

CHARACTERIZATION AND PROPERTIES OF EPOXIDIZED NATURAL
RUBBER TOUGHENED POLY (LACTIC ACID) REINFORCED BY GRAPHENE
NANOFILLER

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DEDICATION

To my beloved husband, Mohamad Shah Erzan bin Shahadan,
And parents, Abdullah bin Sehab and Mariam binti Ahmad,
For their great helps, support and encouragements.

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ABSTRACT

The unvulcanized and dynamically vulcanized poly (lactic acid)/ epoxidized natural rubber (PLA/ENR, PLA/ENR-TPV) blends and a new ternary nanocomposite system based on PLA/ENR/graphene and PLA/ENR-TPV/graphene were prepared. The effect of ENR and ENR-TPV contents (10-30 wt%) on the morphological and mechanical properties of the blends were investigated. On the top of that, the effects of graphene loadings (0-2.0 phr) and different processing methods on the morphological, mechanical and thermal properties of nanocomposites were evaluated. The blends were prepared using a nano-single screw extruder whereas PLA/ENR/graphene and PLA/ENR-TPV/graphene nanocomposites were prepared using both nano-single screw extruder and internal mixer. The tensile and the impact test were carried out to determine the mechanical properties, while the differential scanning calorimeter (DSC) and the thermogravimetric analysis (TGA) were used to investigate the thermal properties. Meanwhile, scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM) were used to observe the morphologies of the blends and nanocomposites. The PLA/ENR and PLA/ENR-TPV blends at 10 wt% of ENR and ENR-TPV loadings showed the highest impact and tensile properties. Thus were selected as basic materials to prepare the nanocomposites. The PLA/ENR/graphene nanocomposites prepared using the internal mixer gave higher mechanical properties and thermal stability than the nano-single screw extruder. The tensile strength, elongation at break and impact strength of the PLA/ENR/graphene and PLA/ENR-TPV/graphene nanocomposites were increased until 1.0 phr of graphene loading. Beyond that these mechanical properties decreased. The PLA/ENR-TPV/graphene nanocomposite exhibited higher tensile strength, elongation at break and impact strength compared with PLA/ENR/graphene nanocomposite. The thermal stabilities of the PLA/ENR/graphene and PLA/ENR-TPV/graphene nanocomposites prepared by both nano-single screw extruder and an internal mixer have improved as the graphene loading increased. From DSC analysis, it was found that the melting temperature, T_m remained unchanged while heat of fusion, ΔH_m and degree of crystallinity, X_c increased as the graphene loading increased since graphene acted as a nucleating agent. The FESEM micrographs revealed good dispersion and distribution of graphene in the PLA/ENR and PLA/ENR-TPV matrix at 1.0 phr of graphene loading that resulting in good interaction between the components. Furthermore, the nanocomposites that prepared using the internal mixer showed better dispersions and distributions of graphene in the matrix thus further enhancing the properties of the nanocomposites.

ABSTRAK

Adunan poli (asid laktik)/getah asli terepoksida tanpa pemvulkanan dan tervulkan secara dinamik (PLA/ENR, PLA/ENR-TPV) dan satu sistem ternari nanokomposit yang baharu berasaskan PLA/ENR/grafin dan PLA/ENR-TPV/grafin telah disediakan. Kesan kandungan ENR dan ENR-TPV (10-30 wt%) terhadap sifat-sifat morfologi dan mekanikal adunan telah diselidiki dan kesan penambahan grafिन (0-2.0 phr) dan kaedah pemprosesan yang berbeza keatas sifat morfologi, mekanikal dan terma nanokomposit telah dinilai. Adunan-adunan telah disediakan menggunakan penyemperit skru tunggal nano manakala PLA/ENR/grafin dan PLA/ENR-TPV grafिन nanokomposit disediakan menggunakan penyemperit skru tunggal nano dan pencampur dalaman. Ujian tegangan dan hentaman telah digunakan untuk mengenalpasti sifat-sifat mekanikal, sementara kalorimetri pengimbasan pembezaan (DSC) dan penganalisis termogravimetri (TGA) telah digunakan untuk mengenalpasti sifat-sifat terma. Sementara itu, mikroskopi elektron imbasan (SEM) dan mikroskopi elektron imbasan pancaran medan (FESEM) digunakan untuk menganalisa morfologi adunan dan nanokomposit. PLA/ENR dan PLA/ENR-TPV pada 10 wt% kandungan ENR dan ENR-TPV telah menunjukkan kekuatan hentaman dan tegangan yang tertinggi. Oleh itu telah dipilih sebagai bahan asas untuk menyediakan nanokomposit. Nanokomposit PLA/ENR/grafin yang disediakan menggunakan pencampur dalaman memberikan sifat-sifat mekanik dan kestabilan terma yang lebih tinggi berbanding penyemperit skru tunggal nano. Kekuatan tegangan, pemanjangan pada takat putus dan kekuatan hentaman PLA/ENR/grafin dan PLA/ENR-TPV/ grafिन nanokomposit meningkat sehingga 1.0 phr muatan grafिन. Selepas nilai itu, sifat mekanikal akan berkurangan. Nanokomposit PLA/ENR-TPV/grafिन menunjukkan kekuatan tegangan, pemanjangan pada takat putus dan kekuatan hentaman yang lebih tinggi berbanding PLA/ENR/grafिन nanokomposit. Kestabilan terma nanokomposit PLA/ENR/grafिन dan PLA/ENR-TPV/grafिन yang disediakan menggunakan kedua-dua penyemperit skru tunggal nano dan pencampur dalaman bertambah baik dengan peningkatan muatan grafिन. Daripada analisa DSC telah menunjukkan suhu lebur, T_m komposit nano kekal tidak berubah manakala haba pelakuran, ΔH_m dan darjah penghabluran, X_c bertambah apabila kandungan grafिन meningkat kerana grafिन bertindak sebagai agen penukleusan. Mikrograf FESEM mendedahkan bahawa serakan dan taburan grafिन adalah baik di dalam matriks PLA/ENR dan PLA/ENR-TPV pada 1.0 phr kandungan grafिन. Oleh itu, menghasilkan interaksi yang baik diantara komponen-komponen. Tambahan pula, nanokomposit yang disediakan menggunakan pencampur dalaman menunjukkan penyerakan dan penyebaran grafिन yang lebih baik dalam matriks sehingga dapat meningkatkan sifat-sifat nanokomposit.

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LIST OF ABBREVIATIONS

ASTM	-	American society of testing and materials
CNT-COOH	-	Functionalized carbon nanotubes
CO ₂	-	Carbon dioxide
DCP	-	Dicumyl peroxide
DTG	-	Derivative thermogram
DSC	-	Differential scanning calorimeter
ENR	-	Epoxidized natural rubber
ENR-TPV	-	Epoxidized natural rubber-thermoplastic vulcanizate
EPDM	-	Ethylene-propylene-diene terpolymer
EVA	-	Ethylene vinyl acetate
FESEM	-	Field emission scanning electron microscope
G	-	Graphene
GNP	-	Graphene nanoplatelets
GNP-L	-	Larger size of graphene
GNP-S	-	Smaller size graphene
GO-ZnO	-	Graphene oxide-zinc oxide
H ₂ O	-	Water
HDPE	-	High density polyethylene
HVA-2	-	N-N'-m-phenylene dimaleimide
LDPE	-	Low density polyethylene
NR	-	Natural rubber

OMMT	-	Organically modified montmorillonite
PCL	-	Poly (caprolactone)
PET	-	Polyethylene terephthalate
PHB	-	Poly (hydroxybutyrate)
Ph-PP	-	Phenolic resin
PLA	-	Poly (lactic acid)
PMC	-	Polymer matrix composite
PNC	-	Polymer nanocomposite
PP	-	Polypropylene
PP-g-MA	-	Maleic anhydride
PS	-	Polystyrene
PVA	-	Poly (vinyl alcohol)
PVC	-	Polyvinyl chloride
SEM	-	Scanning electron microscope
SRT	-	Scrap rubber tyres
TGA	-	Thermogravimetric analysis
TPV	-	Thermoplastic vulcanizate

LIST OF SYMBOLS

%	-	Percent
%w/w	-	Weight per weight percent
ΔH	-	Heat of fusion
$\Delta H_{\text{PLA } 100\%}$	-	Enthalpy for 100% crystalline PLA
$^{\circ}\text{C}$	-	Degree celcius
$^{\circ}\text{C}/\text{min}$	-	Degree celcius per minute
μm	-	Micrometre
g/mL	-	Gram per millilitre
g/mol	-	Gram per mol
GPa	-	Giga pascal
J/m	-	Joule per metre
kg/cm^2	-	Kilogram per centimetre square
kg/m^3	-	Kilogram per metre cube
kN	-	kilo newton
m^2/g	-	Metre square per gram
min	-	Minute
mm	-	millimetre
mm/min	-	millimetre per minute
MPa	-	Mega pascal
nm	-	Nanometre
phr	-	Part per hundred parts of resin

r/min	-	Rotation per minute
rpm	-	Rotation per minute
T _{Deg}	-	Degradation temperature
T _g	-	Glass transition temperature
T _m	-	Melting temperature
T _{onset}	-	Onset temperature
TPa	-	Tera pascal
Wm ⁻¹ K ⁻¹	-	Watt per metre per kelvin
wt%	-	Weight percent
X _c	-	Degree of crystallinity
<i>x</i>	-	Net weight of fraction of PLA

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, world-wide are produced over 200 million tons of plastics each year and 40% of them are used in short-life products such as packaging (Xu, Ma and Hoch, 2016). The plastics that commonly produced are polyethylene includes high density polyethylene (HDPE) and low density polyethylene (LDPE) (29.6%), polypropylene (PP) (18.9%), polystyrene (PS) (7.1%), polyvinyl chloride (PVC) (10.4%), polyethylene terephthalate (PET) (6.9%) and other types of plastic that represent about 19.7% which are approximately 90% of the total plastic production world-wide and most of the plastics are known as “hard to degrade” materials (Li, Tse and I, 2016; Saad and Williams, 2016). This rapid growth of plastic production leads to serious environmental pollution due to half of them are disposed to the environment within a short period (Moura, Nogueira and Veronique Bounor-Lagare, 2012).

Due to the environmental concerns and sustainable issues, the plastic wastes problem can be solved by using bio-based polymers to substitute the conventional petroleum-based polymer which is easily degrading and considered as environmentally friendly material. The bio-based polymer also known as biodegradable polymer where the properties such as mass, molecular weight, and strength of the material may degrade with time when scavenge by microorganisms and produced a by-product such as carbon dioxide (CO₂), water (H₂O), inorganic compounds or biomass (Gorrasi, Milone and Piperopoulos, 2013; Xu et al, 2016). The biodegradable polymer is classified into two groups: i) non-renewable source of raw material and ii) renewable source of raw material. The examples of non-renewable source of raw material are poly (vinyl alcohol) (PVA), poly (caprolactone) (PCL), poly (anhydride), aliphatic co-polyester, and aromatic co-polyester while for the renewable

source of raw material are poly (lactic acid) (PLA), poly (hydroxybutyrate) (PHB), poly (hydroxyl-valerate), and cellulose acetate (Ebnesajjad, 2013). The biodegradable polymer has attracted the interest of many researchers in recent year in various applications such as packaging, agriculture mulch films, and biomedical products (Gorrasi et al, 2013).

PLA is one of the promising and commercially material on the market of bio-based polymer that can replace the conventional petroleum-based polymer (synthetic polymer) in packaging and other engineering applications. PLA is a biodegradable aliphatic polyester that produced via fermentation of the carbohydrate from the renewable agriculture sources such as corn (Auras, Lim and Selke, 2010; Laurence, 2012; Aghjeh, Nazari and Khonakdar, 2015). PLA is highly transparent which behaves as glassy and brittle material that exhibits the tensile strength of 30 to 50 MPa with an elongation at break between 1% to 7% depends on its molecular weight. The tensile modulus of the PLA is between 2 to 4 GPa (Yang, Tang and Xiong, 2015; Ebadi-Dehaghani, Khonakdar and Barikani, 2015; Xu, Ma and Hoch, 2016). The limitation by its brittleness is poor in toughness for the applications that need plastic deformation at high stress level and thermally unstable (Ebadi-Dehaghani et al, 2015; Xu et al, 2016). To overcome the brittleness of the PLA, there are several methods can be used such as processing manipulation, copolymerization, and blending with other polymer, for example, thermoplastic or elastomeric polymer (Zhang, Wang and Huang, 2013).

The epoxidized natural rubber (ENR) has been used in this research as a toughening agent to improve the toughness of PLA. In fact, the ENR is the elastomeric material that has been modified from the natural rubber (NR) and consists of double functionality of crosslinking which are an epoxy group and double bond that makes ENR is a polar material. The ENR can be used as a toughening agent to the rigid polymer since ENR has high impact strength and excellent resistance to puncture and tear (Hazwani Syaza Ahmad, Hanafi Ismail and Rashid, 2016; Mohamad, Zainola, Rahima and Hairul Effendy Ab Maulodb, 2013). Pongtanayut, Thongpin and Santawitee (2013) state that there is partially compatibility between PLA and ENR as compared to PLA/NR at 20 wt% of rubber composition where in PLA/ENR blend system shows very fine particles of the ENR dispersion and ENR acts as the second

phase in the PLA matrix. The ENR also act as stress concentrators that enhance the fracture energy absorption of brittle PLA and resulting in the improvement of the toughness of PLA but the tensile strength had decreased due to the ductile properties of the ENR. According to Zhang et al (2013), they reported that the impact strength and elongation at break of 20 wt% of ENR loading in the ENR50/PLA and ENR20/PLA were increased as compared to pure PLA and this due to the good interfacial adhesion between PLA and ENR while the tensile strength and modulus were reduced. In addition, Akbari, Jawaid and Hassan (2014) reported that addition of 20 wt% of ENR into the PLA/talc composites were improved the impact strength due to the ENR enhancing the mobility of the PLA chains.

The ENR also can be vulcanized by adding a crosslinking agent such as N-N'-m-phenylene dimaleimide (HVA-2), dicumyl peroxide (DCP) and sulphur. In this research, HVA-2 being used as a crosslinking agent to vulcanize ENR. The advantage of using HVA-2 is due to the HVA-2 able to vulcanize rubber in the absence of other catalyst and free radicals source. It's also free from residual chemicals such as zinc oxide, stearic acid and nitrosamines where they possess low cytotoxicity. HVA-2 also has a less rubbery protein that causes allergic responses. HVA-2 also acts as multifunctional radical acceptors to promote a combination of dissimilar polymer radicals to produce a copolymer and create sufficient copolymer to reduce interfacial tension (Hassan, Wahit and Ching, 2003; Ismail Halimatuddahlia and Md Akil, 2005; Kahar, Ismail and Othman, 2013). For the system PLA/epoxidized natural rubber-thermoplastic vulcanizate (ENR-TPV) was reported by Wang, Chen and Xu (2015) where compound was prepared through dynamic vulcanization in the presence of dicumyl peroxide (DCP) as crosslinking agent and they found that the impact strength and elongation at break of the PLA was improved by incorporated with 40 wt% of ENR-TPV while the tensile strength shows decreasing trend but the improvement occurred was better than PLA/ENR itself. Other than that, Thongpin, Kuttanate and Kampuang (2012) stated that the tensile strength and modulus of the PLA/ENR-TPV/OMMT increases while elongation at break decreases as the OMMT loading increases. The thermal stability of PLA/ENR-TPV had enhanced with the incorporation of OMMT. Zurina, Ismail and Ratnam (2008) investigated ENR50/EVA blend that containing HVA-2 as a crosslinking agent and proved that the improvement

in interfacial adhesion, compatibility and tensile strength of the ENR50/EVA blend. The unique combination between PLA and elastomer is the biocompatibility and flexibility of biodegradable blends can be produced (Pongtanayut et al, 2013; Mascia, Hawortha and Vignalib, 2016; Zhang et al, 2016).

Nanofillers with ultrathin size (<100 nm) such as graphene can be used to improve the tensile, impact and thermal properties of polymer blend at lower filler loading (≤ 5 wt%). Toughened PLA can be reinforced by graphene to trigger the significant enhancement in mechanical and thermal properties. Graphene is a carbon material consisting of a single layer or two dimensional sheet with a honeycomb structure or hexagonal packed lattice structure (Bouakaz, Habi and Grohens, 2015; Angelopoulou, Voulgari and Diamanti, 2015). Graphene is used as inorganic nanofillers to enhance the physical, mechanical, thermal and also gas barrier properties to the polymer nanocomposite (Ciu, Kundalwal and Kumar, 2016). Graphene also shows several unique properties such as tensile strength of 130 GPa, high Young's modulus (~ 1.0 TPa), large theoretical specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), and good thermal conductivity ($\sim 5000 \text{ Wm}^{-1} \text{ K}^{-1}$) (Bouakaz et al, 2015). Several studies have been demonstrated that graphene has high reinforcing efficiency in the PLA. Norazlina and Kamal (2015) have conducted the study of graphene modification in PLA nanocomposites and found that PLA/graphene has created good thermal stability by decreasing diffusion pathway of the degradation of by-products such as acidic species, metallic ions or residual products. The tensile strength of the poly (lactic acid)/graphene nanoplatelets (PLA/GNP) has no much different as compared to neat PLA which reported and proven by Pinto et al. (2015). According to She, He and Peng (2014), they found that as the graphene loading increases in the ENR matrix, the tensile strength of the composites was increased while the elongation at break was lower due to the reinforcing of the graphene in the ENR matrix.

This research has an interest in toughening PLA which focused on the incorporation of ENR and ENR-TPV as elastomeric-based materials in PLA matrix to produced PLA/ENR and PLA/ENR-TPV blends. The HVA-2 is selected as a crosslinking agent in the ENR-TPV system. The graphene was incorporated into the

toughened PLA as nanofiller to improve the mechanical and thermal properties of the PLA/ENR and PLA/ENR-TPV blends.

1.2 Problem Statement

There are several limitations of the PLA which are thermally unstable and low deformability that resulting PLA behaves quite glassy and brittle material. To overcome the brittleness, the PLA has been incorporated with an elastomer which is ENR and ENR-TPV to produce PLA/ENR and PLA/ENR-TPV blends which are known as toughened PLA. The incorporation of ENR into the PLA matrix was conducted by previous researchers such as Pongtanayut et al (2013), Zhang et al (2013), and Aghjeh et al (2015) and have been proven that the toughness, elongation at break and impact strength of the PLA/ENR blend system was increased by incorporation of 20 wt% of ENR loading. They also proved that the ENR and PLA were compatible with each other due to their polarity. However, according to Wang et al (2015), they found that the impact strength and elongation at break of the PLA was improved by incorporation of 40 wt% of ENR-TPV. As of our knowledge, ENR-TPV with sulphur and peroxide system had been reported by Wang et al (2015) and Thongpin et al (2012) in toughening of the PLA. In this study, HVA-2 is being used as a crosslinking agent for the PLA/ENR-TPV system since HVA-2 is able to vulcanize rubber in the absence of other catalyst and free radicals source and also there is no work reported on that. The addition of ENR and ENR-TPV into the PLA matrix has caused a reduction in the tensile strength and thermal stability due to the lower modulus and thermal stability of elastomer.

Graphene nanofiller has been used in many polymer systems to enhance the mechanical properties and thermal stability of systems due to a good mechanical and thermal properties of graphene. Norazlina et al (2015) have found that PLA/graphene has shown the improvement in thermal stability by decreasing diffusion pathway of the degradation of by-products and Pinto et al (2015) have proven that the tensile strength and tensile modulus of the PLA/GNP have slightly increased since GNP act

as reinforced filler. According to the She et al (2014), they proved that as graphene loading increased in the ENR matrix, the tensile strength of the composites increased while the elongation at break lowered due to the reinforcing of the graphene in the ENR matrix. In this research, two types of processing method were used which were an internal mixer and nano-single screw extruder where the processing method plays an important role to determine the morphological, mechanical and thermal properties of the blends and nanocomposites.

The PLA/ENR, PLA/ENR-TPV, PLA/graphene and ENR/graphene have been reported in the previous study. Thus, this research is aim to develop a new ternary system based on PLA/ENR/graphene and PLA/ENR-TPV/graphene nanocomposites with improving properties.

1.3 Objectives

The specific objectives of this research are:

1. To determine the effect of ENR and ENR-TPV loading on the morphological and mechanical properties of PLA by using nano-single screw extruder.
2. To investigate the effect of graphene loading of PLA/ENR blends on the morphological, mechanical and thermal properties by comparing with different processing method between nano-single screw extruder and internal mixer.
3. To examine the effect of graphene loading of PLA/ENR and PLA/ENR-TPV blends on the morphological, mechanical and thermal properties by using an internal mixer.

1.4 Scope of the Study

In order to attain the objectives of this research, a few requirements were carried out. A preliminary study of the previous research about PLA, ENR and graphene that related and relevance with this investigation was done in the literature review. The sample preparation was done where firstly the ENR was masticated and compounded with 3 phr of HVA-2 to produce the ENR-TPV. The amount of the HVA-2 was taken from the Zurina et al (2008) since they determined that only 3 phr of HVA-2 was good enough to vulcanize the ENR. Then, PLA/ENR and PLA/ENR-TPV blends were prepared at different ENR and ENR-TPV loading (0, 10, 20 and 30 wt%) by using nano-single screw extruder. The graphene-based nanocomposites were prepared with different loading of graphene (0, 0.5, 1.0, 1.5 and 2.0 phr) by using nano-single screw extruder and internal mixer.

Lastly, the testing and characterization of the blends and nanocomposites were done. For the mechanical testing, tensile properties are evaluated by using the tensile testing machine (Instron Universal Tester) while impact properties of the samples are determined by using impact tester. The thermal behaviour such as glass transition temperature (T_g) and melting temperature (T_m) are analyzed by using differential scanning calorimeter (DSC) while thermal stability of the sample is determined by thermogravimetric analysis (TGA). For the morphological study, scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM) were used to study the dispersion and distribution of the nanofiller in toughened PLA.

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