MECHANICAL, THERMAL, MORPHOLOGICAL AND RHEOLOGICAL PROPERTIES OF POLY(LACTIC ACID)/ NATURAL RUBBER/ CARBON NANOTUBE NANOCOMPOSITES

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ABSTRACT

Inherent brittleness in poly(lactic acid) (PLA) largely limit its wide applications as common biodegradable plastic materials. Thus, PLA toughening through melt blending was prepared by incorporating different ratio of natural rubber (NR) (0% to 20%) as toughening agents to investigate the mechanical, thermal, morphological and rheological properties of the PLA/NR blends. This approach used 9 wt.% of two different types of compatibilizers natural rubber-grafted-maleic anhydride (NR-g-MA) and polylactic acid-grafted-maleic anhydride (PLA-g-MA) in the system to enhance compatibility between PLA and NR. Then, to improve stiffness and strength of the blends, addition 1-8 phr of nanofiller pristine carbon nanotube (CNT) was added into the system to prepare PLA/NR nanocomposites. The result of mechanical properties the blends showed good performance significantly for impact strength. Additionally, thermal properties of the blends and nanocomposites were investigated by using thermogravimetric analysis and differential scanning calorimetry. The results showed an increase in glass transition temperature and thermal stability by addition of CNT. Scanning electron microscopy and nanoscanning electron microscopy were conducted and revealed good dispersion of CNT particles in the PLA matrix at higher amount (8phr). Moreover, X-ray diffraction analysis was carried out for microstructure properties determination for nanocomposites and showed good interactions between PLA and CNTs. Finally, melt flow index and rotational rheometer were used to characterize the rheological properties of the blends and nanocomposites. Increasing for storage modulus and loss modulus were observed in the system with addition of CNT. Experimental data obtained from rheological analysis for all these three systems were used for mathematical model approaches using Power Law and Carreau - Yasuda models to study the rheological behaviour of blends. Power Law model has the best fit and more suitable for shear-thinning behaviour because of low range shear rate system for this particular study compared to Carreau-Yasuda. As a conclusion, additional of compatibilizer and CNT led blend properties to increase significantly in impact strength and thermal stability.

ABSTRAK

Sifat rapuh poli(asid laktik) (PLA) sebahagian besar membataskan keluasan penggunaannya sebagai bahan plastik terbiodegradasi. Oleh itu, pengukuhan PLA melalui pengandungan leburan disediakan dengan mencampurkan nisbah getah asli yang berbeza (0% hingga 20%) sebagai agen pengukuh untuk mengkaji sifat-sifat mekanikal, haba, morfologi dan reologi adunan PLA/NR tersebut. Penggunaan 9% berat dua jenis penserasi yang berbeza (getah asli-cantuman-maleik anhidrida (NR-g-MA) dan asid poli(asid laktik)-cantuman-maleik anhidrida (PLA-g-MA)) di dalam sistem adalah untuk meningkatkan keserasian antara PLA dan NR. Kemudian, bagi meningkatkan kekakuan dan kekuatan adunan, sebanyak 1-8 phr tiub karbon nano asli (CNT) ditambahkan ke dalam sistem untuk menghasilkan PLA/NR komposit nano. Hasil menunjukkan peningkatan ketara untuk sifat-sifat mekanik terutamanya kekuatan hentaman. Tambahan lagi, sifat-sifat terma campuran polimer dan komposit nano dikaji dengan menggunakan analisa termogravimetrik dan kalorimetri imbasan keberbezaan. Keputusan menunjukkan peningkatan suhu peralihan kaca dan kestabilan haba dengan penambahan CNT. Mikroskop elektron imbasan dan mikroskop elektron imbasan nano dijalankan dan mendedahkan serakan zarah CNT adalah lebih baik dalam matrik PLA pada kandungan yang lebih tinggi (8 phr). Selain itu, analisis pembelauan sinar-X telah dijalankan untuk menentukan sifat struktur mikro untuk komposit nano dan menunjukkan ikatan antara PLA and CNT. Akhir sekali, indeks aliran leburan dan reometer putaran digunakan untuk mencirikan sifat reologi campuran dan komposit nano. Peningkatan modulus penyimpanan dan modulus hilang dengan penambahan jumlah CNT. Data yang diperolehi daripada analisis reologi untuk dicerapkan dalam ketiga-tiga sistem ini digunakan dalam kajian model matematik menggunakan model hukum kuasa dan Carreau - Yasuda bagi mengkaji kelakuan reologi campuran tersebut. Model hukum kuasa lebih sesuai terhadap kelakuan penipisan ricih kerana sistem kadar ricih yang rendah digunakan dalam kajian ini berbanding model Carreau-Yasuda. Kesimpulannya, penambahan bahan penserasi dan CNT telah menyebabkan peningkatan sifat campuran terutama kekuatan hentaman dan kestabilan haba.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CNT	-	Carbon Nanotube
CCVD	-	Catalytic Chemical Vapour Deposition
CVD	-	Condensation–Vaporization Densation
DWCNT	-	Double-walled Carbon Nanotube
ENR	-	Epoxidized Natural Rubber
EPR	-	Ethylene Propylene Rubber
EPDM	-	Ethylene propylene diene monomer
MA	-	Maleic Anhydride
MAH-g-EPM	-	Maleic Anhydride grafted Ethylene Propylene Rubber
MA-g-NR	-	Maleic Anhydride grafted Natural Rubber
MA-g-PLA	-	Maleic Anhydride grafted Polylactic Acid
MAH-g-PP	-	Maleic Anhydride grafted Polypropylene
MM	-	Molecular Modelling
MMT	-	Montmorillonite
MW	-	Molecular Weight
MWCNT	-	Multiwalled Carbon Nanotube
MWCNT-g-PLA	-	Multiwalled carbon nanotube grafted Polylactic Acid
NBR	-	Acrylonitrile–butadiene rubber
NR	-	Natural Rubber
NR-g-GMA	-	Glycidyl methacrylate-grafted natural rubber
NR-g-PBA	-	Natural Rubber grafted Poly(butyl acrylate)
NR-g-PMMA	-	Poly(methyl methacrylate) grafted natural rubber
OMLS	-	Organically modified layered silicate
PCV	-	Polyvinyl Chloride
Phr	-	Parts per hundred
PE	-	Polyethylene
PET	-	Polyethylene Terephthalate
PLA	-	Polylactic acid

PP	-	Polypropylene
PS	-	Polystyrene
ROP	-	Ring-opening polymerization
SWCNT	-	Single-walled Carbon Nanotubes
Tc	-	Crystalline Temperature
Tg	-	Glass Transition Temperature
Tm	-	Melting Temperature
ASTM	-	American Society for Testing and Materials
DSC	-	Differential Scanning Calorimetry
MFI	-	Melt Flow Index
SEM	-	Scanning Electron Microscopy
TEM	-	Transmission Electron Microscopy
TGA	-	Thermalgravimetric Analysis
XRD	-	X-ray Diffraction Analysis

LIST OF SYMBOLS

°C	-	Degree Celcius
J/m	-	Joule per Meter
g/10 min	-	Gram per 10 Minutes
g/cm3	-	Gram per Centimeter Cubic
kg	-	Kilogram
wt%	-	Weight Percent
J	-	Joule
%	-	Percentage
MPa	-	Mega Pascal
kg/cm2	-	Kilogram per Centimeter Square
rpm	-	rotation per minute
χ	-	Flory–Huggins interaction
η^*	-	Complex Viscosity
η	-	Viscosity
$\eta\infty$	-	Infinite shear viscosity
γ	-	Frequency
ω	-	Shear rate or angular frequency
λ	-	Time constant

CHAPTER 1

INTRODUCTION

1.1 Research Background

For the past decades, various petrochemical-based polymers were widely contributed in economical, processing and technological aspect. But, after rapid development in these polymers, constant environmental pollution occurred caused by undegradable polymers wastes. Recycling present polymer wastes is a direct and popular approach toward solving the environmental pollution problem. Indeed, developing and using biodegradable polymers is considered as the most utter method for resolving this situation. Due to the public concern regarding these situations, the increasing inclination of manufacturing companies to develop more sustainable products, limited fossil fuel resources, and climate change are significant reasons for governments and companies to find substitutes to crude oil-based products. Green-based polymers present enormous potential to reduce the dependence on fossil fuels and the related environmental impacts. It is a barely new technology but it has been growing concern and a quite lot of them have been industrialized.

Among all these polymers, polylactide (PLA) is one of the biodegradable polymers that can be used as promising alternative to the petroleum based commodity materials, because they can be derived from renewable resources, such as corn, potato, and other agricultural products (Kaci *et al.*, 2012). Polylactic acid (PLA) is a thermoplastic polymer derived from biomass and it is aliphatic polyester producible from renewable resources such as starch and sugar. Apparently, because of its renewability, biodegradability, and greenhouse gas neutrality, it has been emerging as an alternative to conventional petroleum-based polymeric materials. Even though biodegradable polymers have been developed a remarkable speed and the successful situation in this field is quite inspiring, they are far from becoming substitutes for traditional undegradable polymers.

According to Zhang *et al.,* (2011), due to its resource renewability and environmental degradability, PLA holds excellent potential as an alternative to traditional petroleum-based materials. However, there are limitation in their applications in the inherent brittleness, low-melt viscosity, and low-heat distortion temperature. Brittleness, low impact resistance, and high cost, especially, the sensitivity to the temperature of PLA, limit the use of PLA in the engineering field (Zhang *et al.*, 2012). These limits the applications of PLA that driving to replace the conventional thermoplastics (Jaratrotkamjorn *et al.*, 2012).

According to these circumstances, modifications for PLA were approached to improve the properties of PLA. Some techniques such as processing manipulation, copolymerization and blending have been tried to modify the mechanical brittleness of PLA (Zhang *et al*., 2012). Supported by Zhang *et al.*, (2012) stated that; except for chemical modification of PLA, physical blending was suitable to use to improve the properties of PLA. As stated by Liu and Zhang (2011), melt blending of polymers is a much more economical and convenient methodology than synthesizing a new polymers to achieve the properties unattainable with existing polymers. It is common practice where modification of PLA is to blend with flexible polymers. However, the improvement of mechanical properties of PLA is still necessary to obtain such elastomer or rubber with optimum performance (Juntuek *et al*., 2012).

For this particular study, natural rubber (NR) is chosen because is an ideal candidate as toughening agent for PLA. NR is widely used in various applications particularly for tires because of its excellent elastic properties over other synthetic counterparts (Saelao and Phinyocheep, 2005). Jaratrotkamjorn *et al.*, (2012) reported natural rubber is an eco-friendly rubber and derived from a renewable resource. NR should be a good toughening agent due to its high molecular weight and very low glass transition temperature (~-70˚C). This is the reason NR is an interesting candidate as impact modifier for PLA. It has excellent properties with high strength, high resilience, and high elongation at break (Mark, 1970). Even though, impact toughness improvement of PLA is greatly achieved; some drawbacks in strength and stiffness possibly could be a resistance towards polymer blend to obtain optimized properties.

In producing an advanced biodegradable composite in this research, carbon nanotube (CNT) is chosen to promote as nanofiller further enhance in the mechanical, electrical and thermal conductivity performance of PLA as nanofiller. Based on previous studies on CNT, it was considered to be an ideal filler high performance polymer composite. As expected with high aspect ratio and high modulus, experimentally introducing CNTs into a polymer improves remarkably the mechanical properties, crystallization and electrical conductivity of the matrix (Wu *et al*., 2008). Moreover, as nanofillers; CNT can also be more successful than others attending to its reduced diameter and its high surface-volume ratio (Pinto *et al.*, 2015). Therefore, high expectation to further improve PLA properties can be achieved by using CNT as nanofillers in this research.

Unfortunately, the non-polarity of NR makes PLA/NR blends is usually immiscible. Generally, chemically different polymers are immiscible and their blending leads to weak interfacial adhesion and thus poor mechanical integrity (Sadiku-Agboola *et al.*, 2011). In the case of PLA/NR blends, the difference in the polarity and molecular weight of PLA and NR may result in the poor compatibility between PLA and NR. And lead to poor impact strength (Juntuek *et al.*, 2012). Regarding to this problem, it is difficult to achieve an optimum properties because of literally the mechanical properties are strongly dependent on the interfacial characteristic between two components and stabilization of desired morphology or material structure.

This problem can be solved through grafting and improved its rheological, adhesive, thermal and curing performance. One of the classical approaches to improve the adhesion between the phases (reduction in the interfacial tension) is the use of a third component, a compatibilizer by graft copolymerization, which is usually a macromolecule designed to manipulate the interfacial properties (Elias *et al.*, 2007).

Since graft copolymers consisting of chemically identical segments of some polymeric constituents in the blends, they provide the higher phase compatibility resulting in the improved mechanical properties of the obtained finished product (Sookprasert *et al.*, 2017). Therefore, improvement of interfacial interaction between PLA and NR should be made by introducing maleic anhydride grafted NR or PLA in graft copolymerization as compatibilizer.

In this study, rheological mathematical models of non-Newtonian behaviour were required in order to understand the structure-properties relationship of polymer compounds. Despite its importance for industrial applications, the issue of how the rheology of a shear-thinning fluid affects the characteristics of two-phase stratified flow at different flow conditions is not yet completely understood. Only few works have been published on stratified flows in the presence of shear-thinning fluids (Picchi *et al.*, 2017). This may help us to clearly understand to behind of the physical properties of the polymer materials. As the result; in this project, Power Law and Carreau-Yasuda models were applied to describe the effect of shear – thinning behaviour of polymer melts and clearly understand the results from the experimental method in the rheological part. As described in Pinarbasi and Liakopoulus (2995), Carreau-Yasuda fits accurately many experimental viscosity curves over a wide range of shear rate.

1.2 Problem Statement

Limitation in PLA application has been recognized due to its brittleness and poor crystallisation. PLA toughness is one way to overcome this limitation, where natural rubber is chosen as impact modifier in this project. However, the difference in polarity between natural rubber and PLA may led to poor compatibility and poor mechanical properties especially impact strength.

According to the Hwang *et al.,* (2012), the formation of single and oligomeric grafts by grafting of Maleic anhydride onto polyolefins, and proposed that a bridge could be formed between grafted maleic Anhydride and polymer chains. It may lead to improve mechanical properties of polymer. Thus, reactive compatibilizer was used in this study to overcome the limitation in PLA and NR blend.

On the other hand, melt blending PLA with NR may greatly enhance impact toughness but the reductions in tensile strength and stiffness of the PLA materials still remains a challenge. Due to that, in this study CNT will be added as nanofiller or reinforcement agent in order to increase the strength and stiffness of material. Supported by Lee and Khang (2012), CNT is one of the most promising and practical applications of CNTs is their use as reinforcing filler in polymer matrices, with the outstanding improvement in mechanical properties due to their excellent chemical and physical properties such as strength and modulus.

Numerous experiments were conducted to study the properties of the interaction between NR and PLA incorporate with compatibilizers and also its nanocomposites. Corresponding with this, limited research has been carried out to understanding the rheology behaviour of polymers and their nanocomposites which highly useful for predicting the processing behaviour of PLA and its nanocomposites. Studies related to rheological behaviour of pure polymeric melts are well documented, while such studies on molten polymer blends and its nanocomposite are relatively limited, but are indispensable (Djellali *et al.,* 2015). Therefore, study related to understanding rheology behaviour of polymer melt and its nanocomposite was conducted. Accordingly, constitutive equations found in the literature that adequately describe polymer melt will be explored for their application in polymer blends and nanocomposites processing. Particular focus will be given in this project to nonlinear rheological characteristics of viscoelastic materials. For this reason, rheological mathematical models presented by power law model and Carreau – Yasuda model were applied in this particular study to describe the rheological characteristic of the polymer melt.

1.3 Research Objectives

The main objective of this research is to study fundamental science and interaction mechanism of biopolymeric nanocomposite system.

i. To investigate the effects of toughening agent (natural rubber) with different loading on mechanical, thermal, rheological and morphological properties in PLA/NR/CNT blend.
ii. To investigate the effect of compatibilizers (NR-g-MA and PLA-g-MA) on mechanical, thermal, rheological and morphological properties in the PLA/NR blend.
iii. To analyse the effects of different pristine CNT amount on mechanical, thermal, morphological and rheological properties of PLA/NR/Compatibilizers/CNT nanocomposite blend.
iv. To analyse the rheological characteristic of the PLA/NR/CNT with respect to contributions of the materials composition towards the rheological properties by using rheological mathematical models.

1.4 Scopes of Research

In order to achieve the objectives of the research the following scopes of work have been performed:

i. Sample preparations

Sample preparations in this study were involved preparing various samples of polymer blends using different ratio of NR ranging from 5% - 20% and CNT loading (1 - 8 phr). These involved compounding process from raw material feeding, extrusion, pelletizing and compression moulding according to the following sections:

i. PLA/NR blend
ii. Synthesis of compatibilizers (PLA-g-MA and NR-g-MA)
iii. PLA/NR/Compatibilizer blend
iv. PLA/NR/Compatibilizer/CNT nanocomposite

ii. Perform analysis and characterizations:

i. Mechanical Test

Evaluation of toughening effect by conducted Izod Impact test to study the effect of NR and compatibilizer ratio. Tensile test and flexural test also were conducted to study the effect in additional of NR and CNT loading on strength and stiffness of materials.

ii. Thermal properties analysis

Determination of thermal behaviour differential scanning calorimetry (DSC) and thermalgravimetric analysis (TGA) were conducted to analyse glass transition temperature, melting temperatute, percentage of crystallinity, degradation temperature and thermal stability of materials.

iii. Characterizations and morphological study

Scanning electron microscopy (SEM), NanoScanning electron microscopy (NanoSEM) and X-ray diffraction (XRD) analysis were carried out to characterize the morphology of the blends and to investigate the interfacial bonding and distribution between PLA/NR/Compatibilizer/CNT.

iv. Rheological properties analysis

Melt Flow Index (MFI) analysis was run to measure the ability of the materials's melt to flow under pressure and to determine the processing condition for material blends. Rotational rheometer was conducted to discover the rheological properties of PLA/NR/compatibilizer blends. Some important data was collected such as G', G" and complex viscosity as these data were used in modelling approaches.

v. Rheological Mathematical Models

Based on experimental data obtained from rheological analysis, Power Law models and Carreau – Yasuda model were used to obtain mathematical data to describe the rheological characteristic of the polymer melt. Both experimental and mathematical data were compared and analysed the suitability between both data. In this study, rheological theoretical models were approached to predicting the shear-thinning nonlinear rheological behaviour of materials on the effect of additional natural rubber and CNT as nanofiller.

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