UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLY(BUTYLENE ADIPATE-CO-TEREPHTHALATE)/POLY(VINYL CHLORIDE)/CLAY NANOCOMPOSITES

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By

MOHD NAZRI BIN MOHD RAHIM

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January 2010

Chairman: Dr. Nor Azowa Ibrahim, PhD

Faculty: Science

This research focused on blending poly(butylene adipate-co-terephthalate) (PBAT) with poly(vinyl chloride) (PVC) and effect of organoclay on the properties of PBAT/PVC composites.

In order to improve the clay and polymer compatibility, the clay was first converted into the organoclay. The organo-montmorillonite (OMMT) was prepared via ion exchange technique using organic surfactants; octadecylamine (ODA) and dimethyldioctadecyl ammonium bromide (DDOAB). The X-ray Diffraction (XRD) results revealed that the interlayer distance of the sodium montmorillonite (Na-MMT) increases with the formation of the organoclays. The presence and the amount of the alkyl ammonium ions in the organoclays were also characterized using Fourier Transform Infrared spectroscopy (FTIR) and Thermogravimetric Analysis (TGA), respectively.

The PBAT/PVC composite and PBAT/PVC/clay nanocomposites were prepared by melt blending technique using Brabender internal mixer. The effect on the amount of PVC loading on tensile properties of PBAT/PVC composite was studied. The tensile properties of PBAT/PVC composites increased with the increase of PVC loading. At PBAT/PVC composite ratio (50/50), the dynamic mechanical analysis (DMA) result proves that PBAT and PVC formed a miscible system with one glass transition temperature (T_g). Furthermore, the incorporation of PVC results in a gradual increase of the viscosity and decrease of elasticity. The decomposition temperature of PBAT in the composite increased with the addition of the PVC. Scanning electron micrograph (SEM) showed single phase morphology on the tensile fractured surface of PBAT/PVC composite which tend to promote miscibility resulting in good tensile properties. The FTIR spectra indicated a chemical interaction between PBAT and PVC supports the formation of miscible composite.

The nanocomposites were examined by XRD, SEM, transmission electron microscopy (TEM), TGA and Instron Machine. XRD results revealed the expansion of the interlayer spacing of the clay indicates the formation of both intercalated and exfoliated nanocomposites which supported by TEM micrographs (intercalated).

The organoclay behave as compatibilizer agent in PBAT/PVC composites which gave homogenous morphology of PBAT/PVC hence give rise to the enhancement in mechanical properties of nanocomposites. The tensile strength and modulus of the nanocomposite increased while elongation at break decreased with the addition of the clay. Nanocomposites show the characteristic of reinforcing fillers with enhanced in the mechanical properties of PBAT/PVC composites. However the DMA does not exhibit enhancement of the storage modulus indicated that the elastic responses of PBAT/PVC composite towards deformation were not influenced by the presence of organoclay. The TGA showed the presence of clay in PBAT/PVC matrix gave strongly efficient improvement in thermal stability of PBAT/PVC/clay nanocomposites.

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

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT POLI(BUTILENE ADIPATE-CO-TEREPHTHALATE)/POLI(VINIL KLORIDA)/TANAH LIAT

Oleh

MOHD NAZRI BIN MOHD RAHIM

Januari 2010

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Penyelidikan ini tertumpu kepada mengadun poli(butilene adipate-co-terephthalate) (PBAT) dan poli(vinil klorida) (PVC) dan kesan organo-tanah liat ke atas sifat komposit PBAT/PVC.

Untuk meningkatkan keserasian pengadunan tanah liat dengan polimer, tanah liat diubahsuai terlebih dahulu kepada organo-tanah liat. Organo-tanah liat disediakan melalui teknik pertukaran ion menggunakan surfaktan organik; oktadesilamina dan dimetildioktadesil bromida ammonium. Keputusan XRD menunjukkan jarak antara lapisan Na-MMT bertambah dengan pembentukan organo-tanah liat. Kehadiran dan jumlah ion alkil ammonium dalam organ-tanah liat juga ditentukan masing-masing dengan menggunakan FTIR dan TGA.

Komposit PBAT/PVC dan nanokomposit PBAT/PVC/tanah liat telah disediakan dengan kaedah pengadunan leburan menggunakan pencampur dalaman Brabender. Kesan jumlah kandungan PVC kepada ciri-ciri tegangan komposit PBAT/PVC telah dikaji. Ciri-ciri tegangan komposit PBAT/PVC meningkat dengan bertambahnya kandungan PVC. Pada nisbah adunan PBAT/PVC (50/50), keputusan analisis mekanik dinamik (DMA) membuktikan PBAT dan PVC membentuk satu sistem adunan dengan satu suhu peralihan kaca. Adunan bersama PVC menyebabkan peningkatan kelikatan dan pengurangan keanjalan. Suhu penguraian PBAT dalam campuran bertambah dengan pengadunan bersama PVC. Mikrograf pengimbasan electron menunjukkan morfologi satu fasa pada permukaan patah tegang adunan PBAT/PVC menunjukkan keserataan yang membawa kepada ciri-ciri tegangan yang baik. Spektrum FTIR menunjukkan terdapat hubungan kimia antara PBAT dan PVC, yang menyokong pembentukan adunan boleh campur.

Nanokomposit telah diperiksa dengan belauan sinar-X, mikroskopi pengimbasan elektron, mikroskopi penghantaran elektron, analisis termogravimetri dan mesin Instron. Keputusan XRD mendedahkan pengembangan jarak antara lapisan tanah liat menunjukkan terbentuknya nanokomposit jenis interkalasi dan terkelupas yang mana ia disokong oleh imej TEM.

Organo-tanah liat bertindak sebagai ejen keserasian dalam adunan PBAT/PVC yang memberi morfologi seragam seterusnya meningkatan ciri - ciri mekanikal nanokomposit. Kekuatan tegangan dan modulus nanokomposit meningkat manakala pemanjangan pada takat putus menurun dengan penambahan tanah liat. Nanokomposit yang terbentuk menunjukkan peningkatan pada sifat-sifat mekanikal yang merupakan ciri-ciri pengisi pengukuh. Bagaimanapun DMA nanokomposit tidak mempamerkan peningkatan modulus simpanan menunjukkan yang tindak balas elastik campuran PBAT/PVC ke kecacatan tidak dipengaruhi oleh kehadiran organo-tanah liat. Analisis termogravimetri menunjukkan kehadiran lapisan tanah liat dalam matrik PBAT/PVC memberikan peningkatan berkesan terhadap kestabilan terma nanokomposit PBAT/PVC.

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I certify that an Examination Committee has met on **2010** to conduct the final examination of Mohd Nazri Bin Mohd Rahim on his Master of Science thesis entitled "**Preparation and Characterization of Poly(butylene adipate-co-terephthalate)/Poly(vinyl chloride)/Clay Nanocomposites**" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination are as follows:

Chairman, PhD
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This thesis 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 Supervisory Committee were as follows:

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Date: 8 April 2010

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or any other institutions.

MOHD NAZRI BIN MOHD RAHIM

Date: 4 January 2010

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LIST OF ABBREVIATIONS

Å	Amstrong
AAC	Aliphatic-aromatic copolyester
Ar	Aramid
ASTM	American Standard for Testing and Materials
$CaSt_2$	Calcium stearate
CEC	Cation Exchange Capacity
C20A	Cloisite 20A
DSC	Differential scanning calorimetry
DDOA-MMT	Dimetyldioctadecyl ammonium montmorillonite
DEHP	bis-2-ethylhexyl phthalate
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
DOP	Dioctylphthalate
DMA	Dynamic mechanical analysis
DTG	Derivative thermogravimetric
Eb	Elongation at break
ESBO	Epoxidized soya bean oil
FTIR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
HCl	Hydrochloric acid
IUPAC	International Union of Pure and Applied Chemistry
LDPE	Low density polyethylene
MMT	Montmorillonite

Na-MMT	Sodium montmorillonite
NBR	Nitrile butadiene rubber
ODA-MMT	Octadecylamine montmorillonite
OMMT	Organic Montmorillonite
PBAT	Poly(butylene adipate-co-terephthalate)
PBT	Poly(butylene terephthalate)
PCL	Poly(ε-caprolactone)
PGA	Poly(glyco1ic acid)
PLA	Poly(lactic acid)
PLSN	Polymer-layered silicate nanocomposites
PE	Polyethylene
PS	Polystyrene
PP	Polypropylene
PMMA	Poly(methyl methacrylate)
PVC	Poly(vinyl chloride)
rpm	Revolution per minute
SEM	Scanning electron microscope
Tan δ	Tangent delta
TEM	Transmission electron microscope
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
T_m	Melting temperature
TMQ	2,2,4-trimethy-1,2-dihydroquinoline
wt%	weight percentage

XRD	X-ray diffraction
$ZnSt_2$	Zinc stearate
λ	Lambda (wavelength)
µm	micron meter
^oC	Degree Celcius

CHAPTER 1

INTRODUCTION

1.1 Background of the study

In the recent years, the demands for a better performance material are so great to satisfy engineering constraints. For that purpose, polymer is the best choice in term of price and handling. Nevertheless, the properties of pure polymer are not ideal for all applications. In order for polymers to be useful, addition of fillers and reinforcements into the polymer matrix to form composites are necessary.

Polymer blending provides a powerful route to engineering new properties in materials using available polymers. From polymer blending it is possible to produce a range of materials with properties that are superior to that of each individual component polymers. The main advantages of the blended systems are simplicity of preparation and ease of control of physical properties by compositional changes, and also it usually requires little or no extra expenditure compared to new polymer synthesis. However, the miscibility between the constituents of polymer mixture on molecular scale is responsible for material with superior properties (Mohammad *et al.*, 2008).

PBAT is aliphatic aromatic copolyester, which is fully biodegradable. It degrades within a few weeks with the aid of naturally occurring enzymes. It is also known as Ecoflex as the trade name. It has no adverse effect on the environment and has excellent physical properties which can be blended with other biodegradable resins to impart high flexibility. However, most biodegradable polymers based on aliphatic polyesters, such as poly(glyco1ic acid) (PGA), usually have a lower T_g, so their performance and processability could not sometimes match the requirements, thus make it limited usefulness as engineering plastics (Yiwang *et al.*, 2008). Moreover, the high cost of PBAT comparable to that of many general purpose plastics has led to the limitation of its application (Naiwen *et al.*, 2009). So combining PBAT with other stiff polymer is taking into consideration to encounter its weaknesses.

PVC is an important commercial thermoplastic in the world, and one of the most versatile thermoplastic in plastic industry. However pure PVC is a rigid polymer at room temperature and it must be combined with additives in order to provide the properties needed in the finished products. It is efficient to form miscible systems with other substances acting as plasticizers (phthalates, phosphates, adipates, etc.), which are subject to improve flexibility and softness. These plasticizers are expected to reduce the modulus, tensile strength, hardness, density, melt viscosity, glass transition temperature, electrostatic chargeability and volume resistivity of a polymer, while at the same time increasing its flexibility, elongation at break, toughness, dielectric constant and power factor (Matthews, 1996).

Most common plasticizers (dioctylphthalate (DOP), bis-2-ethylhexyl phthalate (DEHP) and diisononyl phthalate (DINP)) are classified as harmful for environment (ecotoxic) (Green Paper, 2000). Thus it makes PVC risky to human health and the environment throughout its entire life cycle, i.e. at the factory, in our homes, and in the trash. Our bodies can be contaminated with poisonous chemicals released during the PVC lifecycle, such as mercury, dioxins, and phthalates, which may pose irreversible life-long health threats (Mustafizur and Christopher, 2004). A promising way to obtain safe and durable PVC is to substitute phthalate with compatible polymer which can behave as plasticizers.

When produced or burned, PVC plastic releases dioxins, a group of the most potent synthetic chemicals ever tested, which can cause cancer and harm the immune and reproductive systems. PVC losses of HCl (dehydrochlorination) thus the active hydrogen is apparently replaced in PVC producing polyene sequences $(CH=CH)_n$. This leads to the thermal degradation of PVC during processing causing by the liberation of hydrogen chloride at labile sites of the PVC molecular chain (Hjertberg and Sorvic, 1983). Therefore, it is necessary to mix PVC with stabilizer in order to prevent and delay degradation by heat and light.

In addition, these plasticizers leached out from the polymer. Many researchers have investigated the approach of using alternative plasticizers to minimize leaching of plasticizers. Polymeric plasticizers have a great advantage in their inherent low volatility and are now being studied as replacements for traditional plasticizers. They can be designed so that they are highly compatible with the host polymer and also leaching and volatility issues have been significantly improved over traditional plasticizers