UNIVERSITI PUTRA MALAYSIA

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DEVELOPMENT OF POLYURETHANE/CLAY NANOCOMPOSITES BASED ON PALM OIL POLYOL

TEUKU RIHAYAT

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, In Fulfilment of the Requirements for the Degree of Doctor Of Philosophy

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DEDICATION

Thanks to my beloved wife, sons, parents and my loving family for their patience and support during the long preparations of this thesis

Abstract of thesis presented to the Senate of Universiti Putra Malaysia
In fulfilment of the requirements for the degree of Doctor of Philosophy

DEVELOPMENT OF POLYURETHANE/CLAY NANOCOMPOSITES BASED ON PALM OIL POLYOL

By

Teuku Rihayat

November 2007

Chairman : Assoc.Prof. Dr. Saari B. Mustapha

Faculty : Engineering

Polyurethanes (PURs) are very versatile polymeric materials with a wide range of physical and chemical properties. PURs have desirable properties such as high abrasion resistance, tear strength, shock absorption, flexibility and elasticity. Although they have relatively poor thermal stability, this can be improved by using treated clay. Polyurethane/clay nanocomposites have been synthesized from renewable sources. A polyol for the production of polyurethane by reaction with an isocyanate was obtained by the synthesis of palm oil-based oleic acid with glycerol. Dodecylbenzene sulfonic acid (DBSA) was used as catalyst and emulsifier. The unmodified clay (kunipia-F) was treated with cetyltrimethyl ammonium bromide (CTAB-mont) and octadodecylamine (ODA-mont). The *d*-spacing in CTAB-mont and ODA-mont were 1.571 nm and 1.798 nm respectively and larger than that of the pure-mont (1.142 nm). The organoclay was completely intercalated in the polyurethane, as confirmed by a wide angle x-ray diffraction (WAXD) pattern.

Polyurethane/clay nanocomposites were prepared by a pre-polymer method and were evaluated by fourier transform infrared (FTIR) spectra to determine micro-domain structures of segmented PU, CTAB-mont-PU 1, 3, 5 wt% and ODA-mont-PU 1, 3, 5 wt%. The morphology of the nanocomposites was characterized by X-ray diffraction (X-RD) and the pattern showed that all of the nanocomposites produced from this work are of the intercalated type. These were further confirmed by transmission electron microscopy (TEM) observation and scanning electron microscopy (SEM) when the surfaces of the materials were studied. Thermal stability was investigated with thermogravimetric analysis (TGA). The results showed that adding clay demonstrated better thermal stability in comparison with the virgin polyurethane. Onset degradation of pure PU is at 200^{o}C, and is lower than that of the CTAB-mont PU and ODA-mont PU which takes place at about 318^{o}C and 330^{o}C, respectively. The mechanical properties (including the dynamic mechanical properties) of pure polyurethane (PU) and PU/clay nanocomposites, were measured. The modified organoclay had a remarkably beneficial effect on the strength and elongation at break of the nanocomposites, which both increased with increasing clay content with the increase of the tensile strength of more than 214% and 267% by the addition of only 5 wt% of the montmorillonite CTAB-mont PU and ODA-mont PU, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

Pembangunan Poliuretana/tanah liat Bernano Komposit Berasaskan Poliol Minyak Sawit

Oleh

Teuku Rihayat

Nopember 2007

Pengerusi : Prof. Madya Dr. Saari B. Mustapha

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Poliuretana (PUR) merupakan bahan polimer yang sangat versatil yang mempunyai ciri-ciri fizikal dan kimia yang sangat luas. PUR juga mempunyai sifat-sifat yang menarik seperti ketahanan lelasan, kekuatan koyak, penyerapan kejutan, fleksibiliti dan kekenjalan yang tinggi. Walaupun PUR mempunyai kestabilan terma yang rendah tetapi ia masih boleh diperbaiki dengan mengunakan tanah liat terawat. Polyurethane/tanah liat bernano komposit telah disintesa daripada bahan boleh diperbaharui. Bahan poliol bagi penghasilan polyurethane melalui tindakbalas dengan isosianat telah diperolehi melalui sintesis asid oleic dari minyak sawit dengan gliserol. Asid dodecylbenzene sulfonic (DBSA) pula berfungsi sebagai pemangkin dan pengemulsi. Tanah liat asal (Kunipia-F) telah dirawat dengan cetyltrimethyl bromide ammonium (CTAB-mont) dan octadodecylamine (ODA-mont). Jarak *d* pada CTAB-mont dan ODA-mont adalah 1.571 nm dan1.798 nm yaitu lebih besar daripada mont tulen (1.142 nm). Tanah liat telah tersisip ke dalam PU sebagai ditunjukkan pada corak WAXD.

PU/tanah liat bernano komposit telah disediakan daripada kaedah prapolimer dan dinilai melalui fourier transform infra red (FTIR) rajah bagi menentukan struktur mikro domain bersegmen PU, CTAB-mont PU 1, 3, 5 wt% dan ODA-mont-PU 1, 3, 5 wt%. Morfologi ke atas nanokomposit telah digambarkan sifatnya melalui belauan X-ray (X-RD) dan corak tersebut menunjukkan bahawa kesemua nanokomposit yang terhasil dalam kajian adalah dari jenis ”*intercalated*”. Kajian lebih lanjut dilakukan dengan menggunakan kaedah “transmission electron microscopy” (TEM) dan “scanning electron microscopy” (SEM) untuk mempelajari permukaan dari bahan material tersebut. Kestabilan terma bahan dikaji melalui analisis termogravimetri (TGA). Kajian menunjukkan penambahan tanah liat menghasilkan kestabilan terma yang lebih baik berbanding PU tulen. Sifat-sifat mekanikal (termasuk sifat-sifat mekanikal dinamik) bagi PU tulen dan PU/tanah liat bernano komposit telah diukur. Kajian mendapati tanah liat berorgano memberikan peningkatan yang memberangsangkan dalam sifat tegang dan suhu peralihan kaca, dimana kedua sifat tersebut meningkat dengan penambahan tanah liat berorgano, dimana kenaikan terhadap kekuatan tegangan sebanyak 214% dan 267% dengan penambahan hanya 5 wt% CTAB-mont PU dan ODA-mont PU.

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I certify that an Examination Committee has met on 15 November 2007 to conduct the final examination of Teuku Rihayat on his Doctor Of Philosophy thesis entitled "Development of Polyurethane/ Clay Nanocomposites Based on Palm Oil Polyol" In accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree.

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Date : 21 February 2008

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 Universiti Putra Malaysia or other institutions.

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TEUKU RIHAYAT

Date : 27 January 2008

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

Å	Amstrong
API	Alliance for the polyurethanes industry
ASTM	American Society for Testing and Materials
C18	Octadecylammonium
C18-MMT	Octadecyl ammonium montmorillonite
CEC	Cation exchange capacity
CTA-MMT	Cetyltrimethyl ammonium montmorillonite
DDA-MMT	Dodecyl ammonium montmorillonite
DMA	Dynamic mechanical analysis
Eb	Elongation at break
EVA	Poly(ethylene-co-vynil acetate)
EVOH	Ethylene vynil alcohol
FTIR	Fourier transforms infrared spectroscopy
GPC	Gel permeation chromatography
HSC	Hard segment concentration
HCl	Hydrochloric acid
HDPE	High molecular weight
HRR	High release rate
MMW	Medium molecular weight
M_W	Molecular weight
MMT	Montmorillonite
MPa	Mega Pascal

MWD	Molecular weight distribution
Na-MMT	Sodium montmorillonite
NCH	Nylon clay hybrid
NR	Natural rubber
PCL	Poly(ε-caprolactone)
phr	Part per hundred
PLA	Poly (L-lactide)
PLS	Polymer layered silicate
PS	Polystyrene
PPMA	Poly (n-propyl methacrylate)
PP-MA	Maleic anhydride modified polypropylene
PUEs	Polyurethane Elastomers
PUR	Polyurethane
PVA	Poly(vynil alcohol)
PVC	Poly vynil chloride
PVCH	Poly(vynilpyridine)
SSC	Soft segment concentration
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TS	Tensile strength
TGDDM	Terafunctional epoxy resin tetraglycidyl diaminodiphenylmethane
Wt%	Weight percent
WAXD	Wide angle x-ray diffraction

XRD	X-ray diffraction
μm	Micrometer
12-mont	12-aminolauric acid modified montmorillonite

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