PERMEABILITY & CHARACTERIZATION STUDY OF (POLYLACTIC ACID) PLA-MODIFIED NA^{+} NANOCOMPOSITES FOR PACKAGING APPLICATION

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A thesis submitted in fulfillment of the requirements for the award of the Degree of Chemical Engineering

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February 2013

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ABSTRACT

One of the most versatile polymers is poly-lactic acid (PLA) which is well known as its biodegradable, high molecular weight, aliphatic polyester derived from renewable resources which is environmentally benign and good processability. In this study, a series of PLA nanocomposite with a different percentage of modified Na^+ with an addition of Polyethylene glycol (PEG) were prepared using the solution intercalation method. The modification of Na+ was done via an ion exchange method by using Copper (II) Chloride as an ion exchange solution with different type of solvent which are water, ethanol and methanol. The existence of the ion exchange between the modifications was confirmed through Atomic Absorption Spectrometry (AAS). The structure of the polymer was examined through X-Ray Diffraction (XRD) while their morphology was illustrated by Scanning Electron Microscopy (SEM). The modification of the Na^+ for every type of solvent was found to be successful where they show their existence of the Transition Metal Ions (TMIs) through AAS and the highest d-spacing was obtained in methanol through XRD with d=14.74 Å. A barrier properties of the film were examined to investigate the amount of water vapor transmit per unit area and time. The permeability of the film was found to decrease with the increase of Na^+ content since 3% of the clay content without an exhibition of Polyethylene Glycole (PEG) shows the lowest Water Vapor Transmission Rate (WVTR). An exfoliation behavior was also found in the structure of PLA with 3% of the clay without the presence of PEG with no peak was detected through XRD.This study indicates that PLA with a modified Na^+ as a filler is better than pure matrix in terms of structure, barrier properties and configuration also could be served as effective nanocomposite for packaging application.

KETELAPAN & KAJIAN PENCIRIAN (POLYLACTIC ACID) PLA- DENGAN PENGUBAHSUAIAN CLAY NANOCOMPOSITES SEBAGAI APLIKASI PEMBUNGKUSAN

ABSTRAK

Salah satu daripada polimer yang paling versatil ialah polimer asid aktik (PLA) yang terkenal dengan berat molekul yang tinggi, boleh dibiodegradasi, poliester alifatik berasal daripada sumber-sumber boleh diperbaharui yang mesra alam dan mempunyai kebolehan untuk diproses dengan baik. Dalam kajian ini, satu siri PLA nanocomposite dengan peratus Na+ berbeza diubah suai dengan tambahan Polyethylene glycol (PEG) disediakan menggunakan kaedah campuran interkalasi. Pengubahsuaian Na+ telah dilakukan melalui kaedah pertukaran ion dengan menggunakan Copper (II) Chloride dengan pelbagai jenis pelarut seperti air, etanol dan metanol. Kewujudan pertukaran antara ion telah disahkan melalui Atomic Absorption Spectrometry (AAS). Struktur polimer telah diperiksa melalui Belauan Sinar-x (XRD) manakala morfologi telah diilustrasi oleh Scanning Electron Microscopy (SEM). Pengubahsuaian Na+ menggunakan semua jenis pelarut didapati telah berjaya menunjukkan kewujudan Transition Metal Ions (TMIs) melalui AAS dan jarak-d tertinggi telah diperolehi dalam metanol melalui XRD dengan d=14.74 Å. Kajian terhaadap ciri-ciri ketelapan filem terhadap jumlah wap air yang boleh melepasi setiap kawasan beserta unit dan masa telah dilakukan. Ketelapan filem didapati berkurang dengan peningkatan kandungan Na+ dimana 3% kandungan Na+ tanpa kehadiran Polyethylene Glycole (PEG) menunjukkan Water Vapor Transmission Rate (WVTR) terendah. Rawakan juga ditemui dalam struktur PLA dengan 3% Na+ tanpa kehadiran PEG dengan tiada puncak dikesan melalui kajian XRD. Hal ini menunjukkan bahawa pengubahsuaian PLA dengan penambahan Na+ lebih baik daripada matriks tulen dari segi struktur, ciri-ciri ketelapan dan tatarajah juga boleh digunakan sebagai nanocomposite berkesan dalam aplikasi pembungkusan.

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AAS	-	Atomic Absorption Spectrometry
EDTA	-	Ethylenediaminetetraacetic acid
MMT	-	Montmorillonite
PEG	-	Polyethylene glycol
PLA	-	Poly-lactic Acid
SEM	-	Scanning Electron Microscopy
TMI	-	Transition Metal Ion
WVTR	-	Water Vapor Transmission Rate
XRD	-	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background Of Study

Since the last few decades, polymers have been chosen as the main resource in the manufacturing field especially in a packaging application since they provide several desired features like softness, transparency and lightness. European Bioplastics (2008) states that in 2007, 260 million metric tonnes per annum polymers produced. Until today, polymers derived from petrochemical-based plastics such as polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), was produced on a large scale production because of their good mechanical performance. However, nowadays the productions of plastics from petrochemicals have to be restricted since they are not easily degraded in the environment and non-totally recyclable. Furthermore, recycling this material was extremely impracticable due to the high cost of consumptions. As a result, most of the plastic waste goes straight to the landfills until today, our earth cannot afford further to receive any municipal waste (Richard et al, 2004). In order to overcome this problem, researchers have discovered the renewable sources based on biomaterials decomposed by natural resources. Currently, the most popular biodegradable polyester is aliphatic polyester. There are a series of biodegradable aliphatic polyesters used for commercial purpose. Among of them are Polyglycolide (PGA), Polycaprolactone (PCL) and Polylactic Acid (PLA). PLA is a biodegradable, low molecular weight, high transparency and good processability. Recently, PLA has been used as a short shelf life packaging product (Siracusa et al, 2008)

Nevertheless, PLA confront with cost and performance issues such as low ductility and brittleness. Singh et al. (2003) also mentioned that another limitation of PLA is its deficiency of gas barrier properties which are the important aspect to access the industry especially in the packaging production. Therefore, new technology has established the integration of polymer and layered silicate to produce nanocomposites to overcome these drawbacks (Okamoto, 2005). Nanocomposites technology is applicable to a wide range of application such as biomedical, transportation, and packaging.

There are three main techniques to be distinguished for preparing polymer nanocomposites which are in situ polymerization, solution intercalation and melt intercalation. In situ polymerization is a mixing of the nanoclay with the monomer then would be followed by polymerization. Melt intercalation consist of blending the organoclay with the polymer matrix in the molten state while solution intercalation can be done by mixing the organoclay in a solution of a polymer in a specific solvent followed by solvent evaporation.

The research in this study represents an effort on modification of the surface of nanoclay to disperse as a filler within PLA to form a nanocomposites by using an ion exchange method. The nanocomposites must chemically be modified to increase the interlayer space between the clay layers in order to maximize the opportunity of an exfoliation structure happened during the formation of polymer. The existence of the ion exchange method was confirmed through AAS. After that, the modified nanoclay will be intercalated with PLA during the formation of polymer nanocomposites. The structure of PLA in this study was confirmed through X-ray diffraction study (XRD) whereas the impact on the resulting morphology PLA/clay nanocomposites were measured by using SEM. Besides, the permeability of the film will be evaluated through ASTM E 95-96 by wet cup test method.

1.2 Problem Statement

New findings of renewable sources of biodegradable Polylactic acid (PLA) by natural resources gave a huge impact to overcome the environmental issues. This polymer however, is too much brittle and ductile in strength and even has a limitation to gas barrier properties. Nevertheless, the PLA properties can improve by adding nanoparticle fillers in pure matrix to offer an additional surface to interact with the pure matrix. In this study, a series of PLA nanocomposite with a different percentage of modified Na+ were prepared by using the solution intercalation method perhaps to provide an improved structure and better barrier properties of polymers.

1.3 Objectives

The objectives of this study are:

- To modify Sodium Cloisite organoclay using metal ion solution (ion exchange method)
- To produce PLA nanocomposite with good barrier properties.

1.4 Scopes Of Study

In order to achieve the objectives of this study, there are four scopes of this study defined which are:

- Modification of organoclay to improve the properties of the nanocomposite by using the ion exchange method. In order to achieve that, Atomic Absorbance Sprectometer (AAS) has been used to verify the existence of the ion exchange in the solution.
- Characterized the structure and morphological of PLA through SEM and XRD
- Fabrication of PLA nanocomposites by solution technique
- Testing the barrier properties of the PLA via the wet cup test method described by ASTM E95-96.

1.5 Rationale & Significance

This study has been done in order to improve the properties of the PLA nanocomposites in terms of permeability also the structure of PLA. In addition, it was done to prove the enhance of the brittleness and ductility of the nanoclay with an addition of a modification of nanofiller within the PLA structure. Consequently, it provides an environmental benign and safe to users.

The nanoclay also achieved the standard performance expected in the packaging application where they concern about the protection of the food quality from the environment and this study has verified its improvement in barrier properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Current Perspectives and Future Prospects: An Overview

The discovery of an era nanotechnology has begun since 1985 when the Toyota Company created the first polymer clay nanocomposite (Usuki et al., 1993). Since that, compounding of polymers with inorganic fillers and fibers was developed leading to novel polymeric materials with tailored thermal and mechanical properties at a lower cost. The field of materials science has lately begun to focus on the quest for composite materials that exhibit the positive characteristics of their initial components. Worldwide, there has been a new and strong desire to modify the structure and composition of materials on the nanometer scale. Thus, we are seeing the foreword of a new and improved class of composites, called as the nanocomposites.

2.2 Polymer Nanocomposite

According to Jordan et al. (2005), nanocomposites is defined as a composite material which at least one dimension of the component is in the nanometer scale (< 100 nm). Nowadays, the term nanocomposites are already common in our daily life where it gains attention from worldwide for current research and development in basically all technical disciplines. The numbers of commercial applications of nanocomposites have been growing at a rapid rate encompass biomedical, transportation, packaging, also electrical and electronic applications.

Naturally, the clay layers tend to bond strongly together, which makes the dispersion of the clay and the polymer matrix are difficult. By inserting the nano-sized inorganic compounds to the polymer matrix, the properties of polymers such as thermal stability and mechanical properties such as adhesion resistance, flexural strength, toughness and hardness can be enhanced and hence this has a lot of applications depending upon the inorganic material present in the polymers. Apart from that, Venkataraman (2005) also concludes that the polymer nanocomposites will increase modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability.

Polymer nanocomposites consist of a polymeric material such as thermoplastics, thermosets, or elastomers with reinforcement of nano-particles. Most commonly used nano-particles include montmorillonite organoclays (MMT), Carbon nanotubes (CNT) as well as graphene. While the thermoplastic or thermosets is used as a matrix in preparation of nanocomposites such as PLA and nylon.

2.2.1 Structure of Polymer Nanocomposites

Most of the packaging industries has focused on clay and silicates as they provide low cost, simple process ability, versatility, and significant improvement (Azeredo, 2009). There are three types of nanocomposites can be obtained depending on the preparation method, polymer matrix, organic cation and layered clay (Alexandre and Dubois, 2000). These methods are phase separated polymer-nanoclay composite, intercalated clay, and exfoliated clay (Blumstein, 1965), (Okamoto, 2005), and (Liu et al., 2006). **Figure 2.1** illustrated the type of nanocomposites structure. However, most of the polymer nanocomposite material's structure does not only have one kind of structure such as simply exfoliated or just intercalated but they usually have a plenty of the mixture of the structure (Huang et al., 2000).