

PROCESSING AND PROPERTIES OF PIB-PUR ELASTOMERS FOR THE PROTECTION OF IMPLANTABLE ELECTRONIC DEVICES

A dissertation submitted for the degree of PhD

Laura Cunningham B.Eng. (Hons)

Dublin City University

Under the supervision of

Dr. Garrett McGuinness

Dr. John O'Rourke, Boston Scientific, Clonmel

Dr. Eithne Lynch, Boston Scientific, Clonmel

School of Mechanical and Manufacturing Engineering

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy (PhD) is entirely my own work, and that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

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Contents

Nomenclature	vii
List of Equations	ix
List of Figures	x
List of Tables.....	xxiii
Abstract.....	xxv
Chapter 1. Introduction	1
1.1 Overview	1
1.2 Physiology of Heart Rate Pathologies	2
1.2.1 Bradycardia	2
1.2.2 Tachycardia	3
1.3 Hermeticity.....	4
1.4 History of Implantable Electronic Devices	6
1.5 The Effect of Water on Electronics	7
Chapter 2. Literature Review	9
2.1 Issues Arising with Advancing Technology.....	9
2.2 Use of Conformal Coatings to Protect Electronics form Corrosion	9
2.3 Polymeric Hermeticity.....	11
2.3.1 Variables of the Polymer	13
2.3.2 The Effect of the Permeating Species	13
2.3.3 Water Vapour Transmission.....	13
2.4 Polymers.....	14
2.4.1 Polydimethylsiloxane (PDMS)	15
2.4.2 Parylene.....	15
2.4.3 Polyimide.....	17
2.4.4 Liquid Crystal Polymer (LCP)	18
2.4.5 Copolymer: Polyether Polyurethane and PDMS	19
2.4.6 Material Properties of Polymers used for Electronic Encapsulation	20
2.5 Polyisobutylene Polyurethane [PIB-PUR].....	22
2.5.1 Polyisobutylene [PIB]	22
2.5.2 Polyurethane [PUR].....	22
2.5.3 Polyisobutylene Polyurethane	23
2.6 Multilayer Encapsulations.....	29
2.7 Literature Review Summary.....	30
2.8 Aims and Objectives.....	31
Chapter 3. Materials and Methods.....	33
3.1 Materials	33

3.1.1	Polyisobutylene Diol.....	33
3.1.2	Lupranat MI.....	33
3.1.3	Crosslinking Agent.....	34
3.1.4	Catalyst.....	35
3.1.5	Polyisobutylene Polyurethane	35
3.1.6	Hydrocarbons	36
3.2	Methods	37
3.2.1	Polymer Formulation	37
3.2.2	Characterisation	37
3.2.3	Mechanical Characterisation Methods	39
3.2.4	Permeation Characterisation Methods.....	43
Chapter 4.	Development of PIB-PUR Processing Route.....	46
4.1	Mechanical Feasibility Testing	46
4.1.1	Initial Method for PIB-PUR.....	46
4.2	Voids within Samples	52
4.2.1	Moisture Contamination.....	52
4.2.2	Surface Contaminants	59
4.2.3	Mixing Regime.....	60
4.2.4	Vacuum and temperature.....	61
4.2.5	Centrifuging.....	63
4.2.6	Preheating Diol and Mould	65
4.2.7	Introduction of Solvents.....	65
4.2.8	Effect of Mould Dimensions.....	69
4.2.9	Protocol for Repeated Evacuations.....	75
4.2.10	Increased Solvent Content	79
4.2.11	Refined Method with High Solvent Content	80
4.3	Conclusion	81
Chapter 5.	Mechanical Characterisation.....	82
5.1	Introduction	82
5.2	Tensile Behaviour	82
5.3	Mullins effect	86
5.3.1	Introduction	86
5.3.2	Experimental Procedure	86
5.3.3	Stress and Modulus Effects	86
5.3.4	Softening	91
5.3.5	Recovery Hysteresis	96
5.4	Degradation.....	103
5.5	Discussion.....	108

5.5.1	Tensile Properties.....	108
5.5.2	Mullins Effect	110
5.5.3	Degradation Properties	111
5.5.4	Conclusion	111
Chapter 6. Permeability and Absorption Characterisation.....		112
6.1	Introduction	112
6.2	Water Vapour Transmission Rate	112
6.2.1	Initial Water Vapour Transmission Rate Testing.....	112
6.2.2	Water Vapour Transmission Rate Analysis	113
6.3	Moisture Absorption	114
6.3.1	Phosphate Buffered Saline Solution Absorption.....	114
6.3.2	Distilled Water Absorption.....	116
6.4	Discussion.....	118
6.4.1	Water Vapour Transmission.....	118
6.4.2	Moisture Absorption	119
6.4.3	Conclusion	122
Chapter 7. Conclusions and Recommendations		123
7.1	Conclusions	123
7.2	Recommendations	124
References.....		126
Appendix A. Patent Application.....		133
Appendix B. Tensile Analysis Data.....		134
B.1	Comparison of Samples from Formulations A and C	134
B.2	Comparison of Samples With and Without Crosslinking Agent (Tween 20)...	134
B.3	Comparing Tensile Data for Formulations A and C	135
B.4	Comparing Tensile Data for Formulations Made With and Without Crosslinking Agent (Tween 20)	136
Appendix C. Cyclic Test Data		138
C.1	Box Plots Comparing Cycles for Formulation A.....	138
C.2	Box plots comparing cycles for formulation AT20	142
C.3	Box plots comparing cycles for formulation C	145
C.4	Box Plots Comparing Cycles for Formulation CT20.....	149
C.5	Comparison of tensile stresses between cycles.....	153
C.6	P Values Comparing Formulations A and AT20.....	154
C.7	P values comparing formulations A and C	154
C.8	P values comparing formulations C and CT20	155
C.9	P Values Comparing Formulations AT20 and CT20.....	155
C.10	P values Comparing the Softening Found in Various Formulations.....	155

C.11 P values comparing the Recovery Hysteresis found in various formulations. 156

Nomenclature

A	The exposed surface area of the material being tested
A	Samples of PIB-PUR made from diol of batch A
AT20	Samples of PIB-PUR made from diol of batch A with Tween 20 as a crosslinking agent
b_k	Width of ends on tensile test dog bone sample
C	Concentration
C	Samples of PIB-PUR made from diol of batch C
CA	Crosslinking Agent
CT20	Samples of PIB-PUR made from diol of batch C with Tween 20 as a crosslinking agent
D	Diffusion Co-efficient
ε	Strain during mechanical testing
E	Young's modulus during mechanical testing
FTIR	Fourier transform infrared spectroscopy
G'	Storage modulus [Pa]
G''	Loss modulus [Pa]
I_0	Intensity of the background spectrum with regards to a sample's FTIR spectrum
I	Intensity in the sample spectrum with regards to a sample's FTIR spectrum
J_x	Flux of penetrating molecules J in the direction x through a membrane
l	Length or thickness of material, pathlength
l_s	Length of narrow portion of tensile test dog bone
LCP	Liquid crystal polymer
LVE	Linear Viscoelastic Region
MDI	Methylene diphenyl diisocyanate
n	Sample size

p	Pressure
P	Permeability Co-efficient
PBS	Phosphate buffered saline
PCB	Printed circuit board
PDMS	Polydimethylsiloxane also known as silicone rubber
PIB	Polyisobutylene
PIB – PUR	Polyisobutylene Polyurethane
ppm	Parts per million
PUR	Polyurethane
PTFE	Polytetrafluoroethylene
PTMO	Poly(tetramethylene oxide)
R	Thermal resistance of the instrumentation
rpm	Rotations per minute
S	Solubility co-efficient of the solute, Henry's constant
SIBS	Poly(styrene-b-isobutylene-styrene)
t	Time
THP	1,1,1- Tris(hydroxymethyl)propane
T20	Tween 20, Polysorbate 20
%T	Percentage transmission (FTIR)
σ	Stress
$W(\%)$	Percentage weight gain associated with moisture absorption
W_t	The weight of the samples after soaking
W_d	The weight of the dried samples before soaking
WVTR	Water vapor transmission rate

List of Equations

Equation 1.1 Howl and Mann Equation	5
Equation 2.1 Permeability co-efficient of a membrane	12
Equation 2.2 Fick's law of diffusion.....	12
Equation 2.3 Henry's law of solubility.....	13
Equation 2.4 Quantity of molecules which penetrate the film described as a function of the diffusion co-efficient, the exposed surface area, the time of exposure, the pressure differential of the solute across the membrane and the thickness of the membrane.....	14
Equation 2.5 Percentage weight gain associated with moisture absorption	20
Equation 3.1 Percentage weight gain associated with moisture absorption	44
Equation 4.1 Null hypothesis for ANOVA analysis of the time study examining the duration of cure at 150°C.....	50

List of Figures

Figure 1.1 Boston Scientific pacemakers, enclosed using titanium casings and ceramic feedthroughs [4]	1
Figure 1.2 Diagram of implanted dual chamber pacemaker from Boston Scientific [14] ..	3
Figure 1.3 The world's first implantable pacemaker by Senning and Elmqvist [22].....	6
Figure 1.4 Phase diagram of water [27]	7
Figure 2.1 Diagram indicating the degree to which various materials are permeable to water vapour taken from Trager [30] © 1977 IEEE	10
Figure 2.2 Chemical Structure of PDMS [38].....	15
Figure 2.3 Chemical structure of repeating unit of Parylene C [41]	15
Figure 2.4 Chemical structure of the repeating unit of Kapton polyimide [51].....	17
Figure 2.5 Chemical structure of the repeating unit of Vectra LCP [54]	18
Figure 2.6 Phases of Liquid Crystal Polymer	18
Figure 2.7 Chemical diagram of a simple diol with functional groups indicated in red....	23
Figure 2.8 Chemical diagram of isocyanate with functional groups indicated in red	23
Figure 2.9 Repeat unit of polyurethane (n)	23
Figure 3.1 Chemical structure of Polyisobutylene diol [103].....	33
Figure 3.2 2,4'-methylene diphenyl diisocyanate [103]	34
Figure 3.3 4,4'-methylene diphenyl diisocyanate [103]	34
Figure 3.4 Polysorbate monolaurate (Tween 20) chemical diagram [103]	34
Figure 3.5 Chemical structure for PIB-PUR containing crosslinking polysorbate [103]	35
Figure 3.6 PIB-PUR with PIB-PUR chains labelled [103]	35
Figure 3.7 Chemical structure of PIB-PUR, constituent chemical residues labelled [103]	36
Figure 3.8 Qualitest Die used to cut tensile samples	39
Figure 3.9 Complement of tensile specimens cut from sample	39
Figure 3.10 Moisture absorption samples cut from sheet.....	39
Figure 3.11 Schematic for lap shear testing.....	40
Figure 3.12 Beginning of tensile test.....	41
Figure 3.13 Displaying strain before failure	41
Figure 3.14 Hanson et al. described the Mullins effect in virgin silica filled PDMS samples [107]. Reprinted from Polymer, 46/24, David E. Hanson, Marilyn Hawley, Robert Houlton, Kiran Chitanvis, Philip Rae, E. Bruce Orler, Debra A. Wroblewski, Stress softening experiments in silica-filled polydimethylsiloxane provide insight into a mechanism for the Mullins effect, 10989 - 10995, 2005, with permission from Elsevier	42

Figure 3.15 Samples in chamber under vacuum.....	43
Figure 3.16 Aluminium mask enclosing PIB-PUR material prior to test WVTR.....	45
Figure 3.17 PIB-PUR material in sealed aluminium mask sitting in open diffusion cell....	45
Figure 3.18 AQUATRON Model 1 from MOCON for water vapour transmission rate testing	45
Figure 4.1 Lap shear results for time study conducted at 100°C for PP-A-PEP 450-L-M0 indicating an increase in lap shear stress. Individual results are in bold, average results are pale in colour.....	48
Figure 4.2 Lap shear results for time study PP-A-PEP 450-L-M1 cured at 150°C indicating an increase in lap shear stress, individual results in bold, average results in pale colour	50
Figure 4.3 Test plan to examine the moisture content of crosslinking agents	53
Figure 4.4 Effect of silica desiccant on PEP 450 from long storage	53
Figure 4.5 Effect of Drierite™ desiccant on PEP 450	54
Figure 4.6 Effect of silica desiccant on fresh PEP 450.....	54
Figure 4.7 Effect of silica desiccant on PEP 550 from long storage	55
Figure 4.8 Effect of silica desiccant on fresh PEP 550.....	55
Figure 4.9 Effect of Drierite™ desiccant on PEP 550	56
Figure 4.10 Effect of silica desiccant on fresh Tween 20	56
Figure 4.11 Effect of Drierite™ desiccant on Tween 20	57
Figure 4.12 Effect of silica desiccant on THP from long storage.....	57
Figure 4.13 Effect of silica desiccant on fresh THP	57
Figure 4.14 Effect of Drierite™ desiccant on THP.....	58
Figure 4.15 Speedmixer DAC 50.1 FV used to mix PIB-PUR material	60
Figure 4.16 Representation of the dual asymmetric mixing employed by the Speedmixer DAC 50.1 FV.....	60
Figure 4.17 Sample of PIB-PUR in 25mm diameter in tub with microbubbles present in uncured PIB-PUR material.....	60
Figure 4.18 Bubbles congregating in the centre of the uncured material after intense mixing.....	61
Figure 4.19 Bubbles congregating in the centre of the uncured material after intense mixing.....	61
Figure 4.20 PP-A-M-M3 mixed at 3500 rpm for 10 mins prior to being placed in the vacuum chamber	62
Figure 4.21 PP-A-M-M3 evacuated at 50°C to 0 ATM 21 times.....	63

Figure 4.22 PP-A-M-M3 after resting in 50°C oven for 16 hrs	63
Figure 4.23 Uncured PP-A-M-M4 mixed at 3500 rpm for 10 mins in 25 mm diameter tub prior to centrifuging	64
Figure 4.24 Uncured PP-A-M-M4 in pipette before centrifuging	64
Figure 4.25 Uncured PP-A-M-M4 after centrifuging at 4000 rpm for 1 hour	64
Figure 4.26 Uncured PP-A-M-M4 after centrifuging at 4000 rpm for 1.5 hours	64
Figure 4.27 Amplitude sweep comparing PIB Diol Batch B without solvent [red] and PIB Diol Batch B with 25% solvent [grey] indicating that both diols with and without the solvent can be classified as liquids as G'' is greater than G'	66
Figure 4.28 Frequency Sweep PIB Diol comparing PIB-Diol Batch B without solvent [red] and PIB Diol Batch B with 10% solvent [grey] and 25% solvent [blue]	66
Figure 4.29 Viscosity comparison of PIB Diol Batch B without solvent [green] and PIB diol, Batch B with 25% solvent [red]	67
Figure 4.30 PP-B-T20-M-M5 containing 0% heptane with 5 evacuations	68
Figure 4.31 PP-B-T20-M-M5 containing 10% heptane with 5 evacuations	68
Figure 4.32 PP-B-T20-M-M5 containing 25% heptane with 5 evacuations	68
Figure 4.33 PP-B-T20-M-M5 with 25% heptane with increased number of evacuations, first void free sample	69
Figure 4.34 PP-B-T20-M-M5 with 25% heptane and increased number of evacuations, first void free sample, Figure 4.33 magnified	69
Figure 4.35 Water Vapour Transmission Mould made of PTFE. Uncured PIB-PUR is placed on the female section on the left. Male section on right is secured in place with allen key screws	70
Figure 4.36 PP-B-T20-M-M6 material preheated and evacuated in PTFE WVTR mould which is ready to be closed	71
Figure 4.37 Cured PP-B-T20-M-M6 after an 8-hour cure at 100°C	71
Figure 4.38 Cured PP-B-T20-M-M6 after an 8-hour cure at 100°C	71
Figure 4.39 Visible bubbles in cured PP-B-T20-M-M6 after an 8-hour cure at 100°C	72
Figure 4.40 PP-B-T20-M-M7 evacuated at 100°C for 3 hrs, uncured at 100°C for 15hrs and cured at 150°C for 1hr open mould filled to 2mm thickness cured	73
Figure 4.41 PP-B-T20-M-M7 evacuated at 100°C for 3 hrs, cured at 100°C for 15hrs and cured at 150°C for 15hrs with burned appearance	73

Figure 4.42 PP-B-T20-M-M7 evacuated at 100°C for 3 hrs, cured at 100°C for 15hrs and cured at 150°C for 15hrs was uncured after 24 hours in oven displaying a dark colour suggesting burning and tacky underside, suggesting insufficient curing	73
Figure 4.43 Uncured PP-B-T20-M-M8 with 25% solvent in mould 25mm x 25mm x 1.5mm	75
Figure 4.44 Cured PP-B-T20-M-M8, voids present	75
Figure 4.45 Cured PP-B-T20-M-M8-1 with voids in sample	75
Figure 4.46 Cured PP-B-T20-M-M8-2 with voids in sample	75
Figure 4.47 Cured PP-B-T20-M-M8-3 with voids in sample	75
Figure 4.48 Uncured PP-B-T20-M-M9 in moulds 25 mm x 25mm x 1.5mm	76
Figure 4.49 Cured PP-B-T20-M-M9-1 no voids present	77
Figure 4.50 Cured PP-B-T20-M-M9-2, small amount of voids present.....	77
Figure 4.51 Cured PP-B-T20-M-M9-3, large amount of voids present	77
Figure 4.52 Cured PP-B-T20-M-M9-4; no voids present.....	77
Figure 4.53 Cured PP-B-T20-M-M9-5; small amount of voids present.....	77
Figure 4.54 Cured PP-B-T20-M-M9-6; no voids present	77
Figure 4.55 Uncured PP-B-T20-M-M9 7-12 in moulds 25mm x 25mm x 1.5mm.....	78
Figure 4.56 Cured PP-B-T20-M-M9 7-12 in moulds 25mm x 25mm x 1.5mm	78
Figure 4.57 Cured PP-B-T20-M-M9-7; no amount of voids present	79
Figure 4.58 Cured PP-B-T20-M-M9-8; no amount of voids present	79
Figure 4.59 Cured PP-B-T20-M-M9-9; small amount of voids present.....	79
Figure 4.60 Cured PP-B-T20-M-M9-10; large amount of voids present	79
Figure 4.61 Cured PP-B-T20-M-M9-11; no voids present.....	79
Figure 4.62 Cured PP-B-T20-M-M9- 12; no voids present	79
Figure 4.63 cured sample of PP-B-T20-M-M10 with increased amount of solvent.....	80
Figure 5.1 Tensile response of samples with formulation A (Batch A with no crosslinker). The average response (n=9) is in dark blue, with standard deviation via error bars	83
Figure 5.2 Tensile response of samples with formulation of AT20 (Batch A with crosslinker). The average response (n=26) of all samples is in dark orange, with standard deviation via error bars.....	83
Figure 5.3 Tensile response of samples with formulation of C (Batch C with no crosslinker). The average response (n=12) of all samples is in dark grey, with standard deviation via error bars	83

Figure 5.4 Tensile response of samples with formulation of CT20 (Batch C with crosslinker). The average of all (n=18) samples is in dark yellow, with standard deviation shown via error bars	84
Figure 5.5 Graph indicating that outliers from group AT20 are from the same sample sheet [purple group sheet 126, green group sheet 117, orange indicates average AT20 response and pale orange individual responses of other AT20 samples	84
Figure 5.6 Comparison of the tensile strain averages from all formulations over the 0% to 25% strain range, with offsets indicating the sample standard deviation of each data set	85
Figure 5.7 Comparison of the tensile strain averages from all formulations from 0% to 1000% strain with error bars indicating the standard deviation of each data set	85
Figure 5.8 Demonstration of Mullins Effect in material type A	87
Figure 5.9 Demonstration of Mullins Effect in material type A with tensile results for material type A for comparison	87
Figure 5.10 Examples of stress values selected for comparison in four consecutive cycles at 100% strain	88
Figure 5.11 Demonstration of Mullins Effect in the material type AT20	88
Figure 5.12 Demonstration of Mullins Effect in material type C	89
Figure 5.13 Demonstration of Mullins Effect in material type CT20	89
Figure 5.14 Softening graph modified from Li et al. [108]. Two upward trajectories of subsequent cycles are highlighted, trajectory A in yellow and trajectory B in orange *..	91
Figure 5.15 Softening graph modified from Li et al. [108]. Area under curve of trajectory A highlighted in yellow *	91
Figure 5.16 Softening graph modified from Li et al. [108]. Area under curve of trajectory B highlighted in orange *	92
Figure 5.17 Softening graph modified from Li et al. [108]. Graph indicating how the softening created by trajectory A can be calculated by the subtraction of the area created by trajectory B from the area created from trajectory A *	92
Figure 5.18 Area underneath the curve of the upward trajectory of the Cycle (ii)	93
Figure 5.19 Indicating the difference in area from the upward trajectory of the second cycle and the downward trajectory of the Cycle (iii)	93
Figure 5.20 Graph indicating the area created by successive upward trajectories and softening - Orange (Softening (i)) Yellow (Softening (ii)) Purple (Softening (iii)) for trial sample from material type A	94

Figure 5.21 Box plots indicating difference between formulations A(blue) (n=8) and C (grey) (n=6) for Softening (iii).....	94
Figure 5.22 Box plots indicating difference between formulations AT20 (orange) (n=9) and CT20 (yellow) (n=10) for Softening (i).....	95
Figure 5.23 Box plots indicating difference between formulations AT20 (orange) (n=9) and CT20 (yellow) (n=10) for Softening (iii)	95
Figure 5.24 Box plots indicating difference between formulations AT20 (orange) (n=9) and CT20 (yellow) (n=10) for Softening (iii)	95
Figure 5.25 Recovery hysteresis graph modified from Li et al. [108]. Orange and yellow highlighted areas indicating the fourth cycle of this hysteresis graph (orange) and the subsequent fifth cycle (yellow) *	97
Figure 5.26 Recovery hysteresis graph modified from Li et al. [108]. Yellow highlighted area indicating the first area to be calculated. The area under the curve of the upward trajectory for the cycle of interest between str strains of 0% and the maximum strain achieved in the previous cycle *	97
Figure 5.27 Recovery hysteresis graph modified from Li et al. [108]. Orange area indicating the second area to be calculated. The area under the curve of the downward trajectory of the previous cycle *	97
Figure 5.28 Recovery hysteresis graph modified from Li et al. [108]. By subtracting the orange area (Figure 5.27) from the yellow area (Figure 5.26) the area indicating the recovery hysteresis for the cycle of interest is found *	97
Figure 5.29 Area underneath the curve created by the upward trajectory of Cycle (iii) to 300% strain.....	98
Figure 5.30 Indicating how the subtraction of the area underneath downward trajectory of Cycle (i) from the upward trajectory of Cycle (ii) creates the area which corresponds to Recovery Hysteresis (iii)	99
Figure 5.31 Graph indicating the area (Recovery Hysteresis (ii)) created by the downward trajectory of Cycle (i) and the upward trajectory of Cycle (ii).....	99
Figure 5.32 Graph indicating the area (Recovery Hysteresis (iii)) created by the downward trajectory of Cycle (ii) and the upward trajectory of Cycle (iii).....	100
Figure 5.33 Graph indicating the area (Recovery Hysteresis (iv)) created by the downward trajectory of Cycle (iii) and the upward trajectory of Cycle (iv).....	100
Figure 5.34 Box plot comparing of formulations A (blue) (n=8) versus AT20 (orange) (n=9) of Recovery Hysteresis (ii).....	101

Figure 5.35 Box plot comparing of formulations A (blue) (n=8) versus C (grey) (6) for Recovery Hysteresis (iii)	101
Figure 5.36 Box plot comparing of formulations A (blue) (n=8) versus C (grey) (n=6) for Recovery Hysteresis (iv)	101
Figure 5.37 Box plot comparing of formulations C (grey) (n=6) versus CT20 (yellow) (n=10) for Recovery Hysteresis (ii)	102
Figure 5.38 Box plot comparing of formulations AT20 (orange) (n=9) versus CT20 (yellow) (n=10) for Recovery Hysteresis (ii)	102
Figure 5.39 Box plot comparing of formulations AT20 (orange) (n=9) versus CT20 (yellow) (n=10) for Recovery Hysteresis (iii)	102
Figure 5.40 Box plot comparing of formulations AT20 (orange) (n=9) versus CT20 (yellow) (n=10) for Recovery Hysteresis (iv)	103
Figure 5.41 Effect of degradation in PBS at 37°C on tensile response for formulation A up to 8 weeks, with standard deviation indicated using error bars (n=4)	103
Figure 5.42 Effect of degradation in PBS at 37°C on tensile response for formulation AT20 up to 8 weeks, with standard deviation indicated using error bars (n=7)	104
Figure 5.43 Effect of degradation in PBS at 37°C on tensile response for formulation C up to 8 weeks, with standard deviation indicated using error bars (n=3)	104
Figure 5.44 Effect of degradation in PBS at 37°C on tensile response for formulation CT20 up to 8 weeks, with standard deviation indicated using error bars (n=7)	105
Figure 5.45 Box Plot differences in formulation A after degradation testing for 20% strain. An increase in stress associated with longer soaking times would not be considered degradation (W0 n=12, W1,2,4,8 n=4)	105
Figure 5.46 Box Plot indicating differences in formulation A after degradation testing for 800% strain. An increase in stress associated with longer soaking times would not be considered degradation (W0 n=12, W1,2 n=3, W4,8 n=4)	106
Figure 5.47 Box Plot indicating differences in formulation AT20 after degradation testing for 20% strain (W0 n=26, W1,2,4,8 n=7)	106
Figure 5.48 Box Plot indicating differences in formulation AT20 after degradation testing for 800% strain (W0 n=25, W1 n=7, W2 n=6, W4 n=5, W8 n=5)	106
Figure 5.49 Box Plot indicating differences in formulation C after degradation testing for 20% strain (W0 n=26, W1 n=7, W2 n=6, W4 n=5, W8 n=5)	107
Figure 5.50 Box Plot indicating differences in formulation C after degradation testing for 800% strain (W0 n=12, W1,2,4,8 n=3)	107

Figure 5.51 Box Plot indicating differences in formulation CT20 after degradation testing for 20% strain (W0 n=18, W1,2,4,8 n=6).....	107
Figure 5.52 Box Plot indicating differences in formulation CT20 after degradation testing for 800% strain (W0 n=18, W1 n=4, W2 n=5, W4 n=6, W8 n=5)	108
Figure 5.53 Bar chart comparing the average ultimate tensile stress (MPa) found during the course of this work, with standard deviations being indicated using error bars. Ultimate tensile strength of non-reinforced PIB-PUR materials from literature with minimum stress reported in solid green with maximum values represented with cross hatched green, Zapp et al. [89] as detailed in [75], Speckhard et al. [86] as detailed in [88], Ojha et al. [88].....	109
Figure 5.54 Bar chart comparing the failure strain (%) found during the course of this work, with standard deviations being indicated using error bars. Failure strain of non-reinforced PIB-PUR materials from literature with minimum stress reported in solid green with maximum values represented with cross hatched green Zapp et al. [89] as detailed in [75], Speckhard et al. [86] as detailed in [88], Ojha et al. [88].....	109
Figure 5.55 Demonstration of Mullins Effect in material formulation A	111
Figure 6.1 Comparison of the average permeation results for the four different material types n=5 with standard deviation denoted by error bars	113
Figure 6.2 Average results for permeation testing with standard deviation (error bars) for formulation A, AT20, C, CT20 (n=5). Time points (A 20.65 hrs, AT20 20.05 hrs, C 21.35 hrs, CT20 20.87 hrs)	114
Figure 6.3 Moisture absorption data for phosphate buffered saline solution absorption for the first 4 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6).....	115
Figure 6.4 Moisture absorption data for phosphate buffered saline solution absorption for 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)	115
Figure 6.5 Box plot indicating average moisture absorption of samples submerged in PBS after 24 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6).....	115
Figure 6.6 Box plot indicating average moisture absorption of samples submerged in PBS after 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)	116
Figure 6.7 Moisture absorption data for distilled water absorption for the first 4 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6).....	116
Figure 6.8 Moisture absorption data for distilled water absorption for 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)	117

Figure 6.9 Box plot indicating average moisture absorption of samples submerged in distilled water after 24 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6).....	117
Figure 6.10 Box plot indicating average moisture absorption of samples submerged in distilled water after 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)	117
Figure 6.11 Water permeability results from this study with data from comparable materials, Polyimide [64], SIBS [64], Parylene C [6] and LCP [57].....	119
Figure 6.12 Average moisture absorption for formulations denoted by solid block colour, with standard deviations seen shown via error bars. Value from Kang et al. [93] shown in green, lowest value shown in solid colour with maximum values shown in cross hatch green whose test conditions was 85°C for 3 days in PBS solution	120
Figure 6.13 Range of moisture absorption seen in H ₂ O comparing to that seen in literature Chang et al. [77]. Solid colour denoting minimum moisture absorption seen, crosshatch denoting highest moisture absorption value seen whose test conditions was 75 ± 1°C for 48 hours, distilled water	121
Figure 6.14 Average moisture absorption for formulations denoted by solid block colour, with standard deviations seen shown via error bars. Formulations studied in this work in comparison to the material properties found in literature for other potential barriers for near hermetic barriers. Parylene [36], [62], Polyimide [109], LCP [55], [57], SIBS [64], PDMS [36], [70]	122
Figure B.1 Box Plot indicated the overlap in tensile values induced in by a 20% strain in samples made from Diol A (blue) (n=9) and Diol C (grey) (n=12) without crosslinking agent Tween 20.....	135
Figure B.2 Box Plot indicating the overlap in tensile values for induced by a strain of 800% strain in samples made from diol A (blue) (n=9) and C (grey) (n=12) without crosslinking agent Tween 20.....	135
Figure B.3 Box Plot indicating the overlap of tensile values induced with 20% strain in samples made from diol batch A (orange) with crosslinking agent Tween 20 (n=26) and batch diol C (yellow) with crosslinking agent Tween 20 (n=18)	136
Figure B.4 Box Plot indicating the overlap of tensile values induced with 800% strain in samples made from diol batch A (orange) with crosslinking agent Tween 20 (n=26) and batch diol C (yellow) with crosslinking agent Tween 20 (n=18)	136
Figure B.5 Box Plot indicating the overlap in tensile values induced with 20% strain in samples made from diol batch A with (blue) (n=9) and without crosslinking agent Tween 20 (orange) (n=26)	136

Figure B.6 Box Plot indicating the overlap in tensile values induced with 800% strain in samples made from diol batch A with (blue) (n=9) and without crosslinking agent Tween 20 (orange) (n=26)	137
Figure B.7 Box Plot indicating the overlap in tensile values induced with 20% strain in samples made from diol batch C with (grey) (n=12) and without crosslinking agent Tween 20 (yellow) (n=18)	137
Figure B.8 Box Plot indicating the overlap in tensile values induced with 20% strain in samples made from diol batch C with (grey) (n=12) and without crosslinking agent Tween 20 (yellow) (n=18)	137
Figure C.1 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)	138
Figure C.2 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)	138
Figure C.3 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)	139
Figure C.4 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)	139
Figure C.5 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)	139
Figure C.6 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol A in the second, third and fourth cycles (n=8 for all cycles) ...	140
Figure C.7 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol A in the second, third and fourth cycles (n=8 for all cycles) ...	140
Figure C.8 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol A in the second, third and fourth cycles (n=8 for all cycles) ...	140
Figure C.9 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol A in the third and fourth cycles (n=8 for all cycles).....	141
Figure C.10 Box Plot indicating the overlap in tensile values induced by a 375% in samples made from diol A in the third and fourth cycles (n=8 for all cycles).....	141

Figure C.11 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol A in the third and fourth cycles (n=8 for all cycles).....	141
Figure C.12 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles (n=9 for all cycles).....	142
Figure C.13 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles (n=9 for all cycles).....	142
Figure C.14 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles (n=9 for all cycles).....	142
Figure C.15 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles (n=9 for all cycles).....	143
Figure C.16 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles (n=9 for all cycles).....	143
Figure C.17 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol A with crosslinking agent Tween 20 in the second, third and fourth cycles (n=9 for all cycles).....	143
Figure C.18 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol A with crosslinking agent Tween 20 in the second, third and fourth cycles (n=9 for all cycles).....	144
Figure C.19 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol A with crosslinking agent Tween 20 in the second, third and fourth cycles (n=9 for all cycles).....	144
Figure C.20 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol A with crosslinking agent Tween 20 in the third and fourth cycles (n=9 for all cycles)	144
Figure C.21 Box Plot indicating the overlap in tensile values induced by a 375% strain in samples made from diol A with crosslinking agent Tween 20 in the third and fourth cycles (n=9 for all cycles)	145

Figure C.22 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol A with crosslinking agent Tween 20 in the third and fourth cycles (n=9 for all cycles)	145
Figure C.23 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)	145
Figure C.24 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)	146
Figure C.25 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)	146
Figure C.26 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)	146
Figure C.27 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)	147
Figure C.28 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol C in the second, third and fourth cycles (n=6 for all cycles) ...	147
Figure C.29 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol C in the second, third and fourth cycles (n=6 for all cycles) ...	147
Figure C.30 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol C in the second, third and fourth cycles (n=6 for all cycles) ...	148
Figure C.31 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol C in the third and fourth cycles (n=6 for all cycles).....	148
Figure C.32 Box Plot indicating the overlap in tensile values induced by a 375% strain in samples made from diol C in the third and fourth cycles (n=6 for all cycles).....	148
Figure C.33 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol C in the third and fourth cycles (n=6 for all cycles).....	149
Figure C.34 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles).....	149

Figure C.35 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles).....	149
Figure C.36 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles).....	150
Figure C.37 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles).....	150
Figure C.38 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles).....	150
Figure C.39 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol C with crosslinking agent in the second, third and fourth cycles (n=10 for all cycles)	151
Figure C.40 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol C with crosslinking agent in the second, third and fourth cycles (n=10 for all cycles)	151
Figure C.41 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol C with crosslinking agent in the second, third and fourth cycles (n=10 for all cycles)	151
Figure C.42 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol C with crosslinking agent in the third and fourth cycles (n=10 for all cycles)	152
Figure C.43 Box Plot indicating the overlap in tensile values induced by a 375% strain in samples made from diol C with crosslinking agent in the third and fourth cycles (n=10 for all cycles)	152
Figure C.44 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol C with crosslinking agent in the third and fourth cycles (n=10 for all cycles)	152

List of Tables

Table 2.1 Material properties of some popular electronic encapsulants.....	21
Table 2.2 Mechanical properties of PIB-PUR from literature	27
Table 2.3 Moisture absorption properties of PIB-PUR from literature.....	29
Table 3.1 Molecular Weights and Specific Gravities of PIB diol batches	33
Table 3.2 Chemical formulae and boiling points of the hydrocarbons, hexane, heptane and octane	36
Table 4.1 Examples of samples of PP-A-PEP 450-L-M0 at 100°C for 1, 2, 4, 8, and 16 hours respectively showing voids present in samples and little evidence of colour change	48
Table 4.2 Examples of samples of PIB-PUR cured at 150°C containing PEP 450 for 1, 2, 4, and 8 hours respectively showing evidence of colour change	51
Table 4.3 Table indicating the effect of desiccation as per Karl Fischer	58
Table 4.4 Thicknesses of PP-B-T20-M-M9 1-6	77
Table 4.5 Thicknesses of PP-B-T20-M-M9 7-12	79
Table 5.1 Table indicating which trajectories used to calculate the various softenings within the cyclic tests.....	92
Table 5.2 Table indicating the trajectories used to calculate the recovery hysteresis within cyclic tests	98
Table 5.3 Mechanical properties of PIB-PUR formulation which arose during the course of this work and mechanical properties from PIB-PUR materials from literature.....	110
Table 6.1 Water permeability results from this study with data from comparable materials, Polyimide [64], SIBS [64], Parylene C [6] and LCP [57].....	118
Table 6.2 Table indicating the moisture absorption properties from this work and those found in literature.....	120
Table 6.3 Moisture absorption properties found during the course of this work and for other potential barriers for near hermetic barriers.....	121
Table B.1 P values for comparison of Diol Batch A and Diol Batch C resulting in the conclusion there is no difference between the batches (all the P values are above the alpha value of 0.05).....	134
Table B.2 P values comparing formulations with and without crosslinking agent demonstrating that there is no significant difference between the formulations (all P values are above the alpha value of 0.05)	135

Table C.1 P values for comparison of tensile stresses (σ) for various cycles (i/ii/iii/iv) at multiple strain points for all formulations F (A, AT20, C and CT20)	153
Table C.2 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations A and AT20	154
Table C.3 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations A and C.....	154
Table C.4 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations C and CT20.....	155
Table C.5 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations AT20 and CT20.....	155
Table C.6 demonstrating P values calculated upon ANOVA analysis comparing the softening effects of between the formulations	156
Table C.7 P values from single factor AVOVA analysis comparing formulations of PIB-PUR	156

Abstract

Processing and Properties of PIB-PUR Elastomers for the Protection of Implantable Electronic Devices

Laura Cunningham

Active implantable medical devices such as cardiac pacemakers are required to work in harsh physiological environments and must be protected in order to prevent device failure. Currently, hermetic packages are constructed using laser welded titanium cases and ceramic feedthroughs. As technology advances and medical devices shrink, the creation of hermetic packages becomes more difficult in smaller devices.

Polyisobutylene (PIB) is a commercially important polymer due to its excellent thermal stability and excellent flexibility at ambient temperature. Many properties have been identified which differentiate PIB from other polymers, a key one being low penetrability to small molecules. A formulation of polyisobutylene diol has been developed by an industrial partner. This diol was developed in order to create a polyisobutylene polyurethane (PIB-PUR), a synthetic rubber anticipated to have low permeability to small molecules and be flexible at ambient temperatures.

A means by which PIB-PUR samples can be fabricated in a laboratory setting was developed. The PIB-PUR samples were seen to exhibit ultimate tensile strengths in the range of 7.66–10.17 MPa and tensile failure strains in the range of 1148–1488%. PIB-PUR samples exhibited the Mullins effect. The water vapour transmission rate was examined for PIB-PUR and seen to be in the range of 0.03–0.04 g.cm/m².day. Moisture absorption rates were also examined for both H₂O and PBS solution for a period of 70 days and seen to be in the range of 0.79–2.24% and 0.57–1.38% respectively. The effect of incorporating polysorbate Tween 20 was examined and did not significantly affect the mechanical and permeability properties of PIB-PUR samples. There was no significant deterioration of mechanical properties over periods of up to 70 days in PBS solution at 37°C.

Finally, the research findings are discussed with respect to the potential of this PIB-PUR material as a suitable candidate to be a near hermetic barrier for encapsulation of implantable electronic devices.

Chapter 1. Introduction

1.1 Overview

As technology becomes more sophisticated, the ability to create ever smaller electronic devices is advancing. This shrinking of electronics provides opportunities for manufacturers to create new types of devices for the treatment of currently neglected disease states. It also offers the chance to miniaturise devices currently being manufactured. The reduction in size of implantable electronic devices such as pacemakers and cardioverter defibrillators allow for more positive experiences for both the patient and the implanting surgeon. Easier implantation, and less perceptible devices when implanted are examples of such advantages. As these medical devices are reduced in size, their packaging becomes more complex. All electronic devices are susceptible to corrosion and subsequent malfunctioning when exposed to moisture and ionic contamination. It is therefore imperative that medical devices containing complex circuitry be protected from the harsh physiological environment in which they operate [1], [2]. These devices are ‘hermetically sealed’ which in this context means being impervious to gas or water penetration [2], [3]. This traditionally entails using titanium casings and ceramic feedthroughs to isolate the electronics from bodily fluids, like those used in the Accolade and Essentio pacemakers from Boston Scientific in Figure 1.1.



Figure 1.1 Boston Scientific pacemakers, enclosed using titanium casings and ceramic feedthroughs [4]

In order to exploit the size reduction achieved by miniaturisation of the electronics, the casing must shrink too. Thinner and smaller titanium case halves become difficult to manipulate in welding glove boxes. When welding casings together the possibility of laser weld blowouts rise, and the risk of damaging underlying components is amplified. The dwindling space within these devices also means further complications when leak testing for hermeticity. Engineers are required to find new methods of protection since traditional methods become increasingly more difficult to implement in a manufacturing environment. Eyes are turning towards new

methods of sealing such as polymeric encapsulation and/or conformal coating. It is believed that achieving a reliable barrier while simultaneously developing a cheaper, more manufacturable alternative to the current industry standard is possible [5]–[9].

1.2 Physiology of Heart Rate Pathologies

In humans and other mammals, the heart consists of four chambers which acts as a double pump. The right side of the heart contains blood at lower pressure and pumps de-oxygenated blood to the lungs. In the lungs CO_2 is exchanged for O_2 and blood returns from the lungs into the left atrium. From the left atrium the oxygenated blood moves into the left ventricle and then is pumped throughout the body. The heart moves blood from one chamber to another, and to and from different areas of the body, by the alternating contraction and release of its atria and ventricles in a systematic and rhythmic way. This is regulated by the electrical myocardium; electrical impulses are generated from the SA node (sinoatrial node) and these impulses causes the atria to contract, forcing blood into the ventricles. This electrical stimulus then travels down through the conduction pathways to the AV node (atrioventricular node). From the AV node the electrical impulse then travels further down the conduction pathway via the bundle of His causing the ventricles to contract, forcing the blood around the body or to the lungs. The pressure within the ventricles then falls post-contraction, allowing the atria to refill with blood. This process repeats, allowing waste products to be removed and nutrients to be distributed throughout the body. Occasionally heart disease can affect how these nodes operate in conjunction with each other, sometimes causing problematic symptoms which can be life threatening if left untreated [10].

1.2.1 Bradycardia

The term bradycardia describes an abnormally slow heartrate. A normal resting heartrate for an adult can range from 60 to 100 beats per minute [11]. When an individual's heartrate falls below 60 beats per minute it can be classified as bradycardia. While some individuals with an abnormally slow heartrate may be asymptomatic and require no treatment others may develop concerning symptoms such as light headedness, confusion, fainting and/or shortness of breath [12]. This may occur when there is insufficient blood pumping throughout the body and will require intervention. Bradycardia can be caused by an issue with the electrical pathways in the heart [11]. When this occurs, there are many interventions at hand for treating physicians to help their patients. However, when medications and surgery to redefine the electrical pathways fail or are inappropriate, patients can be implanted with a pacemaker [11], [12]. Pacemakers are electrical medical devices which deliver small electrical impulses in order to ensure the

reliable beating of the heart [13] thereby allowing sufficient blood to be carried throughout the body. In the current approach, an electrical impulse generator is encased with titanium and implanted subcutaneously below the clavicle as seen in Figure 1.2. Leads carry the electrical impulse from the box to the heart. These leads enter the blood stream through the superior vena cava and enter the heart through the right atrium. Small electrical impulses overpower the electrical impulses generated by the heart and induce a synchronised contraction of the heart [13].

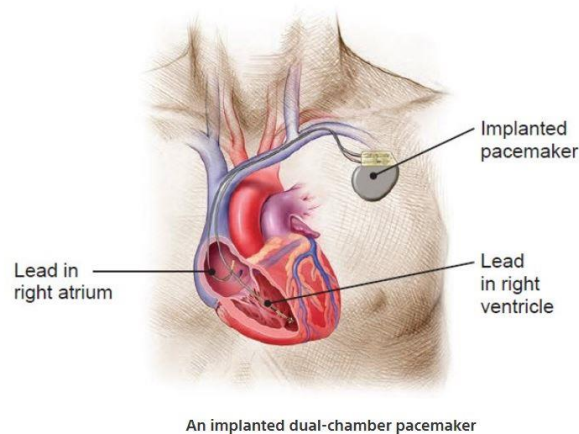


Figure 1.2 Diagram of implanted dual chamber pacemaker from Boston Scientific [14]

1.2.2 Tachycardia

In contrast to bradycardia, tachycardia describes an abnormally fast heartrate, typically anything over 100 beats per minute [15]. Again, it occurs when there is a mis-synchronisation between the pacemaker nodes in the heart caused by irregular electrical impulses. Tachycardia can lead to fibrillation of either the atria or the ventricles [16]. When this occurs, chaotic unsynchronised weak contractions of the heart occur which prevent the heart from effectively pumping blood throughout the body. It can be described as a quivering of the heart rather than a pumping. These weak contractions can cause chest pain, palpitations, dizziness, fatigue, confusion, shortness of breath and fainting [16]. It can also result in death in patients in which it induces a lack of pulse and cardiac arrest [16]. When this occurs, defibrillation is a necessity for the continuation of life. Again, medication and navicardiac ablation can be used to treat tachycardia [15]. However, it may be necessary to implant a cardioverter defibrillator to combat atrial fibrillation [17]. Implantable defibrillators work in much the same way as a pacemaker does and can be implanted in the same fashion. The electrical impulses generated by an implantable cardioverter defibrillator (ICD) are much larger as the threshold needed to stop atrial fibrillation is much greater than that required to induce a contraction [17]. Atrial fibrillation may occur at any point, there is no way to predict when it may occur which leaves

patients with a great deal of uncertainty. There has been a move in recent years to install automated external defibrillators (AEDs) in public places such as sports halls and shopping centres. While this movement is responsible for saving countless lives, there is no guarantee that atrial fibrillation will occur in the vicinity of an AED, that there will be someone present with the training or confidence to perform treatment or that the AED will be sufficiently charged to administer sufficient numbers of shocks. Should fibrillation occur, there is also no guarantee that the heart will reset itself if left without intervention. ICDs monitor the heart and should fibrillation occur, a pulse is generated to reset the heart. The ICDs are designed in such a way that they can deliver multiple shocks if required. This increases the patient's chance of survival.

There are patients with complex cases in which they require both pacing and defibrillation. In that case products are available which provide both forms of treatment.

1.3 Hermeticity

In the medical device industry, the failure of implantable electronic devices can be catastrophic. As many of these devices sustain life, a reduction in performance or full device failure can have devastating effects. Hermeticity is vitally important for the reliability of these devices. They contain advanced electronic circuitry and require protection from harsh, ion rich and corrosive bodily fluids. Hermeticity refers to a state of being impervious to gas flow or moisture penetration [3]. By ensuring the packaging is resistant to moisture ingress, the intended working life of these devices can be protected [18]. As detailed above, an impermeable casing is employed to create a reliable hermetic seal for implantable electronic devices. Described as an impermeable envelope by Donaldson [1], hermetic seals are created using metals, glass and/or ceramics. One reason this is so effective is that the tighter molecular structure of metals and ceramics prevents small molecules such as water vapour from permeating through their bulk material as quickly as in polymers.

Once the titanium casings and ceramic feedthrough have been laser-welded together in an argon-helium environment, the effectiveness of the hermetic seal must be evaluated through a leak test. A satisfactorily low leak rate must be achieved to guarantee a moisture free package for many years and ensure a sufficiently long product life [3]. This test is performed in accordance to standard Mil-STD-883 Test Method 1014. This standard is the most common test for hermeticity for implantable electronic devices in industry today.

This test method contains criteria for many different test conditions for various kinds of packages. For impermeable envelopes Test Condition: A is used. This is detailed as a fine leak

test using helium trace gas and is the most common test condition used. In it a helium leak detector is utilised. A helium leak tester is a mass spectrometer which is tuned to specifically detect the presence of helium in the testing chamber. There are two methods by which this test can be conducted. The first method involves the 'bombing' of the device. This entails pressurising the device in a 100% helium atmosphere. This will allow the helium to penetrate the device through a leak path, should one exist. The amount of helium which manages to enter the package is a function of the leak size, the bomb time and the bomb pressure. The second method involves the backfilling of the device with helium during sealing. After sealing, the device is quickly tested to determine if any helium manages to escape the package, thus giving a check on hermeticity.

After the bombing is completed, the device is connected to the input chamber of the helium leak detector. The amount of helium leaving the package is measured and compared to a standard calibrated leak. This leak rate depends on the size of the leak path and the partial pressure of helium inside the package.

This phenomenon is described by the Howl and Mann Equation, Equation 1.1 [19].

$$R_1 = \frac{L_a P_b}{P_0} \left(\frac{M_A}{M_{He}} \right)^{1/2} \left(1 - \exp \frac{-L_a t_b \left(\frac{M_A}{M_{He}} \right)^{1/2}}{V P_0} \right) \exp \frac{-L_a t_d \left(\frac{M_A}{M_{He}} \right)^{1/2}}{V P_0}$$

Equation 1.1 Howl and Mann Equation

R_1 = The measured leak rate of helium through the leak path ATM cc/s [He].

L_a = the equivalent standard leak rate in ATM cc/s [air].

P_b = The pressure of exposure in absolute ATM.

P_0 = The atmospheric pressure in atmospheres absolute.

M_A = The molecular weight of air (g).

M_{He} = The molecular weight of helium (g).

t_b = The time of exposure to P_b (s).

t_d = The dwell time between releases of pressure and leak detection (s).

V = Internal volume of the package.

Should the package pass both gross and fine leak tests as per the standard, there is little risk of moisture ingress over the lifetime of the device. If a hermetic seal fails, water vapour would be able to penetrate the package. This would allow contaminants such as gasses or moisture to condense on the surface of any active electric components. It is then possible that corrosion and other electrochemical reactions may occur, degrading the device's performance and leading to

device failure. Corrosion is simply a chemical reaction between metal and moisture [20]. The corrosion seen in implanted electronic implants is an electrochemical process by which refined metals transform into a more chemically stable form such as an oxide, hydroxide or sulphide. The structural elements of the circuitry are so small that should the metal corrode, a catastrophic failure could occur. The corrosion of a material is determined by the circuit's local environment and is often dictated by humidity, temperature, electrical potential and surface contamination [21]. Water that has condensed on the surface can bind with ionic contamination such as sodium (Na) or chlorine (Cl) and corrode exposed metal [3].

1.4 History of Implantable Electronic Devices

The hermetic sealing of implantable electronics has been standard practice for decades. However, this was not always the case. In 1958 the first ever implantable pacemaker was developed by Senning and Elmqvist. It was encapsulated in the biocompatible epoxy resin Araldite as shown in Figure 1.3 [22].

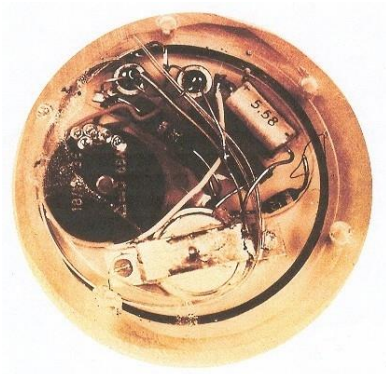


Figure 1.3 The world's first implantable pacemaker by Senning and Elmqvist [22]

Subsequently, pacemakers were encapsulated in epoxy resins and silicone rubbers following the example of the initial prototype device. It was noticed in the 1970s that the epoxy resin began to swell and dissolve inside the human body, inducing failure after a period of implantation [23]–[25]. The swelling of the epoxy also induced mechanical strains on the components. This caused some components to break and the formation of voids in the interface of the epoxy and the circuitry. This space allowed for moisture and other contaminants to condense on the surface. These issues resulted in a transition to the use of titanium casings to enclose the battery and circuitry in the 1970s [3].

The implementation of a hermetic and mechanically stable package did not solve all the issues relating to the closure of these devices. Thomas described the lack of understanding that the effect free moisture has in a hermetically enclosed device [26]. He detailed how the closure of

these devices without a thorough understanding of the environment within can lead to device failure. Packages in an Air Force missile computer were found to contain moisture, helium, freon and carbon dioxide. These were determined to be sufficient to cause the device failure after a short time operating at room temperature [26]. Research such as this has resulted in the current reliable process now practiced.

1.5 The Effect of Water on Electronics

Water plays a key role in failure of electronics. It is therefore vital to understand how it behaves under various conditions in order to predict the likelihood of failure. Water is commonly found in one of three states: solid, liquid or gas. The state at which it is found depends primarily on the surrounding temperature and pressure conditions.

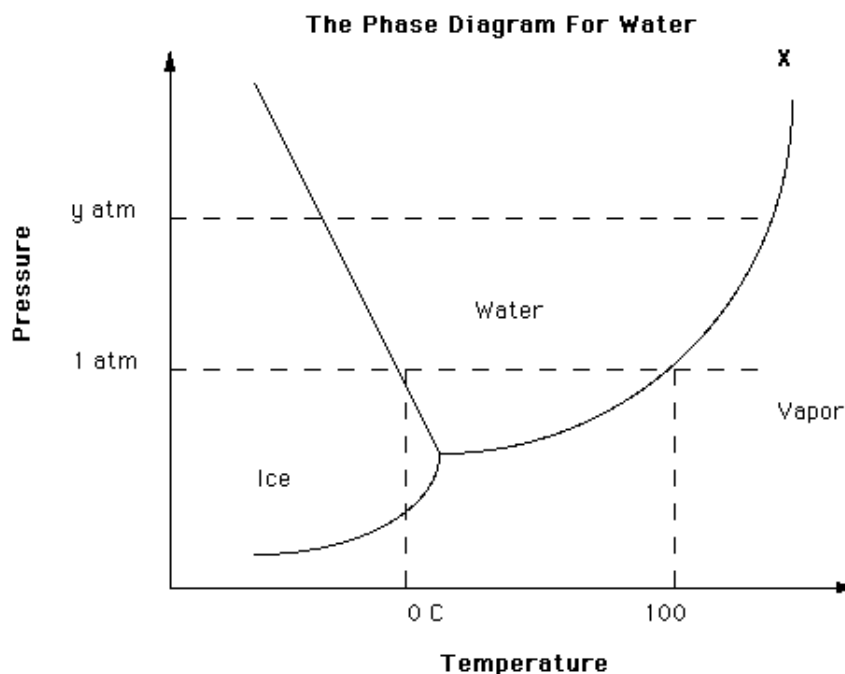


Figure 1.4 Phase diagram of water [27]

The phase diagram of water as shown in Figure 1.4 describes how the surrounding environment affects the physical state of water. The solid lines indicate a change in state of matter between solid (ice), liquid (water) and gas (water vapour). Where all of these lines converge is known as the triple point. This describes the temperature and pressure at which water can exist in all three states of matter: solid, liquid or gas.

The dew point is the environmental temperature at which the atmosphere is fully saturated with moisture vapour. When the atmosphere cools below the dew point, water vapour will condense and turn from a gas to a liquid [28]. At this point, water vapour will instead sublimate

directly to ice. It follows that if the total concentration of water molecules within the package is kept below 6,000 ppm, water vapour can only be converted from gas to solid. This will avoid the corrosive liquid phase. Therefore, 5,000 ppm of water molecules is considered to be allowable in electronic packaging to avoid any corrosive complications [2], [29].

Chapter 2. Literature Review

2.1 Issues Arising with Advancing Technology

Technological advancements over recent decades have expanded the possibilities for electronic intervention in the human body at an ever-increasing rate. The miniaturisation of technology has widened the range of disease states which could be treated with electronic intervention. When designing the packaging for such devices there are a few considerations which must first be considered. In confined areas of the body, it is vital to ensure the implant is of suitable size and form factor. This is seen particularly with retinal, cochlear and neurological implants. In addition to this, applying traditional laser welding techniques to increasingly smaller packages can become difficult. The minimal thicknesses of titanium shells result in a greater risk of inflicting damage on the underlying electronics. This requirement for higher accuracy can cause defects in weld closures. Also, laser welding is an expensive process step. The titanium casings, equipment and the gasses needed to ensure the hermetic seal contribute to this cost. Moreover, should a device fail its hermeticity test the whole unit must be scrapped. This renders the processing completed up to this point useless. The material used cannot be salvaged for use in other devices, contributing to the expense of manufacture. It is for these reasons that a new method of protection should be considered.

2.2 Use of Conformal Coatings to Protect Electronics from Corrosion

There is a second method by which protection may be achieved. Protection may be offered by the introduction of an insulating organic, conformal layer that bonds to the surface of the electronics. A conformal layer in this instance refers to an insulative coating that uniformly adheres to all exposed surfaces. It is a fact that moisture will permeate most materials given sufficient time [30]. Organic materials like polymers are more permeable to gas and liquid than inorganic materials such as metals and ceramics because of their material structure. This is illustrated in Figure 2.1.

If the traditional titanium encapsulation for a pacemaker were to be replaced by a polymer, the amount of moisture within the package would eventually rise. The liquid outside of the device would diffuse within the package. The water molecules would move from the area of high concentration (the body) to an area of low concentration (the free space within the package). However, by conformally coating the electronics, the space in which water vapour is able to condense is removed, provided that the bond is maintained between the polymer and the

substrate [31]. The creation of saline bridges can then be prevented, and the integrity of the electronics can be preserved [1].

Conformal encapsulation can therefore offer 'reliability without hermeticity' [32]. In explanation, a polymer coating will not provide the level of hermeticity that a titanium encapsulation will. However, should a polymer have a sufficient resistance to moisture permeation, due to the limited rate of moisture ingress and the lack of free space for moisture to condense, protection may still be afforded to the underlying components for a period of time. The protection of the device would not be entirely dependent upon the material properties of the encapsulant.

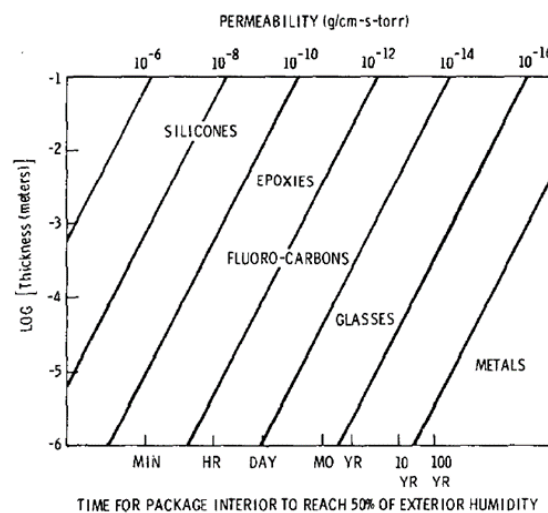


Figure 2.1 Diagram indicating the degree to which various materials are permeable to water vapour taken from Trager [30] © 1977 IEEE

Thin film encapsulation is also particularly attractive to medical device engineers as it occupies less space, is more economical and is easily translated for mass production [33]. The materials used are often flexible. Devices can then be placed in previously unimaginable areas such as within the eye or the ear. These devices are also better able to mimic the mechanical properties of the surrounding tissue. This reduces the stresses translated into the device during movement or during normal functioning [5].

The effectiveness of this type of barrier is dependent primarily on a number of key design choices linked to the properties of the material(s) used to create the conformal coating. Specifically, these include ability to withstand the ingress of contamination and the adhesion of the coating to the substrate. The configuration of the conformal coating, in terms of the amount and type of layers employed, is also critical.

To date the literature provides a plethora of examples of both single and multilayer encapsulations used not only for medical devices but for other electronic devices exposed to harsh environments. Examples include aircraft electronics or devices being exposed to harsh weather.

2.3 Polymeric Hermeticity

Metal and ceramic materials are usually favoured in the manufacturing of implantable electronic devices due to the reliability of their hermeticity. Polymeric materials do not provide an impermeable coating and thus they are generally deemed not to be viable for consideration for long term applications. However, there are significant benefits to choosing polymeric materials if an appropriate polymer and application can be found and married. Polymers reduce cost, weight and size and allow for flexible assemblies.

Permeation is the passing of molecules through a solid material. In order to understand the role that polymers may play in the future of the packaging of implantable medical devices it is imperative that the modes by which species permeate and diffuse into and through these polymers is understood. When coating electronics it is vital that the permeation properties of the encapsulant are known in order to prevent corrosion of the underlying electronics and ultimate failure of the device.

The rate of transmission of a penetrant, either gas, vapour or liquid, through a polymeric material is determined by a number of factors, some of which may be dependent on either the properties of the polymer in question, the permeating species, or on the degree of interaction between the polymer and the penetrant or the environmental conditions. Permeation of a gas or vapour through a polymeric material involves diffusion and can be exacerbated by cracks, pinholes and voids present in the surface. This can lead to rapid deterioration of barrier properties [34]. When there is a uniform coating working to prevent the ingress of contaminants, molecules can still diffuse and permeate through the bulk material.

In 1866 Thomas Graham introduced his theory for gas diffusion through a material. This model describes small molecules permeating a polymeric barrier in four stages.

- i.) Absorption of the permeating species onto the surface of the polymer.
- ii.) Solution of the penetrant into the polymer matrix.
- iii.) Diffusion of the gas or vapour through the wall along a concentration gradient.
- iv.) Desorption from the far surface.

Graham also made other observations:

- i.) Permeation is independent of pressure.
- ii.) An increase in temperature decreases the penetrant solubility but increases the permeability of the membrane.
- iii.) Prolonged exposure to the increased temperature can affect the membranes retention capacity.
- iv.) Variation of thickness of the membranes can affect the permeation rate of penetrants but not the separation characteristics of the material [34].

Permeation through a bulk material is ruled by a simple relationship which is defined as:

$$P = D \times S$$

Equation 2.1 Permeability co-efficient of a membrane

P = Permeability co-efficient of the membrane.

D = Diffusion co-efficient of the solute.

S = Solubility co-efficient of the solute.

Permeability is therefore the product of the diffusion co-efficient which can be calculated using Fick's law of diffusion and the solubility co-efficient which can be which can be calculated using Henry's law of solubility.

Fick's law of diffusion is defined as

$$J_x = -D\left(\frac{dC}{dx}\right)$$

Equation 2.2 Fick's law of diffusion

J_x = Flux of penetrating molecules J in the direction x .

D = Diffusion co-efficient of the solute.

$\frac{dC}{dx}$ = Concentration gradient across the membrane (in the x direction).

It describes how the flux of penetrating molecules J in the direction x is proportional to the concentration gradient of the penetrant across a membrane and is dependent upon the diffusion co-efficient of the membrane (D). It must be noted however that this equation must only be applied to diffusion which is in a steady state [34].

Henry's law of solubility is a gas law and states that 'at a constant temperature the amount of a gas dissolved in a liquid is proportional to the partial pressure of that gas above the liquid'.

$$C = S \times p$$

Equation 2.3 Henry's law of solubility

C = Concentration.

p = Pressure.

S = Solubility co-efficient of the liquid, also referred to as Henry's constant.

By combining these two laws the overall governing law for permeation can be obtained. The main difference between the two laws is the assumption of the pressure differential through the membrane [35]. It is this equation which is used in water vapour transmission rate (WVTR) testing to quantify the permeation rate. This is further described in the experimental methods section.

2.3.1 Variables of the Polymer

The permeation rate of molecules through the polymer film is normally inversely related to the sample's thickness. In general, the permeability co-efficient will be independent of the sample's thickness. A decrease of the permeability co-efficient with increasing thickness can correspond to samples with irregular surfaces or defective films where pinholes or tears can give an apparently high localised permeation rate. It is for this reason that for many packaging applications it is common to use multi-layered structures on the basis that the probability of two pinholes being superimposed is very small, and that the passage of gas is therefore interrupted [34].

2.3.2 The Effect of the Permeating Species

Intuitively the molecular structure plays a significant role in the permeability of a material. Similarly, the molecular structure of the permeating species also plays a large role. Small molecules will diffuse faster through the material than their larger counterparts. Polar molecules diffuse more slowly through polymers than non-polar molecules; this is especially true for polar polymers [34].

2.3.3 Water Vapour Transmission

Water vapour transmission rate tests are typically conducted at 25°C or 38°C across a homogenous, non-porous barrier. The test itself is conducted by clamping the barrier material between two chambers. At one side there is a moist pad which provides the water molecules which permeate the barrier. On the other side there is a humidity sensor which can detect minute changes in the water content of the atmosphere surrounding it. Before beginning the test, the upper section is dried via a stream of dry air through the chamber. When the test begins the inlet and outlet pipes are closed isolating the upper chamber.

Once the equilibrium conditions of water vapour transfer have been calculated within and across the non-porous, homogeneous barrier, the quantity of water vapour permeating through the medium can be calculated by using the Equation 2.4

$$Q = PA t \frac{(p_2 - p_1)}{l}$$

Equation 2.4 Quantity of molecules which penetrate the film described as a function of the diffusion co-efficient, the exposed surface area, the time of exposure, the pressure differential of the solute across the membrane and the thickness of the membrane

Q = Quantity of molecules which penetrate a film.

p_1-p_2 = The difference in water vapour pressure across the sheet.

A = The exposed surface area of the material being tested.

l = The thickness of the material.

P = The permeability co-efficient of the membrane.

2.4 Polymers

When considering polymeric encapsulation for implantable electronic devices it is imperative that the encapsulant material be comprehensively characterised. There are numerous promising polymers which may be suitable as an encapsulant. For instance, silicon rubber is an established material for cable insulation [36]. Parylene C is used as insulation for electronic components used in implants [36]. Polyimide is used in the manufacture of integrated circuits and MEMS chips and various other microelectronic applications [36]. LCPs are known for their role in the manufacture of printed circuit boards and semi-conductors for their use in medical engineering [36]. One issue when looking at polymeric encapsulation for long term implants lies with the bio-stability *in vivo*. Polymers are at risk of degradation through hydrolytic, oxidative, and enzymatic mechanisms which will degrade the polymer's chemical structure [37]. There has been some reserved success with polymeric encapsulation of devices with simple circuits and low voltage components [2]. However, it was noted in Donaldson 1976 [1] that polymeric encapsulation does not provide a true hermetic barrier. Therefore, its use in electronic circuitry for long term applications should be approached with concern. It is important to take into consideration the adhesion of the polymer to the substrate and to ensure the ability to create a void free deposition and cure. Failure to do so will add to osmotic effects and degradation [31].

2.4.1 Polydimethylsiloxane (PDMS)

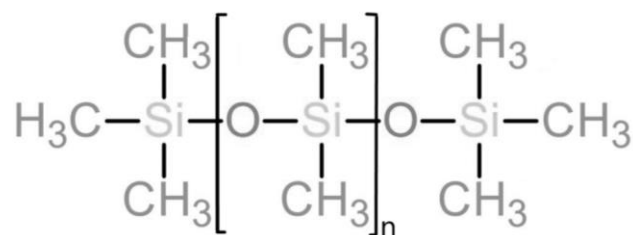


Figure 2.2 Chemical Structure of PDMS [38]

Polydimethylsiloxane, Figure 2.2, is more commonly known as silicon rubber and is a very important material for biomedical implants. It is one of the few polymeric materials that was developed for medical use by the Dow Corning Company [39]. PDMS is manufactured by polymerising the repeating unit dimethyl siloxane through a condensation polymerisation reaction [39]. This results in a backbone consisting of repeating silicon to oxygen bonds and methyl groups. PDMS's material properties make it a popular choice for implantable devices. It is able to maintain its mechanical properties over a wide range of temperatures, -40°C to 185°C [40]. It is used for a variety of implants ranging from contact lenses to breast implants and cables for electronic leads. Typically, in electronics it is used as an insulator as it has excellent electrical properties, such as a low dielectric constant [36], [40]. PDMS also shows resistance to chemical degradation. It is resistant to dilute acids, oxidizing agents and to ketones and alcohols [40]. PDMS exhibits biocompatibility and resistance to degradation *in vivo*. Few molecules can leach out of the PDMS's bulk material [40]. However, it has a relatively high permeability when compared to other materials often used for encapsulation. Its wide usage means that the processability of this material is widely understood and can be easily formed into thin films or moulded [36].

2.4.2 Parylene

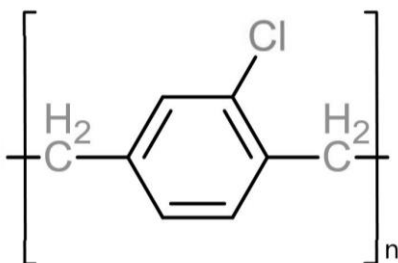


Figure 2.3 Chemical structure of repeating unit of Parylene C [41]

Parylene (poly(p-xylylene)), Figure 2.3 is the name given to a group of thermoplastic linear, semi-crystalline polymers that have found a leading role as a moisture barrier. It is deposited via vapour deposition polymerization. This entails heating the parylene dimer until sublimation occurs, vaporising the dimer into a monomeric gas. This gas is pulled through the machine into the deposition chamber with the pull of a vacuum. When the gas reaches the deposition chamber, it cools down to ambient temperature and deposits on the surface of the substrate and instantaneously polymerises [36], [42]. This method of deposition allows for a conformal and insulative coating, any exposed surface is coated including sharp edges and exposed areas under components [42].

Parylene's material properties make it a popular candidate for thin film protection in the literature. Its high dielectric strength [6] allows it to insulate the underlying electronics from electrical potentials. Perhaps most importantly, it has one of the lowest permeabilities to water when compared to other polymers [43]. Its chemical inertness, flexibility, pin hole free application, and biocompatibility all add to its value in hermeticity [44].

In the last 30 years, parylene has been explored as the sole means of protection for Utah electrode arrays (UEA). Utah electrode arrays were developed to restore function to the nervous system in patients with neurological disorders [45]. Hsu *et al.* examine if Parylene C was sufficient to encapsulate and electrically insulate the UEA interface for a year. Using impedance spectroscopy and leakage current measurements performed at 37°C it was determined that Parylene C created a sufficient barrier. In 2006 Parylene C was used by Li *et al.* to package a retinal prosthesis [43]. Initial results showed an expected lifetime of 20 years, but the study left room for further exploration and development to characterise the reliability of parylene. In 2010 Li was among the inventors in the US patent US 7,774,931. It describes a method for fabricating an integrated intraocular retinal prosthesis device consisting of an initial layer of polymer. This acts as a substrate for a conductive metallic layer which is then covered by a subsequent polymer layer [46].

As recently as 2017, Lecomte *et al.* described a neural probe for recording brain activity protected by Parylene C. Both *in vitro* and *in vivo* tests were completed which showed that the devices remained functional after a 6-month period [47].

Whilst many authors praise the effectiveness of single layer parylene coating encapsulation, Madakasira *et al.* show that even a thick single layer of Parylene C is not an effective barrier [7]. Having tested coatings of thickness of 1, 5 and 10µm they saw no effective improvement in

performance after parylene deposition. That team therefore moved to multilayer encapsulating using both parylene and aluminium oxide coatings to provide a more effective protective layer [7].

The dimer primarily used in the medical device industry is Parylene C. Its electrical and barrier properties make it a good candidate for encapsulation purposes. Parylene is also known for its biocompatibility, and it is recognised by the FDA as a Class VI polymer [44]. Chemical, biological and electrical inertness has meant that it has found a use as an unrestricted encapsulant for chronic implants [36]. Very thin polymer layers on the micrometre scale are created during the deposition process. This results in a very fragile coating which can be very easily damaged as the components proceed down the manufacturing line. Due to its chemical inertness parylene does not often chemically bond to the surface upon which it is deposited. Delamination occurs readily once an initial tear or pinhole has been introduced, as a result of mishandling. This may be combated by activating the surface using plasma [48], adding a silane adhesion agent [5] or texturizing the surface to promote mechanical adhesion [49].

Parylene is a very popular choice when it comes to thin film encapsulation. Its ease of deposition is attractive specifically as it may occur at ambient temperature. It is deposited as a vapour on to the substrate and so it lends itself to pin hole free conformal coating which is essential in this process. Its chemical inertness and its electrical properties allow it to isolate electrical components. Its relatively low water vapour transmission rate of 0.08 g.mm/m²day [6] and water absorption allows it to prevent the transfer of moisture through its material. However, parylene has been noted to fail due to moisture diffusion and interface contamination in both passive and active samples [50].

2.4.3 Polyimide

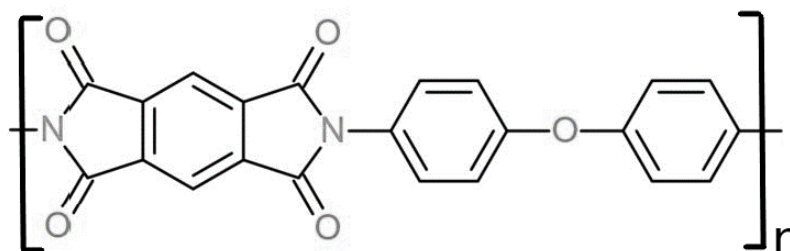


Figure 2.4 Chemical structure of the repeating unit of Kapton polyimide [51]

Polyimide, Figure 2.4 refers to a group of polymers which are created from imide monomers. They are widely used in electronics and have more recently being used in biomedical applications. They also have excellent chemical [52], [53] thermal stability [36], [52] and

dielectric properties [36] to protect electronics. They are durable to repeated bending and twisting and have a low cost of processing [52]. These material properties make polyimides attractive for use as passivation layers in microelectronics to protect circuitry from corrosion, moisture absorption, ion transport and physical damage [52]. However, they have a relative high moisture absorption in relation to other polymers discussed here [36].

2.4.4 Liquid Crystal Polymer (LCP)

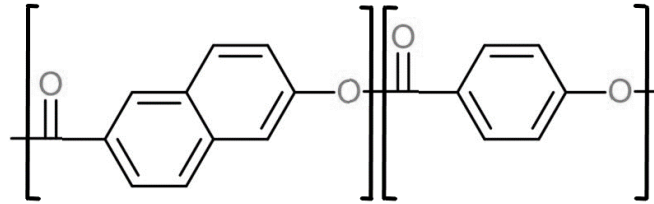


Figure 2.5 Chemical structure of the repeating unit of Vectra LCP [54]

Liquid Crystal Polymers, Figure 2.5 are a group of unique polymers that have found prominence in the electronics industry. They are essentially rod-shaped and rigid molecules. They are unlike any other materials; in that they cannot be considered either crystalline or liquid in entirety but are instead referred to as liquid crystalline. LCPs go through a great deal more phases when subjected to heat than traditional isotropic materials.

In 2011 Lee *et al.* fabricated a neuro-prosthetic device which was monolithically encapsulated with Liquid Crystal Polymer (Vecstar Series, Kuraray Co., Ltd., Tokyo, Japan). According to Lee, LCP is a superior encapsulant when considering moisture absorption. These devices were constructed by bonding LCP based electrode arrays and hemispherical LCP package lids. They were tested by evaluating electrical leakage currents in 37°C and 75°C phosphate buffered saline solutions and were found to be superior to polyimide and Parylene C encapsulated devices [55].

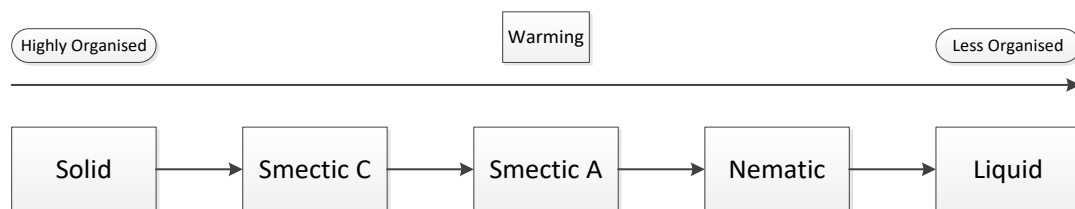


Figure 2.6 Phases of Liquid Crystal Polymer

Figure 2.6 describes the phases of a liquid crystal polymer, in the solid state the LCP's molecules are aligned in ordered configurations. When in the liquid state this alignment remains, and they also form domain structures with characteristic spacing's between the molecules [56]. Some

LCPs are solid at room temperature and have found popularity due to a number of characteristics such as their low co-efficient of thermal expansion [57], low moisture absorption (less than 0.04%) [36], [55], [57], [58] and permeability [36], [57], low permeability to gases [36], low dielectric constant [57], high interfacial adhesion [58], good biocompatibility [58], cost effectiveness [58], mechanical stability [55], flexibility [55] and resistance against various chemicals.

Even though LCPs possess a large range of characteristics that make them desirable packaging materials there are a few things of note. The method by which some LCPs are processed mean that their mechanical properties are not consistent throughout all axes of the material. When looking at extruded uniaxial LCP film, the mechanical properties in the direction in which it was extruded have a magnitude higher than that of the transverse direction [57]. Regardless of this, the literature is still scant on the use of LCP as an encapsulation material for electronics *in vivo*, as the studies associated with the initial enthusiasm for this material await results [36].

2.4.5 Copolymer: Polyether Polyurethane and PDMS

Roopour *et al.* [59] described an exploration of the use of polyurethane for near hermetic coating in biomedical applications. Polyether urethane and polydimethylsiloxane (PDMS) were synthesised. PDMS was incorporated into the backbone of the polymer as a part of the soft segment during the synthesis of the polyurethane. This polyurethane was then studied to determine physical properties and permeability. The PDMS within the copolymer allowed a hydrophobic surface to form. This allowed for a reduction in the uptake of water and moisture permeability in the material. Various tests were carried out by Roopour *et al.* to determine the characteristics of this polymer [59].

The mechanical characteristics were determined using dog bone specimens of 0.1–2mm thickness. These specimens were kept in a desiccator at room temperature for 1 week before tensile testing. The samples were strained at a rate of 20 mm/min until failure. The stress strain curves are obtained using the original cross-sectional area. The Young's modulus was determined by finding the slope of the initial linear region of the curve and the ultimate tensile strength was also determined from the graph [59].

Water uptake was determined using samples of 60mm x 10mm x 0.3–0.4mm. The specimens were dried in a vacuum oven for 24 hours before testing. The weight of these dried samples were recorded (W_d). The specimens were placed in deionised water at 37°C. The wet weight at different immersion times was recorded (W_t) by wiping off the surface water and weighing. The

water absorption was calculating using the Equation 2.5 on the basis of the average of 5 different samples [59].

$$W(\%) = \frac{W_t - W_d}{W_d} \times 100$$

Equation 2.5 Percentage weight gain associated with moisture absorption

W [%] = Percentage weight gain associated with moisture absorption.

W_t = The weight of the samples after soaking.

W_d = The weight of the dried samples before soaking.

The water transmission rates of these specimens were calculated at 37°C. Dry films were placed on the open mouths of test bottles with a radius of 22.5mm containing anhydrous copper sulphate. The samples were then weighed and then immersed in water for 1 week. Copper sulphate acts as a desiccant and drew the water through the film. The water transmission rate was then determined from the weight post immersion [59].

The water vapour transmission rate was determined by covering a conical flask which contained a known amount of deionised water with the polymer and creating a tight seal with parafilm. The measurement of water vapour transport was based on gravimetric determination of vaporised water were recorded daily for 1 week [59].

2.4.6 Material Properties of Polymers used for Electronic Encapsulation

A summation of the material properties of these materials is described in Table 2.1. After testing is complete on these formulations of PIB-PUR, the results of will be compared back to this chart. This will give provide an understanding of how PIB-PUR competes among other near hermetic barriers.

The next section will introduce polyisobutylene polyurethane, which will be the experimental focus of this thesis. SIBS [poly(styrene-b-isobutylene-styrene)] will be discussed in the next section.

Table 2.1 Material properties of some popular electronic encapsulants

	<u>Parylene</u>	<u>Polyimide</u>	<u>LCP</u>	<u>SIBS</u>	<u>PDMS</u>	<u>Copolymer: PEU and PDMS</u> [59]
Ultimate Tensile Strength	69 MPa [36], [62]	392 MPa [36], [63] 2500 MPa [64]	182 MPa [36] 183 MPa [type: MT1300] [65] 190 MPa [MT1310] [66]	12.7 MPa [67] as detailed in [68] 17.7 MPa [68] 10-30 MPa [69]	6.2 MPa [36], [70]	0% PDMS~ 25 – 30 MPa 2% PDMS~ 20 – 25 MPa 10% PDMS~ 15 MPa 50% PDMS~ 7.5 – 10 MPa
Failure Strain	200% [36], [62]	30% [36], [63] 4% [64]	3.4% [36]	700% [64]	600% [36], [70]	0% PDMS~ 550 – 600% 2% PDMS~ 550 – 600% 10% PDMS~ 400 500% 50% PDMS~ 250 – 400%
Young's Modulus	20 MPa [36], [62]	8830 MPa [36], [63]	7800 MPa [type MT1300] [65] 15,000 MPa [type MT1310] [66]	11.2 ± 0.5 MPa [64]	0.1-0.5 MPa [36], [70]	0% PDMS~ 12.5 – 15MPa 2% PDMS~ 10 – 15 MPa 10% PDMS~ 17.5 – 20 MPa 50% PDMS ~25 – 27.5 MPa
Moisture Absorption	0.06% 24 hr [36], [62]	0.7998-3.5327 [67] 1.4% [36], [63] t 23°C for 24 hr in water	<0.04% [55], [57] 0.03% 23°C 50% RH [type MT1300] [36], [65] 0.04% 23°C 50% RH [MT1310] [66]	<0.01% [2 weeks] [64] 1.15% [7 months] [64]	<1% [36], [70]	0% PDMS~ 3% 2% PDMS~ 2.5 – 3% 10% PDMS~ 2% 50% PDMS ~ 1%
WVTR	0.08 g.mm/m ² day [6]	0.56 g.mm/m ² day [64]	0.0508 mm thickness 0.1177 g/m ² day [53] 0.1016 mm thickness 0.0678 g/m ² day [53]	0.241 g.mm/m ² day [64]	Data not found	0% PDMS~ 35 – 40 mg/cm ² [7days] 2% PDMS~ 35 – 40 mg/cm ² [7days] 10% PDMS~ 40 mg/cm ² [7days] 50% PDMS ~ 40 – 45 mg/cm ² [7days]

2.5 Polyisobutylene Polyurethane [PIB-PUR]

2.5.1 Polyisobutylene [PIB]

Polyisobutylene (PIB) is a commercially important polymer due to its thermal stability, excellent flexibility at ambient temperature and low permeability to small molecules. In 1949 PIB was chosen by the National Bureau of Standards (currently the National Institute of Standards and Technology) to be examined in order to establish 'usual' polymeric properties. In this study twenty-seven laboratories across the world collaborated to examine a PIB sample, with the aim to establish what was thought to be standard viscoelastic behaviours of polymers. Instead of achieving this, it was discovered that PIB is not a standard among viscoelastic polymers but rather an exception. Many properties were identified which differentiate PIB from most other polymers. For example, it has markedly low penetrability to small molecule penetrants [60]. It is this low permeability which is most interesting for the purposes of encapsulation of implantable electronics. PIB has not yet been examined as a near hermetic encapsulant for electronic devices and therefore this study aims to determine if it can be a viable option.

The most recognisable form of PIB is in butyl rubber, more formally known as isobutylene isoprene rubber (IIR). It is a synthetic rubber mainly consisting of isobutylene with small amount of isoprene. Butyl rubber has special properties including low permeability to gasses, resistance to oxygen, great electrical properties and resistance to alkalis and acids. Its properties mean butyl rubber has found uses in a range of areas such as medical vial stoppers to tyre inner tubes [61]. Its low permeability to gasses means that the rubber is able to keep liquids and gasses contained. This is attributed to the high proportions of polyisobutylene in the formula.

2.5.2 Polyurethane [PUR]

Polyurethanes are polymers which consist of organic units which are joined by urethane links. They are formed by reacting a polyol with an isocyanate.

Diol

A diol is a chemical compound containing two hydroxyl functional groups.

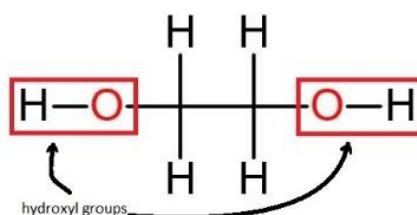


Figure 2.7 Chemical diagram of a simple diol with functional groups indicated in red

Isocyanate

An isocyanate is a material with a functional group of the form $R-N=C=O$. A molecule which contains two of these reactive functional groups is referred to as a diisocyanate (or a polyisocyanate for more than two).

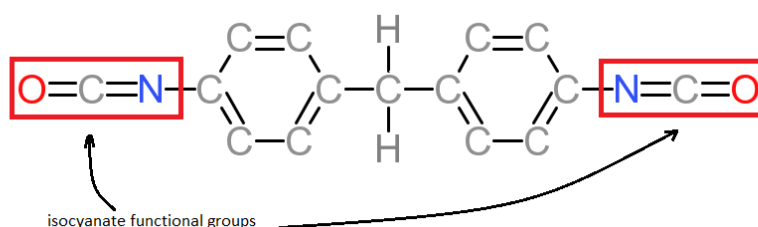


Figure 2.8 Chemical diagram of isocyanate with functional groups indicated in red

Polyurethane

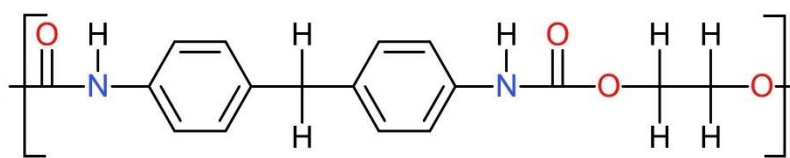


Figure 2.9 Repeat unit of polyurethane (n)

Polyurethanes are formed when isocyanate functional groups react with the hydroxyl groups of a polyol to form a polyurethane polymer matrix. The polyol becomes part of the backbone of the polyurethane forming the soft segment, while the isocyanate acts as a chain extender forming the hard segment.

2.5.3 Polyisobutylene Polyurethane

Kennedy and his group have focused on the synthesis, characterisation, and testing of novel rubbers particularly polyisobutylene based molecular composites since the 1970s [71]–[73]. This followed the discovery of the ability to control the structure of PIB homopolymers, PIB-based prepolymers and complex macromolecular structures which previously was not thought

possible. This triggered the investigation into PIB based materials for biological applications. Previously there had been attempts to prepare polyisobutylene with primary alcohols (diols, triols etc). However, these remained largely unsuccessful [74].

These first generations of polyisobutylene based polyurethanes were received with a great deal of excitement in academic and industrial circles according to Kennedy. However, due to the high cost associated with the manufacturing of PIB diol, research and development was stalled but resumed many years later when the cost of synthesis was mitigated by new discoveries [75].

In the 1980s, Kennedy and his team used a then recently invented polymerization technique, 'the infer method' to produce linear and three-arm star polyisobutylene containing hydroxyl groups [OH] functional groups. The molecular weights of these materials could be highly controlled and could range from 1000 to 5000 [76]. The materials were reported to be colourless, odourless, tasteless, and viscous liquids [76]. Kennedy and his team were able to produce novel polyurethane networks from the linear diols and three-arm star triols when mixed with isocyanates. The polymer was synthesised under a nitrogen atmosphere in a stainless-steel enclosure. The α , ω di(hydroxy) polyisobutylene was dissolved in dry tetrahydrofuran (40%, w/v), mixed with a stoichiometric amount of triphenylmethane triisocyanate. It was then poured on to a teflon pan of dimensions 12 x 12 x 0.5 cm. The mixture was cured at 45°C for two weeks which allowed the solvent to evaporate. The sample was then placed in a vacuum oven and cured at 85°C to 90°C for three days under vacuum [77]. Moisture absorption of about 0.01 – 0.016% moisture absorption over 48 hours at 75°C was found using ASTM D750 [77].

The living polymerization of isobutylene also led to the development of poly (styrene-block-isobutylene-block-styrene) [SIBS] [78], which became the drug eluting coating for the Boston Scientific coronary stent TAXUS [69]. This thermoplastic elastomer has been shown to have excellent biocompatibility [69], [79]–[82]. It is comprised of hard polystyrene end blocks and soft elastomer isobutylene mid blocks [64]. SIBS is an encouraging biomaterial in its own right with a water permeation of 0.24 g.mm/mm²day and a moisture uptake of <0.01 % over two weeks and 1.15% over seven months [64]. The development of SIBS led to the realisation that PIB has exceptional biomaterial properties including its hemocompatibility and tissue compatibility [75].

In the 1990's the research team began to look at biological applications for their novel PIB based materials. Their first use of PIB based biomaterials was in the preparation of bone cements. The molecular structure of PMMA bone cements mean that they were inherently brittle. By

combining PMMAs with covalently bound rubbery PIB domains the team demonstrated the use of PIB in a highly toughened bone cement [74].

PIB based biomaterials also found a use in intervertebral disks, by synthesising PIB carrying cyanoacrylate end groups which polymerized upon exposure to moisture, proteins or other weak nucleophiles. These prepolymers were able to replace intervertebral disks by being injected to the cavity created upon the removal of the herniated nucleus pulposus. Here they were exposed to moisture and then polymerized. The polymer was found to adhere tightly to the surrounding tissue prohibiting the leakage of the polymer into the surrounding tissue [74].

The crosslinking of hydrophilic acrylates and methacrylates with linear and/or three-arm star methacryl-telechelic polyisobutylenes brought about amphiphilic networks and membranes [83], [84]. In 1989 it was determined that a 50/50 proportion of hydrophobic and hydrophilic weight ratios of these polymer networks were biocompatible [85]. This gave rise to the creation of the biocompatible semipermeable PIB based hydrogels. These amphiphilic membranes were fashioned into an artificial (biohybrid) pancreas for the treatment of diabetes Type 1. The membrane enclosed insulin producing porcine cells. These PIB membranes were designed to be 'smart membranes' meaning that they have the ability to change their morphology when exposed to different chemical environments. This encouraged the biocompatibility of the material in the host and also with respect to the porcine pancreatic cells within. As previously stated, they were also designed to be semipermeable which allowed the movement of glucose, metabolic wastes and insulin across the membrane but prevented the movement of antibodies or white blood cells. This protected the insulin producing cells from the host immune system. This was demonstrated by the subcutaneous implantation of this device in a diabetic rat. It was seen that the pig cells produced insulin and a subsequent reduction in the rat's blood glucose levels, which was reversed upon the removal of the artificial pancreas [74].

2.5.3.1 Mechanical Properties of PIB-PURs.

Early iterations of PIB-PUR were found to contain poor mechanical properties, [75], [77], and [86], [87] as detailed in [72]. A large portion of the literature focused on increasing the mechanical properties of PIB-PUR. These poor mechanical properties of PIB-PUR have been heavily detailed in the work detailed by both Kennedy's and Faust's teams. Kang *et al.* [72] and Ojha *et al.* [88] have described these works in the course of their own research into the improvement of these mechanical properties via the addition of PTMO diol into the formulations of polyisobutylene based polyurethanes.

Zapp *et al.* produced polyisobutylene based polyurethanes with ultimate tensile strengths ranging from 10.2 – 33.7 MPa with failure strains of 80 – 320% [89] (as detailed in [72]). In 1985 Speckhard *et al.* again showed low UTS (1-10 MPa) and poor elongation (10-200%) [86] (as detailed in [88]).

Not only did PIB based polyurethanes exhibit poor mechanical properties, Mitzner *et al.* observed that the addition of PIB diol into polyether urethanes significantly reduced their mechanical properties. This was ascribed to the lack of reinforcing H-bridges. The replacement of 10% wt of PTMO diol with PIB diol resulted in a decrease of ultimate tensile strength from 23.4 MPa to 14.2 MPa [90] (as detailed in [88]).

Interest in PIB based polyurethanes waned due to the high cost. However, interest re-emerged following the development of living polymerization of isobutylene leading to the production of diols at reduced cost. At this point, attention turned to the improvement of PIB-PUR's mechanical properties [75]. It was theorised by Kang *et al.* that these low mechanical properties were due to a high degree of phase separation between the hard and soft segments and the lack of H bonds between these segments.

It was then proposed that the addition of PTMO diol in addition to the PIB diol would create gradient interfaces between the polar and non-polar phases and provide improved mechanical properties. The addition of PTMO diols proved to increase the tensile strength and the elongation of the polyurethanes [75].

Jeweajka *et al.* examined the how the addition of PTMO into PIB based polyureas affected the mechanical properties. It was found that the addition of 12% PTMO into the soft segment of the PIB based polyurea greatly increased the mechanical properties with limited impact in the hydrolytic and oxidative stability of the polymer. This supported their hypothesis that the incorporation of PTMO improved the interfacial adhesion between the PIB and urea phases allowing better stress transfer between the hard and soft segments [91].

Erdodi *et al.* then examined the creation of PIB-PURs via the incorporation of PTMO diol into the soft segment of the polyurethane. This resulted in a polyurethane with excellent mechanical properties ranging from 7.2-32.5 MPa stress and elongation range of 211-700% [92]. It was found that by including moderate amounts of PTMO (20% by weight) in the formulations of PIB based polyurethanes that there was a significant increase in mechanical properties.

Similarly, Ojha *et al.* found that the incorporation of a PTMO diol into the soft segment of a polyisobutylene based polyurethane significantly improved the mechanical properties. This was

demonstrated with an increase of tensile strength of 6-9 MPa and an elongation of 150-400% for samples without PTMO to an ultimate tensile strength of approximately 20 MPa and elongations of approximately 700% [88]. Erdodi *et al.* outlined the expectation that by retaining a large amount of PIB diol in the formulation, PIB base polyurethanes were expected to maintain high oxidative, hydrolytic, and enzymatic stability [92].

Kang *et al.* explored the oxidative-hydrolytic stability and biocompatibility of these polyurethanes. As a part of this work tensile studies were performed on urethanes made both and without the addition of PTMO diol. This indicated that there was an increase in the mechanical properties from 14 MPa and 420% to a range of 24.6-27.2 MPa and 740 – 770% [93].

Cozzens *et al.* [94] examined the mechanical, and oxidative stability of polyisobutylene polyurethanes to determine their suitability as a candidate material for electrospun cardiovascular grafts. It was shown that ultimate tensile strengths of these grafts were 1.63-6.53 MPa with failure strains of approximately 103-282%, the strain was dependent on the composition of the polyurethane specifically the ratio of soft segment to hard segment.

Table 2.2 Mechanical properties of PIB-PUR from literature

<u>Mechanical Properties</u>		
<u>Author of Paper</u>	<u>Stress MPa</u>	<u>Strain (%)</u>
Zapp <i>et al.</i> [89] as detailed in [75]	10.2 – 33.7	80 - 320
Speckhard <i>et al.</i> [83] as detailed in [88]	1 – 10	10 – 200
Ojha <i>et al.</i> [88]	6 – 9	150 - 400
Ojha <i>et al.</i> [with PTMO] [88]	20	700
Kang <i>et al.</i> [with PTMO] [93]	24.6 – 27.2	740 - 770

2.5.3.2 Degradation Properties of PIB-PURs

Kennedy *et al.* carried out degradation testing via both dry air and hot water aging. Hot water samples were submerged in water for four days at 85°C then cooled to ambient temperature for testing. Dry aged samples were suspended in a circulating air oven for 48 hrs at 128°C and cooled to ambient temperature before testing. There was negligible difference in the strain experienced at failure but there was up to a 5% decrease in yield stress experienced in samples with a crosslinking density of 3700 and 2100 after hot water exposure. Up to a 3.1 %

deterioration of yield stress in samples which experienced hot air aging across all crosslinking densities tested was observed [76]. Kennedy *et al.* corroborated work previously conducted by Chang *et al.* who also performed hydrolytic stability testing of PIB-PUR materials. This testing was also completed at 85°C for four days and air oven aging was carried out at 128°C for 48 hours. Results from this study also showed for samples with a lower molecular weight (3,400) there was a 5% reduction in tensile strength and elongation, however samples with a larger molecular weight (11,500) did not show significant deterioration. This good retention of mechanical properties was also seen when the PIB-PUR materials were aged at 128°C for 48 hours [77].

Jewrajka *et al.* conducted hydrolytic and oxidative stability experiments by submerging polyureas created from polyisobutylene amines in distilled boiling water for 15 days and stirring them in 36% nitric acid for 12 hours at room temperature. It was found that there was no optical change in either experiment. In the samples submerged in distilled water the tensile strain decreased from 19.5 MPa to 17.5 MPa and 18 MPa to 17.1 MPa. For samples in nitric acid this was seen that the stress decreased from 1.6 MPa to 1.1 MPa, 19.5 MPa to 3.1 MPa and 18 MPa to 2.8 MPa. While this represented a significant change in tensile strength in comparison to the control polymers used (Elaston and Bionate) which disintegrated within 30 minutes of exposure. It shows that these polyisobutylene polyureas exhibited a strong oxidative stability [95].

Kang *et al.* exposed polyisobutylene based polyurethanes to both 35% nitric acid, agitated at 500 rpm for both 4 and 18 hours at room temperature. This resulted in a drop in tensile strength from 31.2-14.0 MPa to 13.0 MPa and 17.4 MPa to 12.5 MPa. Samples also were placed in a H₂O₂/CoCl₂ solution stirred at 150 rpm and kept at 37°C which resulted in a reduction of tensile strength of 14 MPa to 10 MPa [96].

Throughout the literature it was shown that when compared to other control polymers PIB based polymers exhibit strong resistance to oxidation and degradation.

2.5.3.3 Permeability Testing

Chang *et al.* examined two sheets of PIB-PUR with differing molecular weights for oxygen gas permeability in accordance with ASTM D1434. 5cm² disks were tested at 30°C for 89 hours [77]. It was found that when compared to the value for oxygen gas permeability for vulcanized butyl rubber via the Polysar Butyl Handbook (1966) [97] the produced PIB PURs had a much lower permeability value, 202 (cm.mil/100.in².24.h.ATM) versus 650 – 4750 (cm.mil/100.in².24.h.ATM) [74].

2.5.3.4 Moisture Absorption

Chang *et al.* submerged samples in distilled water at $75 \pm 1^\circ\text{C}$ for 48 hours and then blot dried. The percentage of water absorbed was found to be between 0.01-0.016% [77]. Kang *et al.* examined the moisture absorption of PIB based polyurethanes and found it was $0.07 \pm 0.2\%$ the test was carried out at 85°C for 3 days in PBS solution [93].

Table 2.3 Moisture absorption properties of PIB-PUR from literature

<u>Moisture Absorption Properties</u>		
<u>Author of Paper</u>	<u>Moisture Absorption (%)</u>	<u>Test Conditions</u>
Chang <i>et al.</i> [77]	0.01-0.016%	$75 \pm 1^\circ\text{C}$ for 48 hours in distilled water
Kang <i>et al.</i> [93]	$0.07 \pm 0.2\%$	85°C for 3 days in PBS solution

2.6 Multilayer Encapsulations

The materials used for polymeric encapsulation do not always have ideal material properties to ensure near hermeticity. In order to ensure resistance to water, oxygen and ionic permeation the barrier can be improved through the enhancement of adhesion between the substrate and the film or the use of multiple layers [7], [33], [98]. The use of multiple layers allows the packaging engineer to overcome the limitations of a single encapsulant [6].

The most common iteration of a multilayer encapsulation is a bi-layer layout, by which two materials are laid on top on each other to ensure a near hermetic bond. For instance, Wu *et al.* [6] selected an elastomeric silicone for its flexibility, water repellence and abrasion resistance, in addition to parylene with a silane promoter. The parylene compensates for the lack of resistance of the silicone to engine fuel and oil contamination [6].

Because parylene can be easily damaged it is very commonly used in conjunction with another material when forming a near hermetic barrier. In literature it has been used with a thin metallic layer to enhance the hermetic nature of the barrier to prevent the permeation of moisture and gases. Madakasira *et al.* [7] created a multilayer barrier in order to protect plastic solar cells from degradation as a result of exposure to solar light. In the multilayer barrier alternating layers of parylene layers and aluminium oxide were sandwiched together. This combination resulted in favourable electrical and physical properties. The parylene allowed for the electronic isolation

of the photo elastic device. However, parylene is still permeable to oxygen which was mitigated by the aluminium oxide layer. This multilayer was found to be very promising for full protection of organic solar cell degradation [7].

Hogg *et al.* [99] described a hermetic and biocompatible thin film packaging for long term implantable medical devices. This packaging consisted of a high molecular density silicon oxide and parylene C deposited by a novel single chamber thin film deposition process. The parylene layer was vital for permeation and conformity. The silicon oxide also contributes to hermeticity of the coating with a low helium gas permeation. Water permeation of conventional parylene C layers were compared to multilayer stacks consisting of 3 silicon oxide interlayers of 4.7 μm . It was found that by tailoring the thickness ratio between the layers of the coating, the permeation of the direct water exposure could be substantially diminished when compared to conventional single layer parylene C with similar thickness [99].

Kou *et al.* [100] describes water vapour barrier coatings using parylene C. Initially the team tested various thicknesses of parylene C ranging from 2-25 μm . This testing involved 2 electrode printed circuit board (PCB) test boards. They were electrically measured post accelerated aging in an 85°C saline solution in order to gain a baseline minimum for a parylene coat thicknesses. Accelerated life testing was carried out at 85°C on parylene C of thicknesses of 2-9 μm . Immediate failure occurred; it was theorised by Kou *et al.* that this was due to contamination. It was determined that a 25 μm thicknesses was sufficient to provide protection for 11 years using an adapted Arrhenius temperature dependence equation. After cleaning the deposition chamber and subsequent testing it was seen that a 5 μm thickness was satisfactory for short term protection. Water permeation tests were carried out on a multilayer structure comprising of parylene C, oxide and nitride. Single parylene C layers of 9.7 μm thicknesses were compared to 6 multiple interfaced layers of 50 nm oxide and 50 nm nitride. The water vapour transmission rate improved from $4.97 \times 10^{-3} \text{ g.mm/m}^2.\text{day}$ to $2.25 \times 10^{-3} \text{ g.mm/m}^2.\text{day}$ which is an improvement of 54.7% percent [100].

2.7 Literature Review Summary

Technological advancements have allowed for the miniaturisation of electronic medical devices which has increased the variety of disease states that may be treated. However, these advancements have not been made without difficulties. The packaging of these devices is complicated by their shrinking size and thus the consideration of a conformal coating may be prudent. An insulative material that bonds to the surface of the device would in theory prevent

moisture from depositing on the electronics, in turn preventing short circuits and therefore device failure.

In the literature there are numerous kinds of polymers which have been explored as a conformal coating for electronic devices such as parylene and LCP. PIB based polyurethanes were first explored by Kennedy *et al.* in the 1970s. Over the following decades the mechanical properties were explored and subsequently improved via the incorporation of PTMO diol into the soft segment of the polyurethane. Degradation was also examined and found to be minimal. Absorption testing was explored by Chang *et al.* [77] and Kang *et al.* [93]. All of these properties, compounded by polyisobutylene's widely known ability to resist the permeation of moisture and gases give credence to the hypothesis that a polyisobutylene based polyurethane could be an excellent conformal protective coating for an implantable electronic device.

However, there has been minimal exploration of this concept in the literature thus far. This work aims to contribute to this knowledge by achieving the following aims and objectives.

2.8 Aims and Objectives

The industrial partner has created a polyisobutylene diol with a low presence of contamination, confirmed through NMR, considered potentially suitable for implantation. The addition of two hydroxyl groups onto the polyisobutylene chain has created an opportunity to create a polyurethane which may be suitable for the near hermetic encapsulation of electronics *in vivo*.

This project aimed to develop a processing method to create a polyisobutylene polyurethane for the conformal coating of implantable electronic medical devices. The objectives are;

- The development and refinement of a process to fabricate high quality PIB-PUR sheets from a high viscosity diol.
- The identification of tensile mechanical behaviour of fresh and post degradation PIB-PUR samples and the effect of incorporating Tween 20.
- The investigation of the elasticity and strain energy absorption characteristics under multiple consecutive cycles of extension.
- The establishment of the water vapour transmission characteristics for PIB-PUR materials, and investigation of levels of moisture absorption at 37°C in relevant media over protracted periods.

These results will be considered with respect to the requirements of implantable medical devices and by comparison with other materials potentially under consideration for the application.

Chapter 3. Materials and Methods

This chapter provides details of the materials, equipment and experimental procedures used in this research.

3.1 Materials

3.1.1 Polyisobutylene Diol

The polyisobutylene diols (Figure 3.1) used in this study were produced by Boston Scientific Ltd for research purposes. Three batches (A, B and C) were provided to conduct this research. All batches were made in a laboratory setting and therefore were individually characterised as detailed in Table 3.1. The molecular weights and the specific gravity of all three batches differed and were taken into account when calculating stoichiometry for PIB-PUR formulations.

Table 3.1 Molecular Weights and Specific Gravities of PIB diol batches

	Batch A	Batch B	Batch C
Molecular Weight [g.mol ⁻¹]	2029 [101]	1993 [101]	1845 [102]
Specific Gravity [kg.m ⁻³]	0.91 [101]	0.92 [101]	0.92 [102]

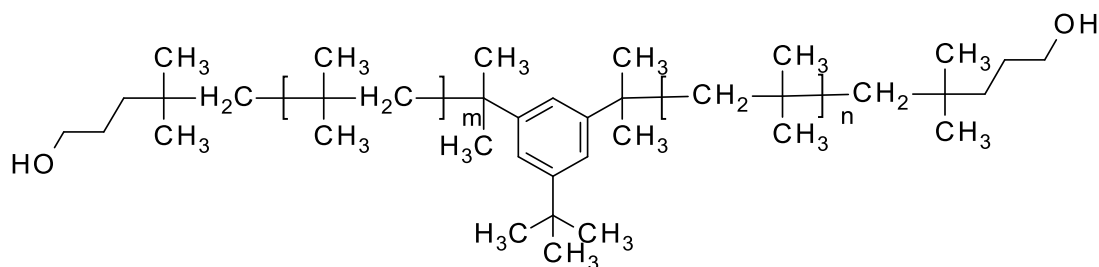


Figure 3.1 Chemical structure of Polyisobutylene diol [103]

3.1.2 Lupranat MI

Lupranat MI is a blend of 2,4 and 4,4'- methylene diphenyl diisocyanate (MDI) procured from BASF (USA), which will be used in the production of these polyisobutylene polyurethanes. It is liquid at room temperature allowing for easier incorporation into the diol than its Lupranat ME counterpart, a pure 4,4' MDI which is solid at room temperature. Figure 3.2 and Figure 3.3 describe 2,4' and 4,4'-methylene diphenyl diisocyanates respectively. They are the diisocyanates employed in this research. These isocyanate functional groups react with hydroxyl groups from a polyol, [PIB diol] or a crosslinking agent [Tween 20] to form a polyurethane.

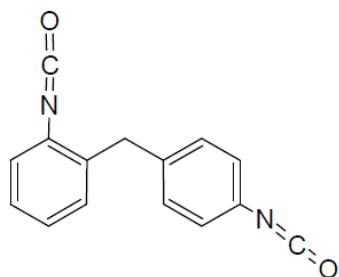


Figure 3.2 2,2',4'-methylene diphenyl diisocyanate [103]

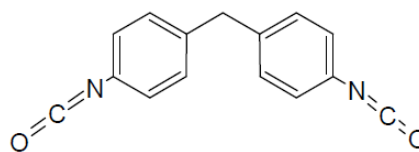


Figure 3.3 4,4'-methylene diphenyl diisocyanate [103]

3.1.3 Crosslinking Agent

3.1.3.1 Tween 20 (Polysorbate)

Tween 20 was procured from Merck via VWR, (Republic of Ireland). Polysorbate, Tween 20, whose molecular structure can be seen in Figure 3.4, is a polysorbate non-ionic surfactant typically used as a detergent in domestic, scientific and pharmacological applications. In this research it is used as a crosslinking agent to create additional bonds with the intention to improve mechanical strength and be a stronger barrier to water vapour ingress.

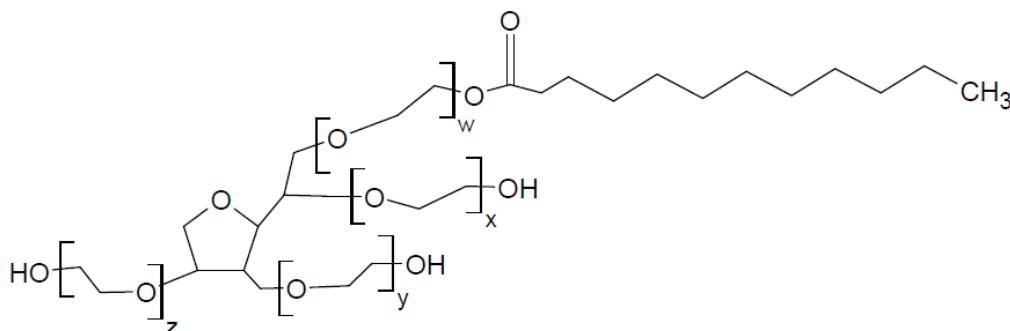


Figure 3.4 Polysorbate monolaurate (Tween 20) chemical diagram [103]

3.1.3.2 Pluracol (PEP) 450, 550

Pluracol 450 and 550 are polyether polyols procured from BASF (USA). Here they were initially used as crosslinking agents and feature in the study when examining the effect of cure duration on the lap shear value of PIB-PUR.

3.1.3.3 THP – 1,1,1- Tris(hydroxymethyl)propane

THP is typically used as a material in the synthesis of polyglycerols and polylactides procured from Sigma Aldrich (USA) product number 93370. In this study it was briefly used as a crosslinking agent in a PIB-PUR formulation in the early stages of development.

3.1.4 Catalyst

3.1.4.1 Tin (II) 2-ethylhexanoate

Tin (II) 2-ethylhexanoate is commonly used as a catalyst in polymeric formulations and procured from Sigma Aldrich (Ireland), product number S3252. In this research it features throughout as the catalyst in all PIB-PUR formulations.

3.1.5 Polyisobutylene Polyurethane

In this research Polyisobutylene (PIB) Polyurethane (PUR) is a polyurethane made from PIB diol and MI Luphanate diisocyanate and in some cases Polysorbate Tween 20, as described in a company patent application [103]. Figure 3.5 shows the chemical diagram for PIB-PUR. In Figure 3.6 the chemical diagram shows the PIB-PUR polymer chains. These chains consist of the diol molecules and the isocyanate molecules which have reacted with each other this is visible in Figure 3.5, Figure 3.6 and Figure 3.7.

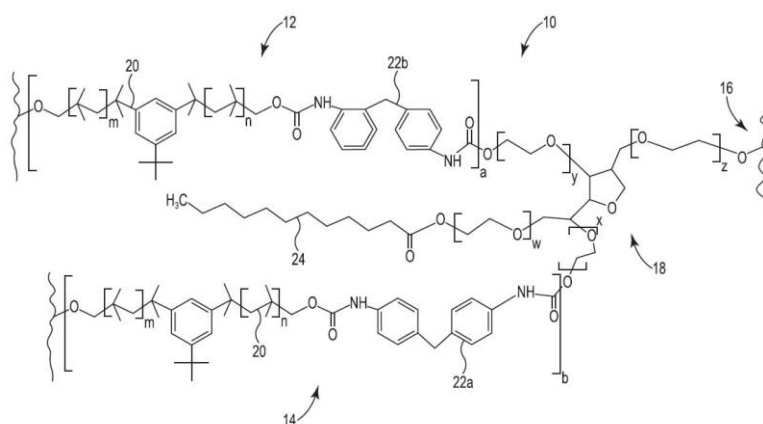


Figure 3.5 Chemical structure for PIB-PUR containing crosslinking polysorbate [103]

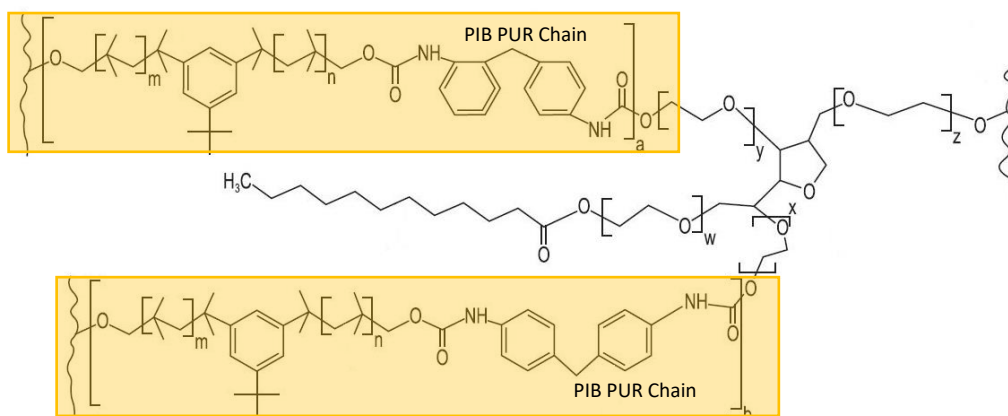


Figure 3.6 PIB-PUR with PIB-PUR chains labelled [103]

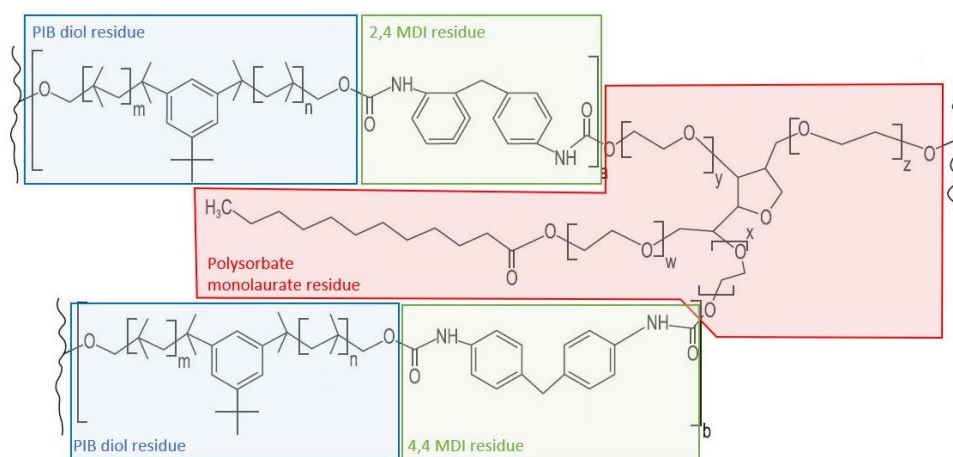


Figure 3.7 Chemical structure of PIB-PUR, constituent chemical residues labelled [103]

3.1.6 Hydrocarbons

The following hydrocarbons were procured from VWR (Ireland) for this study.

- Hexane (catalogue number 24574.323)
- Heptane (catalogue number 24548.298)
- Octane (catalogue number 8.06910.1000)

Hydrocarbons are organic compounds which consist exclusively of carbon and hydrogen. Hexane, Heptane, and Octane are the primary hydrocarbons which feature in this thesis as solvents used to reduce the viscosity of the PIB diol. Hydrocarbons can be extracted from crude oil and are typically volatile and flammable.

Table 3.2 Chemical formulae and boiling points of the hydrocarbons, hexane, heptane and octane

	Hexane	Heptane	Octane
Chemical Formula	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈
Boiling Point	69°C [104]	97-98 °C [105]	125 – 126°C [106]

Hydrocarbons were listed as solvents for Polyisobutylene, in the Polysar Polymer Handbook [97]. These hydrocarbons were all explored as solvents in the production of PIB-PUR. The non-polar nature of hydrocarbons enables them to dilute the polyisobutylene diol and thereby reduce its viscosity.

3.2 Methods

3.2.1 Polymer Formulation

The development of the Polyisobutylene Polyurethane fabrication process is detailed in Chapter 4.

3.2.2 Characterisation

3.2.2.1 Rheology

Amplitude Sweep

When conducting a rheological evaluation of an unfamiliar material the first step is to conduct an amplitude sweep. This will allow the determination of the linear viscoelastic region, which is the region in which testing may be carried out without destroying the structural integrity of the material.

Testing is carried out using an Anton Paar machine and analysed using Anton Paar RheoCompas software. In the programme the amplitude sweep setting is selected, and the strain range is set at 0.01% strain to 100% strain.

The amplitude is tested using parallel plates. Diol is prepared with solvent if required and placed on the bottom plate. The top plate is then affixed to the machine and lowered using programmed settings. Excess material which is pressed out from between the plates is removed using a wooden dowel held perpendicular to the plates.

The storage and loss moduli are then recorded and plotted against the strain rate.

Frequency Sweep

A frequency sweep is also conducted this involves placing material between two parallel plates as above and instead of varying the amplitude of the oscillations, the amplitude of motion was kept fixed, and the frequency is varied. All testing should be conducted within the linear viscoelastic region in order to maintain the material structure. An amplitude of 10% strain was identified to be within the linear viscoelastic region of PIB diol and therefore is a safe amplitude for these materials.

The frequencies examined are 0.1 to 100 rad/s. The storage and loss moduli are recorded and plotted against these frequencies.

Viscosity versus shear rate

Due to the high viscosity of the diol liquid, it is important to understand how and to what degree the addition of solvent to the material would affect the diol viscosity. This is done by examining the material's viscosity versus shear rate.

3.2.2.2 FTIR [Fourier Transform Infrared] Spectroscopy

FTIR is performed to gain better understanding of the molecular structure of materials both before and after curing. Samples are tested on a Thermofisher Nicolet iS50 FTIR Spectrometer with a Smart iTR Attenuated Total Reflectance Sampling Accessory.

The testing surface of the spectrometer is cleaned down using heptane, alcohol, followed by distilled water and subsequently dried with a lint free cloth. The stage is cleaned prior to the analysis of each sample to prevent cross-contamination. A background spectrum is taken before each sample to calibrate the machine. A small amount of the sample is then placed on the stage and held in place with the attenuated arm. An absorbance spectrum is taken and subsequently examined.

3.2.2.3 Sample Selection for Tensile and WVTR Specimens

Each sample's thickness is measured at 25 points, the variance for each sample was calculated and the samples with the least variance are allocated for WVTR testing. The samples with higher variances are used for tensile and moisture absorption specimens.

3.2.2.4 Tensile Test Specimens

Tensile test samples are stamped out using a die from Qualitest TM with the product number DIN 53594 53A Figure 3.8. The die has an overall length of 50mm, a narrow portion length of 16mm and a narrow portion width of 4mm. This punch is placed under a Qualitest™ bench press. The press is pulled down in a swift to ensure a clean cut for the sample with well-defined edges as shown in Figure 3.9.



Figure 3.8 Qualitest Die used to cut tensile samples



Figure 3.9 Complement of tensile specimens cut from sample

3.2.2.5 Moisture Absorption Specimens

Moisture absorption test samples are stamped out using an Osborne Arch Punch, No. 149 with an internal diameter of 25mm. This punch is attached to a fly press. The fly press is pulled down in a swift manner to ensure a clean cut for the sample with well-defined edges as shown in Figure 3.10.



Figure 3.10 Moisture absorption samples cut from sheet

3.2.3 Mechanical Characterisation Methods

Testing of mechanical properties is a fundamental step in the characterisation of any material. It is imperative that its behaviour while under dynamic or static force is understood so that it can be determined how the material may behave if subjected to mechanical stress during its working life.

3.2.3.1 Lap Shear Testing Method

Lap shear testing is a method of testing the strength of curable materials in a single plane. A single lap shear test is detailed in the ASTM standard D1002 and is the simplest but least efficient adhesive test due to eccentric loading in the samples. Single lap shear testing was used as a method to qualify the quality of material being made during exploratory work and thus was not expected to provide large quantities of reliable data.

The test samples typically consist of two metal slides, in this case titanium, which have been cleaned with isopropyl alcohol, acetone and DI water and dried prior to the application of the material to be tested. The material is then placed on a slide which was held in place in the curing fixture. The second slide is then placed on top of the first slide. During curing, the slides are fixed in place in order to keep a defined height of adhesive. Once the material has been fully cured the test sample is placed in a tensile tester and force is applied. The substrate is pulled in opposite directions, the bottom slide is fixed while an upward force is exerted with a displacement of 1.02 cm/min by the top slide as shown in Figure 3.11. The lap shear force of the material is defined as the force required for the bond to fail. In lap shear tests, it is important to examine the failure mode of the specimens, in terms of whether the material fails within the bulk material or at the interface between the metal and the polymer. This is key as it speaks to the inherent strength of the material or its adhesive properties. Should the material fail in the bulk material this would imply that the adhesive strength of the material was higher than that required to shear the bulk material. If the sample fails at the interface of the material and the slide, then the strength of the bulk material was stronger than that of the adhesive strength.



Figure 3.11 Schematic for lap shear testing

3.2.3.2 Tensile Testing Method

Tensile tests are conducted by placing a material under progressively increasing strain. Deformation is typically increased until failure is achieved. The loads induced in the sample are continuously measured. The results are shown in a stress strain curve, from which a plethora of information can be garnered. For the purposes of this study, dumbbells of an overall length of 50 mm, a narrow portion length of 16 mm and a narrow portion width of 4 mm was used. The samples are held in manually tightened grips with added sandpaper to aid the clamping force. Samples are tested with a 5 kN load cell with a strain rate of 100 mm.min^{-1} directly to failure as indicated in Figure 3.12 and Figure 3.13.



Figure 3.12 Beginning of tensile test



Figure 3.13 Displaying strain before failure

3.2.3.3 Cyclic Testing Method to Explore the Mullins Effect

The Mullins effect is a stress softening mechanical response exhibited by rubbers. Under repeated cycles of tensile strain, the polymer exhibits a reduced stress after the initial cycle of extension.

By examining if the Mullins effect is present in this material insight would be gained into the capabilities and the limitations of the material. In the Mullins effect differences are seen in the loading and unloading paths of successive cycles. Hanson *et al.* described this effect in a silica filled PDMS. In their study, the results of which are depicted in Figure 3.14, virgin samples were pulled to 100% strain (red) then to 200% strain (blue) and finally to 300% strain (yellow). For comparison a separate sample which was tested to 300% strain is also displayed (black) [107]. Hanson *et al.* found that the stress strain curve produced is dependent upon the tensile history of the specimen and the maximum loading previously applied to the specimen.

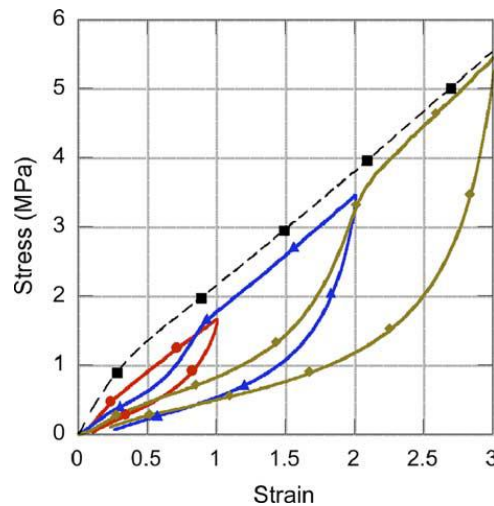


Figure 3.14 Hanson et al. described the Mullins effect in virgin silica filled PDMS samples [107]. Reprinted from Polymer, 46/24, David E. Hanson, Marilyn Hawley, Robert Houlton, Kiran Chitanvis, Philip Rae, E. Bruce Orler, Debra A. Wroblewski, Stress softening experiments in silica-filled polydimethylsiloxane provide insight into a mechanism for the Mullins effect, 10989 - 10995, 2005, with permission from Elsevier

In this study, specimens were exposed to a series of tensile extensions and retractions in order to examine if the Mullins effect held for the various PIB-PUR formulations. These tensile series are composed of the following steps for this study.

1. In the first cycle, the sample is tested at a strain rate of 100 mm/min terminating once a strain of 200% is achieved.
2. The sample is then returned to 0% strain and held at 0% strain for 10 minutes to allow the polymer chains to relax.
3. In the second cycle the sample is then strained to 300% strain at a rate of 100 mm/min.
4. The sample is then returned to 0% strain and again held at 0 % strain for a further 10 minutes.
5. In the third cycle, the sample is strained to 400% strain at a strain rate of 100 mm/min.
6. The sample is again returned to 0% strain and again held at 0 % strain for a further 10 minutes.
7. For the final stage, the sample is tested to failure at a strain rate of 100 mm/min.

3.2.3.4 Degradation Testing Method

Degradation analysis is important in the characterisation of failure of a material and can be used to make some conclusions about the reliability of the material. Here the material is placed in PBS solution and kept at 37°C to mimic the conditions it would undergo *in vivo*.

Tensile specimens are placed in a jar and covered in phosphate buffered saline solution. For each formulation sheet 4 specimens are used. Each jar is labelled with the corresponding sheet

number and formulation. These jars are placed in an oven at 37°C. After 7 days 1 dog bone specimen is removed from each jar, dried and stored before being tensile tested to failure. Samples are subsequently removed at 2, 4, and 8 weeks. The samples are dried using filter paper and stored in aluminium foil for 1 week before testing.

3.2.4 Permeation Characterisation Methods

The evaluation of permeation characteristics is a key stage in the assessment of a new material for coating of electronic devices. As previously stated for all electronic devices, moisture contamination is a key means of failure. Therefore, should a device be expected to perform and protect a patient while implanted, it is crucial that the behaviour of the defensive barrier while exposed to moisture is known.

3.2.4.1 Moisture Absorption Methods

One of the simplest methods to establish how a material will behave when exposed to moisture is a moisture absorbance test by weight gain. For this test, circular specimens of a diameter of 25 mm are stamped out of PIB-PUR sheets as detailed in 3.2.2.5. The specimens were then laid out on aluminium foil on labelled and placed in a vacuum chamber Mophorn 2 Gallon Vacuum Chamber. They are then placed under a vacuum of 0.87 bar for 24 hours at ambient temperature. The vacuum is achieved using a 3CFM single stage vacuum pump with HVAC Lab Vacuum Figure 3.15.

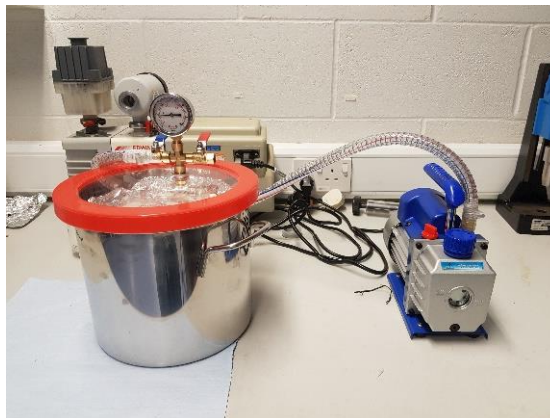


Figure 3.15 Samples in chamber under vacuum

Phosphate Buffered Saline Solution Preparation

Phosphate buffered saline solution is made using Phosphate Buffered Saline (PBS) Tablets, 100ml from VWR Life Science (Ireland). The ratio used is 1 tablet per 100ml of water as per manufacturers specifications.

Distilled Water/Phosphate Buffered Saline Solution Absorption Method

After being held under vacuum for 24 hours the specimens are weighed using a Mettler AE 50 scientific balance to establish their dry weight (W_d).

The samples are then placed in jars containing distilled water or phosphate buffered saline solution and labelled. These jars are then placed in an incubator oven Biotech Galaxy CO₂ Incubator with a constant temperature of 37°C.

Every hour for the first 4 hours, samples are taken out, dried in filter paper, and weighed using the Mettler AE 50 scientific balance. Samples are then weighed at intervals to determine the weight after soaking.

Once the material is saturated, the weight of the sample plateaus and no longer shows an increase (W_t). The moisture absorbance of the material is then calculated for each data point using Equation 3.1.

$$W[\%] = \frac{W_t - W_d}{W_d} \times 100$$

Equation 3.1 Percentage weight gain associated with moisture absorption

$W[\%]$ = Percentage weight gain associated with moisture absorption.

W_t = The weight of the samples after soaking.

W_d = The weight of the dried samples before soaking.

The method for phosphate buffered saline solution absorption mirrors the method describe above for distilled water absorption.

3.2.4.2 Water Vapour Transmission Rate Testing

For this work, water vapour transmission rate was considered to be one of the most important pieces of testing conducted. Determining the amount of water vapour which can permeate through the polymer was crucial. The ASTM standard F1249 describes a method to determine the water vapour transmission rate of flexible plastic sheeting and films which consist of single or multilayer natural or synthetic polymers or foils.

The method consists of a dry chamber separated from a wet chamber of known temperature and humidity by the testing barrier material. The water vapour diffuses through the barrier material from the wet chamber (the area of high concentration of water vapour) to the dry chamber (the area of low concentration of water vapour). In the dry chamber, the water molecules which have permeated through the barrier material mix with the dry gas and are

carried to a pressure-modulated infrared sensor. This sensor measures the infrared energy absorbed by the water vapour and produces an electrical signal. The amplitude of this signal is proportional to the concentration of the water vapour concentration in the dry chamber. This amplitude is then compared to the amplitude produced by a film which has a known water vapour transmission rate. This is then used to calculate the water vapour transmission rate of the material being tested.

Before the samples were tested, they were examined and found to have raised edges created during curing. This may have resulted in a weak seal in the chamber and so were trimmed from 10cm x 10cm to 5cm x 5cm. These were then masked as indicated in Figure 3.16. Once the material is masked it is then placed in the diffusion cell as shown in Figure 3.17 and secured into the machine. In this case the AQUATRON Model 1 from MOCON is used as indicated in Figure 3.18. The WVTR of the film is then measured in accordance to the manufacturer's instructions.



Figure 3.16 Aluminium mask enclosing PIB-PUR material prior to test WVTR



Figure 3.17 PIB-PUR material in sealed aluminium mask sitting in open diffusion cell



Figure 3.18 AQUATRON Model 1 from MOCON for water vapour transmission rate testing

Chapter 4. Development of PIB-PUR Processing Route

4.1 Mechanical Feasibility Testing

Polyisobutylene (PIB) is a commercially important polymer due to its excellent thermal stability and excellent flexibility at ambient temperature. Many properties have been identified which differentiate PIB from most other polymers, such as its low penetrability to small molecules [60]. A formulation of Polyisobutylene diol has been developed by Boston Scientific Ltd. This diol was developed in order to create a polyisobutylene polyurethane (PIB-PUR), another synthetic rubber anticipated to have low permeability to small molecules and be flexible at ambient temperatures. It is an objective of this thesis to investigate processing routes for this material and to uncover its key performance characteristics in relation to implantable electronic applications.

To determine the feasibility of PIB-PUR as a candidate material for creation of a near-hermetic barrier, its mechanical properties were explored. Importance was placed on the materials' lap shear properties because in order to ensure a stable reliable coating it was important to ensure that the material is curable, non-tacky and relatively strong with good adhesion properties. The lap shear analysis examined its adhesion properties to titanium slides. Initial testing was to examine the effect of crosslinking agents on the adhesion properties to the titanium strips. This testing quickly exposed many issues within the manufacturing process.

The first phase of this feasibility testing involved formulating small amounts of PIB-PUR and making lap shear slides using the crosslinking agents THP, Tween 20, Pluracol 450 and Pluracol 550. The purpose of this study was to investigate the ratios of PIB-diol, isocyanate (chain extender), crosslinking agent and silica filler would give sufficient lap shear strength results. A patent application was filed, the details of which can be found in Appendix A [103].

4.1.1 Initial Method for PIB-PUR

Multiple iterations of lap shear samples were made and tested in order to investigate which ratios of PIB diol, isocyanate, crosslinking agent and silica filler would give sufficient lap shear strength results. A target of 0.45 N/mm^2 was set to warrant the continuation of the investigation of PIB-PUR.

For the purposes of clear communication in this chapter, a naming convention will be used to identify the combination of constituents used in each material manufactured. This will take the form:

PP - [PIB batch] – [Cross-linker] – [Sample type] – [Processing Method]

Where: PIB batch may be A, B or C, referring to three batches of the PIB diol synthesised by Boston Scientific.

Cross-linker is identified from the list given above.

Sample type is either lap shear sample (L) or moulded sample (M).

This naming convention will however be simplified later, when a final processing approach is selected.

Initial Method (designated M0).



1. 1g of PIB-diols with a fraction of a drop of Lutidine and 0.1µg of MDI was mixed in a THINKY ARE-250 speed mixer for 10 minutes at 2,000 rpm.
2. If crosslinkers are required for a mixture, weights of 0.123g (Tween 20) 0.34g THP 0.4g PEP 450 and 0.5g PEP 550 were then combined with the solution using the speed mixer for 10 minutes at 2,000 rpm.
3. Titanium slides were cleaned using isopropanol.
4. The mixture was smeared onto one slide, the second slide was then placed on top.
5. Samples were labelled with the date, sample number and initials.
6. Samples were cured in an oven at 100°C for 1, 2, 4, 8 or 16 hours.

The designation for a lap shear sample created using batch A and the PEP 450 cross-linker with Method 0 is therefore PP-A-PEP 450-L-M0.

Samples were tested in lap shear configuration on an Instron Tensile Tester using a 2kN load cell. Initial test results showed little promise. The low lap shear values and tackiness lead to the determination that these samples were not fully cured. It was decided that the time spent curing should be increased to achieve full cure.

A study on the effect of curing time was conducted to determine the optimal time period for curing to be completed. The time study was completed at two temperature values (100°C and 150°C). Samples were cured for 1, 2, 4, 8 and 16 hours respectively. Lap shear tests were then performed and from the resultant values, shear stress at failure increases for higher curing times Figure 4.1.

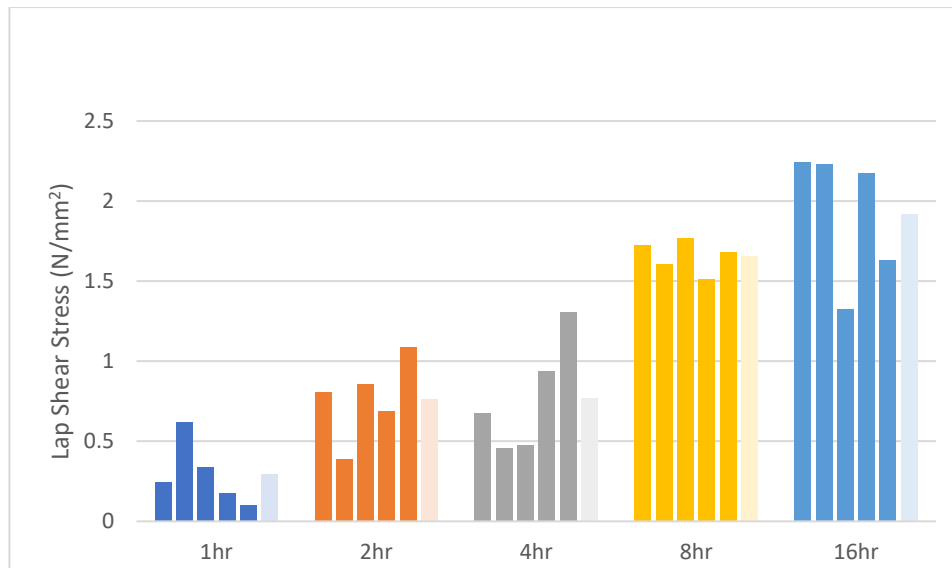


Figure 4.1 Lap shear results for time study conducted at 100°C for PP-A-PEP 450-L-M0 indicating an increase in lap shear stress. Individual results are in bold, average results are pale in colour

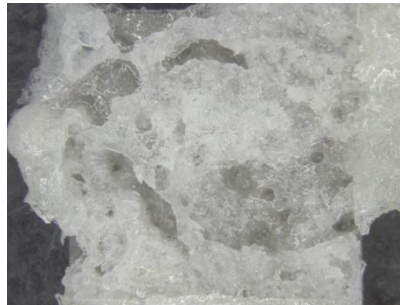
The failure stress continued to increase until the cure time reached 16 hours, when it reached an average load of 1.92 N/mm². Table 4.1 shows images of failed specimens from each of the cure times indicated above, demonstrating voids present in the material.

Table 4.1 Examples of samples of PP-A-PEP 450-L-M0 at 100°C for 1, 2, 4, 8, and 16 hours respectively showing voids present in samples and little evidence of colour change

Hours Cured

Example of PP-A-PEP 450-L-M0

1 hour



2 hours



4 hours



8 hours



16 hours



Method 1 (designated M1)



It was decided to increase cure temperature to 150°C in order to attempt to produce higher quality samples. The method was:

1. 1g of PIB-diol with a fraction of a drop of Lutidine and 0.1µg of MDI was mixed in a THINKY ARE-250 speed mixer for 10 minutes at 2,000 rpm.
2. If crosslinkers [CL] are required for a mixture, weights of 0.123g (Tween 20), 0.34g THP, 0.4g PEP 450 and 0.5g PEP 550 were then combined with the solution using the speed mixer for 10 minutes at 2,000 rpm.
3. Titanium slides were cleaned using isopropanol.
4. The mixture was smeared onto one slide, the second slide was then placed on top.
5. Samples were labelled with the date, sample number and initials.

6. Samples were cured in an oven at 150°C for 1, 2, 4 or 8 hours.

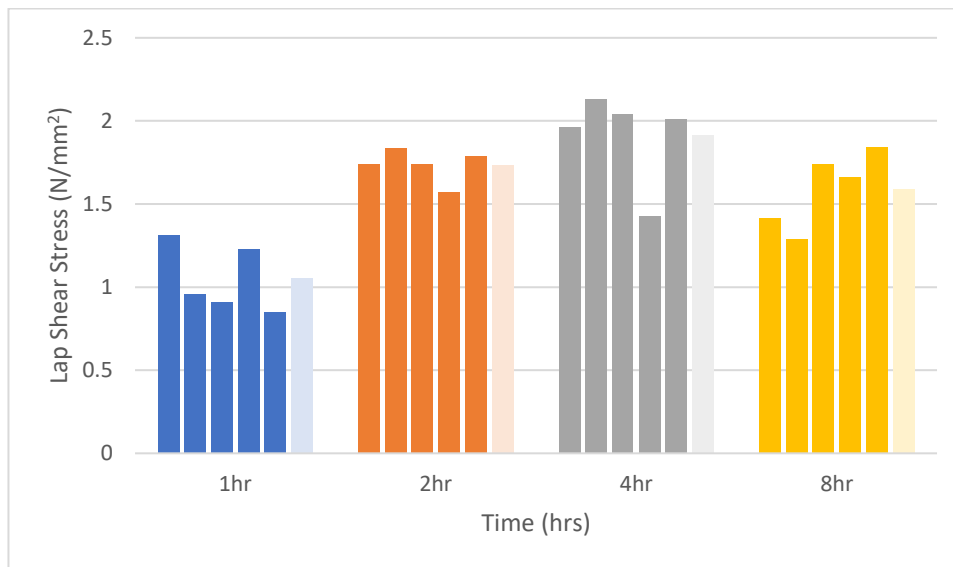


Figure 4.2 Lap shear results for time study PP-A-PEP 450-L-M1 cured at 150°C indicating an increase in lap shear stress, individual results in bold, average results in pale colour

In a study of the effect of curing time with a curing temperature of 150°C we could see a similar increase in load reaching a maximum average of 1.91 N/mm² after 4 hours after which there was a reduction in load as can be seen in the average load of 1.59 N/mm² after 8 hours cure (Figure 4.2).

ANOVA Analysis was conducted to determine if there was a significant difference in the lap shear strengths for samples cured at 150°C with different curing times. The null hypothesis of

$$H_0; \sigma_{1hr} = \sigma_{2hr} = \sigma_{4hr} = \sigma_{8hr}$$

Equation 4.1 Null hypothesis for ANOVA analysis of the time study examining the duration of cure at 150°C

was examined in an ANOVA analysis at 99% confidence in excel. The P value was determined to be 1.84E⁻⁰⁶ allowing the null hypothesis to be rejected, meaning that there is in fact statistical significance in the variance in the lap shear stresses between at least two of the curing times at 150°C. There was also evident discolouration in the samples cured for 8 hours at 150°C. A colour change was noted as visible in

Table 4.2. This suggested that discolouration of the material had occurred at the higher temperature. It was determined that a 4 hour cure at 150°C or a 16 hour cure at 100°C was optimal for lap shear samples.

For all experiments, failure occurred as a bulk failure of the PIB-PUR material rather than as a delamination between the material and the substrate. This means that the bond between the

material and substrate is stronger than the material itself and therefore this interfacial bond should not be the mechanical weak point of the coating.

Table 4.2 Examples of samples of PIB-PUR cured at 150°C containing PEP 450 for 1, 2, 4, and 8 hours respectively showing evidence of colour change

Hours Cured

Example of PP-A-PEP 450–L–M1

1 hour



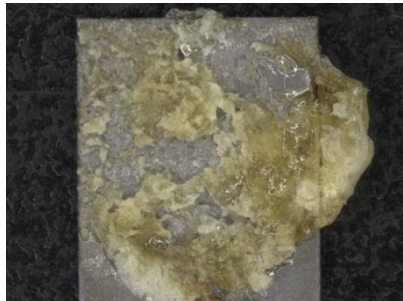
2 hours



4 hours



8 hours



4.2 Voids within Samples

After the lap shear testing, the failure mode of the samples was examined under microscope. In both Table 4.1 and Table 4.2 it could be seen that voids were present across the sample set. Voids would compromise the integrity of a near-hermetic barrier film and therefore it became a main aim of this chapter to identify a method by which void free samples could be repeatably made. Therefore, the first step was to evaluate how the voids became incorporated in the material.

4.2.1 Moisture Contamination

One possible cause of voids in the material is that the components, the crosslinkers specifically, could have been contaminated with moisture. It is possible that during synthesis the H_2O theoretically present within these crosslinkers would react with the isocyanate creating urea and carbon dioxide, producing gas bubbles giving rise to the voids. Until this point materials were kept in a silica desiccant chamber. In order to investigate the moisture content of the crosslinking agents a three-pronged test plan was employed involving crosslinkers (Tween 20, PEP 450, PEP 550, and THP) stored long term at ambient conditions, stored in a silica desiccant or stored in a stronger desiccant Drierite™ (calcium sulphate). A plan was constructed as outlined in Figure 4.3 in order to determine the water content of the crosslinking agents of PIB-PUR and the effect, if any, that desiccation has on the effect of that moisture content.

Samples underwent FTIR testing before any desiccation began. Crosslinking agents were dried out in a vacuum in a Thermo Fisher Vacuum Oven for 48 hours at ambient temperature and then at 40°C for 10 days under a strong vacuum (0 ATM). After desiccation in the oven the samples underwent FTIR testing again in order to note any change in the material composition and then were placed in their respective environments (ambient pressure) in a silica desiccant or in Drierite™. The FTIR spectra were monitored in order to see if there was any reuptake in moisture.

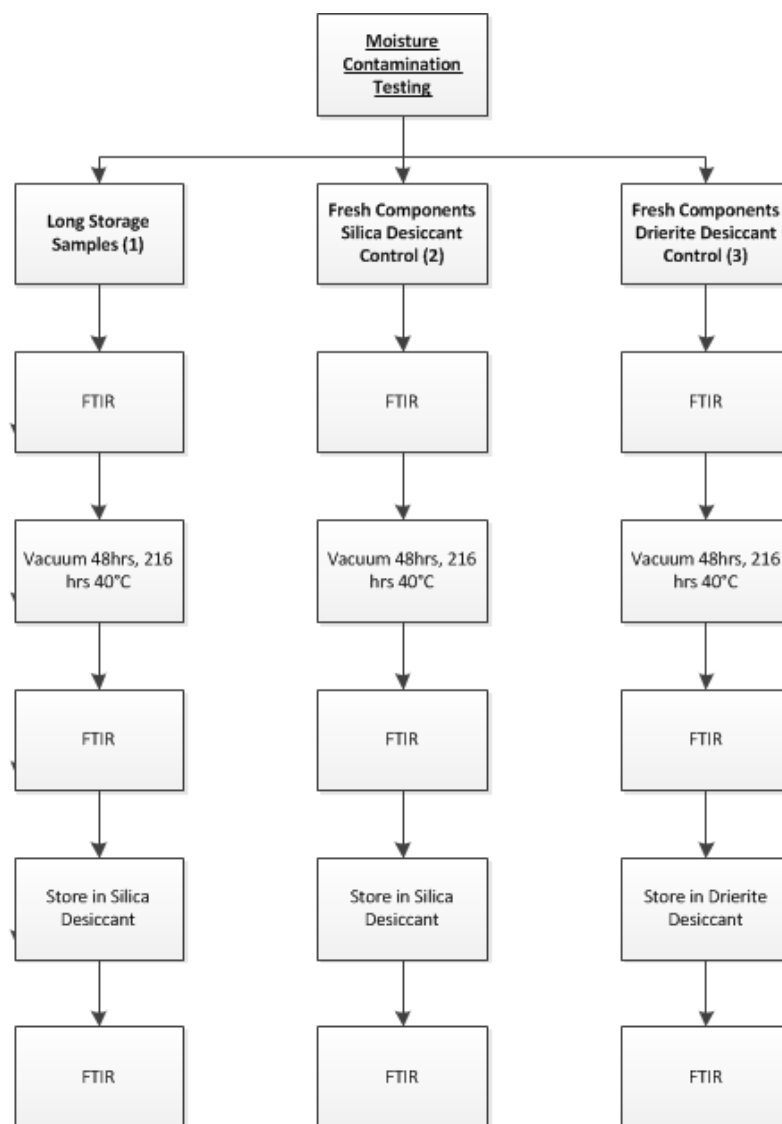


Figure 4.3 Test plan to examine the moisture content of crosslinking agents

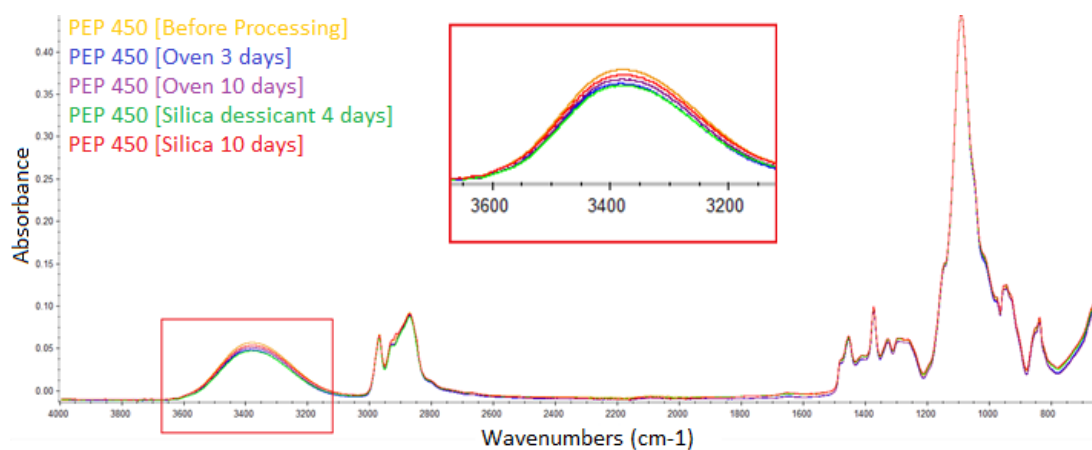


Figure 4.4 Effect of silica desiccant on PEP 450 from long storage

It can be seen from Figure 4.4 that desiccation in both the oven and the silica desiccant had a slight impact in the water content of PEP 450 as can be seen in the peak at 3400 cm⁻¹. The lowest

amount of water was observed after 4 days in the silica desiccant, but the water content seemed to rise by the 10th day in the silica desiccant.

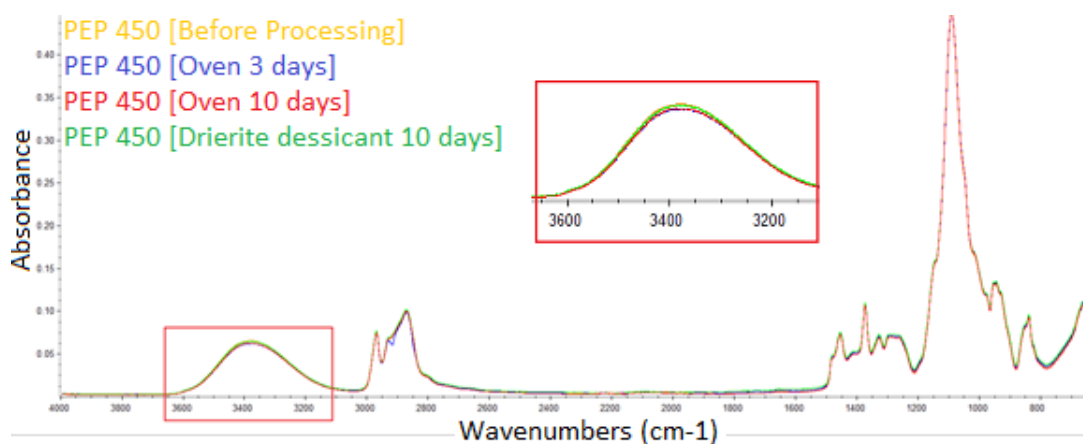


Figure 4.5 Effect of Drierite™ desiccant on PEP 450

Again, the desiccation techniques seemed to have an impact on the water content of PEP 450 with the water content reducing with 10 days in the oven, however the water content was regained after 10 days in a Drierite™ desiccant (Figure 4.5). This was replicated in Figure 4.6 with the fresh sample of PEP 450.

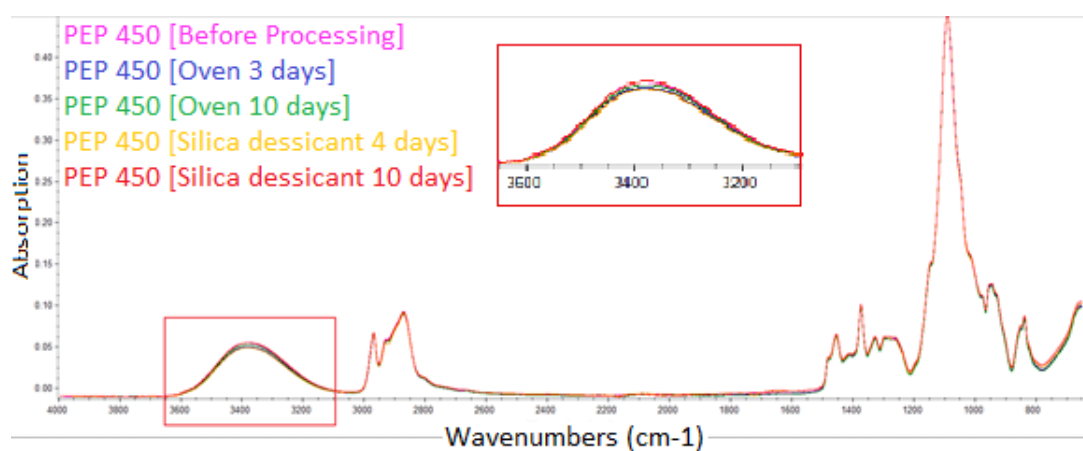


Figure 4.6 Effect of silica desiccant on fresh PEP 450

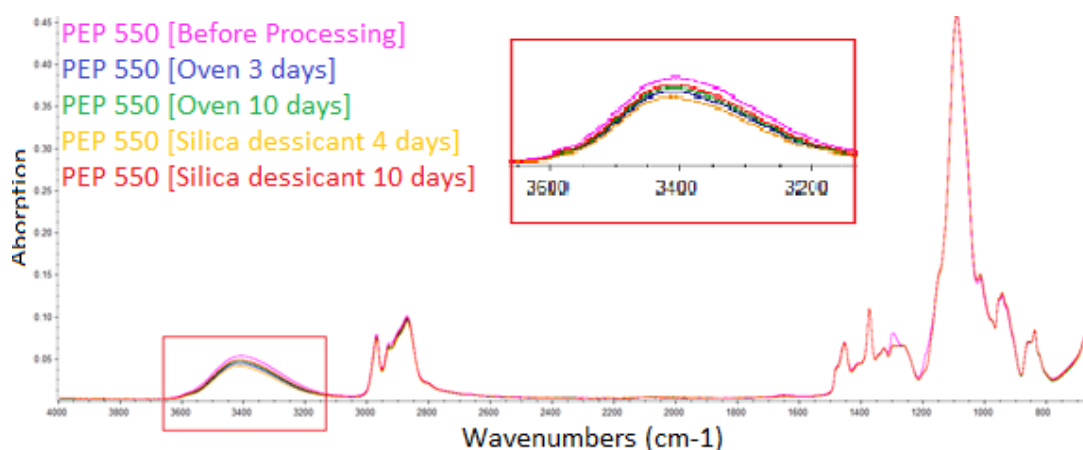


Figure 4.7 Effect of silica desiccant on PEP 550 from long storage

It can be seen from Figure 4.7 that desiccation in both the oven and the silica desiccant had a slight impact in the water content of PEP 550 as can be seen in the peak at 3400 cm^{-1} . The lowest amount of water was observed after 4 days in the silica desiccant, but the water content rose by the 10th day. This trend is again repeated in Figure 4.8.

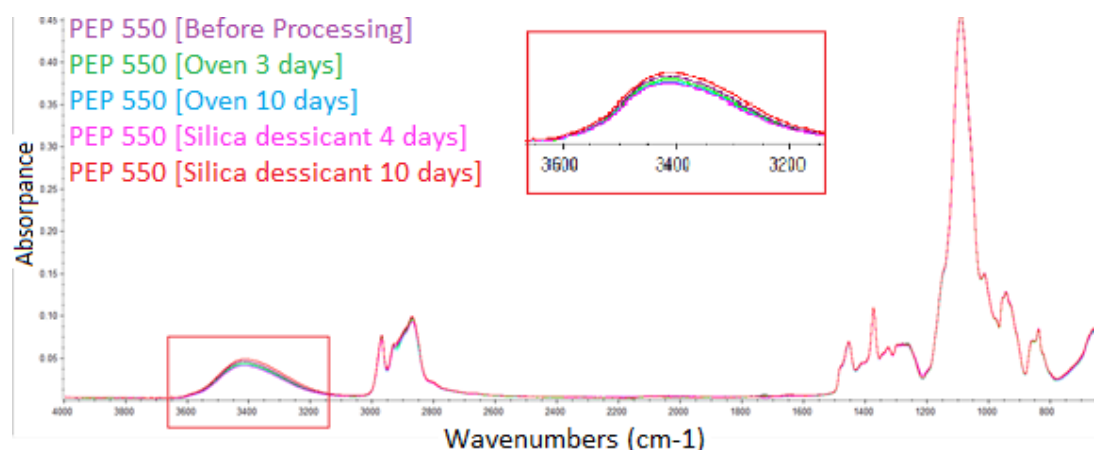


Figure 4.8 Effect of silica desiccant on fresh PEP 550

Figure 4.8 the water content was lowest after 4 days in the silica desiccant with water content showing to have increased by the 10th day in the silica desiccant in fact gaining more OH bonds by the 10th day than was originally contained in the fresh PEP 550 sample.

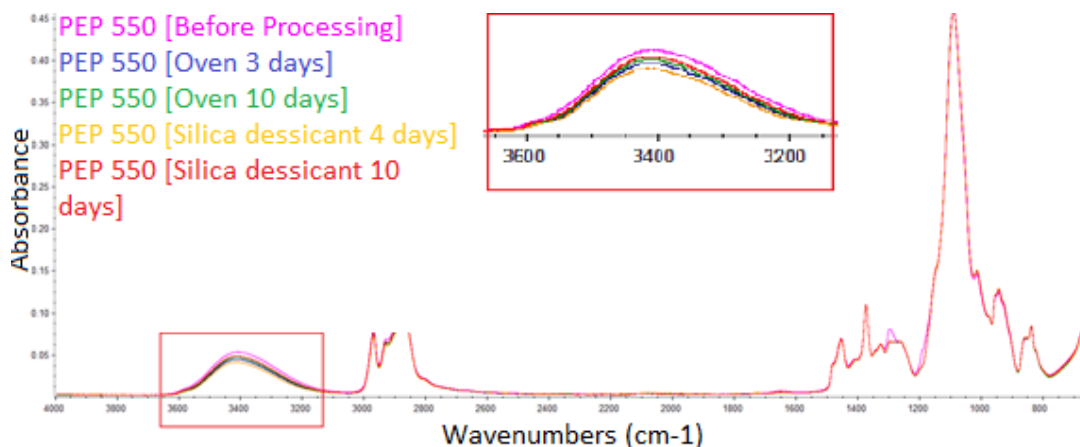


Figure 4.9 Effect of Drierite™ desiccant on PEP 550

Figure 4.9 shows that this trend is also holds with Drierite. Again, the lowest moisture content can be seen after 4 days in the desiccant. Then moisture content then rises to more than was originally contained in the fresh sample.

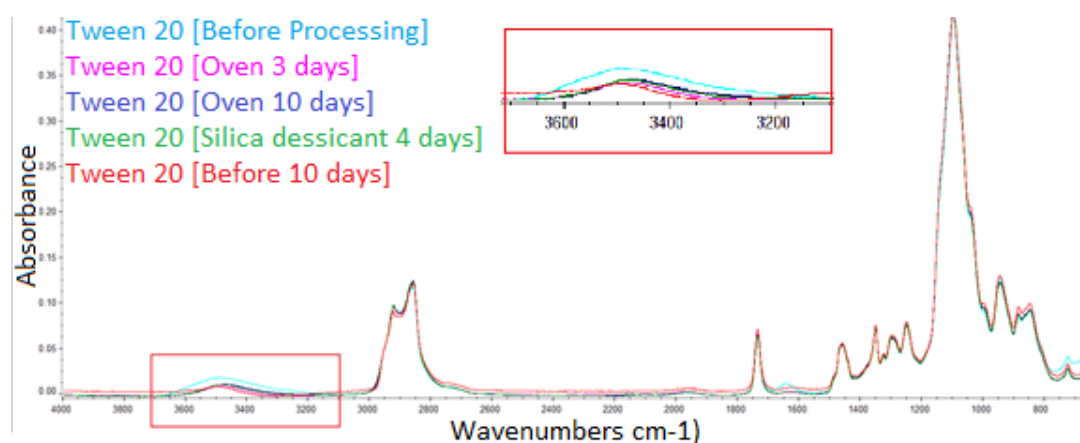


Figure 4.10 Effect of silica desiccant on fresh Tween 20

The FTIR in the Tween 20 sample in Figure 4.10 shows that water remained purged from the sample after 10 days in the silica desiccant.

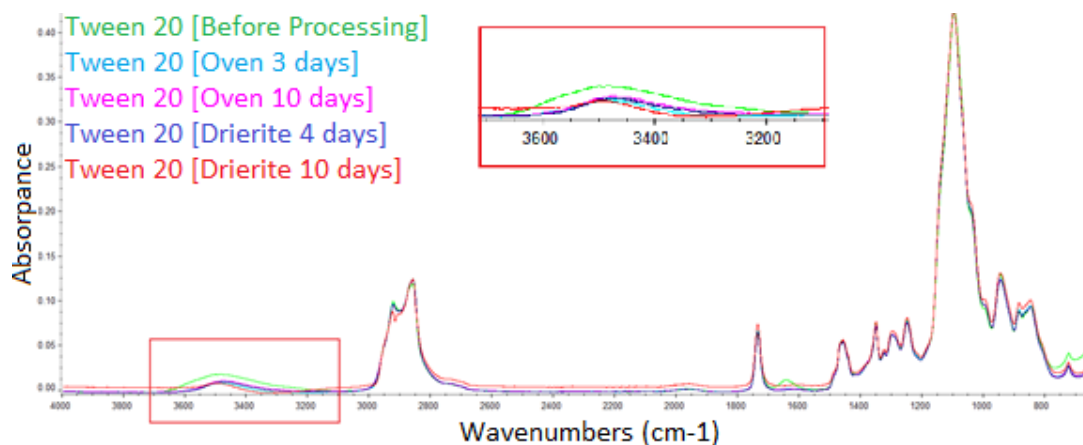


Figure 4.11 Effect of Drierite™ desiccant on Tween 20

As seen in both figures Figure 4.10 and Figure 4.11 the moisture content of Tween 20 did not rise as the other crosslinking agents previously mentioned did after 10 days in their respective desiccants.

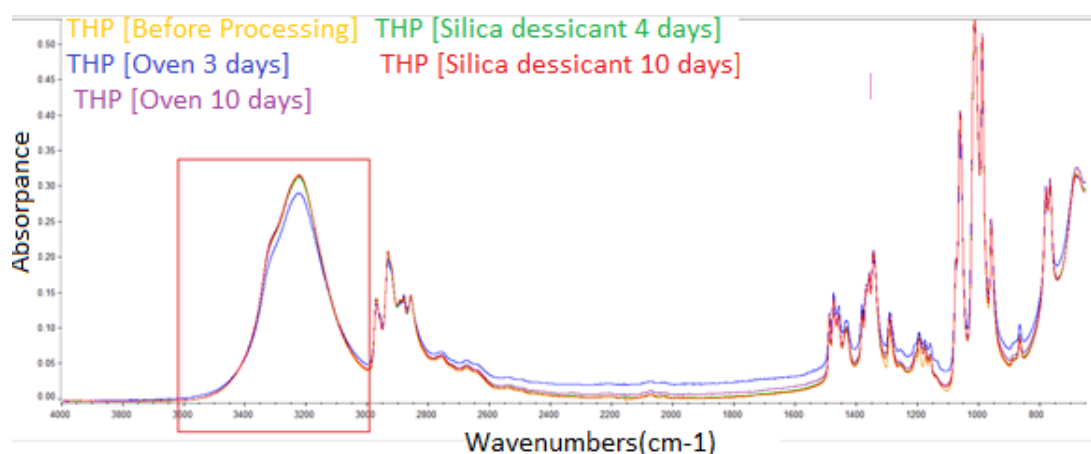


Figure 4.12 Effect of silica desiccant on THP from long storage

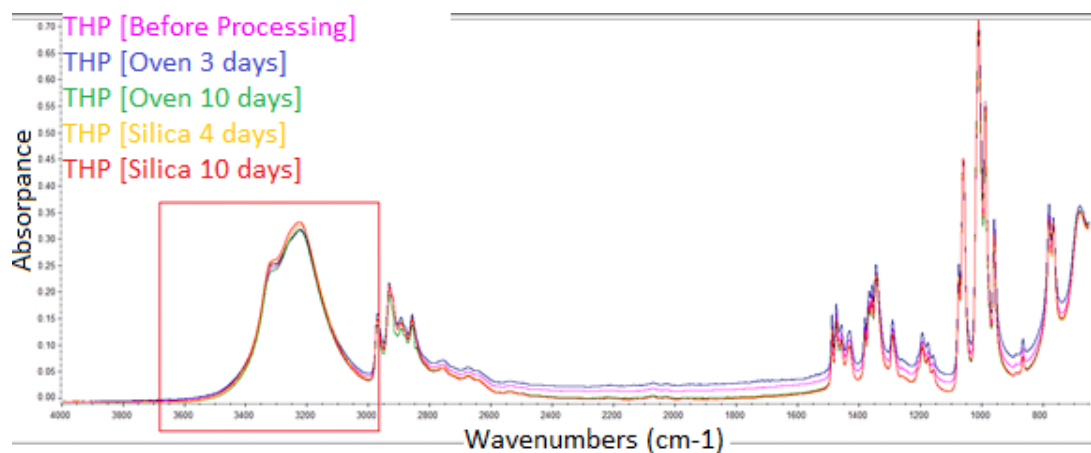


Figure 4.13 Effect of silica desiccant on fresh THP

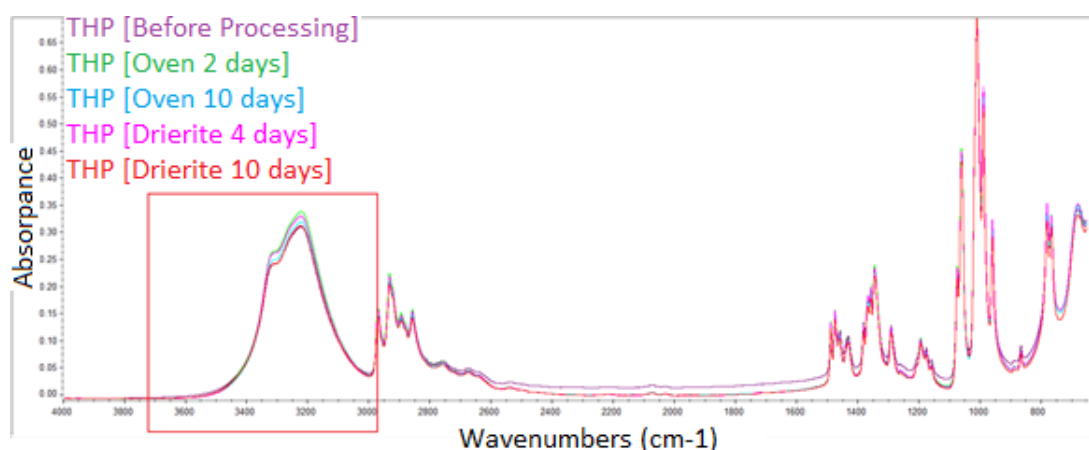


Figure 4.14 Effect of Drierite™ desiccant on THP

As seen in Figure 4.12 and Figure 4.13, the moisture content of THP decreased following the desiccation in the oven however the moisture content began to rise prior to the fourth day in silica desiccant. Figure 4.14 indicates that the dessicant Drierite prevented moisture from re-entering the THP.

In order to quantify the amount of water present in the materials, Karl Fischer analysis was performed. Polysorbate (Tween 20) and Pluracol 450 were selected for further study and were tested post desiccation. It was found that the water content of PEP 450 was comparable to the water content as listed in the technical data sheet. It was also confirmed that water content of Tween 20 had been successfully reduced to a lower content than that of PEP 450. The results can be found in Table 4.3.

Table 4.3 Table indicating the effect of desiccation as per Karl Fischer

<u>Material</u>	<u>% Water Pre-desiccation from specification sheet</u>	<u>Weight (g)</u>	<u>% Water Post desiccation (Drierite)</u>
Polysorbate (Tween 20)	3.0	0.51755	0.475
Pluracol (PEP) 450	0.05	0.57395	0.54

It was therefore concluded that desiccation removed water entrained in Tween 20. Karl Fischer Analysis confirmed what was seen in the FTIR analysis with PEP 450 that after a period of time water molecules migrated into the sample. It was therefore established that Tween 20 should be the crosslinker of choice as it remained purged of its original water content. Further to this investigation PIB-PUR samples were created with the desiccated Tween 20 crosslinker.

Unfortunately, there was no change in the number of voids present in the resulting material (PIB-PUR) and thus it was concluded that moisture contamination was not the primary cause of voids.

Conclusion

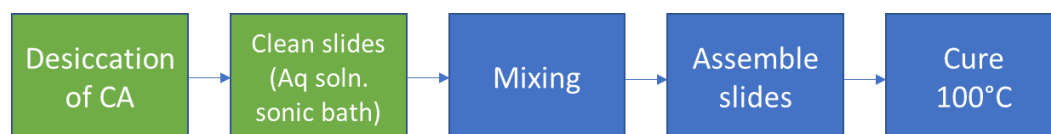
The hypothesis of moisture being a key source of the voids within PIB-PUR was determined to be incorrect. After minimising the water contamination within the samples there was no improvement in the quality of the samples. However as good practice where applicable all samples made from this point forward were made with Tween 20 which was stored in a desiccator containing Drierite as it showed the lowest moisture content post drying.

4.2.2 Surface Contaminants

There was concern that the substrates were not being sufficiently cleaned, and contaminants on the surface could be contributing to the voids in the cured samples. In order to determine if this was in fact the case two cleaning methods were explored. The initial method involved taking the titanium slides and steeping them in heptane and then cleaning them vigorously with a clean lint free cloth. The slides were then placed in isopropanol and again steeped and then cleaned vigorously with a clean lint free cloth. Afterwards the slides were steeped in deionised water and cleaned with a clean lint free cloth. The slides were then dried with clean lint free cloths and placed in an oven at 100°C to ensure all of the water had been removed and to preheat the slides.

Method 2 (designated M2)

The second method [M2] involved steeping the slides in an aqueous solution and placing them in a sonic bath and for an hour. Afterwards the slides were thoroughly rinsed with water and subsequently plasma cleaned. The substrates were then placed in aluminium foil, to ensure that they remained as clean as possible before applying the uncured PIB-PUR. After the examination of both resultant samples, it was determined that cleaning method was not a major factor as there was no noticeable difference in the presence of voids.



Conclusion

The lack of improvement in the number of voids within the sample showed that that the method used to clean the surface of the material has no impact on the end result. As a result, going

forward the cleaning regime, which was previously used, that of cleaning with heptane, isopropanol and DI water and then dried in an oven. This was primarily chosen as access to a plasma cleaner was difficult to achieve on an ongoing basis.

4.2.3 Mixing Regime

In this study the time spent mixing was extended to investigate if this would drive out bubbles within the uncured material. PIB-PUR material is mixed in a Speedmixer DAC 50.1 FV-K shown in Figure 4.15. This mixer works by spinning the sample on 2 axes, the axis of the centre of the drum and the axis of the centre of the tub itself as shown in Figure 4.16.



Figure 4.15 Speedmixer DAC 50.1 FV used to mix PIB-PUR material



Figure 4.16 Representation of the dual asymmetric mixing employed by the Speedmixer DAC 50.1 FV

This typically allows for a quick and uniform mix by inducing turbulence within the material during mixing. It is possible that due to the viscosity of the material, gas present in the sample was unable to fall out during mixing as generally happens with other materials such as silicone. In order to examine this possibility, the sample was reviewed under a microscope after mixing. As shown in Figure 4.17, bubbles were in fact present in the uncured sample.

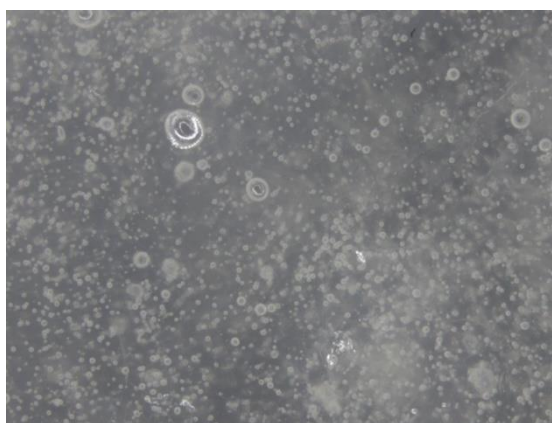


Figure 4.17 Sample of PIB-PUR in 25mm diameter in tub with microbubbles present in uncured PIB-PUR material

Varying mixing speeds & times

At this point it was thought that perhaps a different mixing regime would help. A longer time and a faster mix could generate more force within the material and help the bubbles fall out. The speed and duration of mixing were varied in order to determine if mixing at high speeds for long periods would allow the bubbles to be forced out of the material. This was determined not to be possible. At maximum speed of 3500 rpm for 2 hours, the bubbles started to congregate at the centre of the uncured material as shown in Figure 4.18 and Figure 4.19. It was then determined that this method was not capable of removing the voids from the material. The material may have been too viscous for the gas bubbles to break the internal structure and be released.

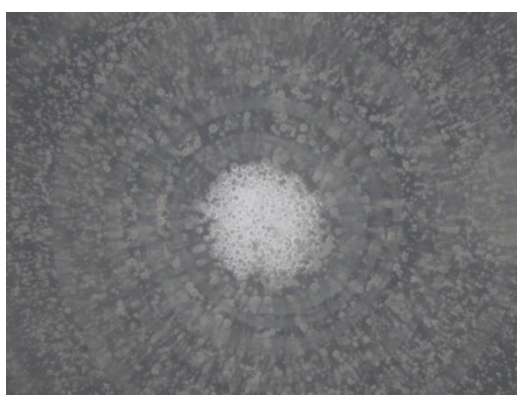


Figure 4.18 Bubbles congregating in the centre of the uncured material after intense mixing

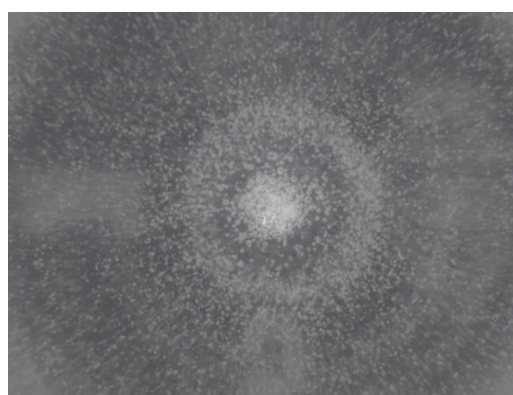


Figure 4.19 Bubbles congregating in the centre of the uncured material after intense mixing

Conclusion

It was suspected that viscosity of the material was too high for the force generated during mixing to allow the bubbles to fall out as is seen with less viscous materials such as silicone. It was determined that any mechanical mixing would incorporate these bubbles within the material and therefore attention should move to removing bubbles after the mixing stage was completed.

4.2.4 Vacuum and temperature

Holding the material under a strong vacuum in a ThermoFisher vacuum oven was examined as a means of removing voids from the uncured polymer. This experiment was carried out in which the material was created using the usual method and mixed at 3500 rpm. As can be seen in Figure 4.20 there were bubbles visible in the mixture.

Method 3 (designated M3)

It was decided to place the material in a vacuum oven at 50°C and repeatedly pull and release vacuums and subsequently cure the material for 16 hrs at 50°C in order to produce high quality, void free samples.



This method consisted of:

1. The sample was made with no crosslinker.
2. The formulation was mixed in a Speedmixer DAC 50.1 FV-K at 3500 rpm for 10 minutes.
3. The material was then placed in a vacuum oven at 50°C and the vacuum was drawn to 0 ATM and released 21 times.
4. The material was then left in the 50°C oven for 16 hrs.



Figure 4.20 PP-A-M-M3 mixed at 3500 rpm for 10 mins prior to being placed in the vacuum chamber

Evacuations were performed using a Thermo Fisher vacuum oven at 50°C by closing the outlet valve and by drawing a vacuum to 0 ATM. The increased temperature was postulated to have allowed the viscosity of the material to reduce. This would have reduced the strength of the molecular bonds within the material and would therefore allowed the gas to be evacuated with greater ease. The vacuum was subsequently released and allowed to return to the ambient 1 ATM. This process was repeated a further 20 times and the change in the material was noted visually as noted in Figure 4.21. As can be seen below, the smaller bubbles were removed. However, the material became pitted and there were larger bubbles visible in material.



Figure 4.21 PP-A-M-M3 evacuated at 50°C to 0 ATM 21 times

In order to remove the pitting on the surface and the bubbles still present in the material, the mixture was put in a vacuum oven and placed under vacuum at 50°C. The result can be seen in Figure 4.22 where the bubbles have not been totally evacuated. This shows that vacuuming and elevated temperature may not be enough to complete the removal of voids but is effective to a degree.

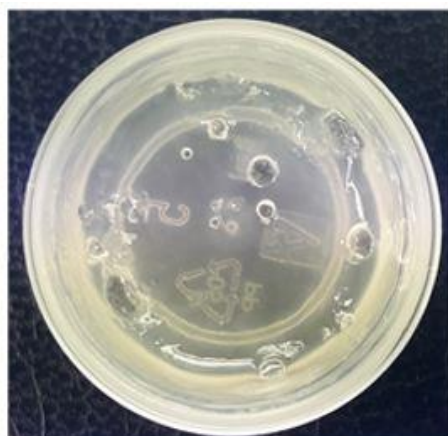


Figure 4.22 PP-A-M-M3 after resting in 50°C oven for 16 hrs

Conclusion

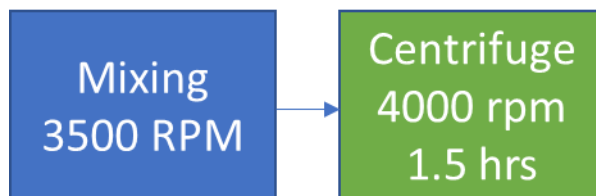
While this method seemed to be beneficial in reducing the amount of bubbles present in the mixture the issue was reintroduced when the applying PIB-PUR mixture to the sample slides. Bubbles were unintentionally reintroduced when placing the mixture on the titanium slides.

4.2.5 Centrifuging

Centrifuging is a common technique used to separate materials in solution, and was incorporated into the fourth method trialled. By spinning the solution at high speeds, the centrifugal force created within the material pulls denser parts of the solution to the perimeter

of the centrifuge. It was thought that if spun at a high enough rate the air pockets created during the mixing process would be forced out of the material.

Method 4 (designated M4)



The centrifuging was performed using the Sartorius 2-6 machine by Sigma at its top speed of 4,000 rpm for 1 minute. It was quickly evident that this did not create sufficient force and so the material was placed at 4000 rpm for a further 30 minutes. But again, due to the viscosity of the mixture it was determined that not enough force was generated to draw the bubbles out of the material even when centrifuged for 90 minutes as seen below in Figure 4.23, Figure 4.24, Figure 4.25 and Figure 4.26.



Figure 4.23 Uncured PP-A-M-M4 mixed at 3500 rpm for 10 mins in 25 mm diameter tub prior to centrifuging

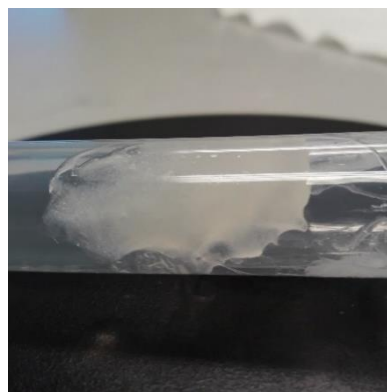


Figure 4.24 Uncured PP-A-M-M4 in pipette before centrifuging

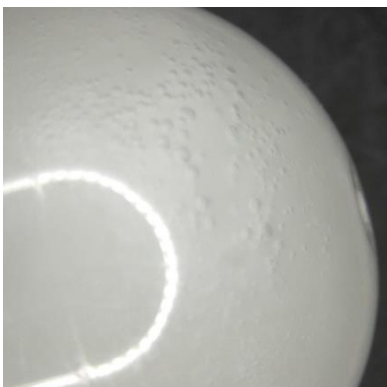


Figure 4.25 Uncured PP-A-M-M4 after centrifuging at 4000 rpm for 1 hour



Figure 4.26 Uncured PP-A-M-M4 after centrifuging at 4000 rpm for 1.5 hours

Conclusion

After centrifuging for 1.5 hours at the machine's maximum speed with no visible improvement, it was concluded that the force generated by the centrifuge was not enough to overcome the viscosity within the uncured PIB-PUR. It was concluded that this viscosity was too large to overcome with the mechanical means at our disposal.

4.2.6 Preheating Diol and Mould

The focus switched to reducing the viscosity of the material, as thus far this was believed to be the main obstacle to removing bubbles. By preheating the mould, it was hoped that the material's viscosity would be lowered to allow voids to be eliminated before curing began.

Preheating the diol base was also attempted to reduce the viscosity of the material. By preheating the PIB-diol base, it was again thought that the viscosity of the material would drop sufficiently and that the other components would be more readily incorporated, creating fewer bubbles during mixing. However, issues arose with this technique when the material began to cure during the mixing stage and even though the material was preheated, the viscosity was not sufficiently reduced to mitigate the amount of bubbles generated during mixing.

Conclusion

The limited improvement seen by both preheating the moulds and the diol base before casting into the moulds were not sufficient.

4.2.7 Introduction of Solvents

It was postulated that the addition of hydrocarbons as solvents would reduce the viscosity of the base material to allow for easier evacuation of gas. Heptane was readily available in the laboratory and was already employed in the process for cleaning purposes.

In order to characterise the flow of the diol and understand the effect of the introduction of a solvent, a rheological study was undertaken. When undertaking a rheological evaluation of any material where the rheological characteristics are unknown it is important firstly to carry out an amplitude sweep. This allows for the identification of the linear viscoelastic region of the material [LVE].

The amplitude sweep was carried out in a parallel plate apparatus set up. It is an oscillatory test in which the sample is deformed through a range of strain values at a fixed frequency. The material underwent a strain range from 0.01% to 100%. In this test measured the storage and loss moduli at these various amplitudes. It can be seen from Figure 4.27 that G'' is above the G'

for both the neat PIB diol and the PIB diol with 25% solvent, thus it can be said that both the samples are ‘fluid’.

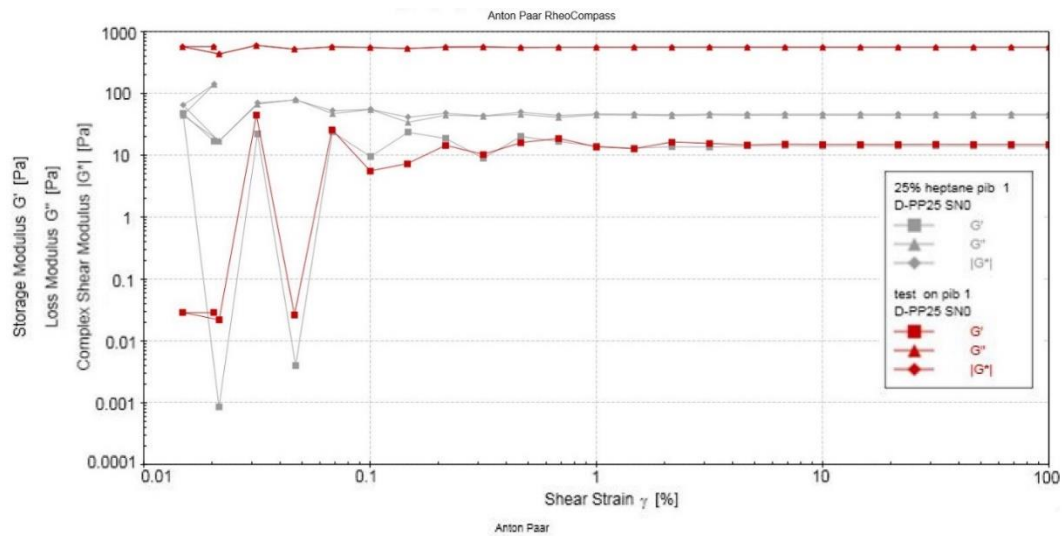


Figure 4.27 Amplitude sweep comparing PIB Diol Batch B without solvent [red] and PIB Diol Batch B with 25% solvent [grey] indicating that both diols with and without the solvent can be classified as liquids as G'' is greater than G'

Frequency sweeps can be utilised to garner information about the internal behaviour and structure of the material. We established a controlled strain would be set at 10% as it was the lowest strain value at which the results came back stable.

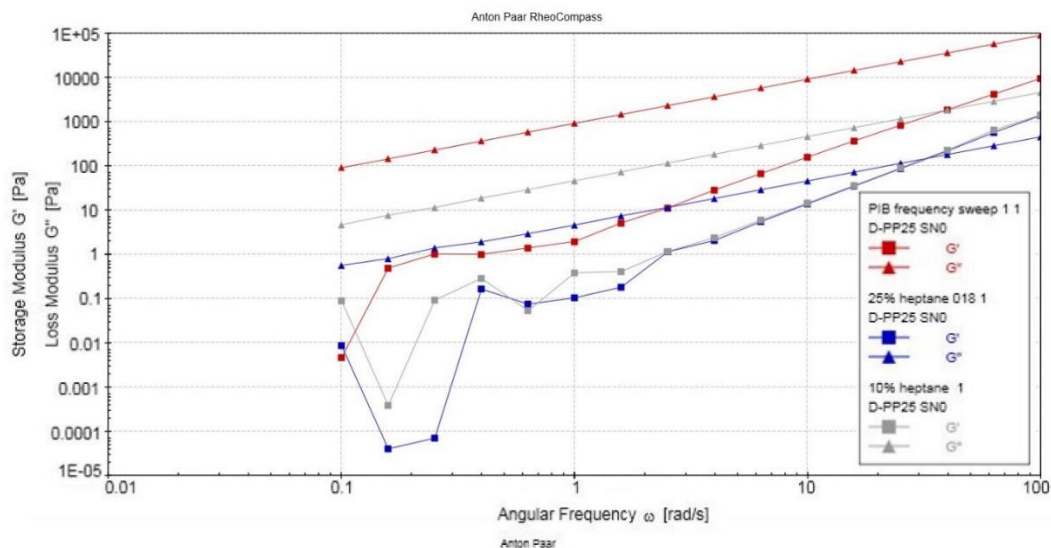


Figure 4.28 Frequency Sweep PIB Diol comparing PIB-Diol Batch B without solvent [red] and PIB Diol Batch B with 10% solvent [grey] and 25% solvent [blue]

The frequency test was conducted with neat diol material from Batch B and again for an addition of 10% heptane and 25% heptane. While in Figure 4.28 the crossover point of G' and G'' are only visible for 25% heptane, the slopes for the 10% solution suggest that they are converging to a

greater degree than those of the neat material. In this test the angular frequency had reached the limit of the apparatus and therefore the higher crossover points could not be identified.

It was observed that when removing the material from its storage container the material would become difficult to move and would hold its shape before flowing off the spatula. The question arose, could this material be exhibiting non-Newtonian properties.

In Figure 4.29 the green line represents the relationship of the PIB diol's [Batch B] viscosity (Pa.s) to the shear rate (s^{-1}) being exhibited. The viscosity is near constant for every shear rate here demonstrating that this diol is ideally viscous and exhibits Newtonian behaviour.

Figure 4.29 also shows the difference in the viscosity as a function of shear rate of both Batch B without any solvent and when 25% solvent is introduced. It is plain to see that there is a large difference in the flow behaviours of both materials. Batch B has very high viscosity, reaching 1000 Pa.s and maintaining that viscosity for the duration of the test regardless of shear rate exhibited on the material. In contrast with the introduction of 25% solvent the viscosity reduces substantially reaching 60 Pa.s near rest reducing further with the application of shear, dropping below 5 Pa.s before increasing rapidly after the 200 s^{-1} . This indicates that an increase in the amount of solvent introduced into material substantially effects the flow characteristics of the material.

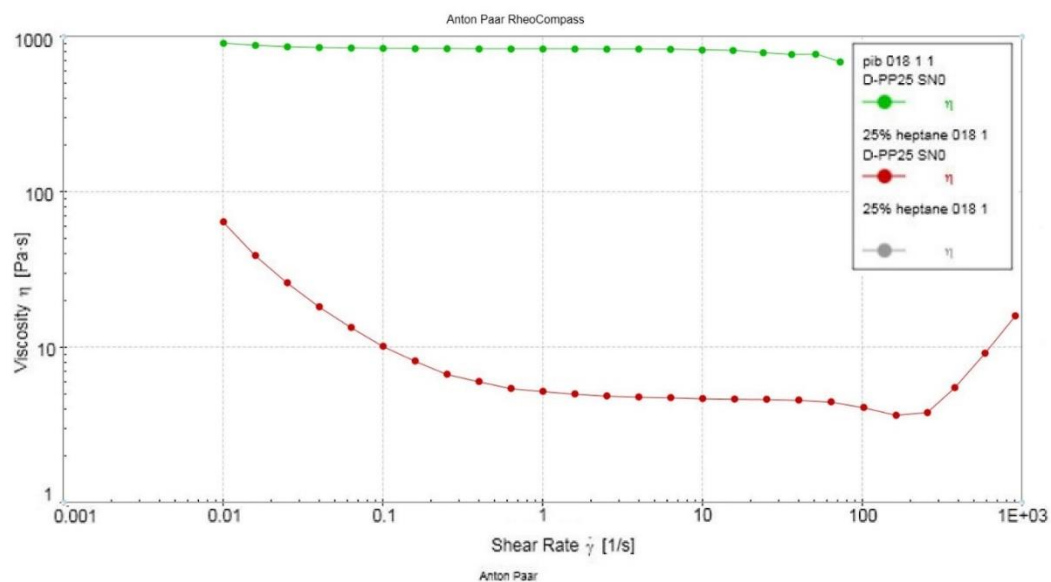


Figure 4.29 Viscosity comparison of PIB Diol Batch B without solvent [green] and PIB diol, Batch B with 25% solvent [red]

Method 5 (designated (M5))



1. Mix PIB-diol and heptane for 15 minutes at 3500 rpm.
2. Add tin (II) octate (catalyst) and MDI Luphranate MI (chain extender).
3. Mix for 5 minutes at 3500 rpm.
4. Add in Polysorbate, Tween 20 and at mix 3500 rpm for 5 minutes.
5. Centrifuge at 4000 rpm for 1 hour in an EFD syringe.
6. Clean and preheat the mould.
7. Eject PIB-PUR mixture onto the preheated mould.
8. Place in a ThermoFisher vacuum oven at 100°C for approximately 1 hr during this time evacuate 5 times.
9. Cure for 8 hours at 100°C.

Samples containing different proportions of solvent (heptane) were created to examine the effect which it had on the number of voids within the sample. Samples of 0, 10 and 25% heptane were formulated with the same method. They were vacuumed repeatedly for 1 hour and allowed to cure at 100°C for 8 hours. Figure 4.30, Figure 4.31, Figure 4.32, Figure 4.33 and Figure 4.34 show how the number of voids reduce with an increased level of solvent.



Figure 4.30 PP-B-T20-M-M5 containing 0% heptane with 5 evacuations



Figure 4.31 PP-B-T20-M-M5 containing 10% heptane with 5 evacuations



Figure 4.32 PP-B-T20-M-M5 containing 25% heptane with 5 evacuations



Figure 4.33 PP-B-T20-M-M5 with **25% heptane** with increased number of evacuations, first void free sample



Figure 4.34 PP-B-T20-M-M5 with **25% heptane** and increased number of evacuations, first void free sample, Figure 4.33 magnified

Conclusion

This study proved to be the most impactful in the reduction in the number of voids within the material. The viscosity of the material was decreased dramatically allowing other techniques to be more effective at removing the bubbles from the solution.

By finding a solution to the removal of bubbles within the sample, void free samples could now feasibly be created. The reduction in the viscosity of the material may have allowed the methods previously explored to be more viable. Methods such as centrifuging, vacuuming at an elevated temperature and pre-heating the moulds were retained as steps in the procedure at this stage.

4.2.7.1 Implications of Solvent Addition Approach for Existing Techniques

Centrifuging

The centrifuging technique was altered. Holders were 3D printed so that pressurised syringes (EFD syringes) could be placed in the centrifuge and the material could be dispensed after centrifuging without the need to transfer the uncured PIB-PUR from test tube to the mould.

Vacuuming

The solvent addition meant that the gas was more readily evacuated from the uncured PIB-PUR while in the vacuum oven.

4.2.8 Effect of Mould Dimensions

4.2.8.1 100mm x 100mm Samples

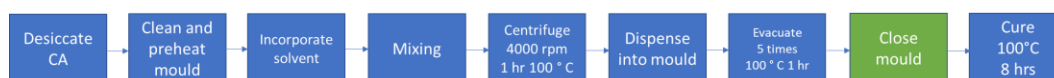
PIB-PUR samples of 100mm x 100mm were desired for WVTR testing as is standard. Due to concerns around the ability to achieve a defined and uniform thickness, a mould was designed and manufactured to achieve a thickness of 0.5 mm. It was machined out of PTFE as seen in Figure 4.35.



Figure 4.35 Water Vapour Transmission Mould made of PTFE. Uncured PIB-PUR is placed on the female section on the left. Male section on right is secured in place with allen key screws

The moulds were cleaned with heptane, isopropanol and deionised water and placed in an oven at 100°C to dry.

Method 6 (designated M6)



1. 6.077g of PIB diol was mixed with 1.519 g of heptane at 3500 rpm for 15 minutes.
2. To this a fraction of a drop of Tin (II) 2-ethylhexanoate (the catalyst) and 0.874μl of MI Luphanate (the chain extender) these were added then mixed for 5 min at 3500 rpm.
3. To this 0.373g of Tween 20 (the crosslinking agent) was added and mixed for 5 min at 3500rpm.
4. The mixture was then divided into 4 EFD syringes.
5. The sample was centrifuged at 4000 rpm for 1 hour.
6. The sample was introduced to the pre-heated mould as seen in Figure 4.36.
7. The mould was then placed back into the oven at 100°C and a vacuum was drawn in a ThermoFisher Vacuum Oven.
8. Then as the sample came to temperature the heptane in the solution evaporated creating bubbles. The sample was evacuated numerous times to prevent over spilling from the mould.
9. The sample continued bubbling and was evacuated for 1 hour.
10. The male section of the mould, which had also been preheated, was placed on the mould and was fixed in place using allen key screws.

11. The mould was clamped between two aluminium plates using a G-clamp.
12. The mould assembly was then removed from the ThermoFisher vacuum oven and placed in an oven for curing.
13. It was then cured at 100°C for 8 hours.
14. The mould assembly was removed from the oven and once cooled, the sample was taken out of the mould.

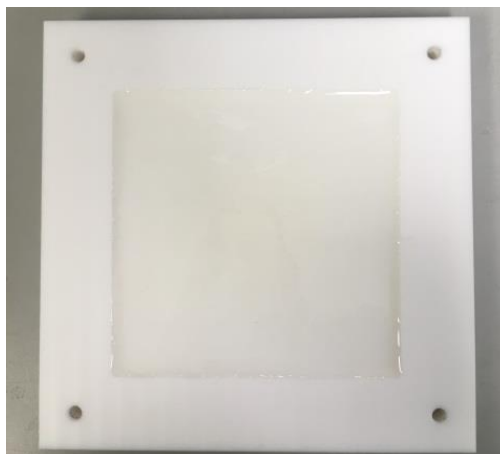


Figure 4.36 PP-B-T20-M-M6 material preheated and evacuated in PTFE WVTR mould which is ready to be closed

There were two sets of issues with this mould. When placing the two aluminium plates, the mould was tightened to such a degree that the mould bowed in the centre causing an uneven thickness and tearing. It was also apparent that material was under cured as the material was still 'tacky' upon opening the mould as demonstrated in Figure 4.37 and Figure 4.38.

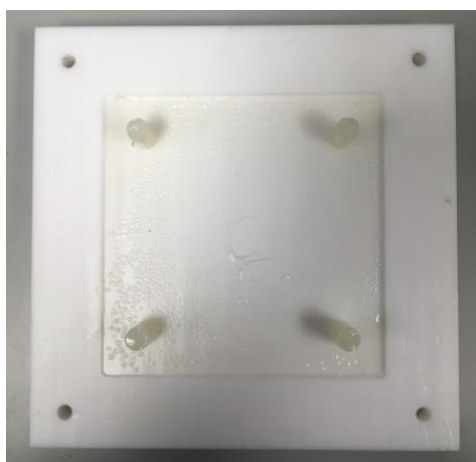


Figure 4.37 Cured PP-B-T20-M-M6 after an 8-hour cure at 100°C

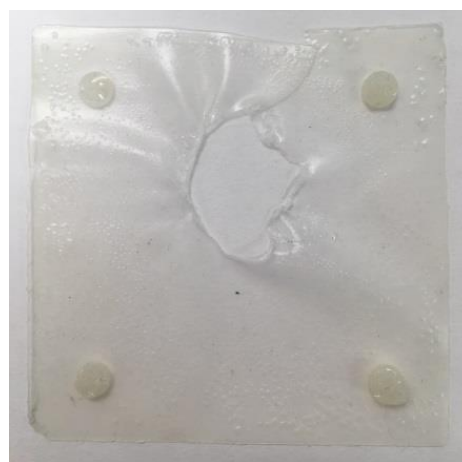


Figure 4.38 Cured PP-B-T20-M-M6 after an 8-hour cure at 100°C

Upon inspection it was also evident that there were bubbles in the cured PIB-PUR (Figure 4.39). This was due to the solvent not being fully evaporated before the lid of the material was placed

on the surface and as the material was heated during cure, the solvent began to evaporate creating gas.



Figure 4.39 Visible bubbles in cured in cured PP-B-T20-M-M6 after an 8-hour cure at 100°C

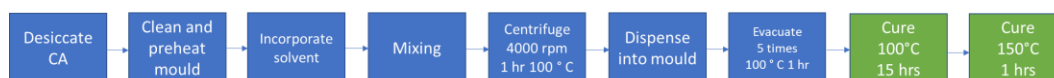
Conclusion

The enclosed mould inhibited the release of the gas from the material. Gas bubbles were trapped within the sample. PTFE moulds easily warped during the curing process and were easily overly tightened resulting in a tear in the centre of the sample. In order to mitigate these problems, the next sample would be made in an open mould.

Creating 100mm x 100mm Samples in Open Mould

The process was repeated without the top (male) part of the mould to allow the solvent to evaporate evenly across the sample.

Method 7 (designated M7)



The moulds were cleaned using heptane, isopropanol and deionised water. They were then dried with clean lint free cloths and then placed in a preheated oven at 100°C for an hour to both preheat the moulds and to ensure that all of the DI water was removed from the mould.

The other steps of Method 5 were repeated with measurements: 19.268g of PIB diol, 4.817g of heptane, a fraction of a drop of Tin (II) 2-ethylhexanoate (the catalyst) and 2.773µl of MI Luphanate (the chain extender). Uncured material can be seen in Figure 4.40.

During processing, deviations from the previous method were as follows:

1. After evacuations, the sample continued bubbling for over 3 hrs.
2. After the sample finished bubbling it was removed from the vacuum oven and was placed in an oven to cure at 100°C for an additional 5 hours.
3. Afterwards it was evident that the sample was still uncured at which time it was placed back in the oven and cured for a further 10 hours at 100°C and 1 hour at 150°C.

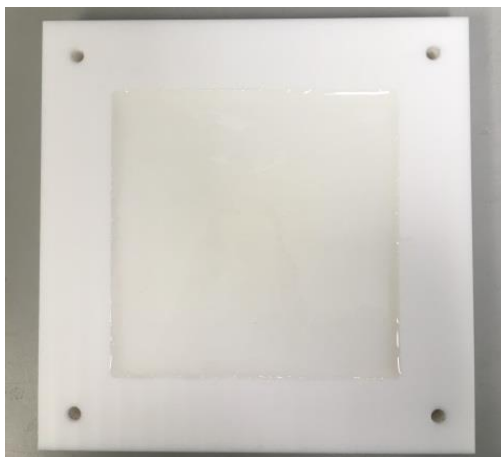


Figure 4.40 PP-B-T20-M-M7 evacuated at 100°C for 3 hrs, uncured at 100°C for 15hrs and cured at 150°C for 1hr open mould filled to 2mm thickness cured

It was apparent that the sample was also unsuitable for WVTR testing as there were a number of bubbles present in the sample and it was still uncured. While the surface had cured, the sample underneath was still tacky as shown in Figure 4.41 and Figure 4.42. The sample also had a deep brown appearance.

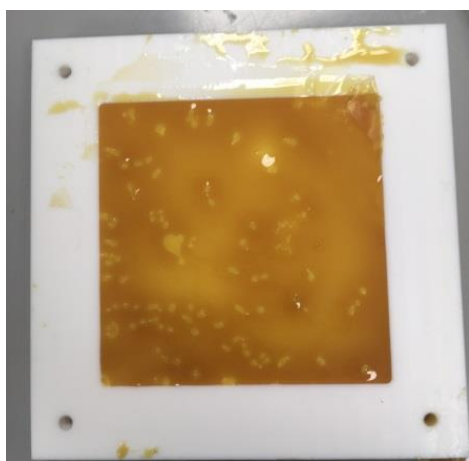


Figure 4.41 PP-B-T20-M-M7 evacuated at 100°C for 3 hrs, cured at 100°C for 15hrs and cured at 150°C for 15hrs with burned appearance



Figure 4.42 PP-B-T20-M-M7 evacuated at 100°C for 3 hrs, cured at 100°C for 15hrs and cured at 150°C for 15hrs was uncured after 24 hours in oven displaying a dark colour suggesting burning and tacky underside, suggesting insufficient curing

Conclusion

The amount of raw material necessary to create samples of this size compounded with the inability to cure, the presence of voids and the previous success with smaller samples suggested that further exploration of the smaller moulds should be carried out before samples of larger sizes are attempted.

4.2.8.2 25mm x 25mm Samples

A set of smaller samples were created for WVTR testing. The sample size was 25mm x 25mm x 1.5mm.

Method 8 (designated M8)



1. The mould was cleaned as in previous iterations using heptane, isopropanol and deionised water and then dried in a 100°C oven for an hour.
2. The sample was also mixed as before using 3.426g of PIB diol, 0.113g of heptane, a fraction of a drop of Tin (II) 2-ethylhexanoate (the catalyst) and 0.493µl of MI Luphanate (the chain extender) then adding 0.210g of Tween 20 (the crosslinking agent).
3. The sample was centrifuged at 4000 rpm for 1 hour. The sample was ejected onto a 100°C pre-heated mould PTFE mould (Figure 4.43).
4. The mould was then placed back into the oven at 100°C and a vacuum was repeatedly drawn.
5. Then as the sample came to temperature the heptane in the solution evaporated out and created bubbles.
6. The sample was then removed from the vacuum oven and placed in another oven and cured at 100°C for an additional 8 hours (Figure 4.44).

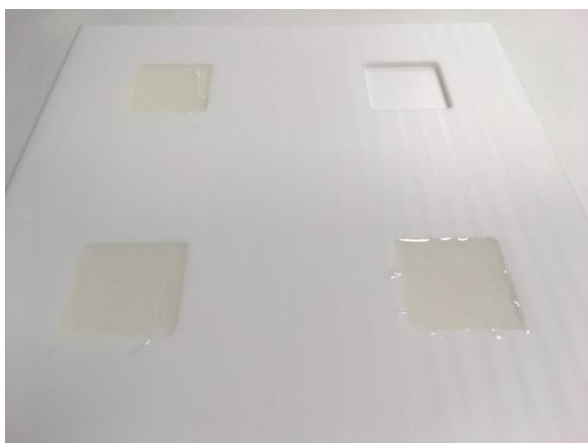


Figure 4.43 Uncured PP-B-T20-M-M8 with 25% solvent in mould 25mm x 25mm x 1.5mm

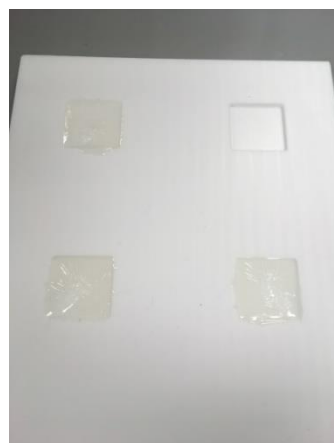


Figure 4.44 Cured PP-B-T20-M-M8, voids present

Afterwards there were large bubbles evident in the samples.



Figure 4.45 Cured PP-B-T20-M-M8-1 with voids in sample

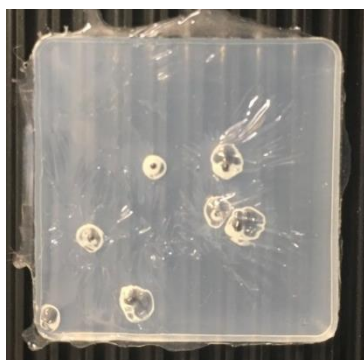


Figure 4.46 Cured PP-B-T20-M-M8-2 with voids in sample

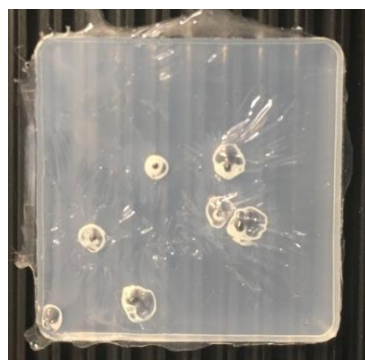


Figure 4.47 Cured PP-B-T20-M-M8-3 with voids in sample

Conclusion

Voids were present as evident in Figure 4.45, Figure 4.46 and Figure 4.47 and the surface had a buckled effect. This suggested that more evacuations were required to have clear and consistent samples.

4.2.9 Protocol for Repeated Evacuations

The number of vacuums drawn were increased. The sample would be subjected to as many vacuums as could be drawn and released over the course of 1 hour.

Method 9 (designated M9)



The previous method (M8) was adjusted to introduce more evacuations to minimise bubbles.

1. The mould was cleaned in the same way as Method 7 using heptane, isopropanol and deionised water then dried in an oven at 100°C.
2. 6.320g of PIB diol was mixed with 1.580g of heptane at 3500 rpm for 15 minutes, a fraction of a drop of Tin (II) 2-ethylhexanoate (the catalyst) and 0.909µl of MI Luphanate (the chain extender), 0.388g of Tween 20 (the crosslinking agent) and then divided into 4 EFDs syringes.
3. The sample was centrifuged at 4000 rpm for 1 hour.
4. The sample was dispensed onto the pre-heated mould PTFE mould. The mould was then placed back into the oven at 100°C and a vacuum was repeatedly drawn and released over the course of 1 hour.
5. As the sample came to temperature the heptane in the solution evaporated, which created voids.
6. The sample was then removed from the Thermo Fisher vacuum oven and placed in a Thermotron oven and cured for at 100°C for an additional 8 hours (Figure 4.48) shows these samples while cooling.

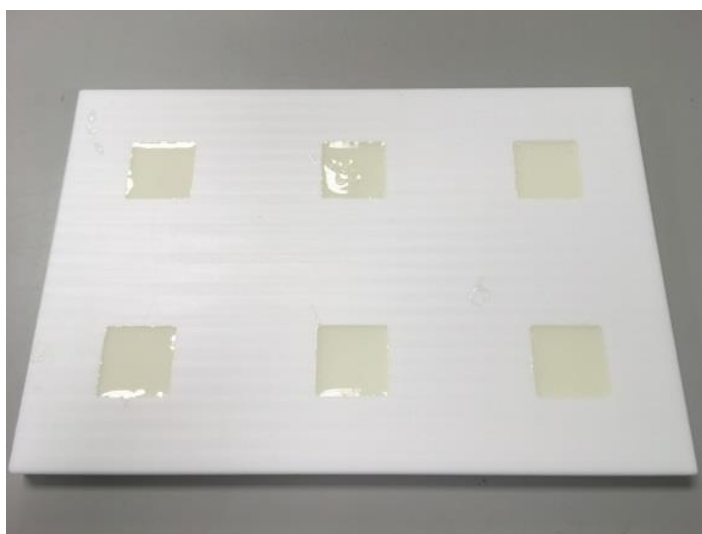


Figure 4.48 Uncured PP-B-T20-M-M9 in moulds 25 mm x 25mm x 1.5mm

Three of the six samples PP-B-T20-M-M9 contained no voids were suitable for WVTR Testing as can be seen in Figure 4.49 to Figure 4.54. Table 4.4 contains thickness measurements for the six samples.

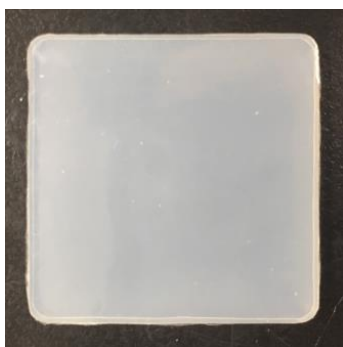


Figure 4.49 Cured PP-B-T20-M-M9-1 no voids present

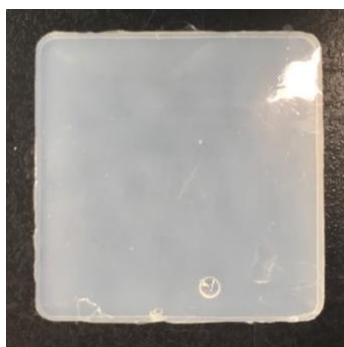


Figure 4.50 Cured PP-B-T20-M-M9-2, small amount of voids present

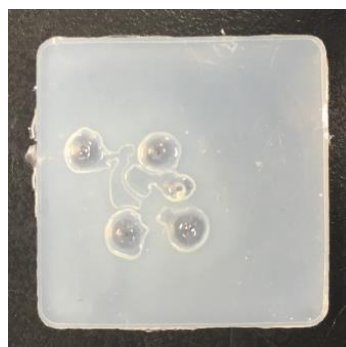


Figure 4.51 Cured PP-B-T20-M-M9-3, large amount of voids present



Figure 4.52 Cured PP-B-T20-M-M9-4; no voids present



Figure 4.53 Cured PP-B-T20-M-M9-5; small amount of voids present

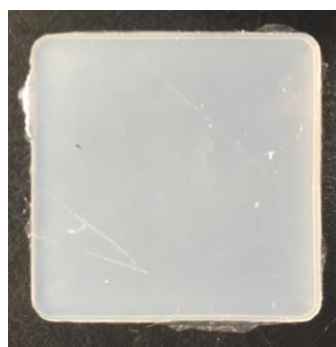


Figure 4.54 Cured PP-B-T20-M-M9-6; no voids present

Table 4.4 Thicknesses of PP-B-T20-M-M9 1-6

PIB PUR	Thickness [mm]
PP-B-T20-M-M9-1	1.76
PP-B-T20-M-M9-2	1.826
PP-B-T20-M-M9-3	2.188
PP-B-T20-M-M9-4	1.736
PP-B-T20-M-M9-5	1.856
PP-B-T20-M-M9-6	1.858

Method 9 (designated M9) Repeated

PP-B-T20-M-M9 was then repeated to create more samples for WVTR testing.

1. The mould was cleaned using n-Heptane, Iso-2-Propanol and DI water and dried in a preheated oven at 100°C for an hour.
2. Samples were created as before using 6.143g of PIB diol, 1.536g of heptane at 3500 rpm, a fraction of a drop of Tin (II) 2-ethylhexanoate (the catalyst) and 0.884µl of MI Luphanate (the chain extender) and 0.377g of Tween 20 (the crosslinking agent).
3. The mixture was divided into 4 EFD syringes and was centrifuged at 4000 rpm for 1 hour after which it was dispensed onto the pre-heated mould PTFE Mould as shown in Figure 4.55.

4. The mould was then placed back into the oven at 100°C and a vacuum was repeatedly drawn consistently for 1 hour. Then as the samples came to temperature the heptane in the solution evaporated out creating bubbles.
5. The samples were then removed from the vacuum oven and placed in an oven and cured for at 100°C for an additional 8 hours (Figure 4.56 shows these samples while cooling).

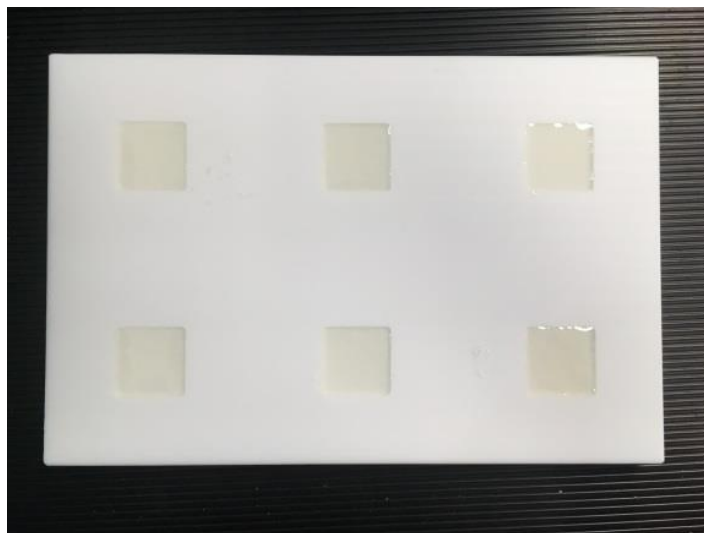


Figure 4.55 Uncured PP-B-T20-M-M9 7-12 in moulds 25mm x 25mm x 1.5mm

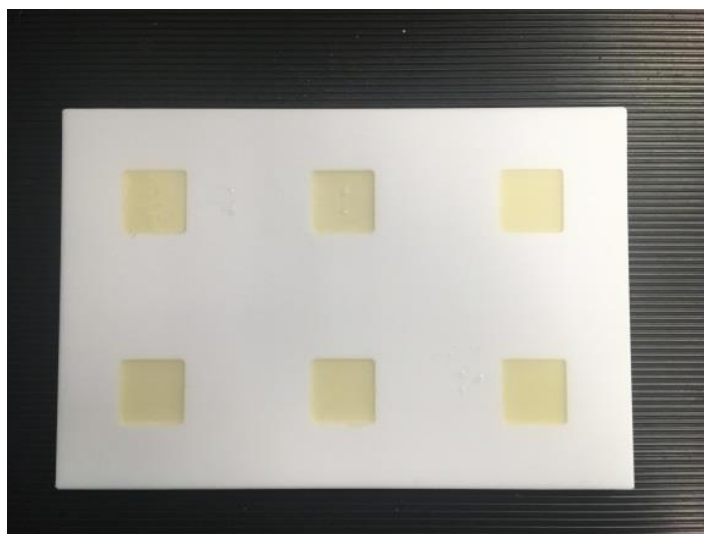


Figure 4.56 Cured PP-B-T20-M-M9 7-12 in moulds 25mm x 25mm x 1.5mm

Four out of the six samples did not have visible voids and were therefore viable for WVTR testing. This can be seen in Figure 4.57 to Figure 4.62. Thickness measurements are also displayed in Table 4.5.

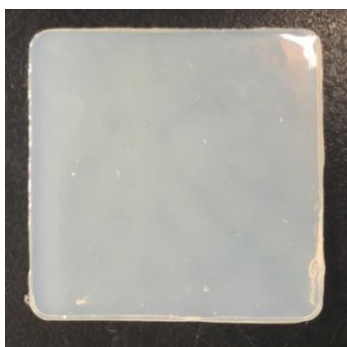


Figure 4.57 Cured PP-B-T20-M-M9-7; no amount of voids present



Figure 4.58 Cured PP-B-T20-M-M9-8; no amount of voids present

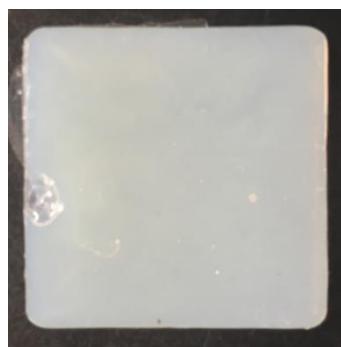


Figure 4.59 Cured PP-B-T20-M-M9-9; small amount of voids present

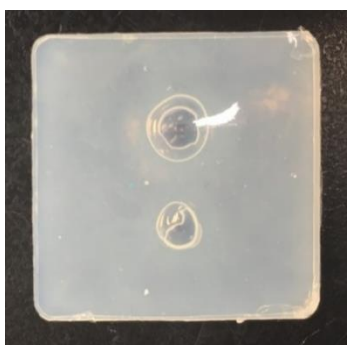


Figure 4.60 Cured PP-B-T20-M-M9-10; large amount of voids present

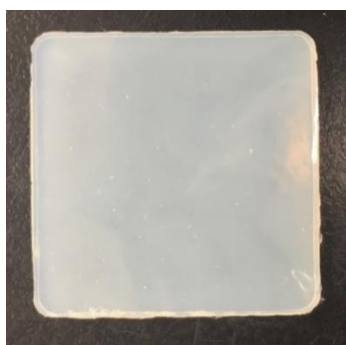


Figure 4.61 Cured PP-B-T20-M-M9-11; no voids present

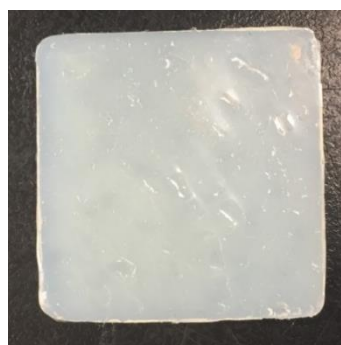


Figure 4.62 Cured PP-B-T20-M-M9-12; no voids present

Table 4.5 Thicknesses of PP-B-T20-M-M9 7-12

PIB-PUR	Thickness [mm]
PP-B-T20-M-M9-7	2.01
PP-B-T20-M-M9-8	1.908
PP-B-T20-M-M9-9	2.018
PP-B-T20-M-M9-10	1.812
PP-B-T20-M-M9-11	1.786
PP-B-T20-M-M9-12	2.098

4.2.10 Increased Solvent Content

To mitigate the high viscosity of the PIB-diol, a substantially higher amount of solvent was added to the diol to facilitate pouring and to achieve thinner samples. In addition to this, steps were taken to ensure that the solvent had evaporated before curing began. Extra time was given to ensure sufficient time to cure samples.



Figure 4.63 cured sample of PP-B-T20-M-M10 with increased amount of solvent

The method involved using 80% heptane by weight, and no catalyst. The resulting sample contained many voids and had high variation in its thickness as indicated in Figure 4.63. However, the mixture was significantly easier to pour, and the viscosity was visibly reduced. The sample was also held at a lower temperature (50°C) for 24 hours to allow the solvent to gently evaporate off without boiling. The sample was also given significantly longer (24 hours) to cure at a slightly lower temperature (90°C) than previously. The step of significantly increasing the solvent content shows promise for producing a more processable material.

4.2.11 Refined Method with High Solvent Content

Method 11 with a refined evaporation and curing protocol is described below.

Method 11 (designated M11)



1. The samples were created for testing by weighing out about 4g of PIB diol. The exact weight was then used to calculate the exact weight of heptane, MI Luphanate, and Tween 20 if applicable.
2. 90% heptane by weight was incorporated into the PIB diol initially by mechanically stirring then in the speed mixer at 2500 rpm for 15 mins.
3. Once it was fully incorporated the MI Luphanate and Tin (II) 2-ethylhexanoate were added and again mixed at 2500 rpm for 10 mins.
4. Tween 20 was then added where applicable and again mixed at 5 mins for 2400 rpm.

5. PTFE moulds, having been cleaned with heptane, isopropanol, and di water and dried in a 70°C oven, the moulds were removed and allowed to cool.
6. The material was then placed into the moulds and labelled with the sample number.
7. The samples were then evacuated repeatedly for 1 hour to 0 ATM at 50°C to remove any bubbles incorporated during the pouring of the mould.
8. Once the evacuation was completed, the solvent was allowed to gently evaporate in the oven at 50°C for 20 hours.
9. Once the 20 hours was complete, the temperature was increased to 90°C and the sample cured for 24 hours. Once these 24 hours were completed the sample was removed from the oven and allowed to cool before demoulding.

With this method high quality, void free samples were reliably obtained. This method was used to create all further samples in this thesis.

4.3 Conclusion

Various methods were explored in the attempt to create void free polymer samples. The key obstacle in this was that the base diol was too viscous to allow the purging of gas from the formulation after the constituent parts had been mixed. Attempts to remove the gas from the material through mechanical means were unsuccessful and the reduction of viscosity via heat alone was ineffective.

In the end the addition of solvent allowed for the sufficient reduction in viscosity that any gas incorporated into the material could escape.

The evaporation of solvent then became an issue. It was determined that holding the material at a warm temperature for 20 hours was sufficient to allow the gentle evaporation of the solvent. A repeatable method for creating PIB-PUR sheets was developed and will be investigated for key functional properties.

Chapter 5. Mechanical Characterisation

5.1 Introduction

Through characterisation of the mechanical properties of materials we can more accurately predict how they will perform when being used in real world applications. It was noted during lap shear testing that bulk material properties were critical rather than material substrate interface. Hence this chapter will focus on tensile mechanical behaviour of PIB-PUR elastomers. A further motivation is that differences in mechanical characteristics can point to underlying structural differences which could have implications for other physical properties.

5.2 Tensile Behaviour

The first objective of this chapter is to characterise the fundamental mechanical behaviour of four material formulations of interest and to investigate potential differences between them.

The material variants being investigated in this chapter have been processed according to the final method described in Chapter 4, utilising diols from either batch A or batch C and, for both these cases, considering cases where the crosslinker, Tween 20 had been added in step 4 versus those where it had not. These were designated A, AT20, C and CT20. Large strain tensile testing was then performed according to the method described in Chapter 3.

At least 9 samples of each of the four formulations were tested under tensile strain with a displacement rate of 100 mm/min. Dog bone samples of length 50 mm were collected and tested in accordance with the method laid out in Chapter 3.

In order to ensure consistent representation of the true initiation of tensile response, a stress value of 0.05 MPa was selected as the threshold signifying the initiation of the experiment. Stress and strain values were then obtained relative to this initial threshold. It was determined that the average stress response would be calculated at designated intervals of strain for each sample. For strain between 0 and 50%, a data point average was taken at every 1% strain. This was to ensure that a detailed representation of the curve was achieved as this could be the most complex region of the response. Subsequently, from 50% strain through to failure, a data point average was taken at 50% strain intervals. For each sample, the data point closest to the intended strain point (within 0.1%) was noted, as was its corresponding stress value. The standard deviations of these stress values were also calculated. As the sample set contained less than 30 values, the sample standard deviation was used as opposed to the population standard deviation which is used for sample sets with $n > 30$.

Figure 5.1, Figure 5.2, Figure 5.3 and Figure 5.4, and show the averaged stress versus strain response for each material formulation (A, AT20, C and CT20) with the standard deviation represented by error bars.

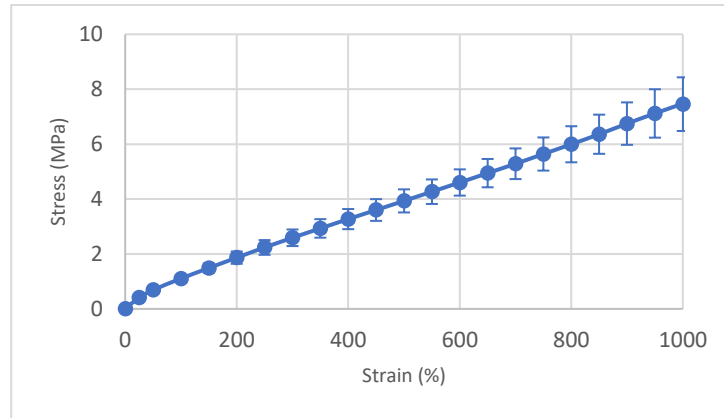


Figure 5.1 Tensile response of samples with formulation A (Batch A with no crosslinker). The average response ($n=9$) is in dark blue, with standard deviation via error bars

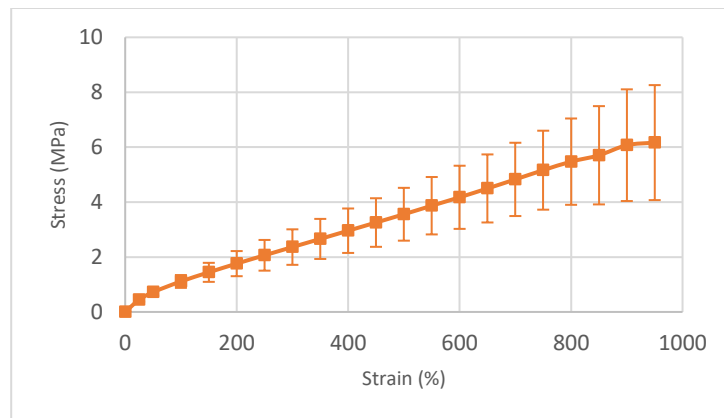


Figure 5.2 Tensile response of samples with formulation of AT20 (Batch A with crosslinker). The average response ($n=26$) of all samples is in dark orange, with standard deviation via error bars

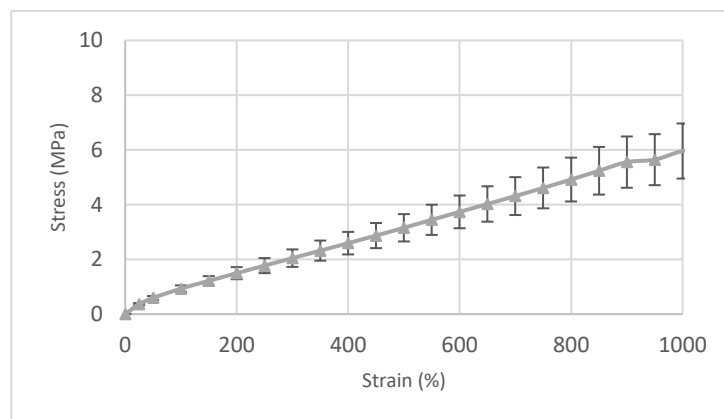


Figure 5.3 Tensile response of samples with formulation of C (Batch C with no crosslinker). The average response ($n=12$) of all samples is in dark grey, with standard deviation via error bars

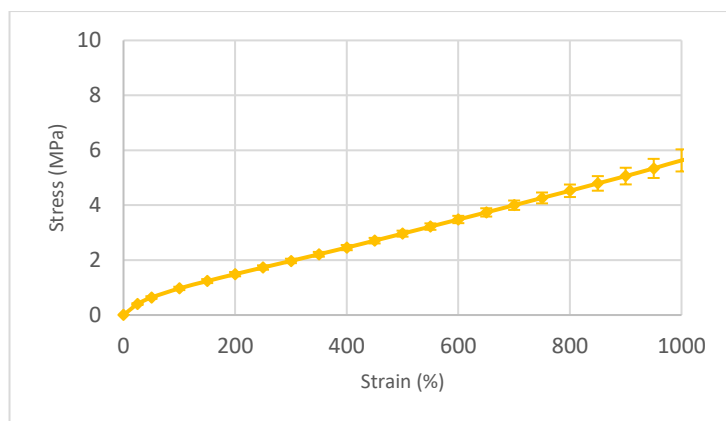


Figure 5.4 Tensile response of samples with formulation of CT20 (Batch C with crosslinker). The average of all ($n=18$) samples is in dark yellow, with standard deviation shown via error bars

There was a notably large standard deviation in formulation AT20 as seen in Figure 5.2. Upon closer inspection it was seen that this large deviation was caused by two groupings of samples, one higher and one lower than the average tensile response. These sample groupings were all identified to have been stamped from the same sheet. The samples with a higher tensile response were identified to have been stamped out from sample sheet #126 [purple] as shown in Figure 5.5. The samples with a lower tensile response were identified to have been stamped out from sample sheet #117 [green] as shown in Figure 5.5.

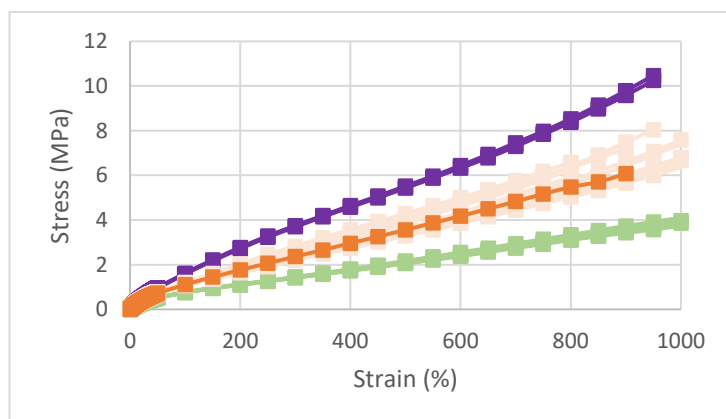


Figure 5.5 Graph indicating that outliers from group AT20 are from the same sample sheet [purple group sheet 126, green group sheet 117, orange indicates average AT20 response and pale orange individual responses of other AT20 samples]

Figure 5.6 shows a comparison of the four material variants over the first 25% strain, while Figure 5.7 shows a comparison of the four material variants up to 1000% strain.

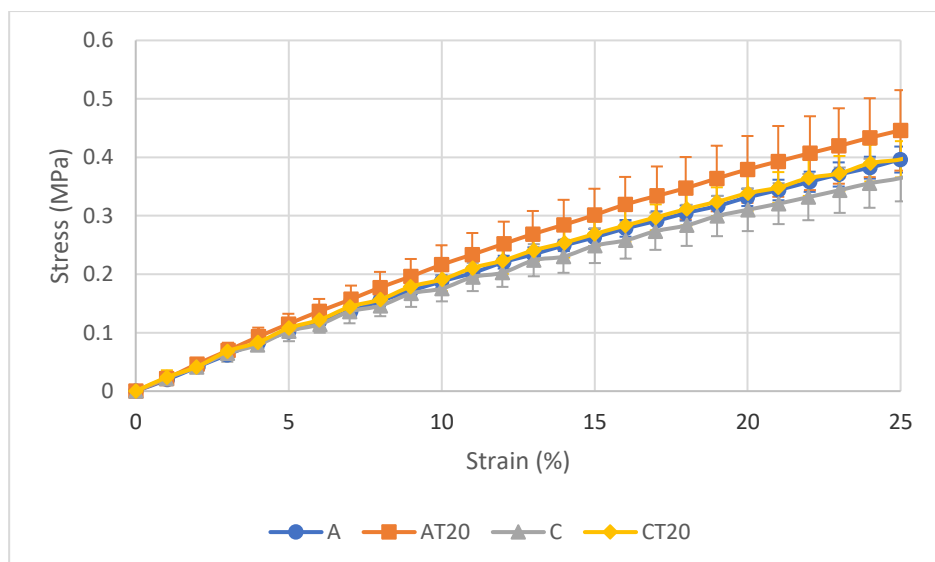


Figure 5.6 Comparison of the tensile strain averages from all formulations over the 0% to 25% strain range, with offsets indicating the sample standard deviation of each data set

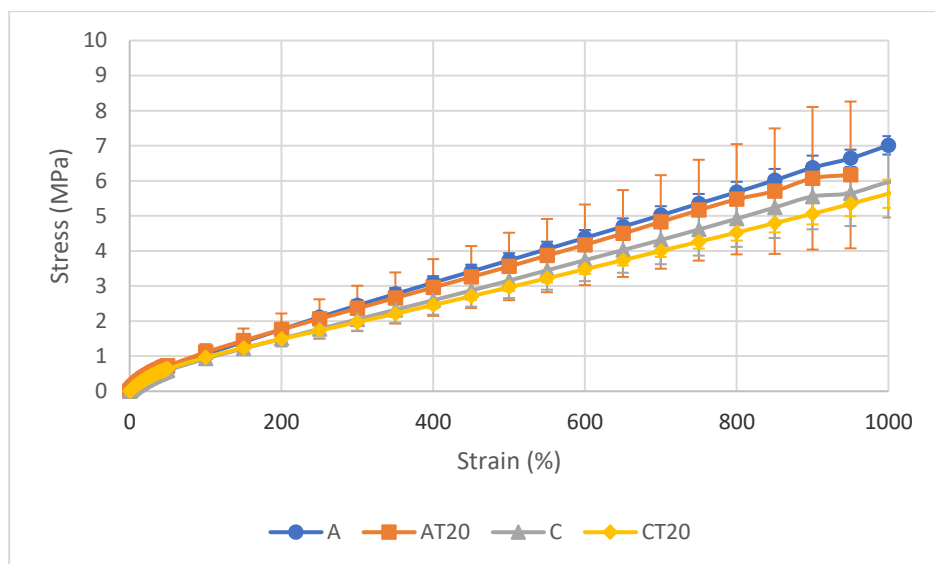


Figure 5.7 Comparison of the tensile strain averages from all formulations from 0% to 1000% strain with error bars indicating the standard deviation of each data set

All formulations appear to have a similar tensile response. ANOVA analysis was conducted to see if formulations made with PIB diol batch A could be said to have significantly different stress responses to formulations made with PIB Diol batch C for two selected strain levels, 20% strain and 800% strain. No significant difference was found between the stresses corresponding to batch A versus those of batch C at either 20% strain or 800% strain (based on a critical alpha value of 0.05). Appendix B contains further details.

Similarly, ANOVA analysis was conducted to test whether formulations created using the Tween 20 crosslinker had significantly different stress levels at the 20% and 800% strain points than the

corresponding formulations made without Tween 20. Again, no significant difference was found. Appendix B contains further details.

5.3 Mullins effect

5.3.1 Introduction

While Polyisobutylene Polyurethane is not expected to experience large stresses or strains when used to coat stiff materials such as printed circuit boards (PCB), it is desirable that the mechanical characteristics and limits of the material are known in order to assess future application opportunities. For example, other materials or devices to be encapsulated could experience large, repeated strains through folding or bending. It is therefore useful to determine whether large strain effects, including hysteretic effects such as the Mullins effect seen in rubbers, are in evidence.

The tests described in the previous section all involved continuous straining of a tensile specimen to the point of failure. Depending on the application, a coating for a flexible medical implant may be required to experience more complex strain events during its working life. Specimens were tested to investigate whether repeated loading and unloading would affect the stress response of these PIB-PUR samples according to the Mullins effect.

5.3.2 Experimental Procedure

In this protocol, tensile samples with the same dimensions as above were subjected to a series of strain cycles. Specifically, the protocol involved extending samples to 200% strain, then returning to 0% strain, followed by a ten-minute interval. Samples were then stretched to 300% strain and again returned to 0% followed by another ten-minute interval. The samples were then strained to 400% strain and subsequently returned to 0% deformation. Following another ten-minute interval, the sample were tested to failure.

5.3.3 Stress and Modulus Effects

5.3.3.1 *Mullins Response for Each Formulation*

In Figure 5.8, for a sample with a PIB diol from batch A and no Tween 20 crosslinker, the Mullins effect appears to be present. The sample follows the normal trajectory from 0 - 200% strain and is then unloaded. The stress path for reloading up to 200% strain is lower than encountered previously. This effect is more pronounced with further and higher strain cycles. To further confirm that the Mullins effect is present, ANOVA analysis was conducted on various strain points to compare consecutive cycles and to determine if the associated stresses are significantly different.

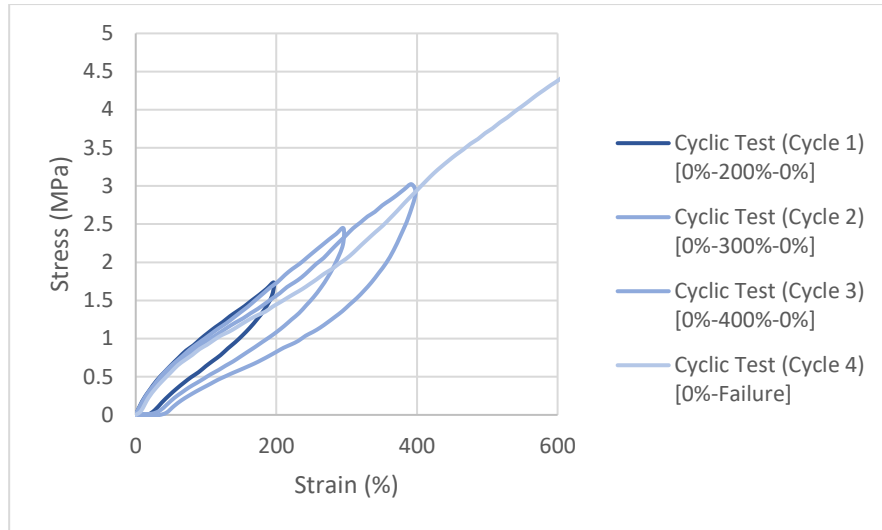


Figure 5.8 Demonstration of Mullins Effect in material type A

Figure 5.9 shows a comparison between the Mullins response to escalating strain cycles, and the tensile response directly to failure of an equivalent sample.

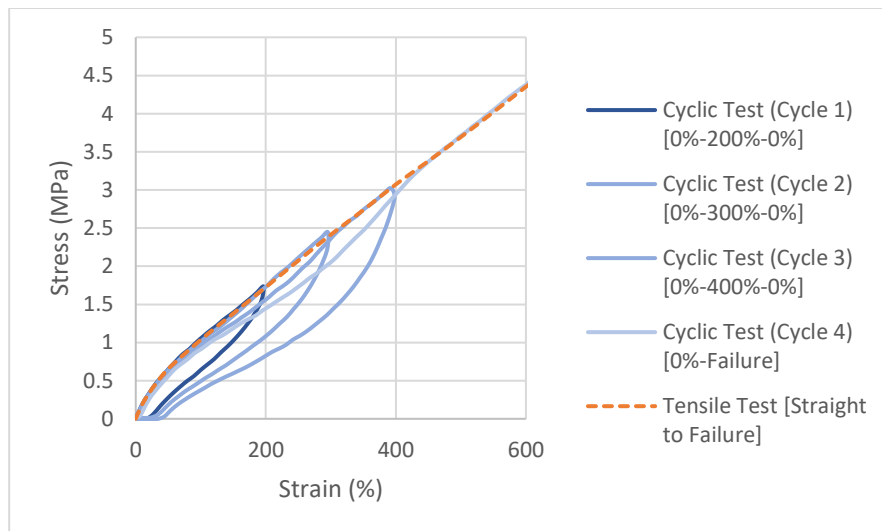


Figure 5.9 Demonstration of Mullins Effect in material type A with tensile results for material type A for comparison

ANOVA analysis was conducted to compare the stress values for the same strain values in consecutive cycles in type A. Figure 5.10 indicates the stress values selected for comparison at 100% strain. Using an alpha value of 0.05 it can be concluded with a 95% certainty that for strains of 100%, 150%, 175%, 195%, 250%, 275% and 295% for successive strains cycles there was a significant difference in the stress induced in the material for an equal amount of strain upon repetition. Box plots demonstrating the differences between cycles for each strain tested are located in Appendix B.

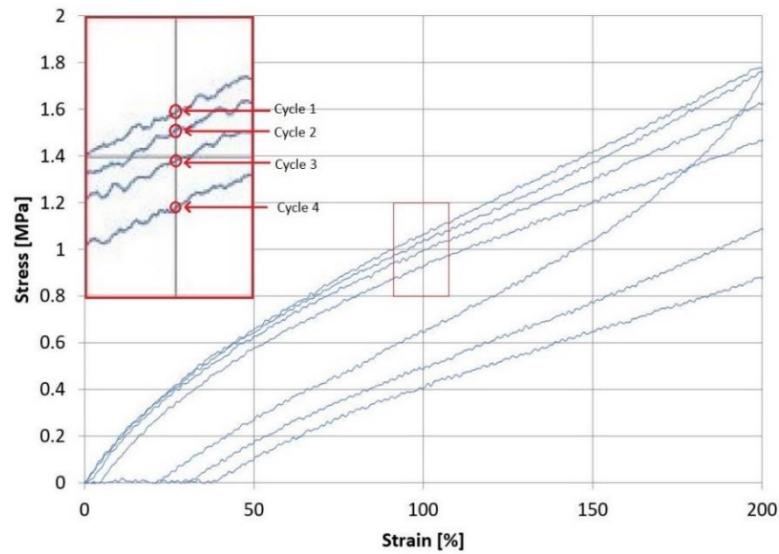


Figure 5.10 Examples of stress values selected for comparison in four consecutive cycles at 100% strain

Figure 5.11 illustrates the Mullins effect in an AT20 sample. ANOVA analysis was conducted to compare the stress values for the same tensile strain between cycles in type AT20. Using an alpha value of 0.05 it can be concluded with a 95% certainty that for strains of 50% and 100% there are significant differences in stresses induced in the material across the cycles. Box plots demonstrating the differences between cycles for each strain tested are located in Appendix B.

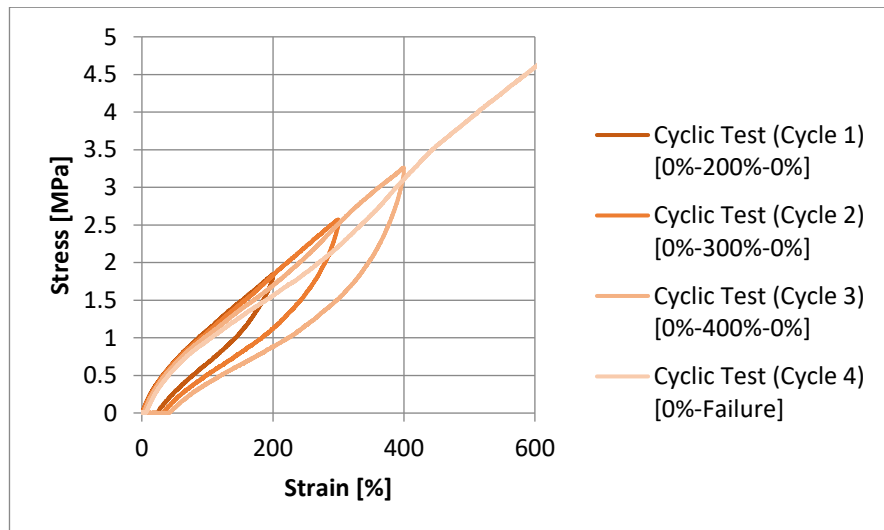


Figure 5.11 Demonstration of Mullins Effect in the material type AT20

Figure 5.12 shows the Mullins effect for material type C. ANOVA analysis was conducted to compare the stress values for the same tensile strain between cycles in material type C. There were no P values which were below the critical alpha value of 0.05. It can therefore be concluded with a 95% certainty there was no statistical difference seen between the cycles in material type

C. Box plots demonstrating the differences between cycles for each strain tested are located in Appendix B.

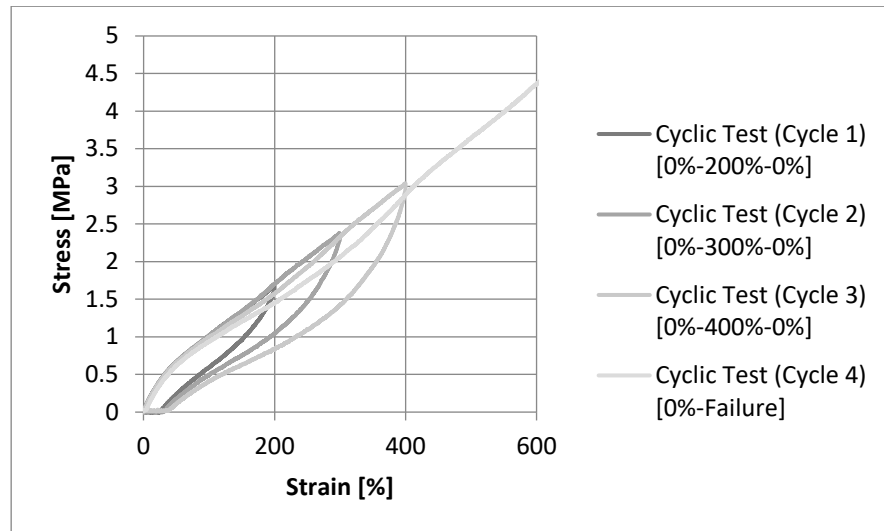


Figure 5.12 Demonstration of Mullins Effect in material type C

Figure 5.13 shows the Mullins effect for material type CT20. ANOVA analysis was conducted to compare the stress values for the same tensile strain between cycles in material type CT20. Using an alpha value of 0.05 it can be concluded with a 95% certainty that for strains of 150%, 175%, 195%, 250%, 275%, 295%, 350%, 375% and 395% there was a statistical difference across cycles. Box plots demonstrating the differences between cycles for each strain tested are located in Appendix B.

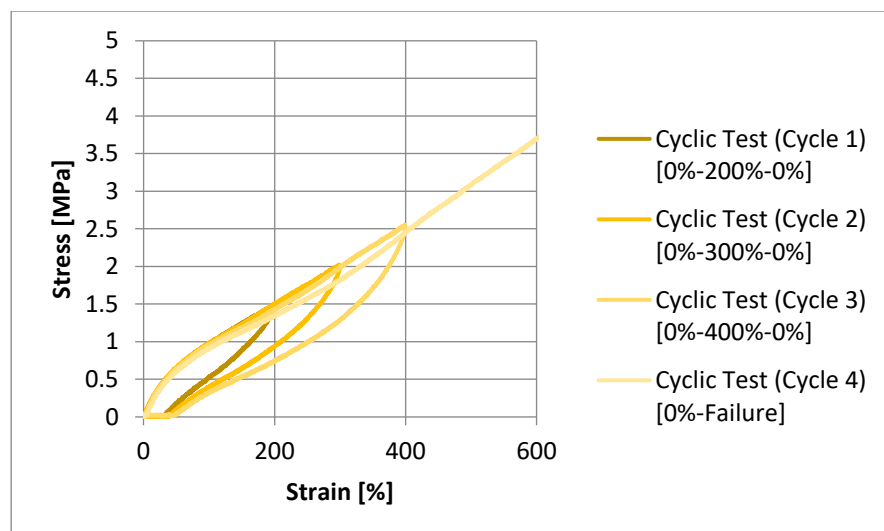


Figure 5.13 Demonstration of Mullins Effect in material type CT20

5.3.3.2 Comparing the Stress Values of Between Formulations

ANOVA analysis was used to compare various material types, to determine if there were any conclusions to be drawn regarding the effect of different batches and the inclusion of crosslinking agent on the mechanical effect of repeated strain cycle. The P values describing these statistical differences can be found in Appendix C. The formulations compared were as follows;

- A and AT20, comparing the effect of the inclusion of crosslinker for material type A.
- A and C, comparing the effect of diol batch.
- C and CT20, comparing the effect of the inclusion of crosslinker for material type C.
- AT20 and CT20, comparing the effect of diol batch.

Effect of T20 on batch A (A versus AT20).

The stress values induced in response to tensile strains and repeated cycles were analysed to determine any statistical differences using an alpha value of 0.05. No significant difference was observed between samples made from the formulations A and AT20 over a range of strain values (as previously indicated) across all cycles. It was therefore concluded that there was no effect in using the crosslinker T20 in formulation A.

Effect of batch where no T20 was used (A versus C).

It can be concluded with a 95% certainty (alpha value of 0.05) that there were significant differences observed at every strain level tested and for every loading cycle between formulations A and C. This suggests that the differences between the diol batches did affect the material response.

Effect of T20 on batch C (C versus CT20).

It can be concluded with a 95% certainty (alpha value of 0.05) that for strain values of 50% and 75% in cycle (iv) there was a significant difference observed in the material between samples made from C and CT20. This suggests that the presence of crosslinker in formulation C may have some influence on mechanical properties.

Effect of batch where T20 was used (AT20 versus CT20).

It can be concluded with a 95% (alpha value of 0.05) certainty that with the exception of the strain value 50% in the cycle (iv) there was significant difference observed in ANOVA analysis of the formulations AT20 and CT20. This suggests again that a difference between batch diol A and

C does have a significant effect on the presence of the Mullins effect for samples containing Tween 20.

5.3.4 Softening

5.3.4.1 Principle

Softening can be graphically described on a stress versus strain graph of a cyclic test as the area enclosed by two consecutive loading trajectories. In Figure 5.14 two upward trajectories of successive cycles are highlighted, trajectory A in yellow and trajectory B in orange [108]. If the area under the curve of trajectory A (yellow) is found, it will encompass the area in yellow in Figure 5.15. Similarly, by finding the area under the curve of the trajectory B (orange) it corresponds to the area in orange in Figure 5.16. By subtracting the area created by trajectory B (orange) from trajectory A (yellow) as indicated in Figure 5.17 the strain softening for that cycle will be found.

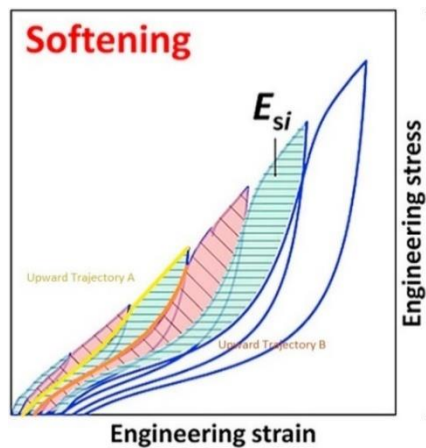


Figure 5.14 Softening graph modified from Li et al. [108]. Two upward trajectories of subsequent cycles are highlighted, trajectory A in yellow and trajectory B in orange *

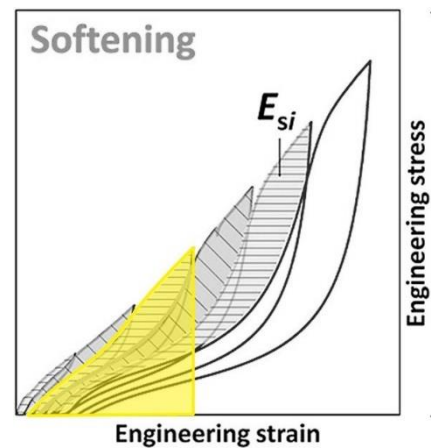


Figure 5.15 Softening graph modified from Li et al. [108]. Area under curve of trajectory A highlighted in yellow *

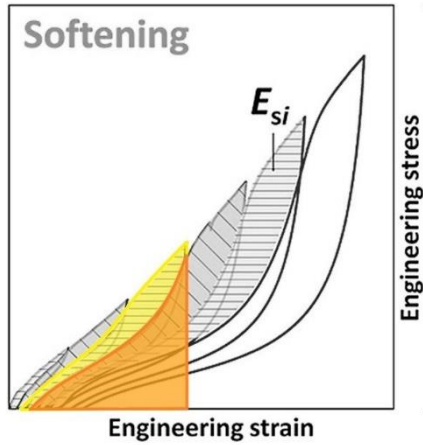


Figure 5.16 Softening graph modified from Li et al. [108]. Area under curve of trajectory B highlighted in orange *

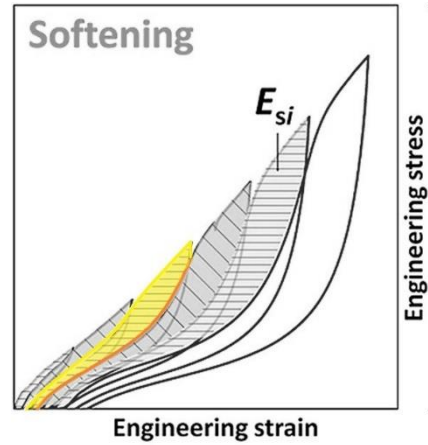


Figure 5.17 Softening graph modified from Li et al. [108]. Graph indicating how the softening created by trajectory A can be calculated by the subtraction of the area created by trajectory B from the area created from trajectory A *

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5.3.4.2 Interpretation of Experiments

The softening of each sample for the four material variants was determined by calculating how much area was enclosed between two successive upward trajectories as indicated in Table 5.1.

Table 5.1 Table indicating which trajectories used to calculate the various softenings within the cyclic tests

	<u>Positive Area</u>	<u>Negative Area</u>
Softening (i)	Upward Trajectory Cycle (i)	Upward Trajectory Cycle (ii)
Softening (ii)	Upward Trajectory Cycle (ii)	Upward Trajectory Cycle (iii)
Softening (iii)	Upward Trajectory Cycle (iii)	Upward Trajectory Cycle (iv)

To calculate the value for Softening (ii), the cycle (ii) and cycle (iii) trajectories were utilised. The green area in Figure 5.18 is created by the upward trajectory of Cycle (ii). The red area in Figure 5.19 is created by the upward trajectory of Cycle (iii). Every 100th data point, corresponding approximately to 10% strain intervals, was taken to determine the area under the curve.

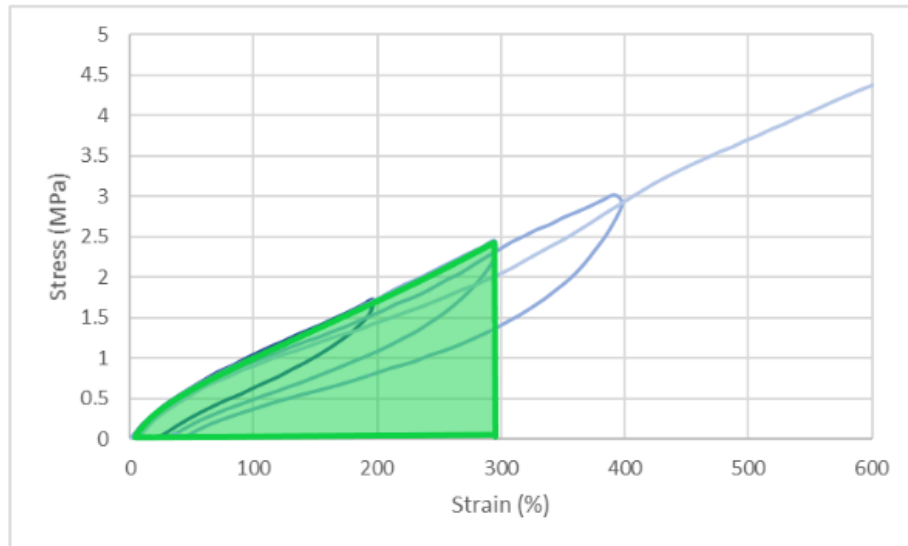


Figure 5.18 Area underneath the curve of the upward trajectory of the Cycle (ii)

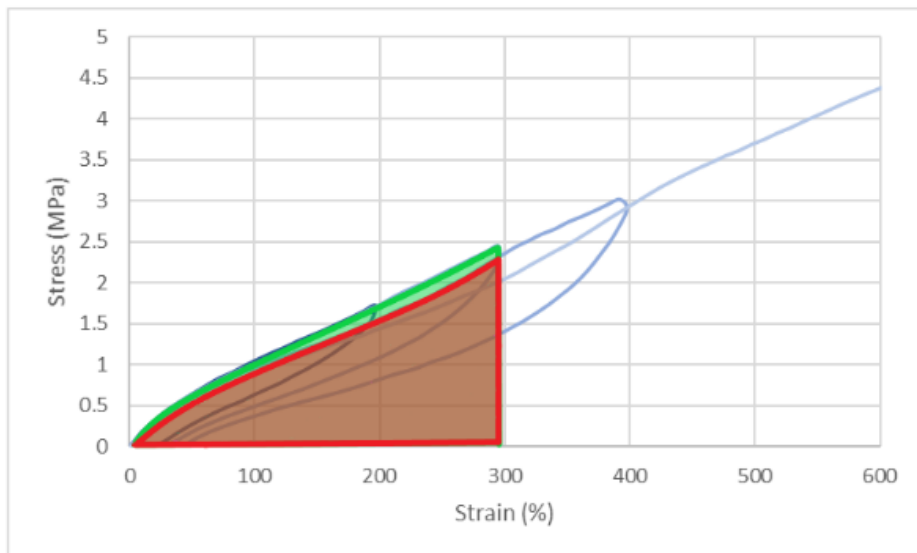


Figure 5.19 Indicating the difference in area from the upward trajectory of the second cycle and the downward trajectory of the Cycle (iii)

The difference between the green area and the red area was then found. This is determined to be the value for Softening (ii). This procedure was then repeated for all other softening areas as indicated in Table 5.1 and Figure 5.20.

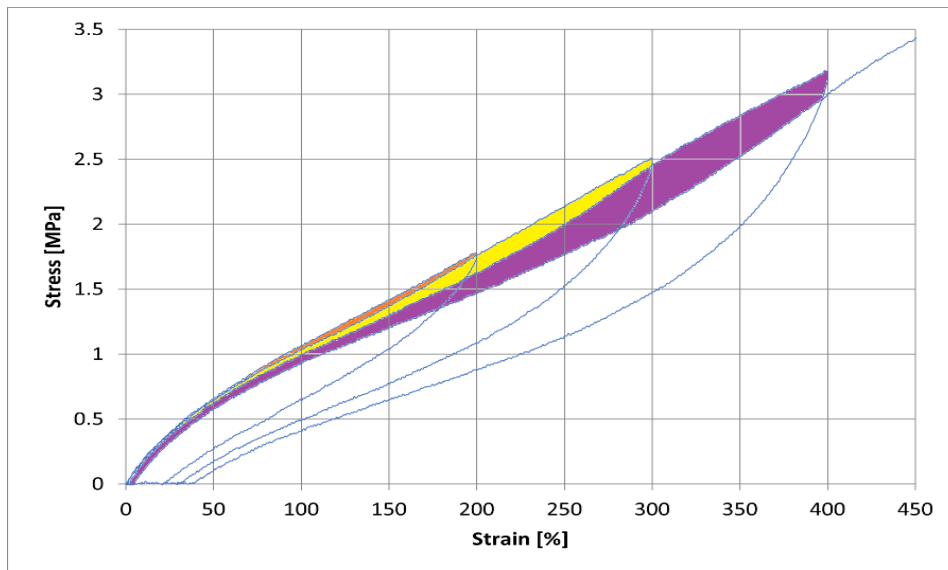


Figure 5.20 Graph indicating the area created by successive upward trajectories and softening - Orange (Softening (i)) Yellow (Softening (ii)) Purple (Softening (iii)) for trial sample from material type A

ANOVA analysis was then conducted on these softening energy densities (calculated areas) to determine if there was any significant statistical difference between formulations. With 95% confidence it was seen that in Cycle (iii) there was a significant difference when comparing the formulations, A and C. A significant difference was also seen for all cycles when comparing the formulations of A and C when the crosslinking agent Tween 20 was incorporated for both. These significant differences are all illustrated in the box plots Figure 5.21, Figure 5.22, Figure 5.23 and Figure 5.24. For all other scenarios no statistical difference was seen.

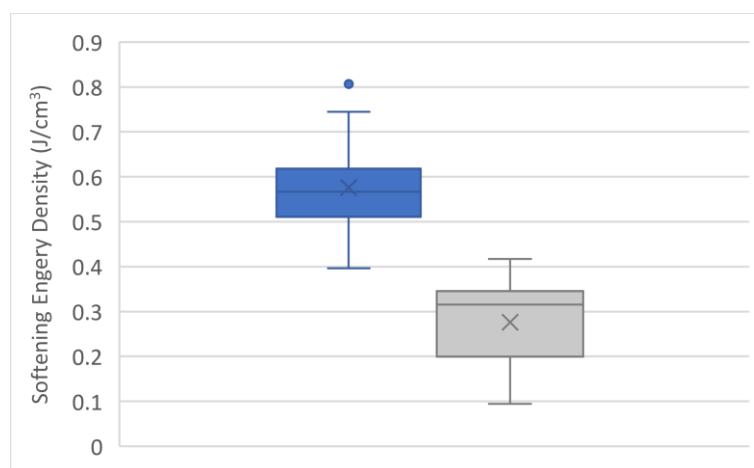


Figure 5.21 Box plots indicating difference between formulations A(blue) (n=8) and C (grey) (n=6) for Softening (iii)

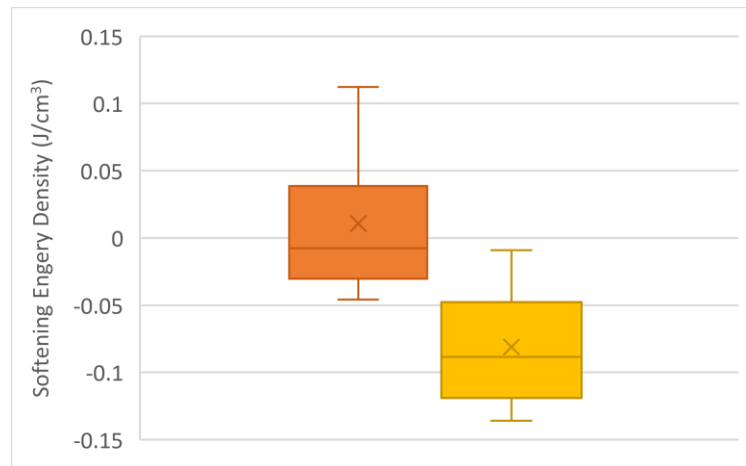


Figure 5.22 Box plots indicating difference between formulations AT20 (orange) (n=9) and CT20 (yellow) (n=10) for Softening (i)

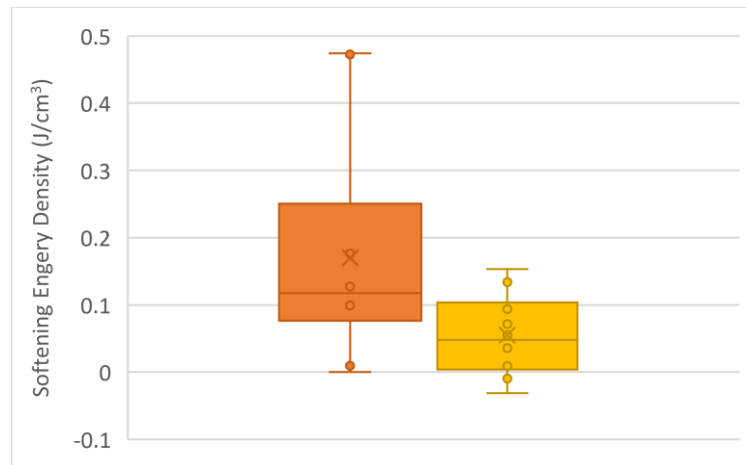


Figure 5.23 Box plots indicating difference between formulations AT20 (orange) (n=9) and CT20 (yellow) (n=10) for Softening (iii)

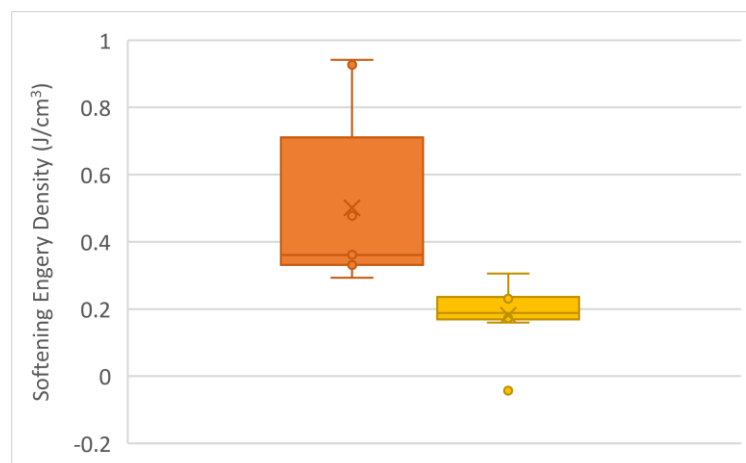


Figure 5.24 Box plots indicating difference between formulations AT20 (orange) (n=9) and CT20 (yellow) (n=10) for Softening (iii)

5.3.5 Recovery Hysteresis

5.3.5.1 Principle

Hysteresis describes how a material behaves when loaded and subsequently unloaded. In hysteresis, more stress is required to reach a level of strain in a polymer than is required for the corresponding strain level during unloading. Recovery hysteresis refers to the difference between the unloading stress path in one cycle and the loading stress path in the subsequent cycle. It describes how well the material 'recovers' its resistance to extension after being unloaded. If no recovery were occurring in the material, the subsequent loading trajectory would follow the same path as the unloading trajectory.

The larger the recovery hysteresis area calculated; the less recovery has occurred. It is calculated by finding the area on a stress versus strain graph which is enclosed by the downward trajectory in question and the subsequent upward trajectory as depicted by the highlighted areas in Figure 5.25, Figure 5.26, Figure 5.27 and Figure 5.28.

First the cycle for which the recovery hysteresis was to be calculated was identified. In Figure 5.25 the hysteresis for the fifth upward loading cycle will be calculated. This cycle is highlighted in yellow, the unloading path for the previous cycle, the fourth cycle is highlighted in orange in Figure 5.25.

The area to be calculated is created by the upward trajectory of the fifth cycle. However, the area for the whole upward trajectory is not taken into account. The area is created from 0% strain to the highest strain achieved by the previous cycle. Here it will be the highest strain achieved in the fourth cycle (indicated in orange) in Figure 5.25, and its impact on the recovery hysteresis is indicated in yellow in Figure 5.26.

The second area to be calculated was created by the downward trajectory of the previous cycle (the fourth cycle as indicated in orange in Figure 5.25). This is straightforward in that the area under the entire downward trajectory is calculated as indicated via the orange highlighted area in Figure 5.27. The recovery hysteresis is then calculated by subtracting the orange area from the yellow area, or more specifically the area underneath the downward trajectory of the previous cycle from the area underneath the upward trajectory of the cycle of interest between 0% strain and the maximum strain experienced in the previous cycle.

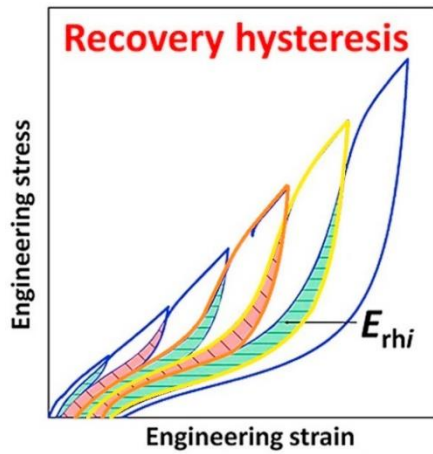


Figure 5.25 Recovery hysteresis graph modified from Li et al. [108]. Orange and yellow highlighted areas indicating the fourth cycle of this hysteresis graph (orange) and the subsequent fifth cycle (yellow) *

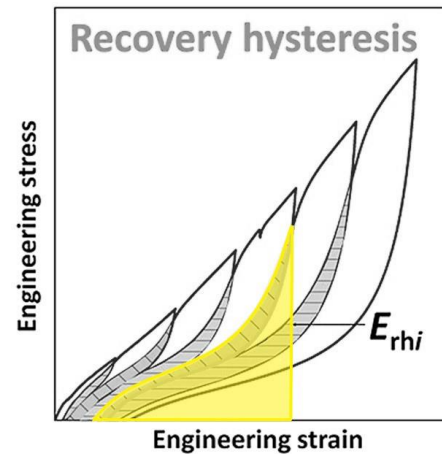


Figure 5.26 Recovery hysteresis graph modified from Li et al. [108]. Yellow highlighted area indicating the first area to be calculated. The area under the curve of the upward trajectory for the cycle of interest between strains of 0% and the maximum strain achieved in the previous cycle *

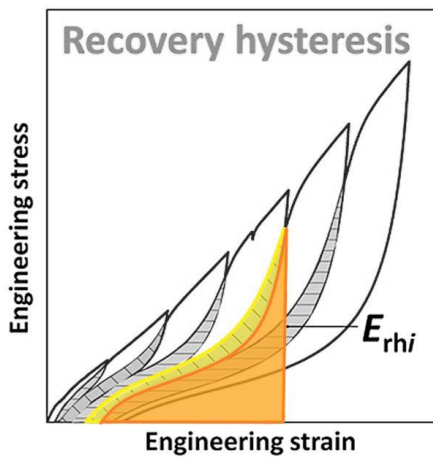


Figure 5.27 Recovery hysteresis graph modified from Li et al. [108]. Orange area indicating the second area to be calculated. The area under the curve of the downward trajectory of the previous cycle *

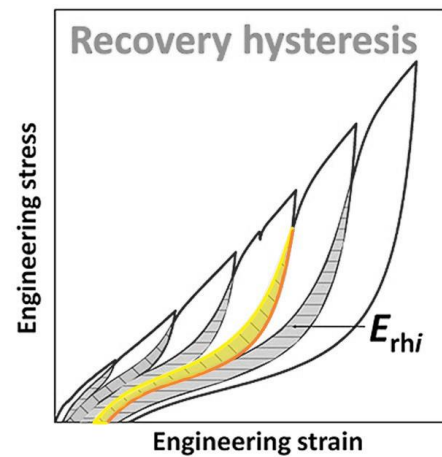


Figure 5.28 Recovery hysteresis graph modified from Li et al. [108]. By subtracting the orange area (Figure 5.27) from the yellow area (Figure 5.26) the area indicating the recovery hysteresis for the cycle of interest is found *

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5.3.5.2 Interpretation of Experiments

Recovery areas were calculated in each of the four formulations (A, AT20, C, CT20) using the trajectories as described in Table 5.2.

Table 5.2 Table indicating the trajectories used to calculate the recovery hysteresis within cyclic tests

	<u>Positive Area</u>	<u>Negative Area</u>
Recovery Hysteresis (ii)	Upward Trajectory Cycle (ii) to 200% Strain	Downward Trajectory Cycle (i)
Recovery Hysteresis (iii)	Upward Trajectory Cycle (iii) to 300% Strain	Downward Trajectory Cycle (ii)
Recovery Hysteresis (iv)	Upward Trajectory Cycle (iv) to 400% Strain	Downward Trajectory Cycle (iii)

To calculate the value for Recovery Hysteresis (iii), Cycle (ii) and Cycle (iii) were utilised. The green area in Figure 5.29 is created by the upward trajectory of Cycle (iii) up to 300%. The red area in Figure 5.30 is created by the downward trajectory of Cycle (ii). These areas were again determined by breaking down the area under the curves into incremental segments.

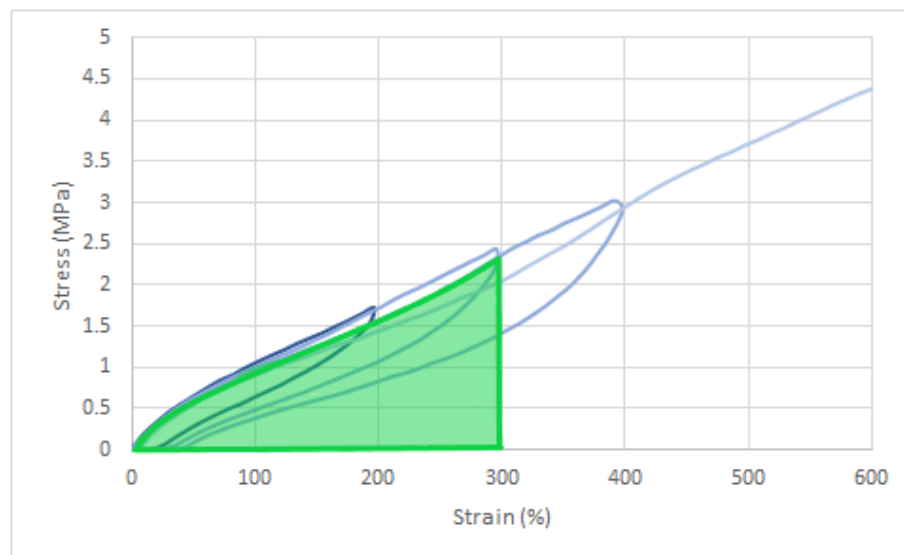


Figure 5.29 Area underneath the curve created by the upward trajectory of Cycle (iii) to 300% strain

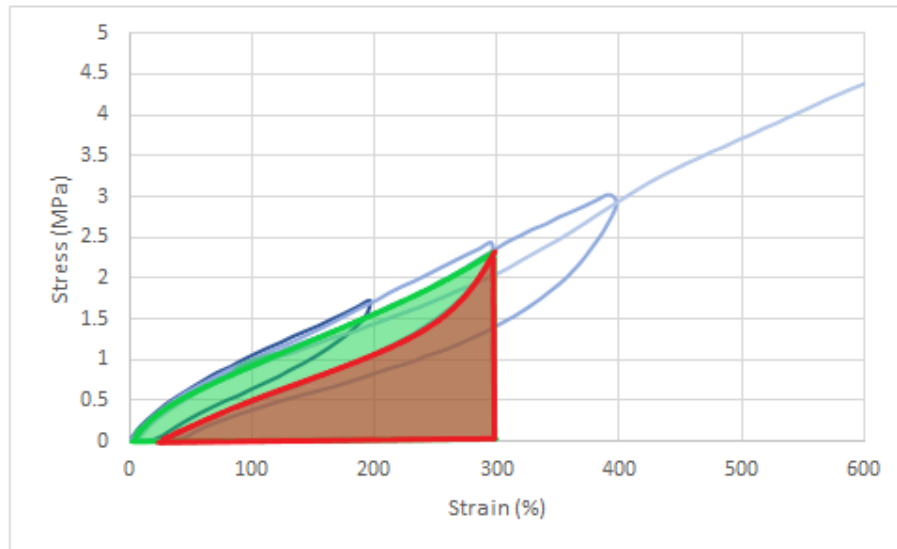


Figure 5.30 Indicating how the subtraction of the area underneath downward trajectory of Cycle (i) from the upward trajectory of Cycle (ii) creates the area which corresponds to Recovery Hysteresis (iii)

The area was calculated in the same way as for softening in the previous section. The strain value was taken as the width value and the stress values were taken as the length. Areas for increments of 10% strain were calculated and summed to get the areas under the desired curves as described in Table 5.2. The procedure was then used to calculate Recovery Hysteresis (ii), as shown in Figure 5.31. The method was repeated for Recovery Hysteresis (iii) as seen in Figure 5.32 and Recovery Hysteresis (iv) in Figure 5.33.

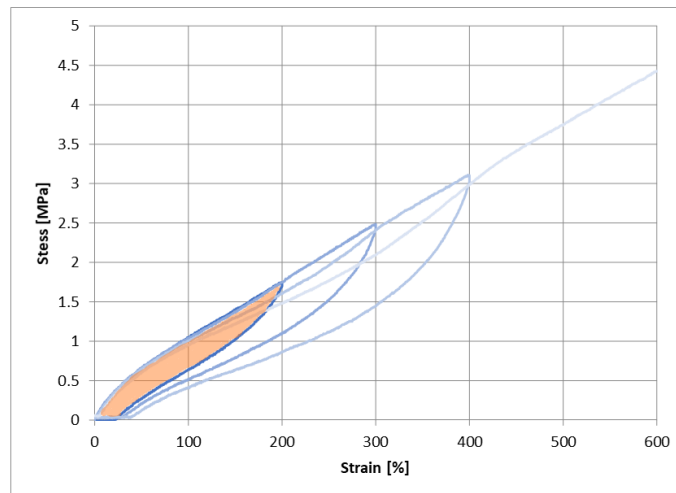


Figure 5.31 Graph indicating the area (Recovery Hysteresis (ii)) created by the downward trajectory of Cycle (i) and the upward trajectory of Cycle (ii)

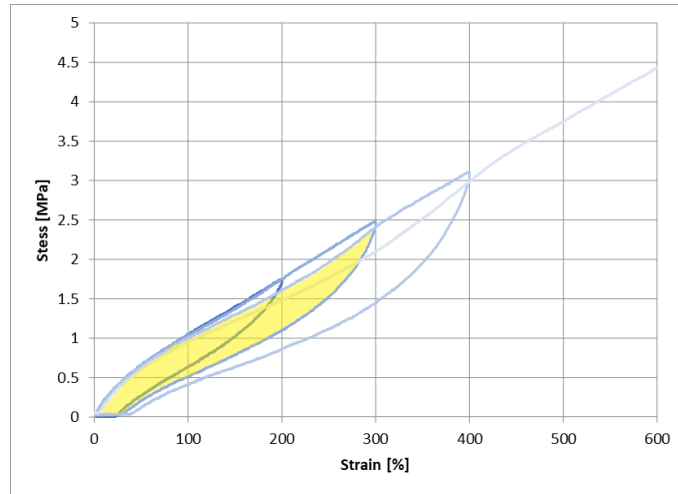


Figure 5.32 Graph indicating the area (Recovery Hysteresis (iii)) created by the downward trajectory of Cycle (ii) and the upward trajectory of Cycle (iii)

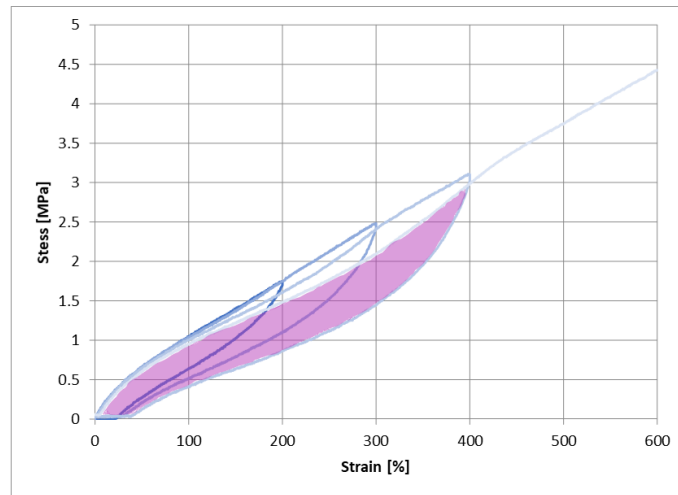


Figure 5.33 Graph indicating the area (Recovery Hysteresis (iv)) created by the downward trajectory of Cycle (iii) and the upward trajectory of Cycle (iv)

The recovery hysteresis area, which corresponds to an energy density (J/cm^3) for each specimen was calculated and ANOVA analysis was then conducted on these areas to determine if there were any significant differences between the four formulations.

With 95% confidence it was seen that in Recovery Hysteresis (iii) (Figure 5.35) and Recovery Hysteresis (iv) (Figure 5.36) there were differences when comparing the formulations, A and C. It was also seen that there were statistically significant differences for Recovery Hysteresis (ii) (Figure 5.38) and Recovery Hysteresis (iii) (Figure 5.39) and Recovery Hysteresis (iv) (Figure 5.40) when comparing the formulations in AT20 and CT20. This mirrors the results seen previously in the analysis of softening. It is also noteworthy that there were small but significant differences seen between formulations A and AT20 (Figure 5.34) and C and CT20 (Figure 5.37) for Recovery Hysteresis (ii). This may indicate Tween 20 has a role in the ability of the material to recover.

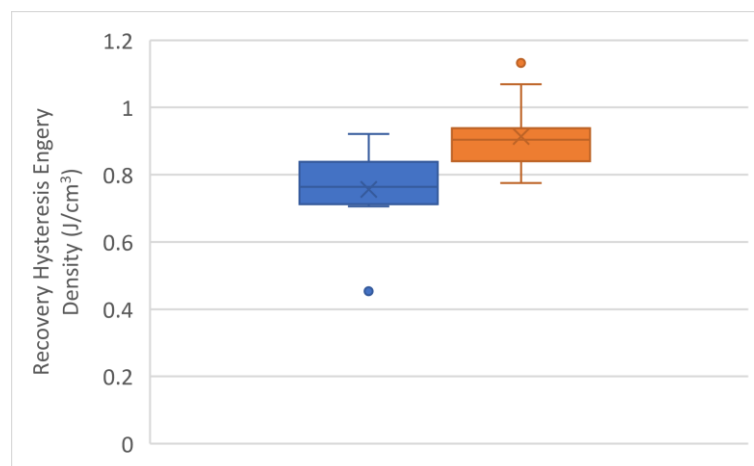


Figure 5.34 Box plot comparing of formulations A (blue) (n=8) versus AT20 (orange) (n=9) of Recovery Hysteresis (ii)

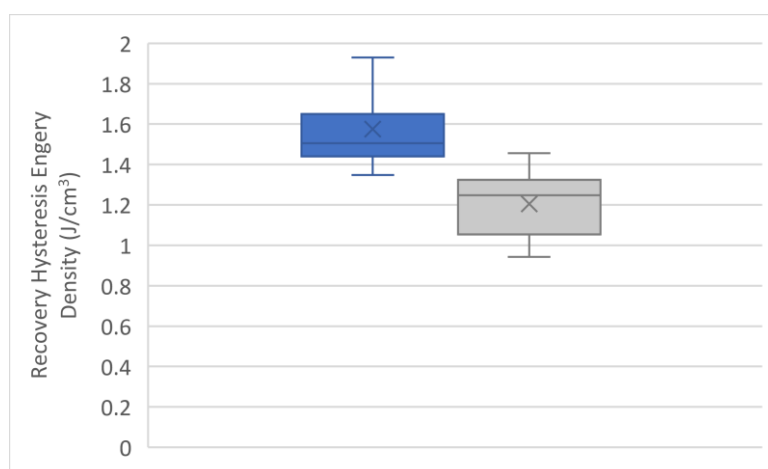


Figure 5.35 Box plot comparing of formulations A (blue) (n=8) versus C (grey) (6) for Recovery Hysteresis (iii)

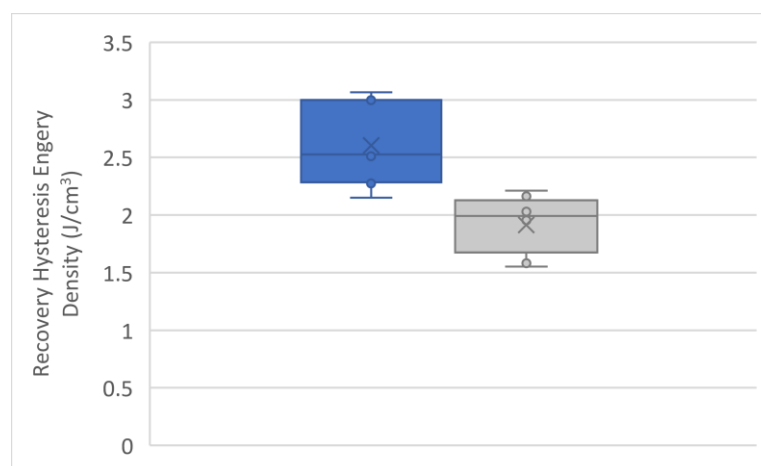


Figure 5.36 Box plot comparing of formulations A (blue) (n=8) versus C (grey) (n=6) for Recovery Hysteresis (iv)



Figure 5.37 Box plot comparing of formulations C (grey) (n=6) versus CT20 (yellow) (n=10) for Recovery Hysteresis (ii)

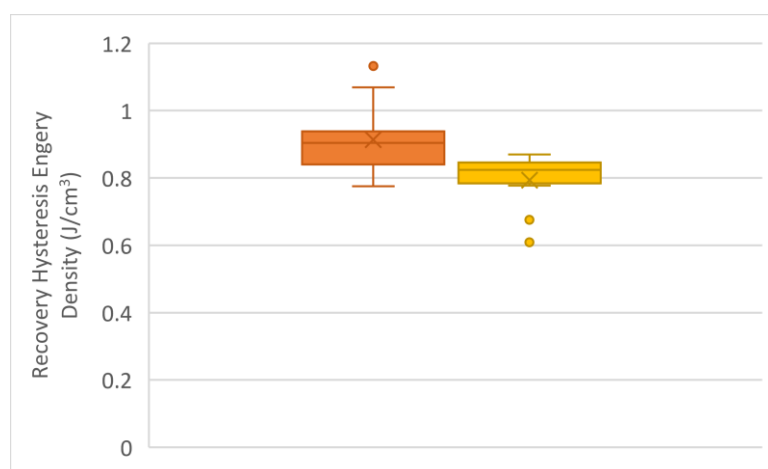


Figure 5.38 Box plot comparing of formulations AT20 (orange) (n=9) versus CT20 (yellow) (n=10) for Recovery Hysteresis (ii)

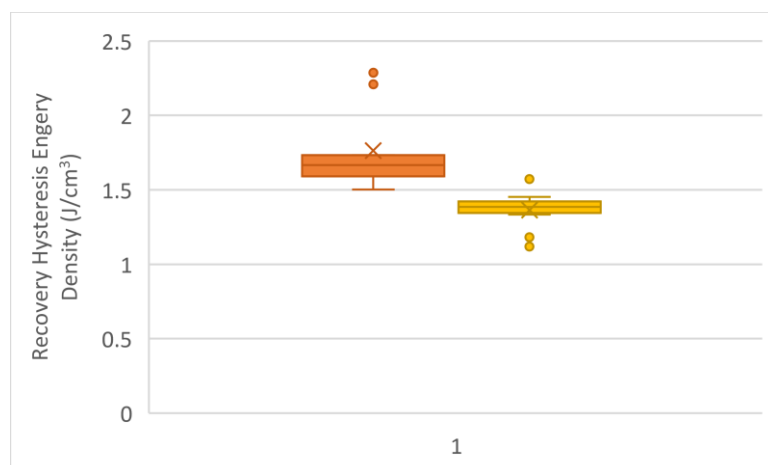


Figure 5.39 Box plot comparing of formulations AT20 (orange) (n=9) versus CT20 (yellow) (n=10) for Recovery Hysteresis (iii)

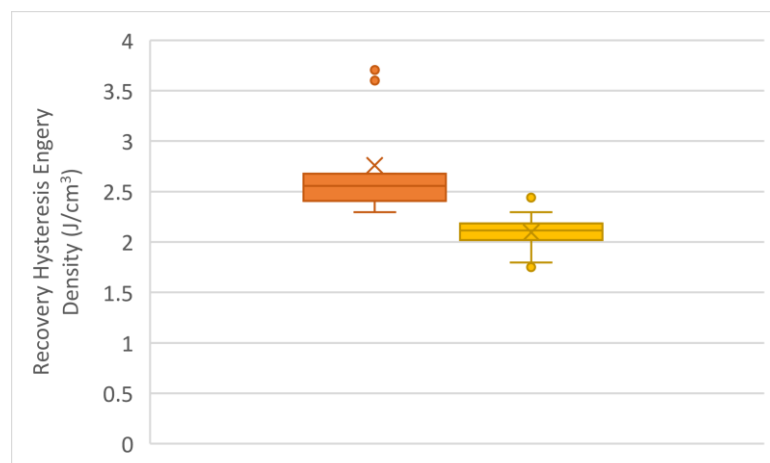


Figure 5.40 Box plot comparing of formulations AT20 (orange) (n=9) versus CT20 (yellow) (n=10) for Recovery Hysteresis (iv)

5.4 Degradation

In order to predict how the mechanical properties of the PIB PUR formulations may be affected when exposed to the harsh environment of the body, degradation tests were employed. Degradation testing was conducted by placing 4 dog bone specimens from each sample sheet in a vial of PBS solution and placing in an oven at 37°C. Specimens were removed at intervals of 1, 2, 4, and 8 weeks and dried with filter paper and stored in aluminium foil for 1 week. The specimens there then tensile tested to failure using the same protocol described in Chapter 3.

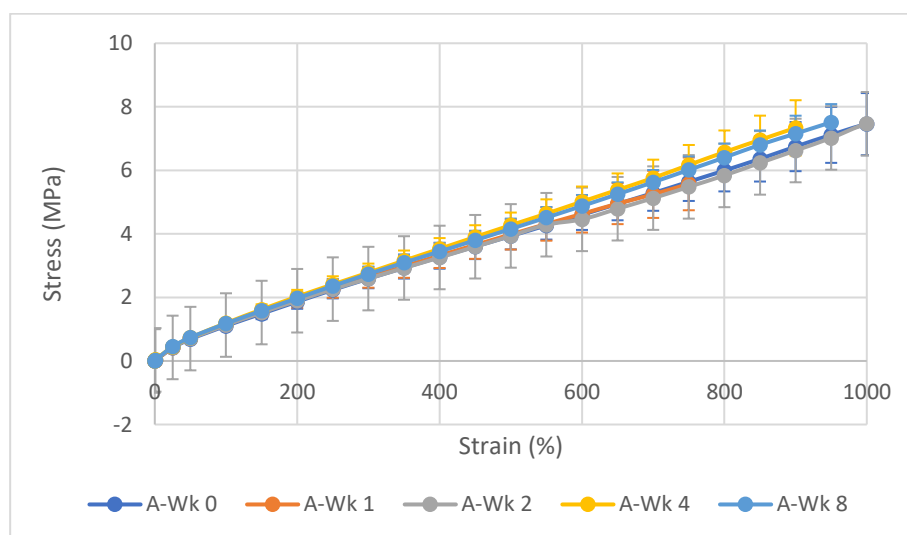


Figure 5.41 Effect of degradation in PBS at 37°C on tensile response for formulation A up to 8 weeks, with standard deviation indicated using error bars (n=4)

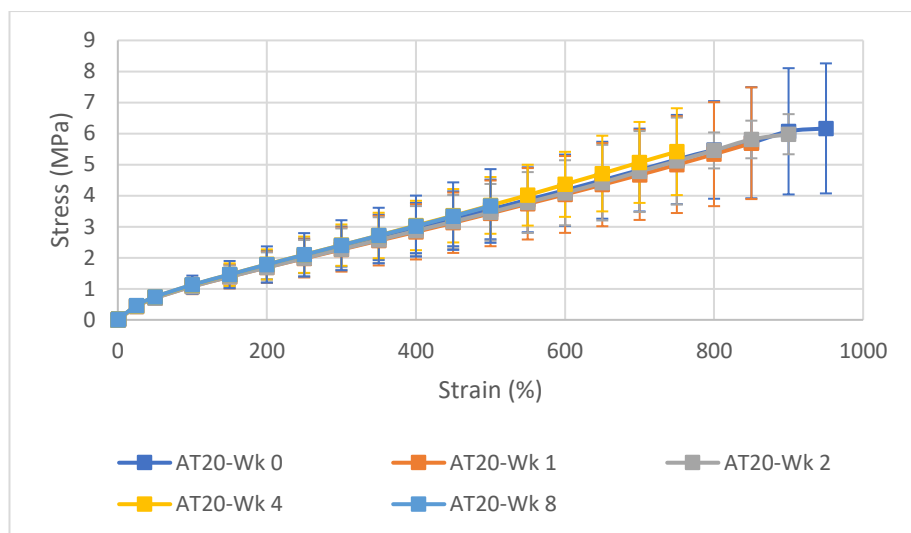


Figure 5.42 Effect of degradation in PBS at 37°C on tensile response for formulation AT20 up to 8 weeks, with standard deviation indicated using error bars (n=7)

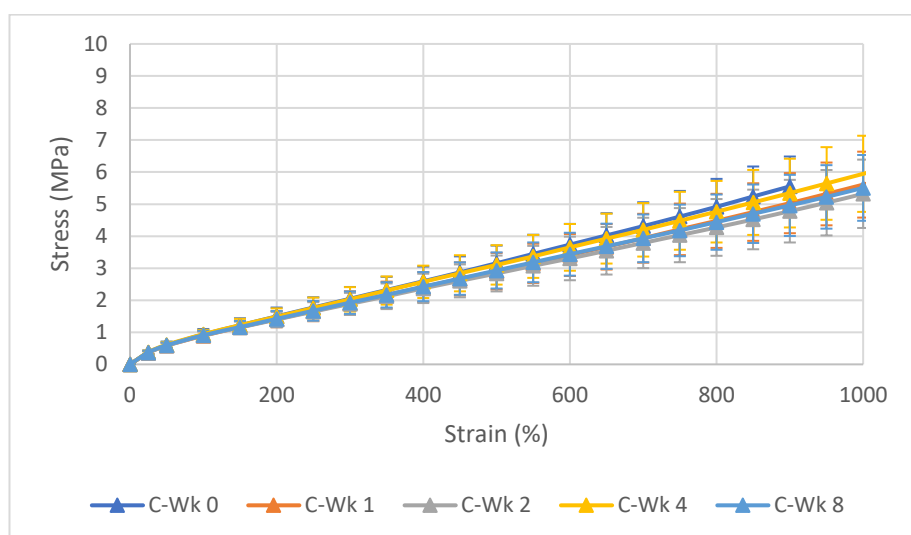


Figure 5.43 Effect of degradation in PBS at 37°C on tensile response for formulation C up to 8 weeks, with standard deviation indicated using error bars (n=3)

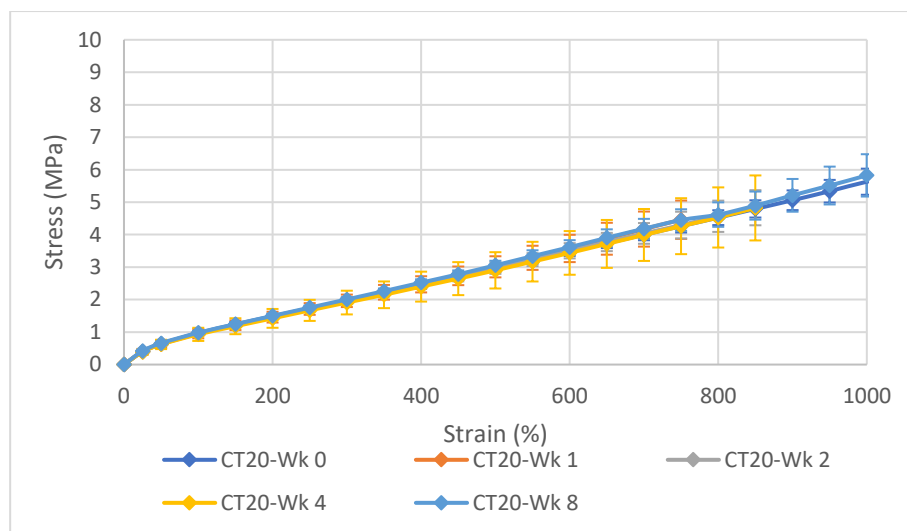


Figure 5.44 Effect of degradation in PBS at 37°C on tensile response for formulation CT20 up to 8 weeks, with standard deviation indicated using error bars (n=7)

ANOVA Analysis was undertaken to determine if there was any statistical difference for the stress induced within the tensile specimens for strains of 20% and 800%. It was determined that with 95% confidence there was no degradation indicated in formulations AT20, C and CT20. Statistical difference was seen for the formulation A for both 20% and 800% as the P values obtained were less than 0.05. From the box and whisker plots below, Figure 5.45 and Figure 5.46, it can be seen that there is a slight increase in the stress induced for both strains for subsequent weeks. This accounts for the statistical difference. However, this would not be considered degradation as it represents an increase in mechanical properties. It can therefore be summarised that there was no degradation seen in samples held in in Phosphate Buffered Saline Solution at 37°C for up to 8 weeks.

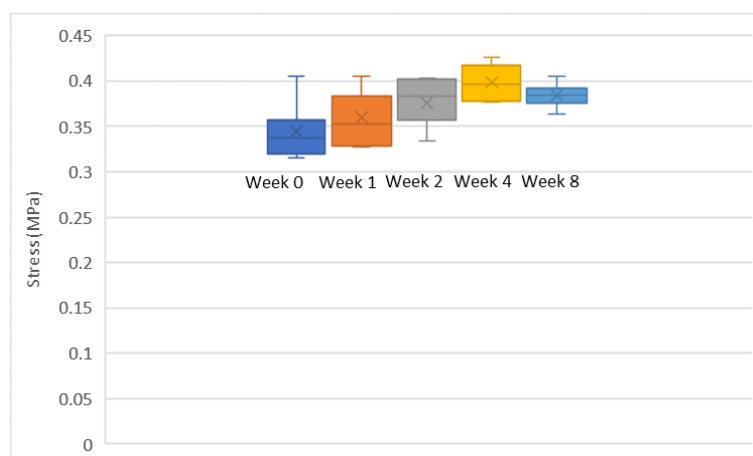


Figure 5.45 Box Plot differences in formulation A after degradation testing for 20% strain. An increase in stress associated with longer soaking times would not be considered degradation (W0 n=12, W1,2,4,8 n=4)

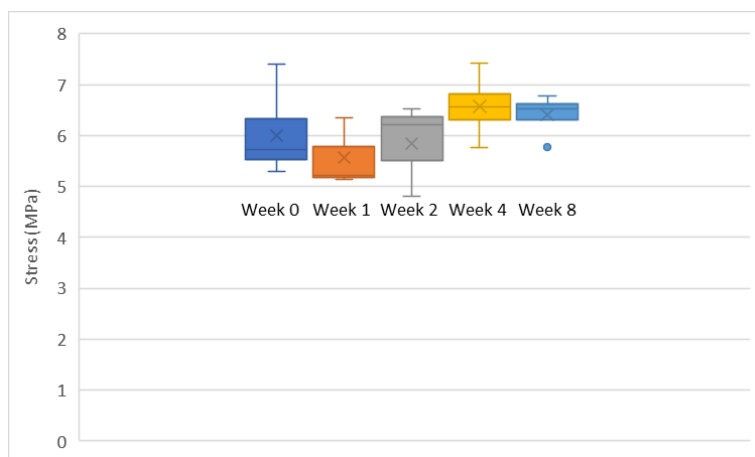


Figure 5.46 Box Plot indicating differences in formulation A after degradation testing for 800% strain. An increase in stress associated with longer soaking times would not be considered degradation (W0 n=12, W1,2 n=3, W4,8 n=4)

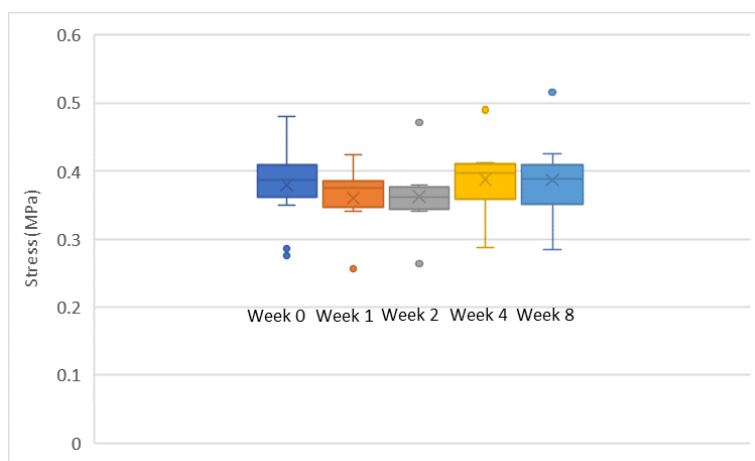


Figure 5.47 Box Plot indicating differences in formulation AT20 after degradation testing for 20% strain (W0 n=26, W1,2,4,8 n=7)

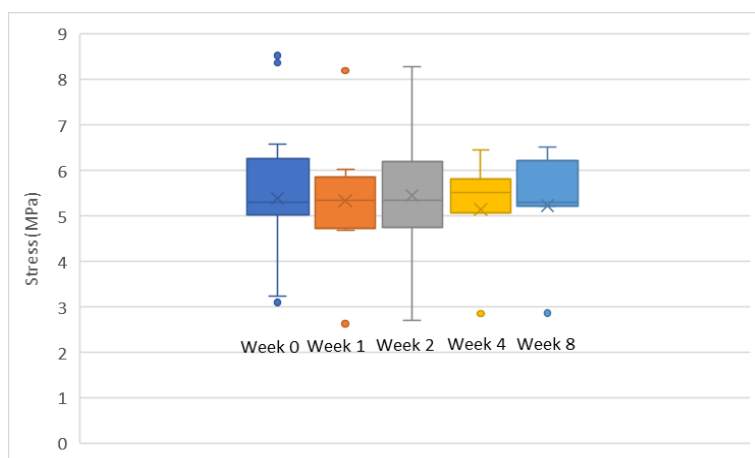


Figure 5.48 Box Plot indicating differences in formulation AT20 after degradation testing for 800% strain (W0 n=25, W1 n=7, W2 n=6, W4 n=5, W8 n=5)

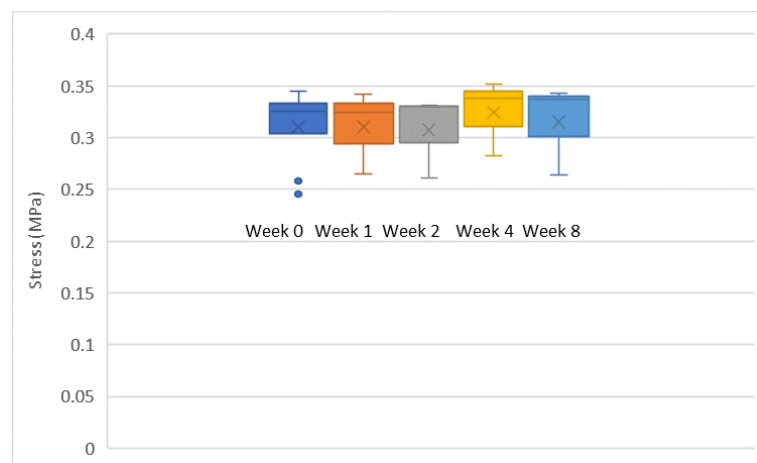


Figure 5.49 Box Plot indicating differences in formulation C after degradation testing for 20% strain (W0 n=26, W1 n=7, W2 n=6, W4 n=5, W8 n=5)

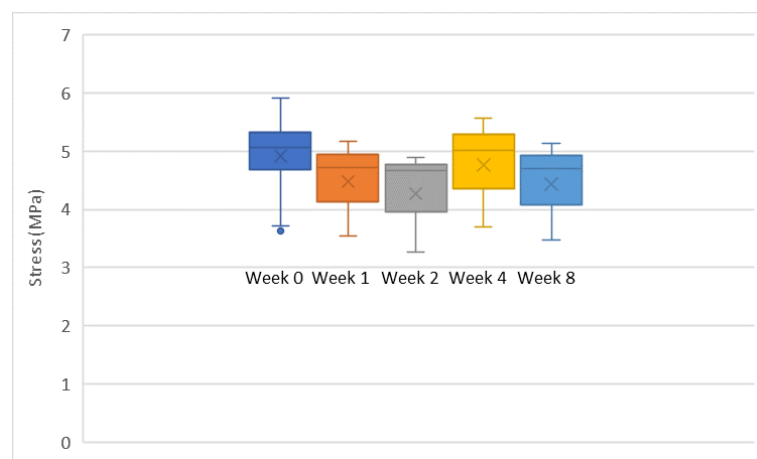


Figure 5.50 Box Plot indicating differences in formulation C after degradation testing for 800% strain (W0 n=12, W1,2,4,8 n=3)

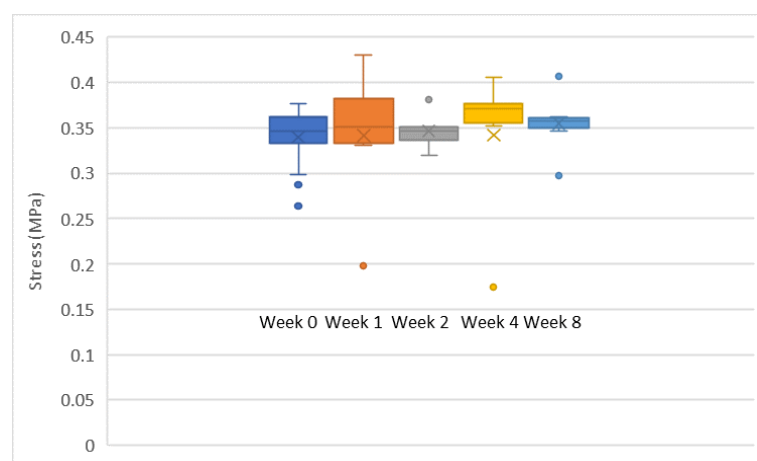


Figure 5.51 Box Plot indicating differences in formulation CT20 after degradation testing for 20% strain (W0 n=18, W1,2,4,8 n=6)

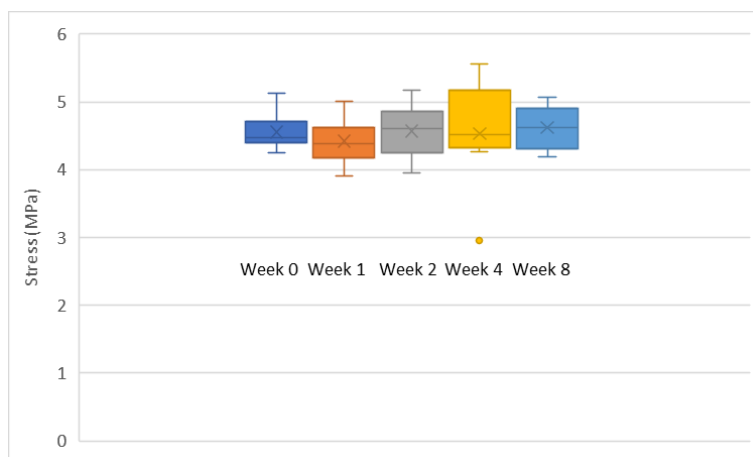


Figure 5.52 Box Plot indicating differences in formulation CT20 after degradation testing for 800% strain (W0 n=18, W1 n=4, W2 n=5, W4 n=6, W8 n=5)

5.5 Discussion

5.5.1 Tensile Properties

In most aspects of the mechanical analysis there was no significant difference in samples made with and without Tween 20. One exception is in the analysis of the effect of T20 on batch C when examining the Mullins effect. It was anticipated that the polysorbate's addition would enhance the mechanical properties of the material. This was found not to be the case as there was no statistical increase in ultimate tensile stress or failure strain for the samples. The most notable aspect of the results was the consistency between different versions of the PIB-PUR formulation, indicating that the properties are not highly sensitive to material variations.

Zapp *et al.* [89] as detailed in [75] observed strength values of 10.2 to 33.7 MPa with an elongation of 80% - 320% strain. Ojha *et al.* [88] incorporated PTMO diol into the soft segment of the polyurethane with the aim of improving the mechanical properties of their material. These properties were successfully increased from a range of strength values of 6-9 MPa with elongation of 150% - 400% to 20 MPa strength with 700% elongation.

The mechanical strengths of these PIB-PUR formulations were comparable to those found in the literature as seen in Table 5.3 and Figure 5.53. The range of the average ultimate tensile strength experienced at breakage of these samples was in the range of 7-10 MPa. Note that this is a minimum average threshold as failure at the grips was observed in many cases. Nonetheless this indicated that the strengths of the materials are at least comparable to literature values.

The elongation of this material however was observed to be significantly higher than that seen in the literature as can be seen in Table 5.3 and Figure 5.54. Speckhard *et al.* [86] as detailed in [88] determined the failure elongation of non-reinforced PUB PUR to be 1-200% elongation [86]

as detailed in [88]. The range seen in this work was between 1168 - 1488% strain before failure. As mentioned above failure at the grips was observed in many cases. This represents a remarkable increase in a fundamental material property relative to literature observations. This may be attributable to the processing route involving high quantities of solvent, as it appears not to be dependent on variations of the material formulations.

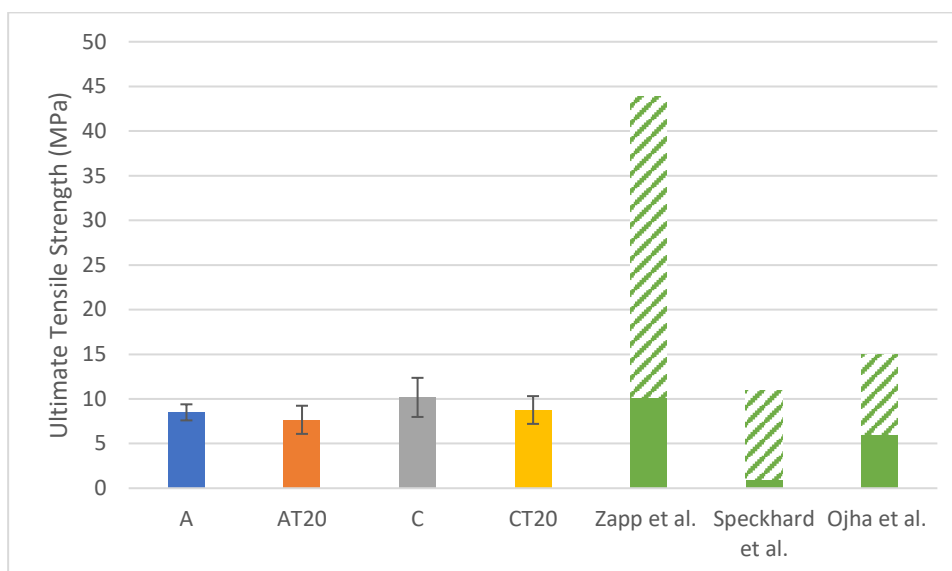


Figure 5.53 Bar chart comparing the average ultimate tensile stress (MPa) found during the course of this work, with standard deviations being indicated using error bars. Ultimate tensile strength of non-reinforced PIB-PUR materials from literature with minimum stress reported in solid green with maximum values represented with cross hatched green, Zapp et al. [89] as detailed in [75], Speckhard et al. [86] as detailed in [88], Ojha et al. [88]

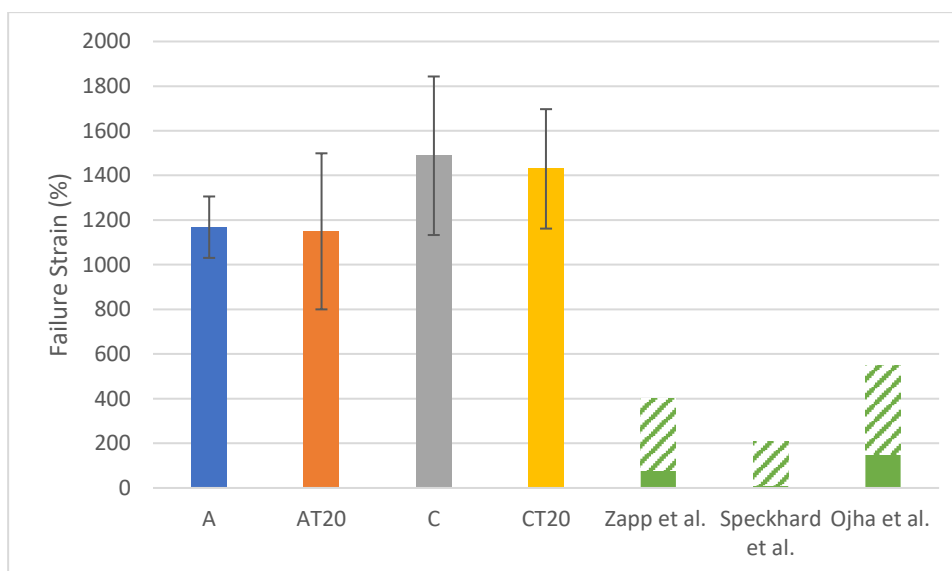


Figure 5.54 Bar chart comparing the failure strain (%) found during the course of this work, with standard deviations being indicated using error bars. Failure strain of non-reinforced PIB-PUR materials from literature with minimum stress reported in solid green with maximum values represented with cross hatched green Zapp et al. [89] as detailed in [75], Speckhard et al. [86] as detailed in [88], Ojha et al. [88]

Table 5.3 Mechanical properties of PIB-PUR formulation which arose during the course of this work and mechanical properties from PIB-PUR materials from literature

<u>Mechanical Properties</u>		
<u>Material/Study</u>	<u>Ultimate Tensile Stress</u> <u>MPa</u>	<u>Failure Strain (%)</u>
A (n=9)	8.5*	1168*
AT20 (n=26)	7.66*	1148*
C (n=12)	10.17*	1488*
CT20 (n=18)	8.76*	1428*
Zapp <i>et al.</i> [89] as detailed in [75].	10.2 – 33.7	80 - 320
Speckhard <i>et al.</i> [86] as detailed in [88].	1 – 10	10 – 200
Ojha <i>et al.</i> [88].	6 – 9	150 - 400
Ojha <i>et al.</i> [with PTMO] [88].	20	700
Kang <i>et al.</i> [with PTMO] [93]	24.6 – 27.2	740 - 770

*These values include cases where the sample failed at the grips. These values therefore represent minimum threshold average values for both ultimate tensile strain and failure strain.

5.5.2 Mullins Effect

It can be seen from the stress/strain cycle plots that the Mullins effect was present in these PIB-PUR samples. This can be concluded due to the reduction in stress response as the material is strained repeatedly as evident in Figure 5.55. No previous literature describing the Mullins effect in PIB-PUR elastomers was found.

Erdodi *et al.* [92] investigated hysteresis in PIB based polyurethanes. Their aim was to understand the effect of PIB molecular weight, hard segment content and the incorporation of PTMO on hysteresis. Their experiments involved subjecting tensile specimens to 300% strain for 10 cycles. It was found that the highest hysteresis was found during the first cycle. This high initial hysteresis was due to permanent deformation in the hard segment of the polymer. This was corroborated by the finding that polymers with higher proportions of hard segment

exhibited a higher degree of hysteresis. It was also determined that the incorporation of PTMO into the soft segment of the polymer had little effect on the total hysteresis.

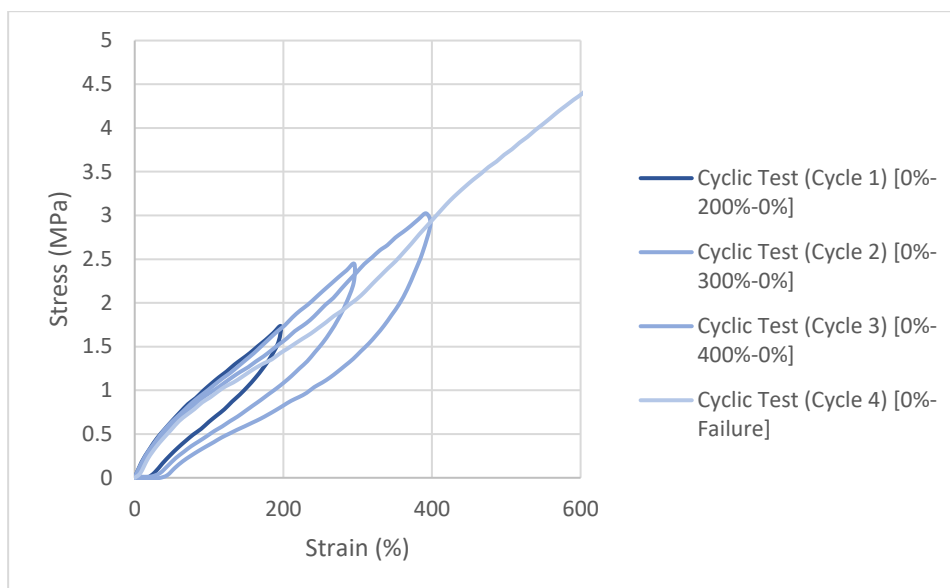


Figure 5.55 Demonstration of Mullins Effect in material formulation A

5.5.3 Degradation Properties

Across the literature PIB-PUR showed a low degree of degradation when placed in a variety of solutions when compared to controls. In this work this was corroborated by the lack of degradation seen at eight weeks of submersion in PBS at 37°C. It can therefore be concluded that the four versions of this material are mechanically stable in PBS at 37 °C for a period of at least 8 weeks. This work adds to the information found by Chang *et al.* who saw that there was little degradation evident when submerged in water at 85°C for 4 days and when samples were dry aged in air for 48 hours at 128°C [77].

5.5.4 Conclusion

The PIB-PUR materials created in this project have shown interesting and repeatable mechanical properties, which indicate the robust nature of the process developed in the course of this study. The four material variants will now be brought forward for further characterisation with respect to water vapour transmission and moisture absorption.

Chapter 6. Permeability and Absorption Characterisation

6.1 Introduction

Permeability and absorption characterisation are very important stages in the evaluation of a new material intended for the coating of implantable electronic devices. As previously stated, moisture contamination is a key failure mechanism for electronics and can be detrimental to the life of an implanted medical device and therefore to patient safety and health. A thorough understanding of the moisture permeability is imperative to forming recommendations on any coating which would form a protective layer for a medical device *in vivo*. In this work two forms of characterisation were conducted, water vapour transmission rate and moisture absorption testing.

6.2 Water Vapour Transmission Rate

Water vapour transmission is an important functional property for the considered application, as it is a fundamental property required to determine PIB-PUR's feasibility as a barrier material for protection against moisture ingress. Therefore, quantification of water vapour permeation is imperative. Water vapour transmission rate experiments measure the permeability of films, coatings, or membranes to water vapour.

When examining the literature for data on comparator materials it was noted that there are inconsistencies in the meanings of various terminologies in relation to permeation and water vapour transmission rate testing. For the purposes of this work the units used are $\left(\frac{g.cm}{m^2.day}\right)$ for 1 ATM partial pressure. Both water vapour transmission rate $\left(\frac{mg}{m^2.day}\right)$ and permeation values $\left(\frac{mg.mil}{m^2.day}\right)$ were obtained for each experiment. These permeation values were then converted to $\frac{g.cm}{m^2.day}$ for 1 ATM partial pressure. Due to a variation in thickness between samples, permeation values were used for the basis of comparison between formulations.

6.2.1 Initial Water Vapour Transmission Rate Testing

Preliminary WVTR testing was conducted early in the PIB-PUR process development. The purpose of these tests was to provide an initial indication of the potential of the overall approach for achieving low water vapour transmission rates. Five samples from BT20 were tested by RDM Test Equipment in Hertfordshire UK. Tests were carried out at 37.8/37.9°C with relative humidity in the wet chamber set at 100% and with ambient temperature at 23°C. Samples were of 6.25 cm² area and 2 mm thickness. However, the samples were required to be

masked, reducing the testing area to 1cm². The permeation ranged from 0.011 to 0.103 g.cm/(m².day).

Notwithstanding the relatively large variation in permeation results for these samples, which could be attributed to the underdeveloped nature of the process at the time, some samples showed promising water vapour transmission rate properties. This contributed to the decision to focus on refining the process prior to final characterisation of the water vapour transmission rate.

6.2.2 Water Vapour Transmission Rate Analysis

Once the final process had been developed, five samples each of formulation A, AT20, C, and CT20 were sent to RDM Test Equipment for WVTR testing. Results were found as per Figure 6.1 and Figure 6.2. ANOVA analysis was performed to determine if there were any significant differences (95% confidence interval) between permeation values for these formulations. It was found that there was in fact no difference between formulations made from diols of different molecular weights, A versus C, or AT20 versus CT20. However, there were significant differences found between formulations A and AT20. It was established via the F test and displayed graphically in Figure 6.2 that higher permeation rates were found in AT20 samples.

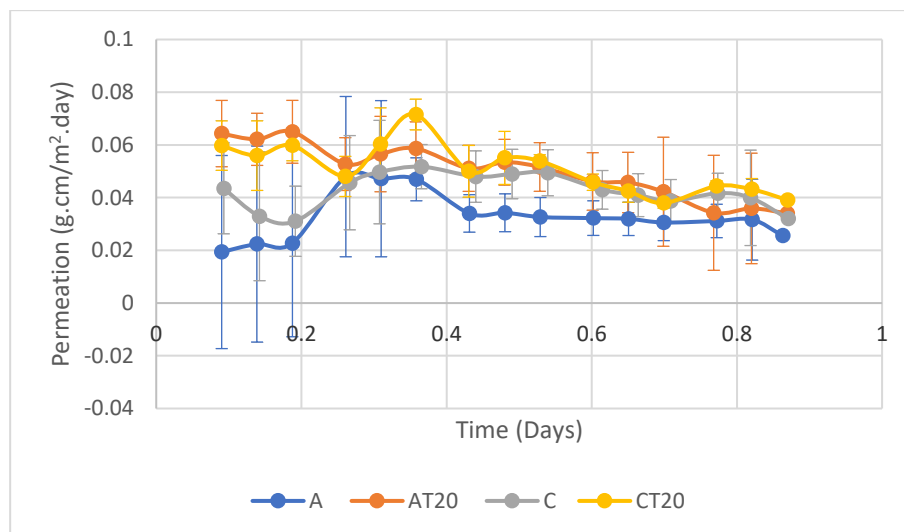


Figure 6.1 Comparison of the average permeation results for the four different material types n=5 with standard deviation denoted by error bars

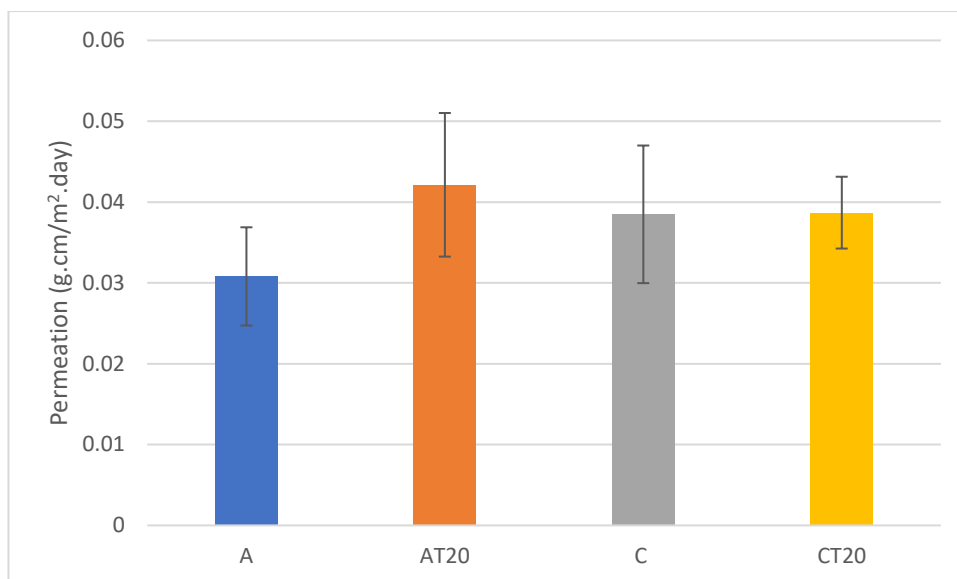


Figure 6.2 Average results for permeation testing with standard deviation (error bars) for formulation A, AT20, C, CT20 (n=5). Time points (A 20.65 hrs, AT20 20.05 hrs, C 21.35 hrs, CT20 20.87 hrs)

6.3 Moisture Absorption

Two types of moisture absorption studies were undertaken to examine how PIB-PUR formulations behave when submerged in either phosphate buffered saline solution or distilled water.

Specimens were placed in a vacuum for 24 hours and then weighed. These samples were subsequently submerged in either PBS solution or distilled water. After a given period of time samples were removed from solution, blot dried with filter paper, weighed and then replaced in the relevant solution. The difference in weight was found and expressed as a percentage of the original dry weight. This was found to have increased over time, as expected for both solutions.

6.3.1 Phosphate Buffered Saline Solution Absorption

Figure 6.3 shows moisture absorption by weight (W_t) over the first 4 hours of immersion based on 25 mm diameter samples. ANOVA analysis was conducted for values obtained at 24 hours and at 70 days. This compared moisture absorption between the four different sample types.

For samples submerged in PBS there were statistical differences seen with a 95% confidence between formulations A and C at both the 4 hour (Figure 6.3 and Figure 6.5) and 70 day time points (Figure 6.4 and Figure 6.6) and also between the formulations C and CT20 at the 70 day mark.

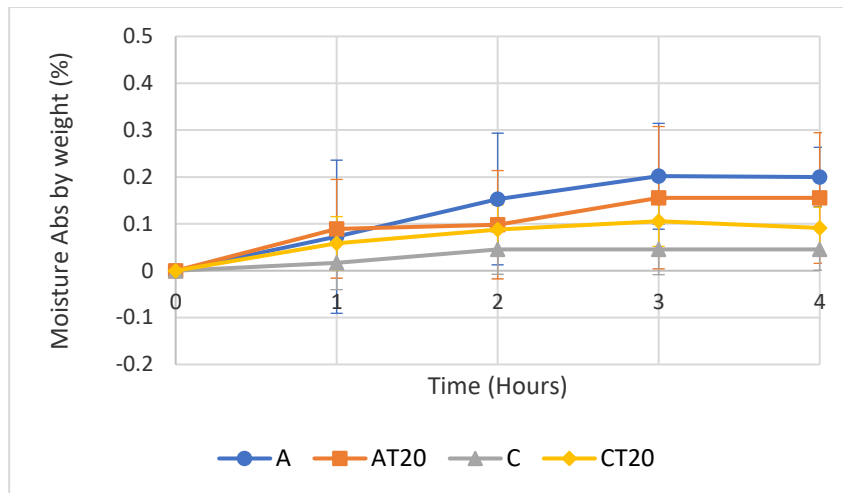


Figure 6.3 Moisture absorption data for phosphate buffered saline solution absorption for the first 4 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

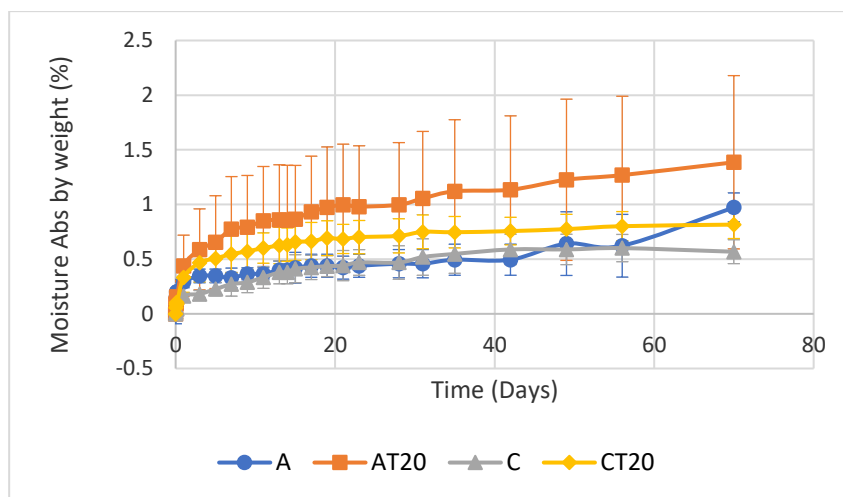


Figure 6.4 Moisture absorption data for phosphate buffered saline solution absorption for 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

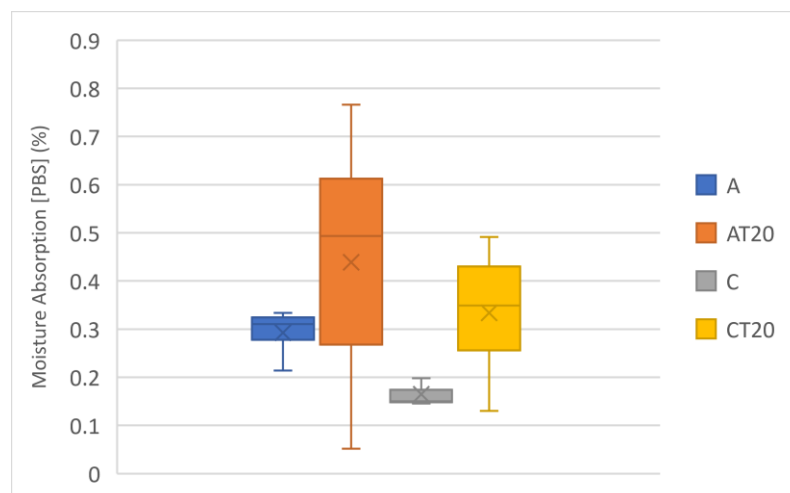


Figure 6.5 Box plot indicating average moisture absorption of samples submerged in PBS after 24 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

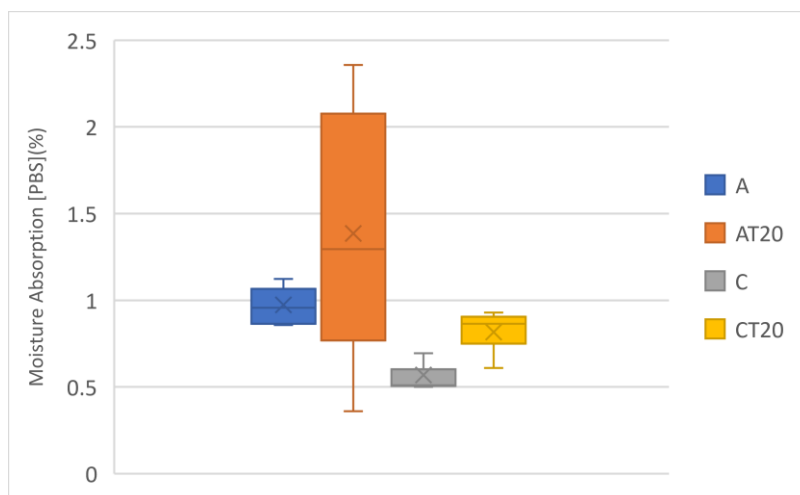


Figure 6.6 Box plot indicating average moisture absorption of samples submerged in PBS after 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

6.3.2 Distilled Water Absorption

Figure 6.7 shows moisture absorption by weight (W_t) over the first 4 hours of immersion based on 25mm diameter samples. Figure 6.8 shows moisture absorption by weight (W_t) over the first 70 days of immersion based on 25 mm diameter samples. ANOVA analysis was conducted for values obtained at 4 hours and at 70 days. This compared moisture absorption between the four different sample types in distilled water. For samples submerged in distilled water statistical differences were seen between the formulations of A versus AT20 and C versus CT20 after 4 hours as depicted in Figure 6.7 and Figure 6.9. There were no statistical differences seen after 70 days in Figure 6.8 and Figure 6.10.

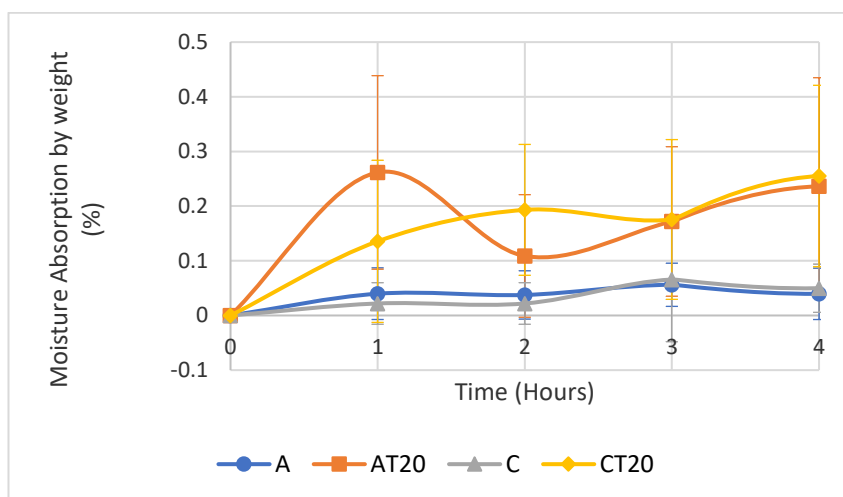


Figure 6.7 Moisture absorption data for distilled water absorption for the first 4 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

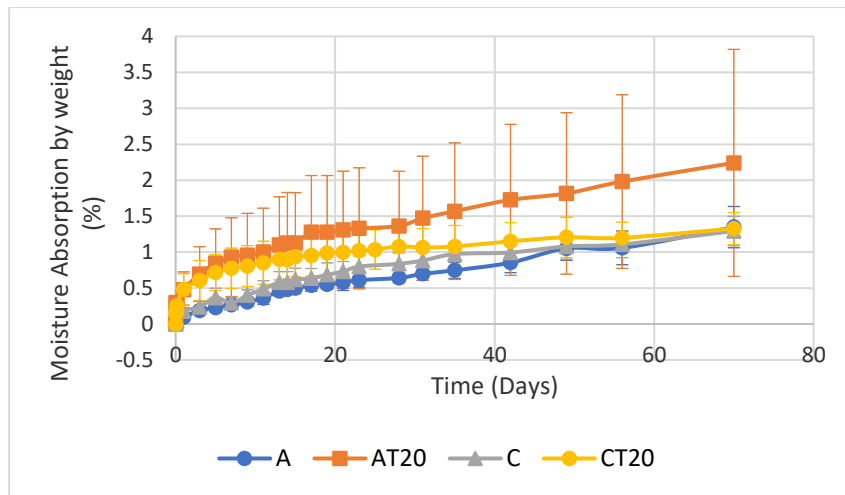


Figure 6.8 Moisture absorption data for distilled water absorption for 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

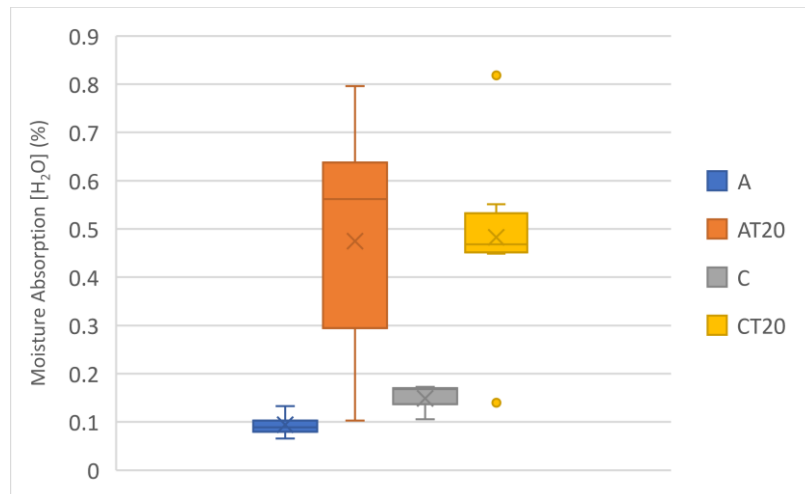


Figure 6.9 Box plot indicating average moisture absorption of samples submerged in distilled water after 24 hours. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

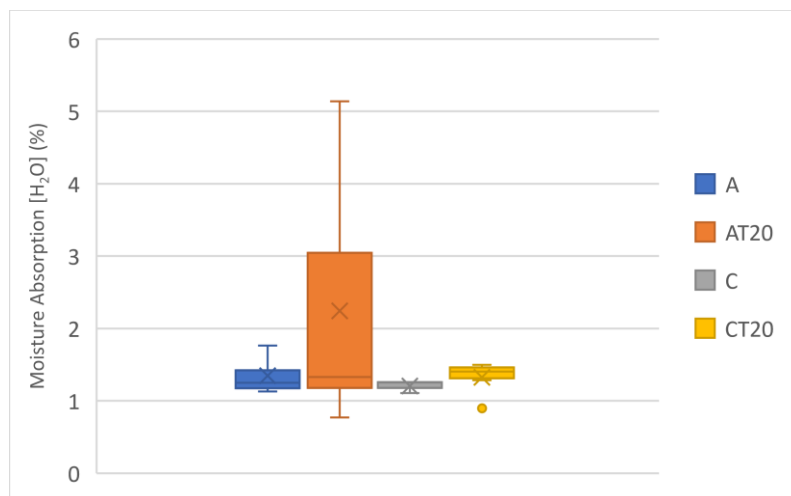


Figure 6.10 Box plot indicating average moisture absorption of samples submerged in distilled water after 70 days. A (n=4) AT20 (n=7) C (n=3) CT20 (n=6)

6.4 Discussion

6.4.1 Water Vapour Transmission

For the formulations examined in this thesis the average permeability was seen to be 0.03 – 0.04 g.cm/m²day. When looking at the water vapour transmission rate for other potential near hermetic barriers in Table 6.1 and Figure 6.11 it was seen that the permeability for these formulations of PIB-PUR were marginally larger than those seen for SIBS and significantly larger than those reported for Parylene C and LCP.

Table 6.1 Water permeability results from this study with data from comparable materials, Polyimide [64], SIBS [64], Parylene C [6] and LCP [57]

<u>Material</u>	<u>Permeability to Water Vapour</u>
A	0.03 g.cm/m ² day
AT20	0.04 g.cm/m ² day
C	0.038 g.cm/m ² day
CT20	0.039 g.cm/m ² day
Parylene	0.08 g.mm/m ² day [6] (0.008 g.cm/m ² day)
Polyimide	0.56 g.mm/m ² .day [64] (0.056 g.cm/m ² day)
LCP	0.1177 g/m ² day for 0.0508 mm thickness [57] (5.98 x10 ⁻⁴ g.cm/m ² day) 0.0678 g/m ² day for 0.1016 mm thickness [57] (6.89x10 ⁻⁴ g.cm/m ² day)
SIBS	0.241 g.mm/m ² day [64] (0.0241 g.cm/m ² day)

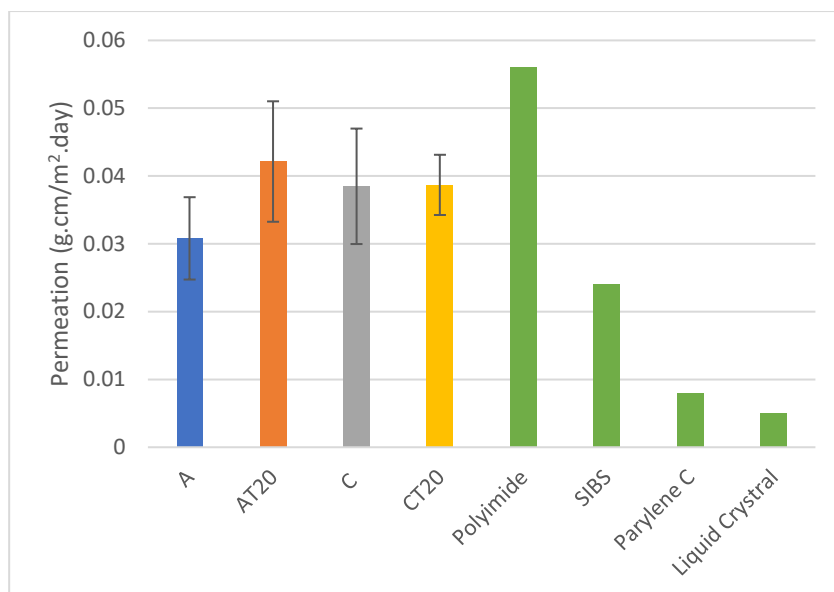


Figure 6.11 Water permeability results from this study with data from comparable materials, Polyimide [64], SIBS [64], Parylene C [6] and LCP [57]

Permeability to water vapour for PIB PUR was found to be between 0.03 and 0.04 g.cm/m².day. Permeability to water vapour reported for SIBS, parylene C and liquid crystal polymer was found to be lower. The permeation value of PIB-PUR was found to be a degree higher than parylene C and liquid crystal polymer in particular. On permeability alone PIB-PUR does not confer any advantages to materials currently considered near hermetic. However, this must be considered in context with other material properties with regards to any desired application.

6.4.2 Moisture Absorption

The literature showed that compared to other PIB-PUR materials for which data was available there was a relatively high degree of water absorption, as can be seen in Table 6.2. Figure 6.12 and Figure 6.13 give a graphical representation of the range of PIB-PUR moisture absorption properties obtained from literature compared to those found in this study. In the course of this work an average moisture absorption for each material under investigation was found for 70 days in 37°C in both water and PBS. In this work it was seen that at 70 days at 37°C in H₂O a moisture absorption range of 1.29% - 2.24% was observed. When PIB-PUR was submerged in PBS at 37°C, a range of 0.57% - 1.39% was seen at 70 days. This difference is possibly due to the longer time that the polymer was submerged in the present study. Water vapour transmission data was not found for the PIB-PUR materials described in the work by Chang *et al.* and Kang *et al.*

Table 6.2 Table indicating the moisture absorption properties from this work and those found in literature

Moisture Absorption Properties		
Author of Paper	Moisture Absorption (%)	Test Conditions
<i>A [H₂O/PBS]</i>	1.34/0.97	37°C for 70 days
<i>AT20 [H₂O/PBS]</i>	2.24/1.39	37°C for 70 days
<i>C [H₂O/PBS]</i>	1.29/0.57	37°C for 70 days
<i>CT20 [H₂O/PBS]</i>	1.33/0.82	37°C for 70 days
<i>Chang et al. [77].</i>	0.01-0.016%	75 ± 1°C for 48 hours, distilled water
<i>Kang et al. [93].</i>	0.07 ± 0.2%	85°C for 3 days in PBS solution

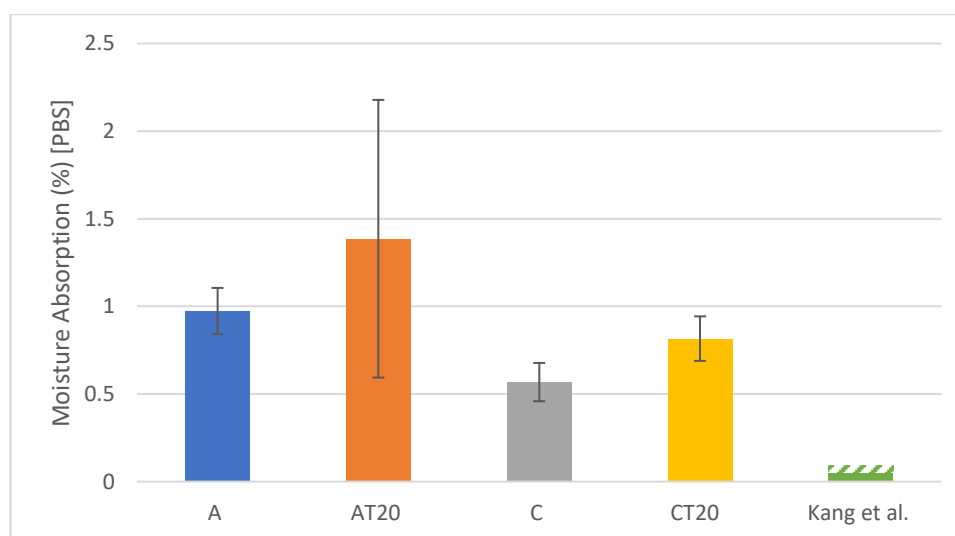


Figure 6.12 Average moisture absorption for formulations denoted by solid block colour, with standard deviations seen shown via error bars. Value from Kang et al. [93] shown in green, lowest value shown in solid colour with maximum values shown in cross hatch green whose test conditions was 85°C for 3 days in PBS solution

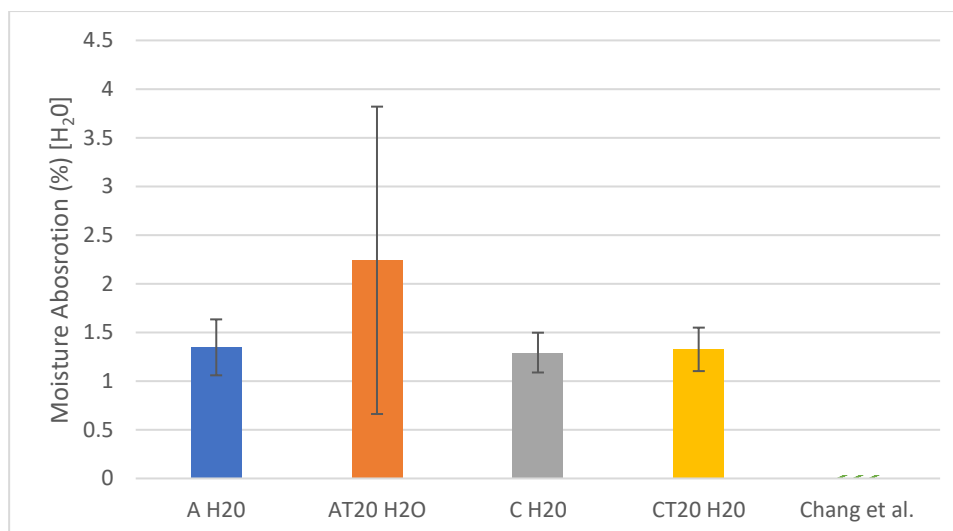


Figure 6.13 Range of moisture absorption seen in H₂O comparing to that seen in literature Chang et al. [77]. Solid colour denoting minimum moisture absorption seen, crosshatch denoting highest moisture absorption value seen whose test conditions was 75 ± 1°C for 48 hours, distilled water

When looking at comparative materials' moisture absorption in order to contextualise the values obtained in the course of this research, it was seen that, in the majority of studies, moisture absorbance was evaluated using H₂O.

It was seen that the moisture absorption for these formulations of PIB-PUR were a degree larger than those seen for SIBS, Parylene C and LCP which is described in Table 6.3 and Figure 6.14.

Table 6.3 Moisture absorption properties found during the course of this work and for other potential barriers for near hermetic barriers

<u>Material</u>	<u>Moisture Absorption</u>
A	1.02% 37°C for 70 days H ₂ O
AT20	2.24% 37°C for 70 days H ₂ O
C	0.79% 37°C for 70 days H ₂ O
CT20	1.32% 37°C for 70 days H ₂ O
Parylene	0.06% 24 hr [36], [62]
Polyimide	0.7998-3.5327 [109] 1.4% [36], [63] at 23°C for 24 hr in water
LCP	<0.04% [55], [57]

	0.03% 23°C 50% RH [type MT1300] [36], [65] 0.04% 23°C 50% RH [MT1310] [66]
SIBS	<0.01% [2 weeks] [64] 1.15% [7 months] [64]
PDMS	<1% [36], [70]

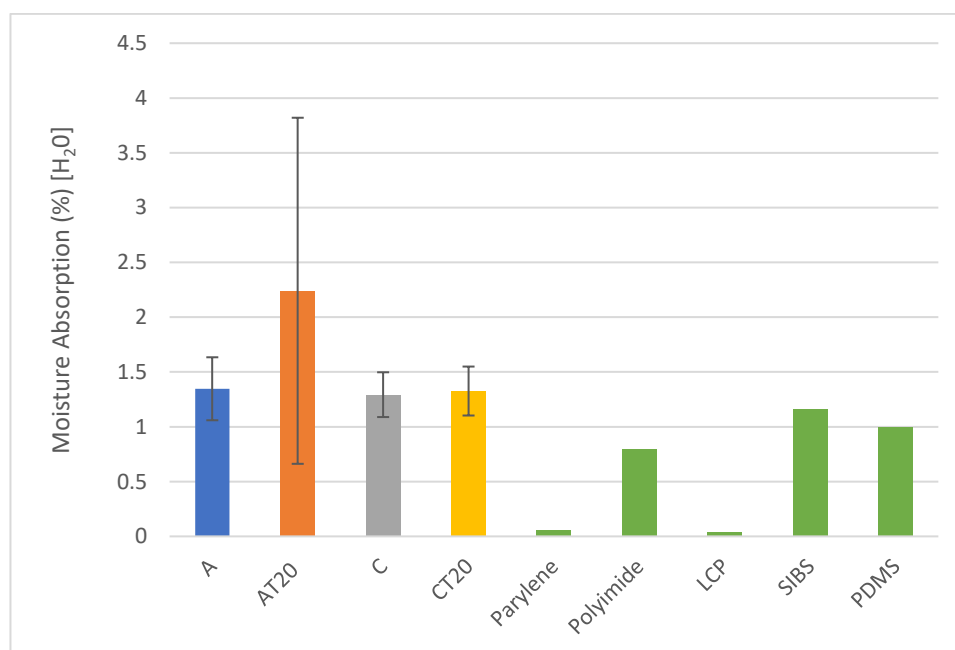


Figure 6.14 Average moisture absorption for formulations denoted by solid block colour, with standard deviations seen shown via error bars. Formulations studied in this work in comparison to the material properties found in literature for other potential barriers for near hermetic barriers. Parylene [36], [62], Polyimide [109], LCP [55], [57], SIBS [64], PDMS [36], [70]

6.4.3 Conclusion

The PIB-PUR materials studied in the course of this project have again showed repeatable permeability and absorption properties, which again point to the repeatable nature of the process developed. It is evident that both the permeability and absorption characteristics for these PIB-PUR materials are not as hermetic with respect to water vapour or moisture as the comparative materials described in literature. Nonetheless due to their very different mechanical properties and the still promising degree of permeability demonstrated, the materials may find applications in relation to more flexible substrates or devices.

Chapter 7. Conclusions and Recommendations

7.1 Conclusions

The objective of this study was to achieve high quality void free PIB-PUR materials with a high degree of impermeability for potential implant applications. Due to the highly viscous nature of the PIB diol, there was a high degree of difficulty in processing the material without entrapping gas. A solution was found by decreasing the viscosity using relatively high proportions of solvents. A detailed processing method was developed to produce void free PIB-PUR samples using the highly viscous PIB diol.

The following conclusions can be made based on the studies conducted in this thesis.

- Consistent tensile mechanical properties were obtained for samples produced according to the developed method. These properties were insensitive to batch variation and the inclusion of a crosslinker. This suggests a robust processing method that produces materials with predictable properties.
- The PIB-PUR materials exhibited a high degree of extensibility with considerably higher failure strains than those quoted in the literature for other PIB-PUR formulations. Ultimate tensile strains were within the range of other studies on PIB-PUR materials.
- The Mullins effect was observed in all of the PIB-PUR materials tested. This appears to be the first demonstration of this property in PIB-PUR elastomers. Softening and recovery hysteresis were also evident and have been characterised in detail. Comparisons between the four formulations were conducted and were found to be largely similar with some specific exceptions.
- There was no degradation evident after 8 weeks when placed in phosphate buffered saline solution at 37°C. This aligns with the hydrolytic stability of PIB based polyurethanes described in the literature.
- The permeation rate of water vapour with respect to PIB-PUR was lower than values available for polyurethane and polyimide but higher than values for SIBS, Parylene C and Liquid Crystal Polymer. These PIB-PUR samples also showed similar or higher moisture absorption properties to those materials previously mentioned.

Parylene is the gold standard for near hermeticity. It is quite fragile and is prone to delamination should a scrape or imperfection in the coating occur. This disadvantage is a reason a more robust coating could be considered, despite not meeting the same hermeticity standards. An alternative could be a multilayer encapsulation featuring a primary layer of parylene C, protected by an outer conformal coating of PIB-PUR. Liquid crystal polymer is a rigid plastic whose tight material structure inhibits the permeation of water molecules. However, it lacks the flexibility of PIB-PUR which may be important in some applications.

7.2 Recommendations

PIB-PUR exhibits potential for implant applications in which robust flexible coatings may be needed. On foot of this current study the following recommendations for future work can be made.

- It is recommended that immediate future studies would concentrate on refinement and improvement of the process with a single representative formulation. Efforts could focus on ways to limit the amount of solvent required and determine the effect on permeability and other properties. A further desirable outcome would be to shorten the overall processing time and to develop a processing method for the coating of substrates without introducing voids.
- If PIB-PUR is to be applied as a conformal coating, then it would be valuable to further evaluate its ability to adhere to various substrates. A more comprehensive lap shear study would provide more information about its adhesive properties.
- The examination of delamination would also be prudent. By conformally coating a printed circuit board and submerging the device in PBS it would be possible to determine if any evidence of delamination is present. This would also provide the opportunity to observe how long a PIB-PUR coated PCB would remain functional in a moist environment providing more insight into its potential for implantable electronic applications.
- One area of research omitted from this study is the examination of the insulative properties of the material. Going forward it would be recommended to conduct dielectric studies in order to understand how PIB-PUR might insulate a printed circuit board and protect from short circuiting.

- In addition to that, electro impedance spectroscopy would also be useful and allow for the examination of how the impedance of the material would change whilst being degraded. While this and other research showed little to no degradation it would be important to understand if the material's impedance can be expected to alter whilst implanted.

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(54) **THERMOSET
POLYISOBUTYLENE-POLYURETHANES
AND METHODS FOR MAKING**

(71) Applicant: **Cardiac Pacemakers, Inc.**, St. Paul,
MN (US)

(72) Inventors: **Joseph T. Delaney, JR.**, Minneapolis,
MN (US); **Michael J. Kane**, St. Paul,
MN (US); **Laura Cunningham**,
Drogheda (Co. Louth) (IE)

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ABSTRACT

A thermoset polyisobutylene network polymer includes a polyisobutylene diol residue, a diisocyanate residue, and at least one crosslinking compound residue selected from the group consisting of a residue of a sorbitan ester and a residue of a branched polypropylene oxide polyol.

Patent: Thermoset Polyisobutylene-Polyurethanes and Methods for making [103].

Appendix B. Tensile Analysis Data

B.1 Comparison of Samples from Formulations A and C

It was postulated that there is no significant difference in tensile properties between the samples made from Diol Batch A and their counterparts made with Diol Batch C. Samples were obtained by cutting dog bone samples from a sheet of PIB-PUR for the specific formulation being tested. For all samples cut from the same sheet the average was found. These averages were when used to conduct ANOVA analysis. An alpha value of 0.05 was used for each hypothesis. In Table B.1, for all hypotheses, the corresponding P values were larger than the alpha value 0.05. Therefore, the null hypotheses can be accepted with a 95% certainty. We can conclude that there is no significant difference between the batches.

Table B.1 P values for comparison of Diol Batch A and Diol Batch C resulting in the conclusion there is no difference between the batches (all the P values are above the alpha value of 0.05)

<u>Hypothesis</u>	<u>P- Value</u>
$\sigma_A 20\% = \sigma_C 20\%$	0.278252
$\sigma_A 800\% = \sigma_C 800\%$	0.125869
$\sigma_{A T20} 20\% = \sigma_{C T20} 20\%$	0.062925
$\sigma_{A T20} 800\% = \sigma_{C T20} 800\%$	0.11383

B.2 Comparison of Samples With and Without Crosslinking Agent (Tween 20)

It was postulated that there was no significant difference between the samples made with and without crosslinking agent Tween 20 it was found that all the corresponding P values were larger than the alpha value 0.05. Samples made with and without crosslinking agent were compared via ANOVA single factor analysis. Multiple dog bone samples were cut from sheets of the appropriate formulation. Average stress values for all of these samples from a common sheet were again found for strains at 20% and 800%. These values were then utilised in ANOVA analysis with an alpha value of 0.05.

Therefore, the null hypotheses can be accepted with a 95% certainty. Therefore, it can be concluded that there is no significant difference between the formulations.

Table B.2 P values comparing formulations with and without crosslinking agent demonstrating that there is no significant difference between the formulations (all P values are above the alpha value of 0.05)

<u>Hypothesis</u>	<u>P- Value</u>
$\sigma_A 20\% = \sigma_A T20 20\%$	0.138181
$\sigma_A 800\% = \sigma_A T20 800\%$	0.890379
$\sigma_C 20\% = \sigma_C T20 20\%$	0.122965
$\sigma_C 800\% = \sigma_C T20 800\%$	0.594065

B.3 Comparing Tensile Data for Formulations A and C

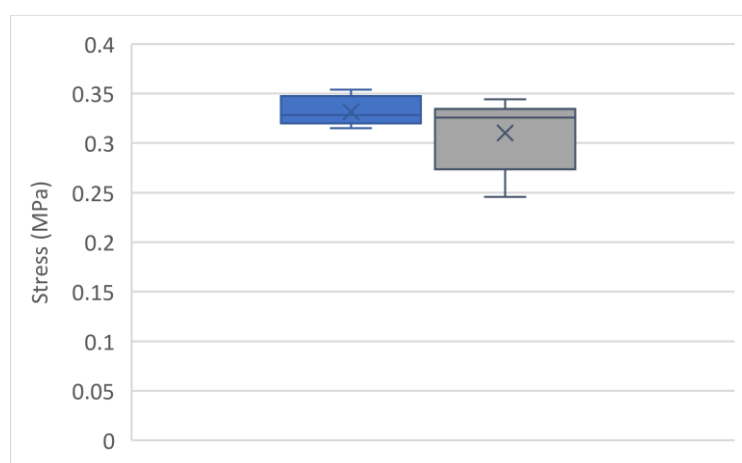


Figure B.1 Box Plot indicated the overlap in tensile values induced in by a 20% strain in samples made from Diol A (blue) (n=9) and Diol C (grey) (n=12) without crosslinking agent Tween 20

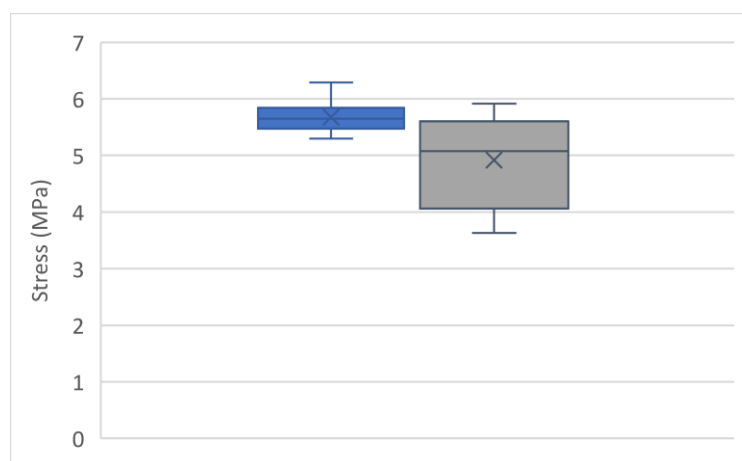


Figure B.2 Box Plot indicating the overlap in tensile values for induced by a strain of 800% strain in samples made from diol A (blue) (n=9) and C (grey) (n=12) without crosslinking agent Tween 20

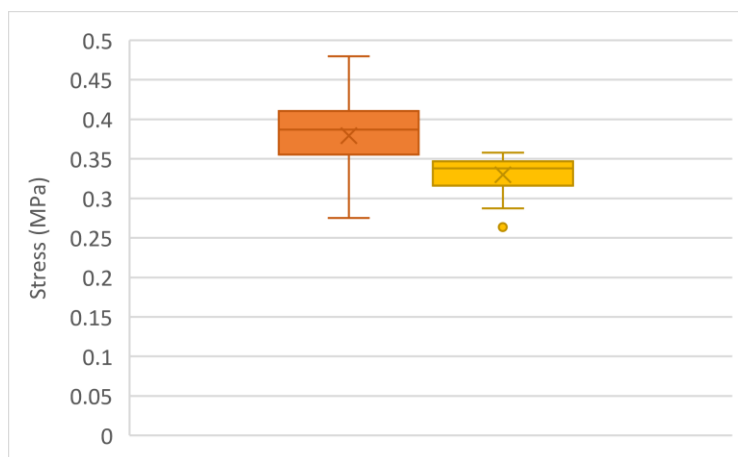


Figure B.3 Box Plot indicating the overlap of tensile values induced with 20% strain in samples made from diol batch A (orange) with crosslinking agent Tween 20 (n=26) and batch diol C (yellow) with crosslinking agent Tween 20 (n=18)

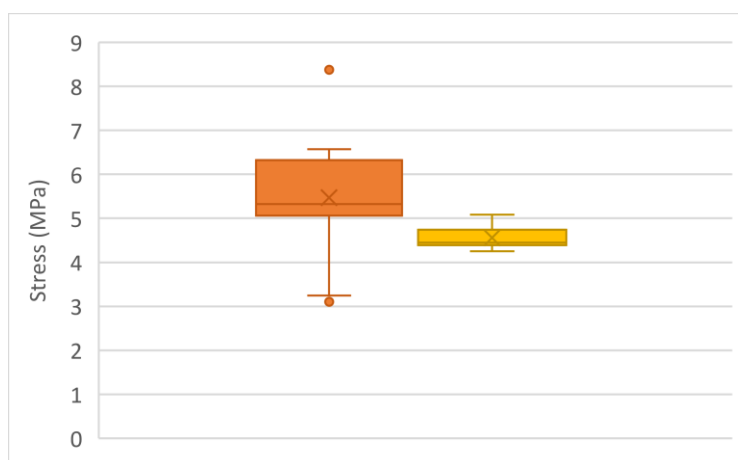


Figure B.4 Box Plot indicating the overlap of tensile values induced with 800% strain in samples made from diol batch A (orange) with crosslinking agent Tween 20 (n=26) and batch diol C (yellow) with crosslinking agent Tween 20 (n=18)

B.4 Comparing Tensile Data for Formulations Made With and Without Crosslinking Agent (Tween 20)

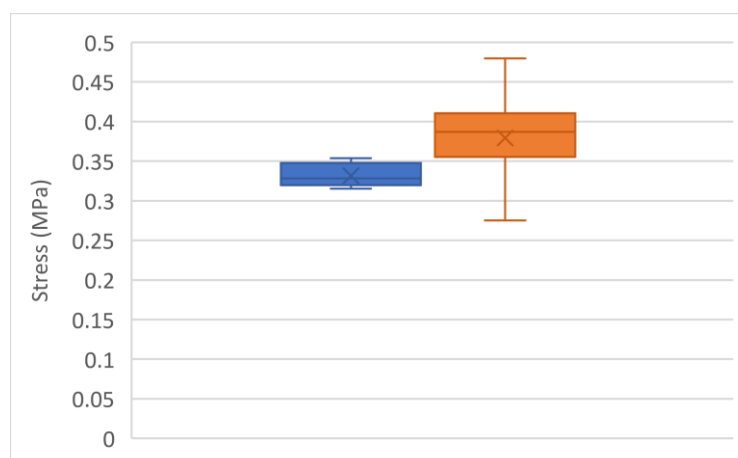


Figure B.5 Box Plot indicating the overlap in tensile values induced with 20% strain in samples made from diol batch A with (blue) (n=9) and without crosslinking agent Tween 20 (orange) (n=26)

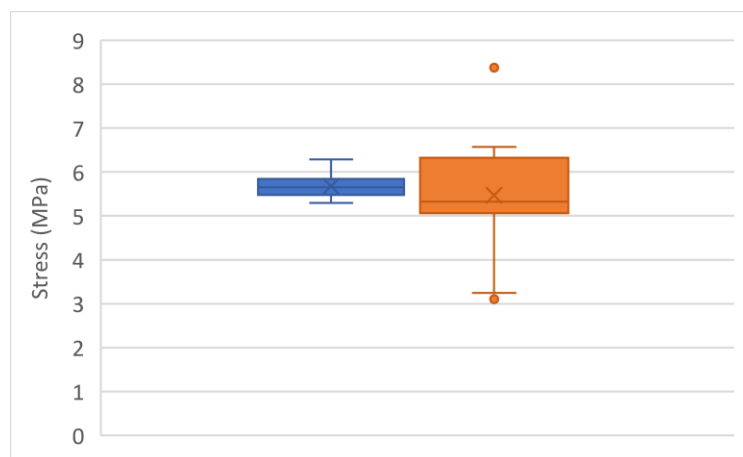


Figure B.6 Box Plot indicating the overlap in tensile values induced with 800% strain in samples made from diol batch A with (blue) (n=9) and without crosslinking agent Tween 20 (orange) (n=26)

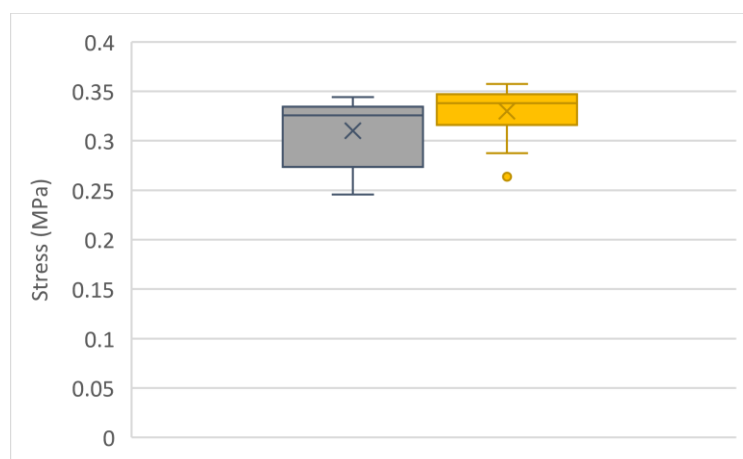


Figure B.7 Box Plot indicating the overlap in tensile values induced with 20% strain in samples made from diol batch C with (grey) (n=12) and without crosslinking agent Tween 20 (yellow) (n=18)

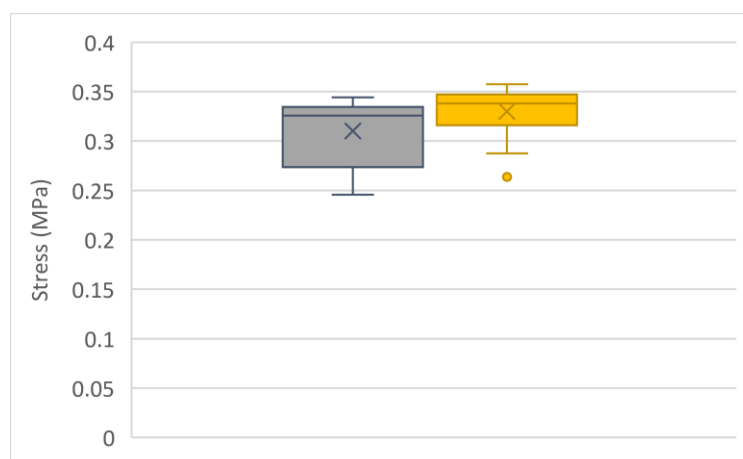


Figure B.8 Box Plot indicating the overlap in tensile values induced with 20% strain in samples made from diol batch C with (grey) (n=12) and without crosslinking agent Tween 20 (yellow) (n=18)

Appendix C. Cyclic Test Data

The following box plot Figures represent tensile stress for repeated loading cycles as illustrated in Figure 5.10.

C.1 Box Plots Comparing Cycles for Formulation A

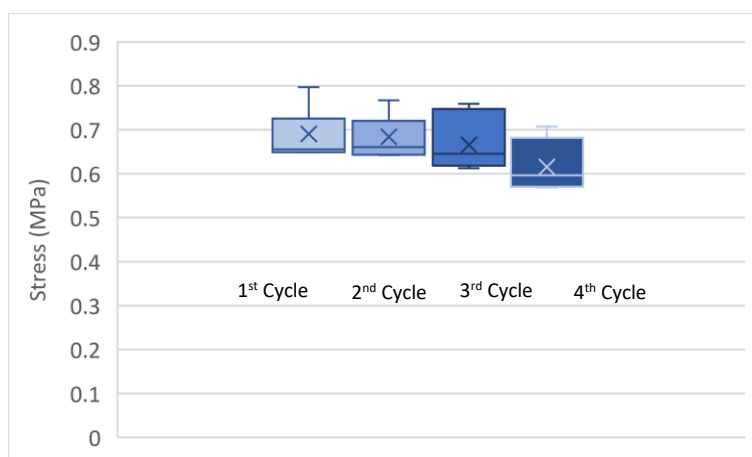


Figure C.1 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol A in the first, second, third and fourth cycles ($n=8$ for all cycles)

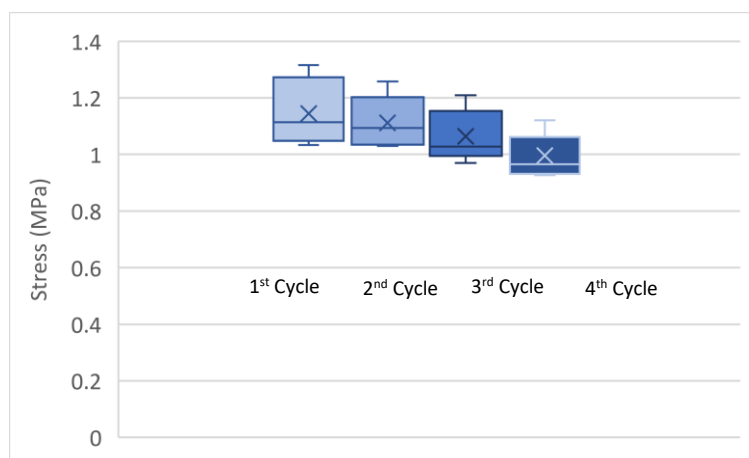


Figure C.2 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol A in the first, second, third and fourth cycles ($n=8$ for all cycles)

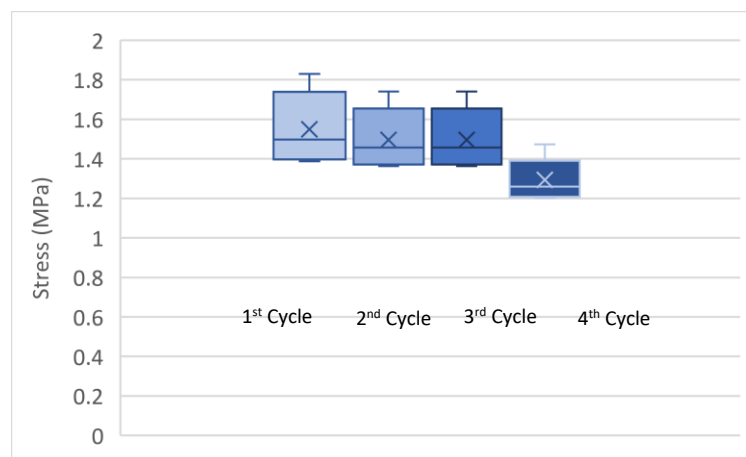


Figure C.3 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)

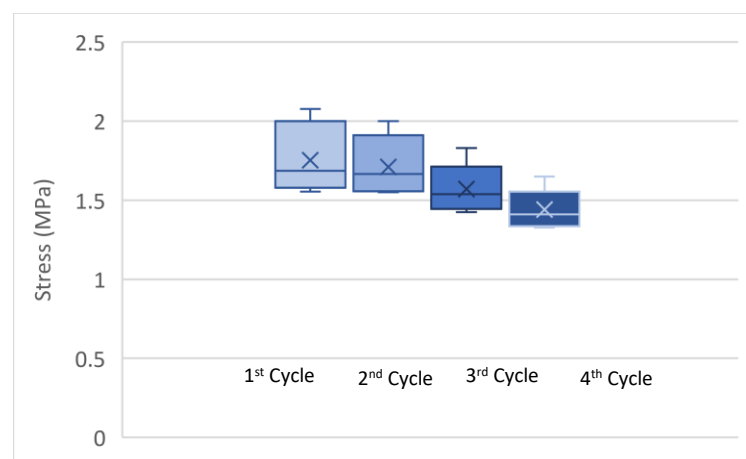


Figure C.4 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)

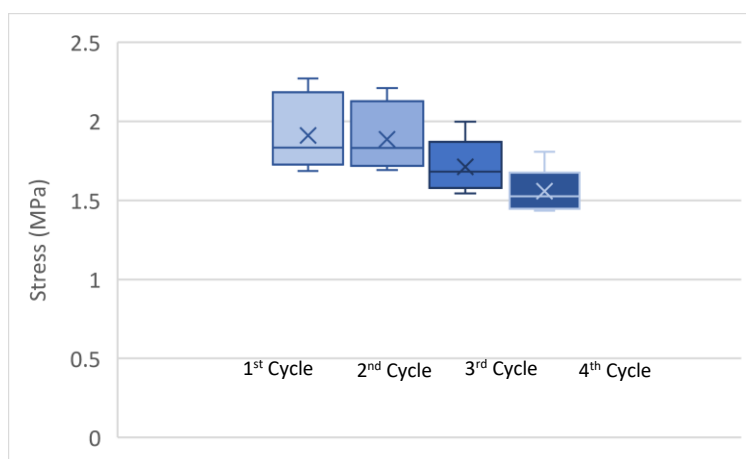


Figure C.5 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol A in the first, second, third and fourth cycles (n=8 for all cycles)

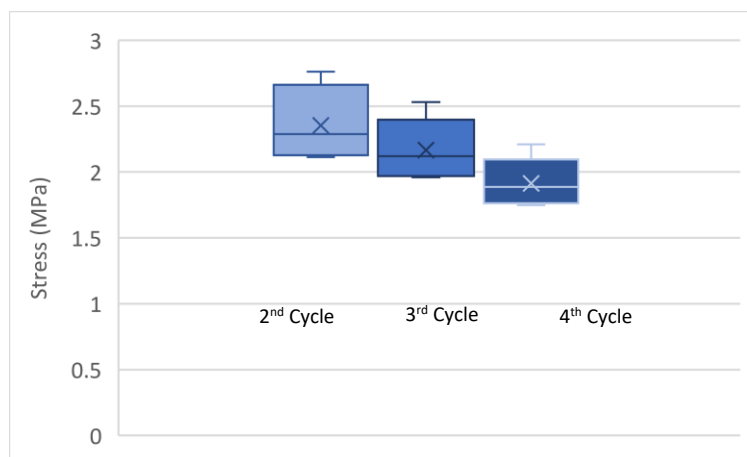


Figure C.6 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol A in the second, third and fourth cycles (n=8 for all cycles)

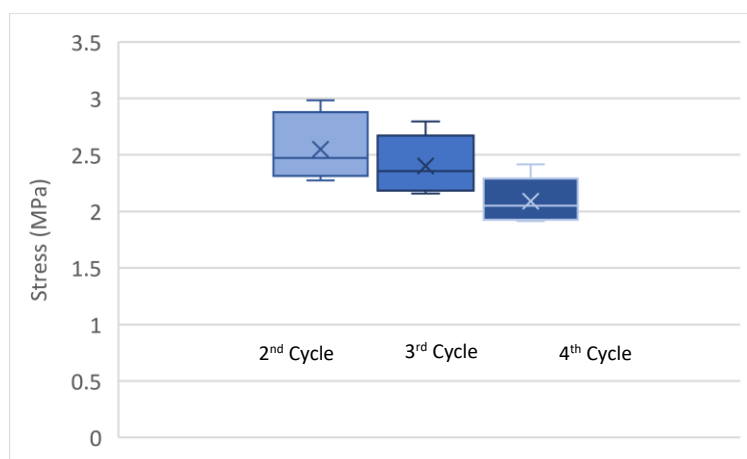


Figure C.7 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol A in the second, third and fourth cycles (n=8 for all cycles)

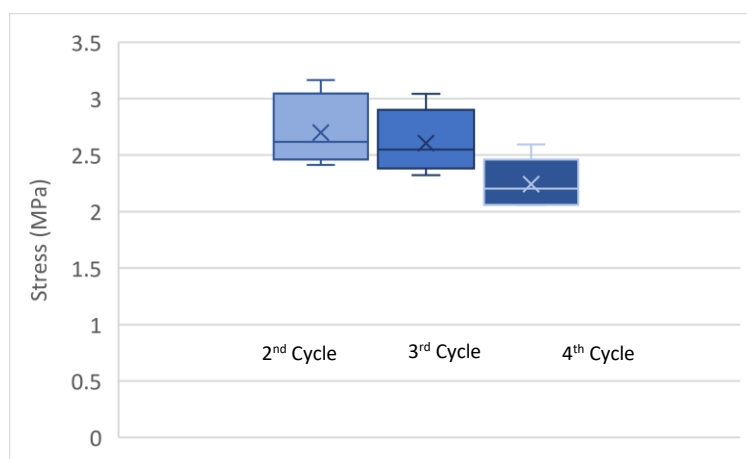


Figure C.8 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol A in the second, third and fourth cycles (n=8 for all cycles)

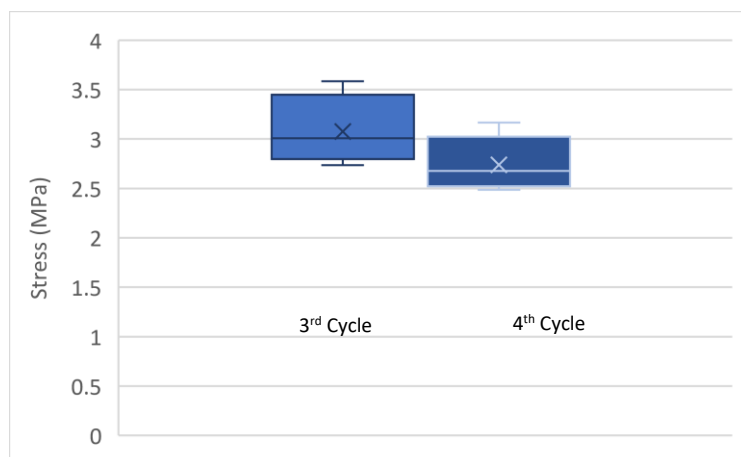


Figure C.9 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol A in the third and fourth cycles (n=8 for all cycles)

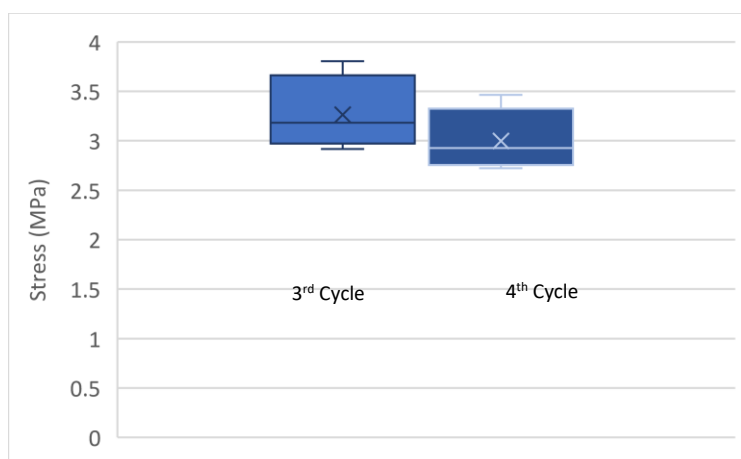


Figure C.10 Box Plot indicating the overlap in tensile values induced by a 375% in samples made from diol A in the third and fourth cycles (n=8 for all cycles)

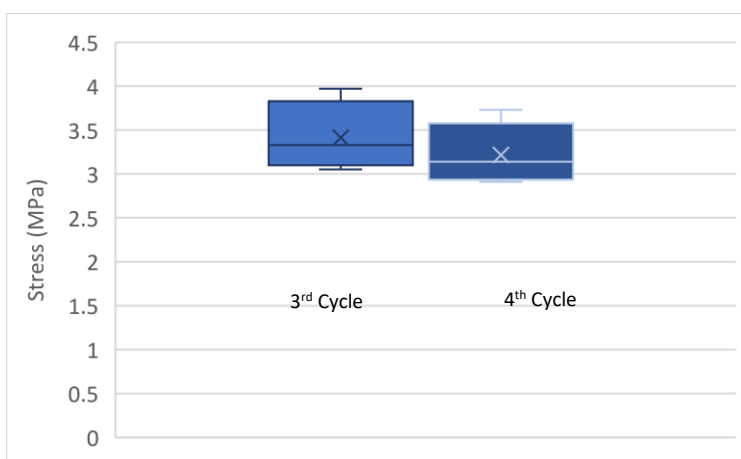


Figure C.11 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol A in the third and fourth cycles (n=8 for all cycles)

C.2 Box plots comparing cycles for formulation AT20

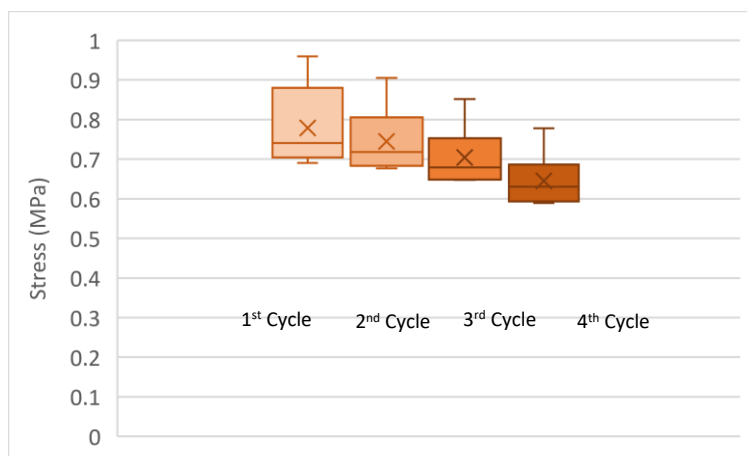


Figure C.12 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles ($n=9$ for all cycles)

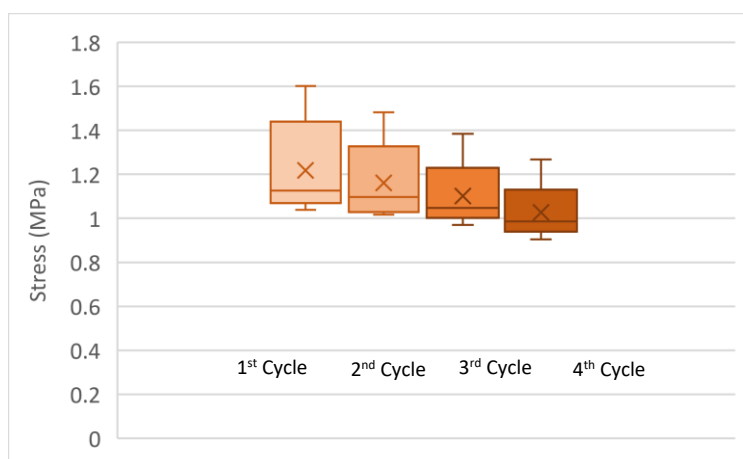


Figure C.13 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles ($n=9$ for all cycles)

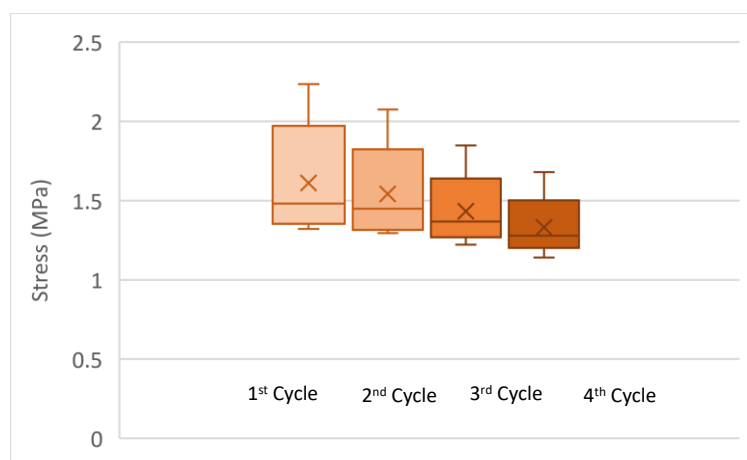


Figure C.14 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles ($n=9$ for all cycles)

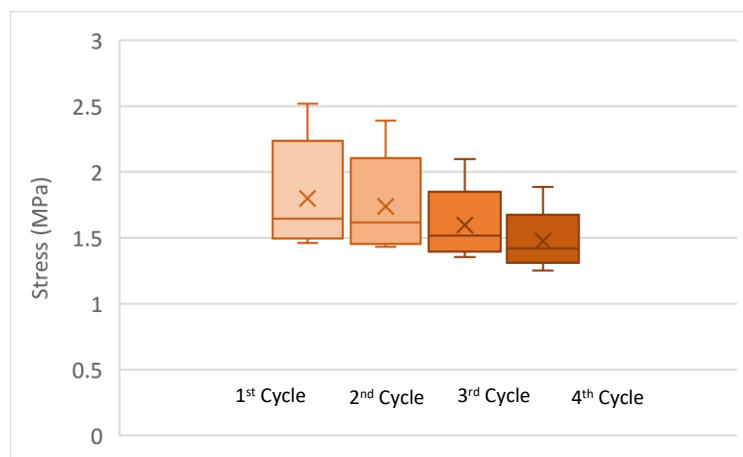


Figure C.15 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles (n=9 for all cycles)

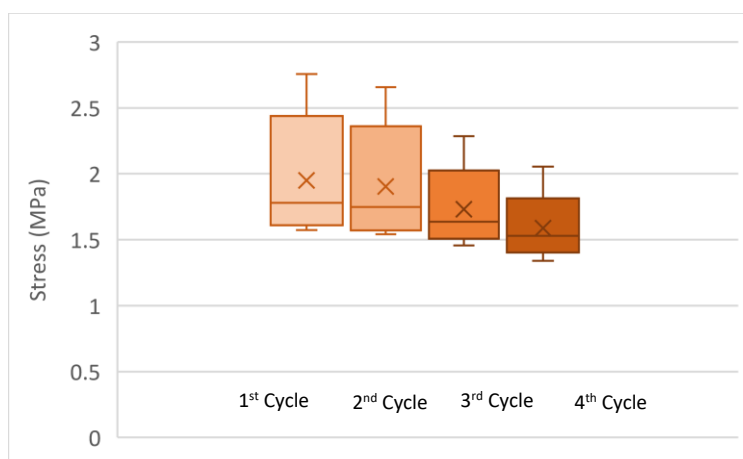


Figure C.16 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol A with crosslinking agent Tween 20 in the first, second, third and fourth cycles (n=9 for all cycles)

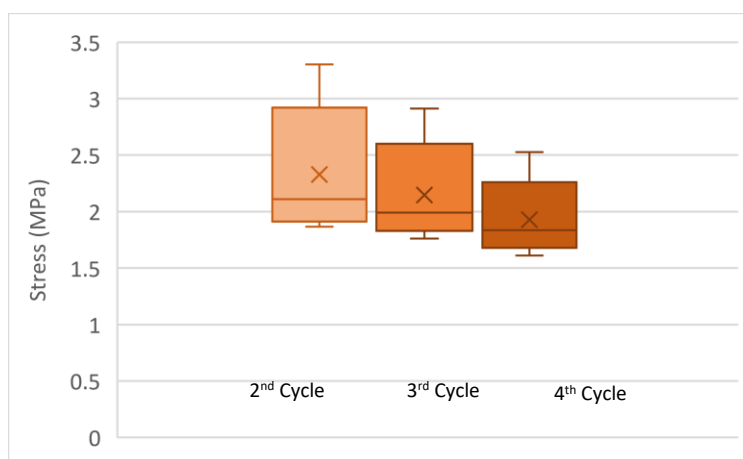


Figure C.17 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol A with crosslinking agent Tween 20 in the second, third and fourth cycles (n=9 for all cycles)

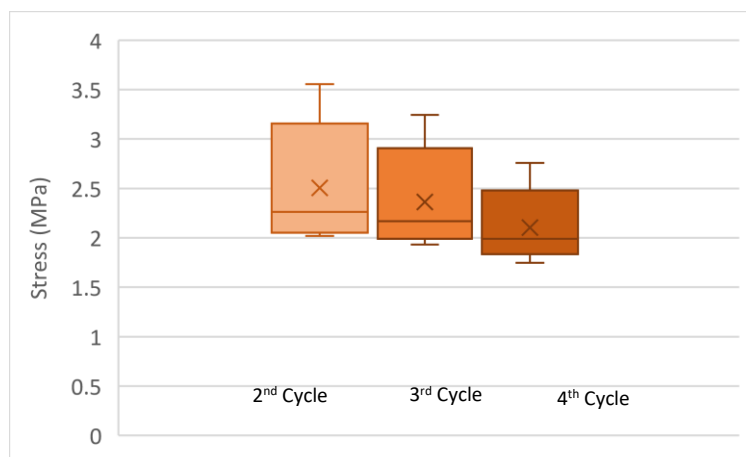


Figure C.18 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol A with crosslinking agent Tween 20 in the second, third and fourth cycles (n=9 for all cycles)

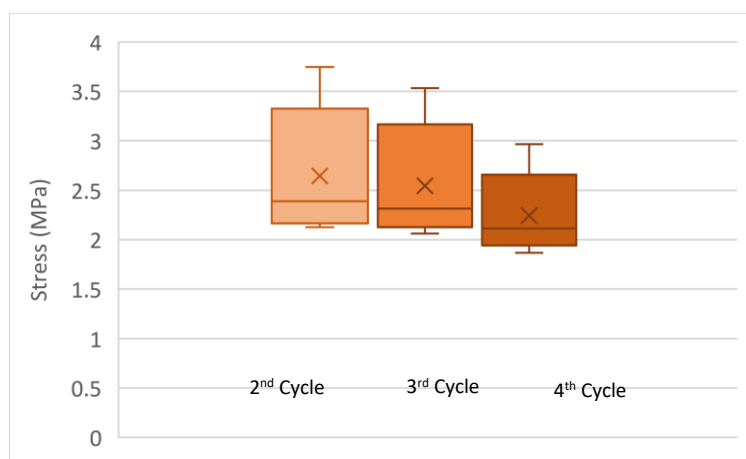


Figure C.19 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol A with crosslinking agent Tween 20 in the second, third and fourth cycles (n=9 for all cycles)

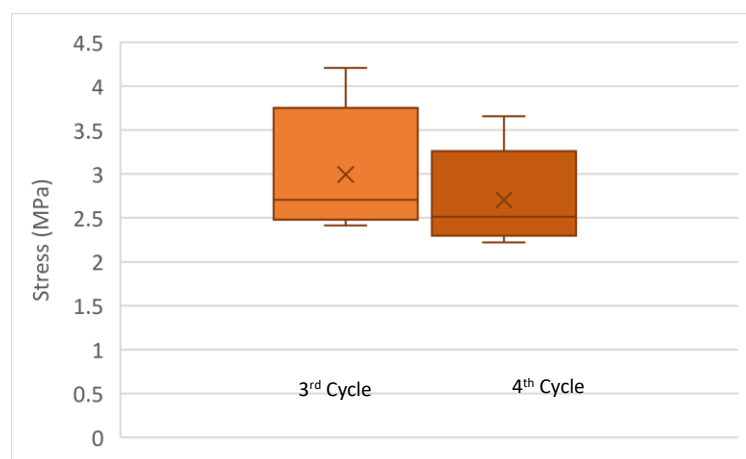


Figure C.20 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol A with crosslinking agent Tween 20 in the third and fourth cycles (n=9 for all cycles)

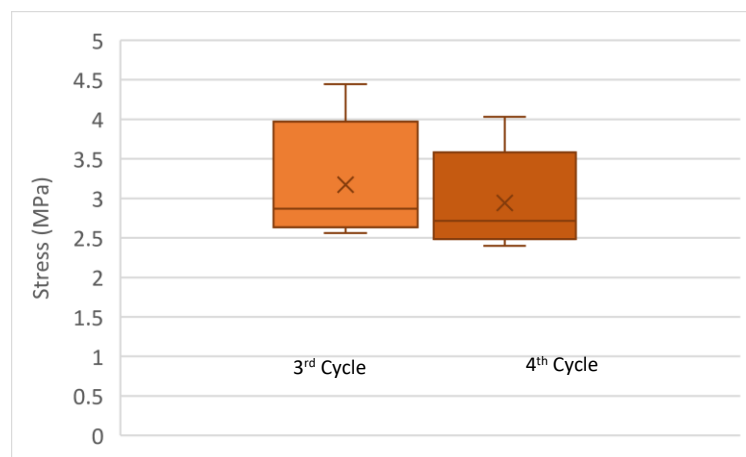


Figure C.21 Box Plot indicating the overlap in tensile values induced by a 375% strain in samples made from diol A with crosslinking agent Tween 20 in the third and fourth cycles ($n=9$ for all cycles)

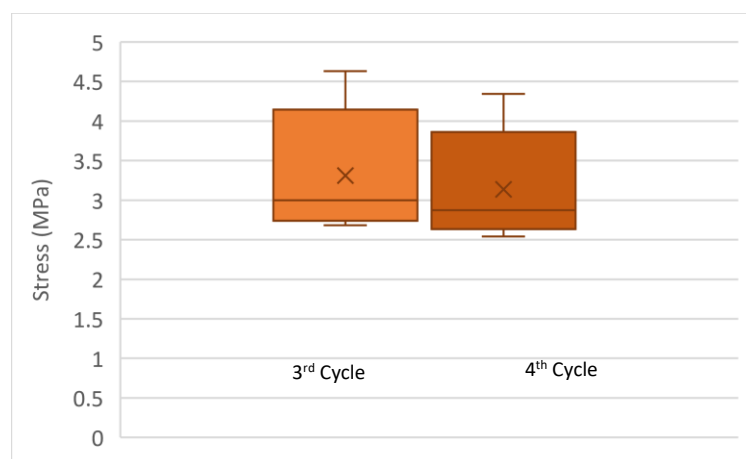


Figure C.22 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol A with crosslinking agent Tween 20 in the third and fourth cycles ($n=9$ for all cycles)

C.3 Box plots comparing cycles for formulation C

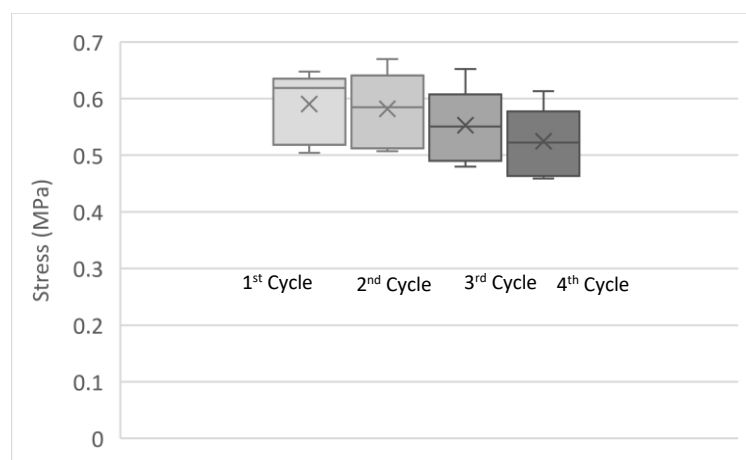


Figure C.23 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol C in the first, second, third and fourth cycles ($n=6$ for all cycles)

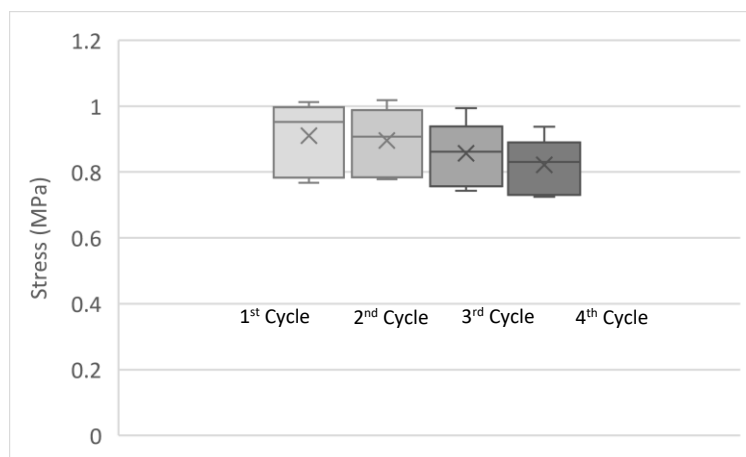


Figure C.24 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)

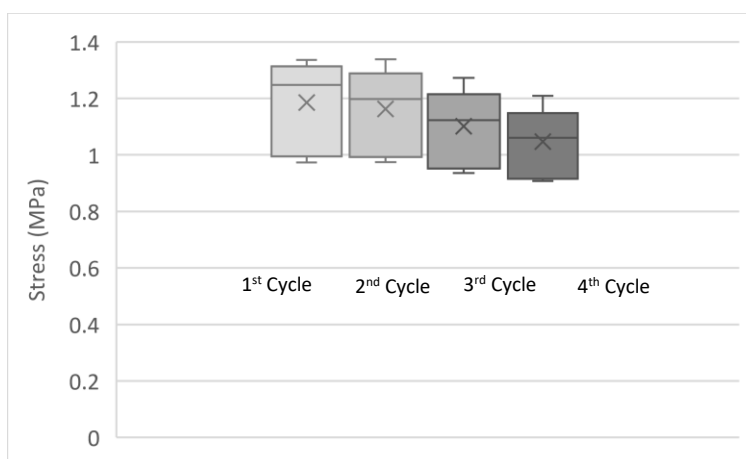


Figure C.25 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)

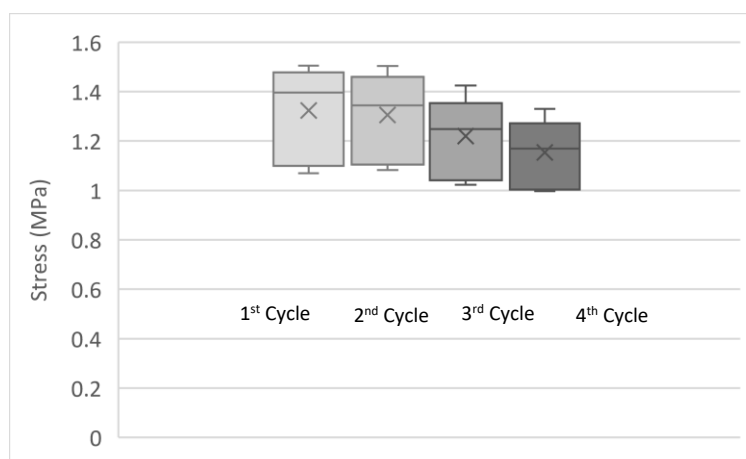


Figure C.26 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)

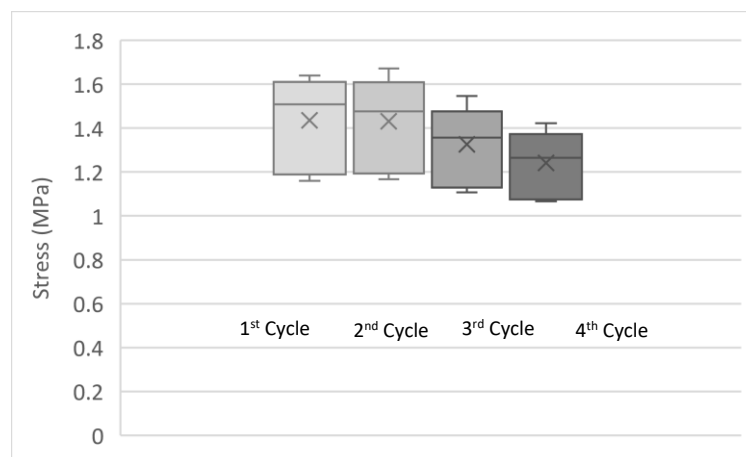


Figure C.27 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol C in the first, second, third and fourth cycles (n=6 for all cycles)

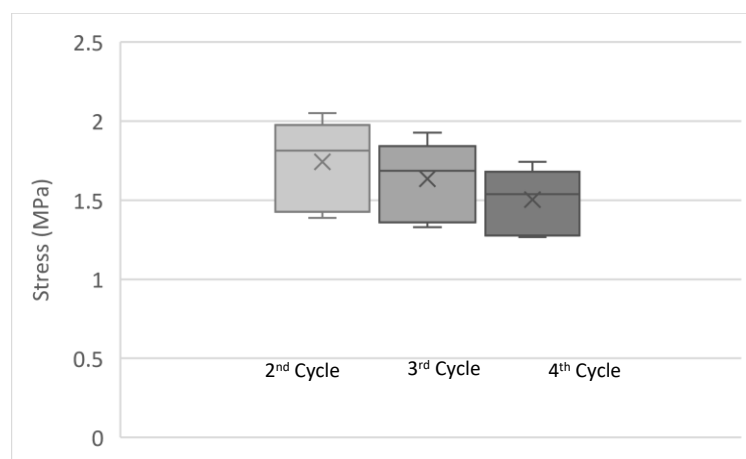


Figure C.28 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol C in the second, third and fourth cycles (n=6 for all cycles)

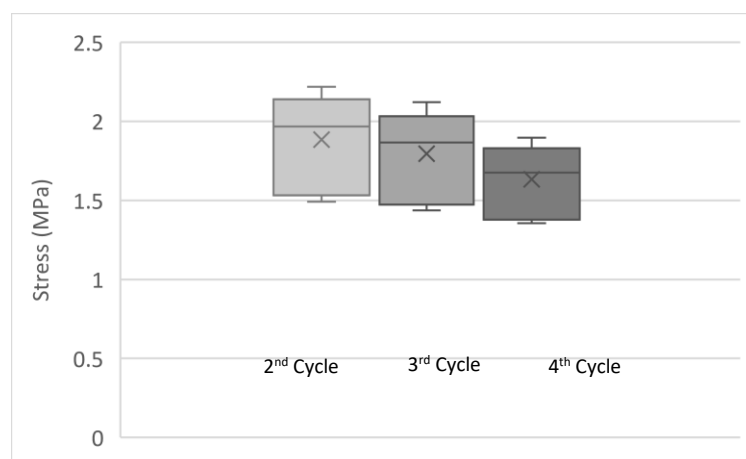


Figure C.29 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol C in the second, third and fourth cycles (n=6 for all cycles)

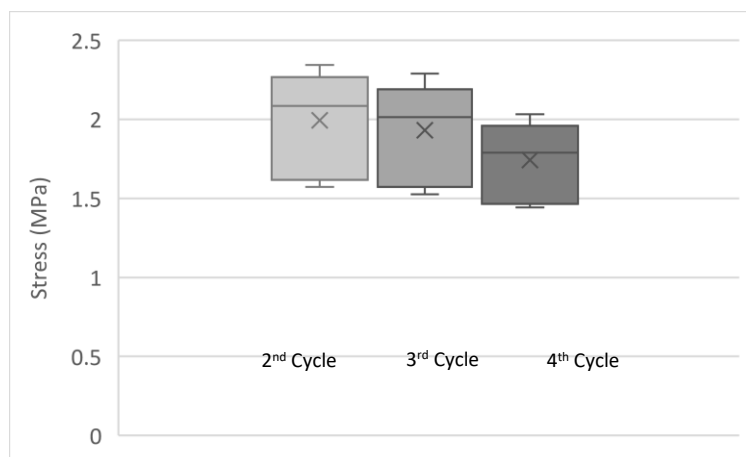


Figure C.30 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol C in the second, third and fourth cycles (n=6 for all cycles)

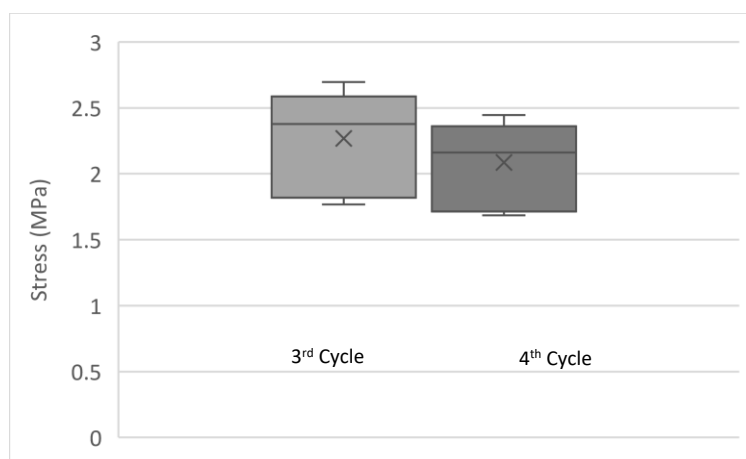


Figure C.31 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol C in the third and fourth cycles (n=6 for all cycles)

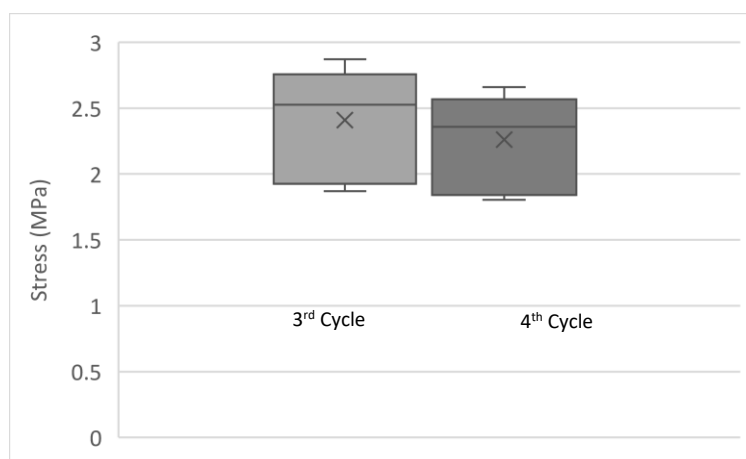


Figure C.32 Box Plot indicating the overlap in tensile values induced by a 375% strain in samples made from diol C in the third and fourth cycles (n=6 for all cycles)

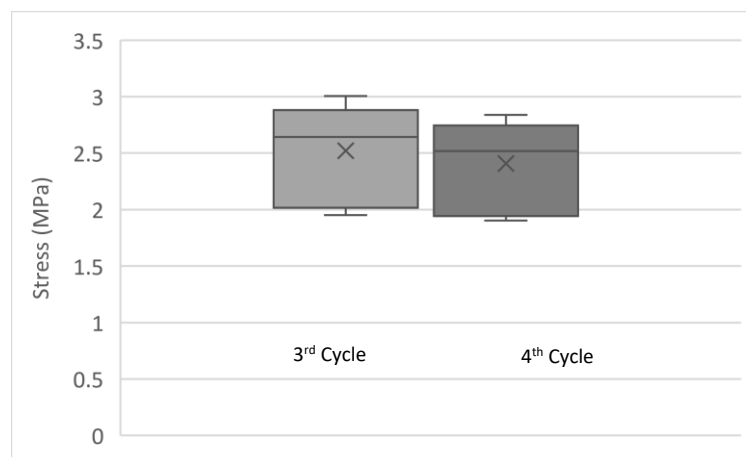


Figure C.33 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol C in the third and fourth cycles ($n=6$ for all cycles)

C.4 Box Plots Comparing Cycles for Formulation CT20

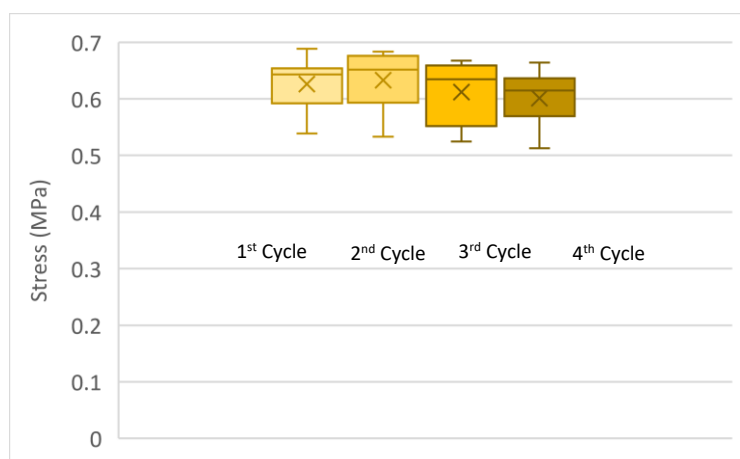


Figure C.34 Box Plot indicating the overlap in tensile values induced by a 50% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles ($n=10$ for all cycles)

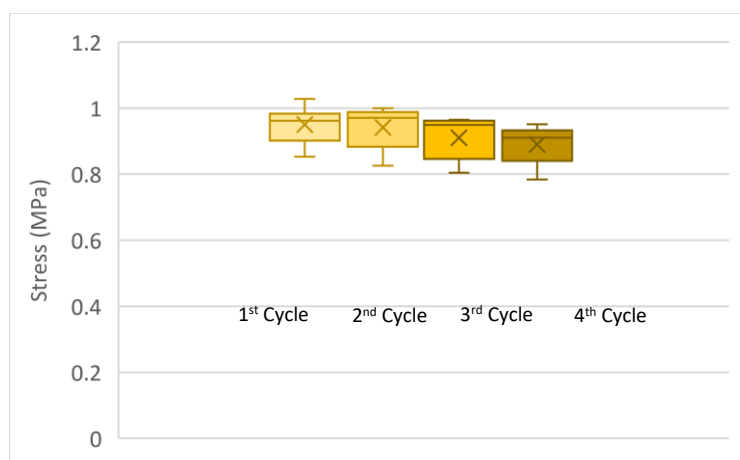


Figure C.35 Box Plot indicating the overlap in tensile values induced by a 100% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles ($n=10$ for all cycles)

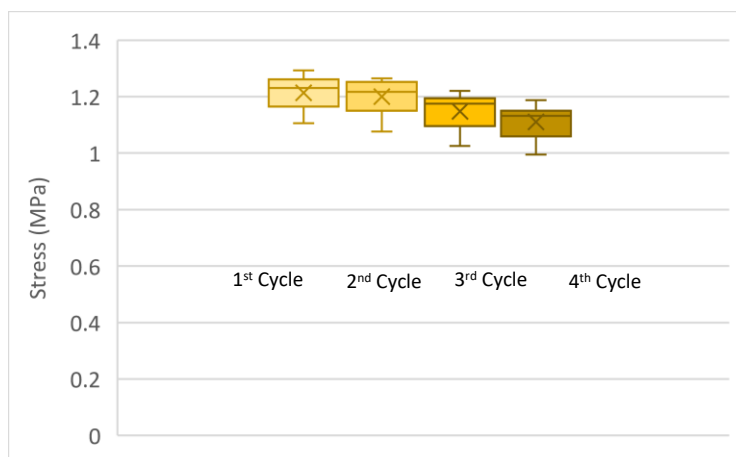


Figure C.36 Box Plot indicating the overlap in tensile values induced by a 150% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles)

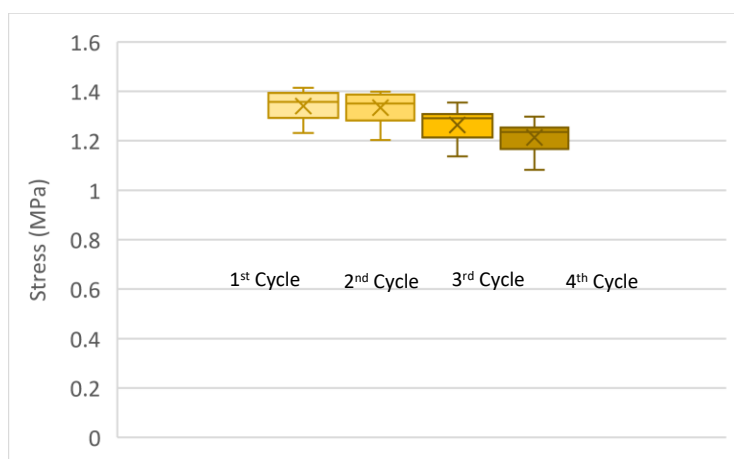


Figure C.37 Box Plot indicating the overlap in tensile values induced by a 175% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles)

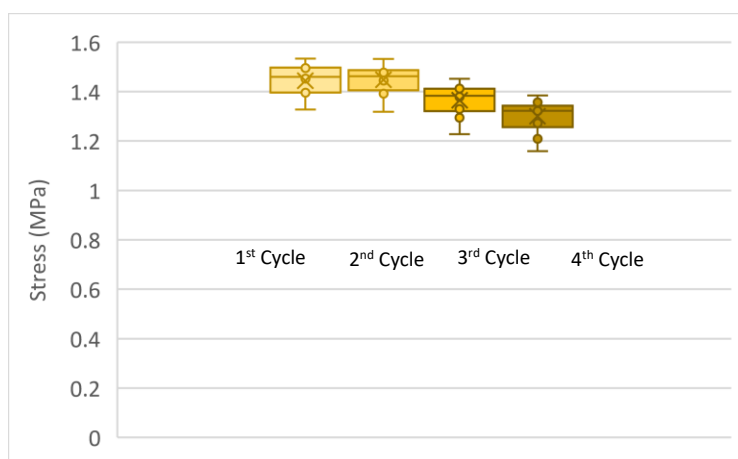


Figure C.38 Box Plot indicating the overlap in tensile values induced by a 195% strain in samples made from diol C with crosslinking agent in the first, second, third and fourth cycles (n=10 for all cycles)

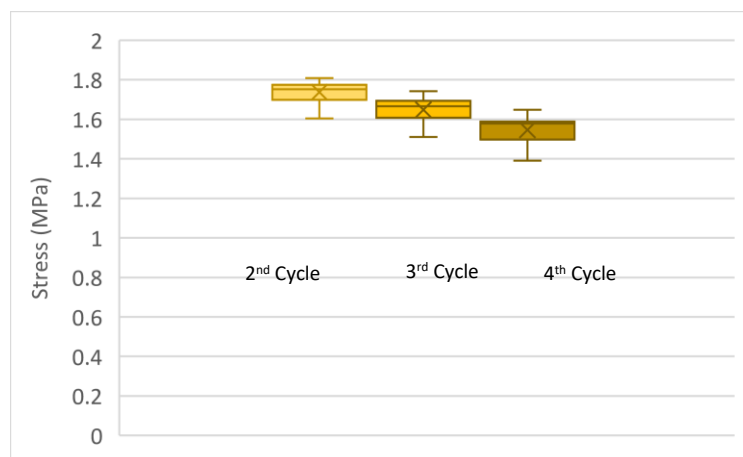


Figure C.39 Box Plot indicating the overlap in tensile values induced by a 250% strain in samples made from diol C with crosslinking agent in the second, third and fourth cycles (n=10 for all cycles)

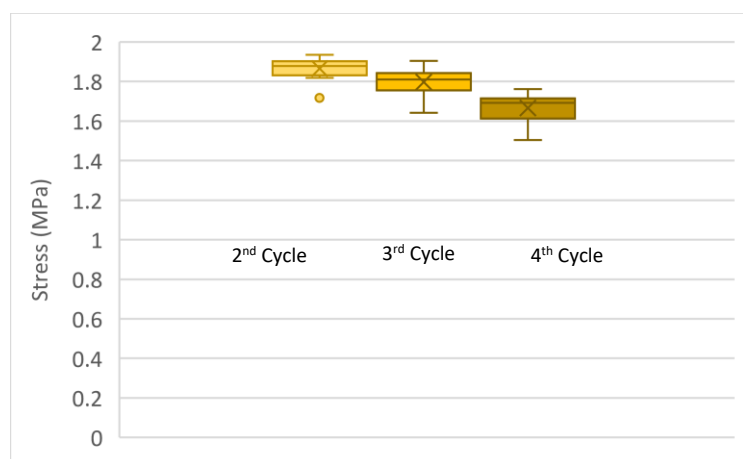


Figure C.40 Box Plot indicating the overlap in tensile values induced by a 275% strain in samples made from diol C with crosslinking agent in the second, third and fourth cycles (n=10 for all cycles)

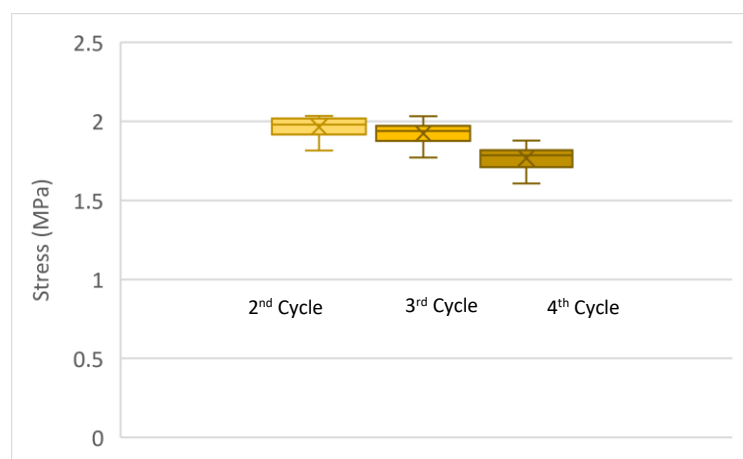


Figure C.41 Box Plot indicating the overlap in tensile values induced by a 295% strain in samples made from diol C with crosslinking agent in the second, third and fourth cycles (n=10 for all cycles)

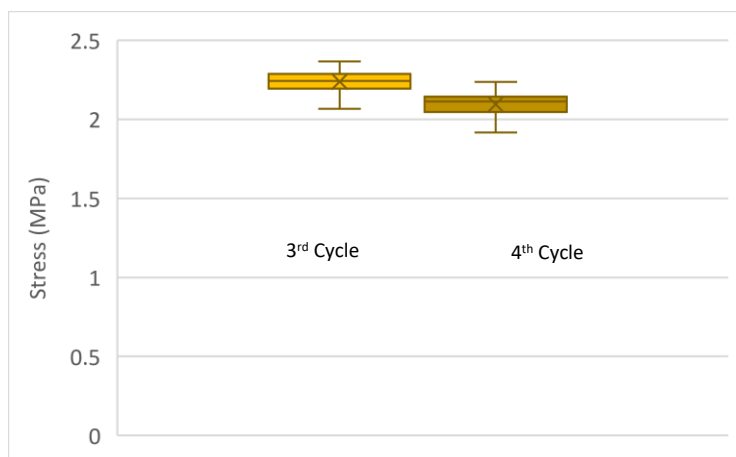


Figure C.42 Box Plot indicating the overlap in tensile values induced by a 350% strain in samples made from diol C with crosslinking agent in the third and fourth cycles (n=10 for all cycles)

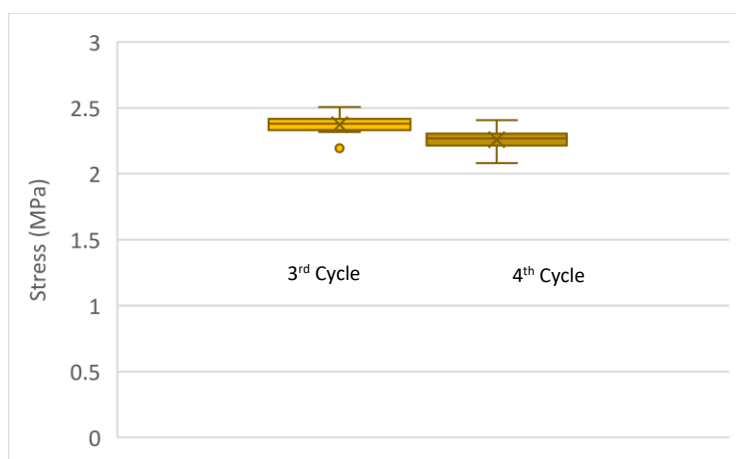


Figure C.43 Box Plot indicating the overlap in tensile values induced by a 375% strain in samples made from diol C with crosslinking agent in the third and fourth cycles (n=10 for all cycles)

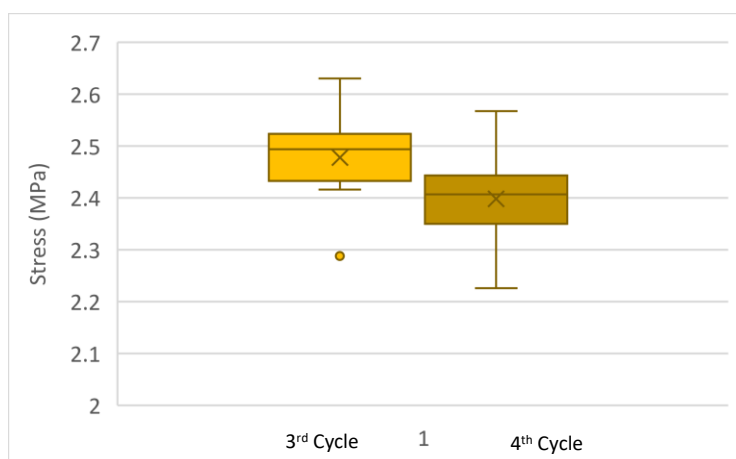


Figure C.44 Box Plot indicating the overlap in tensile values induced by a 395% strain in samples made from diol C with crosslinking agent in the third and fourth cycles (n=10 for all cycles)

C.5 Comparison of tensile stresses between cycles

Table C.1 P values for comparison of tensile stresses (σ) for various cycles (i/ii/iii/iv) at multiple strain points for all formulations F (A, AT20, C and CT20)

<u>Hypothesis</u>	<u>P-Value</u> <u>Formulatio</u> <u>n F (A)</u>	<u>P-Value</u> <u>Formulatio</u> <u>n F (AT20)</u>	<u>P-Value</u> <u>Formulatio</u> <u>n F (C)</u>	<u>P-Value</u> <u>Formulatio</u> <u>n F (CT20)</u>
$\sigma_{F 50\% (i)} = \sigma_{F 50\% (ii)} = \sigma_{F 50\% (iii)}$ $= \sigma_{F 50\% (iv)}$	0.0704	<u>0.0420</u>	0.2095	0.5020
$\sigma_{F 100\% (i)} = \sigma_{F 100\% (ii)} = \sigma_{F 100\% (iii)}$ $= \sigma_{F 100\% (iv)}$	<u>0.0195</u>	<u>0.0420</u>	0.3640	0.1091
$\sigma_{F 150\% (i)} = \sigma_{F 150\% (ii)} = \sigma_{F 150\% (iii)}$ $= \sigma_{F 150\% (iv)}$	0.0166	0.3065	0.3393	<u>0.0024</u>
$\sigma_{F 175\% (i)} = \sigma_{F 175\% (ii)} = \sigma_{F 175\% (iii)}$ $= \sigma_{F 175\% (iv)}$	<u>0.0084</u>	0.3279	0.3022	<u>0.0002</u>
$\sigma_{F 195\% (i)} = \sigma_{F 195\% (ii)} = \sigma_{F 195\% (iii)}$ $= \sigma_{F 195\% (iv)}$	<u>0.0067</u>	0.3280	0.2883	<u>1.47E⁻⁰⁵</u>
$\sigma_{F 250\% (ii)} = \sigma_{F 250\% (iii)} = \sigma_{F 250\% (iv)}$	<u>0.0088</u>	0.2490	0.3007	<u>5.06E⁻⁰⁶</u>
$\sigma_{F 275\% (ii)} = \sigma_{F 275\% (iii)} = \sigma_{F 275\% (iv)}$	<u>0.0110</u>	0.3569	0.3452	<u>4.42E⁻⁰⁶</u>
$\sigma_{F 295\% (ii)} = \sigma_{F 295\% (iii)} = \sigma_{F 295\% (iv)}$	<u>0.0152</u>	0.3986	0.3881	<u>6.61E⁻⁰⁶</u>
$\sigma_{F 350\% (iii)} = \sigma_{F 350\% (iv)}$	0.06999	0.4128	0.4378	<u>6.61E⁻⁰⁶</u>
$\sigma_{F 375\% (i)} = \sigma_{F 375\% (ii)}$	0.1725	0.5486	0.5679	<u>0.0012</u>
$\sigma_{F 395\% (i)} = \sigma_{F 395\% (ii)}$	0.3375	0.6672	0.6908	<u>0.0081</u>

Bold and underlined numbers indicate significant values.

C.6 P Values Comparing Formulations A and AT20

Table C.2 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations A and AT20

	P-Value Cycle (i)	P-Value Cycle (ii)	P-Value Cycle (iii)	P-Value Cycle (iv)
$\sigma_{A 50\%} = \sigma_{AT20 50\%}$	0.200621	0.328107	0.665336	0.738154
$\sigma_{A 75\%} = \sigma_{AT20 75\%}$	0.370952	0.497329	0.659232	0.167158
$\sigma_{A 100\%} = \sigma_{AT20 100\%}$	0.523179	0.632318	0.712182	0.094035
$\sigma_{A 150\%} = \sigma_{AT20 150\%}$	0.739248	0.802593	0.840408	0.092182
$\sigma_{A 175\%} = \sigma_{AT20 175\%}$	0.833715	0.915923	0.903257	0.822981
$\sigma_{A 200\%} = \sigma_{AT20 200\%}$	0.916567	0.9829	0.989519	0.852077
$\sigma_{A 250\%} = \sigma_{AT20 250\%}$		0.870035	0.873238	0.973192
$\sigma_{A 275\%} = \sigma_{AT20 275\%}$		0.822869	0.810174	0.993369
$\sigma_{A 300\%} = \sigma_{AT20 300\%}$		0.783076	0.744779	0.928422
$\sigma_{A 350\%} = \sigma_{AT20 350\%}$			0.739713	0.823579
$\sigma_{A 375\%} = \sigma_{AT20 375\%}$			0.723938	0.781856
$\sigma_{A 400\%} = \sigma_{AT20 400\%}$			0.73205	0.753412

C.7 P values comparing formulations A and C

Table C.3 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations A and C

	P-Value Cycle (i)	P-Value Cycle (ii)	P-Value Cycle (iii)	P-Value Cycle (iv)
$\sigma_{A 50\%} = \sigma_{C 50\%}$	<u>0.003617</u>	<u>0.002148</u>	<u>0.002659</u>	<u>0.005413</u>
$\sigma_{A 75\%} = \sigma_{C 75\%}$	<u>0.002211</u>	<u>0.000855</u>	<u>0.001536</u>	<u>0.001837</u>
$\sigma_{A 100\%} = \sigma_{C 100\%}$	<u>0.001772</u>	<u>0.000891</u>	<u>0.001116</u>	<u>0.001044</u>
$\sigma_{A 150\%} = \sigma_{C 150\%}$	<u>0.001782</u>	<u>0.001214</u>	<u>0.001062</u>	<u>0.001169</u>
$\sigma_{A 175\%} = \sigma_{C 175\%}$	<u>0.002084</u>	<u>0.001251</u>	<u>0.001145</u>	<u>0.00108</u>
$\sigma_{A 200\%} = \sigma_{C 200\%}$	<u>0.002004</u>	<u>0.001532</u>	<u>0.001154</u>	<u>0.001187</u>
$\sigma_{A 250\%} = \sigma_{C 250\%}$		<u>0.001214</u>	<u>0.001122</u>	<u>0.001418</u>
$\sigma_{A 275\%} = \sigma_{C 275\%}$		<u>0.001177</u>	<u>0.001037</u>	<u>0.001358</u>
$\sigma_{A 300\%} = \sigma_{C 300\%}$		<u>0.001184</u>	<u>0.001012</u>	<u>0.001224</u>
$\sigma_{A 350\%} = \sigma_{C 350\%}$			<u>0.001134</u>	<u>0.001172</u>
$\sigma_{A 375\%} = \sigma_{C 375\%}$			<u>0.001217</u>	<u>0.002125</u>
$\sigma_{A 400\%} = \sigma_{C 400\%}$			<u>0.001269</u>	<u>0.001183</u>

C.8 P values comparing formulations C and CT20

Table C.4 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations C and CT20

	P-Value Cycle (i)	P-Value Cycle (ii)	P-Value Cycle (iii)	P-Value Cycle (iv)
$\sigma_{C\ 50\%} = \sigma_{C\ T20\ 50\%}$	0.161609	0.083694	0.056773	<u>0.019322</u>
$\sigma_{C\ 75\%} = \sigma_{C\ T20\ 75\%}$	0.250681	0.12693	0.09775	<u>0.038383</u>
$\sigma_{C\ 100\%} = \sigma_{C\ T20\ 100\%}$	0.280274	0.211563	0.157968	0.067691
$\sigma_{C\ 150\%} = \sigma_{C\ T20\ 150\%}$	0.533149	0.4195	0.306017	0.15969
$\sigma_{C\ 175\%} = \sigma_{C\ T20\ 175\%}$	0.722154	0.568742	0.396919	0.222862
$\sigma_{C\ 200\%} = \sigma_{C\ T20\ 200\%}$	0.888499	0.762689	0.527329	0.320325
$\sigma_{C\ 250\%} = \sigma_{C\ T20\ 250\%}$		0.962172	0.788818	0.491168
$\sigma_{C\ 275\%} = \sigma_{C\ T20\ 275\%}$		0.919188	0.904819	0.609062
$\sigma_{C\ 300\%} = \sigma_{C\ T20\ 300\%}$		0.857515	0.816328	0.69255
$\sigma_{C\ 350\%} = \sigma_{C\ T20\ 350\%}$			0.87703	0.869127
$\sigma_{C\ 375\%} = \sigma_{C\ T20\ 375\%}$			0.832757	0.961474
$\sigma_{C\ 400\%} = \sigma_{C\ T20\ 400\%}$			0.820539	0.984034

C.9 P Values Comparing Formulations AT20 and CT20

Table C.5 P values gathered from one factor ANOVA analysis comparing the stress values (σ) associated with various strain points for formulations AT20 and CT20

	P-Value Cycle (i)	P-Value Cycle (ii)	P-Value Cycle (iii)	P-Value Cycle (iv)
$\sigma_{A\ T20\ 50\% (i)} = \sigma_{C\ T20\ 50\% (ii)}$	<u>0.00127</u>	<u>0.005165</u>	<u>0.011301</u>	0.161302
$\sigma_{A\ T20\ 75\% (i)} = \sigma_{C\ T20\ 75\% (ii)}$	<u>0.0014</u>	<u>0.002003</u>	<u>0.003495</u>	<u>0.022276</u>
$\sigma_{A\ T20\ 100\% (i)} = \sigma_{C\ T20\ 100\% (ii)}$	<u>0.001748</u>	<u>0.002084</u>	<u>0.002107</u>	<u>0.009752</u>
$\sigma_{A\ T20\ 150\% (i)} = \sigma_{C\ T20\ 150\% (ii)}$	<u>0.002687</u>	<u>0.002421</u>	<u>0.001563</u>	<u>0.003702</u>
$\sigma_{A\ T20\ 175\% (i)} = \sigma_{C\ T20\ 175\% (ii)}$	<u>0.002734</u>	<u>0.003095</u>	<u>0.001675</u>	<u>0.003018</u>
$\sigma_{A\ T20\ 200\% (i)} = \sigma_{C\ T20\ 200\% (ii)}$	<u>0.002796</u>	<u>0.003904</u>	<u>0.001721</u>	<u>0.002635</u>
$\sigma_{A\ T20\ 250\% (i)} = \sigma_{C\ T20\ 250\% (ii)}$		<u>0.003354</u>	<u>0.002021</u>	<u>0.002478</u>
$\sigma_{A\ T20\ 275\% (i)} = \sigma_{C\ T20\ 275\% (ii)}$		<u>0.003188</u>	<u>0.002338</u>	<u>0.001893</u>
$\sigma_{A\ T20\ 300\% (i)} = \sigma_{C\ T20\ 300\% (ii)}$		<u>0.002997</u>	<u>0.003729</u>	<u>0.001843</u>
$\sigma_{A\ T20\ 350\% (i)} = \sigma_{C\ T20\ 350\% (ii)}$			<u>0.002685</u>	<u>0.002227</u>
$\sigma_{A\ T20\ 375\% (i)} = \sigma_{C\ T20\ 375\% (ii)}$			<u>0.002512</u>	<u>0.00235</u>
$\sigma_{A\ T20\ 400\% (i)} = \sigma_{C\ T20\ 400\% (ii)}$			<u>0.002419</u>	<u>0.002843</u>

C.10 P values Comparing the Softening Found in Various Formulations

Table C.6 contains P values of softening response, to determine if statistical differences are present between formulations.

Table C.6 demonstrating P values calculated upon ANOVA analysis comparing the softening effects of between the formulations

<u>P-Values</u>	<u>Softening (i)</u>	<u>Softening (ii)</u>	<u>Softening (iii)</u>
A/AT20	0.175945	0.800705	0.473553
A/C	0.90097	0.133081	<u>0.001442</u>
C/CT20	0.334348	0.165814	0.096558
AT20/CT20	<u>0.003786</u>	<u>0.029465</u>	<u>0.00173</u>

C.11 P values comparing the Recovery Hysteresis found in various formulations

Table C.7 contains P values of recovery hysteresis response, to determine if statistical differences are present between formulations.

Table C.7 P values from single factor AVOVA analysis comparing formulations of PIB-PUR

P Values	Recovery Hysteresis (i)	Recovery Hysteresis (ii)	Recovery Hysteresis (iii)
A/AT20	0.030090803	0.154983544	0.49219465
A/C	0.264853804	0.007352684	0.002588198
C/CT20	0.021688542	0.072684455	0.166287063
AT20/CT20	0.023793422	0.000914408	0.00170717