# SYNTHESIS AND CHARACTERIZATION OF EPOXIDIZED NATURAL RUBBER/CLAY NANOCOMPOSITES

**By**

**NG SU FANG**

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**SYNTHESIS AND CHARACTERIZATION OF EPOXIDIZED NATURAL RUBBER/CLAY NANOCOMPOSITES**

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**October 2004**

**Chairman : Professor Wan Md. Zin bin Wan Yunus, Ph.D.**

**Faculty : Science**

Sodium montmorillonite (Na-MMT) was modified by alkyl ammonium ions by cation exchange process. The influence of long chain primary (octadecylammonium ion) and quaternary alkylammonium ions (cetyltrimethylammonium ions) on the clay structure was studied. X-ray diffraction (XRD) analyses show that the basal spacings of cetyltrimethylammonium-montmorillonite (CTA-MMT) and octadecylammonium-montmorillonite (ODA-MMT) increase from 12.78 Å for Na-MMT to 19.76Å and 29.83 Å, respectively, after the organo-modification. The infrared spectra of CTA-MMT show the presence of the peaks at 2920 and 2850 $cm^{-1}$ while ODA-MMT at 2928 $cm^{-1}$ and 2854 $cm^{-1}$, which correspond to the C-H asymmetric and symmetric stretching vibrations, respectively. This suggests that both cetyltrimethylammonium ($CTA^{+}$) and octadecylammonium ions ($ODA^{+}$) are sorbed into the silicate layers of Na-MMT. CHNS elemental analysis and density analysis showed that more $ODA^{+}$ are intercalated in the Na-MMT layer when the initial concentration of the octadecylamine is increased.

However the effect is not significant when the CTAB concentration is varied. ENR50/clay nanocomposites were prepared by melt and solution blendings by introducing various amounts of CTA-MMT and ODA-MMT. XRD analyses of the nanocomposites show that there are increments of basal spacing for ENR50/clay nanocomposites prepared by both methods. This indicates that ENR50 is successfully intercalated into the interlayer galleries of the organoclays. Transmission electron microscopy (TEM) showed that the nanocomposites are of intercalated type. The effect of CTA-MMT and ODA-MMT in the rubber matrix on the curing, crosslink density, mechanical properties and thermal stability were also studied. Vulcametric curves show that both ENR50/ODA-MMT and ENR50/CTA-MMT nanocomposites had shorter times than that of the ENR50/Na-MMT microcomposite. An increment of more than 2.5 times in the tensile strength and a highest crosslink density were observed in ENR50/ODA-MMT nanocomposite with 5 phr ODA-MMT content. High moduli were also observed in the compounds incorporated with CTA-MMT and ODA-MMT. ENR50/ODA-MMT nanocomposite with 15 phr of ODA-MMT content has the highest modulus and the lowest elongation at break. TGA studies reveal that ENR50/ODA-MMT nanocomposites with 10 and 15 phr ODA-MMT contents have the highest $T_{max}$, which occurs at 415$^{o}$C.

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

**SINTESIS DAN PENCIRIAN GETAH ASLI TEREPOKSIDA/TANAH LIAT NANOKOMPOSIT**

Oleh

**NG SU FANG**

**Oktober 2004**

**Pengerusi : Profesor Wan Md Zin bin Wan Yunus, Ph.D.**

**Fakulti : Sains**

Natrium montmorillonite (Na-MMT) diubahsuai dengan menggunakan ion alkil ammonium melalui proses penukaran kation. Pengaruh alkilamina primer (ion oktadesilammonium) dan alkilamina kuatenari (ion setiltrimetilammonium) berantai panjang kepada struktur tanah liat telah dikaji. Analisis pembelauan sinar-X (XRD) menunjukkan ruang jarak antara lapisan dalam setiltrimetilammonium-montmorillonite (CTA-MMT) dan oktadesillammonium-montmorillonite (ODA-MMT) telah meningkat masing-masing daripada 12.78 Å untuk Na-MMT kepada 19.76 Å and 29.83Å selepas pengubahsuaian organo. Spektra inframerah (FTIR) menunjukkan kehadiran puncak di 2920 dan 2850 $cm^{-1}$ pada CTA-MMT manakala ODA-MMT di 2928 $cm^{-1}$ dan 2854 $cm^{-1}$ disebabkan oleh masing-masing getaran regangan asimetrik dan simetrik C-H. Ini mencadangkan kedua-dua ion setiltrimetilammonium ($CTA^+$) dan oktadesilammonium ($ODA^+$) telah dijerap ke dalam lapisan silika. Analisis CHNS dan ketumpatan menunjukkan lebih $ODA^+$ telah diinterkalasi ke dalam lapisan silika apabila kepekatan

oktadesilamina yang digunakan telah ditingkatkan. Akan tetapi, kesan ini tidak ketara apabila kepekatan CTAB berubah. ENR50/tanah liat nanokomposit telah disediakan melalui kaedah pengadunan leburan dan larutan dengan pelbagai kuantiti CTA-MMT dan ODA-MMT. Analisis XRD menunjukkan bahawa terdapatnya peningkatan ruang antara lapisan untuk ENR50/tanah liat nanokomposit yang disediakan dengan kedua-dua kaedah ini. Ini menunjukkan ENR50 telah berjaya diinterkalasikan ke dalam ruang antara lapisan tanah liat terubahsuai. Mikroskopi elektron penyebaran (TEM) menunjukkan bahawa nanokomposit adalah jenis interkalasi. Kesan CTA-MMT dan ODA-MMT dalam matrik getah ke atas pematangan, ketumpatan rangkai-silang, pencirian mekanikal dan kestabilan terma telah dikaji. Lengkungan vulkametrik menunjukkan bahawa ENR50/ODA-MMT dan ENR50/CTA-MMT nanokomposit mempunyai masa skorj yang pendek berbanding dengan ENR50/Na-MMT mikrokomposit. ENR50/ODA-MMT nanokomposit dengan 5 bahagian per seratus getah (bsg) ODA-MMT menunjukkan peningkatan kekuatan tensil sebanyak 2.5 kali dan ketumpatan rangkai-silang yang tertinggi. Sebatian dengan CTA-MMT dan ODA-MMT juga menunjukkan modulus yang tertinggi. ENR50/ODA-MMT nanokomposit dengan 15 bsg ODA-MMT mempunyai modulus tertinggi dan pemanjangan pada takat putus yang terendah. Kajian termogravimetri menunjukkan ENR50/ODA-MMT nanokomposit dengan 10 and 15 bsg ODA-MMT mempunyai $T_{max}$ tertinggi yang berlaku pada $415^{o}C$.

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I certify that an Examination Committee met on 18th October 2004 to conduct the final examination of Ng Su Fang on her Master of Science thesis entitled "Synthesis and Characterization of Epoxidized Natural Rubber/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 Committee are as follows:

**Mohd. Zobir Hussein, Ph.D.**
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

**Anuar Kassim, Ph.D.**
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

**Mohamad Zaki Ab. Rahman, Ph.D.**
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

**Jamil Ismail, Ph.D.**
Associate Professor
School of Chemical Sciences
Universiti Sains Malaysia
(Independent Examiner)

_____
**GULAM RUSUL RAHMAT ALI, Ph.D.**
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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

**Wan Md. Zin B. Wan Yunus, Ph.D.**
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

**Mansor B. Ahmad, Ph.D.**
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

**Zainal Abidin Talib, Ph.D.**
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

_____
**AINI IDERIS, Ph.D.**
Professor
Dean of Graduate Studies
Universiti Putra Malaysia

Date:

## 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 other institutions.

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**NG SU FANG**

Date:

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