

**PREPARATION AND PROPERTIES OF  
POLY(LACTIC ACID)/HALLOYSITE  
NANOTUBE NANOCOMPOSITES**

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**PREPARATION AND PROPERTIES OF POLY(LACTIC ACID)/  
HALLOYSITE NANOTUBE NANOCOMPOSITES**

**by**

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A.2	Paper 2 Polymer-Plastics Technology and Engineering (Published)
A.3	Paper 3 Journal of Polymer Environment (Published)
A.4	Paper 4 Journal of Thermal Analysis and Calorimetry (Published)
A.5	Paper 5 Journal of Thermoplastic Composite Materials (Published)
A.6	Conference Proceeding 1 (MAMIP2012) International, Malaysia
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## LIST OF ABBREVIATIONS

Al-OH	Alumino
ASTM	American Society for Testing and Materials
BaSO <sub>4</sub>	Barium sulfate
BRPBA	British Rubber Producers Research Association
CaCO <sub>3</sub>	Calcium carbonate
CNT	Carbon nanotube
DSC	Differential scanning calorimetry
EBS	N,N'-ethylenebis(stearamide)
ENR	Epoxidized natural rubber
EOC-g-MA	Ethylene-octene copolymers
EPDM	Ethylene propylene diene monomer rubber
EPR-g-MA	Ethylene-propylene rubber grafted maleic anhydride
FESEM	Field Emission Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HDPE	High-density polyethylene
HIPS	High-impact polystyrene
HNT	Halloysite nanotubes
HPC	Hydroxypropyl cellulose
MH	Magnesium hydroxide
OMMT	Organo-montmorillonite
OOT	Oxidative onset temperature
OTR	Oxygen transmission rate

PA6	Polyamide 6
PAA	Poly(acrylic acid)
PBS	Poly(butylene succinate)
PEG	Poly(ethylene glycol)
PET	Poly(ethylene terephthalate)
PHBHH	Poly [(3-hydroxybutyrate) -co-(3-hydroxyhexanoate)]
PLA	Poly(lactic acid)
POE	Polyethylene-octene copolymer
PP	Polypropylene
PVC	Poly(vinyl chloride)
RH	Relative humidity
RID	Refractive index detector
SEBS-g-MA	Maleic anhydride grafted styrene-ethylene/butylenes-styrene copolymers
SiO <sub>2</sub>	Silica
Si-OH	Silanols
TbC	Tributyl citrate
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV	Ultra-violet
CI	Carbonyl index

## LIST OF SYMBOLS

$E_a$	Activation energy of water diffusion
$T_{cc}$	Cold crystallization temperature
$W$	Corrected energy absorbed by breaking the test specimen
$T_c$	Crystallization temperature
$T_{dl}$	Decomposition temperature
$T_5$	Decomposition temperature at 5 % weight loss
$\chi_c$	Degree of crystallinity
$D$	Diffusion coefficient
$\Delta H_f$	Enthalpy for 100% crystalline PLA
$\Delta H_m$	Enthalpy of melting
$R$	Gas constant (8.314 J/K mol)
$T_g$	Glass transition temperature
$D_o$	Initial diffusion coefficient of the sample
$T_m$	Melting temperature
$w_{PLA}$	Net weight fraction of the PLA
$T_{onset}$	Onset decomposition temperature
$P_{O_2}$	Oxygen permeability coefficient
$M_t$	Percentage change at time, $t$
$M_m$	Percentage of maximum moisture absorption
$T$	Temperature
$W_w$	Weight of specimen after exposure to water
$W_d$	Weight of specimen prior exposure to water

# **PENYEDIAAN DAN SIFAT NANOKOMPOSIT POLI(ASID LAKTIK)/NANOTIUB HALOISIT**

## **ABSTRAK**

Dalam penyelidikan ini, nanotub haloisit (HNT) telah digunakan untuk meningkatkan sifat-sifat poli(asid laktik) (PLA). Nanokomposit PLA/HNT telah disediakan dengan kaedah penyebatian leburan diikuti oleh pengacuan mampatan. Tiga jenis pengubahsuai hentaman, iaitu kopolimer stirena-etilena/butilena-stirena tercantum maleik anhidrida (SEBS-g-MA), *N,N'*-etilenabis(stearamida) (EBS), dan getah asli terepoksida (ENR) telah digunakan untuk memperliat nanokomposit PLA. Sifat-sifat nanokomposit PLA/HNT telah dicirikan oleh ujian mekanik (ujian tegangan, lenturan, hentaman), analisis termal (kalorimetri pengimbasan pembezaan (DSC) dan analisis termogravimetri (TGA)), analisis morfologi (iaitu ujian mikroskopi elektron imbasan pancaran medan (FESEM) dan mikroskopi elektron pemancaran (TEM)), dan spektroskopi inframerah jelmaan Fourier (FTIR). Kekuatan hentaman bagi nanokomposit PLA/HNT telah meningkat sebanyak 300% dengan penambahan 15 wt% ENR. Dengan penambahan EBS dan ENR, HNT yang terserak halus dapat meningkatkan kesan penukleusan dan membantu dalam proses penghabluran bagi PLA. Walau bagaimanapun, penambahan SEBS-g-MA dan HNT melambatkan pembentukan kumin hablur yang bersaiz besar di dalam PLA. Kinetik penyerapan air bagi nanokomposit PLA/HNT adalah mengikut kelakuan hukum resapan Fickian pada suhu rendaman 30°C dan 40°C. Bagi sampel terdedah kepada 50°C, penyerapan air mematuhi hukum Fick di peringkat awal. Namun, semakin lama direndam, sampel tersebut didapati tidak lagi mematuhi hukum Fick dan

kehilangan berat berlaku. Hal ini disebabkan oleh hidrolisis PLA pada suhu rendaman yang tinggi yang telah disahkan melalui perubahan pH, pengurangan berat molekul, peningkatan nilai-nilai indeks karbonil (CI), dan perubahan sifat termal. Daripada keputusan TGA, didapati bahawa penguraian tunggal berlaku ketika keadaan nitrogen, manakala proses penguraian dua-peringkat telah berlaku dalam keadaan oksigen. Penambahan EBS dan ENR dapat meningkatkan kestabilan termal bagi PLA/HNT di bawah keadaan oksigen. Nanokomposit PLA/HNT6/ENR5 mempunyai kestabilan termo-beroksida yang tinggi di bawah atmosfera oksigen. Selain itu, penambahan 5 wt% ENR dalam nanokomposit PLA/HNT6 menganjukkan suhu permulaan pengoksidaan (OOT) kepada suhu yang lebih tinggi (dari 239.5°C kepada 296.5°C). Nanokomposit PLA/HNT6/ENR5 telah menunjukkan nilai pekali kebolehtelapan oksigen ( $P_{O_2}$ ) yang terendah ( $1.567 \times 10^{-4} \text{ cm}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$ ). Walau bagaimanapun, penambahan SEBS-g-MA tidak dapat meningkatkan sifat-sifat halangan gas oksigen bagi nanokomposit PLA/HNT. Daripada analisis spektroskopi UV-Vis, penambahan pengubahsuaian hentaman di dalam nanokomposit PLA/HNT telah mengurangkan penembusan cahaya dan hampir tiada cahaya UV dihantar melalui filem pada 300 nm. Namun, kesemua nanokomposit PLA/HNT kekal lutsinar melalui pengamatan visual. Kesimpulannya, penambahan ENR dalam nanokomposit PLA/HNT dapat meningkatkan sifat-sifat nanokomposit polimer secara efektif dari segi kekuatan hentaman, tenaga pengaktifan resapan air ( $E_a$ ), OOT, dan ciri-ciri halangan gas oksigen.

**PREPARATION AND PROPERTIES OF POLY(LACTIC ACID)/  
HALLOYSITE NANOTUBE NANOCOMPOSITES**

**ABSTRACT**

In this research, halloysite nanotube (HNT) was used to improve the properties of poly(lactic acid) (PLA). The PLA/HNT nanocomposites were prepared using melt compounding followed by compression molding. Three types of impact modifiers i.e., maleic anhydride grafted styrene-ethylene/butylene-styrene copolymer (SEBS-g-MA), *N,N'*-ethylenebis(stearamide) (EBS), and epoxidized natural rubber (ENR), were used to toughen the PLA nanocomposites. The properties of PLA/HNT nanocomposites were characterized by mechanical tests (i.e., tensile, flexural, and impact tests), thermal analysis (i.e., differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)), morphological analysis (i.e., field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM)), and Fourier transform infrared spectroscopy (FTIR). The impact strength of PLA/HNT nanocomposites was increased significantly to approximately 300% by the addition of 15 wt% ENR. A finely dispersed HNT could eventually increase its nucleation effect and assist in the crystallization process of PLA whilst in the presence of EBS and ENR. Nevertheless, the presence of SEBS-g-MA and HNT retard the formation of large crystallites of PLA. The kinetics of water absorption of PLA/HNT nanocomposite fitted Fickian diffusion behaviour at immersion temperatures of 30°C and 40°C. For the samples exposed to 50°C, the water uptake followed Fick's law during the initial stages, but at longer time periods, deviations and weight loss were observed. This may have been due to the hydrolysis of PLA at

higher immersion temperatures, which was confirmed by the pH change, reduction of molecular weight, increase in carbonyl index (CI) values, and thermal property changes. From the TGA results, it was found that single decomposition took place in the nitrogen atmosphere, while a double-stage decomposition process occurred in the oxygen atmosphere. The incorporation of EBS and ENR could improve the thermal stability of PLA/HNT under oxygen atmosphere. The PLA/HNT6/ENR5 nanocomposites exhibited high thermo-oxidative stability under oxygen atmosphere. Furthermore, the addition of 5 wt% of ENR in PLA/HNT6 nanocomposites increased the oxidation onset temperature (OOT) (from 239.5°C to 296.5°C). The PLA/HNT6/ENR5 showed the lowest oxygen permeability coefficient ( $P_{O_2}$ ) value of approximately  $1.567 \times 10^{-4} \text{ cm}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$ . However, the incorporation of SEBS-g-MA could not improve the oxygen gas barrier properties of PLA/HNT nanocomposites. From the UV-Vis spectroscopy analysis, the incorporation of impact modifiers in PLA/HNT nanocomposites decreases light transmittance and nearly no UV light can be transmitted through thin film at 300 nm. Nevertheless, all PLA/HNT nanocomposites remain transparent from visual view. In summary, the addition of ENR in PLA/HNT nanocomposites can effectively improve the properties of polymer nanocomposites in term of impact strength, activation energy of water diffusion ( $E_a$ ), OOT, and oxygen gas barrier properties among the others impact modifiers.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of research

The disposal of petroleum-based plastics and the restricted availability of petrochemical resources is a global concern. In recent years, biopolymers have been a focus of academic and industrial research in the context of sustainable development and reduced impact on the natural environment. Recent developments pertaining to the economical manufacturing of lactic acid from renewable agricultural resources (e.g. corn, potato, sugar beet, sugar cane) have made poly(lactic acid) (PLA) one of the most important biodegradable polymers (Garlotta, 2001; Yu et al., 2006; Cai et al., 2013). PLA offers good mechanical properties (i.e. high strength and modulus), a high degree of transparency, facile processability, good biocompatibility and excellent biodegradability. Thus, PLA is considered as a potential alternative to non-degradable polymers in various applications such as food packaging, automotive parts, disposable tableware, sutures, electronic and electrical devices, and drug delivery device (Martin & Averous, 2001; Krikorian & Pochan, 2003; Arroyo et al., 2010; Shin et al., 2011). However, it should be noted that PLA still faces some challenges e.g. inferior impact performance, low thermal stability, poor gas barrier properties and slow crystallization rate (Nam et al., 2006; Song et al., 2013). Blending is usually a practical and economic approach to improve the properties of PLA. Incorporating micro- or nano-fillers into PLA is a promising way improves the mechanical properties, thermal stability, gas barrier, and crystallization behaviour of PLA.