TENSILE, THERMAL AND UV-RESISTANCE PROPERTIES OF POLY(LACTIC ACID)/ZINC OXIDE TREATED HALLOYSITE NANOTUBES NANOCOMPOSITES

by

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LIST OF ABBREVATIONS

APTES	3-aminopropyltriethoxysilane
ASTM	American Society for Testing and Materials
ATR-FTIR	Attentuated Total Reflectance-Fourier Transform Infrared
BI	Browning Index
Cu	Copper
Cs	Chitosan
C15A	Cloisite 15A
C30B	Cloisite 30B
DAS	3-(2-aminoethyl)aminopropyltriethoxysilane
EB	Elongation at break
EBS	Ethylenebis(stearamide)
EPDM	Ethylene Propylene Diene Monomer
Fe^{2+}	Ferum (II) ions
Fe^{3+}	Ferum (III) ions
FESEM	Field Emmision Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
GPC	Gel Permeation Chromatography
GRAS	Generally Recognised as Safe
HDPE	High Density Polyethylene
HNT	Halloysite Nanotubes
H_2O_2	Hydrogen Peroxide
I_{co}	Carbonyl Index
MMT	Montmorillonite
M_n	Number Average Molecular Weight

M_w	Weight Average Molecular Weight
ODP	Octadecyl Phosphonic Acid
OMHNT	Organomodified Halloysite Nanotubes
PE	Polyethylene
PI	Polydispersity Index
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Polystyrene
SDS	Sodium Dodecyl Sulfate
TAS	3-[2-(2-aminoethyl)aminoethyl]aminopropyltrimethoxysilane
TEM	Transmission Electron Microscopy
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
TiO_2	Titanium Dioxide
T_m	Melting Temperature
T_{max}	Maximum Decomposition Temperature
UV	Ultraviolet
UV-DRS	Ultraviolet-Visible Diffuse Reflectance Spectroscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
UVR	Ultraviolet Blocking Ratio
VR	Visible Shielding Ratio
XRD	X-ray Diffraction
YI	Yellowing Index
ZnO	Zinc Oxide

LIST OF SYMBOLS

a*	Redness chromaticity coordinates
b*	Yellowness chromaticity coordinates
ΔE^*	Colour differences
K	Shape factor
L*	Lightness chromaticity coordinates
λ	Wavelength
n_c	average Number of Random Chain Scissions
wt %	weight percentage

SIFAT-SIFAT TEGANGAN, TERMA DAN RINTANGAN UV NANOKOMPOSIT POLI(ASID LAKTIK)/ NANOTIUB HALOISIT TERAWAT ZINK OKSIDA

ABSTRAK

Matlamat kajian ini adalah untuk menghasilkan poli(asid laktik)/nanotiub haloisit (PLA/HNT) nanokomposit (dengan dan tanpa rawatan zink oksida (ZnO)) yang mempunyai kestabilan foto yang tinggi. HNT dirawat ZnO dengan kestabilan cas, struktur dan sifat-sifat morfologi yang optimum telah berjaya disintesis menggunakan teknik tanpa pelarut. Seterusnya, HNT-ZnO (1: 2) (formulasi optimum) dicampukan dengan PLA, dan kesan HNT dirawat ZnO pada pelbagai bebanan (1, 3, 5, 7, 10 wt%) terhadap sifat-sifat mekanikal, haba dan rintangan UV nanokomposit PLA/HNT telah dinilai. PLA/HNT-ZnO-3 menunjukkan pengimbangan dalam moduli tegangan, kekuatan tegangan dan elongasi di patah. Terma stability untuk kedua-dua PLA/HNT-ZnO dan PLA/HNT adalah lebih tinggi daripada PLA. Keputusan UV-Vis menunjukkan bahawa penambahan ZnO secara substansial meningkatkan keupayaan penyekatan UV dalam PLA nanokomposit di samping mengekalkan ketelusan sederhana di filem. Dengan pendedahan pada ujian luluhawa dipercepat selama tempoh 0, 30 dan 60 hari, PLA/HNT nanokomposit dengan rawatan ZnO menampil penurunan dalam indeks penguning (YI) dan tidak banyak perubahan dalam warna filem telah diperhatikan. Nilai YI yang rendah menunjukkan rintangan UV yang lebih tinggi dalam filem PLA/HNT-ZnO berbanding dengan PLA/HNT. Tambahan, kajian FTIR juga menunjukkan pengurangan nilai indeks karbonil (I_{CO}) PLA/HNT-ZnO pada peringkat awal 30 hari. Hal ini boleh dikaitkan dengan kehadiran HNT-ZnO, menyebabkan nanokomposit PLA kurang terdedah

kepada foto degradasi, selanjutnya kejadian penguntingan rantai yang kurang serta penurunan dalam berat molekul PLA telah dilihat.

TENSILE, THERMAL AND UV-RESISTANCE PROPERTIES OF POLY(LACTIC ACID)/ZINC OXIDE TREATED HALLOYSITE NANOTUBES NANOCOMPOSITES

ABSTRACT

The aim of this research is to prepare poly(lactic acid)/halloysite nanotube PLA/HNT nanocomposites (with and without zinc oxide (ZnO) treatment) with high photostability. ZnO treated HNT with optimum charge stability, structural and morphological properties were successfully fabricated via a solvent free technique. Thereafter, HNT-ZnO (1:2) (the optimum formulation) was incorporated into PLA, and the effects of ZnO treated HNT at various loadings (1, 3, 5, 7, 10 wt%) were evaluated on the mechanical, thermal and UV resistance properties with respect to PLA/HNT nanocomposites. PLA/HNT-3 shows a balance in tensile modulus, tensile strength and elongation at break. The thermal stability of both PLA/HNT-ZnO and PLA/HNT are higher than that of PLA. UV-Vis results demonstrated that addition of ZnO substantially enhanced the UV-blocking ability of PLA nanocomposites whilst maintaining moderate transparency in film. Upon exposure to accelerated weathering test for a period of 0, 30 and 60 days, PLA/HNT nanocomposites with ZnO treatment showed decreased in the yellowing index (YI) and not much change in colour of films was noted. The low YI values denote that the UV resistance was higher in PLA/HNT-ZnO films as compared to PLA/HNT. In addition, FTIR studies revealed the decrease in carbonyl index (I_{CO}) values of PLA/HNT-ZnO at the initial stage of 30 days. This is associated that in presence of HNT-ZnO, the PLA nanocomposites are less susceptible to photodegradation, as less occurance of chain scission and lesser reduction in the molecular weight of PLA were discerned.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Petroleum based polymers is one of the most common and persistent pollutants in ocean waters, beaches and landfills worldwide. A considerable part of them are seen coming from the streets, some going through the drains with the rain, and eventually reach into the rivers and lakes, and finally to the oceans. For that reasons, in the past decades, biodegradable polymers as an alternatives to petroleum-based polymers have been investigated and have attracted much attention as feasible alternatives in various applications such as biomedical products, films for argo-industry, nanocomposites for technical applications in automotive parts and electrical-electronic devices and more recently, packaging materials.

Poly(lactic acid) are undoubtedly one of the most promising candidates on the market of biodegradable polymers. They are produced from renewable resources such as sugar cane or corn, which are biodegradable and compostable. According to Gross and Kalra (2002), PLA degrades primarily by hydrolysis and not microbial attack on disposal. Therefore, even at high humidity, for PLA to encounter contamination by fungi, mold, or other microbes is exceptionally rare. It is of this unusual characteristic of a PLA that has been acknowledged as attractive packaging materials, which accommodate polymer to be in direct contact with foods for extended period of time. In addition, PLA have very little or no toxicity and possess high mechanical performance, comparable to those of commercial polymers which makes it more attractive (Ghanbarzadeh & Almasi, 2013). Due to that, more recently, nanoparticles for the production of high-performance materials based on PLA was intensively studied. Improvement on the quality and properties of PLA by introducing nano-sized particles is necessary to make this a competitive material among the polymers used in the industry.

Owing to its naturally abundance and high aspect ratio, halloysite nanotubes (HNT), are presently being popularised as reinforcing fillers in the studies of polymer nanocomposites. These natural aluminosilicate nanotubes have demonstrate improvement in properties for polymer such as its tensile strength, Young’s modulus, impact properties, flexural properties, and storage modulus (Liu et al, 2013; Wu et al, 2013; Stoclet et al, 2014; Chen et al, 2015). It is their unique nanoscale crystal structure, low density of hydroxyl functional groups, and their rod-like geometry that furnish HNT with good filler dispersion in a polymer matrix. Since this relatively new nanocomposites are potentially interesting for various applications (especially in food packaging), it is important to have clearer information about their performances, as well as their stability during aging conditions.

In most outdoor applications, the main element in fabricating polymeric material is the ability to resist UV light. It is of particular concern, as UV light is the key factor causing changes in the surface chemistry of the composites commonly known as photodegradation. Islam et al. (2010) and Bolio-Lopez et al. (2013) described that long exposure time to UV-radiation extensively reduces the molecular mass, stress and strain at break thus affecting the aesthetic appeal of PLA films. Following numerous studies of PLA based-clay nanocomposites, it prevails that oxidative degradation of these materials are more significant as compared to pristine PLA. Some studies proposed that the fast degradation could attribute to the catalytic effect of transition metal impurities of clay nanofillers (Bocchini et al, 2010; Bocchini & Frache, 2013; Gaaz et al, 2017). Therefore, considering these drawbacks of PLA/HNT nanocomposites on the photostability, the need for an improved novel nanocomposite formulation has arisen.

Among the metal oxide nanofillers, zinc oxide (ZnO) nanoparticles have gained considerable attention among researchers due to their low cost, easy availability, biocompatibility and possibility of performing surface modifications with different functional groups (Diez-Pascual & Diex Vicente, 2014). These nanoparticles are non-toxic and they have long been recognised and accepted as a safe additive by the United States Food and Drug Administration (USFDA, 21CFR182.8991). In recent years, manipulating ZnO into the polymeric matrix or as additives to a coating have substantially prove to increase the shelf-life of packaged product, as well as improve the photostability, due to their excellent UV absorption ability. Furthermore, ZnO have been considered as a potential candidate as reinforcing fillers in polymer composites. They possess exceptional mechanical properties, low coefficient of thermal expansion and high thermal conductivity, which exhibited improvement in thermal, mechanical, and other relevant properties of PLA (Pantani et al, 2013; Shankar et al, 2018).

Recently, surface modifications are being focused on HNT to enhance good interface compatibility with polymer. The exterior surface of HNT which comprised of silicates can typically interacts well with guest molecules through hydrogen bonding or Van der Waals forces as they are weakly charged. One of the promising tools that are widely used in increasing loading efficiencies is by grafting molecules onto the host site (Yuan et al, 2015; Guo et al, 2016). In the light of this study, modification of HNT by immobilising ZnO nanoparticles on the tubular nanotubes was investigated. ZnO nanoparticles can be used to integrate its UV-filtering properties with HNT apart from its reinforcing ability via the covalent bonding (Li et al, 2015). Further, the influence of ZnO on improving the properties of PLA/HNT nanocomposites as packaging material was thoroughly studied and particularly its function as an UV protective agent, have been highlighted by further exposed under the accelerated weathering test. It is known that polymer materials will undergo photochemical degradation when exposed to UV radiation (Tochacek et al, 2014). Thus, by surface modification of HNT (ZnO treated HNT), it could potentially assist in developing PLA/HNT nanocomposites of particular interest for outdoor application. Up to date, there is no study reported yet investigating the UV performances and weathering properties of PLA/HNT and PLA/HNT-ZnO nanocomposites. However, it is known that when PLA product is exposed to sunlight during its usage, the low wavelength and high energy UV radiation could lead to PLA degradation due to the presence of carbonyl group in its chemical structure which can absorb UV radiation at about 280 nm via n- π^* electron transition (Castro-Aguirre et al, 2016). Therefore, if the service life of the PLA product could be prolonged reasonably depends on its application, then the carbon footprint of the PLA can be reduced.

1.2 Problem Statement

The ultraviolet (UV) degradation of polymers has huge importance since the resistance to ageing, especially to UV light, is a key factor for outdoor applications. Therefore, the goal of the present work was to study the effect of HNT treated ZnO on the UV stability of PLA. Initially, in the fabrication of HNT-ZnO, an optimum loading ratio of zinc acetate dihydrate to HNT is to be taken into consideration. This is because tuning this parameter plays a crucial step, as the amount/distribution of the synthesised ZnO nanoparticles will have an influence in enhancing the UV absorption and thermal stabilization of the polymer nanocomposites. Moreover, HNT treated ZnO need to be fabricated because studies in the literature have showed that HNT naturally possess some metal impurities (for instance Fe^{2+}, Fe^{3+} iron ions), which can attribute to a huge impact on polymer oxidation. During UV weathering process, HNT can have pro-degradant effects on PLA photodegradation attributed to the chromophoric impurities of HNT having an inductive effect on the radical oxidation mechanism of PLA (Therias et al, 2017). Subsequently, this reveals that PLA/HNT nanocomposites without treatment will be highly susceptible to photo-oxidation upon weathering resulting in formation of discolouration and brittle products. Therefore, in order to control the photo-oxidative degradation in PLA/HNT nanocomposite, it is of interest to treat HNT with ZnO to enable further protection of nanocomposites against UV radiation for outdoor purposes.

1.3 Objectives

The aim of this research was to study the thermal, mechanical and typically focuses on the UV shielding properties, played by ZnO nanoparticles in the composition of PLA/HNT nanocomposites. In order to accomplish this goal, the following specific objectives were considered:

1. To determine the optimum zinc acetate dihydrate loading for the HNT treatment in order to obtain ZnO treated HNT nanofiller.
2. To determine the effects of HNT-ZnO on the tensile, thermal and UV-resistance properties on the PLA/HNT nanocomposites.
3. To investigate the effects of accelerated weathering on the properties of PLA/HNT nanocomposites (with and without ZnO treatment).

1.4 Scope of the Study

The outlined route in present study exploited the utilisation of ZnO in preparation of PLA/HNT nanocomposites and compared that to the untreated PLA/HNT nanocomposites. The goal was to demonstrate that ZnO treated HNT has the potential to provide efficient UV protection on polymer nanocomposites, improving their stability against photo-degradation for uses as packaging materials. Herein, scopes of the study are broken down into three main parts. The first part involved fabrication and characterisation of HNT-ZnO by manipulating the precursor ratio concentrations as described in Chapter 3. This was followed by the preparation of PLA nanocomposites via melt compounding with different weight percentage loadings (i.e. 1, 3, 5, 7, 10 wt%). Further, in this second stage that optimising the thermal, mechanical and particularly UV properties of PLA/HNT and PLA/HNT-ZnO was investigated via several analytical and spectroscopic techniques. Finally, the third study on the possibilities of PLA degradation process by comparing the optimum nanocomposites formulation of PLA/HNT nanocomposites with and without ZnO treatment. The accelerated weathering was carried out and the changes in physical and structural properties were monitored using colourimeter, Fourier transform infrared spectroscopy (FTIR), and Gel permeation chromatography (GPC).

1.5 Thesis Outline

This thesis is comprised of five chapters.

Chapter 1 represents the introduction part of the thesis, which gives preliminary view on the research background and problem statement of this research. This chapter also includes the overall outline of this dissertation.

Chapter 2 reveals the literature review part of the thesis, which contains adequate information on the literature done by past researcher; giving general information about the overview of PLA, HNT, ZnO as well as comprehensive literature review of PLA-based nanocomposites and its photodegradation mechanism towards UV exposure.

Chapter 3 represents the materials and methods. In this context, detailed explanation on fabrication of materials, the characterisation method utilised and general synthetic pathway are provided.

Chapter 4 displays the results and discussion of the project. Elaboration on the experimental results for the prepared ZnO treated HNT as well as the fabricated PLA/HNT nanocomposite with and without ZnO treatment are extensively discussed.

Chapter 5 denotes the conclusion of the project. This chapter provides summary based on the objectives of the project and suggest recommendation for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanocomposites

A nanocomposite, by definition is the fabrication and exploitation of structures with at least one dimension in the nanometre length scale (10^{-9} m) that creates novel properties and phenomena to the materials (Lagaron & Lopez-Rubio, 2011; Peelman et al, 2013).

Meanwhile, bio-nanocomposite is assign to an emerging class of biohybrid materials that show dimensions in the nanometer range (1–100 nm), resulting from the combination of biopolymers such as poly(lactic acid), polysaccharides, proteins, and nucleic acids with inorganic solids appearing no less than one measurement on the nanometer scale (Darde et al, 2007; Pande & Sanklecha, 2017,).

Distinctly, polymer is the primary phases, having continuous character which acts as a matrix to reinforce particles (discontinuous nanodimensional phase) having at least one dimension in the nanometre range (i.e. < 100 nm). The latter plays an important structural role in nanocomposite which exhibited much improved mechanical, barrier and optical properties as compared to neat biopolymers owing to its nanometre particles size as depicted in Figure 2.1 (Rhim & Ng, 2007; Rhim et al, 2013; Othman, 2014).

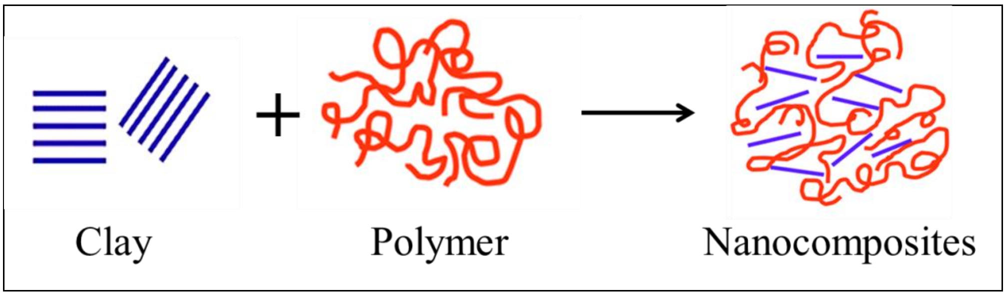

Figure 2.1: Illustration of the formation of nanocomposites (Othman, 2014).