MECHANICAL, THERMAL, MORPHOLOGICAL AND FLAMMABILITY PROPERTIES OF HALLOYSITE NANOTUBE REINFORCED COMPATIBILIZED POLY(ETHYLENE TEREPHTHALATE) / POLYPROPYLENE NANOCOMPOSITES

NOORZILAWANI CHE ABDUL RAZAK

UNIVERSITI TEKNOLOGI MALAYSIA

MECHANICAL, THERMAL, MORPHOLOGICAL AND FLAMMABILITY PROPERTIES OF HALLOYSITE NANOTUBE REINFORCED COMPATIBILIZED POLY(ETHYLENE TEREPHTHALATE) / POLYPROPYLENE NANOCOMPOSITES

NOORZILAWANI CHE ABDUL RAZAK

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Polymer)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

FEBRUARY 2016

‘For my beloved husband, my lovely Mom and Dad, my sisters and my brothers’

ACKNOWLEDGEMENTS

Alhamdulillah, all praises be to Allah for His generous blessing and grace bestowed upon me during the course of this research.

I would like to express my gratitude to my supervisor, Prof. Dr. Azman Hassan for his endless advice, guidance and encouragement throughout the period of this research. Thank you very much for his willingness, time and comments in evaluating my research papers and my thesis prior to submission. May Allah reward him and his generation abundantly according to his riches in kindness, insha Allah. I would also like to thank to my co-supervisor, Dr. Sani Amril Samsudin for his help, guidance and advice during my period of study.

I also wish to express my appreciation to all the lecturers in the Department of Polymer Engineering for their help and support in my research. Sincere thanks are also accorded to all the lab assistant and laboratory technician for their help and enjoyable working environment.

A special thanks to my family. Words cannot express how grateful I am for all of the sacrifices that you've made on my behalf. Your prayer for me was what sustained me thus far. I would also like to thank all of my friends who supported me throughout the course of this research. Last but not least, I would like to dedicate this thesis to my beloved husband, Ahmad Syawal, who spent sleepless nights with and was always my support in the moments when there was no one to answer my queries.

ABSTRACT

The effects of two types of compatibilizers and halloysite nanotubes (HNT) on poly(ethylene terephthalate) (PET)/polypropylene (PP) blends were investigated. Blends of PET/PP in various compositions ranging from 20 – 50 wt% of PP were prepared via twin screw compounding. Polypropylene grafted maleic anhydride (PP-g-MAH) and styrene-ethylene/butylene-styrene grafted maleic anhydride (SEBS-g-MAH) at composition 0 – 10 phr respectively were used as compatibilizers. Mechanical test showed that when PP was incorporated into PET, tensile modulus increased significantly. Both tensile and flexural strengths of the blends showed considerable improvement at 4 phr PP-g-MAH and the impact strength of the blends significantly increased at 8 phr of SEBS-g-MAH. Scanning electron microscopy micrographs confirmed the excess amount of compatibilizer induced agglomerations that limited the enhancement of the mechanical properties. PET/PP/PP-g-MAH 70/30/4 phr was chosen as the optimum composition for the next series of study. The incorporation of HNT into compatibilized blends increased all the mechanical properties. Thermogravimetric analysis data showed that the thermal stability of compatibilized PET/PP filled with HNT was higher than the unfilled blends, while the limiting oxygen index test showed that flammability decreased with the increasing amount of HNT. Transmission electron microscopy revealed that there were interactions between HNT and compatibilized PET/PP blend. X-ray diffraction analyses indicated limited intercalation of HNT occurred in PET/PP nanocomposites. Fourier transform infrared spectroscopy analysis showed the existence of hydrogen bonds between silicon monoxide of HNT with the polar groups of PET and PP-g-MAH. The optimum composition in terms of mechanical properties of compatibilized PET/PP filled HNT was achieved at 2 phr loading of HNT.

ABSTRAK

Kesan dua jenis penserasi dan tiub nano haloisit (HNT) pada campuran poli (etilena teraftalat) (PET)/polipropilena (PP) telah disiasat. Campuran PET/PP dalam komposisi yang terdiri daripada 20 - 50% PP telah disediakan menggunakan adunan skru berkembar. Polipropilena tercangkuk malik anhidrida (PP-g-MAH) dan stirena-etilina/butadiena-stirena tercangkuk malik anhidrida (SEBS-g-MAH) dengan komposisi campuran masing-masing dari 0 - 10 phr telah digunakan sebagai penserasi. Ujian mekanikal menunjukkan bahawa apabila PP dimasukkan ke dalam PET, tegangan modulus meningkat dengan ketara. Kedua-dua tegangan dan kekuatan lenturan campuran menunjukkan peningkatan yang besar pada 4 phr PP-g-MAH dan kekuatan hentaman kesan daripada campuran meningkat dengan ketara pada 8 phr SEBS-g-MAH. Mikroskopi elektron penskanan mengesahkan jumlah penserasi yang berlebihan cenderung untuk mendorong penggumpalan yang mengehadkan peningkatan sifat-sifat mekanik. PET/ PP/PP-g-MAH 70/30/4 phr telah dipilih sebagai komposisi optimum bagi siri kajian yang seterusnya. Penambahan HNT ke dalam campuran berpenserasi telah meningkatkan semua sifat mekanikal. Analisis termogravimetri menunjukkan bahawa kestabilan haba PET/PP berpenserasi diisi HNT adalah lebih tinggi daripada campuran tidak berpengisi manakala, ujian indeks pengehad oksigen menunjukkan kebolehbakaran menurun dengan peningkatan jumlah HNT. Mikroskop elektron penghantaran menunjukkan bahawa terdapat interaksi antara HNT dan campuran penserasi PET/PP. Analisis pembelauan sinar-X menunjukkan berlaku interkalasi terhad antara HNT dan campuran PET/PP. Analisis spektroskopi inframerah transformasi fourier menunjukkan kewujudan ikatan hidrogen antara silikon monoksida dari HNT dengan kumpulan berkutub dari PET dan PP-g-MAH. Komposisi optimum dari segi sifat mekanikal PET/PP berpenserasi diisi HNT dicapai pada 2 phr HNT.

TABLE OF CONTENTS

CHAPTER	TITLE		PAGE
	DECLARATION		ii
	DEDICATION		iii
	ACKNOWLEDGEMENTS		iv
	ABSTRACT		v
	ABSTRAK		vi
	TABLE OF CONTENTS		vii
	LIST OF TABLES		xi
	LIST OF FIGURES		xii
	LIST OF ABBREVIATIONS		xv
	LIST OF SYMBOLS		xvii
	LIST OF APPENDICES		xviii
1	**INTRODUCTION**		1
	1.1	Background of the study	1
	1.2	Problem statements	3
	1.3	Objectives of research	4
	1.4	Scope of research	5
2	**LITERATURE REVIEW**		7
	2.1	Polyethylene Terephthalate (PET)	7
	2.2	Polypropylene	9
	2.3	Polymer blends	11
	2.4	PET/PP blends	11
	2.5	Role of compatibilizers in polymer blends	13

2.5.1 Applications of PP-g-MAH and SEBS-g-MAH as compatibilizers 14
2.6 Halloysite Nanotubes (HNT) 22
2.6.1 Morphologies and properties of halloysite nanotubes (HNT) 22
2.7 Polymer nanocomposites 24
2.7.1 Processing techniques of nanocomposites 24
2.7.1.1 Melt intercalation 24
2.7.1.2 Solution dispersion method 25
2.7.1.3 *In-situ* polymerization 25
2.7.2 PET/PP nanocomposites 26
2.8 Recent studies of halloysite nanotubes (HNT) 27
2.9 Recent studies on the flammability properties of HNT 30

3 METHODOLOGY 33
3.1 Materials 33
3.1.1 Polyethylene Terephthalate 33
3.1.2 Polypropylene 34
3.1.3 Halloysite Nanotubes 35
3.2 Blend formulations 36
3.3 Preparation of PET/PP nanocomposites 38
3.3.1 Pre-mixing 38
3.3.2 Twin Screw Extrusion 38
3.3.3 Injection Molding 38
3.4 Mechanical properties of PET/PP blends and nanocomposites 39
3.4.1 Tensile Test 39
3.4.2 Flexural Test 39
3.4.3 Izod Impact Test 39
3.5 Characterization of PET/PP blends 40
3.5.1 Scanning Electron Microscopy 40
3.6 Flammability test 40
3.6.1 Limiting oxygen index 40

	3.7	Characterization of HNT filled PET/PP nanocomposites	41
		3.7.1 Fourier Transform Infrared Spectroscopy Analysis	41
		3.7.2 X-ray Diffraction Analysis	41
		3.7.3 Transmission Electron Microscopy	41
	3.8	Thermal analysis	42
		3.8.1 Thermogravimetric Analysis	42
4	**RESULTS AND DISCUSSION**		43
	4.1	Effect of PP contents on PET/PP blends	43
		4.1.1 Mechanical properties	43
		4.1.2 Morphological properties	48
		4.1.2.1 Effect of PP contents on morphologies of PET/PP blends	48
	4.2	Effect of PP-g-MAH and SEBS-g-MAH loading on PET/PP blends	50
		4.2.1 Mechanical properties	50
		4.2.2 Morphological properties	59
		4.2.2.1 Effect of PP-g-MAH and SEBS-g-MAH contents on morphologies of PET/PP blends	59
	4.3	Effect of HNT contents on PET/PP/PP-g-MAH blends	63
		4.3.1 Mechanical properties	63
	4.4	TEM Morphology	70
	4.5	Flammability properties	74
	4.6	Thermal properties	75
		4.6.1 Thermogravimetric analysis (TGA)	75
	4.7	X-ray Diffraction analysis	78
	4.8	FTIR properties of HNT filled PET/PP nanocomposites	81
5	**CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK**		84
	5.1	Conclusions	84
	5.2	Recommendations	85

REFERENCES 87

Appendices A – C 94 - 100

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	General properties of PET	8
2.2	Properties of isotactic PP	10
2.3	Band position and the observed bands in the lattice region of halloysite	23
3.1	Properties of polyethylene terephthalate (PET)	34
3.2	Properties of Polypropylene (SM240)	35
3.3	HNTs properties from Applies Mineral Inc.	35
3.4	Formulation of PET/PP blends used in the first series of the study	36
3.5	Formulation of PET/PP/compatibilizers used in the second series of the study	36
3.6	Sample composition of PET/PP/PP-g-MAH/HNT	37
4.1	Data of LOI test of PET/PP/PP-g-MAH/HNT nanocomposites	74
4.2	The thermal stability parameters of PET/PP/PP-g-MAH blends with various loading of HNT	78
4.3	FTIR bands and assignments of HNT and PET/PP/PP-g-MAH blend	82

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Transesterification process to produce PET	8
2.2	Hydrolysis of PET	9
2.3	Typical characteristics of PP	11
2.4	SEM micrographs of the PET/PP blends (80/20)	12
2.5	SEM micrographs for the fracture surfaces	17
2.6	Dispersed phase size as a function of the amount of copolymer	18
2.7	Crystalline structure of HNT	22
2.8	Scheme of entrapment mechanism of thermal decomposition of PP/HNT nanocomposites	30
2.9	Heat release rate of neat PP and PP/HNT nanocomposites	31
2.10	HRR curves of LLDPE/HNT composites	32
4.1	Effect of PP content on the tensile strength of PET/PP blends	44
4.2	Effect of PP content on the tensile modulus of PET/PP blends	45
4.3	Effect of PP content on the flexural strength of PET/PP blends	46
4.4	Effect of PP content on the flexural modulus of PET/PP blends	47
4.5	Effect of PP content on the impact strength of PET/PP blends	48
4.6	SEM micrographs of fracture surface of PET/PP blends	50
4.7	Effect of PP-g-MAH and SEBS-g-MAH content on the tensile strength of PET/PP blends	51
4.8	Effect of PP-g-MAH and SEBS-g-MAH content on the tensile modulus of PET/PP blends	52

4.9	Effect of PP-g-MAH and SEBS-g-MAH content on the flexural strength of PET/PP blends	54
4.10	Effect of PP-g-MAH and SEBS-g-MAH content on the flexural modulus of PET/PP blends	55
4.11	Effect of PP-g-MAH and SEBS-g-MAH content on the impact strength of PET/PP blends	56
4.12	Proposed chemical reactions between PET, PP and PP-g-MAH	58
4.13	Proposed chemical reactions between PET, PP and SEBS-g-MAH	59
4.14	SEM micrographs taken from impact fractured surface of uncompatibilized PET/PP blend	61
4.15	SEM micrographs taken from impact fractured surface of compatibilized PET/PP blends	62
4.16	SEM micrographs taken from impact fractured surface of PET/PP blends	62
4.17	Effect of HNT contents on tensile strength of PET/PP/PP-g-MAH blends	64
4.18	Effect of HNT contents on tensile modulus of PET/PP/PP-g-MAH blends	65
4.19	Effect of HNT contents on flexural strength of PET/PP/PP-g-MAH blends	66
4.20	Effect of HNT contents on flexural modulus of PET/PP/PP-g-MAH blends	67
4.21	Effect of HNT contents on impact strength of PET/PP/PP-g-MAH blends	68
4.22	Proposed chemical bonding between PP-g-MAH and HNT	69
4.23	TEM images of PET/PP/PP-g-MAH/HNT nanocomposites	71
4.24	Inter-tubular interactions	72
4.25	TEM images of zig-zag structure formed by face-to-edge (black arrow) and edge-to-edge (white arrow) interactions between HNT	73
4.26	TGA curve of PET/PP/PP-g-MAH blends with various loading of HNT	77
4.27	DTG curve of PET/PP/PP-g-MAH blends with various loading of HNT	77
4.28	XRD pattern of pure HNT	79
4.29	XRD pattern of PET/PP/PP-g-MAH/HNT nanocomposites with different loading of HNT	80
4.30	The FTIR spectra of pure HNT and PET/PP/PP-g-MAH blend	81

4.31	The FTIR spectra of PET/PP/PP-g-MAH/HNT nanocomposites with various loading of HNT	83

LIST OF ABBREVIATIONS

ASTM	-	American Standard Test Method
BPO	-	Benzoyl peroxide
CNT	-	Carbon nanotubes
DCP	-	Dicumyl peroxide
DMT	-	Dimethyl terephthalate
DSC	-	Differential Scanning Calorimetry
EG	-	Ethylene glycol
E-GMA	-	Ethylene glycidyl methacrylate copolymer
E-EA-GMA	-	Ethylene ethylacrylate glycidyl methacrylate terpolymer
E-MeA-g-MA	-	Maleic anhydride modified ethylene methyl acrylate copolymer
EPM	-	Ethylene-propylene copolymer
FTIR	-	Fourier Transform Infrared Spectroscopy
HDPE	-	High density polyethylene
HDT	-	Heat distortion temperature
HNT	-	Halloysite nanotubes
L/D	-	Length to diameter ratio
LOI	-	Limiting oxygen index
MA	-	Maleic anhydride
MMT	-	Montmorillonite
PA 6	-	Polyamide 6
PET	-	Poly(ethylene) terephthalate
Phr	-	Parts per hundred
PP	-	Polypropylene
PP-g-MAH	-	Maleic anhydride grafted polypropylene
PS	-	Polystyrene
PTA	-	Purified terephthalic acid

SEBS-g-MAH	-	Maleic anhydride grafted styrene-ethylene/butylene-styrene
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis
UV	-	Ultra violet
XRD	-	X-ray diffraction

LIST OF SYMBOLS

T_c	-	Crystallinity temperature
T_g	-	Glass transition temperature
T_m	-	Melting temperature
phr	-	Part per hundred
mm	-	Millimetre
mm/min	-	Millimetre per minute
i.e.	-	That is
kV	-	Kilovolts
wt%	-	Weight percent
˚C/min	-	Degree celcius per minute
J/m	-	Joule/metre
%	-	Percent
°C	-	Degree Celcius
h	-	Hour
MPa	-	Mega pascal

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Limiting oxygen equipment and end-product	94
B	Abstract of publications in international journal	96
C	Abstract of scopus and proceeding through international conference	98

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Blending is a technique in which at least two polymers are added together to create a new material with enhanced properties or reduced cost. It offers the advantage of reduced research and development expense compared to the development of new monomers and polymers to yield a similar property profile (Koysuren *et al.*, 2010). The role of polymer blend technology is pervasive in the products of our everyday life. In the rapidly emerging technology, polymer blend can quickly respond to the developing needs, much faster than the time needed in creating new monomer or developing new polymer. As a result, many research have been done to explore the advantages of the polymer blends.

Several studies on polyethylene terephthalate (PET) blends with other polymers such as high density polyethylene (HDPE), polyamide 6 (PA6), and polystyrene (PS) has been investigated (Ávila and Duarte, 2003; Retolaza *et al.* 2005; and Ryan and Brian, 2008). PET is a low cost high performance thermoplastic polymer resin of the polyester resin. It is commonly used nowadays in synthetic fibers, thermoforming, electronics and packaging applications. PET may exist both as an amorphous and as a semi-crystalline polymer depending on its processing and thermal history. The semi crystalline material might appear transparent or opaque and white depending on its crystal structure and spherulite size. Currently, blends of PET with other polymers have been extensively investigated in order to explore new applications of PET other than packaging and electronics (Lee *et al*., 2000 and Ryan and Brian, 2008). PET offers many excellent physical properties. Nevertheless, the shortcomings of PET such as low impact strength, low rate of crystallization and low heat distortion temperature (HDT) have limited the use of its in certain applications (Wang *et al*., 2006).

The combination of polypropylene (PP) with PET offers some advantages due to the attractive properties of PP such as low density and high HDT. PP could facilitate crystallization of PET by heterogeneous nucleation and further raising blend stiffness (Papadopoulou and Kalfoglou, 2000). In addition, the lower permeability of PET towards water vapor and oxygen could be usefully utilized in packaging materials if the morphology of the alloy is optimized. PET/PP blend could be expected to combine the barrier properties of both components since the permeability of PET to gases is much lower than PP and permeability to water is higher than PP. The moisture sensitivity of PET may reduce due to the hydrophobic nature of PP and facilitate crystallization of PET (Papadopoulou and Kalfaglou, 2000).

Most of the physical blends are highly incompatible and this includes PET/PP blend. Hence, the constituents tend to form aggregations, resulting in separated phases that lead to inhomogeneous blends with poor interphase adhesion resulting in poor mechanical properties. It is also difficult to obtain a good dispersion in polymer blends, particularly for combinations of nonpolar with polar polymers (Calcagno *et al*., 2008). In order to overcome the problem of immiscible blend, some modifications of the interfaces or compatibilization are then necessary to obtain useful polymeric product with desired properties.

There are many types of compatibilizers used in PET/PP blends. Some of the compatibilizer that are widely used are polypropylene grafted maleic anhydride (PP-g-MAH), LLDPE-g-MAH, maleic anhydride grafted styrene-ethylene/butylene-styrene (SEBS-g-MAH), polypropylene grafted acrylic acid (PP-AA) and vinyl acetate (EVA) based graft copolymers (Lim and Chow, 2012; Calcagno *et al.*, 2008; Wang *et al.*, 2006; Papadopoulou and Kalfaglou, 1999; Oromiehie *et al*., 1997; and Dimitrova *et al.*, 2000). In this study, PP-g-MAH and SEBS-g-MAH were used as the compatibilizers because it has been proven both of the compatibilizers provide good dispersion in the blends, thus, improve the compatibility of blends and PET and PP composites (Lim and Chow, 2012; Calcagno *et al.*, 2008; Papadopoulou and Kalfaglou, 2000; Oromiehie *et al*., 1997).

Nowadays, there are many applications which demands the use of the reinforced materials and development of nanocomposites has been widely used with this purpose. In addition, polymer nanocomposite can often offer property profile combinations that are not easily obtained with new polymeric structures. The numerous inorganic fillers such as montmorillonite (MMT), halloysite nanotubes (HNT) and carbon nanotubes (CNT) are being used in the polymer composite industry with the objectives of reduction in the overall cost as well as acquiring the required material properties (Calcagno *et al.*, 2008; Du *et al.*, 2010 and Yesil and Bayram, 2011).

1.2 Problem statements

It is known that PET/PP blends are incompatible. In order to overcome the compatibility issues and improved properties of PET/PP blends, the compatibilizer was added into the blends. Although compatibilized PET/PP blends may have good properties, continues effort must be done to improve the materials to be more competitive.

In recent years, halloysite nanotubes (HNT) have been widely used to reinforce the polymer matrices such as PP, ethylene propylene diene monomer (EPDM) and PA 6. The incorporation of HNT can improve the properties of blends significantly. Addition of HNT can increase impact strength without sacrificing flexural modulus, strength and thermal stability. Besides that, a previous study suggested that HNT is promising as flame retardant fillers (Du *et al.*, 2006). In addition, HNT are much cheaper than other nanoparticles such as CNT, thus in this study, HNT will be used to produce PET/PP composites.

Studies of the effect of HNT on polymer nanocomposites of various matrices have been investigated (Jia *et al.*, 2009; Marney *et al.*, 2008; Ismail *et al*., 2009 and Handge *et al.*, 2010). Study on the effect of HNT on PET/PP composites however has not been reported.

1.3 Objectives of research

The main objective of this study is to develop a new material with better mechanical and flammability properties based on compatibilized PET/PP composites filled with halloysite nanotubes (HNT) as fillers. The main objective can be further divided into:

1) To determine the effects of blend ratio on the mechanical properties of PET/PP blends.
2) To study the effects of compatibilizers types and loading on the mechanical properties of the PET/PP blends.
3) To investigate the effect of HNT loading on the mechanical and flammability properties of the PET/PP nanocomposites.
4) To study the effects of HNT loading on the thermal and morphological properties of the PET/PP blends.

1.4 Scope of research

This research involved the preparation of samples (uncompatibilized and compatibilized PET/PP blend and PET/PP nanocomposites) includes the following stages:

i) Dry blending,
ii) Melt blending of samples,

Twin screw extruder was used to produce pellets of PET/PP blends followed by injection moulding of PET/PP. The content of PP was varied from 0, 20, 30, 40, 50 and 100 wt% each. Two different types of compatibilizer, which are PP-g-MAH and SEBS-g-MAH were added into PET/PP blends. The ratios of PP-g-MAH and SEBS-g-MAH were varied from 0, 2, 4, 6, 8 and 10 phr each. The inorganic fillers, HNT were used to reinforce the polymer matrix while equally improving the mechanical and flammability properties of the composite. HNT ratios were at 0, 2, 4, 6, 8 and 10 phr.

The tests below were done for characterization of the samples:

i) Mechanical properties of PET/PP blending with varying percentages of PP, compatibilizers and HNT were determined especially,

a) Tensile properties (ASTM D638)
b) Flexural properties (ASTM D790)
c) Impact properties (ASTM D256)

ii) Scanning Electron Microscopy (SEM) were carried out to examine the phase morphology of the uncompatibilized and compatibilized PET/PP blends with different ratios of PP and compatibilizers loading.

iii) The flammability properties of PET/PP nanocomposites with varying percentages of HNT were investigated using Limiting Oxygen Index (LOI) test in accordance to ASTM 2863.

iv) Thermogravimetric Analysis (TGA) was done to determine the thermal stability and thermal properties of the nanocomposites.

v) X-ray Difraction (XRD) Analysis and Transmission Electron Microscopy (TEM) were carried out to examine the phase morphology of the nanocomposites.

vi) Fourier Transform Infrared Spectroscopy (FTIR) was done to characterize the functional group exist in compatibilized PET/PP blend filled with HNT.

REFERENCES

Abdolrasoul O. and Meldrum I.G. (1999). Characterization of polyethylene terephthalate and functionalized polypropylene blends by different methods. *Iranian Polymer Journal*. 8 (3):1026-1265.

Alfredo C. E. (2008). *Industrial Polymers*. Munich: Hanser Publishers.

Akbari M., Zadhoush A. and Haghighat M. (2007). PET/PP blending by using PP-g-MA synthesized by solid phase. *Journal of Applied Polymer Science*. 104: 3986-3993.

Baoli O., Duxin L. and Yuejun L. (2009). Compatibilizing effect of maleated polypropylene on the mechanical properties of injection molded polypropylene/polyamide 6/functionalized-TiO_2 nanocomposites. *Composites Science and Technology*. 69: 421–426.

Berthier P. (1826). Analyse de I'halloysite. *Annales de Chimie et de Physique*. 32: 332-335.

Bhattacharya Sti N., Musa Rasim Kamal and Guota Rahul K. (2008). *Polymeric nanocomposites:theory and practice*. Carl Hanser Verlag: Munich.

Brydson J. A. (1999). *Plastics materials*. (7th ed.). Butterworth: Heinemann.

Calcagno C.I.W., Mariani C.M., Teixeira S.R., and Mauler R.S. (2008). The role of the MMT on the morphology and mechanical properties of the PP/PET blends. *Composite Science and Technology*. 68: 2193-2200.

Chen H., Pyda M., and Cebe P. (2009). Non-isothermal crystallization of PET/PLA blends. *Thermochimia Acta 492*. 61-66.

Cheung M. K. and Chan D. (1997). Mechanical and Rheological Properties of Poly(ethylene terephthalate)/ Polypropylene Blends. *Polymer International*. 43(3): 281-287.

Chongprakobkit S., Opaprakasit M. and Chuayjuljit S. (2007). Use of PP-g-MA prepared by solution process as compatibilizer in polypropylene/polyamide 6 blends. *Journal of Metals, Materials and Minerals*. 17(1): 9-16.

Chiu H. T. and Hsiao Y.K. (2006). Compatibilazation of poly(ethylene terephthalate)/polypropylene blends with maleic anhydride grafted polyethylene-octene elastomer. *Journal of Polymer Research*. 13: 153-160.

Deng S., Zhang J., Ye L. and Wu J. (2008). Toughening epoxies with halloysite nanotubes. *Polymer*. 49: 5119-5127.

Dimitrova T.L., Mantia L., .F.P., Pilati F., Toselli M., Valenza A. and Visco A. (2000). On the compatibilization of PET/HDPE blends through a new class of copolyester. *Polymer*. (41): 4817-4824.

Du M., Guo B. and Jia D. (2006). Thermal stability and flame retardant effects of halloysite nanotubes on poly(propylene). *European Polymer Journal*. 42: 1362-1369.

Du M., Guo B. and Jia D. (2010). Newly emerging applications of halloysite nanotubes: a review. *Polymer International*. 59: 574-582.

Du M., Guo B., Cai X., Jia Z., Liu M. and Jia D. (2008). Morphology and properties of halloysite nanotubes reinforced polypropylene nanocomposites. *E-polymer*. 130: 1–14.

Du M., Guo B., Liu M. and Jia D. (2006). Preparation and characterization of polypropylene grafted halloysite and their compatibility effect to polypropylene/halloysite composite. *Polymer Journal*. 38(11): 1198-1204.

Ferry M.H. & Becker A.V. (2004). *Handbook of Polymer Science and Technology*. Bangalore, New Delhi: CBS Publishers & Distributors.

Frost R.L. and Shurvell H.F. (1997). Raman microprobe spectroscopy of halloysite. *Clays and Clay Minerals*. 45(1): 68–72.

Ganguly A. and Bhowmick A. K. (2009). Effect of polar modification on morphology and properties of styrene-(ethylene-co-butylene)-styrene triblock copolymer and its montmorillonite clay-based nanocomposites. *Journal of Materials Science*. 44(3): 903-918.

Gartner C., Suarez M., Lopez B. L. (2008). Grafting of maleic anhydride on polypropylene and its effect on blending with poly(ethylene terephthalate). *Polymer Engineering and Science*. 48(10).

Guo B., Zou Q., Lei Y. and Jia D. (2009). Structure and performance of polyamide 6/halloysite nanotubes nanocomposites. *Polymer journal*. 41(10): 835-842.

Handge, U. A., Hedicke-Hochstotter K. and Altstadt V. (2010). Composites of polyamide 6 and silicate nanotubes of the mineral halloysite: Influence of molecular weight on thermal, mechanical and rheological properties. *Polymer*. 51(12): 2690-2699.

Heino M., Kirjava J., Hietaoja P. and Seppala J. (1997). Compatibilization of polyethylene terephthalate/polypropylene blends with styrene–ethylene/butylene–styrene (SEBS) block copolymers. *Journal of Applied Polymer Science*. 65(2): 241-249.

Hillier S. and Ryan P.C. (2002). Identification of halloysite (7Å) by ethylene glycol solvation: the ‘MacEwan effect’. *Clay Minerals*. 37: 487-496.

Inuwa I. M., Hassan A., Samsudin S. A., Mohamad Haafiz M. K., and Jawaid M. (2015). Interface modification of compatibilized polyethylene terephthalate/ polypropylene blends: Effect of compatibilization on thermomechanical properties and thermal stability. *Journal of Vinyl & Additive Technology*. DOI: 10.1002/vnl.21484.

Inuwa I. M., Hassan A., Samsudin S. A., Mohamad Haafiz M. K., and Jawaid M., Majeed K. and Abdul Razak N. C. (2014). Characterization and mechanical properties of exfoliated graphite nanoplatelets reinforced polyethylene terephthalate/polypropylene composites. *Journal of Applied Polymer Science*. 131(15).

Ismail, H., Pooria Pasbakhsh, Ahmad Fauzi M. N. and Abu Bakar A. (2009). The effect of halloysite nanotubes as a novel nanofiller on curing behaviour, mechanical and microstructural properties of ethylene propylene diene monomer (EPDM) nanocomposites. *Polymer-Palstics Technology and Engineering*. 48: 313-323.

Jamaludin N. A., Inuwa I. M., Hassan A., Othman N. and Jawaid M. (2015). Mechanical and thermal properties of SEBS-g-MA compatibilized halloysite nanotubes reinforced polyethylene terephthalate/polycarbonate/ nanocomposites. *Journal of Applied Polymer Science*. 132(39).

Jia, Z., Luo, Y., Guo, B., Yang, B., Du, M. and Jia, D. (2009). Reinforcing and flame-retardant effects of halloysite nanotubes on LLDPE. *Polymer-Plastics Technology and Engineering*. 48(6): 607-613.

Joseph H. K. (2006). *Polymer nanocomposites: Processing, Characterization and Applications*. McGraw-Hill Nanoscience and Technology Series.

Joussein E., Petit S., Churchman J., Theng B., Righi D. and Delvaux B. (2005). Halloysite clay minerals — a review. *Clay Minerals*. 40(4): 383-426.

Kalfoglou N.K., Skafidas D.S. and Kallitsis J.K. (1995). Comparison of compatibilizer effectiveness for PET/HDPE blends. *Polymer.* 36(23): 4453-4462.

Kordjazi Z. and Ebrahimi N. G. (2009). Rheological behavior of noncompatibilized and compatibilized PP/PET blends with SEBS-g-MA. *Journal of Applied Polymer Science.* 116: 441-448.

Lan T and Pinnavaia T. J. (1994). Clay-reinforced epoxy nanocomposites. *Chemical Materials.* 6: 2216-2219.

Lecouvet B., Sclavons M., Bourbigot S., Devaux J. and Bailly C. (2011). Water-assisted extrusionas a novel processing route to prepare polypropylene/halloysite nanotube nanocomposites: Structure and properties. *Polymer*. 52: 4284-4295.

Lee W. J., Ki H. L., Dong C. L., Jin S. Y., In J. C., Hyoung J. C. and Kwang H. L. (2000). Alternating copolymers as compatibilizer for blends of poly(ethylene terephthalate) and polystyrene. *Journal of Applied Polymer Science*. 78(11): 1998-2007.

Lepers J.C., Favis B.D. and Tabar R. J. (1997). The Relative Role of Coalescence and Interfacial Tension in Controlling Dispersed Phase Size Reduction during the Compatibilization of Polyethylene Terephthalate/Polypropylene Blends. *Journal of Polymer Science: Part B: Polymer Physics*. 35: 2271-2280.

Lepers J.C., Favis B.D. and Lacroix C. (1999). The influence of partial emulsification on coalescence suppression and interfacial tension reduction in PP/PET blends. *Journal of Polymer Science Part B: Polymer Physics*. 37(9): 939-951.

Li, Q., Wu, C. and Zhu, P. (2011). Effect of maleic-anhydride-grafted polypropylene as a compatibilizer on the properties of polypropylene/(modified carbon black) composites. *Journal of Vinyl and Additive Technology.* 17(4): 260-264.

Lim, S.R. and Chow, W.S. (2012). Impact, thermal, and morphological properties of functionalized rubber toughened-poly(ethylene terephthalate) nanocomposites. *Journal of Applied Polymer Science*. 123(5): 3173-3181.

Lou C. W., Lin C. W., Lei C. H., Su K. H., Hsu C. H., Liu Z. H. and Lin J. H. (2007). PET/PP blend with bamboo charcoal to produce functional composites. *Journal of Materials Processing Technology*. 428–433.

Marney D.C.O, Russell L.J., Wu D.Y., Nguyen T., Cramm D., Rigopoulos N., Wright N. and Greaves M. (2008). The suitability of halloysite nanotubes as a fire retardant for nylon 6. *Elsevier polymer degradation and stability*. 93(10): 1971-1978.

Messersmith P. B. and Giannelis E. P. (1994). Synthesis and characterization of layered silicate-epoxy nanocomposites. *Chemical Materials*. 6: 1719-1725.

Ning, N. Y., Yin, Q. J., Luo, F., Zhang, Q., Du, R. and Fu, Q. (2007). Crystallization behavior and mechanical properties of polypropylene/halloysite composites. *Polymer*. 48(25): 7374-7384.

Nwabunma D. and Kyu T. (2007). *Polyolefin Composites*. Wiley-Interscience, A John Wiley & Sons, Inc., Publication.

Oromehie, A. R., Hashemi S. A., Meldrum I. G. and Waters D. N. (1997). Functionalisation of Polypropylene with Maleic Anhydride and Acrylic Acid for Compatibilising Blends of Polypropylene with Poly(ethylene terephthalate). *Polymer International*. 42(1): 117-120.

Pang Y.X., Jia D.M., Hu H. J. Hourston D. J. and Song M. (2000). Effects of a compatibilizing agent on the morphology, interface and mechanical behaviour of polypropylene/poly(ethylene terephthalate) blends. *Polymer*. 41: 357-365.

Papadopoulou C.P. and Kalfoglou N.K. (2000). Comparison of compatibilizer effectiveness for PET/PP blends: their mechanical, thermal and morphology characterization. Polymer 41: 2543-2555.

Pasbakhsh P., Ismail H., Ahmad Fauzi M. N. and Abu Bakar A. (2009). Influence of maleic anhydride grafted ethylene propylene diene monomer (MAH-g-EPDM) on the properties of EPDM nanocomposites reinforced by halloysite nanotubes. *Polymer Testing*. 28: 548-559.

Pasquini N. (2004). *Polypropylene Handbook*. (2^{nd} ed.). Munich: Hanser.

Paul C.P. and Michael M.C. (1997). *Fundamentals of Polymer Science An Introductory Text*. (2^{nd} ed.). The Pennsylvania State University: CRC PRESS.

Paul D.R. & Bucknall C.B., (1999). *Polymer Blends*. Volume 2: Performance. John Wiley & Sons: A Wiley-Interscience Publication.

Peacock J.A. and Calhoun A. (2006). *Polymer chemistry; properties and applications*. Cincinnati: Hanser Gardner Publications.

Pooria P., Ismail H., Ahmad Fauzi M.N. and Abu Bakar A. (2010). EPDM/modified halloysite nanocomposites. *Applied Clay Science*. 48: 405-413.

Prashantha K., Lacrampe M.F. and Krawczak P. (2011). Processing and characterization of halloysite nanotubes filled polypropylene nanocomposites based on masterbatch route: effect of halloysites treatment on structural and mechanical properties. *eXPRESS Polymer Letters*. 5(4): 295-307.

Pruthtikul R. and Liewchirakorn P. (2010). Preparation of polypropylene graft maleic anhydride (PP-g-MA) via twin screw extrusion. *Advanced Materials Research.* 93(94): 451-454.

Pulickel M. Ajayan, Linda S.S. and Paul V.B. (2003). *Nanocomposite Science and Technology*. Weinheim: WILEY-VCH GmbH & Co. KGaA.

Qiu W., Endo T. and Hirotsu T. (2005). A novel technique for preparing of maleic anhydride grafted polyolefins. *European Polymer Journal*. 41(9): 1979-1984.

Retolaza A., Eguiazabal J.I. and Nazabl J. (2005). Reactive Processing Compatibilization of Direct Injection Molded Polyamide-6/Poly(Ethylene Terephthalate) Blends. *Journal of Applied Polymer Science*. 97: 564 - 574.

Ryan J. S. and Brian S. M. (2008). Solid-state blending of poly(ethylene terephthalate) with polystyrene: Extent of compatibilization and its dependence on blend composition. *Polymer Engineering and Science*. 649-655.

Su Z., Jiang P., Li Q., Wei P. and Zhang Y. (2004). Toughening of polypropylene highly filled with aluminium hydroxide. *Polymers & Polymer Composites*. 13: 139-150.

Singh B. (1996). Why does halloysite roll - A new model. *Clays and Clay Minerals.* 44(2): 191–196.

Thomas S. and Weimin Y. (2009). Advances in polymer processing: From macro to nano scales. Woodhead Publishing in Materials.

Tripathi D. (2002). *Practical guide to polypropylene*. RAPRA Technology Ltd.

Ulrich A.H, Katrin H. H. and Altstadt V. (2010). Composites of polyamide 6 and silicate nanotubes of the mineral halloysite: Influence of molecular weight on thermal, mechanical and rheological properties. *Polymer.* 51: 2690-2699.

Vaia R. A. and Giannelis E. P. (1997). Polymer melt intercalation in organically-modified layered silicates: Model predictions and experiment. *Macromolecules* 30: 8000-8009.

Wang M. J (1998). Effect of polymer-filler and filler-filler interactions on dynamic properties of filled vulcanizates. *Rubber Chemical Technology*. 71(3): 520-89.

Wang Y., Gao J., Ma Y. and Agarwal U. S. (2006). Study on mechanical properties, thermal stability and crystallization behavior of PET/MMT nanocomposites. *Composites Part B: Engineering*. 37(6): 399-407.

Yano K., Usuki A., Okada A., Kurauchi T. and Kamigaito O. (1993). Synthesis and properties of polyimide-clay hybrid. *Journal of polymer science, Part A: polymer chemistry*. 31:2493-2498.

Yesil S. and Bayram G. (2011). Poly(ethylene terephthalate)/carbon nanotube composites prepared with chemically treated carbon nanotubes. *Polymer Engineering and Science*. 1286-1300.

Yoon, B. S., Joang, J. Y., Suh, M. H., Lee, Y. M. and Lee, S. H. (1997). Mechanical properties of polypropylene/polyamide 6 blends: Effect of manufacturing processes and compatibilization. *Polymer Composites.* 18(6): 757-764.

Yousef A. M. (2011). Thermal and mechanical properties of polyethylene terephthalate/polycarbonate nanocomposites modified by lanthanum acetyl acetonate hydrate. *Polymer-Plastics Technology and Engineering*. 50: 635-645.

Zhao M. and Liu P. (2008). Halloysite nanotubes/polystyrene (HNTs/PP) nanocomposites via in situ bulk polymerization. *Journal of thermal analysis and calorimetry*. 94(1): 103-107.

Zhang Y., He X., Ouyang O. and Yang H. (20013). Palladium nanoparticles deposited on silanized halloysite nanotubes: synthesis, characterization and enhanced catalytic property. *Scientific reports*. 3: 2948.