

Contents

	<u>Page No.</u>
Title Page	i
Dedication	ii
Approval of the viva-voce board	iii
Certificate	iv
Acknowledgements	v
Declaration	vi
List of Symbols	vii
List of Abbreviations	viii
Abstract	ix
Contents	x

CHAPTER 1 **Introduction** **1–34**

1.1	Polymer-clay nanocomposite	5
1.2	Polyurethanes	5
1.3	Thermoplastic Polyurethane (TPU)	9
1.4	TPU-clay Nanocomposites	10
1.5	Literature Review on TPU-clay Nanocomposites	12
1.5.1	Structure and Morphology	12
1.5.2	Mechanical Properties	15
1.5.3	Thermal Properties	18
1.5.4	Rheological Characteristics	20
1.6	TPU-Laponite clay Nanocomposites	22
1.7	Summary of the Literature Review	24
1.8	Scope and Objectives	25
1.9	References	27

CHAPTER 2 Experimental 35–48

2.1	Materials Used	35
2.1.1	Thermoplastic Polyurethane (TPU)	35
2.1.2	Nanoclays	35
2.1.3	Other Chemicals	36
2.2	Modification of Nanoclays	38
2.2.1	Ionic Modification of Laponite	38
2.2.2	Covalent Modification of Laponite	39
2.2.3	Dual Modification of Laponite	40
2.3	Preparation of Nanocomposites	41
2.3.1	Solution Mixing Technique	41
2.3.2	Synthesis of TPU	41
2.3.3	Preparation of TPUCN by <i>Ex-situ</i> Technique	42
2.3.4	Preparation of TPUCN by <i>In-situ</i> Technique	42
2.4	Characterization Techniques Adopted	44
2.4.1	Fourier Transform Infrared Spectroscopy (FTIR)	44
2.4.2	Solid State NMR Spectroscopy	44
2.4.3	X-Ray Diffraction (XRD) Studies	44
2.4.4	Transmission Electron Microscopy (TEM)	45
2.4.5	Field Emission Scanning Electron Microscopy (FESEM)	45
2.4.6	Atomic Force Microscopy (AFM)	45
2.4.7	Differential Scanning Calorimetry (DSC)	45
2.4.8	Thermogravimetric Analysis (TGA)	46
2.4.9	Dynamic Mechanical Analysis (DMA)	46
2.4.10	Rubber Process Analyzer (RPA)	46
2.4.11	Tensile Property Studies	47

CHAPTER 3 Characterization of Modified Nanoclays 49–65

3.1	Introduction	49
3.2	FTIR Studies of Clay with and without Modification	49
3.2.1	Ionic Modification	49
3.2.2	Covalent Modification	51
3.2.3	Dual Modification	51
3.3	Solid State NMR Spectroscopy of the Modified Clays	53
3.3.1	Ionic Modification	53
3.3.2	Covalent Modification	54
3.3.3	Dual Modification	54
3.4	Wide Angle X-ray Diffraction (WAXRD) Studies	58
3.4.1	Ionic Modification	58
3.4.2	Covalent Modification	59
3.4.3	Dual Modification	59
3.5	Thermogravimetric Analysis of Nanoclays	60
3.5.1	Ionic Modification	60
3.5.2	Covalent Modification	62
3.5.3	Dual Modification	62
3.6	Conclusions	63
3.7	References	63

CHAPTER 4A TPU-clay Nanocomposite based on Modified Laponite and Cloisite® 67–89

4A.1	Introduction	67
4A.2	Wide Angle X-Ray Diffraction	67
4A.3	Transmission Electron Microscopy	70
4.3.1	Morphology of Solution Cast Nanocomposites	70
4.3.2	Morphology of Annealed Nanocomposites	70

4A.4	Field Emission Scanning Electron Microscopy	73
4A.5	Atomic Force Microscopy	74
4A.6	Differential Scanning Calorimetry	75
4A.7	Dynamic Mechanical Analysis	76
4A.8	Thermogravimetric Analysis	81
4A.9	Isothermal TGA	84
4A.10	Conclusions	88
4A.11	References	88

CHAPTER 4B **Rheological Characteristics of TPUCN 91–112**
 Based on Modified Laponite and Cloisite®

4B.1	Introduction	91
4B.2	Strain Sweep	92
4B.3	Temperature Sweep	96
4B.4	Frequency Sweep	98
	4B.4.1 Effect on Complex Viscosity at 140 °C	99
	4B.4.2 Effect on Complex Viscosity at 170 °C	103
	4B.4.3 Effect on Modulus at 140 and 170 °C	106
4B.5	Stress Relaxation	108
	4B.5.1 A Brief Theoretical Background on Stress Relaxation	108
	4B.5.2 Instantaneous (0.1 s) and 30 s Stress Relaxation time at 120 °C	109
4B.6	Conclusions	111
4B.7	References	111

CHAPTER 5 **TPUCN based on Modified
Laponite RDS** **113–134**

5.1 Introduction 113

5.2	Wide Angle X-Ray Diffraction (WAXRD)	113
5.3	Transmission Electron Microscopy	115
5.4	Field Emission Scanning Electron Microscopy	118
5.5	Differential Scanning Calorimetry	119
5.6	Dynamic Mechanical Analysis	120
5.7	Dynamic Rheological Analysis	123
5.7.1	Strain Sweep	123
5.7.2	Temperature Sweep	125
5.7.3	Frequency Sweep	127
	5.7.3.1 Effect on Complex Viscosity at 140 °C	127
	5.7.3.2 Effect on Complex Viscosity at 170 °C	127
5.7	Thermogravimetric Analysis	128
5.8	Isothermal TGA	131
5.9	Conclusions	133
5.10	References	134

CHAPTER 6 TPUCN based on Covalent and Dual Modified Laponite RD 135–149

6.1	Introduction	135
6.2	Wide Angle X-Ray Diffraction (WAXRD)	135
6.3	Transmission Electron Microscopy	137
6.4	Differential Scanning Calorimetry	139
6.5	Dynamic Mechanical Analysis	140
6.6	Dynamic Rheological Analysis	144
6.6.1	Strain Sweep	144
6.6.2	Temperature Sweep	145
6.6.3	Frequency Sweep	145
	6.6.3.1 Effect on Complex Viscosity at 140 °C	145
	6.6.3.2 Effect on Complex Viscosity at 170 °C	146
6.7	Thermogravimetric Analysis	147
6.8	Isothermal TGA	147

6.9	Conclusions	149
6.10	References	149

**CHAPTER 7 *Ex-situ and In-situ Prepared TPUCN 151–174*
based on Dual Modified Laponite RD**

7.1	Introduction	151
7.2	Wide Angle X-Ray Diffraction (WAXRD)	151
7.2.1	WAXRD at Lower Angular Range	151
7.2.2	WAXRD at Higher Angular Range	154
7.3	Transmission Electron Microscopy	158
7.4	Differential Scanning Calorimetry	161
7.5	Dynamic Mechanical Analysis	163
7.6	Dynamic Rheological Analysis	165
6.6.1	Strain Sweep	165
6.6.2	Temperature Sweep	167
6.6.3	Effect on Complex Viscosity at 140 °C	168
7.7	Tensile Properties	170
7.8	Thermogravimetric Analysis	172
7.9	Conclusions	174
7.10	References	174

CHAPTER 8 Summary and Conclusions 175–180

8.1	Summary and Conclusions	175
8.2	Contribution of the Present Work	179
8.3	Limitations and Scope for Future Work	180