

PROPERTIES AND CHARACTERIZATION OF POLY LACTIC
ACID/NATURAL RUBBER/GRAPHENE NANOCOMPOSITE

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ABSTRACT

Natural rubber toughened poly lactic/graphene (PLA/NR/graphene) nanocomposites were prepared by two different processes known as in-situ melt mixing process (conventional) and integration of latex compounding - melt mixing process. These two processes were employed to compare the state of graphene dispersion and distribution in the nanocomposite. The objectives of this research comprise the effect of different processing methods and graphene content on the morphology, mechanical and thermal properties of PLA/NR/graphene nanocomposite. The composition of PLA/NR blend was fixed at 80/20 wt% and the graphene content was varied at 0.1-0.4 phr. Mechanical properties were studied by tensile, flexural and impact test. The tensile and impact strength were slightly improved with increasing of graphene loading (from 0.1-0.3 phr) indicating that graphene significantly effective in increasing the mechanical properties of toughened PLA nanocomposite. The PLA/NR/graphene nanocomposite was characterized by field emission scanning electron microscopy and scanning electron microscopy. Integration of latex compounding and melt mixing process showed better graphene distribution and dispersion compared to the conventional processing method. Differential scanning calorimetry and thermogravimetric analysis were used to determine the temperature profile: glass transition temperature (T_g), melting temperature (T_m) and cold crystallization temperature (T_{cc}) and also to access thermal stability of the nanocomposite. The results also revealed that the PLA/NR blend was reinforced and toughened simultaneously by graphene. The simultaneous improvement in tensile strength and toughness could be attributed to the homogeneous dispersion of graphene in PLA/NR/graphene nanocomposite. The integration of latex compounding and melt mixing process had given a promising method to homogeneously dispersed graphene in the polymer matrix.

ABSTRAK

Nanokomposit polilaktik asid/grafin diperkuat getah asli (PLA/NR/grafin) telah dihasilkan menggunakan dua proses berlainan dikenali sebagai proses percampuran leburan secara in-situ (lazim) dan melalui proses integrasi penyebatan lateks-percampuran leburan. Kedua-dua proses digunakan untuk membandingkan keadaan penyebaran dan pengagihan grafina di dalam nanokomposit. Objektif-objektif penyelidikan meliputi kesan kaedah proses yang berbeza dan kandungan grafina terhadap morfologi, sifat-sifat mekanikal dan sifat-sifat termal nanokomposit PLA/NR/grafin. Komposisi sebatian PLA/NR ditetapkan pada peratusan berat 80/20 serta kandungan grafina diubah pada 0.1- 0.4 phr. Sifat-sifat mekanikal telah dikaji melalui ujian tegangan, lenturan dan impak. Kekuatan ketegangan dan kekuatan impak sedikit meningkat oleh kemasukan grafina (dari 0.1-0.3 phr) menunjukkan bahawa grafina adalah sangat berkesan dalam meningkatkan sifat-sifat mekanikal bagi nanokomposit PLA diperkuat getah asli. Nanokomposit PLA/NR/grafin telah dicirikan dengan menggunakan mikroskop pengimbasan medan pelepasan electron dan mikroskop pengimbasan elektron. Proses integrasi penyebatan lateks dan percampuran leburan menunjukkan pengagihan dan penyebaran grafina yang lebih baik berbanding kaedah pemprosesan lazim. Kalorimetri pengimbas perbezaan dan analisis thermogravimetrik telah digunakan untuk menentukan profil suhu: suhu peralihan kaca (T_g), suhu lebur (T_m) serta suhu penghabluran sejuk (T_{cc}) dan juga menguji kestabilan termal nanokomposit. Keputusan menunjukkan bahawa sebatian PLA/NR telah diperkukuh dan diperkuat oleh grafina. Peningkatan kekuatan dan ketahanan boleh disebabkan oleh penyebaran grafina yang sekata di dalam nanokomposit PLA/NR/grafin. Proses integrasi merupakan kaedah yang memberikan penyebaran grafina yang sekata di dalam matriks polimer.

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LIST OF ABBREVIATION

ASTM	-	American Society of Testing and Materials
CaCl ₂	-	Calcium chloride
CaCO ₃	-	Calcium carbonate
CNT	-	Carbon nanotubes
DSC	-	Differential scanning calorimetry
ENR	-	Epoxidized natural rubber
FESEM	-	Field Emission Scanning Electron Microscopy
GNPs	-	Graphene nanoplatelets
HA	-	High ammonium latex
IR	-	Isoprene rubber
KOH	-	Potassium hydroxide
MST	-	Latex mechanical stability
NBR	-	Nitrile butadiene rubber
NR	-	Natural rubber
PCL	-	Poly captolactone
PE	-	Polyethylene
PET	-	Polyethylene terephthalate
PLA	-	Poly lactic acid
PP	-	Polypropylene
PS	-	Polystyrene
rGO	-	Reduced graphene oxide
SBR	-	Styrene butadiene rubber
TGA	-	Thermogravimetric analysis
VFA	-	Volatile fatty acid
xGNP	-	Graphene nanoplatelets

LIST OF SYMBOLS

%	-	Percentage
°C	-	Celcius
°C/min	-	Celcius per minute
g/cm ³	-	Gram per centimeter cube
GPa	-	Gigapascal
J	-	Joule
J/g	-	Joule per gram
J/m	-	Joule per meter
kV	-	Kilovoltage
m	-	Meter
m ² /g	-	Meter square per gram
mJ/m ²	-	Milijoule per meter square
mm	-	Milimeter
mm/min	-	Milimeter per minute
MPa	-	Megapascal
mW	-	MiliWatt
nm	-	Nanometer
phr	-	Part per hundred resin
rpm	-	Revolution per minute
T _{cc}	-	Cold crystallization temperature
T _d	-	End decomposition temperature
T _g	-	Glass transition temperature
T _m	-	Melting temperature
T _o	-	Onset degradation temperature
TPa	-	Terapascal
wt%	-	Weight percentage
X _c	-	Degree of crystallinity
ΔH _c	-	Entalphy fusion of crystallization

ΔH_m - Entalphy fusion of PLA

CHAPTER 1

INTRODUCTION

1.1 Background

Polymers are widely used around the world for various applications due to their advantages such as light weight, low cost and easy to process. However, the usage of the commodity synthetic polymers has become a great concern due to the high impact of plastic waste in daily use. One of the possible solutions to this problem is by replacing synthetic polymers with biodegradable polymers (Matta *et al.*, 2014). In recent years, biodegradable polymers derived from natural resources have gained much interest as they can be alternative to petroleum-based polymeric materials as well as a solution to waste disposal problem. Hence, development of materials is an important issue in order to decrease the environmental impact of the plastic production and waste (Pongtanayut *et al.*, 2013).

Poly lactic acid (PLA) is one of the materials that derived from the biomass which exhibit high physical and mechanical properties combined with excellent biodegradability and biocompatibility properties (Bitinis *et al.*, 2011). However, its inherent brittleness, low toughness and low elongation at break usually limit their usage in most of the applications (Talbamrung *et al.*, 2016). In order to modify the drawback, many strategies have been employed such as processing manipulation, copolymerization and blending (Zhang *et al.*, 2013). Pongtanayut *et al.* (2013), reported that the blending of PLA with other polymer is more practical and cheaper

compared to the copolymerization with other monomers which are widely used but failed in commercial application. Among all of these methods, blending with the biodegradable polymer is the most convenient approaches for toughening PLA.

One of the best materials for toughening PLA is natural rubber (NR) which improved in physical and mechanical properties (Bitinis *et al.*, 2011). NR is one of the good toughening agents due to its high molecular weight and very low glass transition temperature (-70°C). Research by Jaratrotkamjorn *et al.* (2012) revealed that toughness and ductility of the PLA/NR blend were increased compared to the virgin polymer. In this research, toughening of PLA was focused on the use of NR latex/graphene masterbatch by the latex compounding method. The rubber particles behave as toughening agent and enhancing fracture energy absorption of brittle polymers and ultimately resulting improves in toughness (Pongtanayut *et al.*, 2013).

Polymer nanocomposites are one of the new options besides the conventionally filled polymer. The properties of nanocomposites are markedly enhancing when compared to the pure polymer due to the present of dispersion of the nanometer size filler into the polymer matrix. It occupied outstanding properties included mechanical strength, enhancement in solvent and heat resistance and also reduces flammability (Varghese and Karger-Kocsis, 2003). Polymer based nanocomposites have become important, which begin with the interesting observation of exfoliated clay, and currently on carbon nanotubes (CNT), graphene, nanoscale size filler and also modified fibers (Paul and Robeson, 2008).

Graphene is a material which presents high aspect ratio, thus being able to react with a large interfacial interaction between the polymer matrix and the nanofiller, resulting in effective loads transfer and increased strength (Pinto *et al.*, 2016). The addition of graphene into a polymer matrix has improved the properties of the nanocomposites with good application in various industries (Dhand *et al.*, 2013). The theoretical tensile strength and Young's modulus of graphene measured to be 130 GPa and 11.0 TPa respectively which were higher than the tensile strength nano-sized steel or CNT (Chee *et al.*, 2015). However, graphene is difficult to disperse well in the polymer matrix due to the high π - π interaction between the

graphene. Thus, graphene must be dispersed at a reasonable concentration, with a right solvent, and dispersed in the appropriate period of time (Johnson *et al.*, 2015).

Basically, there are three main methods that are used to disperse graphene into the polymer matrix which are in-situ polymerization, solvent blending and melt blending. Generally, in-situ polymerization and solvent blending give better dispersion compared to melt blending (Jiang *et al.*, 2013). Kim *et al.* (2010), (2011) prepared polyurethane/graphene and polyethylene/graphene composites via in-situ polymerization, melt blending and solution blending. The result showed that the in-situ polymerization and solution blending gives good dispersion compared to melt blending. An elastomeric compound which mostly exists as latex form may be one of the appropriate material that can be a polymer matrix for the graphene. Latex compounding offers satisfactory dispersion and performance which also reduces the incompatibility between the rubber and fillers in the rubber matrix (Gui *et al.*, 2016).

From the previous research, there were only a few of polymer/graphene composites prepared using melt blending, while others were focusing on solvent blending and in-situ polymerization. However, both of these methods have some limitations which involve poisonous solvent and do not convenient for the industrial processing (Verdejo *et al.*, 2011). Latex compounding method has mostly been applied to prepare polymer/graphene composite with various kind of polymer, such as polyethylene (Cao *et al.*, 2012), polypropylene (Song *et al.*, 2011), polystyrene (Tkalya *et al.*, 2010) and polycarbonate (Yoonessi and Gaier, 2010). By using this latex compounding method, nanofiller particles are wrapped by the polymer latex particles and form dissociate network (Jiang *et al.*, 2013).

Both latex compounding and melt blending method were used together in this research to prepare PLA/NR/graphene nanocomposites. Latex compounding is one of the suitable methods to exfoliate and disperse the graphene homogeneously. On the other hand, melt blending is the method used to combine both NR latex/graphene masterbatch with PLA polymer. Corresponding to the benefits of two methods, nanocomposites exhibit greater improvement in mechanical and thermal properties.

1.2 Problem Statement

PLA is one of the widely use biodegradable polymer due to its comparable properties with the petroleum- based polymer such as high strength and modulus. However, brittleness, low elongation at break and low in toughness are the drawback of the PLA and limit its applications (Bijarimi *et al.*, 2014). Therefore, these properties needed to be improved for many potential applications. Pongtanayut *et al.* (2013) showed that the toughness of PLA improved by blending with natural rubber and epoxidized natural rubber. Moreover, in the previous research, Bitinis *et al.* (2011) reported the natural rubber was used as a second phase polymer to overcome the brittleness of PLA and toughened the thermoplastic. Generally, the rubber particle act as stress concentrators, initiating and terminating craze in the brittle polymer matrices and improved the fracture energy absorption (Ishida *et al.*, 2009). However, the significant decrease in tensile strength and modulus of the blends were observed. Adding fillers into plastics is usually implemented in the plastics to improve the mechanical properties. Polymer/graphene composites showed significant improvement in mechanical, thermal, electrical properties and flame retardancy by adding of small amount of graphene. Graphene is an encouraging filler for polymer composites, however, the irreversible aggregation when introducing into the polymer is a challenge for property improvements and restricts its application (Jiang *et al.*, 2013). Currently, there are only a few methods have been reported in dispersion of graphene in the latex composites such as mechanical stirring, in-situ reductions, ultrasonically assisted mixing and two roll mill processing (Li *et al.*, 2013) The latex compounding method introduced to reduce the incompatibility between the filler and polymer. Besides, the method reduced the agglomeration of the filler and resulted in the good dispersion. From the previous study by Tkalya *et al.* (2010), the polymer/graphene composites exhibited better dispersion and improved properties by latex compounding method. Research by Xing *et al.* (2014) also stated that the latex compounding method gives an excellent dispersion of graphene and strong interfacial between graphene and latex were achieved. Therefore, this work was aimed at clarifying the method of compounding and graphene loading of PLA/NR/graphene nanocomposites influences the mechanical and thermal behaviour of the nanocomposites.

1.3 Research Objectives

The objectives of this study comprise the followings:

1. To study the effect of different processing method between latex compounding and in-situ mixing method of graphene on morphology, mechanical and thermal properties of PLA/NR/graphene nanocomposites.
2. To investigate the effect of different loading of graphene on mechanical and thermal properties of latex compounding and in-situ mixing method of PLA/NR/graphene nanocomposites.

1.4 Scope of Study

In this study, the PLA/NR/graphene nanocomposite was prepared by two different methods. The first method is known as the integration of latex compounding masterbatch and melts mixing method, and the second method is the in- situ mixing process in the twin screw extruder. The composition of PLA/NR blends was fixed at 80/20 wt% and the graphene loading was varied from 0.1-0.4 phr. The effect of different processing methods and graphene loadings in the PLA/NR/graphene nanocomposites on morphology, mechanical and thermal properties were investigated. Mechanical properties of the nanocomposites were investigated by a tensile test, flexural test and impact test. The thermal stability and thermal properties of the nanocomposites were determined by differential scanning calorimetry and thermogravimetric analyzer. Field emission scanning electron microscopy and scanning electron microscopy were conducted to evaluate the morphological properties based on the impact fracture surface of the nanocomposites.

The results and discussions on the finding covered in Chapter 4 of this research. Particular emphasis was given to the PLA/NR/graphene nanocomposites

preparation methods, optimum filler content for the nanocomposites, improvement of filler dispersion, and last but not least the nanocomposite mechanical and thermal properties.

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