EFFECT OF GRAPHENE ON MECHANICAL PROPERTIES AND FLAME RETARDANCY OF POLYCARBONATE/ ACRYLONITRILE BUTADIENE STYRENE NANOCOMPOSITES

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A dissertation submitted in fulfillment of the requirements for the award of the degree of Master of Science (Polymer Technology)

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> > 2014

To my beloved parents and sister

First and foremost, I would like to acknowledge my supervisor, Prof. Dr. Azman Bin Hassan, for his encouragement, guidance and inspiration throughout this research.

I wish to express my deep appreciation to all the lecturers from Department of Polymer Engineering who have directly or indirectly contributed towards the success of my research project. I also wish to thanks all the technicians of laboratories of polymer engineering for their help in my research.

Most importantly, I would like to extend my sincere thanks to my family for their continuous love and encouragement, for always believing in me and never failing to provide me any support.

ABSTRAK

Polikarbonat/akrilonitril butadiena stirena (PC/ABS) komposit nano yang mengandungi platelet nano grafin (GNPs) dan bisfenol A bis (difenil fosfat) (BDP) telah berjaya dihasilkan dengan menggunakan penyemperit skru berkembar berlawanan arah dan diikuti dengan pengacuan suntikan. Di dalam kajian ini BDP telah digunakan sebagai bahan perencat api. Sifat-sifat mekanikal komposit nano telah dikaji melalui ujian tegangan, lenturan dan hentaman. Termogravimetri analisis (TGA) digunakan untuk menilai sifat-sifat terma komposit nano, dan morfologi komposit nano diperhatikan melalui imbasan elektron mikroskop (FESEM). Struktur kimia komposit nano PC/ABS telah diuji melalui fourier infra merah (FTIR). Kebolehbakaran komposit nano telah diukur dengan menggunakan indeks penghad oksigen (LOI) dan UL94. Sifat-sifat mekanikal adunan PC/ABS meningkat apabila GNPs dan BDP digabungkan. 3wt.% kandungan GNPs memberikan nilai maksimum bagi kekuatan sifat regangan, modulus Young dan sifat kebolehlenturan bagi komposit nano. Analisis TGA mendedahkan kestabilan terma PC/ABS/BDP dan komposit nano telah meningkat dengan ketara berbanding dengan yang PC/ABS. Ini dapat dilihat apabila 1wt.% GPNs digunakan 20% suhu kehilangan berat (T20) meningkat sebanyak 23 °C. Baki hasil pembakaran PC/ABS/GNPs3 meningkat secara dramatik sebanyak 64 % apabila 10 wt.% BDP ditambah. Sinergi dalam LOI dan UL94 telah diperhatikan untuk PC/ABS/GNPs3/BDP10 dibandingkan dengan PC/ABS/BDP. GNPs telah tersebar dengan baik didalam adunan PC/ABS seperti didedahkan oleh FESEM. Interkalasi GNPs turut diperhatikan apabila BDP ditambah kepada komposit nano. Spektrum FTIR menunjukkan bahawa penambahan GNPs ke dalam PC/ABS matriks tidak membawa apa-apa perubahan ketara dalam struktur kimia. Walau bagaimanapun beberapa interaksi ikatan hidrogen antara GNPs dan campuran PC/ABS dicadangkan.

TABLE OF CONTENTS

CHAPTER		TITLE	PAGE	
	DECL	ARATION	ii	
	DEDICATION			
	ACKN	IOWLEDGEMENTS	iv	
	ABSTRACT			
	ABSTRAK TABLE OF CONTENTS			
	LIST	OF TABLES	xi	
	LIST OF FIGURES LIST OF ABBREVIATION			
	LIST	OF SYMBOLS	xvi	
1.	INTR	ODUCTION	1	
	1.1	Background of the Study	1	
	1.2	Problem Statement	4	
	1.3	Objective of the Study	5	
	1.4	Scope of the Study	6	
2.	LITE]	RATURE REVIEW	7	
	2.1	Polycarbonate	7	
		2.1.1 Application of PC	8	
		2.1.2 Advantages and disadvantage of PC	9	
	2.2	Acrylonitrile-butadiene-styrene	10	
		2.2.1 Applications of ABS	12	
		2.2.2 Advantage and disadvantage of ABS	12	
	2.3 Polymer Blends		13	

		2.3.1 Blend of ABS and PC	15
		2.3.2 Overview of PC/ABS blends	19
	2.4	Halogen-free flame-retardants	21
		2.4.1 Reason for adding flame retardants to polymers	22
		2.4.2 Bis phenol A bis (diphenyl phosphate)	23
		2.4.3 Flame retardancy of BDP on ABS/PC blends	25
	2.5	Nanocomposite technology	30
	2.6	Fillers	32
		2.6.1 Graphene nanoplatelets	
		2.6.2 Polymer graphene nanocomposites	36
	2.7	Nanocomposite Preparation Methods	37
3.	METH	IODODLOGY	40
	3.1	Materials and methods	40
	3.2	Blend preparation	41
	3.3	Mechanical testing	42
		3.3.1 Tensile test	42
		3.3.2 Flexural test	43
		3.3.3 Impact test	43
	3.4	Thermal properties	44
		3.4.1 Thermogravimetric analysis (TGA)	44
	3.5	Chemical characterization and morphological analysis	45
		3.5.1 Fourier transform infra-red spectroscopy (FTIR)	45
		3.5.2 Field emission scanning electron microscopy	
		(FESEM)	45
	3.6	Flame retardancy analysis	46
		3.6.1 Limiting oxygen index (LOI)	46
		3.6.2 UL-94 properties	46
4	RESU	LTS AND DISCUSSION	47
	4.1	Mechanical properties	47
		4.1.1 Tensile strength of PC/ABS/GNPs nanocoposites	47
		4.1.2 Young modulus of PC/ABS/GNPs nanocoposites	49

	4.1.3 Elongation at break of PC/ABS/GNPs nanocoposites	50
	4.1.4 Flexural strength of PC/ABS/GNPs nanocoposites	51
	4.1.5 Impact strength of PC/ABS/GNPs nanocoposites	54
	4.1.6 Tensile strength of PC/ABS/BDP and	
	PC/ABS/GNP3/BDP nanocomposites	55
	4.1.7 Young modulus of PC/ABS/BDP and	
	PC/ABS/GNP3/BDP nanocomposites	57
	4.1.8 Flexural test of PC/ABS/BDP and	
	PC/ABS/GNP3/BDP nanocomposites	60
	4.1.9 Impact strength of PC/ABS/BDP and	
	PC/ABS/GNP3/BDP nanocomposites	62
4.2	Thermal properties	64
	4.2.1 Thermogravimetry analysis	64
4.3	Flame retardancy analysis	71
	4.3.1 Limiting oxygen index of PC/ABS/GNPs	
	nanocomposites	71
	4.3.2 Limiting oxygen index of PC/ABS/BDP and	
	PC/ABS/GNP3/BDP nanocomposites	73
	4.3.3 UL-94 properties of PC/ABS/GNPs nanocomposites	73
	4.3.4 UL-94 properties of PC/ABS/BDP and	
	PC/ABS/GNP3/BDP nanocomposites	74
4.4	Morphological study	76
	4.4.1 Field emission scanning electron microscopy	76
	4.4.2 Fourier transform infra-red spectroscopy	79
CONC	LUSION AND RECOMMENDATION	82
5.1	Conclusion	82
5.2	Recommendations for future works	83

5

REFERENCES

85

Х

LIST OF TABLES

TITLE

TABLE NO.

2.1	Mechanical properties of PC, ABS and their blends	16
2.2	The physical and chemical properties of BDP	24
2.3	Physical properties of neat PC/ABS and the blend	
	fire retarded with BDP	26
2.4	Properties of GNPs, CNT, nano sized steel, and polymers	35
3.1	General properties of BDP	40
3.2	General Properties of GNPs	41
3.3	Compounding formulations for PC/ABS/GNPs/BDP	42
3.4	Dimension specification for Izod impact test specimen	44
4.1	TGA and DTG results of PC/ABS, PC/ABS/GNPs,	
	PC/ABS/BDP and PC/ABS/GNPs/BDP	71
4.2	Effect of GNPs content on the LOI values of all	
	PC/ABS nanocomposites	72
4.3	The effect of BDP and BDP with GNPs on the LOI values	
	of PC/ABS nanocomposites	73
4.4	The UL-94 results of PC/ABS/GNPs nanocomposites	74
4.5	UL-94 results for PC/ABS / BDP and PC/ABS/GNP3/BDF	P 75

PAGE

LIST OF FIGURES

NOTITLE PAGE

2.1	Reaction of bisphenol A (BPA) and phosgene COCl_2	10
2.2	Chemical structure of ABS	11
2.3	Stress-strain curve for PC, ABS and their blends	16
2.4	Tensile properties of ABS/PC blends	17
2.5	Effect of blend ratio on impact properties of ABS/PC ble	end 18
2.6	Plot of fire hazard (heat release capacity) versus	
	materials'cost. Plot courtesy	23
2.7	Chemical structure of RDP	24
2.8	Chemical structure of BDP	24
2.9	Thermogravimetry curves for TPP, RDP, and BDP. Hea	ting
	rate 10°C/min, argon flow 60 cm3/min	25
2.10	The oxygen index data for various PC/ABS blends	
	flame retarded by aryl phosphates	26
2.11	Thermogravimetry curves of neat PC/ABS (3:1) and	
	the blend fire retarded with aryl phosphates	27
2.12	Izod impact strength of various PC/ABS blends	
	fire retarded with aryl phosphates)	28
2.13	Representative specimens after UL 94 vertical test (0,	
	original size of all specimens; 1, PC/ABS; 2,	
	PC/ABS + PTFE; 3, PC/ABS + BDP; 4,	
	PC/ABS + PTFE + BDP; 5, PC/ABS + RDP + PTFE;	
	6, PC/ABS + TPP + PTFE).	29
2.14	GNP (top left) is a carbon atoms honeycomb	
	structure. Graphite (top right) is stack of graphene	
	layers. Carbone nanotube (bottom left) is a rolled up	

	cylinder of graphene	34
4.1	Effect of GNPs content on tensile strength of PC/ABS	
	nanocomosite	48
4.2	FESEM images of PC/ABS/GNPs3	49
4.3	Effect of GNPs content on Young's modulus	
	of PC/ABS nanocomposites	50
4.4	Effect of GNPs content on elongation at break	
	of PC/ABS nanocomposites	51
4.5	Effect of GNPs content on (a) flexural strength	
	and (b) flexural modulus of ABS/PC nanocomosite	53
4.6	Effect of GNPs content, on impact strength	
	of PC/ABS nanocomposites	54
4.7	Effect of BDP content and GNP3/BDP content	
	on tensile strength and elongation at break of PC/ABS.	56
4.8	FESEM images of PC/ABS/GNPs3/BDP10	57
4.9	Effect of BDP content, Yong's modulus of (a)	
	PC/ABS blend and (b) PC/ABS/GNPs3 nanocomposite	59
4.10	Effect of BDP and GNPs3/BDP content on	
	flexural strength and flexural modulus of PC/ABS	61
4.11	Effect of BDP and GNPs3/BDP content on	
	impact strength of PC/ABS	63
4.12	TGA and DTG curves of PC/ABS and	
	PC/ABS/GNPs nanocomposites	66
4.13	(a) TGA and (b) DTG curves for the PC/ABS and	
	PC/ABS/BDP in different percentage of BDP	68
4.14	(a) TGA and (b) DTG results of PC/ABS, PC/ABS/GNPs,	
	PC/ABS/BDP and PC/ABS/GNPs/BDP	70
4.14	UL-94 results for all PC/ABS samples	75
4.15	FESEM images of (a-d) PC/ABS (e-h) PC/ABS/GNPs	
	and (f-l) PC/ABS/GNPs 3 with 10 wt.% BDP content	78
4.16	FTIR spectra of (a-b) GNPs, PC/ABS and	
	(c).PC/ABS/GNPs, PC/ABS/BDP10)	76

xiii

LIST OF ABBREVIATION

ABS	-	Acrylonitrile-butadiene-styrene
ASTM	-	American standard testing methods
BDP	-	Bisphenol A bis(diphenyl phosphate)Safety
BEP	-	Bisphenol A bis(diethyl phosphate)
CNT	-	Carbon nanotube
CO_2	-	Carbon dioxide
DSC	-	Differential scanning calorimetry
EVA	-	Ethylene-vinyl acetate
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared
GNPs	-	Graphene nanoplatelets
HRR	-	Heat release rate
LOI	-	Limiting oxygen index
Mw	-	Molecular weight
N_2	-	Nitrogen
O_2	-	Oxygen
PA6	-	Polyamide 6
PC	-	Polycarbonate
PDMS	-	Poly dimethylsiloxane
PEN	-	Poly(ethylene-2,6-naphthalate)
Phr	-	Parts per hundred
PHRR	-	Peak heat release rate
PLA	-	Poly(lactic acid)
PLS	-	Polymer/layered silicate
PMMA	-	Poly methyl methacrylate
PP	-	Poly(propylene)
PS	-	Poly(styrene)

PVA	-	Poly(vinyl alcohol)
PVC	-	Poly(vinyl chloride)
RDP	-	Resorcinol bis(diphenyl phosphate)
SWCNT	-	Single wall carbon nanotube
t _{ign}	-	Ignition time
TGA	-	Thermogravimetric analysis
TPP	-	Triphenyl phosphate
UL 94	-	Universal laboratory burning champer
VST	-	Vicat softening temperature
wt. %	-	Weight percentage
xGnP	-	Exfoliated graphene nanoplatelets
XRD	-	X-ray diffraction

LIST OF SYMBOLS

Å	-	Angstrom
	-	Diffraction angle (°)
λ	_	X-ray wavelength (Å)
μm	-	Micrometer

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Recently polymeric materials are structured by "on-demand properties". They are also performance through the blending a kind of polymer with the other polymers, additives or fillers. The ability to combine the existing polymer into new composites with commercialize properties, that offers the advantage of reducing the research and development cost compared to the development of new monomer and synthesize modern polymer to yield a comparable property configuration. Polymer blending has been accepted as a significant technique to make new and valuable polymeric products. The resulting material may obligate properties superior toward the components by blending polymers. However it can be attractive to industry as much less costly and time saving approach to meet the need for high performance material than would be the synthesis and development of an entirely.

One of the engineering thermoplastics with the widely used in a variety of high performance application is polycarbonate (PC). It is a kind of ductile thermoplastic compare to the other polymers such as nylon, polyesters, etc. The application of PC is limited by the notch sensitivity in thicker samples and by the processing properties. It is shown that addition of small amount of modifier such as polyolefins, ABS to PC can improve the notch sensivity and other mechanical and processing properties of net PC.

Acrylonitrile-butadiene-styrene (ABS) is the largest-volume engineering thermoplastic resin. It consists of two phases. The main construction of ABS is the styrene - acrylonitrile (SAN) that formulate a continuous matrix, and the second phase is referred to the composed of dispersed poly butadiene particles that contain the layers of SAN grafted on to their surface. The compatible of these two phases are prepared by SAN layers. ABS resins are commonly used in polymer blends, notably with PC to increase its mechanical properties. The PC/ABS blends are known to possess high impact strength and many other desirable properties. Since it can be easily processed.

PC/ABS blends have been widely utilized as an engineering thermoplastic. Many studies have been carried out on ABS/PC blends (Balakrishnan *et al.*, 1998; Chiang and Hwung, 1987; Choi *et al.*, 2000; Lee *et al.*, 2008; Ogoe *et al.*, 1996). Between the interesting finding of these studies are that ABS supplies the advantages of economics, processability and more certain impact resistance, while PC contributes the improvement of tensile, flexural, thermal properties and flammability to the blends. Investigation of the deformation behavior of PC/ABS alloy is important for their engineering application and extensive works have been carried out.

Notomi *et al.* (2000) has experimented the tensile deformation and fracture of PC/ABS blend. Fang *et al.* (2006) expanded a three-dimensional displacement measurement system to experimental study the large tensile deformation behavior of PC/ABS alloy. Seelig and van der Giessen (2002) numerically analyzed the localized plastic deformation in PC/ABS blend with respect to its dependence on strain rate. Yin *et al.*(2008) studied the viscoelastic deformation behavior of PC/ABS blends with DMA and static relaxation tests.

Since thermoplastics, include PC/ABS blends, are easily combustible, flameretarding formulation are desirable to reduce the probability of burning in the initial phase of a fire. The flame retardant makes disruption of the burning process so that it is terminated within an acceptable period of time, preferably before ignition actually occurs. Environmental regulations have restricted the use of halogen FR additives because of the generation of toxic gases and high levels of smoke this has initiated a search for alternative FR additives (Kashiwagi *et al.*, 2005).

Recently, worldwide interests in halogen-free flame retardants (FRs) have been mounting in the light of possible or potential health and environment hazards associated with the application of halogenated FRs (Morgan, 2006). Many kinds of halogen-free FRs have been developed, such as boron-containing compounds, phosphorus-containing compounds, nitrogen-containing compounds, siliconcontaining compounds as well as some inorganic. Among them, the phosphoruscontaining compounds or aryl phosphates are the most promising halogen-free FRs. For instance red phosphorus, triphenyl phosphate (TPP), resorcinol bis(biphenyl phosphate) (RDP), and bisphenol A bis(biphenyl phosphate) (BDP) are widely used in polyolefin, polycarbonate (PC), and PC/ABS alloys. The flame retardancy mechanisms of aryl phosphates in PC/ABS were examined by (Levchik and Weil, 2004). Within all flame retardants used in PC/ABS, aryl phosphates, including BDP would be a successful alternative for flame retardants containing halogen. The BDP volatilizes in the temperature interval of 320-500°C, which is higher than that of RDP (280-460°C). Thus, BDP is the most thermally persistent of the three phosphates, probably because of its higher molecular weight (Levchik and Weil, 2004).

Nanoparticle fillers are highly attractive for this purpose because they can simultaneously improve the flammability and physical properties of polymer nanocomposites (Feyz *et al.*, 2011). Nanocomposite technology has been described as the new frontier of material science due to the employment of a few amount of nano filler which enhances mechanical, thermal, dimensional and barrier performance properties significantly (Alexandre and Dubois, 2000; LeBaron *et al.*, 1999). Among of nano fillers single layer two-dimensional graphene nanoplates

(GNPs) is considered as the strongest material along with high surface area and aspect ratio (Lee et al., 2008). In addition, manufacturing cost for GNPs is lower compared to other high performance carbon-based nano structured materials, such as carbon nanotubes (CNTs) (Kuilla et al., 2010). Therefore GNPs would be an interesting candidate as new reinforcing nano filler to enhance the properties of polymers (H. Kim et al., 2010). A number of literatures have been dedicated to investigate potential of GNPs for improving the electrical, mechanical, thermal, and flame retardant properties of polymers. The present study focused on the effect of GNPs on the properties of PC/ABS blends. No systematic studies have been done so far to investigate the properties of PC/ABS/GNPs nanocomosites. Higginbotham et al. (2009) prepared graphene oxide (GO) with PC, ABS, and high-impact polystyrene for the purpose of evaluating the flammability reduction and material properties of the resulting systems which resulted in improvement in thermal, mechanical and electrical properties. Wang et al.(2011) also studied synergistic effect of GNPs on anti-dripping, fire resistance of intumescent flame retardant and mechanical properties of poly butylene succinate (PBS) composites due to the nanoreinforcement and unique physical properties of GNPs.

1.2 Problem Statement

Blending of polymers offers a simple and relatively cheap way to develop novel materials with a number of valuable properties. Studies on blending ABS with PC polymers had received considerably attentions due to their compatibility, rigidity and chemical resistance (Herpels and Mascia, 1990). In general PC/ABS blends are low hardness and expensive, so many researchers and industrialists are trying to introduce the alternative materials such as filler into this blend to enhance mechanical properties as well as improving the thermal properties at a cheaper cost. In recent years, studies on graphite derivatives (whether that of micro and nano-scale particles) incorporated into a single polymeric matrix such as EVA by Kim *et al.*(2009) and PC by Higginbotham *et al.* (2009) polymers has received much attention and favorable results had been obtained due its availability, low cost and high aspect ratio and non-toxicity. Detaile study on the characterization of PC/ABS/GNPs nanocomposites has not been reported in the literature.

The blends of PC/ABS are widely used for flame-retardant electrical and electronic enclosures. However, they are easily combustible mainly because of major drawback of ABS which is high flammable. Therefore, to overcome this problem variety of flame retardants were used however, further investigation on the affect of halogen free flame retardants such as BDP is needed. It is expected that the incorporation of BDP and GNPs would enhance the mechanical properties as well as thermal properties improvement. Meanwhile BDP can offer enhancement of flame retardancy of related blends. Moreover, the possibility of synergistic effect between GNPs and BDP for improvement of flame-retardancy and mechanical properties will be expected.

1.3 Objectives of the Study

The overall aim of the present work was to improve the mechanical properties and flame resistant performance of PC/ABS blends by incorporation of GNPs and BDP into the polymer matrix. The objectives of this study are as follows:

- 1. To determine the effects of GNPs as nano fillers on mechanical, flame retardancy and thermal properties of PC/ABS blends.
- To study on the effect of BDP as flame retardant on mechanical, flame retardancy and thermal properties of GNPs filled PC/ABS nanocomposites.

1.4 Scope of the Study

The scope of the study covered the preparation of the blend formulation to conducting various tests on the samples. According to Tjong and Meng (2000) and Jin *et al* (1998) the blends were consisted of a fixed PC/ABS blend composition of 70/30 blend. The halogen-free flame retardant which is BDP was introduced into the polymer matrix. In addition, the content of GNPs also varied to evaluate the effect of filler loading on the composites.

- 1. Fabrication of PC/ABS /BDP blends using twin screw extruder.
- 2. Fabrication of PC/ABS/ GNPs nanocomposite using twin screw extruder.
- 3. Fabrication of PC/ABS/ BDP/GNPs using twin screw extruder.
- 4. Fabrication of The composite and nanocomposite specimens via injection molding for analysis.
- 5. Evaluating the physical and mechanical properties of the prepared blend and nanocomposite by means of tensile strength, tensile modulus, and elongation at break, flexural test and Izod impact test.
- 6. Characterizing the thermal and structural properties of the of the prepared blend and nanocomposite using, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) and Fourier transform infra-red (FTIR) spectroscopy.
- 7. Evaluating the flame retardancy properties of the prepared blend and nanocomposite using UL-94 and limiting oxygen index (LOI).

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