

STUDY ON THERMAL, WATER BARRIER AND
MECHANICAL PROPERTIES OF
POLYURETHANE CLAY NANOCOMPOSITE
PREPARED BY SOLUTION INTERCALATION
METHOD



NORAYUNI BINTI AZIZI

MASTER OF ENGINEERING (CHEMICAL)
UNIVERSITI MALAYSIA PAHANG

STUDY ON THERMAL, WATER BARRIER AND MECHANICAL
PROPERTIES OF POLYURETHANE CLAY NANOCOMPOSITE
PREPARED BY SOLUTION INTERCALATION METHOD



FEBRUARY 2016

THESIS STATUS VALIDATION FORM

UNIVERSITI MALAYSIA PAHANG

DECLARATION OF THESIS AND COPYRIGHT

Author's Full Name : NORAYUNI BINTI AZIZI

Date of Birth : 2nd JANUARY 1989

Title : STUDY ON THERMAL, WATER BARRIER AND MECHANICAL PROPERTIES OF POLYURETHANE CLAY NANOCOMPOSITE PREPARED BY SOLUTION INTERCALATION METHOD

Academic Session : SEMESTER 2 2015/2016

I declare that this thesis is classified as:

<input type="checkbox"/>	CONFIDENTIAL	(Contains confidential information under the Official Secret Act 1972)*
<input type="checkbox"/>	RESTRICTED	(Contains restricted information as specified by the organization where research was done)*
<input type="checkbox"/>	OPEN ACCESS	I agree that my thesis to be published as online open access (Full text)

I acknowledge that Universiti Malaysia Pahang reserve the right as follows:

1. The Thesis is the Property of Universiti Malaysia Pahang
2. The Library of Universiti Malaysia Pahang has the right to make copies for the purpose of research only.
3. The Library has the right to make copies of the thesis for academic exchange.

Certified by:

(Student's Signature)

(Supervisor's Signature)

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of degree of Master of Engineering in Chemical Engineering.

(Supervisor's Signature)

Full Name : PROF. MADYA DR. KAMAL BIN YUSOH

Position : SENIOR LECTURER,
FACULTY OF CHEMICAL AND NATURAL RESOURCES
ENGINEERING,
UNIVERSITI MALAYSIA PAHANG

Date :



UMP

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or other institutions.

(Student's Signature)

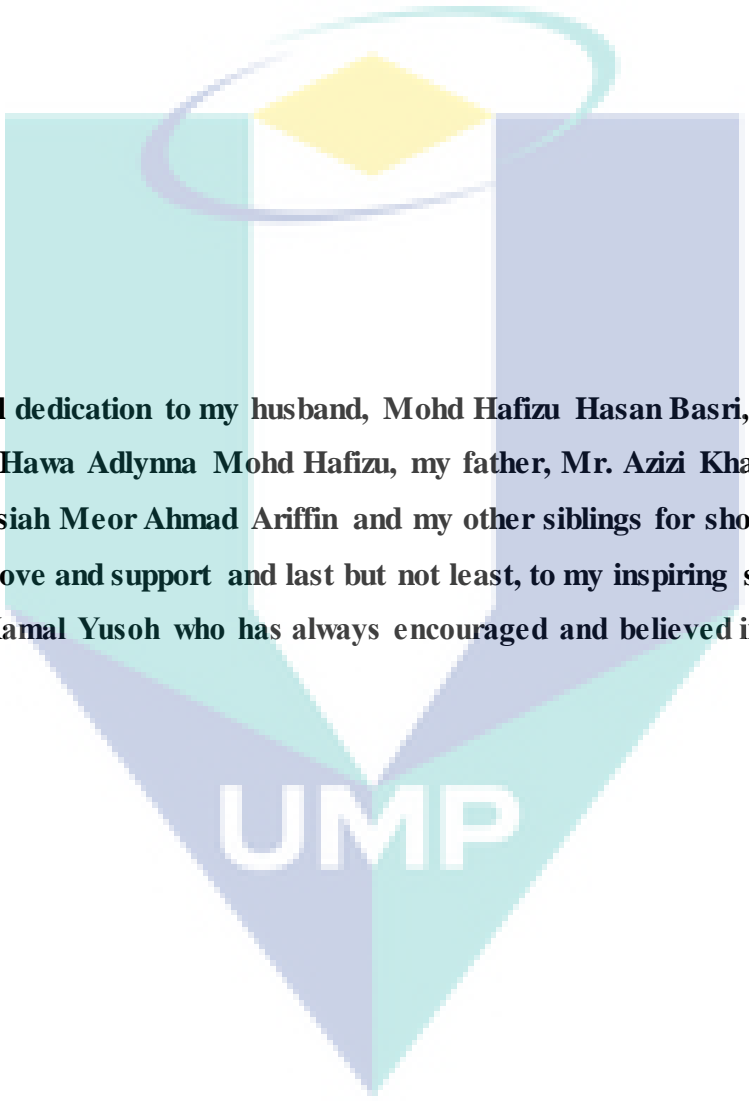
Full Name : NORAYUNI BINTI AZIZI

ID number : MKC12014

Date :



UMP

The logo of UMPA (Universiti Malaysia Perlis) is a shield-shaped emblem. It features a central white diamond with a yellow square inside it, surrounded by a purple and teal oval. The shield is divided into four quadrants: top-left is teal, top-right is purple, bottom-left is purple, and bottom-right is teal. The letters 'UMP' are written in white at the bottom of the shield.

Special dedication to my husband, Mohd Hafizu Hasan Basri, my beloved daughter, Hawa Adlyna Mohd Hafizu, my father, Mr. Azizi Khalid, my mother, Mrs. Norsiah Meor Ahmad Ariffin and my other siblings for showering me with endless love and support and last but not least, to my inspiring supervisor, Dr Kamal Yusoh who has always encouraged and believed in me...

ACKNOWLEDGEMENTS

I am grateful and would like to extend my sincerest gratitude to my supervisor, Dr Kamal bin Yusoh for his continuous encouragement and constant support in making this research possible. It was his endless faith and believes in me that motivated me in completing this research. I truly appreciate his consistent support, invaluable guidance and incipient ideas from the first day of my post graduate life to these concluding moments. I am truly grateful and sincerely thank him for all the time spent in correcting my mistakes and mentoring me throughout this path.

My sincere thanks to all my team mates in the research group and the staffs of the Faculty of Chemical and Natural Resources Engineering (FKKSA) lab, Institute of Postgraduate Studies (IPS), and to all whom helped me in many ways and making this research a successful one. I would also like to extend my gratitude to Universiti Malaysia Pahang for the research grants, RDU1203109 and RDU130341 that enabled a smooth flow of the experimental works.

I acknowledge my sincere indebtedness and gratitude to my family for their endless love and sacrifice throughout my life. I am truly grateful for their sacrifices, patience and continuous faith in me. It was their devotion that became my source of strength and motivation. Special thanks to my family members and friends whom supported me throughout this work.

The logo of Universiti Malaysia Pahang (UMPA) is a large, stylized shield shape. It is divided into four quadrants by a white 'V' shape pointing downwards. The top-left and bottom-right quadrants are light blue, while the top-right and bottom-left quadrants are light purple. The letters 'UMPA' are written in white, bold, sans-serif font across the center of the shield.

UMPA

Abstract

In this thesis, a series of polyurethane (PU) nanocomposite was fabricated by using the solution intercalation polymerization by employing chloroform with the incorporation of nanoclay Cloisite B30. The interaction between the nanoclay Cloisite B30 and PU matrices is the major factor in determining the structure in the PU nanocomposite, which was aimed at achieving a good dispersion with slighter agglomerates. The thermal characterization was conducted through thermal conduction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal conductivity of the PU nanocomposite increased with increase in the nanoclay loading. The results show that there was significant effect of the nanoclay on lowering the melting temperature of the PU nanocomposite. Hence, the thermal degradation behaviour of PU increased by the incorporation of the nanoclay up to 16 °C for 96 % PU/4 % B30. The addition of the nanoclay results in the enhancement of the thermal stability. The morphology of PU nanocomposite was investigated using the field emission scanning emission microscopy (FESEM), scanning emission microscopy (SEM) and X-ray diffraction (XRD), while chemical structure analysis was analysed using Fourier transform infrared spectrometer (FTIR). FESEM micrographs demonstrated fewer agglomerates formed in the PU nanocomposite while an even distribution of nanoclay in SEM was obtained. The degree of crystallinity of PU nanocomposite was directly increased according to Cloisite B30 content, which shows that good intercalated structure has been attained. FTIR indicated that there was no chemical structure alteration in PU nanocomposite. The barrier properties of the PU nanocomposite films were studied through the water absorption and water permeability analysis. Water absorption analysis presented that the highest percentage of water absorption was in the 98% PU/2% B30 with 14.9 %. Meanwhile, the water permeability revealed an improvement through the increase in nanoclay loading due to the formation of the tortuosity of the transport path in the PU nanocomposite. The highest decrement in the water permeation rate amounting to 56 % for 3 bar and 68 % for 4 bars were obtained in 98% PU/2% B30 however for 2 bar, there was no volume of water penetrate through the sample. The tensile strength and elongation of the PU nanocomposite at break were improved by the incorporation of the nanoclay. The tensile stress for the pristine PU was valued at 0.40 MPa while the highest tensile stress at 0.93 MPa was observed for the sample with 96 % PU/4 % B30 film. Meanwhile, the percentage of the elongation at break of the sample is the maximum with 106 % for the sample with 96 % of PU/4 % of B30. The results exhibited that the tensile strength and elongation at break of the nanocomposites dramatically increased with the incorporation of the nanoclay. This improvement was dependent on the content of the nanoclay as well as the formation structure of the nanoclay in the PU matrices.

Abstrak

Dalam thesis ini, sebuah siri nanokomposit poliuretana (PU) telah disintesis dengan menggunakan larutan interkelasi pempolimeran dengan menggunakan klorofom yang disebatikan dengan *nanoclay* Kloisit B30 . Penyebaran diantara *nanoclay* Kloisit B30 dan matrik PU adalah faktor utama dalam mengenalpasti struktur di dalam nanokomposit PU yang bertujuan untuk mencapai penyerakan yang sempurna dengan jumlah penggumpalan yang sedikit. Perincian sifat terma dilakukan dengan menggunakan teknik konduktiviti terma, alat analisis termogravimetrik (TGA) dan kalorimetri imbasan pembezaan (DSC). Kekonduksian terma dari nanokomposit PU meningkat seiring dengan peningkatan *nanoclay* sedikit demi sedikit. Hasil kajian menunjukkan bahawa terdapat kesan ketara didapati daripada *nanoclay* pada takat lebur nanokomposit PU. Justeru, penurunan sifat terma PU meningkat melalui sebatian *nanoclay* sehingga 16°C pada sampel 96 % PU/4 % B30. Penambahan *nanoclay* menunjukkan peningkatan pada kestabilan terma. Morfologi nanokomposit PU telah dikaji menerusi mikroskop elektron pengimbas pancaran medan (FESEM), mikroskopi elektron imbasan (SEM), pembelauan sinar-X (XRD) manakala analisa struktur kimia telah dikaji oleh spektroskopi inframerah transformasi Fourier (FTIR). Fotomikro daripada FESEM menunjukkan sedikit penggumpapan kecil terjadi di dalam nanokomposit PU sementara penyebaran yang sekata didapati daripada *nanoclay* menerusi SEM. Darjah penghabluran nanokomposit PU meningkat secara langsung seiring dengan kandungan Kloisit B30 yang menunjukkan pencapaian struktur interkelasi yang baik. FTIR mengindikasikan bahawa tidak ada ubahsuaian struktur kimia pada nanokomposit PU. Ciri-ciri kemeresapan filem nanokomposit PU telah dikaji menerusi analisis penyerapan air dan kebolehtelapan air. Analisa penyerapan air menunjukkan peratusan penyerapan air yang tertinggi adalah pada kadar 98% PU/2% B30 dengan 14.9%. Manakala, sifat ketelapan air berubah dengan penambahan jumlah *nanoclay* yang disebabkan oleh pertambahan rintangan saluran pergerakan di dalam nanokomposit PU. Nilai susutan tertinggi bagi ujian ketelapan air menunjukkan 56% bagi 3 bar manakala 68% bagi 4 bar didapati pada sampel 98% PU/2% B30 walaupun bagaimanapun bagi ujian ketepatan air pada 2 bar, tiada sebarang isipadu air telap menerusi sampel. Tahap ketegangan dan pemanjangan sampel kesemua nanokomposit PU telah menunjukkan hasil yang diperbaiki dengan penggabungan sebatian *nanoclay*. Tekanan tegangan bagi PU asli telah dinilai pada 0.40 MPa sementara tekanan tegangan yang tertinggi adalah pada 0.93 MPa telah didapati bagi sampel 96% PU/4% B30. Manakala, peratus untuk pemanjangan pada takat putus tahap maksimum ialah 106% untuk sampel dengan 96% PU/4% B30. Keputusan yang diperoleh telah mempamerkan kekuatan tegangan dan pemanjangan nanokomposit PU pada takat putus meningkat secara mendadak seiring dengan penggabungan sebatian *nanoclay*. Peningkatan yang ditunjukkan ini adalah bergantung pada kandungan *nanoclay* serta pembentukan struktur *nanoclay* di dalam matrik PU.

TABLES OF CONTENTS

	Page
TITLE PAGE	i
THESIS STATUS VALIDATION FORM	ii
SUPERVISOR’S DECLARATION	iii
STUDENT’S DECLARATION	iv
DEDICATION	v
ACKNOWLEDGEMENTS	vi
ABSTRACT	vii
ABSTRAK	viii
TABLE OF CONTENTS	ix
LIST OF TABLES	xiii
LIST OF FIGURES	xiv
LIST OF SYMBOLS	xviii
LIST OF ABBREVIATION	xx
CHAPTER 1 – INTRODUCTION	
1.1 Research Background	1
1.2 Problem Statements	4
1.3 Research Objectives	6
1.4 Scopes of Research	7
1.5 Significance of Research	8
CHAPTER 2 – LITERATURE REVIEW	
2.1 Introduction	9
2.2 Polymer	9
2.3 Diisocyanate	10
2.4 Polyols	10
2.4.1 Polyethers	11
2.4.2 Polyesters	12

2.4.2.1	Dibasic acid type	12
2.4.2.2	Polycaprolactone	12
2.4.2.3	Polycarbonate	13
2.5	Polyurethane (PU)	13
2.6	Organically modified layered silicate	19
2.7	Dispersion of nanocomposite	23
2.9.1	Phase separated/unmixed/immiscible nanocomposite	26
2.9.2	Intercalated nanocomposite	27
2.9.3	Exfoliated nanocomposite	27
2.8	Type of intercalation polymerization	29
2.10.1	Solution intercalation polymerization	29
2.10.2	Melt intercalation polymerization	30
2.10.3	In-situ intercalation polymerization	31
2.9	Polymer nanocomposite	33
2.10	Polyurethane nanocomposite	34
2.11	Physical and mechanical properties of polyurethane nanocomposite	35
2.12	Morphological Analysis	38
2.12.1	Field Emission Scanning Electron Microscopy (FESEM)	38
2.12.2	Scanning Electron Microscopy (SEM)	41
2.12.3	X-Ray Diffraction (XRD)	43
2.13	Chemical Structure Analysis	46
2.13.1	Chemical analysis using Fourier Transform Infrared Spectrometer (FTIR)	46
2.14	Thermal Analysis	48
2.14.1	Thermal Conductivity Test	48
2.14.2	Thermogravimetric Analysis (TGA)	52
2.14.3	Differential Scanning Calorimetry (DSC)	54
2.15	Diffusivity Analysis	60
2.15.1	Water Absorption Test	60
2.15.2	Water Permeability Test	63
2.16	Mechanical Analysis	67

CHAPTER 3 – METHODOLOGY

3.1	Introduction	71
3.2	Materials	72
	3.2.1 Polyurethane	72
	3.2.2 Chloroform	73
	3.2.3 Nanoclay Cloisite B30	74
3.3	Fabrication of Pristine PU	75
3.4	Fabrication of PU Nanocomposite	76
3.5	Morphological Analysis	77
	3.5.1 Field Emission Scanning Electron Microscopy (FESEM)	77
	3.5.2 Scanning Electron Microscopy (SEM)	79
	3.5.3 X-Ray Diffraction (XRD)	82
3.6	Chemical Structure Analysis	83
	3.6.4 Fourier Transform Infrared Spectrometer (FTIR)	83
3.7	Thermal Analysis	84
	3.7.1 Thermal Conductivity Test	84
	3.7.2 Thermogravimetric Analysis (TGA)	85
	3.7.3 Differential Scanning Calorimetry (DSC)	85
3.8	Diffusivity Analysis	86
	3.8.1 Water Absorption Test	86
	3.8.2 Water Permeability Test	87
3.7	Mechanical Analysis	89

CHAPTER 4 – RESULT AND DISCUSSION

4.1	Introduction	90
4.2	Morphological Analysis	92
	4.2.1 Morphology Analysis using Field Emission Scanning Electron Microscopy (FESEM)	92
	4.2.2 Morphology Analysis using Scanning Electron Microscopy (SEM)	96
	4.2.3 Morphology Analysis using X-Ray Diffraction (XRD)	100

4.2.4	Mechanism Involved	105
4.3	Chemical Structure Analysis	108
4.3.1	Chemical Analysis using Fourier Transform Infrared Spectrometer (FTIR)	108
4.4	Thermal Properties of Polyurethane Nanocomposite	111
4.4.1	Thermal Analysis using Thermal Conductivity Test	111
4.4.2	Thermal Analysis using Thermogravimetric Analysis (TGA)	114
4.4.3	Thermal Analysis using Differential Scanning Calorimetry (DSC)	120
4.5	Barrier Properties of Polyurethane Nanocomposite	123
4.5.1	Barrier Analysis using Water Absorption Test	123
4.5.2	Barrier Analysis using Water Permeability Test	127
4.6	Mechanical Properties of Polyurethane Nanocomposite	133
4.6.1	Mechanical Analysis using Tensile Strength Test	133
CHAPTER 5 – CONCLUSION AND RECOMMENDATION		
5.1	Conclusions	138
5.2	Recommendation For Future Work	140
REFERENCES		
APPENDICES		
A	Fabrication of Polyurethane Nanocomposite	156
B	List of Publications	160

LIST OF TABLES

Table no.	Title	Page
2.1	PU properties and characteristics	17
2.2	Cloisite MMT clay organic modifier and chemical structure	21
2.3	Results measured by DSC	57
3.1	Physical and chemical properties of PU	72
3.2	Physical and chemical properties of chloroform	73
3.3	Physical and chemical characters of Cloisite B30	74
3.4	The weight fraction of all samples involved	76
4.1	XRD summarize data for pristine PU and variable compositions	101
4.2	The degree of crystallinity of pristine PU and PU nanocomposite	103
4.3	Summary of characteristic of Infrared absorption bands involved	109
4.4	Maximal degradation of samples involved	114
4.5	TGA data of compositions involved in nitrogen gas	119
4.6	DSC data for pristine and PU nanocomposite	120

The logo for UMP (Universiti Malaysia Perlis) is a large, downward-pointing triangle. It is composed of four smaller triangles meeting at the center. The top-left and bottom-right triangles are light blue, the top-right and bottom-left triangles are a slightly darker blue, and the central area is white. The letters 'UMP' are printed in a bold, white, sans-serif font across the white central area.

UMP

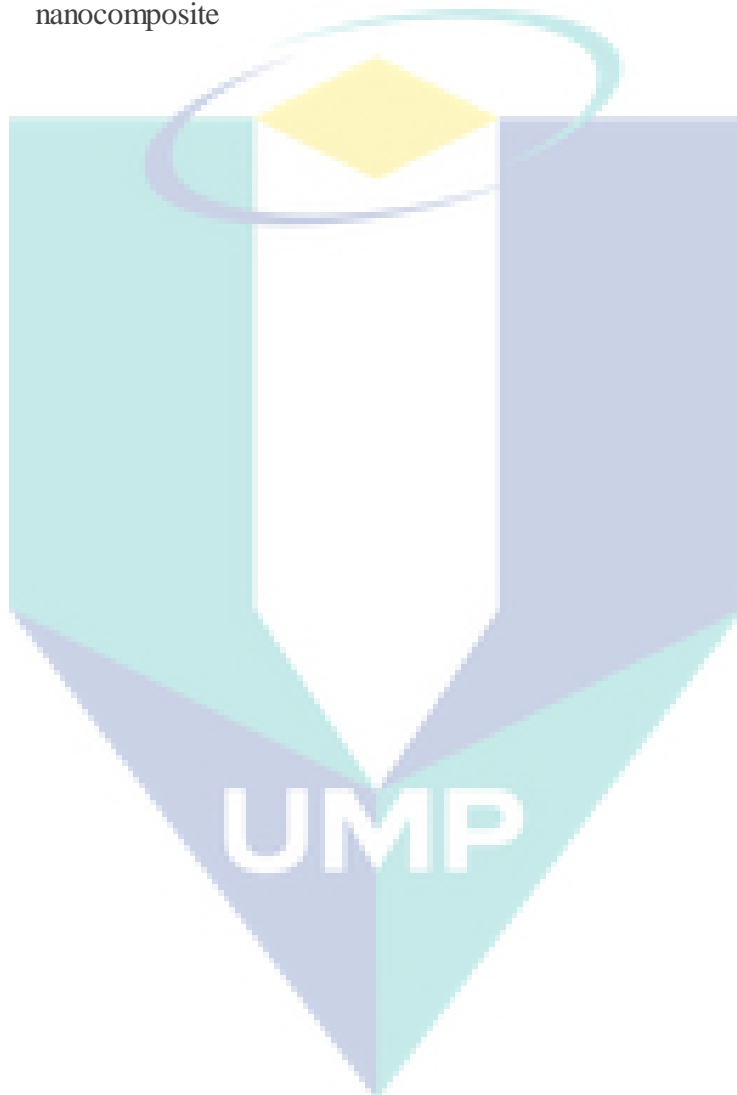
LIST OF FIGURES

Figure no.	Title	Page
2.1	The manufacturing route of the polypropylene glycol (PPG) and polytetramethylene glycol (PTMEG)	11
2.2	(a) Reaction of diisocyanate and polyols to produce prepolymer and (b) Chain extension with hydroxyl groups of diols	15
2.3	The molecular structure of PU that consists of soft and hard segment and repetitive segments	16
2.4	Chemical structure of MMT nanoclays	20
2.5	Schematic illustration of nanoclay structure in nanoscale sized	22
2.6	Schematic shows the preparation of polymer nanocomposite	23
2.7	Schematic showing polymer clay nanocomposite classification	25
2.8	The corresponding TEM and WAXS results of different types of dispersion of nanoclay in polymeric matrixes	26
2.9	The schematic illustration of nanocomposite structure that ordinarily occur in polymer nanocomposite	28
2.10	Melt intercalation polymerization method	30
2.11	Transmission electron microscopy of the cross section view of polyurethane organoclay nanocomposite	34
2.12	Nanotechnology that will be applied in PU	35
2.13	Nano insulation materials' position as thermal insulation for concrete	37
2.14	The presence of CNTs in polymer resin	39
2.15	FESEM fractured surface micrograph of the MWCNT (3wt%)/PCL-based PU composite	40
2.16	SEM surface structure observation of (a) 3% of unmodified MMT (Cloisite Na ⁺) in starch and (b) 5% of organically modified MMT (Cloisite B30) in starch	42
2.17	Schematic illustration of XRD diffractogram patterns	44
2.18	Schematic diagram of XRD principle of Bragg reflection	45

	analogy	
2.19	Thermal conductivity of series of carbon nanotube	51
2.20	Cross section of TA Instruments DSC QA10	55
2.21	Diagram of determination way for thermal character of material by DSC	56
2.22	DSC results obtained at a scan rate of 10 K/min under nitrogen gas atmosphere, (a) annealed at 90 °C for 2 h and (b) at 180 °C for 30 min	58
2.23	Regular arrangement of platelets with the main direction perpendicular to the diffusion direction	64
2.24	Conceptual of the diffusion of water through partially intercalated and exfoliated nanocomposites	65
2.25	The degree of delamination of nanocomposite (W is the thickness of the silicate layered stacked)	66
2.26	Tensile strength versus elongation with different clay contents	69
2.27	Schematic illustration of formation of hydrogen bonds in Nylon-6/montmorillonite nanocomposite	69
3.1	Polyurethane chemical structure	72
3.2	FESEM employed for this experimental work	78
3.3	Schematic diagram of SEM	80
3.4	SEM employed for this experimental work	81
3.5	XRD Miniflex by Rigaku equipment	82
3.6	Thermo Scientific FTIR Nicolet Avatar 370 DTGS Model spectrometer	83
3.7	KD2 Pro by Decagon Devices	84
3.8	The arrangement of permeability cell for water permeability testing	87
3.9	Universal Testing Machine Instron 3300 Series	89
4.1	The illustration of the samples produced (a) pristine PU, (b) 99.5% of PU/0.5% B30, (c) 99% of PU/1% B30, (d) 98% of	91

	PU/2% B30 and (e) 96% of PU/4% B30	
4.2	FESEM micrographs of (a) pristine B30 and (b) pristine PU	93
4.3	Illustration of (a) 99.5% of PU/0.5% B30, (b) 99% of PU/1% B30, (c) 98% of PU/2% B30 and (d) 96% of PU/4% B30	94
4.4	SEM micrographs demonstrate sample figure of (a) pristine B30, (b) pristine PU, (c) 99.5% of PU/0.5% B30, (d) 99% of PU/1% B30, (e) 98% of PU/2% B30 and (f) 96% of PU/4% B30	97
4.5	XRD diffractogram obtained for samples (a) pristine PU, (b) 99.5% PU/0.5% B30 (c) 99% PU/1% B30 (d) 98% PU/2% B30 and (e) 96% PU/4% B30	104
4.6	Sketch of the modification of nanoclay interlayers by organic onium cations	106
4.7	FTIR spectra of all the samples prepared	108
4.8	Illustration of –CH bonding	110
4.9	Plot of experimentally thermal conductivity during this experimental work	112
4.10	Thermogravimetric and derivative curves of pristine	116
4.11	Thermogravimetric and derivative curves of 99.5% PU/0.5% B30	116
4.12	Thermogravimetric and derivative curves of 99% PU/1% B30	117
4.13	Thermogravimetric and derivative curves of 98% PU/2% B30	117
4.14	Thermogravimetric and derivative curves of 96% PU/4% B30	118
4.15	The graph of water absorption percentage by all samples involved	124
4.16	The graph of volume water uptake by all samples involved	125
4.17	Water absorption coefficient at temperature of room temperature	126
4.18	The result of the water permeability rate for different pressure	128
4.19	The sketch of the tortuosity of water molecules transport path passing through the PU nanocomposite structure	129
4.20	Diffusion coefficient for every sample at 2 bar	131

4.21	Diffusion coefficient for every sample at 3 bar	131
4.22	Diffusion coefficient for every sample at 4 bar	132
4.23	The tensile strength in MPa for various composition of Cloisite B30	134
4.24	The Young's modulus of different loading in PU nanocomposite	135
4.25	The elongation percentage of different loading in PU nanocomposite	136



LIST OF SYMBOLS

n	an integer
λ	X-ray wavelength
d	inter-plane spacing
θ	diffraction angle giving the primary diffraction peak
W_1	weight after water absorption
W_0	dried weight of the sample
M_s	weight of the sample after absorption
M_t	initial mass of the specimen of weight of the specimen after 24 hours
ρ_w	specific density of water
V_c	volume of the dry sample
C_t	instantaneous capacity
C_0	capacity of dry sample
ϵ_w	dielectric constant of water (78.3 at 25 °C)
M_i	initial mass of the specimen
A_w	liquid contact area of the specimen
t	time taken which is 24 hours
G	gradient from graph attained
V	volume of permeant
l	sample thickness
A	area of sample
ΔP	pressure drop across the sample
k	thermal conductivity measured
Q	heat flow measured
A	cross-sectional area of the material
t	time
L	length of the material in the direction of heat flow
ΔT	temperature difference across the material

T_g	glass transition temperature
T_m	melting temperature
ΔH_m	enthalpy of fusion
T_c	crystallization temperature
X_c	percent of the crystallinity
C_p	specific heat
ΔH_f	the heat of fusion for completely crystallized PU
Φ	mass fraction of the Cloisite B30
N_2	nitrogen gas
D	the diffusion coefficient (for water permeability analysis)
P	Permeability
S	Solubility of the permeant
ZnO	zinc oxide
PP	polypropylene
D	thermal diffusivity (for thermal conductivity analysis)
ρ	density of the sample
K_{eff}	effective thermal conductivity
K_m	conductivity coefficients of polymer matrix
K_f	conductivity coefficients of filler particles
n	empirical factor for the shape of filler particles
\emptyset	volume fraction of filler in polymer matrix

LIST OF ABBREVIATIONS

B30	Cloisite [®] 30B
PU	Polyurethane
FESEM	Field emission scanning emission microscopy
SEM	Scanning emission microscopy
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectrometer
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
TDI	toluene diisocyanate
MDI	4,4-diphenylmethane diisocyanate
NDI	1,5-naphthalene diisocyanate
PTMEG	polytetramethylene glycol
PPG	polypropylene glycol
BDO	butanediol
MMT	Montmorillonite
SiO ₄	Silicon tetraoxide
Si ₄ O ₁₀	Kind of mineral component
Na ⁺	Sodium ion or Cloisite [®] Na ⁺ (unmodified clay)
HDT	heat deflection temperature
CLTE)	coefficient of linear thermal expansion
15A	Cloisite [®] 15A
20A	Cloisite [®] 20A
93A	Cloisite [®] 93A
25A	Cloisite [®] 25A
10A	Cloisite [®] 10A
2M2HT	dimethyl, dehydrogenated tallow, quaternary ammonium salt
MT2EtOH	methyl, tallow, bis-2-hydroethyl, quaternary ammonium salt

TEM	transmission electron microscopy
HCN	hydrogen cyanide
CN ⁻	cyanide anion
N	nitrogen
NIM	nano-insulation materials
C	Carbon
H	Hydrogen
O	Oxygen
ASTM	American Society for Testing and Materials code
MWNTs	multiwalled carbon nanotubes
CNTs	Carbon nanotubes
12COOH-mont	aminolauric acid nanocomposite
Pt	platinum
KBr	potassium bromide
IR	infrared
BZD-mont	benzidine nanocomposite
KH550-Sp	g-aminopropyltriethoxysilane
TSPU	thermo-sensitive PU
PPy	polypyrrole
PCL3000	Polycaprolactone diols
PPG600	polypropylene glycol
IPDI	Isophorone diisocyanate
BDO	1,4-butanediol
DMPA	Dimethylpropionic acid

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Polymers are widely used in daily life. Polymers incorporated with nanoclay have gained much attention to develop functional polymer composite field since the past two decades (Okada and Usuki, 2006) and this material is chosen in application of biomaterial devices which have led to various application (Styan, 2006). In spite of that, polymer nanocomposite attributes positive result to be applied in many fields. It improve the properties of pristine polymer in term of mechanical, thermal, electrical, chemical resistant and more. Major industries broadly rely on the polymer nanocomposite such as academic, government and industrial laboratories regarding to the potential application in many fields (Yang, 2001; Kim, 2008). Moreover, it is easy in the process of producing polymer nanocomposite. The speedy progress of polymer nanocomposite commonly depends on the easy processing and inexpensive raw materials, besides being very useful in daily life and offering many essential properties (Sukhummek, 2005).

Nanocomposite is a novel kind of composite (Bal et. al., 2012) and it has an important role in determining the alteration of the polymer properties (Kojima et. al., 1993). There are several types of nanoclay that is available in the current market. The development of nanocomposite attracts many researchers and industries to develop a new technology. Scientific and technical review state the development of properties of polymer with the incorporation with the nanoclay and demonstration often unfamiliar yet beneficial for the material properties (Turro et. al., 2009). Generally, polymer matrices inserted in between the nanoclay layers to build the polymer nanocomposite

which has better properties than the phase alone. Moreover, the mechanical and thermal properties of nanocomposite have raised its significant development (Kojima, 1993). Even though there are many types of additives offered, nanoclay is the one that environmental friendly additive. The nanoclay Na^+ has been modified to be different kind of nanoclay and all the classified nanoclay has its own advantages. Additionally, additives such as nanocomposite show a high alteration of characteristics beyond what traditional polymer composites possess (Chang et. al., 1995).

Polyurethane (PU) elastomers are built by phase-separated microdomain with two major segments (Yao, 2005, Styan, 2006; Sigamani, 2010). The soft segment has flexible nature besides having a very low transition glass which below than the room temperature (T_g), whereas the hard segment of PU skeleton has T_g above than the room temperature and a rigid crystalline nature (Sigamani, 2010). Due to the PU elastomers unique properties, PU deserves one of the most versatile classes of polymeric materials nowadays (Vedprakash, 1998). Furthermore, PU elastomers offer good manners in many aspects including the mechanical, electrical, thermal and chemical resistant properties which have been widely used in many applications. However, the major thing that needs to be understood is the relationships between morphology and the other properties for the material.

In the history of development of PU nanocomposite, Air Force Research Laboratory found that this kind of polymer nanocomposite is a novel class of insulation material by means in reducing the manufacturing cost, lightening weight and exhibiting better ablative performance and insulation characteristics (Chang et. al., 1995). Moreover, the nano-scale dimension of PU nanocomposite gives a huge enhancement as compared to the pristine PU. This may enhance the usage of PU as the significant improvement made and it is a comparatively a new class of composite material. Simultaneously, the compatibility of PU matrices and nanoclay particles make up the development of properties in term of morphological structure and the dispersion efficiency of particles (Piszczyk, 2012). This may resulted that PU nanocomposite is the chosen material to be applied in many applications.

REFERENCES

- Abedini R. and Nezhadmoghadam A. (2010). Application of Membrane in Gas Separation Processes: Its Suitability and Mechanisms. *Petroleum & Coal*. 52 (2), 69-80.
- Alexandre B. et. al. (2009). Water Barrier Properties of Polyamide 12/Montmorillonite Nanocomposite Membranes: Structure and Volume Fraction Effects. *Journal of Membrane Science*. 328 (2009), 186 – 204.
- Alexandre M. and Dubois P. (2000). Polymer-layered Silicate Nanocomposites: Preparation, Properties and Uses of a New Class of Materials. *Material Science Engineering Report*. 28 (2000), 1 – 63.
- Al-Homoud M. S. (2004). Performance Characteristics and Practical Applications of Common Building Thermal Insulation Materials. *Building and Environment*. 40 (2005), 353 – 366. Elsevier.
- Al-Sanea S. A. and Zedan M. F. (2002) Optimum insulation thickness for building walls in a hot-dry climate. *International Journal of Ambient Energy*. 23 (3) (2002), 115 – 126.
- American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) (2001). *Handbook of Fundamentals*. Atlanta, GA, USA. (Chapter 23).
- Anjayan P. M., Schadler L. S. and Braun P. V. (2006). *Nanocomposite Science and Technology*. (1st ed.) Deutsche, Germany: WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Atkinson. S. C. (2013). *Crystal Structures and Phase Transitions in the Rare Earth Oxides*. Ph.D. Thesis. University of Salford, Salford, UK.
- Azizi N. (2012). *Biodegradable Behaviour of Polylactic Acid Nanocomposite Based on Modified Nanoclay*. Bachelor Thesis. Universiti Malaysia Pahang, Gambang.
- Bai J. B. and Allaoui A. (2003). Effect of the Length and the Aggregate Size of MWNTs on the Improvement Efficiency of the Mechanical and Electrical Properties of Nanocomposites-Experimental Investigation. *Composites: Part A*. 34 (2003), 689 – 694.
- Bal A. et. al. (2012). A Novel Type Nanocomposite Coating Based on Alkyd-Melamine Formaldehyde Resin Containing Modified Silica: Preparation and Film Properties. *Journal of Applied Polymer Science*. 125 (S1), E85 – E92.
- Balandin, A. A. (2011). Thermal Properties Of Graphene And Nanostructured Carbon Materials. *Nature Materials*. 10 (2011), 569 – 581.
- Bang C. and Partners. (2010). Integration of Nanotechnology Materials for Green Building (I) Impacting Design and Construction. p.10, February 2010 (accessed 13 July 2012).

- Baysal G. et. al. (2013). Comparison Dielectric and Thermal Properties of Polyurethane/Organoclay Nanocomposites. *Thermochimica Acta*. 566, 305 – 313.
- Becker O. et. al. (2002). Morphology, Thermal Relaxations and Mechanical Properties of Layered Silicate Nanocomposites Based Upon High-Functionality Epoxy Resins. *Polymer*. 43 (16), 4365 – 4373.
- Behi. M. and Mirmohammadi. S. A. (2012). Investigation on Thermal Conductivity, Viscosity and Stability of Nanofluids. Master of Science. Royal Institute of Technology.
- Beyer G. (2002). Nanocomposites: A New Class of Flame Retardants for Polymers. *Plastics, Additives and Compounding*. 4 (10), 22 – 27.
- Bharadwaj R. K. (2001). Modeling the barrier properties of polymer-layered silicate nanocomposites. *Macromolecules*. 34 (2001), 9189 – 9192.
- Bhatia. A. (2008). *Experimental Study of Structure and Barrier Properties of Biodegradable Nanocomposites*. Master Thesis. RMIT University.
- Bhattacharya S. N, Kamal M. R. and Gupta R. K. (2008). *Polymeric Nanocomposites*. Munich: Carl Hanser Publishers.
- Bonilla G. et. al. (2006). Ternary Interpenetrating Networks of Polyurethane-Poly(Methyl Methacrylate)-Silica: Preparation by The Sol-Gel Process and Characterization of Films. *European Polymer Journal*. 42 (2006), 2977 – 2986.
- Bruzaud S. et. al. (2013). A Study of Morphological, Thermal, Rheological and Barrier Properties of Poly(3-Hydroxybutyrate-Co-3-Hydroxyvalerate) / Polylactide Blends Prepared by Melt Mixing. *Polymer Testing*. 32 (2013), 842 – 851.
- Cai X. X. et. al. (2012). Morphology Evolution of Immiscible Polymer Blends as Directed by Nanoparticle Self-Agglomeration. *Polymer*. 53 (2012). 259 – 266.
- Cai. D. (2009). *Development of High Performance Carbon Nanotube/Polymer Composites*. PhD Thesis Loughborough University.
- Chan C. M., Wu J., Li J. X. and Cheung Y. K. (2002). Polypropylene/Calcium Carbonate Nanocomposites. *Polymer*. 43 (10) 2981 – 2992.
- Chang J. H. and An Y. U. (2002). Nanocomposites of Polyurethane with Various Organoclays: Thermomechanical Properties, Morphology and Gas Permeability. *Journal of Polymer Science Part B – Polymer Physics*. 40 (2002), 670 – 677.
- Chang T. C. et. al. (1995). Thermo-Oxidative Degradation of Phosphorus-Containing Polyurethane. *Polymer Degradation Stability*. 49 (3), 353 – 360.
- Chattopadhyay D. K. and Raju K. V. S. N. (2007). Structural Engineering of Polyurethane Coatings for High Performance Applications. *Progress in Polymer Science*. 32 (2007), 352 – 418. Elsevier.

- Chau D. V. (2012). A Study on Water Absorption and Its Effects on Strength of Nano Organoclay-epoxy Composites. *Journal of Applied Sciences*. 12 (2012), 1939 – 1945.
- Chen H. et. al. (2012). Study on Thermal Properties of Polyurethane Nanocomposites Based on Organosepiolite. *Polymer Degradation and Stability*. 97 (2012), 242 – 247.
- Chen T. K. et. al. (2000). Synthesis and Characterization of Novel Segmented Polyurethane/Clay Nanocomposites. *Polymer*. 41 (2000), 1345 – 1353.
- Chen X. et. al. (2013). Influences of Coupling Agent on Thermal Properties, Flammability and Mechanical Properties of Polypropylene/Thermoplastic Polyurethanes Composites Filled with Expanded Graphite. *Journal of Thermal Analysis and Calorimetry*. 115 (2014), 689 – 695.
- Chen Y. et. al. (2004). Preparation and Characterization of Nanocomposite Polyurethane. *Journal of Colloid and Interface Science*. 279 (2004), 370 – 378.
- Chen Y. et. al. (2007). The Polyurethane Membranes with Temperature Sensitivity for Water Vapor Permeation. *Journal of Membrane Science*. 287 (2007), 192 – 197.
- Chen-Chi M. M. et. al. (2005). Synthesis, Thermal, Mechanical and Rheological Properties of Multiwall Carbon Nanotube/Waterborne Polyurethane Nanocomposite. *Composites Science and Technology*. 65 (2005), 1703 – 1710.
- Chiu H. T., Chiu S. H. and Wu J. H. (2003). Study on Mechanical Properties and Intermolecular Interaction of Silicone Rubber/Polyurethane/Epoxy Blends. *Journal of Applied Polymer Science*. 89 (2003), 959 – 970.
- Cho J. W. and Paul D. R. (2001). Nylon 6 Nanocomposites by Melt Compounding. *Polymer*. 42 (2001), 1083 – 1094.
- Chon C. H. et. al. (2005). Empirical Correlation Finding the Role of Temperature and Particle Size for Nanofluid (Al_2O_3) Thermal Conductivity Enhancement. *Applied Physics Letter*. 87 (15), 429 – 431.
- Choudalakis G. and Gotsis A. D. (2009). Permeability of Polymer/Clay Nanocomposites: A Review. *European Polymer Journal*. 45 (2009), 967 – 984. Elsevier.
- Chu H. S. et. al. (1999). Thermal Conductivity of Polyurethane Foams. *International Journal Heat Mass Transfer*. 42 (1999). 2211 – 2217. Elsevier.
- Ciprari D. L. (2004). *Mechanical Characterization of Polymer Nanocomposites and the Role of Interphase*. Master Thesis. Georgia Institute of Technology.
- Clemison I. R. (2008). Castable Polyurethane Elastomers. (1st Ed.). United States of America: CRC Press: Taylor & Francis Group.

- Corcione C. E. and Frigione M. (2012). Characterization of Nanocomposites by Thermal Analysis. *Materials*. 5 (2012), 2960 – 2980.
- Corcione C. E. and Frigione M. (2012). Characterization of Nanocomposites by Thermal Analysis. *Materials*. 5 (2012), 2960 – 2980.
- Danley R. L. (2002). New Heat Flux DSC Measurement Technique. *Thermochemical Acta*. 395 (1 – 2), 201 – 208.
- Das C. K. et. al. (2012). Mechanical and Crystalline Behavior of Polymeric Nanocomposites in Presence of Natural Clay. *Open Journal of Applied Sciences*. 2 (2012), 277 – 282.
- DUNA-Corradini (2011). Polyurethane/Polyisocyanurate for CRYOGENIC INSULATION [Brochure]. Modena, Italy: DUNA-Group Technical Documentation Center.
- Duquesne et. al. (2001). Thermal Degradation of Polyurethane and Polyurethane/Expandable Graphite Coatings. *Polymer Degradation and Stability*. 74 (2001), 493 – 499.
- Dylewski R. and Adamczyk J. (2011). Economic and Environmental Benefits of Thermal Insulation of Building External Walls. *Building and Environment*. 46 (2011), 2615 – 2623. Elsevier.
- Eastman J. A. et. al. (2001). Anomalously Increased Effective Thermal Conductivities of Ethylene Glycol Based Nanofluids Containing Copper Nanoparticles. *Applied Physics Letters*. 78, 718 – 720.
- European Commission – DG Environment. (2010). Green Public Procurement Thermal Insulation Technical Background Report.
- Fischer H. (2003). Polymer Nanocomposites: From Fundamental Research to Specific Applications. *Material Science Engineering Part C*. 23 (2003), 763 – 772.
- Gacitua W. et. al. (2005). Polymer Nanocomposites: Synthetic and Natural Fillers a Review. *Clencia y Tecnologia*. 7 (3), 159 – 178.
- Gao F., Chen S. and Hull J.B. (2001). Layer Expansion of Layered Silicates in Solid Polymer Matrices by Compression. *Journal of Material Science Letter*. 20 (19), 1807 – 1810.
- Gersappe D. (2002). Molecular Mechanisms of Failure in Polymer Nanocomposites. *Physical Review Letters*. 89 (5), 058301 – 1 – 4.
- Giannelis E. P. (2000). In Nanostructured Films and Coatings. G.M. Chow et al. (Ed.) Polymer-Layered Silicate Nanocomposites: Emerging Scientific and Commercial Opportunities. (367 – 372). Kluwer Academic Publishers.
- Grassie N. and Zulfiqar M. (1978). *The Effect of the Fire Retardant Ammonium Polyphosphate on the Thermal Degradation of Polyurethane*. In Scott G. (Ed.)

- Developments in Polymer Stabilisation, Vol 1.* 197 – 217. London: Applied Sciences.
- Haines P. J., Reading M. and Wilburn F. W. (1998). *Differential Thermal Analysis and Differential Scanning Calorimetry*. In Brown M. E. (Ed.) *Handbook of Thermal Analysis and Calorimetry*, vol 1. (279 – 361). The Netherlands: Elsevier Science BV.
- Han Z. and Fina A. (2010). Thermal Conductivity of Carbon Nanotubes and Their Polymer Nanocomposites: A Review. *Progress in Polymer Science*. 36 (7), 914 – 944.
- Hartwig G. et. al. (1999). Effect of Water Absorption in Polymers at Low and High Temperatures. *Polymer*. 40 (1999), 3433 – 3441.
- Hentschel T. and Munstedt H. (2001). Kinetics of The Molar Mass Decrease in a Polyurethane Melt: A Rheological Study. *Polymer*. 42 (2001), 3195 – 3203.
- Hercule K. M. et. al. (2011). Preparation and Characterization of Waterborne Polyurethane Crosslinked by Urea Bridges. *International Journal of Chemistry*. 3 (2), 88 – 96.
- Herrera-Alonso J. M. (2009). *Polymer/Clay Nanocomposites as Barrier Materials Used for VOC Removal*. Ph.D. Thesis. Virginia Polytechnic Institute and State University. Blacksburg, VA.
- Hong J. H. et. al. (2005). Electrospinning of Polyurethane / Organically Modified Montmorillonite Nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*. 43 (2005), 3171 – 3177.
- Hosokawa A. et. al. (2007). Nanostructured Shape Memory Alloys for Biomedical Applications. *Material Science Forum*. 539 – 547(2007), 505 – 510.
- Hu Y. et. al. (2000). Measurement of Water Vapor Transmission Rate in Highly Permeable Films. *Journal of Applied Polymer Science*. 81 (2000), 1624 – 1633.
- Huggett J. M. and Shaw H. F. (1997). Field Emission Scanning Electron Microscopy a High-Resolution Technique for the Study of Clay Minerals in Sediments. *Clay Minerals*. 32 (1997), 197 – 203.
- Hussain F. et. al. (2006). Review article: Polymer-Matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. *Journal of Composite Materials*. 40 (17), 1511 – 1565.
- Jatav G. K. et. al. (2013). Characterization of Swelling Behaviour of Nanoclay Composite. *International Journal of Innovative Research in Science, Engineering and Technology*. 2 (5), 1560 – 1563.
- Javni I. et. al. (2000). Rigid Polyurethane Foams Based on Soy-Bean Oil. *Journal Applied Polymer Science*. 77 (2000), 467 – 473.

- Javni I. et. al. (2000). Thermal Stability of Polyurethane Based on Vegetable Oil. *Journal Applied Polymer Science*. 77 (2000), 1723 – 34.
- Jelle B. P. (2011). Traditional, State-of-Art and Future Thermal Building Insulation Materials and Solutions – Properties, Requirements and Possibilities. *Energy and Building*. 43 (2011), 2549 – 2563. Elsevier.
- Jelle B. P. et. al. (2010). The High Performance Thermal Building Insulation Materials and Solutions of Tomorrow. *Thermal Performance of the Exterior Envelopes of Whole Buildings XI International Conference (Buildings XI)*. 5 – 9 December 2010. Clearwater Beach, Florida, U.S.A.
- Jordan J. et. al. (2005). Experimental Trends in Polymer Nanocomposites. *Materials Science and Engineering A*. 393 (2005), 1 – 11.
- Jullok N. et. al. (2012). Sorption and Diffusivity Study of Acetic Acid and Water in Polymeric Membranes. *Chemical Engineering Science*. 78 (2012), 14 – 20.
- Jung Y. C., Sahoo N. O. and Cho J. W. (2005). Polymeric Nanocomposites of Polyurethane Block Copolymers and Functionalized Multi-Walled Carbon Nanotubes as Crosslinkers. *Macromolecular Rapid Communications*. 27 (22), 126 – 131.
- Kane M. C. (2008). Permeability, Solubility and Interaction of Hydrogen in Polymers- An Assessment of Materials for Hydrogen Transport. Savannah River National Laboratory, Washington Savannah River Company. Washington, United States. WSRC-STI-2008-00009, Rev. 0
- Kaushik A., Ahuja D. and Salwani V. (2011). Synthesis and Characterization of Organically Modified Clay/Castor Oil Based Chain Extended Polyurethane Nanocomposites. *Composites: Part A*. 42 (2011), 1534 – 1541.
- Kaynakli O. (2012). A Review of the Economical and Optimum Thermal Insulation Thickness for Building Applications. *Renewable and Sustainable Energy Reviews*. 16 (2012), 415 – 425.
- Khudyakov I. V. et. al. (2009). Polyurethane Nanocomposites. *Designed Monomers and Polymers*. 12 (2009), 279 – 290.
- Kim T. et. al. (2008). Strengthening and Thermal Stabilization of Polyurethane Nanocomposites with Silicon Carbide Nanoparticles by a Surface – Initiated-Polymerization Approach. *Composites Science and Technology*. 68 (2008), 164 – 170.
- King J. A. et. al. (2008). Synergistic Effects of Carbon Fillers in Electrically and Thermally Conductive Liquid Crystal Polymer Based Resins. *Polymer Composites*. 29 (4), 421 – 428.
- Kline D. E. (1961). Thermal Conductivity Studies of Polymers. *Journal of Polymer Sciences*. 50 (154), 441 – 450.

- Kochetov, R. (2009). Thermal Behavior of Epoxy Resin Filled With High Thermal Conductivity Nanopowders. *IEEE Electrical Insulation Conference, Montreal*. 524 – 528.
- Kojima Y. (1993). Synthesis of Nylon 6-Clay Hybrid. *Journal of Materials Research*. 8 (1993), 1179 – 1184.
- Kojima Y. et. al. (1993). Gas Permeabilities in Rubber-Clay Hybrid. *Journal Material Science Letters*. 12 (1993), 889 – 890.
- Koo J. H. (2006). *Polymer Nanocomposites: Processing, Characterization and Applications*. (First Edition). United States of America: McGraw-Hill: Nanoscience and Technology Series.
- Krishnamoorti R. and Vaia R. A. (2001). *Polymer Nanocomposites: Synthesis, Characterization and Modeling*. ACS Symposium 804. ACS, Washington, DC.
- Krishnamoorti R. et. al. (1996). Structure and Dynamics of Polymer-Layered Silicate Nanocomposites. *Chemistry Materials*. 8 (1996), 1728 – 1734.
- Kuan H. C. et. al. (2005). Synthesis, Thermal, Mechanical and Rheological Properties of Multiwall Carbon Nanotube/Waterborne Polyurethane Nanocomposite. *Composites Science and Technology*. 65 (2005), 1703 – 1710.
- Kumlutas D., Tekce H. S. and Tavman I. H. (2007). Effect of Particle Shape on Thermal Conductivity of Copper Reinforced Polymer Composites. *Journal of Reinforced Plastics and Composites*. 26 (1), 113 - 121.
- Labde. R. (2010). *Preparation and Characterization of Polyethylene Terephthalate/Montmorillonite Nanocomposites by In-situ Polymerization Method*. Master Thesis. University of Toledo.
- Lambda N, M. K., Woodhouse K, A., Cooper S, L. (1998). Polyurethanes in Biomedical Applications. CRC Press: New York. 205 – 241.
- Lan T., Kaviratna P. D. and Pinnavaia T. J. (1995). Mechanism of Clay Tactoid Exfoliation in Epoxy-Clay Nanocomposites. *Chemistry of Materials*. 7 (11), 2144 – 2150.
- Larena A. et. al. (1994). Crystallinity Degree of Polyethylene Diffraction and Density Methods: An Evaluation of the Interfacial Contribution Tubular Blown Films Evaluated by X-ray. *Polymer Plastic Technology Engineering*. 33 (1994), 551 – 559.
- LeBaron P. C., Wang Z. and Pinnavaia T. J. (1999). Polymer-Layered Silicate Nanocomposites: An Overview. *Applied Clay Science*. 15 (1999), 11 – 29.
- Lewis. O. D. (2008). *A Study of the Influence of Nanofiller Additives on the Performance of Waterborne Primer Coatings*. Ph.D. Thesis Loughborough University.

- Li J. H. and Yu B. M. (2011). Tortuosity of Flow Paths through a Sierpinski Carpet. *Chinese Physical Letter*. 28 (3), 034701-1 – 034701-3.
- Liu J. et. al. (2011). Nanoparticle Dispersion and Aggregation in Polymer Nanocomposites: Insights from Molecular Dynamics Simulation. 27 (12), 7926 – 7933.
- Lligadas G. et. al. (2007). Poly(Ether Urethane) Networks from Renewable Resources as Candidate Biomaterials: Synthesis and Characterization. *Biomacromolecules*. 8 (2), 686 – 692.
- Lu Y. and Larock R. C. (2008). Soybean-Oil-Based Waterborne Polyurethane Dispersions: Effects of Polyol Functionality and Hard Segment Content on Properties. *Biomacromolecules*. 9 (11), 3332 – 3340.
- Lukas K. and LeMaire P. K. (2009). Differential Scanning Calorimetry: Fundamental Overview. *Resonance*. 807 – 817.
- Lutter S. et. al. (2008). Potential of the Ecological Footprint for Monitoring Environmental Impacts from Natural Resource Use: Analysis of the Potential of the Ecological Footprint and Related Assessment Tools for Use in the EU's Thematic Strategy on the Sustainable Use of Natural Resources. Report to the European Commission, Directorate General for the Environment.
- Malmberg C. G. and Maryott A. A. (1956). Dielectric Constant of Water from 0 °C to 100 °C. *Journal of Research of the National Bureau of Standards*. 56 (1), 1 – 8.
- Markova-Deneva I. (2010). Infrared Spectroscopy Investigation of Metallic Nanoparticles Based on Copper, Cobalt and Nickel Synthesized through Borohydride Reduction Method (Review). *Journal of the University of Chemical Technology and Metallurgy*. 45 (4), 351 – 378.
- Marquis D. M. et. al. (2011). Properties of Nanofillers in Polymer. In Cuppoletti J. (Ed.) *Nanocomposites and Polymers with Analytical Methods*. (261 – 284). InTech Europe.
- Matahwa H. et. al. (2011). *Block, Graft, Star and Gradient Copolymer Particles*. In Mittal V. (Ed.) *Advanced Polymer Nanoparticles: Synthesis and Surface Modifications*. (99 – 131). CRC Press: Taylor & Francis Group.
- McBane J. E. et. al. (2011). Biodegradation and In Vivo Biocompatibility of A Degradable, Polar / Hydrophobic / Ionic Polyurethane for Tissue Engineering Applications. *Biomaterials*. 32 (2011), 6034 – 6044.
- McLauchlin A. R. (2009). *Development of a Novel Organoclay for Poly(Lactic Acid) Nanocomposites*. Ph.D. thesis. Loughborough University.
- Mintsa H. A. et. al. (2009). New Temperature Dependent Thermal Conductivity Data for Water-Based Nanofluids. *International Journal of Thermal Sciences*. 48(2), 363 – 371.

- Mishra. A. K. (2010). *Thermoplastic Polyurethane-Modified Laponite Clay Nanocomposites*. Ph.D. Thesis. Indian Institute of Technology, Kharagpur.
- Mittal V. (2007). Gas Permeation and Mechanical Properties of Polypropylene Nanocomposites with Thermally-Stable Imidazolium Modified Clay. *European Polymer Journal*. 2007 (43), 3727 – 3736.
- Mittal V. (2007). Polypropylene-Layered Silicate Nanocomposites: Filler Matrix Interactions and Mechanical Properties. *Journal Thermoplastic Composite Material*. 2007 (20), 575 – 599.
- Mittal V. (2012). *In-situ Synthesis of Polymer Nanocomposites*. In Mittal V. (Ed.) *Polymer Nano- Micro- & Macrocomposites: In-situ Synthesis of Polymer Nanocomposites*. (1 – 25). WILEY-VCH Verlag GmbH & Co. KGaA.
- Mittal V. (2012). Mechanical and Gas Barrier Properties of Polypropylene Layered Silicate Nanocomposites: A Review. *The Open Macromolecules Journal*. 6 (2012), 37 – 52.
- Mukhopadhyaya P. et. al. (2002). Effect of Surface Temperature on Water Absorption Coefficient of Building Materials. *Journal of Thermal Envelope and Building Science*. 26 (2), 179 – 195.
- Muller C. M. O., Laurindo J. B. and Yamashita F. (2012). Composites of Thermoplastic Starch and Nanoclays Produced by Extrusion and Thermopressing. Carbohydrate. *Polymers*. 89 (2012), 504 – 510.
- Naranjo A. et. al. (2008). *Plastics Testing and Characterization*. Germany: Hanser.
- Nataraj S., Yang K. and Aminabhavi T. (2012). Polyacrylonitrile-Based Nanofibers – A State of – The Art Review. *Progress in Polymer Science*. 37 (2012) 487–513.
- Nawani P. et. al. (2010). Characterization of Nanoclay Orientation in Polymer Nanocomposite Film by Small-Angle X-Ray Scattering. *Polymer*. 51 (2010), 5255 – 5266.
- Nayak P. L. And Pradhan K. C. (2012). Synthesis and Characterization of Polyurethane Nanocomposite from Castor Oil-Hexamethylene Diisocyanate (HMDI). *Advances in Applied Science Research*. 3 (5), 3045 – 3052.
- Nikkeshi S., Kudo M. and Masuko T. (1998). Dynamic Viscoelastic Properties and Thermal Properties of Powder-Epoxy Resin Composites. *Journal of Applied Polymer Science*. 69 (1998), 2593 – 2598.
- Odian G. (2004). *Principles of Polymerization*. (4th Ed.). Hoboken, New Jersey: John Wiley & Sons, Inc.
- Odion G. (2004). *Principles of Polymerization*. Step Polymerization. (4th Ed.). New Jersey, USA: John Wiley & Sons, Inc.

- Okada A. and Usuki A. (2006). Twenty Years of Polymer-Clay Nanocomposites. *Macromolecular Materials and Engineering*. 291 (2006), 1449 – 1476.
- Olad A. and Naseri B. (2010). Preparation, Characterization and Anticorrosive Properties of a Novel Polyaniline/Clinoptilolite Nanocomposite. *Progress in Organic Coatings*, 67 (3), 233 – 238.
- Pan F. S., Cheng Q. L., Jia H. P. and Jiang Z. Y. (2010). Facile approach to polymer-inorganic nanocomposite membrane through a biomineralization-inspired process, *Journal of Membrane Science*. 357 (2010), 171–177.
- Pattanayak A. and Jana S. C. (2005). Thermoplastic Polyurethane Nanocomposites of Reactive Silicate Clays: Effects of Soft Segments on Properties. *Polymer*. 46 (2005), 5183 – 5193.
- Paul D. R. and Robeson L. M. (2008). Polymer Nanotechnology: Nanocomposites. *Polymer*. 49 (15), 3187 – 3204.
- Pavlidou S., Papaspyrides C. D. (2008). A Review on Polymer-Layered Silicate Nanocomposites. *Progress in Polymer Science*. 33(2008). 1119-1198.
- Pendse S. (2005). *Effect of Nanoclay on the Morphological Properties of Poly (Ethylene Terephthalate) in Relation to Fracture Toughness*. Master Thesis. University Of North Texas, USA.
- Pennycook S. J. et. al. (2007). In *Scanning Microscopy For Nanotechnology: Techniques and Applications*. Zhou W. and Wang Z. L. (Ed.) Scanning Transmission Electron Microscopy for Nanostructure Characterization. (152 – 191). New York, NY: Springer.
- Peters E. N. (2007). Plastics: Thermoplastics, Thermosets, and Elastomers. In Kutz M. (Ed.). *Handbook of Materials Selection*. New York, USA: John Wiley & Sons, Inc.
- Pinnavaia T. J. and Beall G. W. (2000). *Polymer-Clay Nanocomposites*. New York, USA: JohnWiley & Sons.
- Piszczyk L. et. al. (2012). Preparation and Characterization of Rigid Polyurethane–Polyglycerol Nanocomposite Foams. *European Polymer Journal*. 48 (2012), 1726 – 1733.
- Pradhan. N. R. (2010). *Thermal Conductivity of Nanowires, Nanotubes and Polymer-Nanotube Composites*. PhD Thesis Worcester Polytechnic Institute.
- Pradittham et. al. (2014). Surface Modified CaCO₃ by Palmitic Acid as Nucleating Agents for Polypropylene Film: Mechanical, Thermal and Physical Properties. *Energy Procedia*. 56 (2014), 264 – 273.
- Qi J. H. and Boyce M. C. (2004). Constitutive Model for Stretch-Induced Softening of the Stress-Stretch Behavior of Elastomeric Materials. *Journal of Mechanics and Physics of Solids*. 52, 2187 – 2205.

- Qi H. J. and Boyce M. C. (2004). Stress Strain Behavior of Thermoplastic Polyurethane. *Mechanics of Materials*. submitted for publication
- Ram A. (1997). *Fundamentals of Polymer Engineering*. (1st Ed.). New York, USA: Plenum Press.
- Rawlins J. W. and Mendon S. K. (2009). In *Coatings, Adhesives and Laminates*. In Bhattacharya A., Rawlins J. W. and Ray P. (Ed.) *Polymer Grafting and Crosslinking*. (273 – 318). John Wiley & Sons, Inc.
- Ray S. S. and Okamoto M. (2003). Polymer/Layered Silicate Nanocomposites: A Review from Preparation to Processing. *Progress in Polymer Science*. 28 (2003), 1539 – 1641.
- Reynaud E. et. al. (2001). Nanofillers in Polymeric Matrix: A Study on Silica Reinforced PA6. *Polymer*. 42 (21), 8759 – 8768.
- Roy M. et. al. (2005). Polymer Nanocomposite Dielectrics – The Role of the Interface. *IEEE Transactions Dielectrics Electric Insulation*. 12 (4), 629 – 643.
- Russ M. et al. (2013). Length-Dependent Electrical and Thermal Properties of Carbon Nanotubeloaded Epoxy Nanocomposites. *Composites Science and Technology*. 81 (2013), 42 – 47.
- Russo P. et. al. (2013). Tensile Properties, Thermal and Morphological Analysis of Thermoplastic Polyurethane Films Reinforced with Multiwalled Carbon Nanotubes. *European Polymer Journal*. 49 (2013), 3155 – 3164.
- Rutter A. et. al. (2013). In Situ Application Of Activated Carbon And Biochar To PCB-Contaminated Soil And The Effects Of Mixing Regime. *Environmental Pollution*. 182 (2013), 201 – 208.
- Salahuddin N. et. al. (2010). Synthesis and Characterization of Polyurethane/Organo-Montmorillonite Nanocomposites. *Applied Clay*. 47 (2010), 242 – 248.
- Schmidt H. et. al. (2005). Testing Water Vapour Permeability through Porous Membranes. *FIBRES & TEXTILES in Eastern Europe April / June 2005*. 13 (2), 66 – 68.
- Schmitt F. et. al. (1998). Dimeric Isocyanates in Polyurethane Powder Coatings. *Progress in Organic Coatings*. 34 (1998), 227 – 235.
- Seo W. J. et. al. (2006). Synthesis and Properties of Polyurethane/Clay Nanocomposite by Clay Modified with Polymeric Methane Diisocyanate. *Journal of Applied Polymer Sciences*. 101 (5), 2879 – 2883.
- Shah et. al. (2002). Moisture Diffusion through Vinyl Ester Nanocomposites Made with Montmorillonite Clay. *Polymer Engineering and Science*. 42 (9), 1852 – 1863.
- Sharma V. and Kundu P. P. (2008). Condensation Polymers from Natural Oils. *Progress of Polymer Sciences*. 33 (12), 1199 – 1215.

- Shawyer M. and Pizzali A. F. M. (2003). The Use of Ice on Small Fishing Vessels. Food and Agriculture Organization of the United Nations.
- Shyang C. W. (2008). Tensile and Thermal Properties of Poly(Butylene Terephthalate)/Organo-Montmorillonite Nanocomposites. *Malaysian Polymer Journal*. 3 (1), 1 – 13.
- Sigamani N. S. (2010). *Characterization of Polyurethane at Multiple Scales for Erosion Mechanisms under Sand Particle Impact*. Master Thesis. Texas A & M University.
- Sime. K. J. (1998). *Characteristics and Surface Analysis of Polymer Interfaces used in Dye Diffusion Thermal Transfer Printing*. PhD Thesis. Loughborough University.
- Simon G. P. et. al. (2004). Thermal Stability and Water Uptake of High Performance Epoxy Layered Silicate Nanocomposites. *European Polymer Journal*. 40 (2004), 187 – 195.
- Slavutsky A. M., Bertuzzi M. A. and Armada M. (2012). Water Barrier Properties of Starch-Clay Nanocomposite Films. *Brazilian Journal of Food Technology*. 15 (3), 208 – 218.
- Song M. and Cai D. (2012). *In-situ Synthesis of Polymer Nanocomposites*. In Mittal V. (Ed). *Polymer Nano- Micro- & Macrocomposites: In-situ Synthesis of Polymer Nanocomposites*. (169 – 244). WILEY-VCH Verlag GmbH & Co. KGaA.
- Srubar W. V. et. al. (2012). Characterizing the Effects of Ambient Aging on the Mechanical and Physical Properties of Two Commercially Available Bacterial Thermoplastics. *Polymer Degradation and Stability*. 97 (2012), 1922 – 1929. Elsevier.
- Styan K. (2006). *Polyurethane Organosilicate Nanocomposites for Novel Use as Biomaterials*. Ph.D. Thesis. University Of New South Wales.
- Sukhummek B. (2005). *Polyurethane / Poly(Ethyl Methacrylate) Interpenetrating Polymer Network Organoclay Nanocomposites*. Ph.D. Thesis. Loughborough University.
- Sultana and Khan. (2013). Water Absorption and Diffusion Characteristics of Nanohydroxyapatite (nHA) and Poly(hydroxybutyrate-co-hydroxyvalerate-) Based Composite Tissue Engineering Scaffolds and Nonporous Thin Films. *Journal of Nanomaterials*. 2013, 1 – 8.
- Tea S. (2011). *Polymeric Nanoparticles for the Modification of Polyurethane Coatings*. Ph.D. Thesis. Universitat Bayreuth.
- Tekce H. S., Kumlutas D. and Tavman I. H. (2004). Determination of the Thermal Properties of Polyamide-6 (Nylon-6)/Copper Composite by Hot Disk Method, In: Proceedings of the 10th Denizli Material Symposium, Denizli. 296 – 304.

- Thomson T. (2004). *Polyurethanes as Specialty Chemicals: Principles and Applications*. (1st Edition). United States of America: CRC Press LLC.
- Tijing L. D. et. al. (2012). Antibacterial and Superhydrophilic Electrospun Polyurethane Nanocomposite Fibers Containing Tourmaline Nanoparticles. *Chemical Engineering Journal*. 197 (2012), 41 – 48.
- Tjong S. C. (2006). Structural and Mechanical Properties of Polymer Nanocomposites. *Materials Science and Engineering R*. 53 (2006), 73 – 197.
- Tjong S. C. and Meng Y. Z. (2003). Impact-Modified Polypropylene/Vermiculite Nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*. 41 (19), 2332 – 2341.
- Tripathy D. K. and Barick A. K. (2011). Preparation, Characterization And Properties Of Acid Functionalized Multi-Walled Carbon Nanotube Reinforced Thermoplastic Polyurethane Nanocomposites. *Materials Science and Engineering B*. 176 (2011), 1435 – 1447.
- Tsekmes I. A. et. al. (2013). Thermal Conductivity of Polymeric Composites: A Review. 2013 IEEE International Conference on Solid Dielectrics. 978-1-4673-4459-3/13. 678 – 681.
- Turro N. J. et. al. (2009). *Principles of Molecular Photochemistry: An Introduction*. University Science Books, Sausalito, California.
- Ulutan S. and Balkose D. (1996). Diffusivity, Solubility and Permeability of Water Vapor in Flexible PVC/Silica Composite Membranes. *Journal of Membrane Science*. 115 (1996), 217 – 224.
- Vaia R. A. and Giannelis E. P. (1997). Polymer Melt Intercalation in Organically-Modified Layered Silicates: Model Predictions and Experiment. *Macromolecules* 30 (25), 8000 – 8009.
- Valek R. and Hell J. (2011). Impact Properties of Polymeric Nanocomposites with Different Shape of Nanoparticles. NANOCON 2011.
- Vedprakash M. et. al. (1998). Self-Preservation of the Drop Size Distribution Function, and Variation in the Stability Ratio for Rapid Coalescence of a Polydisperse Emulsion in a Simple Shear Field. *Journal of Colloid and Interface Science*. 197, 57 – 67.
- Wacharawichanant S., Sahapaibounkit P. and Saeueng U. (2011). Study on Mechanical and Morphological Properties of Polyoxymethylene/Al₂O₃ Nanocomposites. *TIChE International Conference 2011*. pp002-1 – pp002-5
- Wang Z. and Pinavaia T. J. (1998). Nanolayer Reinforcement of Elastomeric Polyurethane. *Chemistry of Materials*. 10 (1998), 3769 – 3771.
- Ward W. J. et. al. (1991). Gas Barrier Improvement using Vermiculite and Mica in Polymer Films. *Journal of Membrane Science*. 55 (1991), 173 – 180.

- Weber. E. H. (2001). *Development and Modelling of Thermally Conductive Polymer/Carbon Composites*. Ph.D. Thesis. Michigan Technology University.
- Webster D. C. and Chattopadhyay D. K. (2009). Thermal Stability and Flame Retardancy of Polyurethanes. *Progress in Polymer Science*. 34 (2009), 1068 – 1133.
- Wei S. Q., Bai Y. P. and Shao L. (2008). A Novel Approach to Graft Acrylates onto Commercial Silicones for Release Film Fabrications by Two-Step Emulsion Synthesis. *European Polymer Journal*. 44 (2008), 2728–2736.
- Weidenfeller B. et. al. (2004). Thermal Conductivity, Thermal Diffusivity, and Specific Heat Capacity of Particle Filled Polypropylene. *Journal of Composites Part A: Applied Science and Manufacturing*. 35(4), 423 – 429.
- Woo E. M. and Tseng Y. C. (1999). Glass Transition and Miscibility in Blends of Two Semicrystalline Polymers: Poly(Aryl Ether Ketone) and Poly(Ether Ether Ketone). *Journal of Polymer Science, Polymer Physics*. 37 (1999), 1485 – 1494.
- Wu C. L., Zhang M. Q., Rong M. Z. and Friedrich K. (2002). Tensile Performance Improvement of Low Nanoparticles Filled-Polypropylene Composites. *Composites Science and Technology*. 62 (10), 1327 – 1340.
- Wynne K. J. and Makal U. (2005). Water Induced Hydrophobic Surface. U. S. National Library of Medicine. 21 (9), 3742 - 3745.
- Xiong J. et. al. (2006). The Thermal and Mechanical Properties of A Polyurethane/Multi-Walled Carbon Nanotube Composite. *Carbon*. 44 (2006), 2701 – 2707.
- Yang Q, Zhong C. and Wang W. (2001). Correlation and Prediction of the Thermal Conductivity of Amorphous Polymers. *Fluid Phase Equilibria*. 181 (2001), 195 – 202.
- Yanilmaz M. et. al. (2012). Thermal Properties of Polyurethane Based Composites. *Smartex Research Journal*. 1 (1), 85 – 87.
- Yano K. et. al. (1993). Synthesis and Properties of Polyimide–Clay Hybrid. *Journal of Polymer Science, Part A: Polymer Chemistry*. 31 (1993), 2493 – 2498.
- Yao N. and Wang Z. L. (2005). *Handbook of Microscopy for Nanotechnology*. USA: Kluwer Academic Publishers.
- Yao. K. (2005). *High Performance Polyurethane-Organoclay Nanocomposites*. Ph.D. Thesis Loughborough University.
- Youn J. R. and Song Y. S. (2005). Influence of Dispersion States of Carbon Nanotubes on Physical Properties of Epoxy Nanocomposites. *Carbon*. 43 (2005), 1378 – 1385.

Yusoh K. (2010). *Subsurface and Bulk Mechanical Properties of Polyurethane Nanocomposite Films*. Ph.D. Thesis. Loughborough University, Leicestershire.

Zanetti M. et. al. (2001). Synthesis and Thermal Behaviour of Layered Silicate-EVA Nanocomposites. *Polymer*. 42 (10), 4501 – 4507.

Zemboui I. et. al. (2013). A Study of Morphological, Thermal, Rheological and Barrier Properties of Poly(3-Hydroxybutyrate-Co-3-Hydroxyvalerate)/Polylactide Blends Prepared by Melt Mixing. *Polymer Testing*. 32 (2013), 842 – 851.

