

MECHANICAL AND FLAMMABILITY PROPERTIES OF GRAPHENE
REINFORCED COMPATIBILIZED POLY(LACTIC ACID) / POLY(BUTYLENE
ADIPATE-CO-TEREPHTHALATE) NANOCOMPOSITES

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To my beloved mother, father and family members

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ABSTRACT

Graphene nanoplatelets (GNP) reinforced, glycidyl methacrylate (GMA) compatibilized blends of PLA/PBAT nanocomposites were prepared by melt extrusion followed by injection molding. GMA act as compatibilizer with contents of 3, 5 and 8 parts per hundred (phr) were added to the base formulation PLA/PBAT (75/25 weight percent). GNP reinforced nanocomposites 2, 4 and 6 phr were prepared and characterized by using universal testing machine, impact tester, field emission scanning electron microscope (FESEM), x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), limiting oxygen index (LOI) and UL-94V. Compatibilization of the blends with 8 phr GMA results in a blend with highest notched Izod impact strength. The impact strength was enhanced more than 10 times compared to the uncompatibilized blend. Tensile and flexural strengths of test specimens were evaluated and the results revealed that with the presence of GNP nanoplatelets, moderate improvement in stiffness and strength of the nanocomposites were observed. The morphological studies from FESEM micrograph showed the GNP nanoplatelets were embedded and reasonably evenly distributed in the polymer matrix. The thermal stability based on TGA results and the flame retardancy of the GNP reinforced nanocomposites were generally improved with increasing nanofillers content with the optimum at 6 phr. The FTIR analysis did not show chemical interaction between GNP nanoplatelets and polymer matrix although the mechanical and thermal properties of the GNP reinforced nanocomposites were moderately improved.

ABSTRAK

Nanoplatlet graphene (GNP) diperkukuhkan, adunan PLA/PBAT komposit nano diserasikan dengan glisidil metakrilat (GMA) telah disediakan melalui proses penyemperitan leburan diikuti dengan pengacuanan suntikan. GMA yang bertindak sebagai penyerasi dengan kandungan 3, 5 dan 8 phr telah ditambah ke dalam formulasi PLA/PBAT (75/25 peratus berat). GNP diperkukuhkan komposit nano 2, 4 dan 6 phr telah disediakan dan dicirikan dengan menggunakan mesin pengujian universal, pengujian impak, mikroskopi bidang pelepasan imbasan elektron (FESEM), pembelauan sinar-x (XRD), Fourier spektroskopi infra merah (FTIR), analisis termogravimetri (TGA), kalorimetri imbasan pembezaan (DSC), indeks had oksigen (LOI) dan UL-94V. Adunan yang berserasian dengan 8 phr GMA menghasilkan nilai kekuatan hemtaman yang tertinggi. Kekuatan hemtaman telah dipertingkatkan lebih daripada 10 kali ganda berbanding dengan adunan yang tidak berserasian. Kekuatan tegangan dan lenturan telah diuji dan keputusan menunjukkan bahawa dengan kehadiran GNP platlet nano, peningkatan yang sederhana dalam lenturan dan tegangan pada komposit nano diperhatikan. Kajian morfologi daripada mikrograf FESEM menunjukkan GNP nanoplatlet tertanam dan tertabur sama rata secara munasabah dalam matriks polimer. Kestabilan terma dan rencat nyalaan komposit nano GNP diperkukuhkan umumnya dipertingkatkan dengan penambahan pengisi nano optimum pada 6 phr. Analisa FTIR tidak menunjukkan interaksi kimia antara GNP platlet nano dengan matriks polimer walaupun sifat-sifat mekanikal dan terma GNP diperkukuhkan komposit nano telah dipertingkatkan secara sederhana.

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LIST OF ABBREVIATION

ABS	-	Acrylonitrile Butadiene Styrene
ASTM	-	American Standard Testing Methods
ATH	-	Aluminium Trihydroxide
BA	-	Butylene Adipate Unit
BT	-	Butylene Terephthalate Unit
CaCO ₃	-	Calcium Carbonate
DSC	-	Differential Scanning Calorimeter
DTG	-	Derivative Thermogram
EGMA	-	Ethylene-Glycidyl Methacrylate
EPO	-	Epoxidized Palm Oil
FESEM	-	Field Emission Scanning Microscopy
FTIR	-	Fourier Transformation Infra-Red Spectroscopy
GMA	-	Glycidyl Methacrylate
GNP	-	Graphene Nanoplatelets
GNS	-	Graphene Nanosheets
GOS	-	Graphene Oxide Sheet
GPa	-	Giga Pascal
HDPE	-	High Density Polyethylene
HCN	-	Hydrogen Cyanide
iPP	-	Isotactic Polypropylene
LDPE	-	Low Density Polyethylene
LLDPE	-	Linear Low Density Polyethylene
LOI	-	Limiting Oxygen Index
MDH	-	Magnesium Hydroxide
MMT	-	Montmorillonite

MPa	-	Mega Pascal
mPOE	-	Poly(ethylene octane)
MWCNTs	-	Multi-Walled Carbon Nanotubes
Na	-	Sodium
N ₂	-	Nitrogen
O ₂	-	Oxygen
OMMT	-	Organo-modified Montmorillonite
PA	-	Polyamide
PBAT	-	Poly(butylene adipate-co-terephthalate)
PBS	-	Poly(butylene succinate)
PBSA	-	Poly(butylene-succinate-co-adipate)
PEG	-	Polyethylene Glycol
PET	-	Polyethylene Terephthalate
phr	-	Part Per Hundred
PLA	-	Poly(lactic acid)
PLS	-	Polymer/Layered Silicates
PP	-	Polypropylene
PPO	-	Polyphenylene Oxide
PVA	-	poly(vinyl alcohol)
SEM	-	Scanning Electron Microscopy
TBT	-	Tetrabutyl Titanate
TGA	-	Thermogravimetric Analysis
TMI	-	Transition Metal Ion
TPa	-	Tera Pascal
UL	-	Underwriter Laboratory
wt. %	-	Weight Percentage

LIST OF SYMBOLS

$^{\circ}\text{C}$	-	Degree Celsius
T_c	-	Cold Crystallization Temperature
T_m	-	Melting Temperature
T_i	-	Initial Degradation Temperature
T_{10}	-	Degradation Temperature at 10 %
T_{50}	-	Degradation Temperature at 50 %
ΔH_c	-	Enthalpy of Crystallization
ΔH_m	-	Enthalpy of Melting
X_c	-	Degree of Crystallinity
ΔY	-	Polymer Degradation
%	-	Percentage
\AA	-	Angstrom
d	-	d-spacing
θ	-	Theta

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In the recent years, polymers from renewable resources have attracted an escalating amount of attention due to two major reasons: environmental concerns and the realization of petroleum resources are limited. Considerable interest has been focuses on biodegradable polymers due to their environmental friendly property comparing to conventional non-degradable or slowly degradable synthetic petrochemical based polymeric materials (Zhao *et al.*, 2010). Furthermore, increased volume of domestic and industrial waste accumulated in the landfills and sites has created environmental problems, which it urges the development of biodegradable polymers from renewable resource based in order to reduce the consumption of petroleum based polymers in various applications.

One of the biodegradable polymer that widely used in to substitute the conventional petroleum based polymer is polylactide or poly(lactic acid) (PLA). PLA is the favorite in the emerging biopolymer market with the best availability and the most attractive cost structure. PLA is linear, a type of aliphatic thermoplastic polyester, derived from renewable resources, such as corn starch, sugarcane, tapioca roots, chips or starch. PLA polymers are considered biodegradable and compostable. However, PLA similar to polystyrene, it has characteristic of brittleness and stiff polymer with low elongation at break, poor melt strength, narrow processing window

and low thermal stability (Al-Itry, Lamnawar and Maazouz, 2012). These reasons limit their large scale applications.

Another fully biodegradable polymer, poly(butylene adipate-co-terephthalate) (PBAT), gains more attention researchers interest in useful applications recently. PBAT is an aliphatic-aromatic copolyester. It has high toughness, high flexible, high biodegradability and higher elongation at break than most biodegradable polyesters. It degrades within a few weeks with the support of naturally occurring enzymes. PBAT is suitable for packaging films application and this polymer has been hardly studied for other application like medical devices. The main limitations towards wider industrial and medical applications of PBAT are its poor thermal and mechanical properties that limit its access to some sectors (Fukushima *et al.*, 2012).

In view of PBAT high toughness and biodegradability, PBAT is a promising candidate for toughening of PLA. It has been studied that the elongation at break and toughness of blends of PLA and PBAT increased dramatically with the increase of PBAT content (5-20 %) (Jiang, Wolcott and Zhang, 2006). The blends showed decreased of tensile strength and modulus. This means the flexibility of PLA has been increased by incorporation of PBAT. The failure mode changed from brittle fracture of neat PLA to ductile fracture of the blends. Pivsa-Art *et al.* (2011) reported that the maximum tensile strength and impact strength were reached with the blend of equal amount 20 wt. % of PBAT in PLA.

Experiments found that the addition of the compatibilizers led to a highly homogeneous structure, while phase separation occurred in the absence of compatibilizers. Glycidyl methacrylate (GMA) grafted polymers are often used as reactive compatibilizers in polyester blends. It is usually believed that epoxy groups can react with carboxyl or hydroxyl groups of polyester. The end hydroxyl and/or carboxyl groups of PLA can react with epoxy groups via nucleophilic substitution under appropriate conditions. It is reported that GMA modified poly(ethylene octane)

(mPOE) have significant toughening effect on PLA (Su *et al.*, 2009). Zhang *et al.* (2009) found that incorporation of GMA as reactive processing agent in PLA/PBAT blends was greatly increased the toughness without severe loss in tensile strength. The impact strength of the blend was also significantly improved at 1 wt. % of GMA addition but ultimately trend to be saturated with increasing GMA. Besides, Kumar *et al.* (2010) achieved optimum impact strength at 75/25 ratio of PLA/PBAT blend.

Blending different polymers and compounding the polymer with inorganic particles have been the traditional and direct approaches in developing new polymeric materials with targeted properties. Nanoparticles have shown positive enhancements when compounded with polymers. Since last decade, nanoparticles become more popular and it has been replaced micron-sized particles in properties enhancement. Nanoparticles such as modified silicate platelets have enhanced gas barrier properties, toughness, mechanical strength, thermo-mechanical strength and reduce flammability with only small amount of organoclay compared to the traditional inorganic composites. The properties of nanocomposites are highly dependent on the dispersion of the particles in the polymer matrix and the interaction between the polymer and the particles. Pavlidou and Papaspyrides (2008) had specifically reviewed recent advances in the field of polymer-layered silicate nanocomposites which had attracted both academic and industrial attention because they exhibited dramatic improvement in properties at very low filler contents, including flammability of various nanocomposites. Pluta *et al.* (2002) found that polylactic acid/montmorillonite nanocomposites loaded with 3 wt. % of organo modified montmorillonite reduced flammability and char formation was observed, compared to the microcomposites and pure PLA.

Development of polymer nanocomposites has been attracting growing research effort worldwide over the last few decades due to the advantages of polymer nanocomposite's inherent mechanical properties, light weight and added value properties. Polymer nanocomposites based on graphene have attracted great attention

in recent years. A number of researchers have studied and investigated polymer based graphene nanocomposites materials.

El Achaby and Qaiss (2013) compared the properties of high density polyethylene (HDPE)/graphene nanosheets (GNS) and HDPE/Multi-Walled Carbon Nanotubes (MWCNTs) nanocomposites with 0.5 %, 1 % and 3 % nanofiller contents were prepared using the melt mixing method. They found that the HDPE/GNs nanocomposites showed better properties than HDPE/MWCNTs nanocomposites at identical filler content due to high specific surface area and nanoscale 2-D flat surface of GNs which result in an enhanced mechanical interlocking with the polymer chains and enlarged interphase zone at filler–polymer interface.

Milani *et al.* (2013) studied the properties of isotactic polypropylene/graphene nanosheet nanocomposites (iPP/GNS). From a mechanical perspective, they found that there was an excellent balance between a significant increase in Young's modulus and a slight reduction in the elongation at break compared to neat iPP. The reinforcing effect of graphene incorporation was confirmed by the increase of the storage modulus with nanosheet content.

Chieng *et al.* (2014) investigated effects of graphene nanoplatelets (GNP) in poly(lactic acid) (PLA)/polyethylene glycol (PEG) blends. The prepared nanocomposites not only showed enhanced thermal stability but also exhibited a significant improvement in tensile properties at a low GNP loading. The tensile properties demonstrated that the addition of 0.3 wt. % of GNP led to an increase of up to 32.7 %, 69.5 % and 21.9 % in tensile strength, tensile modulus and elongation at break of the nanocomposites, respectively.

1.2 Problem Statement

Polymer blends are one of the convenient approaches to tailor the material cost and to improve the material properties. Polymer blending is a method for obtaining properties that the individual do not possess and has been widely used for various kinds' polymers. Blending of PLA with other biodegradable polymers and nanoparticles offers the possibility of improving the degradation rate, permeability characteristics, flammability, drug release profiles, thermal and mechanical properties.

PLA can become one of the most preferred commodity plastics in the future. However, the higher price of aliphatic biodegradable polymer limits their general application. This problem can be overcome by blending two components of biodegradable polymer. Example blending of PLA/PBAT with compatibilizer is significant interest, since it could lead to the development of a new range of biodegradable polymeric materials with enhanced mechanical properties and wider its applications. According to Kumar *et al.* (2010) findings, incorporation of 3 – 5 wt. % GMA increased the impact strength of PLA/PBAT blend. Incorporation of 5 wt. % of nanoclay reinforced the blend matrix. Use of nanoparticles in PLA often exhibits remarkably improved mechanical and various other properties as compared with virgin PLA.

PLA has very poor flame retardance which restricts its application and development in many fields. So the flame retardancy property has been an importance task. Kumar *et al.* (2010) did not study the flammability and stiffness of PLA/PBAT nanocomposites. Incorporation of GNP is expected to further enhance mechanical properties as well as flame retardancy of PLA/PBAT/GMA compatibilized blends. With these properties modifications, the utilization of PLA/PBAT composites will be more widen to various potential applications such as packaging materials, electronic and electrical devices, mechanical and automotive

parts, etc. which can be an alternative replacement to nonrenewable polymers like polyolefins in future.

1.3 Objective of the Study

The overall objective of this study is to develop a new polymeric material based on PLA / PBAT nanocomposites.

The objectives of this study can be further divided into:

1. To study the effect of GMA content as compatibilizer on mechanical properties of PLA/PBAT blends.
2. To evaluate the effect of GNP content as nanofillers on mechanical and flame retardancy properties of reinforced compatibilized PLA/PBAT nanocomposites.

1.4 Scope of the Study

The scope of the study covered the preparation of the PLA/PBAT blends with formulation fixed at 75:25 ratios. This 75:25 ratio composition is based on the optimum impact strength that determined by Kumar *et al.* (2010). GMA as compatibilizer was incorporated into PLA/PBAT blends. In addition, GNP was

introduced into optimum PLA/PBAT/GMA blend to further evaluate the effect of filler loading and flame retardant on the composites.

1. Evaluation of the mechanical properties by means of tensile, flexural and impact test.
2. Characterize the thermal and morphology of the nanocomposites by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infra-red spectroscopy (FTIR), x-ray diffraction (XRD) and scanning electron microscopy (SEM).
3. Evaluation of the flame retardancy properties of the nanocomposites by using limiting oxygen index (LOI) and UL-94V.

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