UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER/CLAY, POLY(ETHYLENE-CO-VINYL ACETATE)/CLAY AND NATURAL RUBBER/POLY(ETHYLENE-CO-VINYL ACETATE)/CLAY NANOCOMPOSITES

JAMALIAH BT SHARIF

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By

JAMALIAH BT SHARIF

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

October 2005

DEDICATED TO

My beloved family
Hubby: Mohd Mustafah
Daughters: Dr Nadia and Syaza
Sons: Yasir, Anas, Farid and Hilmi
Daughter inlaw: Amelia
For their prayers and
moral support

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

PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER/CLAY, POLY(ETHYLENE-CO-VINYL ACETATE)/CLAY AND NATURAL RUBBER /POLY(ETHYLENE-CO-VINYL ACETATE)/CLAY NANOCOMPOSITES

By

JAMALIAH BT SHARIF

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Chairman: **Professor Wan Md Zin Wan Yunus, PhD**

Faculty: **Science**

This thesis describes the preparation, characterization and physicochemical properties of natural rubber/clay, poly(ethylene-co-vinyl acetate)/clay and natural rubber /poly(ethylene-co-vinyl acetate)/clay nanocomposites.

In order to improve the clay and polymer compatibility, the clay was first converted into the organoclay. The organoclays were prepared from sodium montmorillonite (Na-MMT) through cation exchange reaction using cetyltrimethyl ammonium bromide, octadecyl ammonium chloride or dodecyl ammonium chloride. The x-ray diffraction (XRD) results reveal that the interlayer distance of the Na-MMT increases with the formation of the organoclays. The presence of the alkyl ammonium ions in the organoclays was also studied by the Fourier transforms infrared spectroscopy (FTIR). The amount of alkyl ammonium ions intercalated into the clay galleries increases with the increase of alkyl ammonium chain length as shown by elemental analysis and thermogravimetric analysis (TGA) results.

The nanocomposites were prepared by melt blending the natural rubber (NR), poly (ethylene-co-vinyl acetate) (EVA) or blend of both NR and EVA with the organoclays. The compounds were then crosslinked with an electron beam (EB) irradiation. The XRD patterns showed that all of the nanocomposites produced from this work are of intercalated-type. These were further confirmed by transmission electron microscopy (TEM) observation. Scanning electron microscopy (SEM) study on the cryo-fractured surface reveals that the pure Na-MMT dispersed in the polymer matrix in large agglomerated form while the modified Na-MMT separated into small aggregates and dispersed homogeneously in the polymer matrix.

The optimum irradiation dose for crosslinking of NR, EVA and NR/EVA nanocomposites was determined. The formation of radiation induced crosslinking in NR, EVA and NR/EVA blend was not inhibited with the presence of dodecyl ammonium montmorillonite (DDA-MMT) but it was affected by the presence of dimetyl dehydrogenated tallow montmorillonite (C20A). The tensile modulus of all the nanocomposites increases with the increase of the clay content of up to 10 phr. The tensile strength and elongation at break of the NR/clay nanocomposites increases with the increase of organoclays up to 3 phr and decreases with further increase of the organoclay content. However, the tensile strength of EVA/clay and NR/EVA/clay nanocomposites remains constant with the increase of the organoclay content of up to 5 phr but decreases with the increase of organoclay content of up to 10 phr. The elongation at break of both EVA/clay and NR/EVA/clay decreases slightly with the increase of organoclay content. Electron beam irradiation of the nanocomposites increases the tensile modulus and tensile strength further but decreased the elongation at break.

The dynamic storage modulus of all nanocomposites increases with the increase of organoclay concentration in the investigated temperature range. The shifting of the glass transition temperature (T_g) indicates improved adhesion between the polymer matrix and the clay layers. TGA analysis reveals that the nanocomposites undergo slower thermal degradation than that of the pure polymer or conventional composite of the polymer with unmodified sodium montmorillonite. The decomposition temperature of the nanocomposites increase with the increase of organoclay content of up to 5 phr and beyond that the decomposition temperature remains constant or decreases.

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

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT GETAH ASLI/ TANAH LIAT, POLI(ETILENA-KO-VINIL ASETAT)/TANAH LIAT DAN NANOKOMPOSIT GETAH ASLI/ POLI(ETILENA-KO-VINIL ASETAT)/TANAH LIAT

Oleh

JAMALIAH BT SHARIF

Oktober 2005

Pengerusi: **Professor Wan Md Zin Wan Yunus, PhD**

Fakulti: **Sains**

Tesis ini menerangkan penyediaan, pencirian dan sifat kimia dan fizik nanokomposit getah asli/tanah liat, poli(etilena-ko-vinil asetat)/tanah liat dan getah asli/poli(etilena-ko-vinil asetat)/tanah liat.

Untuk meningkatkan keserasian pengadunan tanah liat dengan polimer, tanah liat diubahsuai terlebih dahulu kepada organo-tanah liat. Organo-tanah liat disediakan daripada sodium montmorillonit (Na-MMT) melalui tindak balas penukar kation menggunakan cetiltrimetil ammonium bromida, oktadesil ammonium klorida atau dodesil ammonium klorida. Keputusan belauan sinar-x (XRD) menunjukkan jarak antara lapisan Na-MMT bertambah dengan pembentukan organo-tanah liat. Kehadiran ion alkil ammonium dalam organo-tanah liat juga ditentukan dengan menggunakan spektroskopi infra-merah pengubah Fourier (FTIR). Jumlah ion alkil ammonium yang termasuk ke dalam lapisan tanah liat bertambah dengan pertambahan panjang rantai alkil ammonium seperti yang ditunjukkan oleh keputusan analisis unsur dan analisis termogravimetri (TGA).

Nanokomposit telah disediakan daripada getah asli (NR), poli(etilena-ko-vinil asetat) (EVA) dan adunan NR dan EVA melalui pengadunan leburan dengan organo-tanah liat. Sebatian telah ditautsilang dengan sinaran alur elektron. Keputusan XRD menunjukkan bahawa semua nanokomposit yang dihasilkan daripada kerja ini adalah daripada jenis ‘intercalated’. Keputusan ini seterusnya disokong oleh pemerhatian mikroskop transmisi elektron (TEM). Kajian mikroskop imbasan elektron (SEM) ke atas permukaan sampel kriopatahan menunjukkan Na-MMT berselerak di dalam matrik polimer dalam bentuk agglomerat (gabungan aggregate kecil) yang besar manakala organo-tanah liat terpecah kepada aggregat yang lebih kecil dan bertabur secara homogen di dalam matrik polimer.

Dos optima penyinaran untuk pembentukan tautsilang NR, EVA dan NR/EVA nanokomposit telah ditentukan. Kehadiran dodesil ammonium monmorilonit (DDA-MMT) didapati tidak merencat pembentukan tautsilang yang diaruh oleh sinaran tetapi terencat dengan kehadiran dimetil dihidrogenated tallow ammonium montmorillonit (C20A). Modulus tegangan bagi semua nanokomposit meningkat dengan peningkatan kandungan organo-tanah liat hingga 10 bps. Kekuatan tegangan dan pemanjangan pada takat putus bagi NR/tanah liat nanokomposit meningkat dengan peningkatan organo-tanah liat sehingga 3 phr dan menurun dengan penambahan organo-tanah liat sehingga 10 phr. Walau bagaimanapun bagi EVA/tanah liat dan NR/EVA/tanah liat nanokomposit, kekuatan tegangan tidak berubah dengan peningkatan organo-tanah liat sehingga 5 phr tetapi menurun dengan

peningkatan organo-tanah liat seterusnya. Pemanjangan pada takat putus menurun dengan peningkatan kandungan tanah liat. Penyinaran alur elektron ke atas nanokomposit telah meningkatkan lagi modulus tegangan dan kekuatan tegangan dan mengurangkan pemanjangan pada takat putus.

Modulus simpanan dinamik (G') bagi semua nanokomposit bertambah dengan pertambahan kandungan organo-tanah liat pada julat suhu kajian. Peningkatan pada suhu peralihan kaca (T_g) menunjukkan terdapat lekatan yang lebih baik di antara matrik polimer dengan lapisan tanah liat. Analisis termogravimetri menunjukkan nanokomposit menjalani degradasi lebih lambat berbanding polimer tulen atau komposit biasa antara polimer dan sodium montmorillonit yang tidak dirawat. Suhu penguraian nanokomposit meningkat dengan peningkatan kandungan organo-tanah liat sehingga 5 phr selepas takat ini suhu penguraian akan tetap atau menurun.

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LIST OF SYMBOLS AND ABBREVIATIONS

Å	Amstrong
APP	Ammonium polyphosphate
bsg	Bahagian seratus getah
C18	Octadecylammonium
C18-MMT	Octadecyl ammonium montmorillonite
C20A	Cloisite 20A
C30B	Methyl-tallow-bis-2-hydroxyethyl quartenary ammonium montmorillonite
C6A	Dimethyl dihydrogenated tallow ammonium montmorillonite.
CEC	Cation exchange capacity
CHNS	Carbon, hydrogen, nitrogen and sulfur
CTA-MMT	Cetyltrimethyl ammonium montmorillonite
DDA-MMT	Dodecyl ammonium montmorillonite
DIOM	Dioctadecyl dimethyl ammonium montmorillonite
DMA	Dynamic mechanical analysis
DMDS-MMT	dimethyl distearyl ammonium bromide modified MMT
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric
EB	Electron beam
Eb	Elongation at break
ENR	Epoxidized natural rubber
EPDM	Ethylene-propylene-diene monomer
EVA	Poly (ethylene-co-vinyl acetate)