisation component. The observed changes in the elastic response of the specimen are consistent with this qualitative argument. Billinghamurst (1969) has observed that the shear modulus of polyvinylchloride (PVC), natural rubber and polyethylene (PE) increases under N₂ gas pressure. However, the PTFE specimen showed an initial increase in the modulus followed by plasticisation of the same on further pressurisations. This effect was not detected with an impenetrable pressure media or indeed with helium. It was proposed that since PTFE has a granular structure the high pressure gas entered in between the granules and decreased the modulus through plasticisation. A similar study was later conducted by Jones-Parry and Tabor (1974) and it was observed that the shear modulus of a number of polymers increased with the application of N₂ gas pressure. It was proposed that the applied pressure does not simply 'press' the molecules closer together, it also 'slides' them into new positions. Recently, Briscoe and Mahgerefteh (1986) have suggested that much of the peculiar plasticisation effects of N₂ gas on PTFE are attributable to non-isothermal effects in the earlier experiments.

7.2.3 Crack Detection During Nitrogen Gas Decompression

During the rapid reduction of the ambient gas pressure it is known that the

silicone elastomer is severely damaged internally (Chapter 8). It has been possible to follow the inflation of the specimen during this process (Chapter 6). In the following paragraphs it will be shown that with the help of the mode-1, ultrasonic arrangement, the initiation and growth of internal cracks during the gas decompression cycle can also be monitored.

The changes in the ultrasonic signal attenuation, 1 MHz frequency component, for the unfilled silicone elastomer are given in Figure 7.6. At the start of the ambient N₂ gas decompression the signal attenuation is probably only due to the absorption of sound in the material. Sound waves cause adiabatic compressions and rarefactions as they propagate through materials. There is a momentary temperature rise in the compressions and a momentary fall in the rarefactions. Heat energy is taken from the compressions and restored to the rarefactions, this process decreases the energy of the wave and causes attenuation (McGonnagle, 1961, p. 218). The signal attenuation in the silicone elastomer begins to increase as the decreasing ambient pressure reaches a critical value of ca. 17 MPa from ca. 27 MPa; Figure 7.6. The generation of randomly oriented lesions makes the system ultrasonically inhomogeneous. The internal cracks or bubbles contain the absorbed gas and therefore two materials of different density and sound velocity meet at these interfaces. The specimen now contains boundaries at which the acoustic impedance (density x velocity) changes abruptly. When these cracks are just nucleating and their sizes are still smaller than the signal wave length, scattering of the signal occurs. This process has been exemplified by the scattering of light by small water droplets in fog (Krautkramer and Krautkramer, 1977, p. 108). The attenuation augments rapidly with further decreases in pressure. The cracks grow and become comparable to the wave length, the signal is probably split into various reflected and transmitted waves. This process repeats itself due to the presence of numerous cracks distributed in the matrix. Thus the original pulse is divided into partial waves which are attenuated along their long and complex path. Due to the

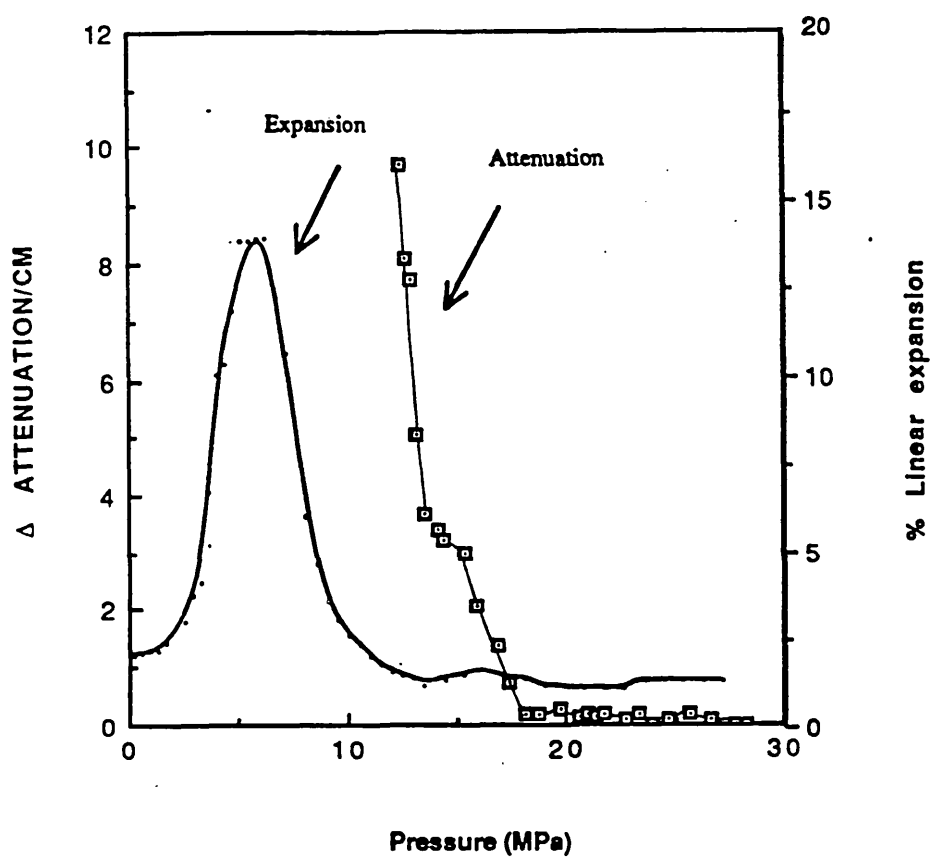


Figure 7.6: Change in ultrasonic signal attenuation for the silicone elastomer specimen during ambient high pressure N_2 gas decompression. The specimen inflation under similar conditions is also shown.

numerous echoes with different transit times, the so-called 'grass' is produced in the received signal. The effect of this disturbance cannot be counteracted by increasing the transmitter voltage or by the amplification of the received signal, because in doing so the 'grass' or noise also increases. Hence, no back wall signal is identified by the transducer as the decreasing pressure reaches ca. 12.5MPa (Figure 7.6). A gross volumetric inflation of ca. 50% was observed during this process (Chapter 6). The expansion profile is again shown in Figure 7.6. It will be realised that the signal attenuation starts to increase even when there is no significant volume inflation with reference to the start of the decompression. As the elastomer begins to expand and the internal cracks grow the detectable back wall echoes are lost. It is concluded from these results that the silicone elastomer specimen was ruptured while the volumetric strain was only ca. 5%. This is consistent with the negative hydrostatic stress model for crack generation proposed by Gent and Lindley (1959a) and Lindsey (1967).

The resonance frequency of the ultrasonic transducers used was 1 MHz. If the average value of the sound velocity through the silicone elastomer under pressure is taken as 1100 m.s⁻¹, the signal wave length is about 1 mm. The ultrasonic flaw detection within a material depends upon the signal wave length. Therefore, it is reasonable to suppose that the N₂ gas induced crack sizes at ca. 12.5 MPa are of the order of the wave length. The detection resolution could be improved by employing higher frequency transducers. However, they were not used because the high frequency signals were attenuated more heavily due to higher matrix energy absorption (Krautkramer and Krautkramer, 1977; Vary, 1980; Goebells, 1980). The 1 MHz transducer had been selected because the received signals had an acceptable signal to noise ratio for the specimen lengths used in the experiments.

7.2.3.1 Acoustic Emission Technique for Crack Detection

The nucleation and development of the internal cracks have also been studied by an acoustic emission (A.E.) technique. An aluminium wave guide in the shape of a flat umbrella was moulded into the unfilled silicone elastomer specimen for this purpose. The acoustic emission transducer (R-15, Physical Acoustics Corporation, USA) was attached to the wave guide, with a thin layer of the acoustic couplant. This arrangement was adopted to avoid any emissions occurring from the sliding friction between the inflating specimen and the transducer face. Initial experiments showed this to be a major source of emissions. The acoustic emission signals detected by the transducer were channelled through a preamplifier operating at a gain of 25 to an acoustic emission registerer (RIF-MEPh1-1, Moscow Engineering and Physics Institute). The registerer operated above a threshold of 100×10^{-3} volt. At lower threshold levels the gas decompression noise and other electrical noises in the laboratory were also picked up and produced a high noise to signal ratio. The events were captured after every tenth of a second and digitally displayed. They were also plotted on a chart recorder. The acoustic event counts with respect to the decreasing N_2 gas pressure are given in Figure 7.7. The specimen inflation profile under similar conditions is again shown in the figure. It is observed that the detectable events occur towards the later stages of the decompression. In relation to the specimen inflation curve, the bursts of events occur while the test specimen is rapidly expanding. After reaching the maximum, the detected number of events decrease rapidly. On the basis of these results it is concluded that this technique can only provide information about crack development and not nucleation.

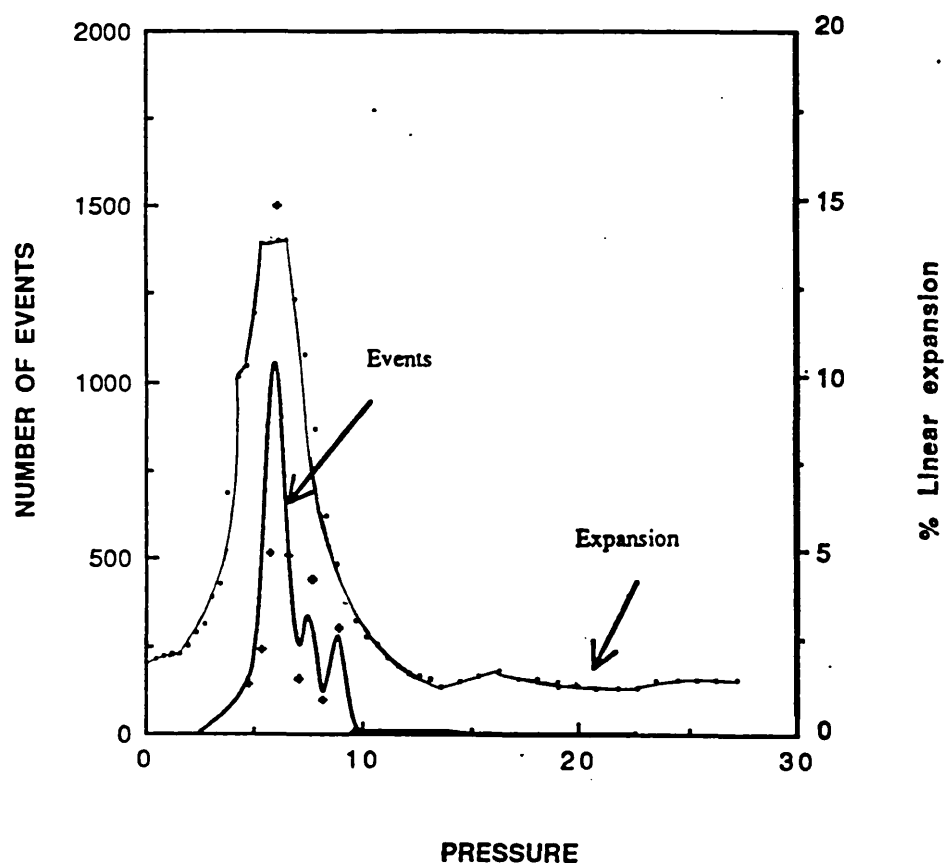


Figure 7.7: Acoustic emission event counts for the silicone elastomer specimen during ambient high pressure N_2 gas decompression. The specimen inflation under similar conditions is also shown.

7.3 MATERIAL PROPERTIES IN HIGH PRESSURE CO₂ GAS ENVIRONMENT

In this section the effects of high pressure CO₂ gas on the properties of the silicone elastomer and few liquids such as distilled water and silicone fluid will be presented and discussed.

7.3.1 Ultrasonic Velocity Changes in Certain Fluids

In the CO₂ gas pressurisations of the water it is realised that the increase in sound speed is unlike the linear rise observed under the hydrostatic and the N₂ gas pressures; Figure 7.8. In this case there is a sharp increase in the velocity which later seems to level off with further rise in the ambient CO₂ gas pressure. Each measurement was taken after ca. 45 minutes of a pressure step. The experimental temperature was maintained at 42°C. Similar results were obtained at ca. 35°C and are also plotted on the same graph (Figure 7.8). The probable explanation for this non-linear behaviour is the significant solubility of CO₂ gas in water. At a pressure of ca. 20 MPa and ca. 42°C, the solubility of CO₂ in water has a value of ca. 6.3% on weight basis (Perry and Chilton, 1983, p. 3-96). The absorbed CO₂ probably forms carbonic acid (H₂CO₃) with the water and contributes towards an increase in the system density. Hence, in this case the experiment is sensing the velocity of sound in carbonic acid rather than in water.

When the ambient CO₂ gas pressure is released the quality of the ultrasonic pulse-echo signal remained unaffected down to a pressure of ca. 6 MPa. A further decrease in the pressure caused severe dispersion of the signal. The same phenomenon was experienced even when the gas pressure was reduced at a relatively slow rate and the decompression was completed in ca. 15 minutes. The signal dispersion is certainly due to the bubbling out of the absorbed gas which

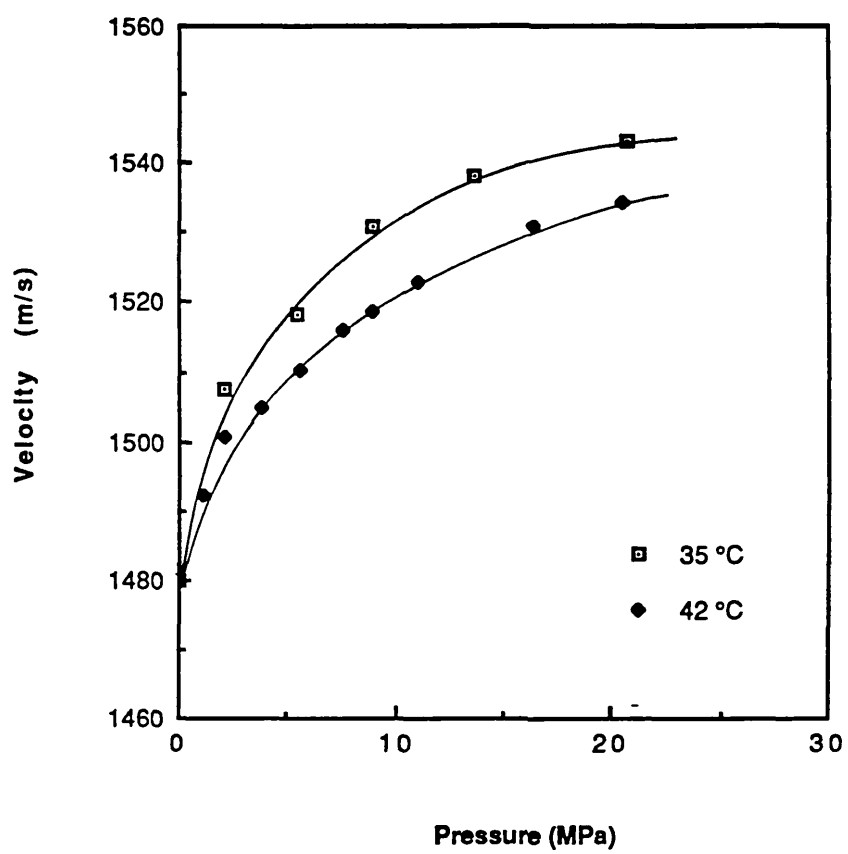


Figure 7.8: Velocity of sound in the distilled water as a function of CO₂ gas pressure.

could be seen even after another 10 minutes, when the water container was removed from the pressure vessel. As mentioned earlier (Chapter 4), for these reasons water was not favoured as a signal transmitting medium in the mode-2 of the ultrasonic experimental technique for the CO₂ gas environments. Mercury was found to be unaffected by the CO₂ gas pressurisations and depressurisations and was therefore used in this experimental arrangement. A silicone fluid (Dow Corning, 400 cp) has also been investigated. Signal dispersions similar to that encountered in the water were experienced during the decompression. In the pressurisation stage the observed changes in the sound velocity are presented in Figure 7.9. The experiment was only performed up to a pressure of ca. 10 MPa at a temperature of ca. 42°C. It is realised that initially there is a ca. 4% decrease in the velocity of sound for a pressure of ca. 3 MPa. Subsequent pressurisations resulted in a rise and a ca. 4% increase with reference to the original value is observed at ca. 10 MPa. At a fixed temperature, CO₂ gas pressure will have two counteracting effects on the system properties. One effect is due to the CO₂ absorbed in the liquid and the other is caused by the increasing hydrostatic pressure. The initial decrease in the velocity is probably due to the former. As the pressure increases the latter effect dominates and the increase in sound velocity is observed.

7.3.2 Ultrasonic Velocity Changes in Silicone Elastomers

The changes in sound velocity for the silicone elastomer as a result of CO₂ gas pressurisations are given in Figure 7.10. The experiment was only performed up to a pressure of ca. 10 MPa. The reasons for this limitation on the upper pressure have already been explained in Chapter 6. It is observed that after a slight increase, the velocity of sound in the material starts to decrease (Figure 7.10). The actual decrease reaches ca. 21% at a pressure of ca. 10 MPa. These data are in a

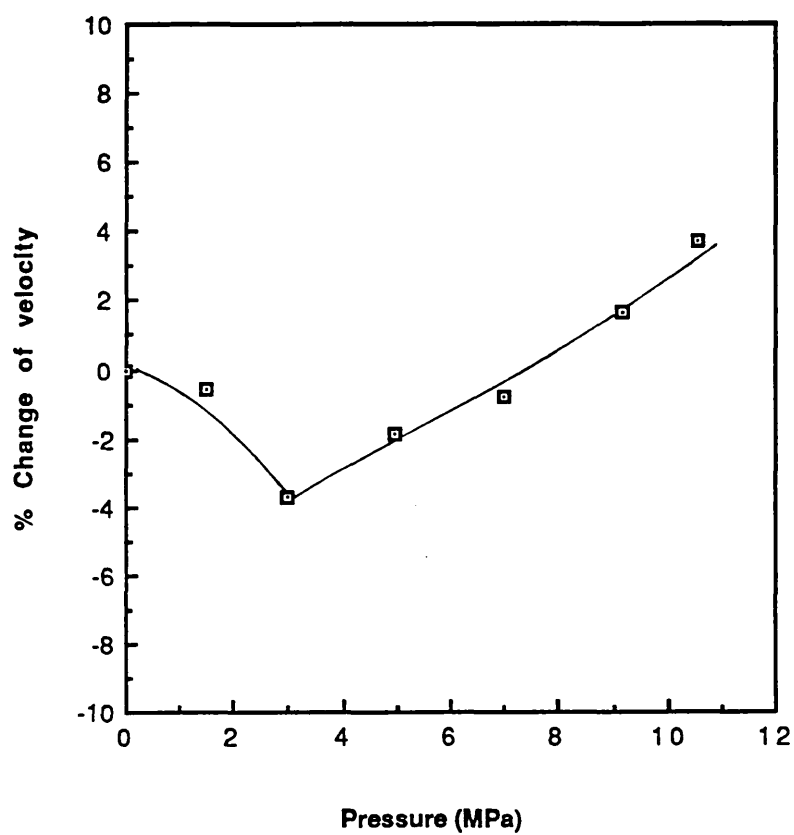


Figure 7.9: Percentage change in ultrasonic velocity for the silicone fluid (400 cp), as a function of CO₂ gas pressure, 42°C.

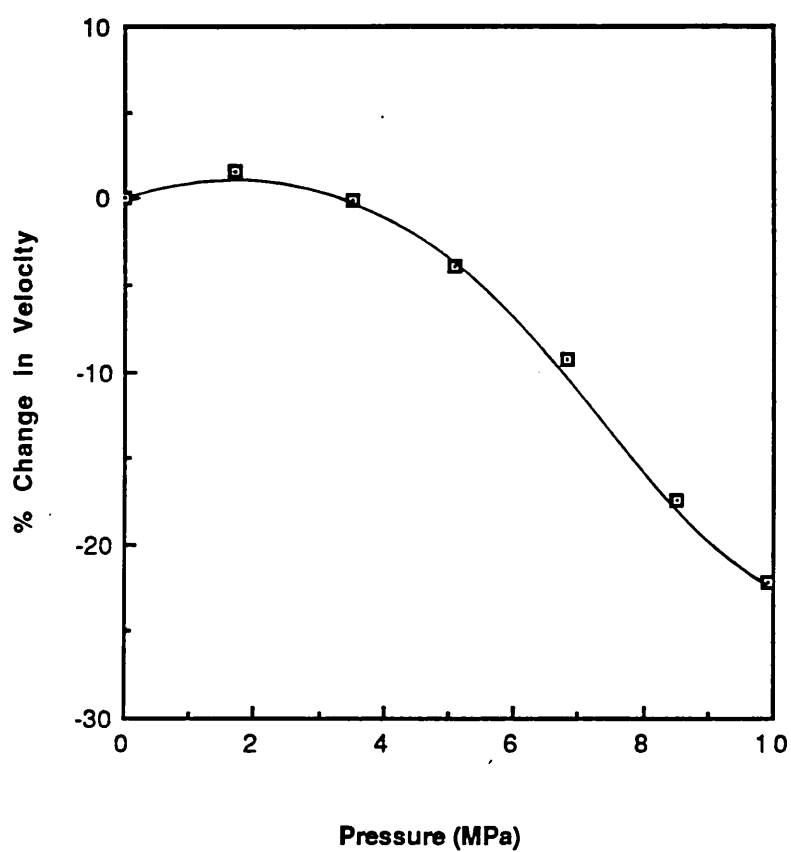


Figure 7.10: Percentage change in ultrasonic velocity for the unfilled silicone elastomer specimen as a function of CO₂ gas pressure, 42°C.

marked contrast to those obtained for the silicone fluid where the situation is almost the reverse. The velocity decrease in the elastomer is probably attributable to the plasticisation effects of the absorbed CO₂ gas (Wang *et al*, 1982; Sefcik, 1986 a, b; Hirose *et al*, 1986; Hojo and Findley, 1973). A decrease in the velocity of sound in plasticised PVC has been observed by Wada, (1954). The plasticisers used were dioctyl phthalate (DOP) and tricreyl phosphate (TPP). It was observed that the decrease in sound velocity was proportional to the extent of the plasticiser addition. Wada and Yamamoto (1956) also detected that the velocity of sound in a number of glassy polymers dropped suddenly at temperatures above the glass transitions. The velocities of sound in a thin slab of polystyrene under CO₂ gas pressures have been measured by Wang *et al* (1982). It was found that the velocity decreased continuously up to a pressure of ca. 20 MPa. However, there was a gradual increase with further increases in the pressure. It was noted that while taking these measurements the dilation of polystyrene reported by several other researchers (Sefcik, 1986b; Wissinger and Paulaitis, 1987) has not been considered; these data are therefore unreliable. In the present study the specimen length was maintained constant while measuring the velocity changes.

The velocity of sound in the silicone elastomer specimen swollen by cyclohexane solvent has also been measured. In this case the measured velocity is 1160 m.s⁻¹ as against 1052 m.s⁻¹ in the unswollen state; an unusual inverse in the velocity. The test specimen had dilated volumetrically by more than 145% after being allowed to equilibrate for more than 7 days. The amount of solvent absorbed was of the order of 100% by weight. The large swelling probably causes the molecular chain segments to uncoil to a certain extent and therefore they are in a state of strain. Mullins (1959), cited in Treloar (1975, p. 145), noted that at a high degree of swelling the effects of limited network extensibility can produce a significant increase in modulus.

7.3.3 Moduli Changes Under CO₂ Gas Pressure

The calculated changes in the modulus of the silicone elastomer specimen as a function of CO₂ gas pressure are given in Figure 7.11. The shape of this curve closely follows that of the velocity curve shown in Figure 7.10. There is a slight increase initially, which is followed by a drop in the modulus with further pressurisations. A 30% decrease in the longitudinal modulus is observed for a pressure of ca. 10 MPa. The absorbed gas appears to produce significant plasticisation of the system. Under similar conditions a reduction in glass transition temperatures for certain polymers has also been reported (Chiou, 1985). However, in certain cases the gas induced increase in molecular chain mobility may cause crystallisation in polymers. This effect is normally favoured by the application of pure hydrostatic pressure. The trend of the curve in Figure 7.11 at high pressures indicates that at a certain higher pressure the decrease in the modulus will level off and may even show an increase, as observed by Wang *et al* (1982) for polystyrene.

7.3.4 Crack Detection During CO₂ Gas Decompression

The changes in the ultrasonic signal attenuation relative to the value at the start of the CO₂ gas decompression (ca. 10 MPa) are given in Figure 7.12. In this experiment, a commercial transducer had been employed. The depressurisation from ca. 10 MPa to the atmospheric pressure was completed in ca. 15 minutes. The decompression rate was kept lower than previously because it was assumed that faster rates will damage the transducer. However, interesting results have been obtained. It is observed that at a pressure of ca. 8.25 MPa down to 7.5 MPa the ultrasonic signal attenuation exhibits a slight decrease. Under these conditions an increase is expected. This unusual behaviour can be attributed to the

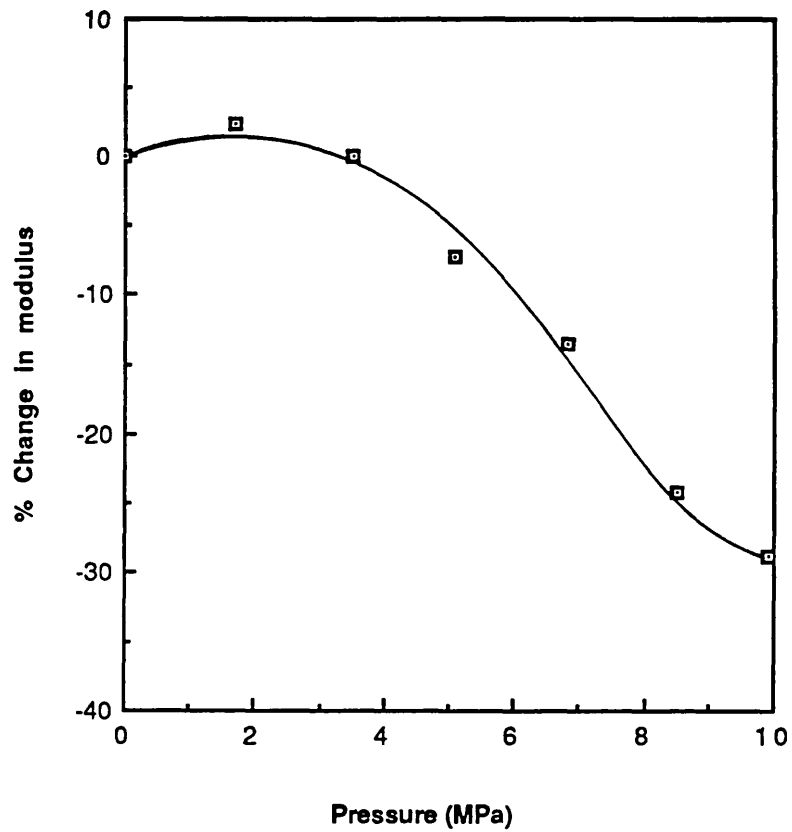


Figure 7.11: Percentage change in the modulus for the unfilled silicone elastomer specimen as a function of CO₂ gas pressure.

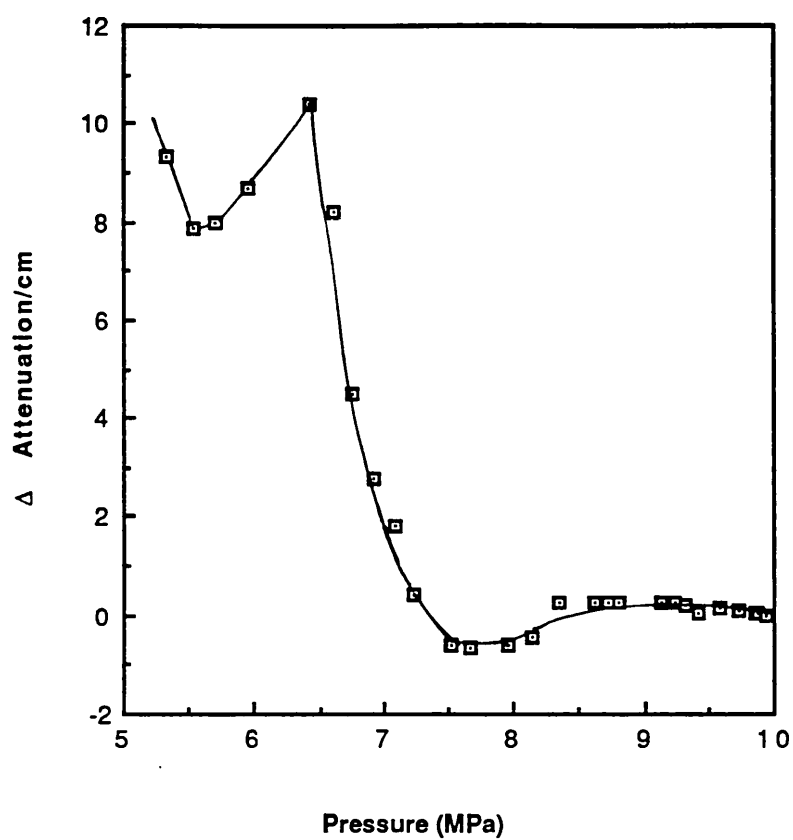


Figure 7.12: Change in ultrasonic signal attenuation for the unfilled silicone elastomer specimen as a function of ambient high pressure CO_2 gas decompression.

CO₂ desorption from the specimen, resulting in declustering of the high concentration localised zones of CO₂ (Chapter 6). A further fall in the ambient pressure results in an increase in the signal attenuation. This is probably due to the formation of the internal cracks/bubbles. However, once again there is a decrease in the attenuation followed by complete loss of the signal. It is known that CO₂ gas decompression results in large cracks in the unfilled silicone elastomer matrix and the crack surfaces are smooth (Chapter 8). It is proposed that the formation of bubbles would result in an increase in signal attenuation and their collapse causes the crack surfaces to heal. The second decrease in the attenuation is ascribed to the collapse of gas bubbles in the matrix and hence to crack healing. The inception of large number of cracks or bubbles later, disperse the ultrasonic signals completely.

7.4 CONCLUSIONS

The ultrasonic method (mode-1) can be used to determine a number of material properties in various high pressure pneumatic environments. The changes in the longitudinal modulus of the silicone elastomer under gas pressure and the inception of internal cracks during the depressurisations have been monitored. The high pressure N₂ and CO₂ gaseous ambients have markedly different effects on the material properties. The N₂ gas influence was more akin to that produced by pure hydrostatic pressure. An increase in the modulus of the silicone elastomer was exhibited, whilst, the high pressure CO₂ induced plasticisation of the matrix.

The linear increase in the sound velocity for water was less significant under the N₂ gas pressure than under a nominally equivalent pure hydrostatic pressurisation. Under the CO₂ gas pressure the velocity increase was non-linear and seemed to level off at higher pressures. In this case the velocity of sound in carbonic acid was being measured. Marked dispersions of the ultrasonic signals occurred in the water and the silicone fluid during the CO₂ gas decompressions.

Such behaviour was not observed with the N₂ gas.

The silicone elastomer specimen started to rupture at a small volumetric strain of ca. 5% at a decreasing N₂ gas pressure of ca. 17 MPa. The damage augmented with further decreases in the pressure. The fracture behaviour was consistent with the negative hydrostatic stress model. In the CO₂ gas decompression, the signal attenuation characteristics revealed that crack healing occurs when the bubbles produced in the matrix collapse on loosing the gas from inside into the ambient.

The acoustic emission technique has not been employed extensively. However, it has been demonstrated that it can also be used for studying the gas induced damage process. This method may be quite useful for highly filled specimens through which the transmission of ultrasonic signals is more difficult and sometimes even impossible.

CHAPTER EIGHT

GAS INDUCED DAMAGE IN ELASTOMERIC COMPOSITES

8.1 INTRODUCTION

This chapter will mainly discuss the nature of the gas induced damage incurred in the various polymeric systems exposed to different decompression environments. The processes that lead to the 'explosive decompression' damage have been described in Chapters 2 & 3. The effects of several factors that influence the extent and the type of the damage will be discussed on the basis of the experimental information obtained. The maximum experimental pressure was ca. 21 MPa. The equilibrium temperature was maintained at ca. 42°C for the CO₂ gas pressure media and ca. 20°C for the N₂ gas. The saturation times allowed were ca. 3 hours and the depressurisation times were ca. 90 seconds. The Chapter is divided mainly into three parts. The first section deals with the visual inspection of the damaged specimens soon after the various pressurisation and depressurisation cycles. The minimum time after which the damage could be assessed was 10 to 15 minutes. This was the time required to disassemble the pressure vessel and remove the test specimens. The second part describes the results of a study where the damaged specimens were sectioned and examined by the various optical techniques to determine the pattern and the orientation of the gas induced cracks. The role of matrix-filler interface quality on the crack initiation, growth and geometry is considered. Finally, the results of a series of mechanical deformation experiments conducted on different damaged specimens will be described. The purpose of this part of the study was to establish the relationship between the loss in specimen coherence caused by the presence of internal cracks and their influence on the

mechanical properties of the damaged samples.

An interesting phenomenon of internal bubble formation occurred in the carbon black filled silicone elastomer. The liquid elastomer with 20% by weight carbon black (particle size 5×10^{-6} m and surface areas $3 \times 10^3 \text{ m}^2 \cdot \text{Kg}^{-1}$) was placed in an oven at ca. 150°C to cure. When the oven was opened after ca. 2 hours the volume of the cured specimen was observed to have increased by more than 100%. The specimen was cut open and gas bubbles of ca. 2 mm diameter were found internally; Figure 8.1. However, this behaviour was not observed when a similar specimen was allowed to cure at room temperature. The carbon black appears to have behaved like the blowing agents used in certain polymer foaming processes. This simple experiment illustrates the potential problems encountered when using porous fillers as reinforcements for elastomeric composites which may be subjected to explosive decompression.

8.2 VISUAL INSPECTION

Several types of damage can occur after an explosive decompression, diametric surface cracks, surface blisters, internal ring cracks, internal micro cracks or voids and in certain cases catastrophic fragmentation of the sample. The test specimens were visually inspected soon after the experiments were completed (10-15 min). A first order estimate for the extent of damage and the changes in physical state were made. In the silicone elastomer specimens there was no detectable changes in the sample dimensions, however, the test samples which were originally transparent, generally, turned opaque with a milky appearance. A few days after the experiment the milky appearance was lost and the major internal cracks could then be clearly observed; Figure 8.2. The most likely reason for this effect is retention of a certain quantity of the initially absorbed gas in small discrete domains in the matrix. The excess gas desorbs slowly and the specimen becomes

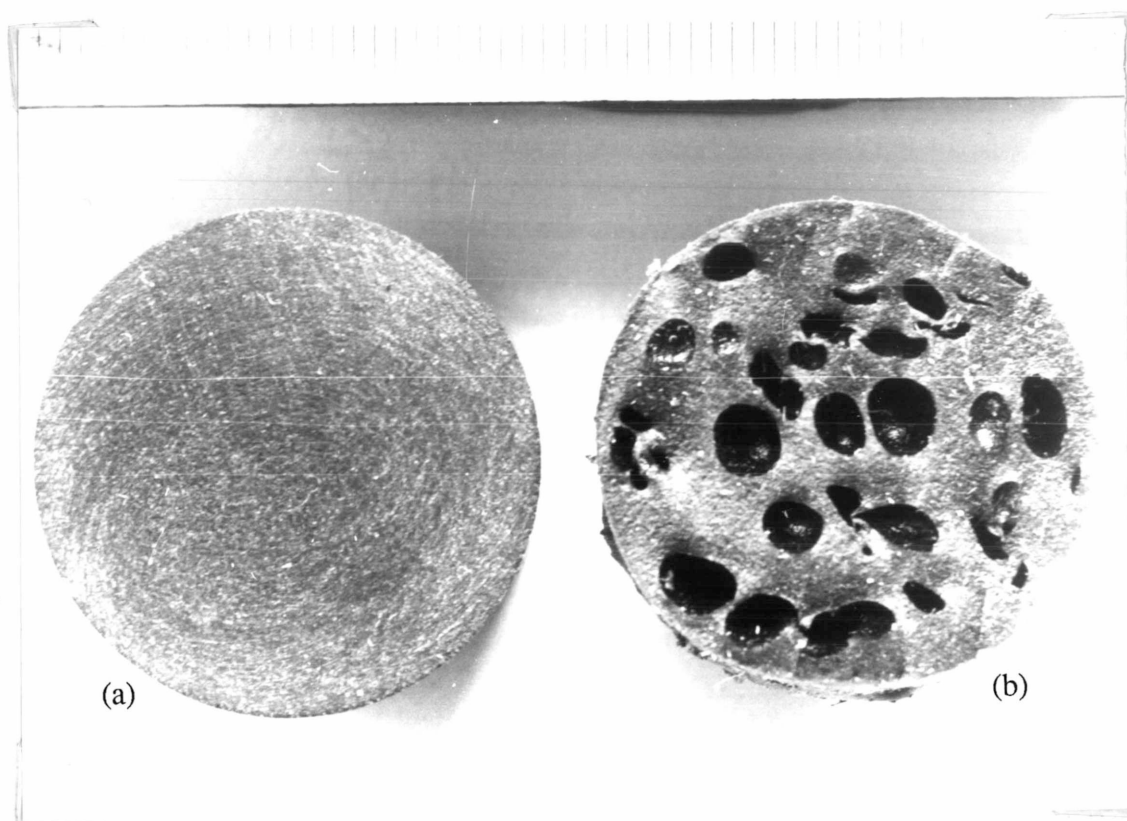


Figure 8.1: Silicone elastomer specimen filled with 20% (w/w) carbon black; (a), cured at 20°C; (b), cured at 100°C.

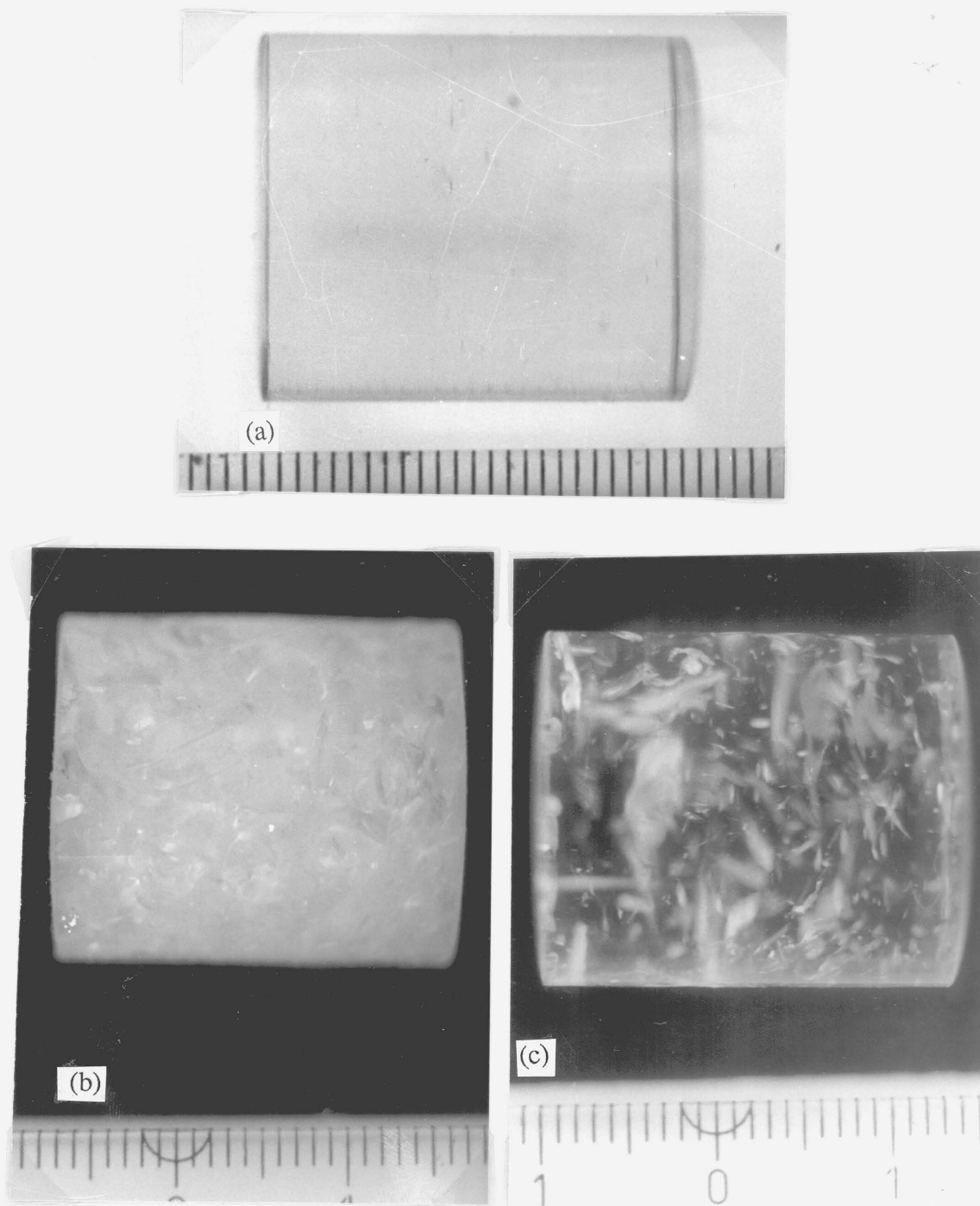


Figure 8.2: Appearance of the silicone elastomer specimen at various stages of the explosive decompression experiment; (a), before the experiment; (b), 20 min after the experiment, (c), 24 hours after the experiment.

clearer as the small cracks and bubbles heal. In the silicone elastomer systems, surface cracks were not detected in all test specimens. They only appeared in the CO₂ gas damaged unfilled test pieces and the samples with the clean unmodified glass beads as the filler. The presence of such cracks at a surface, which penetrate into the bulk of a specimen, was an indication of diametric specimen 'splitting' and hence the occurrence of catastrophic damage. The surface blisters, which are pockets of trapped gas at the surface of an explosively decompressed specimen, were only detected in the nitrile rubber specimens after the CO₂ decompressions. They completely disappeared as the absorbed gas escaped, typically after more than 24 hours. Sectioning of the blister sites revealed subsurface splits. The occurrence of surface blisters with CO₂ gas and other hydrocarbon gases and their disappearance after some time has also been reported by Wolcott and Straznides (1985) and Cox (1985). The blisters were not observed on the nitrile rubber surfaces after the rapid N₂ gas decompressions. It is believed that the permeability of a gas in a polymer strongly contributes to the extent of this phenomenon. The permeability of CO₂ gas in polydimethyl siloxane has been reported as $24.2 \times 10^{-15} \text{m}^3(\text{STP}) \cdot \text{s}^{-1} \cdot \text{m}^{-1} \cdot \text{Pa}^{-1}$ while in nitrile rubber it has a much lower value of $0.23 \times 10^{-15} \text{m}^3(\text{STP}) \cdot \text{s}^{-1} \cdot \text{m}^{-1} \cdot \text{Pa}^{-1}$ (Lomax, 1985). Thus, owing to low gas permeability in the latter system the gas desorption was hindered and resulted in surface blisters; a view which is also supported by the findings of other researchers. Potts (1985), has reported that PTFE and silicone elastomer are materials with an excellent resistance to blister formation.

The physical appearance of the cylindrical PTFE specimens used in this study remained unaltered by the rapid decompression of the high pressure CO₂ gas and N₂ gas ambients.

It is worthwhile to mention the behaviour of the elastomeric O-ring seal of the pressure vessel cap. After a CO₂ gas pressurisation-depressurisation cycle the seal was found to be swollen and removal of the pressure vessel cap immediately

after the experiment was difficult. The sealing performance also deteriorated after a number of similar experiments. Frequent replacement of the seal was therefore necessary.

8.3 OPTICAL METHODS

The sectioning of the explosively decompressed silicone elastomer specimens revealed the pattern and the orientation of the internal cracks; Figure 8.3. The transparent silicone elastomer readily underwent crack healing and the fracture lines disappeared and were not detected easily. In order to highlight the cracks they were impregnated with a black ink. It is noted that all the silicone elastomer test specimens have two distinctly different types of cracks. The larger and axially symmetrical cracks form surfaces of approximately the same shape as the specimen but of a smaller dimension. In the cylindrical samples they are axially symmetrical and circular in nature. A similar crack pattern has been observed by Briscoe *et al* (1986) and George (1984). In addition, relatively smaller and randomly oriented internal cracks are also visible in the matrices; Figure 8.3.

The presence of these two types of cracks can be explained by the help of the gas induced rupture model proposed recently by Liatsis (1989). In this model an elastomeric specimen saturated with high pressure gas is regarded as a 'pressure vessel' during rapid ambient pressure release. In this situation, two types of stress fields are assumed to act on the system simultaneously. The first is generated by the overall triaxial expansion of the specimen that occurs due to the negative hydrostatic pressure produced inside the test piece. The second type of stress field is generated due to the internal pressure profiles developed during gas desorption. The outer regions of the specimen desorb gas more rapidly than the interior. They are in a state of tension relative to the inner parts. Shear stresses are generated between the two regions which lead to the formation of large circumferential

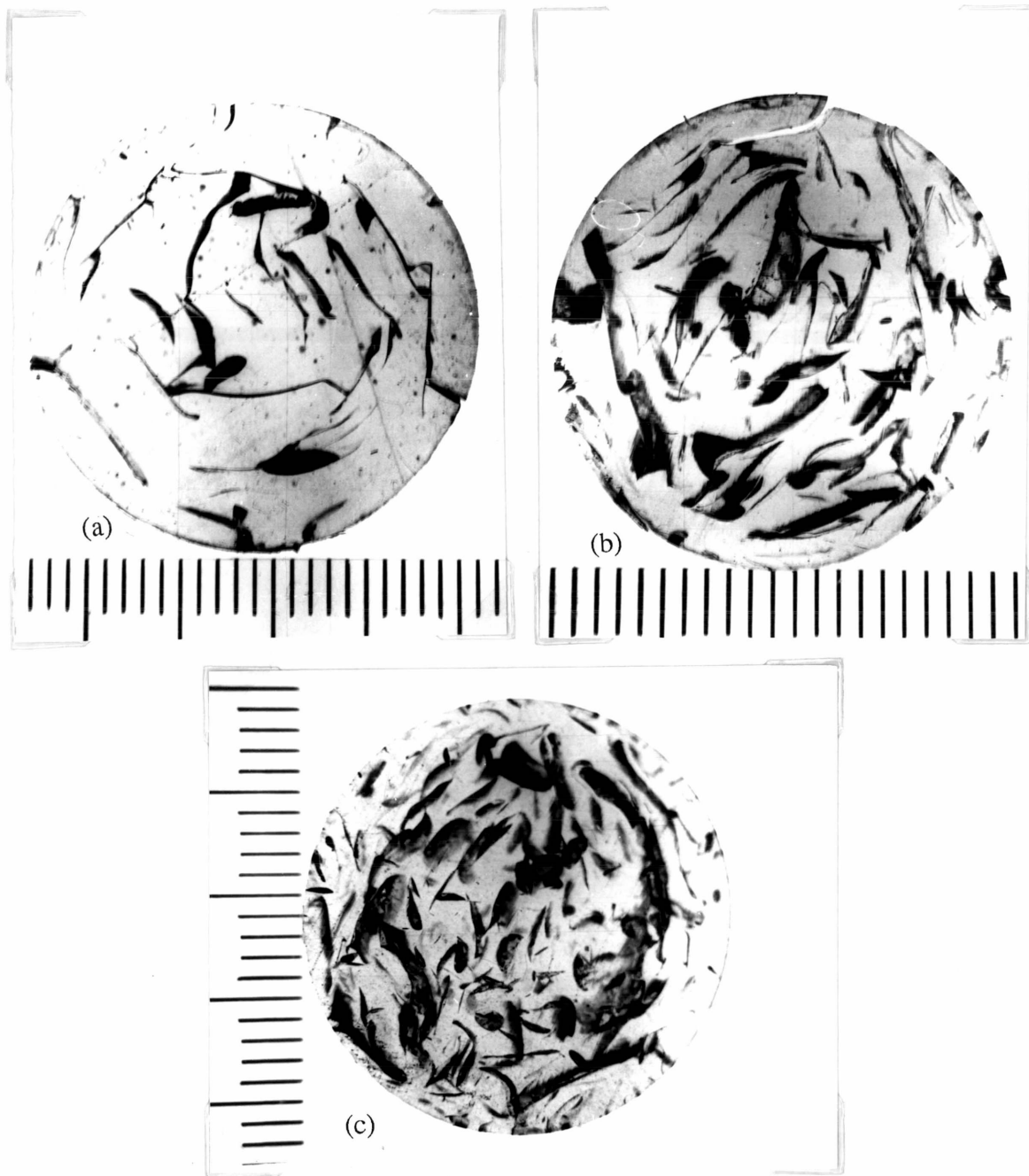
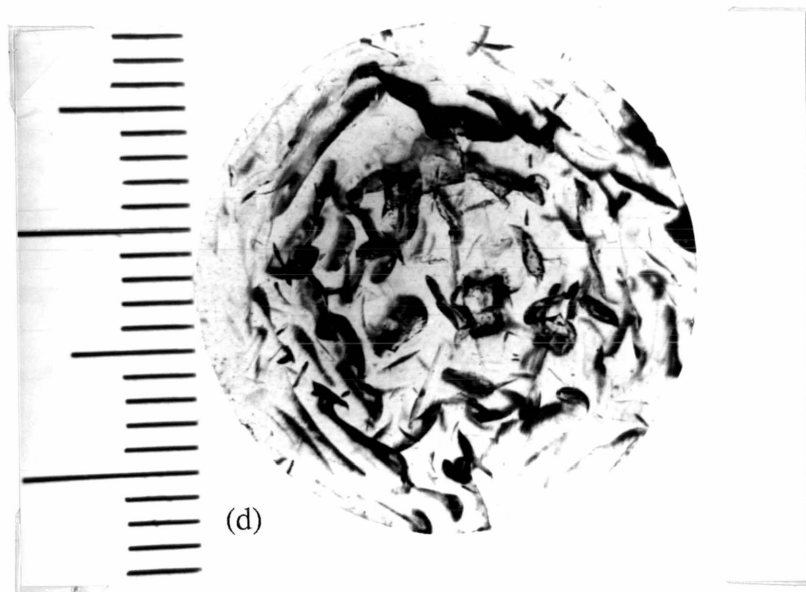


Figure 8.3: Cross section of the CO₂ gas damaged specimens; (a), unfilled; (b), untreated filler; (c), release agent treated filler; (d), silated filler; (e), primered filler.



internal cracks. The smaller randomly oriented cracks are produced by the relatively uniform triaxial expansion of the specimen.

8.3.1 Effect of Ambient Gas on Internal Rupture

A distinct difference has been observed between the specimens damaged by the CO₂ gas and the N₂ gas. The silicone elastomer specimens, with or without the glass beads, disrupted with the N₂ gas seem to have foamed. There were a large number of small cracks in the elastic solids and it was difficult to distinguish amongst them on the basis of crack size and number, Figures 8.4 a, b. However, the various silicone elastomer composites damaged by the CO₂ gas could be differentiated on this basis. The solubility of CO₂ gas in the elastomer is seven times greater than that of the N₂ gas (Chapter 5). Therefore, during decompression there is a larger flux of the absorbed CO₂ leaving the specimen than in the case of the absorbed N₂ gas. Sekhar and Van Der Hoff (1971) observed that the degree of dewetting/cavitation in filled elastomers increases with the solubility of the absorbed gases. Similarly, Villamizar and Han (1978), while studying foaming of liquid polymers, found that excessive amounts of the blowing agent brought about coalescence of small bubbles and gave rise to a small number of large bubbles. They also observed while considering CO₂ and N₂ gases as blowing agents that with the N₂ gas, the distribution of bubble size was more uniform. Gent and Tompkins (1969a) have reported that with less soluble gases the rate of bubble growth in an elastomer is slower than that with more highly soluble gases. Probably for these reasons N₂ gas is popular as a foaming agent for polymers (Hobbs 1975, Chanda and Roy 1987). The high pressure dissolved CO₂ gas also plasticises the silicone elastomer in contrast to the N₂ gas where the modulus has been detected to increase (Chapter 7). These factors will also influence the fracture response of the specimens during the explosive decompression with these gases.

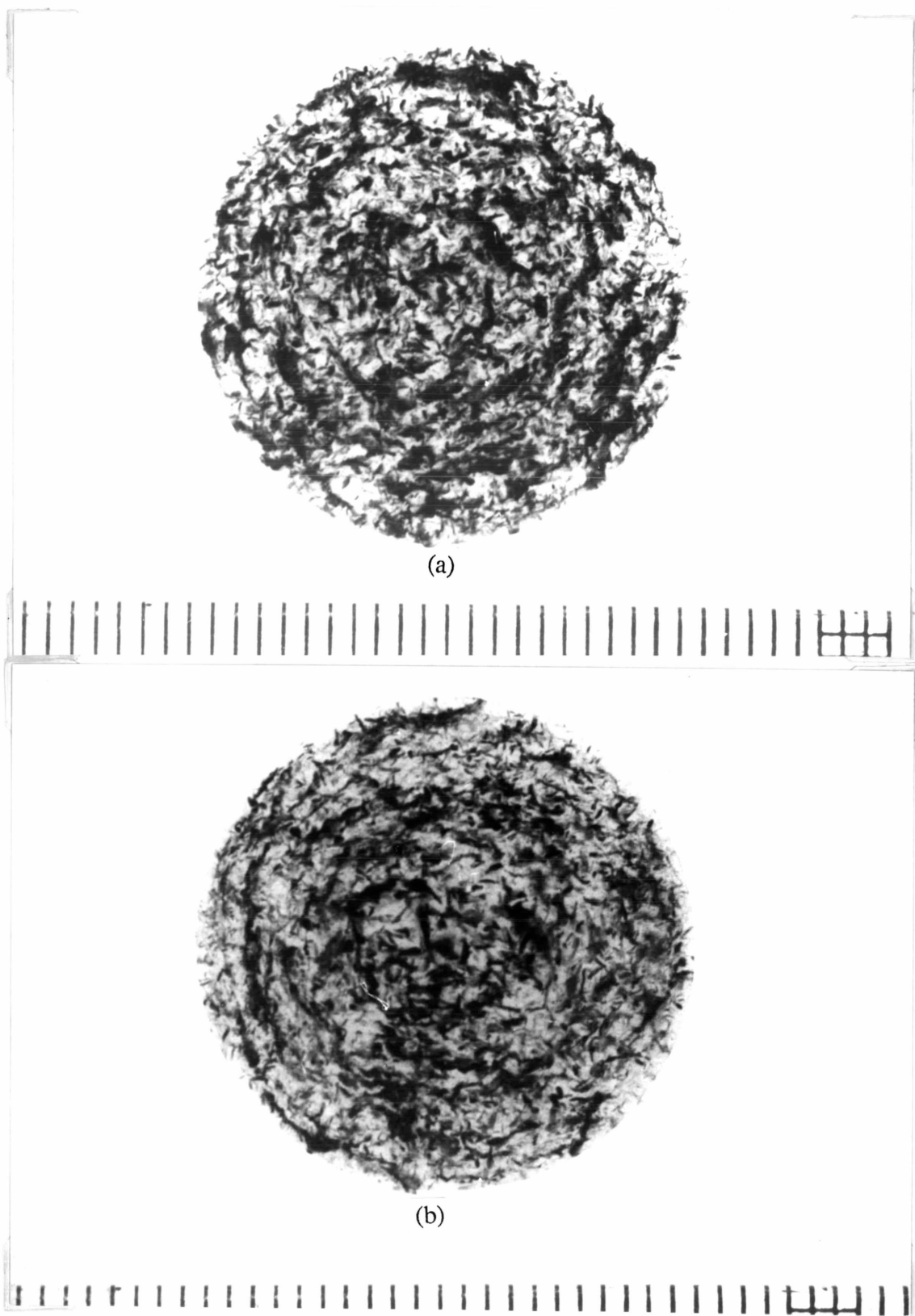


Figure 8.4: Cross section of the N_2 gas damage specimen; (a), unfilled; (b), filled (0.5%).

These data, and also the observations made in this study, indicate that the crack growth will be more catastrophic in a plasticised material. Olf and Peterlin (1975) have studied the crazing behaviour of polypropylene in various gaseous environments. It was proposed that gas adsorption resulted in a reduction in the polymer surface energy and consequently made the system more susceptible to the cracking process.

The lateral depth of the internal cracks from the specimen surface is related to the saturation time and the ambient gas pressure. Longer saturation times cause the cracks to occur over larger regions of the elastomeric specimen. A cross-section from the middle of a N₂ gas damaged silicone elastomer specimen that was allowed to equilibrate for only ca. 15 minutes is shown in Figure 8.5. It suggests that the diffusing gas had penetrated up to the point where the cracks stopped. A coherent core remains. A saturation time of ca. 3 hours was found to be sufficient for the penetrating gas to completely saturate the ca. 25 x 25 mm cylindrical silicone elastomer specimen and a more general disruption of the sample was observed.

The number of cracks, the mean crack lengths and the percentage area of the cracks in different CO₂ gas damaged silicone elastomer specimens are given in Table 8.1. The large axially symmetrical cracks were mainly oriented in circumferential planes normal to the axis of the cylindrical specimens. Therefore, they did not produce large crack-area contributions in the visual analysis. The smaller randomly oriented cracks made proportionally larger contributions. The specimen with no filler particles have the smallest number of cracks (Figure 8.3a) and also have the lowest crack area in the cross-section. In the absence of the filler particles the mean crack length is comparatively large. The most notable shift with the addition of the filler particles is that, irrespective of the matrix-filler interface quality, there is an increase in the number of cracks observed. The second generalisation drawn from Table 8.1, is that the strong interface systems show a significantly greater crack area than the unfilled and weak interface systems. It may

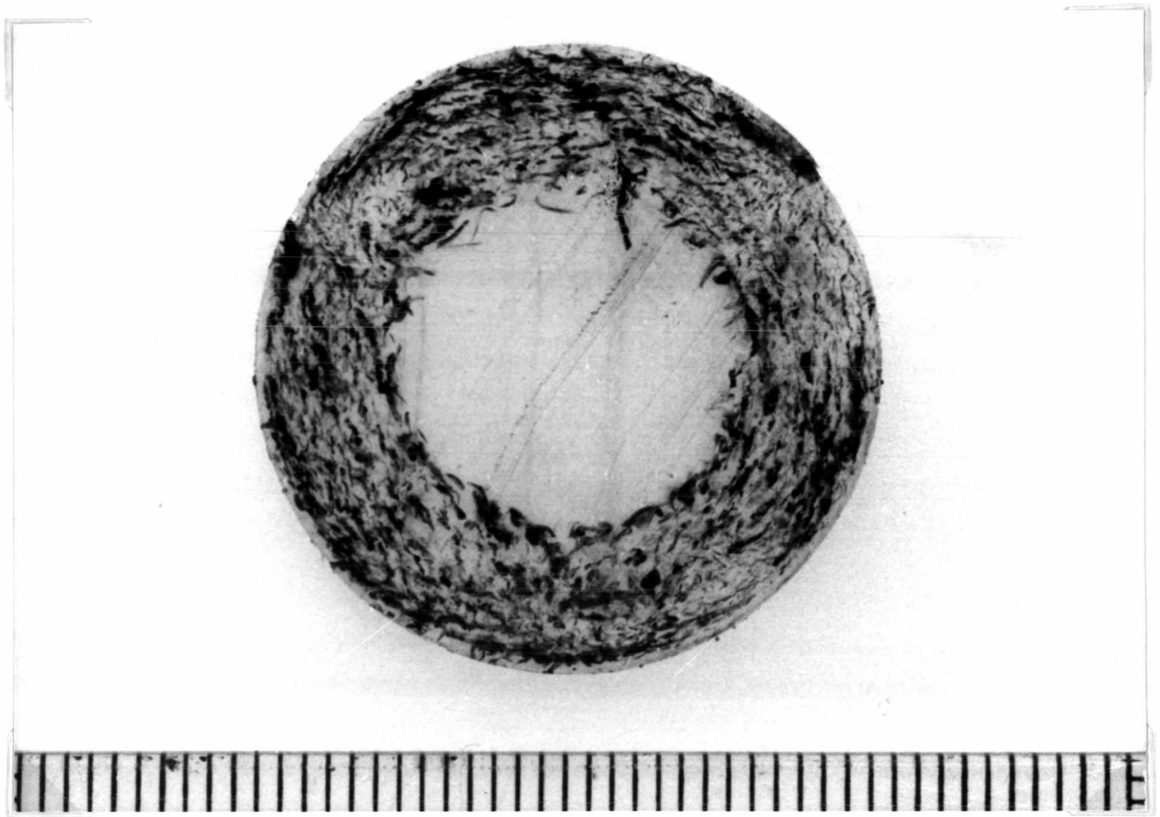


Figure 8.5: Lateral depth of the N_2 gas induced internal rupture (saturation time 15 min).

Specimen Type	% Crack Area	Crack Number	Mean Crack Length (mm)
Clear	8.5	79	10.5
Clean Filler	18.4	146	7.0
Release	25.0	255	6.0
Silated	28.0	207	3.0
Primered	30.0	128	3.0

Table 8.1: Optical assesment of damage in the various silicone elastomer specimens after carbon dioxide decompression.

be concluded that the strong interfaces produce crack patterns with a greater range of orientation in the specimen. The presence of rigid inclusions increase the capacity of the system for energy dissipation by inducing multiple and randomly oriented internal failures. They prevent individual cracks from becoming unstable and growing catastrophically.

In the nitrile rubber specimens subjected to the CO₂ gas decompressions only circumferential ring cracks are detected in the cross-sections; Figure 8.6. No internal rupture was observed with N₂ gas. However, the PTFE specimens remained unaffected in both the cases. The solubility of N₂ gas in nitrile rubber and PTFE is comparatively low. These polymers also have higher hardness and moduli than the silicone elastomer which may make them more resistant to explosive decompression damage.

8.3.2 Microscopic Study of the Internal Rupture

A closer examination of the cracks in the various transparent silicone elastomer specimens with low filler concentrations revealed the interfacial and the cohesive nature of the damage. It is observed that in the system where the glass beads were coated with the release agent and the internal interfaces were weak the failure mode is interfacial; Figure 8.7. This was not the case when the fillers were treated with the commercial adhesion promoter and the interfaces were strong. The internal interfaces with the clean unmodified filler particles did not arrest crack growth and were debonded when they intercept an approaching crack; Figure 8.8. These filler particles sometimes also appeared to dewet and initiate a crack. The criteria for adhesive failure proposed by Gent (1980) suggests that in the silicone elastomer specimens containing rigid inclusions, the possible mode of rupture is cohesive even when the filler particles are treated with the release agent (Appendix). The possible explanation for a behaviour contrary to the criterion mentioned



Figure 8.6: Typical ring cracks in the cross section of CO₂ gas damaged nitrile rubber.

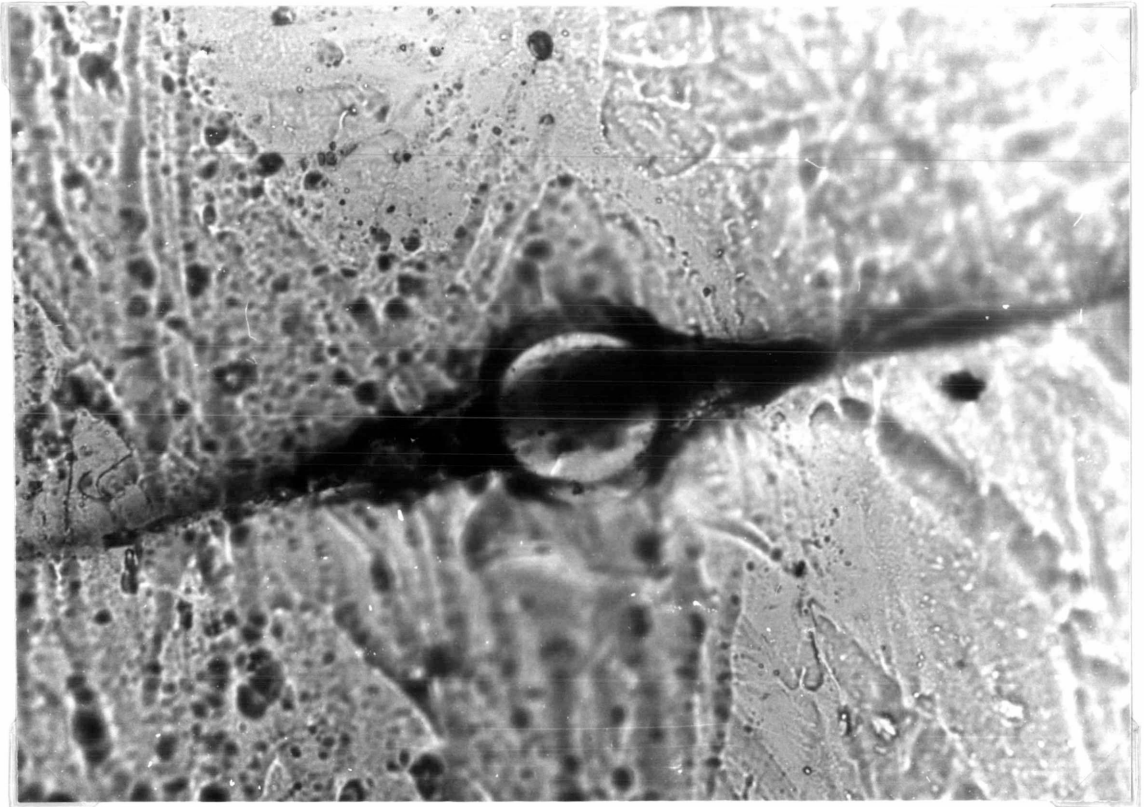


Figure 8.7: Internal crack initiated from a release agent coated filler particle.

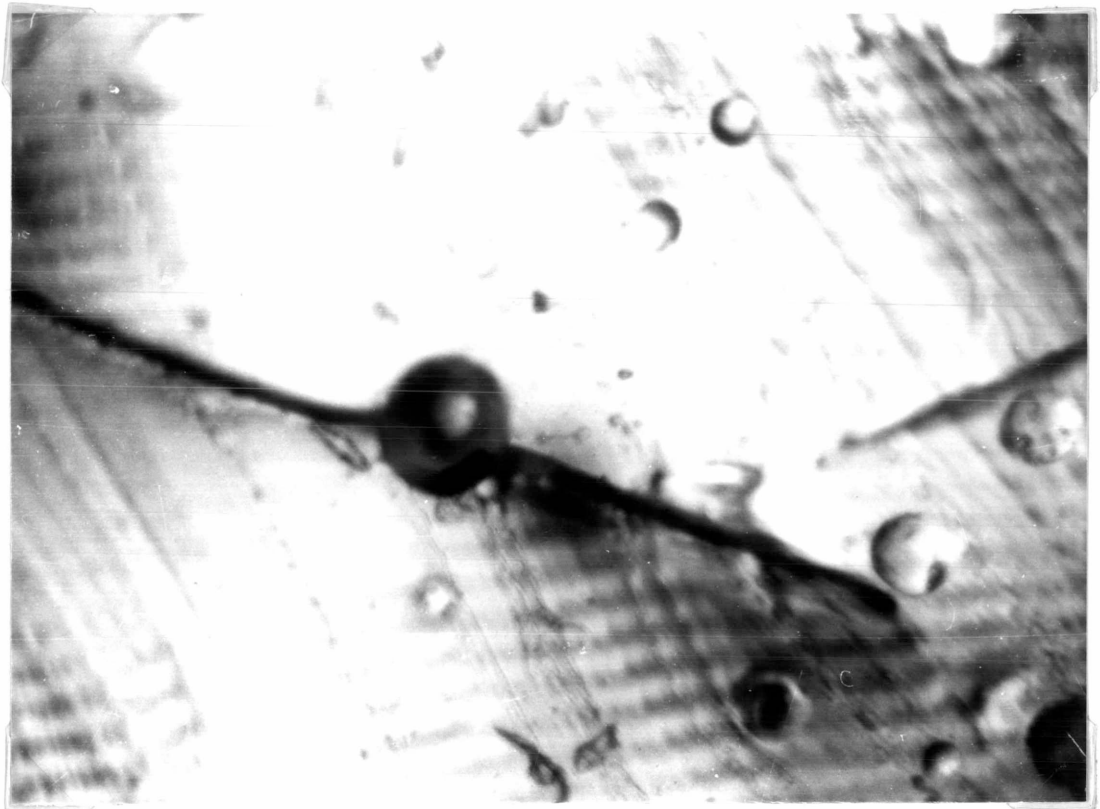


Figure 8.8: Interfacial rupture of an internal untreated interface.

above may be advanced by noting that the high pressure CO₂ gas, is absorbed in a significantly large quantity in the elastomeric matrix. The absorbed gas is thus able to penetrate the weak interfaces and reside between the filler particles and the matrix. It has been observed that the normalised amount of the absorbed gas in the composite silicone elastomer specimens with weak internal interfaces is higher than the unfilled specimen. The details of this effect have been discussed in Chapter 5. Hence the presence of the CO₂ gas may have weakened the interfaces further and the adhesive strength is lowered below the cohesive strength of the matrix. Oberth and Bruenner (1965) have detected that a solvent penetrant was able to dewet weak interfaces in a particulate composite while the strong interfaces remained intact. Thus during the decompression vacuoles are formed around the filler particles by the expansion of the gas present at the interfaces. These vacuoles inflate into the matrix and generate new surfaces. This process relieves the large negative triaxial stresses acting on the specimen. It probably also facilitates rapid desorption of the gas present in the matrix by short circuit diffusion and prevents unstable crack growth. In the specimen with the release agent coated fillers the particles are mostly detected at the centre of the crack; Figure 8.7. The wedge shape of the crack, on either side of the filler particle, indicates that the particle is the nucleating site for the fracture. In this system, although the number of cracks are the maximum, the individual sizes are relatively small; Figure 8.3(c).

The appearance of the system with stronger internal interfaces is consistent with no matrix-filler dewetting during decompression. The strong interfaces either arrest the cohesive crack growth or change its direction; Figure 8.9. The modified filler surfaces form strong adhesive bonds with the matrix which result in tougher layers of polymer around the filler particles. The high pressure gas seems to be unable to penetrate and corrupt the interfaces. This view is substantiated by the observation that the normalised amount of the absorbed gas in the system with strong interfaces is lower than that taken up by the unfilled specimen (Chapter 5).

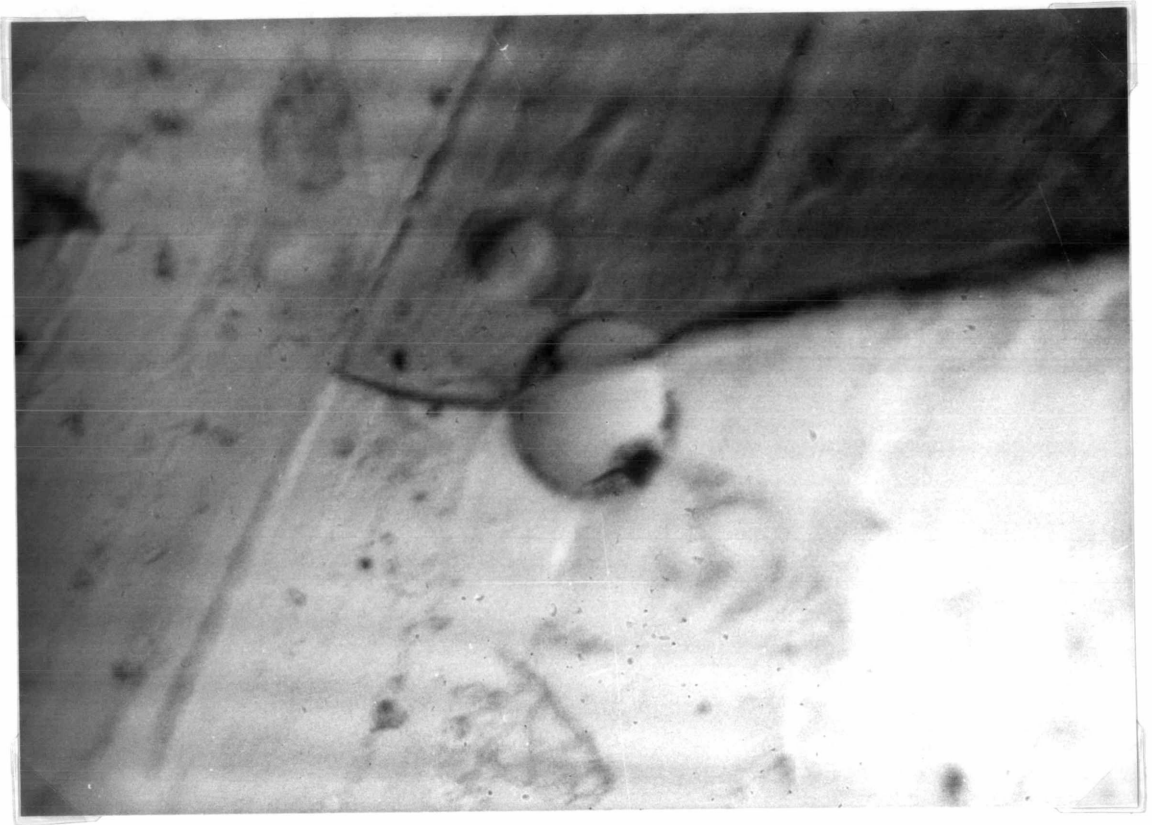


Figure 8.9: Crack arrested at a strong internal interface.

During the decompression the matrix remains attached to the filler particles and cavitation of the matrix occurs. A SEM photograph of a strong interface with a cohesive crack in its vicinity is shown in Figure 8.10a. Another SEM micrograph; Figure 10b, shows a broken filler particle in the path of a propagating crack. The glass bead might have broken during the explosive decompression or while sectioning of the specimen; in either case it indicates that the strong interface between the primer coated filler particle and the silicone elastomer matrix remains intact even under the extreme stresses that were sufficient to break the glass bead. The estimated number of cracks in this system are low; Table 8.1.

Model interfaces between the silicone elastomer and the surface modified sheets of glass were also explosively decompressed with CO₂ gas. It is observed that the elastomer detached cleanly from the untreated glass substrate; Figure 8.11a, whilst in the case of the strong, primered interface, the elastomeric layer did not detach. A large cohesive crack occurred in the matrix adjacent to the interface; Figure 8.11b.

The microscopic examination of the N₂ gas damaged cross-sections revealed that the internal cracks in all the silicone elastomer composites were cohesive in nature. As mentioned earlier, the amount of N₂ gas absorbed in the silicone elastomer is considerably less than CO₂ gas (ca. 7 times). The presence of filler particles, even with weak interfaces, did not augment the normalised gas absorption (Chapter 5). Hence, the interfaces are apparently not corrupted by this gas. During the explosive decompression the cracks did not nucleate from the interfaces and only matrix cavitation occurred.

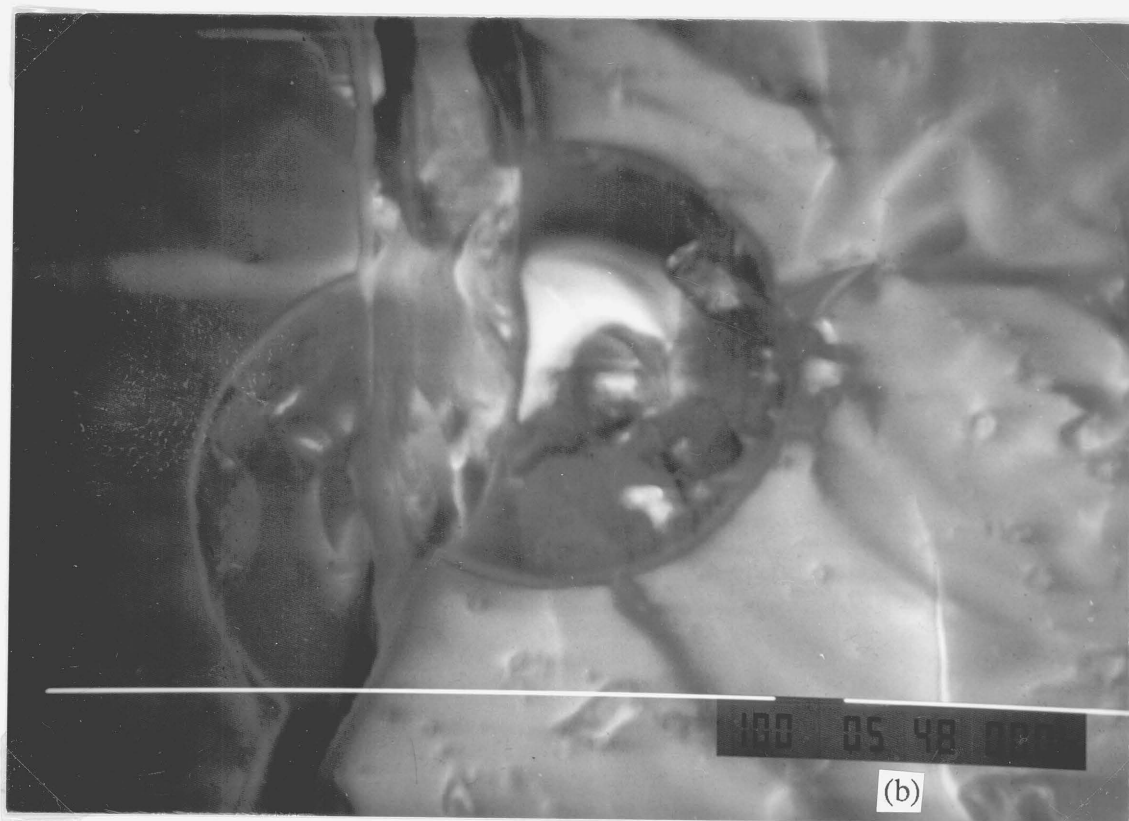
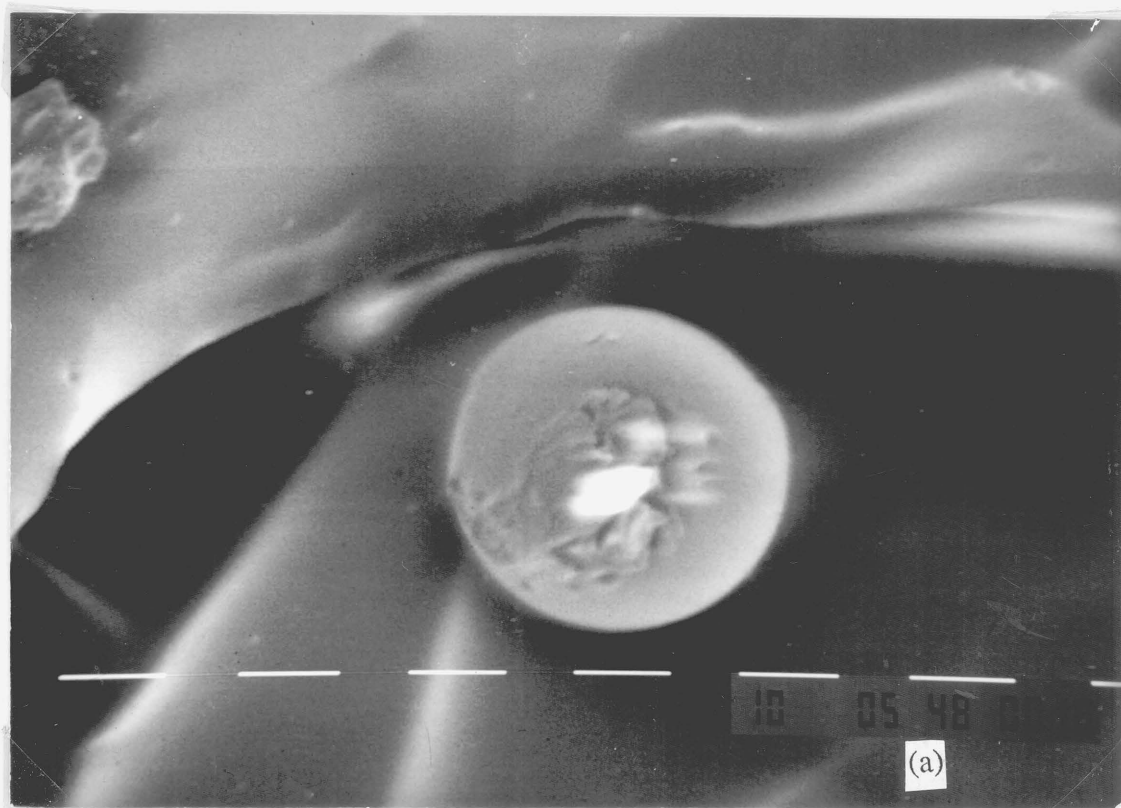


Figure 8.10: SEM micrograph of internal interfaces treated with the adhesion promoter; (a), cohesive rupture of the matrix; (b), broken glass bead in the crack path.

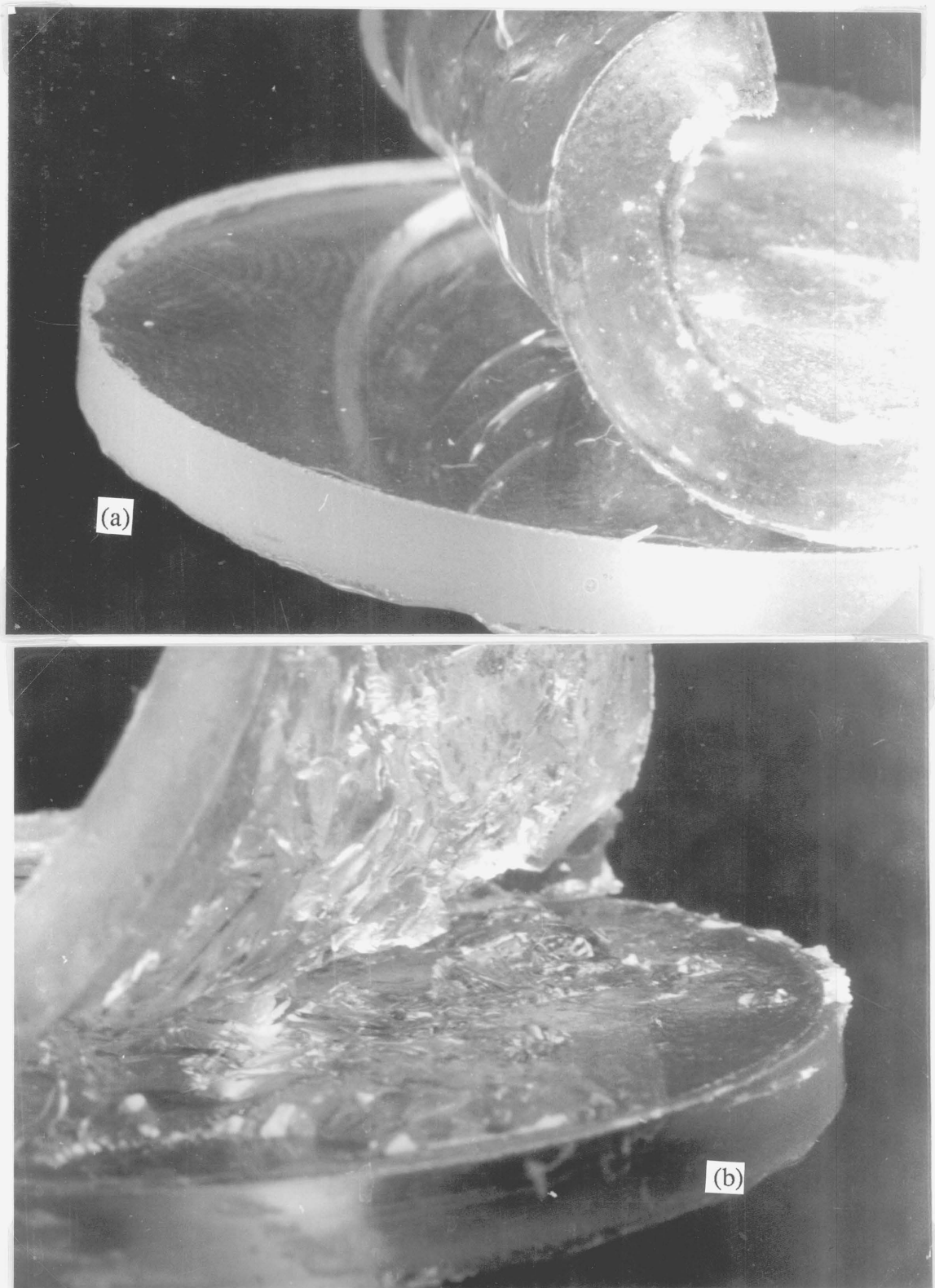


Figure 8.11: Model silicone elastomer-glass interfaces; (a), interfacial failure for the weak interface; (b), Cohesive failure for the strong interface.

8.4 MECHANICAL PROPERTIES OF THE DAMAGED SPECIMENS

8.4.1 Diametric Compression

A number of mechanical methods have been used to quantify the extent of the overall gas induced damage produced in the various silicone elastomer specimens. The general sensitivity of the different systems to explosive decompression damage incited by the CO₂ and the N₂ gases is apparent from Figures 8.12 a, b. The compressive stress against diametric strain for the various specimens with an aspect ratio of ca. 1 is presented. The reference specimen of an undamaged silicone elastomer shows the elastic response of a crack-free matrix under similar conditions. The diametric compression produces a range of compressive and tensile stress fields in the elastomeric specimens. The compressive load is seen to increase nonlinearly with the decrease in specimen thickness. This is because the area under the load increases. Lindley (1966) proposed that for a cylindrical specimen of diameter 'd' and at a deformation 'x', the load is carried by a rectangular cross-section, ABCD, of the sample; Figure 8.13. The load is applied to the two parallel sides of varying breadth 'b'. The increasing width of the load bearing area can be approximated by using the following expression:

$$x = d (1 - \cos \theta) \quad (8.1)$$

where 'θ' is the angle corresponding to the changing width of the load bearing sides. The reduction in stiffness for the CO₂ gas damaged specimens, relative to the undamaged matrix, is apparent even at low values of strain. The differences between the two reflect the extent of the internal damage. A more succinct ranking is provided by Figure 8.14, where the stress differences, referred to the undamaged sample, are plotted against the imposed strains. The form of the plots are similar

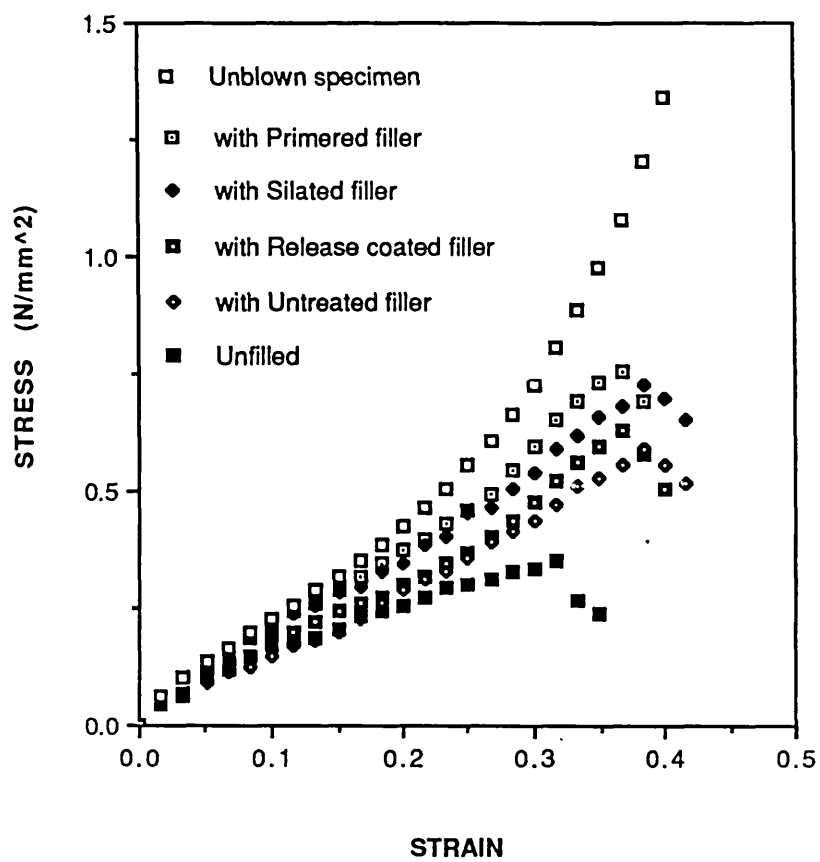


Figure 8.12a: Stress as a function of diametric strain for the various CO₂ gas damaged silicone elastomer specimens.

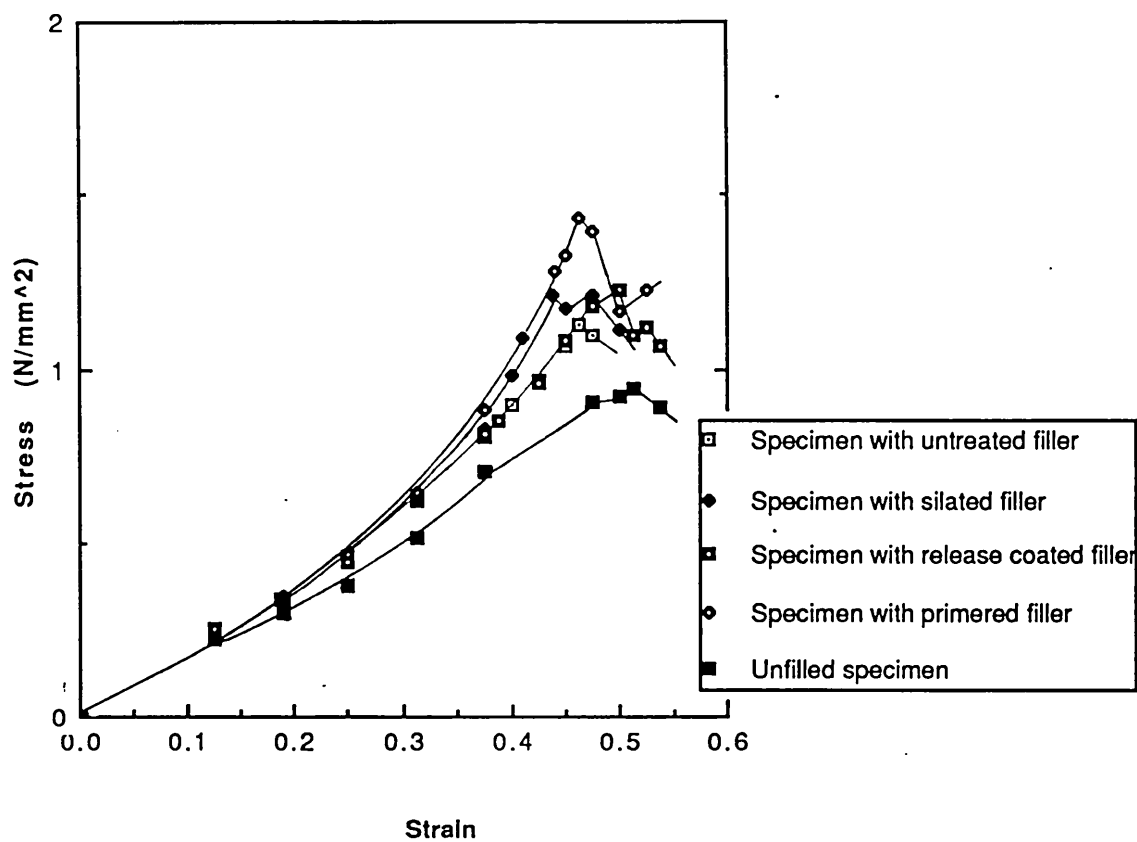


Figure 8.12b: Stress as a function of diametric strain for the various N_2 gas damaged silicone elastomer specimens.

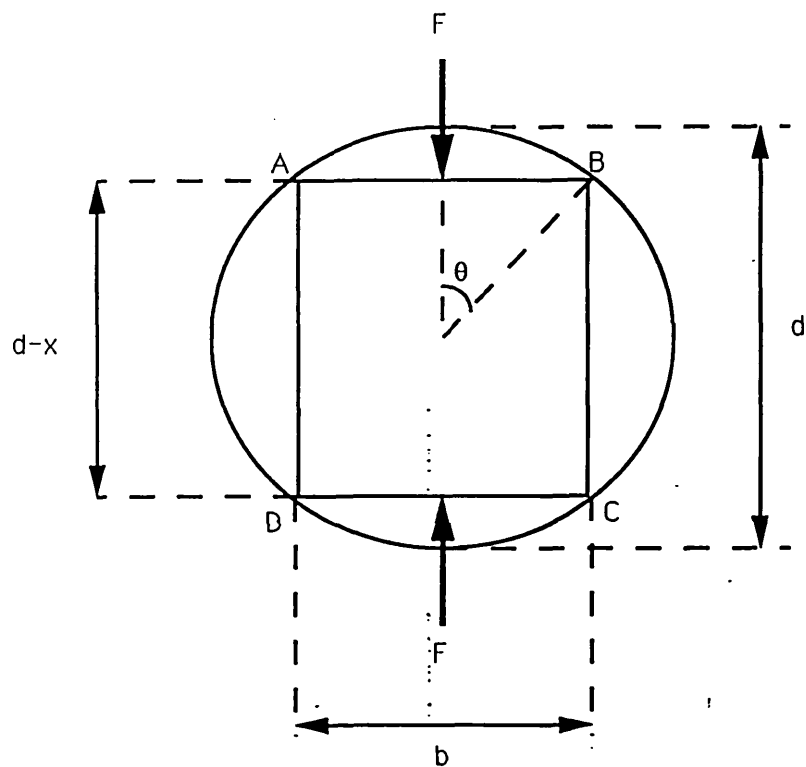


Figure 8.13: Cross section of a cylindrical specimen. The rectangle ABCD is the shape assumed for the rubber carrying the load (Lindley, 1966).

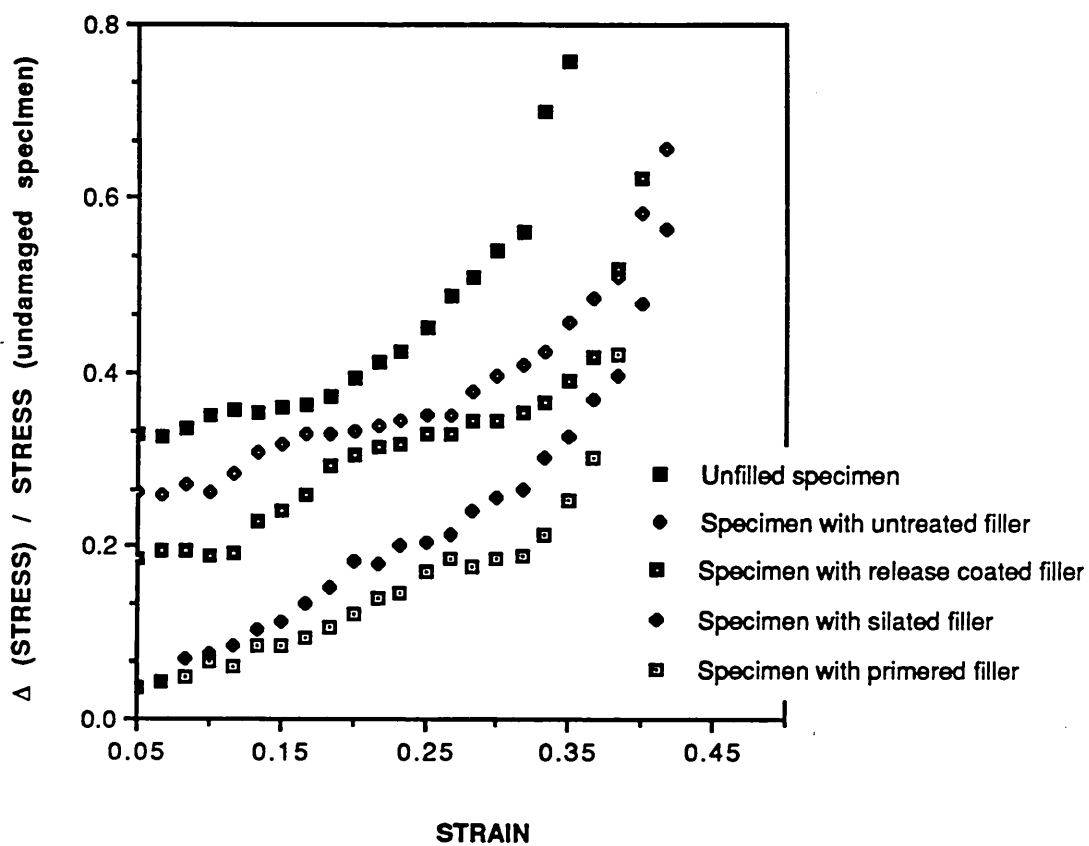


Figure 8.14: Normalised stress as a function of diametric strain for the various CO₂ gas damaged silicone elastomer specimens.

for each sample although the absolute values of the normalised stress difference, at a given strain, are dissimilar. Table 8.2 gives the values of the normalised stress differences at 20% strain. Table 8.3 gives the fracture energy values for model interfaces at an arbitrarily chosen crack velocity of $0.2 \text{ m}\cdot\text{s}^{-1}$. Comparison of these two tables shows a reasonably good correlation between the loss of stiffness in the CO_2 gas damaged specimens and the inverse of the interface quality.

As mentioned earlier, the N_2 gas induced damage was characteristically different from that instigated by the CO_2 gas decompression. The mechanical response of the two sets of specimens is also different. All the N_2 gas damaged silicone elastomer composites follow the a similar stress-strain curve for diametric strains of up to ca. 20%; Figure 8.12b. At higher strains the difference in their response becomes evident. The trends for the stresses, in the various samples at a given strain of say 40% again scales with the inverse of the interface quality. However, the unfilled damaged specimen is more compliant throughout than all the other specimens.

The values of the yield stress and strain are found to be higher for the N_2 gas damaged systems than for the CO_2 gas disrupted specimens; Figure 8.12 a, b. Also, the N_2 gas damaged specimens did not simply fracture and split into pieces. The smaller internal cracks appear to grow in steps and joint together to relieve the stored strain energy. Further crack propagation is resisted until higher values of strain. Thus, the yielding of the specimens seem to follow a stick-slip process and therefore the stress-strain curves are irregular in the yield region (Figure 8.12b). In the case of the CO_2 gas damaged specimens the internal crack growth is more catastrophic at the yield points; Figure 8.12a. The internal lacerations extended to split the specimens. It is observed that the broken surfaces are smoother, unlike those for the N_2 gas disrupted specimens; Figure 8.15 a, b. In the latter case, the surfaces are rough, manifesting the presence of smaller internal cracks that had joined together to produce this surface. The surface gave

Specimen Type	Normalised Stress
Clear	0.4
Untreated	0.32
Release	0.3
Silated	0.18
Primered	0.12

Table 8.2: Normalised stress at 20% diametric strain for the various carbon dioxide gas damaged specimens.

Specimen Type	Fracture Energy (J/m ²)
Release	6.5
Untreated	8.5
Silated	12.8
Primered	72.0

Table 8.3: Interfacial fracture energy at a crack velocity of 0.2m/s

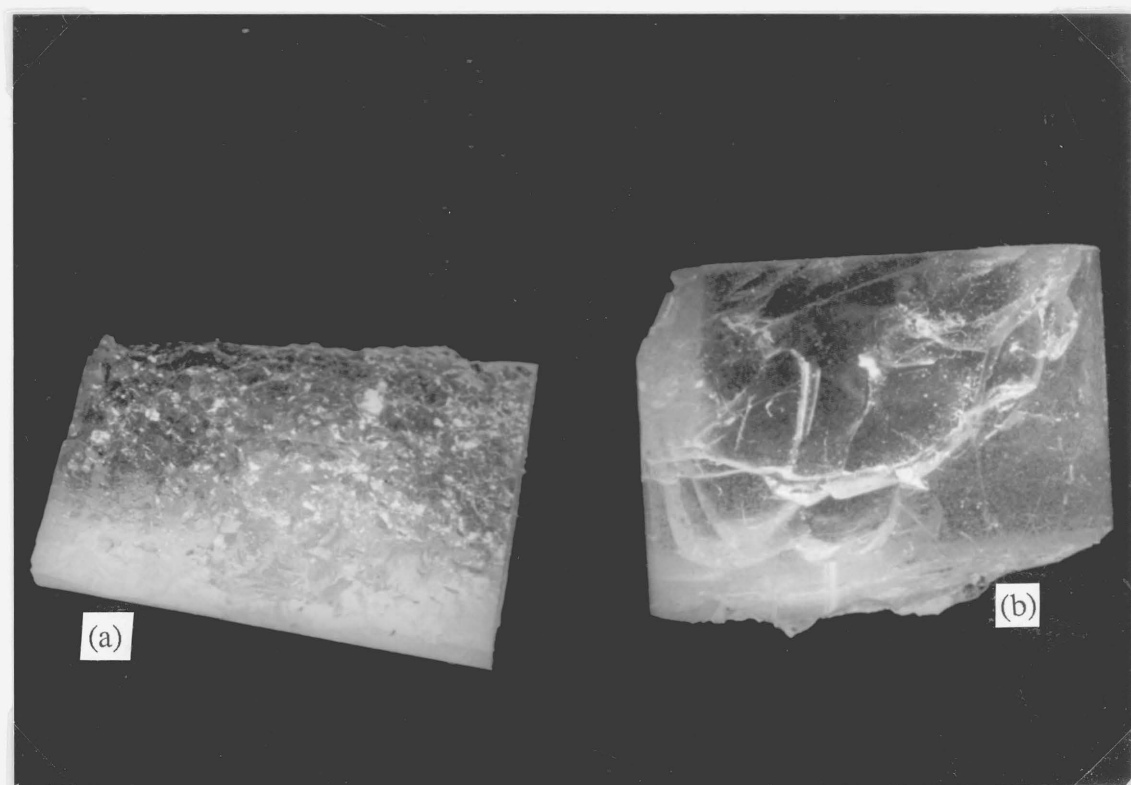


Figure 8.15: Surface of internal cracks for the silicone elastomer; (a), N_2 gas damaged; (b), CO_2 gas damaged.

the appearance of a torn-out section of a closed cell foam.

8.4.2 Cyclic Diametric Compression

The behaviours of the various test samples subjected to cyclic diametric strains are given in Figures 8.16 a, b. The data indicate the extent of the additional crack growth in cyclic loading. The N₂ gas damaged specimens only appear to be effected during the first few 30% compression cycles, when the load requirement decreases. The specimens become rather insensitive to subsequent deformations. In the case of the CO₂ gas damaged specimens, two systems appear to be impassive to additional crack growth; the specimen with strong internal interfaces and the unfilled system. These samples have the least number of cracks; Table 8.1. The fatigue sensitivity actually scales quite well with the observed number of cracks. The specimen with the release agent coated filler particles is most fatigue sensitive and it has the highest crack population.

8.4.3 Dynamic Mechanical Testing

The dynamic mechanical testing of the various CO₂ gas damaged specimens was performed over a range of temperatures, whilst maintaining the straining frequency constant. The loss angle as a function of temperature is given in Figure 8.17. The cyclic strain opens and closes the cracks and the additional viscoelastic loss seems to be associated with the dissipation energy consumed in peeling the internal cracks and friction between the crack faces. The magnitude of this work is related to the total crack area and the geometric disposition of the cracks. The crack area is a function of both the total crack number in the test specimen and their length. The large axially symmetrical cracks will be most active. It has been speculated earlier that the axial crack symmetry is inversely related to the

crack area sensed in the axial plane of the specimen (projected axis area). The relationship observed between the magnitude of the measured loss and the inverse of the axially sensed crack area is consistent with this proposition. In Figure 8.17, the value of the viscoelastic loss is seen to decrease with an increase in the test temperature. This behaviour is due to the fact that with an increase in test temperature moduli of the cross-linked elastomers increase (Van Krevelen and Hoftyzer, 1976, p 278). In the course of these experiment it was observed that the loss modulus component of the complex modulus dropped significantly with an increase in temperature and the storage modulus component increased slightly over the temperature range investigated.

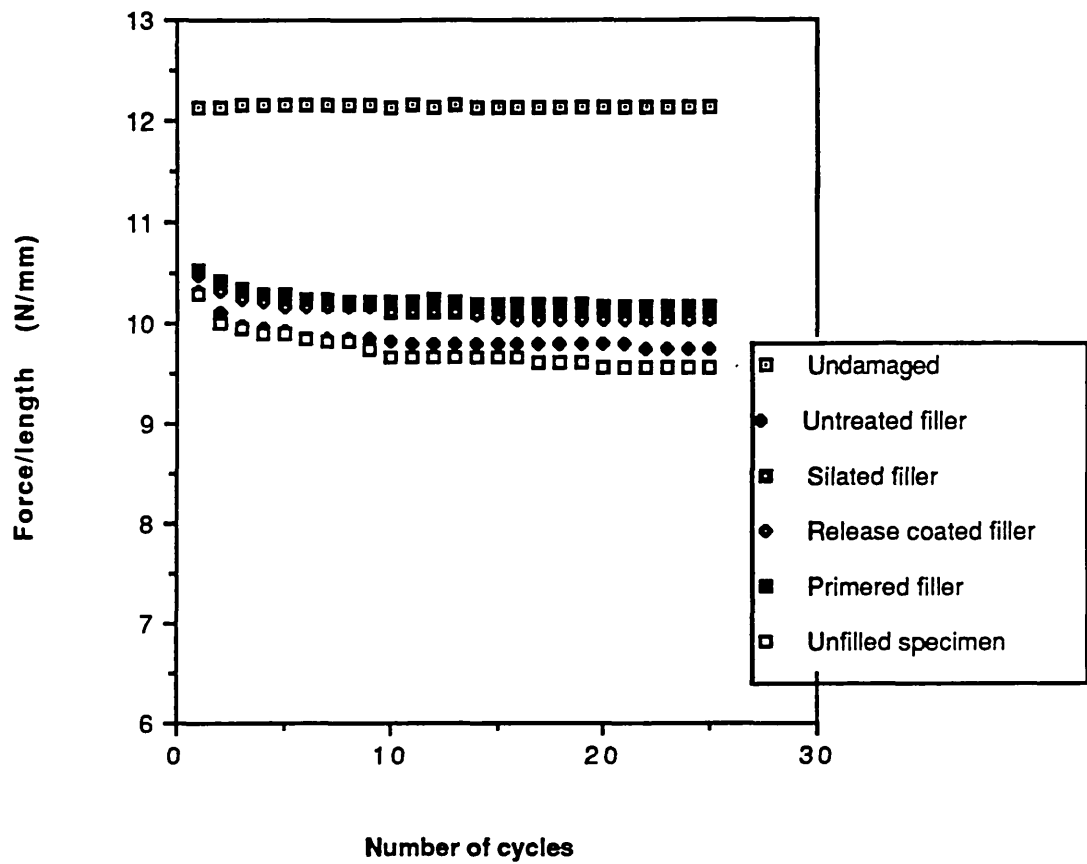


Figure 8.16a: The force requirement for 30% diametric strain for the various N₂ gas damaged silicone elastomer specimens as a function of cyclic loading.

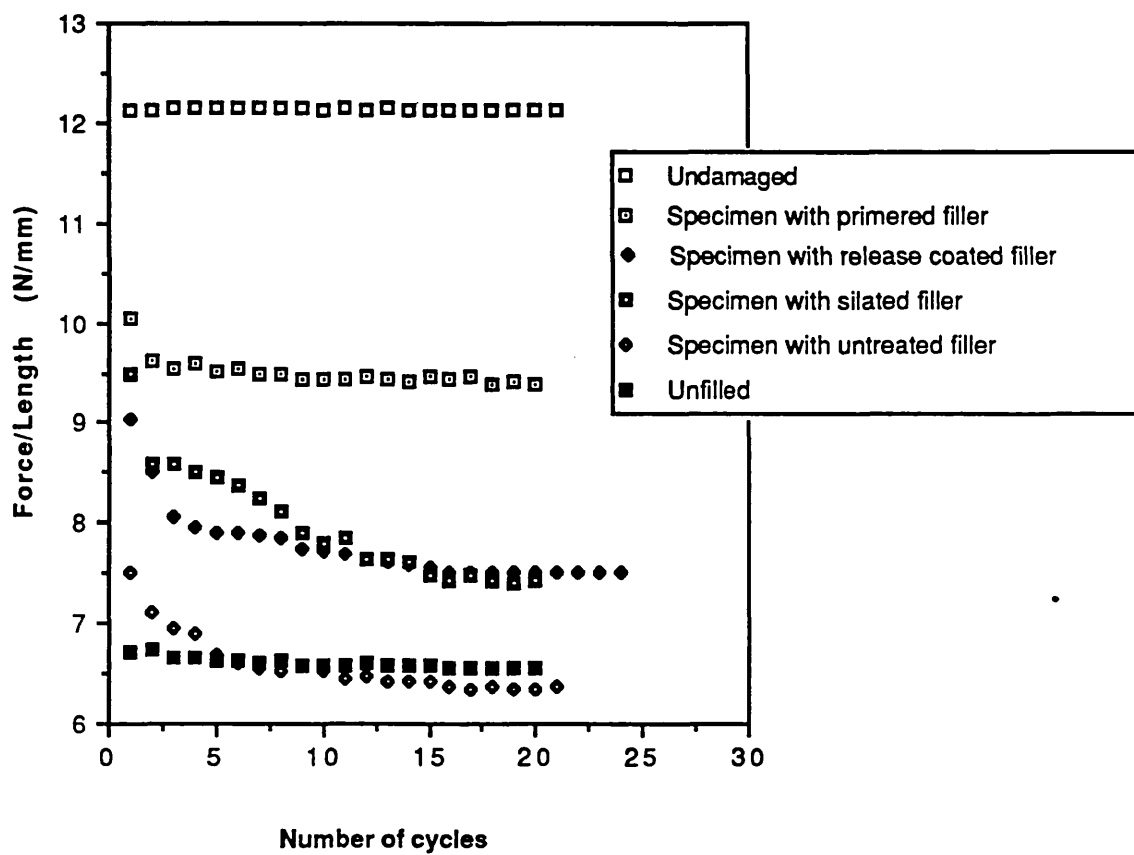


Figure 8.16b: The force requirement for 30% diametric strain for the various CO₂ gas damaged silicone elastomer specimens as a function of cyclic loading.

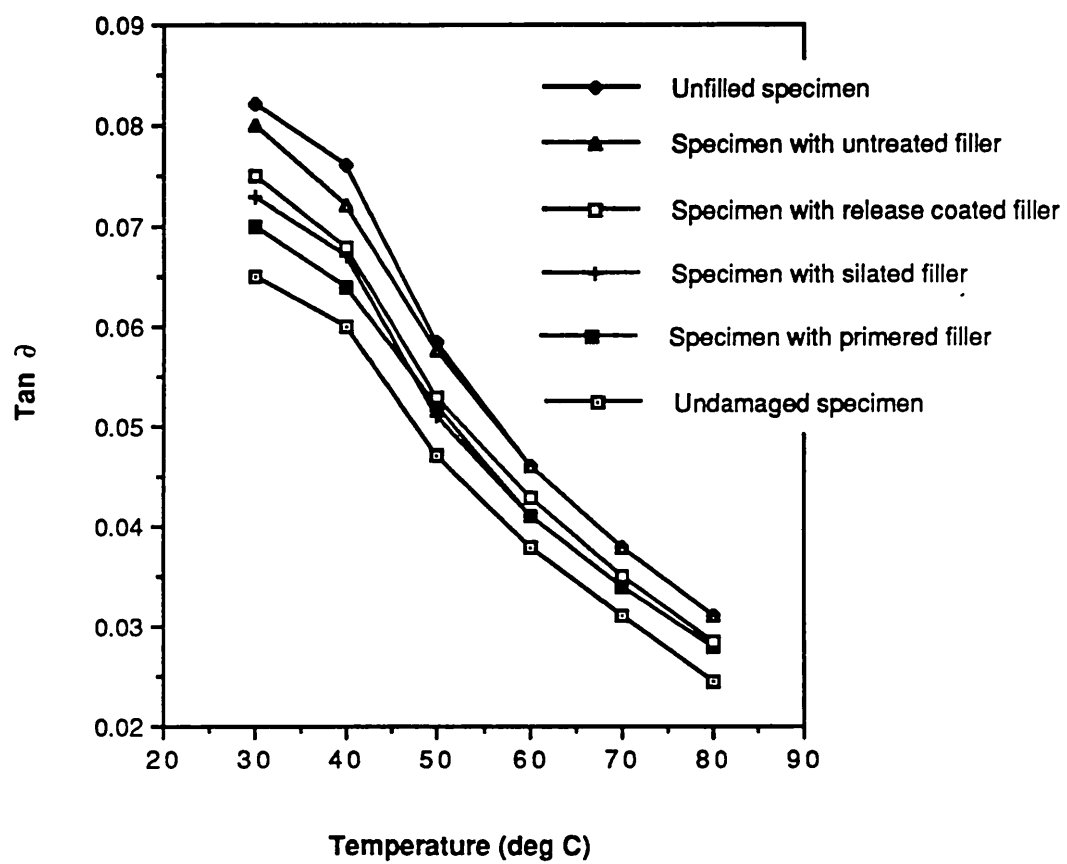


Figure 8.17: Loss Tangent for the various CO₂ gas damaged silicone elastomer specimens

8.5 CONCLUSIONS

The rapid release of the excess high pressure gas from the ambient of saturated elastomeric specimens resulted in internal rupture of the test pieces. In the silicone elastomer systems, generally, two types of cracks were observed; the large circular cracks which follow the circumference of the specimen and the randomly oriented smaller cracks in the bulk. The overall rupture induced by the explosive decompression of the different gases was peculiar. The damage produced by the N_2 gas was less pernicious than that incited by the CO_2 gas. The nitrile rubber specimens incurred no detectable damage after the rapid decompression of the former. However, the silicone elastomer test specimens appeared to have foamed with the occurrence of a large number of small internal cracks. The presence of filler particles in the elastomeric matrix in this case does not seem to effect the degree of damage. For the CO_2 gas decompression, the fillers significantly modified both the nature and the extent of the internal rupture. The rigid inclusions tended to suppress unstable crack growth. They not only decreased the mean crack size but also the crack number increased as did the randomness of the crack orientation. The effect of matrix-filler interfacial quality also played an important role in the failure mechanism. The weak interfaces were easily corrupted by the high pressure absorbed CO_2 gas. This promoted dewetting of the particles in the dynamic gas desorption stress fields and also the lesions acted as inflation centres. The strong matrix-particle interfaces remained adamant and led to cavitation failures in the elastomeric matrix away from the interfaces. The various mechanical tests that were performed also indicated the extent of damage. It was noted that the resistance to explosive decompression damage was improved by the introduction of filler particles. The coherence loss by the various composite specimens was inversely related to the matrix-filler interfacial quality.

CHAPTER NINE

CONCLUSIONS

This thesis has considered various aspects of the phenomena which result from the application of a pneumatic or hydrostatic stress to a polymeric matrix. Various stress transmission media have been investigated. In particular, two gaseous systems N_2 and CO_2 have been examined in great detail. In addition, a variety of experiments have been carried out using mercury to generate a purely triaxial stress field. The general conclusions are that whilst the hydrostatic stresses transmitted by mercury are purely compressive in nature, those produced by CO_2 gas induce an element of plasticisation and swelling of the chosen systems. In some respects N_2 gas represents an intermediate in these cases. These statements underline a subtle problem which requires detailed interpretation in the description of the responses of polymeric systems to hydrostatic stresses in particular those produced by gaseous media. In simple terms, an impermeable fluid such as mercury which has been used extensively in this study reduces the free volume of the matrix. In this case the polymer becomes compressed and as a result there will be associated changes in the mechanical and diffusive characteristics of the system. In contrast the systems under a gaseous stress field, such as that generated by CO_2 , will not only transmit, for reasons yet to be explained in detail, an effective triaxial stress of the sort transmitted by mercury but also because of the sorptive ability produce an internal pressure which will cause the system to swell. A gas such as

N_2 which has less affinity for the matrices studied in this work will actually, it seems, produce a response which is more similar to that produced by mercury than by CO_2 . The particular study described in this thesis has focussed on the behaviour of a silicone elastomer which has been filled to various extents with glass filler particles of varying interface quality. Additional data are provided for a nitrile rubber and a PTFE to exemplify their responses to the application of either a pure triaxial stress or a gaseous stress. The conclusions offered here mainly refer to the results of the study of the silicone elastomer system. The quality of the interface between the silicone elastomer matrix and the glass filler particles has been varied in a very deliberate way and characterised independently using a blister test. It has been possible to deduce, in detail, the role of interface quality on the way in which the various stress media have influenced a variety of responses of the polymeric matrices studied. This is particularly true of the responses caused by gaseous environments including CO_2 and N_2 .

The thesis has addressed two particular types of gas-polymer interactions. The significant part of the thesis has dealt with what may be usefully described as equilibrium characteristics. Data have been presented on the equilibrium mass sorption, the equilibrium volumetric strains and in addition certain parameters associated with the mechanical changes in the elastomers such as the modulus. The various changes have been investigated as a function of the interface quality created between the matrix and the filler particles. A related but entirely separate study has been made for the behaviour of these systems when the ambient pressure was rapidly reduced. The important features of these sorts of processes are the dimensional changes associated with the decreasing ambient pressure and also the generation of internal cracks and fissures during the release of the pneumatic stress fields. The later part of the thesis is devoted to describing the consequences of this type of decompression cycle upon the mechanical coherence of the specimens

studied. This part of the study has involved visual and mechanical characterisation of the damaged samples. A central theme in the interpretation of these dynamic data is the belief that the rupture is produced by the generation of hydrostatic tensile fields within the interior of these specimens during the decompression cycle.

An important part of the current study has been the development of a range of relatively novel experimental techniques to investigate the properties of the gas-polymer systems under high pressures using ultrasonic transducers. These transducers have not only enabled the characterisation of the equilibrium state to be deduced but also the behaviour of the systems during the transient conditions when the ambient pressure was reduced. These types of data have revealed the changes in the dimensions of the specimens at equilibrium and during the transient pressure conditions. They have also allowed the detection of the generation and development of internal flaws during the decompression cycle. In addition, the techniques have provided a measure of the acoustic modulus of the specimen at various stages during the pressurisation history. The same technique has allowed the tentative identification of what may be reasonably called a clustering phenomenon in the CO₂ gas-silicone elastomer system at high ambient pressure when the gas is in the supercritical state.

Before dealing in detail with the specific conclusions derived from this thesis, it is useful to bring forward the major inferences which are relevant to the description of the current study. First of all, it should be pointed out that none of the experimental data and the analysis which are offered here contradict those which are outlined in Chapters 2 and 3. In some cases it is clear that the general interpretation of the current data would be more reasonably described using one model rather than the other but there is no conflict in general terms. However, an important feature of the current work, it is believed, is based upon the study of the problem which is associated with the way that gases at high pressures influence the mass sorption and dilation behaviour of polymeric systems. The situation with the

silicone elastomer which has been extensively studied here is well developed. The central issue does seem to be the rather peculiar role of the ambient triaxial stress which produces a compressive stress and the dilational stress which is associated with the sorption phenomena. In the current work this has been examined in detail in the context of filled systems and in this way a number of new and interesting results emerge. The essence of the phenomena does seem to be the role of the hydrostatic pressure, either external or internal, upon the properties of the polymeric matrix. A unifying parameter which goes through the current work is the influence of the effective hydrostatic stress within the polymer created by the ambient and influenced by the interfaces in the composite material. The work carried out here and the precedents does seem to suggest that the presence of an interface within a composite will modify the hydrostatic fields which are generated by the external and internal stresses because of the resistive forces produced by the interface. This facet of the work was originally developed by Gent and others in a particular context and is very relevant in the present case. Much of the data presented here which describes the variation of the mass gas sorption and the volumetric changes as a function of the interface quality can be interpreted simply as being due to the constraining influences of the interfaces within the systems. Strong interfaces appear to inhibit volumetric changes and hence suppress gas mass sorption. The studies on thin layers of the elastomer confirm this idea. The interfacial constraints generated by the interfacial shear stresses effectively increase the stiffness of the matrix. It is not necessary to invoke the formation of 'special' polymer surface layers. This increase in stiffness prevents dilation and hence mass sorption. Weak interfaces on the other hand do not provide this constraint and what is more provide sites, in some circumstances, for additional gas mass sorption.

The present study has focused very much on the experimental study of the three parameters. These were the equilibrium mass sorption, the equilibrium volumetric changes and the inception and growth of cracks within the systems

during explosive decompression cycles. Data are also presented for the gross volumetric changes during the explosive decompression cycle. All of the data, with the exception of the mass sorption data, were accumulated by the use of the ultrasonic probes including the acoustic emission probes. It is believed that these probes do offer a unique opportunity to study the behaviour of polymers in high pressure gas environments. It is particularly noteworthy that the ultrasonic technique which is able to sense the linear strain as well as the attenuation of the signals was able to identify the crack initiation that certainly occurred at ca. 5% volumetric strain during the N₂ gas decompression. During the CO₂ gas depressurisation the formation of internal cracks/bubbles and their healing have also been detected. The same technique has also been able to distinguish between the behaviour of unfilled and filled systems of various interfacial qualities during various decompression ramps. The acoustic method also provides unique values of acoustic modulus and hence probably the Young's modulus of the system in high pressure gas environments. It will be recalled that in the case of the N₂ gas environment the modulus is a monotonic increasing function of pressure, whilst, for the CO₂ gas environment a substantial plasticisation is evident. The acoustic method also detected, tentatively, the CO₂ clustering phenomenon in the silicone systems. In the latter, the experimental evidence is consistent with this suggestion but must be substantiated by independent evidence. It is interesting to speculate that these cluster centres could also provide the sources of internal rupture within the specimens without resorting to the arguments that intrinsic flaws must be present to provide rupture centres.

The application of a pneumatic gas stress to a polymer invariably produces an increase in the gas mass sorption. The same stress, depending upon the extent of the sorption, will produce an overall volumetric strain in the system and hence the polymer is under a very peculiar state of stress. The polymer appears to be

suffering from a form of a triaxial stress similar to that produced by mercury for example but also an internal swelling stress similar to that produced by swelling solvents such as cyclohexane. The more it swells the more it will absorb, *vice versa*. CO₂ gas is a swelling solvent, it dilates the system and the sorption is large. N₂ gas swells the samples less and the sorption is also less. It has been found that at the higher pressures the CO₂ gas sorption is an order of ca. 7 greater than that of N₂ gas. In the former case the specimen dilation was 14 times more than that for the latter. It is likely that similar variations in the volumetric changes and the solubility will be found with other gaseous systems. In the broad generic terms, at low to moderate pressures, the mass sorption characteristics of the systems follow the sort of equivalence classically proposed by van Amerongen (1964) for the absorption of gases in liquids and in polymers. In this respect the silicone elastomers are merely crosslinked liquids.

Previously it was concluded that the presence of the internal interfaces, of various interfacial qualities, affects both the equilibrium volumetric changes and also the mass sorption. In simple interpretive terms, the presence of strong interfaces has been argued as inhibiting the swelling because of the interfacial constraints. If the swelling is constrained by the strongly bonded interfaces then the mass sorption is also reduced. If the interfaces are weak there is a prospect of vacuole formation and excess sorption at the interface is possible. This has been observed in the present work. Hence, there is no particular difficulty in rationalising the present equilibrium data for the filled systems in terms of the interfacial quality. Strong interfaces suppress dilation and hence mass sorption. Weak interfaces may do so and in addition in the worse possible cases with the strongly absorbing gases, such as CO₂ in this study, they enhance gas sorption. The general result seems to be that under an equilibrium pneumatic pressure, polymers for a variety of reasons, are in a peculiar state of hydrostatic

compression/tension and when the pressure is released the stress fields are modified.

The work in this thesis has not speculated in detail upon what might occur in physical terms when the ambient pressure is reduced. Clearly it could be argued that the internal and external (swelling and compressive) stresses act independently. The 'pressure vessel' model has been referred to as a means of interpreting the crack geometry in unfilled systems. Somehow, the removal of the hydrostatic stress combined with the development of a pressure gradient (and hence a reduction in the local swelling stresses) produces a hydrostatic tension field either throughout the sample or in localised zones adjacent to the filler particles. It is proposed that this negative hydrostatic stress is the source of the crack initiation and growth. The changes from the equilibrium state have been shown to have substantial consequences upon the survival of the coherence of the polymeric matrices. In this study CO₂ gas is seen to be far more damaging than N₂ gas because it is absorbed to a higher degree and also induces a higher sorptive dilational strain. For both these environments significant inflation commences towards the later stages of the explosive decompression and the specimens revert to their original dimensions shortly after the experiment. The role of the tensile stress fields is exemplified in a very pronounced way when the sources of crack damage which are created during explosive decompression are examined. In the absence of localised hydrostatic tension fields of the sort produced by the filler interfaces large axially symmetrical cracks are produced. However, when the filler particles are present then the fields that are produced seem to have a localised hydrostatic tension component and smaller, more randomly oriented cracks are generated. The interface quality also plays an important role in the generation of cracks in the failed systems. The data in Chapter 8 illustrates that the weak interfaces act as flaws while the strong interfaces probably act as crack arresting sites. The visual examination of the crack geometry, orientation, size and disposition is generally interpretable in terms of the observed

erosion in the mechanical properties of the explosively decompressed specimens. This is particularly useful facet of the current study as it does illustrate that the proper choice of the mechanical evaluation technique can provide an insight into the nature and the extent of the damage and in particular the role filler particles might play in arresting or promoting damage of this sort.

In summary, the present thesis serves to demonstrate two important things. First of all, the consequence of the interactions between a hydrostatic stress and a solvation stress within the polymeric matrix. The situation is complicated but is still rationalisable in simple terms in particular for the systems that contain filler particles of various interfacial qualities. In addition, the thesis demonstrates that the use of ultrasonic probes may provide comprehensive and unique information, not only on the equilibrium characteristics of these systems, but also on the way in which they respond when the ambient pressure is reduced.

APPENDIX

CRITERION FOR DETACHMENT AND CAVITATION OF AN ELASTIC MATRIX FROM A RIGID SPHERICAL INCLUSION

A criterion for detachment/cavitation of an elastic matrix from a rigid inclusion is considered. The minimum detachment stress is given by (Gent, 1980):

$$\delta_a^2 = 4 \pi G_a E / 3 r$$

where ' G_a ' is the bond fracture energy in $\text{J}\cdot\text{m}^{-2}$, ' E ' is the Young's modulus of the matrix in MPa and ' r ' is the radius of the inclusion in μm . The critical stress ' σ_c ' for matrix cavitation near a spherical inclusion is given by (Gent, 1980; Oberth and Bruenner, 1965; Gent and Park, 1984):

$$\sigma_c = 5 E / 12$$

If the system is under a superimposed pressure, an additional force equal to the pressure will be necessary before matrix cavitation or filler dewetting can occur.

The experimentally determined tensile modulus of the silicone elastomer is 1.4 MPa and the average radius of the glass beads has been taken as 30 μm . The interfacial fracture energy was taken from Table 8.3. The cavitation stress for this system is calculated as $0.625 \times 10^6 \text{ N/m}^2$. The dewetting stresses for the various interfaces are given in the Table A below.

<u>Matrix-Filler Interface</u>		<u>Dewetting Stress</u> ($\times 10^6$ N/m ²)
(1)	Untreated	1.334
(2)	Release coated	1.147
(3)	Silated	1.637
(4)	Primered	3.8832

Table A: Dewetting stress for the various silicone elastomer composites with different matrix-filler interface quality.

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