UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLY(BUTYLENE SUCCINATE)/ POLY(BUTYLENE ADIPATE-COTEREPHTHALATE) ORGANO-CLAY NANOCOMPOSITES

CHIENG BUONG WOEI
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By

CHIENG BUONG WOEI

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Master of Science

June 2010

DEDICATION

To my beloved family
for their endless love, concern and encouragement …

To my beloved Loo Yuet Ying
for her romantic love, support, understanding and care…

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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CHIENG BUONG WOEI

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Chairman : Nor Azowa Ibrahim, PhD

Faculty : Science

The present research aims at studying the influence of organoclay on the properties of poly(butylene succinate)/poly(butylene adipate-co-terephthalate), PBS/PBAT blend. The organoclay was modified via cation exchange method using organic surfactants; protonated octadecylamine (ODA), cetyltrimethylammonium (CTA) and dimethyldioctadecylammonium (DDOA). The characterizations of organoclays were carried out by the Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Thermogravimetric analysis (TGA). XRD and FTIR results indicated sodium montmorillonite (Na-MMT) was successfully modified to be organoclay through cation exchange method. XRD showed that the basal spacing of clay increased with the formation of organoclays.

The PBS/PBAT blends were successfully prepared by melt blending technique. FTIR spectra revealed that the blends involved only physical interaction. Tensile strength and modulus decreased as the PBAT contents increased. SEM of the PBS/PBAT clearly demonstrated a two-phase morphology, which indicated the immiscibility of the components.

The PBS/PBAT nanocomposites were prepared by melt intercalation technique. The expansion of the basal spacing of the clay indicated the formation of intercalated as well as exfoliated types of nanocomposites which supported by XRD diffractograms and TEM images. FTIR spectra showed that there is strong interaction between clay and PBS/PBAT polymer matrix which gives rise to improvement in tensile properties. Tensile modulus increased with clay loading up to 7 wt% while improvements in tensile strength were limited. Tensile strength increased up to 1 wt% of clay while elongation at break decreased with the addition of clay.

The thermogravimetric analysis showed the presence of clays give significant improvement in thermal stability, particularly organoclay. The DMA analysis showed an increase in the storage modulus and loss modulus with the addition of organoclay into PBS/PBAT blend compared with neat PBS/PBAT. Furthermore, the presence of organoclay influenced the morphology of the PBS/PBAT blend which showed more homogeneous and single phase morphology. This revealed that the organoclay acts as compatibilizer for the immiscible PBS/PBAT polymer blend. Biodegradability results indicated that nanocomposites exhibit the same or a higher level of biodegradability compared with the PBS/PBAT blend.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai
memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT POLI(BUTILENA SUKSINAT)/POLI(BUTILENA ADIPAT-KO-TERAFITALAT) ORGANO-TANAH LIAT

Oleh

CHIENG BUONG WOEI

Jun 2010

Pengerusi **: Nor Azowa Ibrahim, PhD**

Fakulti **: Sains**

Matlamat kajian ini adalah untuk mengetahui kesan penggunaan organo-tanah liat ke atas sifat poli(butilena suksinat)/poli(butilena adipat-ko-terafitalat) (PBS/PBAT). Sampel organo-tanah liat disediakan melalui tindak balas penukar kation meggunakan surfaktan; oktadesilamina (ODA), setiltrimetilamonium (CTA), dan dimetildioktadesilamonium (DDOA). Pencirian organo-tanah liat dijalankan menggunakan spektroskopi penukar Fourier infra-merah (FTIR), pembelauan sinar-X (XRD) dan termogravimetrik (TGA). Keputusan XRD dan FTIR menunjukkan bahawa natrium montmorillonit (Na-MMT) telah berjaya diubahsuai menjadi organo-tanah liat melalui tindak balas penukar kation. Keputusan XRD menunjukkan bahawa jarak basal bertambah dengan pembentukan organo-tanah liat.

Adunan PBS/PBAT berjaya disediakan dengan teknik pengadunan leburan. FTIR menunjukkan bahawa adunan tersebut hanya melibatkan interaksi fizikal. Kekuatan tegasan dan modulus menurun dengan menambah kandungan PBAT. SEM mempamerkan morfologi dua fasa dan menujukkan adunan tersebut tidak bercampur.

Nanokomposit PBS/PBAT telah disediakan dengan teknik pengadunan leburan. Pengembangan ruangan basal tanah liat menunjukkan pembentukan nanokomposit jenis interkalasi atau terkelupas yang mana ianya disokong oleh diffraktogram XRD dan imej TEM. Spektrum FTIR menunjukkan terdapat interaksi yang kuat antara tanah liat dan PBS/PBAT polimer matrik dan memberi peningkatan dalam kekuatan regangan. Kekuatan modulus meningkat dengan kandungan tanah liat sehingga ke 7 wt%, sementara itu, peningkatan dalam kekuatan regangan adalah terhad. Kekuatan regangan meningkat sampai ke tahap 1wt% tanah liat manakala pemanjangan pada takat putus menurun dengan penambahan kandungan tanah liat.

Analisis termogravimetrik menunjukkan kehadiran tanah liat memberi peningkatan yang signifikan terhadap kestabilan terma, khususnya organo-tanah liat. Analisis DMA menunjukkan peningkatan dalam modulus simpanan dan modulus bebas dengan penambahan organo-tanah liat kepada PBS/PBAT berbanding dengan PBS/PBAT yang asal. Selain itu, kehadiran organo-tanah liat mempengaruhi morfologi adunan PBS/PBAT yang menunjukkan permukaan yang lebih homogen dan morfologi fasa tunggal. Ini menunjukkan bahawa organo-tanah liat bertindak sebagai unsur keserasian terhadap PBS/PBAT adunan yang tidak bercampur. Keputusan kebolehbiorosotan menunjukkan bahawa nanokomposit mempamerkan kebolehan yang sama atau lebih tinggi berbanding dengan kebolehbiorosatan adunan PBS/PBAT.

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Last but not least, I would like to express my deepest gratitude to my beloved family members for their continuous understanding and moral support throughout the period of my study. Special thanks to Universiti Putra Malaysia for the financial support under the Graduate Research Fellowship (GRF).

APPROVAL

I certify that a Thesis Examination Committee has met on 28 Jun 2010 to conduct the final examination of Chieng Buong Woei on his degree thesis entitled “Preparation and characterization of poly(butylene succinate)/poly(butylene adipate-co-terephthalate) organo-clay nanocomposites” in accordance with University Colleges Act 1971 and the Constitution of Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 12 August 2010

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

CHIENG BUONG WOEI

Date: 1 July 2010

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APES	Aliphatic polyester-based
CEC	Cation Exchange Capacity
CTAB	Cetyltrimethylammonium bromide
CTA-MMT	Cetyltrimethylammonium treated montmorillonite
DDOAB	Dimethyldioctadecylammonium bromide
DDOA-MMT	Dimethyldioctadecylammonium treated montmorillonite
DMA	Dynamic Mechanical Analysis
DTG	Derivative thermogravimetric
FTIR	Fourier Transform Infrared spectroscopy
HDPE	High Density Polyethylene
HCI	Hydrochloric acid
MMT	Montmorillonite
Na-MMT	Sodium Montmorillonite
ODA	Octadecylamine
ODA-MMT	Octadecylamine treated montmorillonite
OMLS	Organic modified layered silicate
PBAT	Poly(butylene adipate-co-terephthalate)
PBS	Poly(butylene succinate)
PCL	Poly(ε-caprolactone)
PLA	Poly(lactic acid)
PLLA	Poly (L-lactic acid)
PLSN	Polymer layered silicate nanocomposite
PE	Poly(ethylene)

PS	Poly(styrene)
PP	Poly(propylene)
PMMA	Poly(methyl methacrylate)
PVC	Poly(vinyl chloride)
rpm	Revolutions per minute
SEM	Scanning Electron Microscope
Tan δ	Tangent delta
TEM	Transmission Electron Microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric Analysis
XRD	X-ray diffraction
Wt%	Weight percentage
λ	Lambda
^oC	Degree Celcius

CHAPTER 1

INTRODUCTION

1.1 Background

Human beings depend a lot on great invention of science. One of the inventions is polymer which greatly brings many benefits to our mankind. Very few polymers are used commercially in their pure state without any additives. Several types of material are added to most of polymers to improve or modify their properties, such as plasticizers added to lower the glass transition or reduce the amount of crystallinity which softens the final product, silanes or other bonding agents added to composite to induce the bonding between polymers, finely divided rubber is added to brittle polymers to toughen them, both glassy and rubbery polymer are cross-linked to improve elastomer behavior or to control swelling, carbon black or silicas are added to rubber formulations to improve tear resistance and raise the modulus, fillers are added to reduce price and etc.

However, these polymer materials are non-biodegradable, thus widely used of these polymers for disposable applications significantly damaging the earth's ecosystem. The environmental effect of polymer plastic wastes brings global concern to a worrying status. Considerable attention has been paid to biodegradation polymers, mainly owing to increase interest for preservation of environment. Many efforts have been made to solve problems generated by plastic waste, particularly by one-time-use disposable commodity materials. Most of the research attention was focused on the replacement of petro-based plastics by biodegradable material with similar mechanical properties. Biodegradable polymers have been considered as most promising materials for this purpose.

One of the methods to improve these biodegradable polymers is to develop nanocomposites using these materials. Nanocomposites constitute one of the most developed areas of nanotechnology. These materials being refer to composite components with nanoscale dimensions. Commonly, such fillers have at least one dimension in nanometer range and typically 1 to 20 nm (Komarneni, 1992).

Montmorillonite clay was the most common filler that widely been used in the preparation of nanocomposites with polymers. Polymer layered silicate (PLS) nanocomposites are a combination of nanometer sized montmorillonite clay platelets with a polymer matrix. These nanocomposites usually exhibit superior properties to those of the pristine polymer and conventional inorganic particle filled composite materials because of the synergistic effects from the two constituting components and the strong interaction between the high specific area nanoclay and the polymer. This confinement of the chains and strong interaction between the clay and polymer render the nanocomposite with remarkable improvements of material properties. These improvements include increased tensile properties, high storage modulus, high heat distortion temperature, decreased gas permeability and flammability, and increased biodegradability rate of biodegradable polymers (Sinha Ray and Okamoto, 2003b).

All of these improvements strongly depend on the structure and properties of the montmorillonite clay. The montmorillonite clay is usually modified with large surfactant cations, such as a long chain alkylammonium to improve the wetting ability with the polymer matrix. After the organotreatment, the polymer matrix and the clay surface have better affinity, which is essential to the dispersion of clay platelets, but this would confine the chains and segmental movement around the platelets.

1.2 Biodegradable Polymer

Biodegradable polymers have received much attention in the last two decades because of potential applications in the fields related to environmental protection. Biodegradable polymers are a degradable polymer in which the degradation is results from the action of naturally occurring microorganism such as bacteria, fungi and algae. A lot of scientific research is focused on the development and commercialization of biodedegradable polymers. They can be obtained from renewable resources like corn, starch, wood cellulose, etc. However, they can also be derived from the petrochemicals resources. Due to comparatively higher cost, small-scale, and certain properties limitations compared to conventional plastics, biodegradable polymers in general are not prevalent in the mainstream of plastic industry. However, the conventional plastics such as polystyrene (PS), polypropylene (PP), polyethylene (PE) and poly(vinyl chloride) (PVC) are resistant to biodegradation.

Although biodegradable polymers have started making inroads into the commercial applications, there is lot of potential in the improvement of their properties for large scale or mass level applications. Some of the widely available biodegradable polymers are poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), poly(caprolactone) (PCL), poly(butylene succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT), thermoplastic starch, cellulose and etc (Tokiwa and Calabia, 2007). Most biodegradable polymers belong to thermoplastics. However, thermoplastic from polyolefins are not biodegradable, even if some of them have prooxidant additives making them photo and/or thermodegradable, the assimilation of oligomers or monomers by microorganism is not yet totally proved.

1.3 Poly(butylene succinate)

Poly(butylene succinate) PBS is a biodegradable aliphatic thermoplastic which synthesized by polycondensation of 1,4-butanediol with succinate acid with many desirable properties including biodegradability, melt processability and thermal and chemical resistance. It can be processed in the field of textiles into melt-blown, multifilament, monofilament, flat and split yarn (Fujimaki, 1998). The structure of PBS is shown in the Figure 1.1. PBS has a promising future because both the monomers used in the condensation polymerization can be obtained from the renewable resources such as corn, sugarcane, and etc. Various chemical companies are in the process of developing the technology to produce succinic acid from renewable resources at bulk level. Therefore, the PBS can be categorized into the green and sustainable class of polymeric materials. Some examples of its potential applications include shampoo bottles, beverage bottles, food trays, shopping bags, cups, and etc.