Polylactic acid/ Thermoplastic Starch/Montmorillonite Nanocomposite: Morphological, Tensile Properties, Water Absorption and Degradation Behavior

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Polylactic acid/ Thermoplastic Starch/Montmorillonite Nanocomposite: Morphological, Thermal, Tensile Properties, Water Absorption and Degradation Behavior

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To my beloved mother and father

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ABSTRACT

Polylactic acid/ Tapioca starch/ Montmorillonite nanocomposites were prepared with different loadings of nanoclay (MMT) via twin screw extruder then compressed into plates for using in various tests. The effects of different loadings of MMT on mechanical, thermal, morphological properties, water absorption and biodegradation behavior of nancocomposites were investigated. Tensile properties were studied as some mechanical properties through this research. The thermal properties were characterized by using differential scanning calorimeter (DSC). Morphological properties of nanocomposites were studied through field emission scanning electron microscope (FESEM) and x-ray diffraction (XRD). Tensile strength increased by increasing the percentage of MMT in polymer matrix. Optimum amount for Young's modulus and percentage of elongation at break were determined among the five samples and these results are in fine agreement with XRD results that prove the intercalated and exfoliated structure of nanocomposites. The results of DSC showed that MMT increased melting temperature and crystallization temperature of matrix but reduction in glass transition temperature was observed. During the water absorption test, amount of water intake decreased by increasing the content of MMT in nanocomposite structure. Biodegradation study exhibited that incorporation of this type of nanoclay has growing effect on degradation rate of nanocomposites.

ABSTRAK

Polylactic asid/ Tapioca kanji/ Montmorillonite nanocomposit telah disediakan dengan pembebanan yang berbeza nanoclay (MMT) melalui penyemperit skru kembar kemudian dimampatkan ke dalam plat untuk menggunakan dalam pelbagai ujian. Kesan pemebanan yang berbeza MMT pada mekanikal, hartanah, haba morfologi, penyerapan air dan kelakuan biodegradasi daripada nanocomposites disiasat. Sifat tensil telah dikaji sebagai beberapa sifat mekanik melalui penyelidikan ini. Sifat haba telah dicirikan dengan menggunakan meter kalori pengimbasan kebezaan(DSC). Sifat morfologi nanokomposit dikaji melalui pelepasan bidang mikroskop electron imbasan (FESEM) dan pembelauan sinar-X (XRD). Kekuatan tegangan meningkat dengan meningkatkan peratusan MMT di dalam matriks polimer. Jumlah optimum untuk modulus Young peratusan pemanjangan telah ditentukan di kalangan lima sampel dan keputusan ini adalah dalam perjanjian halus dengan keputusan XRD. Sifat haba telah dicirikan dengan menggunakan meter kalori pengimbasan kebezaan(DSC). Keputusan menunjukkan bahawa MMT meningkat suhu peralihan kaca diperhatikan. Semasa jumlah ujian penyerapan air, pengambilan air menurun dengan meningkatkan kandungan MMT dalam struktur komposit nano. Kajian biodegradasi mempamerkan bahawa penubuhan jenis daripada nanoclay ini telah berkembang kesan ke atas kadar degradasi nanokomposit.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

PLA	Polylactic acid
TPS	Thermoplastic Starch
MMT	Montmorillonite
OMLS	Organically Modified Layered Silicate
MA	Maleeic Anhydride
Phr	Parts per Hundred
Tc	Crystalline Temperature
Tg	Glass Transition Temperature
Tm	Melting Temperature
ASTM	American Standard Test Method
FESEM	Field Emission Scanning Electron Microscope
XRD	X-Ray diffraction
DSC	Differential scanning calorimetry

CHAPTER 1

INTRODUCTION

1.1 Introduction

Recently, most plastics are derived from natural gas and crude oil that are not renewable resources. Small portions of plastics can be recycled or reused, while others are disposed in landfills. The latter contributes to the largest municipal solid waste due to theirs undegradable characters and consequently pollutes the environment. In recent years, plastics made from natural resources and biodegradable materials such as starch, polylatice acid (PLA) and poly-3-hydroxybutyrate (PHB) have received many attentions (Kolybaba *et al*, 2003). However, biodegradable polymer materials exhibit problems in processing characteristics and mechanical properties. By blending two or more polymers can reduce this problem (Vašková *et al.*, 2008). Biodegradable polymers are classified in three categories: synthetic polymers, naturally occurring processible bacterial polymers and blends of polymers and additives that are easily consumed by microorganism. Synthetic polymers and natural polymers that have enzymatically or hydrolytically labile bonds or groups are degradable.

Starch is one of natural polymers which has attracted much attentions since 1970s due to its total biodegradability, renewability, abundance and low cost. Native starch cannot be used directly because of poor mechanical properties, processability and stability of this polymer (Lu *et al.*, 2009). Various chemical and physical modifications are needed to improve the properties of starch. Blending, graft copolymerization and derivation are some examples of modifications that have been investigated so far. If the crystalline structure of native starch is destroyed in presence of plasticizer, thermoplastic starch will be obtained. This process is called gelatinization. Thermoplastic starch (TPS) has low oxygen permeability, so it can be used as a good barrier for oxygen in biodegradable packaging applications. TPS is a hydrophilic material and must be blended with other polymers to produce materials that suitable for many applications (Lu *et al.*, 2009).

Another important group of biodegradable polymer is polylactic acid (PLA). It is aliphatic, linear thermoplastic polyester which is synthesized by the ring opening polymerization of lactic monomers or condensation polymerization of the lactic acid monomers (Tzong and Cheng, 2006). PLA can also be produced from lactic acid that obtained from 100% renewable and agricultural resources such as sugar beets and starch. Biocompatibility, biodegradability, mechanical properties and thermal plasticity characters of PLA, make this polymer attractive for disposable and biodegradable plastic substituent and it is a growing polymer for various applications such as tissue engineering, drug delivery, food packaging and bottle containers (Jie *et al*., 2011).

However, PLA has few disadvantages. It is more expensive than conventional plastics and rate of degradation is slow in comparison with the rate of waste accumulation (Tianyi and Xiuzhi , 2000). In spite of good barrier properties to aromas, PLA has high permeability to oxygen, water vapor and carbon dioxide. The other disadvantages are it has poor thermal stability and inherent brittleness, thus limits its applications in many areas such as packaging and agriculture films. To overcome these problems, PLA should be modified for improving its properties and reduce its cost (Xiaogang *et al*, 2008).

The blend of PLA with other low cost biodegradable materials has been investigated (Jie *et al*., 2011). The preparation of starch/ PLA composites resulting in reducing the overall cost dramatically, improving the thermal properties and enhancing the biodegradability of blends (Kim *et al.*, 1998). A major problem of this blend is incompatibility of the hydrophilic starch with the hydrophobic PLA that makes a weak adhesion between these two components. This resulted poor mechanical properties of final blends (Zhang *et al.*, 2009). To overcome this problem and to improve the interfacial adhesion of blend, reactive compatibilization with Maleic Anhydride was studied (Woo *et al.,* 2007). Glycerol, formamide and water are used separately or combined as plasticizer to obtain thermoplastic starch during gelatinization process (Aouada *et al.,* 2011).

Meanwhile, poor mechanical and barrier properties of biopolymer are improved by using of layered silicates or nanoclays for producing nanocomposites. Saponite, hectorite and montmorillonite (MMT) are different clays that are used in polymer layered silicate (PLS). These clays are naturally abundant, economical and environmentally friendly (Xiaozhi *et al*., 2008). Polymer-Clay Nanocomposite, PCN is a class of clay filled polymer that has high application in food packaging industries. Several properties of PCN can be improved in comparison with neat polymer counterparts. Some of these improvements include: increase in heat resistance and flame retardancy, reduction in weight, superior mechanical strength, improved barrier properties against moisture and volatiles, ultraviolet, oxygen and carbon dioxide. (Sudip *et al.*, 2006). However, type of polymer and nanoclay and the extent of dispersion of nano particle in the polymer matrix would give major impact to the properties (Gopakumar *et al.*, 2002; Hotta and Paul, 2004; Morawiec *et al.*, 2005).

1.2 Problem Statement

Thermoplastic starch (TPS) and polylactic acid (PLA) are two biodegradable polymers that are increasingly being used for the replacement of petrochemical-based polymers. However, these polymers have some limitations that restrict the use of these materials such as brittleness, poor barrier and mechanical properties. Studies showed that the incorporation of clay montmorillonite (MMT) could enhance the properties of these polymers (Aouada *etal.* 2011; Sudip *et al.*, 2006; Mishra *et al.*, 2011). Research of PLA/ starch/MMT blends has been done (Arroyo *et al.*, 2010). This current study focuses on the effects of different loadings of MMT on various properties of nanocomposites. Few questions arise from this research are:

i. Does MMT affect tensile properties of nanocomposite
ii. Does MMT affect the thermal and morphological behavior of nanocomposite
iii. Does MMT affect the amount of water intake and degradation rate of nanocomposite

1.3 Objective of study

Biodegradable polymers have attracted more attentions over last two decades because of their environmental friendly characters and abundance natural resources. In the food packaging industry, apart from the degradability and cost of materials, some properties such as thermal, mechanical and barrier properties are important. The objectives of this study are:

i. To determine the effects of MMT content on tensile and morphological properties of PLA/starch nanocomposite.

ii. To characterize the thermal properties, degradation and water absorption behavior of nanocomposite samples.

1.4 Scope of study

The following activities have been carried out to achieve the objectives of this research:

1. Sample preparation:
   - i. Blending of PLA/starch/MMT via twin-screw extruder at different MMT loadings and pelletizing
   - ii. Compression moulding the PLA/starch/MMT nanocomposite into plates

2. Sample testing and characterizations
   - i. X-Ray diffraction (XRD)
   - ii. Field Emission Scanning Electron Microscopy (FESEM)
   - iii. Differential scanning calorimetry (DSC)
   - iv. Tensile properties
   - v. Water absorption analysis
   - vi. Biodegradability studies

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