UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER/BENTONITE NANOCOMPOSITES

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MASTER OF SCIENCE
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2004

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By

MOHAMMAD HUSSEIN AL-KHAWALDEH

Thesis Submitted to the School of Graduate Studies,
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for the Degree of Master of Science
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DEDICATION

بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

قَالُواْ سُبۡحَٰنَكَ لَا عِلۡمَ لَنَآ إِلَّا مَا عَلَّمۡتَنَآۖ إِنَّكَ أَنتَ ٱلۡعَلِيمُ ٱلۡحَكِيمُ ٣٢

Surat Al-Baqara.

Especially dedicated to my beloved parents....
my wife and kids......

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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November 2004

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

Faculty : Science

Natural rubber/bentonite nanocomposites were prepared from deproteinised natural rubber (dp-NR) and modified bentonite clay by both solvent casting and blending methods. To prepare the nanocomposites by the solvent method, the rubber was first dissolved in toluene and then mixed by stirring with the modified clay at room temperature. In the blending method, the rubber was first softened for 1 minute in an internal Haake mixer and then blended with the modified clay at 60°C.

Modification of the clay by replacing the clay's sodium ions with alkylammonium (cetyltrimethylammonium (CTA), dodycelammonium (DDA) and octadecylammonium (ODA)) groups was carried out through an ion-exchanger process. Elemental

analysis indicated that 0.59 mmol of CTA, 0.75 mmol of DDA and 0.98 mmol of ODA were sorbed by 1 g of the clay. FTIR spectra of the modified clays showed a peak at about 3000 cm^{-1}, which indicated the presence of the amine group stretching. The increase in the degradation temperature of DDA, CTA and ODA in the organobentonite implied that there was a strong intermolecular interaction between the alkylammonium ions and the bentonite.

The nanocomposites produced were characterized by XRD and TEM. It was found the nanometer-scale silicate layers of organoclay were completely exfoliated in dp-NR if the organoclay concentration in the composites was less than 1%. However, increase the clay contents to 3% or higher, produced intercalated nanocomposites. The mechanical properties obtained were found to be affected strongly by the organoclay content and the type of alkylammonium groups. Tensile properties of the nanocomposites prepared using the ODA treated bentonite is better than that of the nanocomposites pretreated with the other alkylammonium groups. In addition, mechanical properties of the nanocomposites also effected by the method of their preparation. The solvent casting technique improved several mechanical properties of the nanocomposites compared with those of the nanocomposites produced by the blending method.

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

SINTESIS DAN PENCIRIAN NANOKOMPOSIT GETAH ASLI-BENTONIT

Oleh

MOHAMMAD HUSSEIN AL-KHAWALDEH

November 2004

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

Fakulti: **Sains**

Nanokomposit getah asli-bentonit telah disediakan daripada getah asli nyahprotein dan tanah liat bentonit terubahsuai menggunakan kaedah pengacuan pelarut dan kaedah adunan leburan. Bagi kaedah pelarut, getah asli dilarutkan didalam pelarut toluena dan kemudian ianya dikacau bersama dengan tanah liat terubahsuai pada suhu bilik. Untuk kaedah pengadunan leburan, getah asli terlebih dahulu dilembutkan selama satu minit didalam pencampur dalaman Haake sebelum dicampurkan dengan tanah liat terubahsuai pada suhu 60°C.

Pengubahsuaian tanah liat dilakukan melalui penukaran ion natrium dari tanah liat dengan kumpulan alkil ammonium

(setiltrimetilamonium (CTA), dodesilamonium (DDA) dan oktadesilamonium (ODA)). Analisis unsur menunjukkan 0.59 mmol CTA, 0.75 mmol DDA dan 0.98 mmol ODA telah diserap oleh satu gram tanah liat. Spektrum FTIR bagi tanah liat terubahsuai menunjukkan kewujudan puncak pada 3000 cm^{-1}, menunjukkan kewujudan regangan kumpulan amonium. Peningkatan suhu digradasi bagi DDA, CTA dan ODA bagi bentonit–organo mencadangkan terdapatnya interaksi molekul yang kuat di antara ion alkil ammonium dengan bentonit.

nanokomposit yang terhasil dicirikan dengan menggunakan XRD. Lapisan silikat pada skala nanometer bagi tanah liat-organo terekpoliasi sepenuhnya jika kandungan tanah liat organo didalam komposit kurang daripada satu peratus. Walau bagaimanapun, meningkatkan kandungan tanah liat kepada 3 peratus menghasilkan nanonomposit yang interkalasi. Sifat mekanikal komposit dipengaruhi oleh kandungan tanah liat organo dan jenis kumpulan alkil ammonium. Nanokomposit yang disediakan menggunakan tanah liat bentonit terubahsuai ODA menunjukkan kelebihan dari segi kekuatan regangan berbanding nanokomposit yang menggunakan kumpulan alkilamonium yang lain. Sifat mekanikal bagi nanokomposit juga bergantung kepada kaedah penyediaan dimana teknik pelarut memberikan peningkatan beberapa ciri bagi nanokomposit berbanding dengan nanokomposit yang disediakan menggunakan kaedah pencampuran adunan leburan.

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I certify that an examination committee met on **8 November 2004** to conduct the final examination of **Mohammad Hussein Al-khawaldeh** on his **Master** thesis entitled "PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER/BENTONITE NANOCOMPOSITES" in accordance with Universiti Putra Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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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**. The members of the Supervisory Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citation, 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.

MOHAMMAD HUSSEIN AL-KHAWALDEH

DATE:

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INTRODUCTION

Nanocomposites

Polymer layered nanocomposites have been the focus of attention of many researchers (Usuki et al., 1993a). They are a new class of composite materials, in which clay as a layered silicate is dispersed in nanoscale size in polymer matrix (Takeichi et al., 2001). Nanocomposites exhibit very different physical and chemical properties from their bulk counterparts because of the nanometer scale dispersion of reinforcement agents and the high surface-to-volume ratio (Arroyo et al., 2003).

The dispersion of clay particles in a monomer or polymer matrix can result in the formation of three types of composite materials (Lan et al., 1995). The first type is conventional composites that contain clay tactoids with layers aggregated in an unintercalated face to face form (Figure 1(a)). In this case the clay tactoids are dispersed simply as a segregated phase resulting in poor mechanical properties of the composite material. The second type is intercalated polymer clay nanocomposites, which are formed by the insertion of one or more molecular layers of polymer into the clay host galleries (Figure 1(b)). The last type is exfoliated polymer clay nanocomposites, characterized by low clay content of the composites (Figure 1(c)). Exfoliated polymer clay nanocomposites are especially desirable for improved properties because of the homogeneous dispersion of clay and huge inter facial area between polymer and clay (Fu and Qutubuddin, 2001).

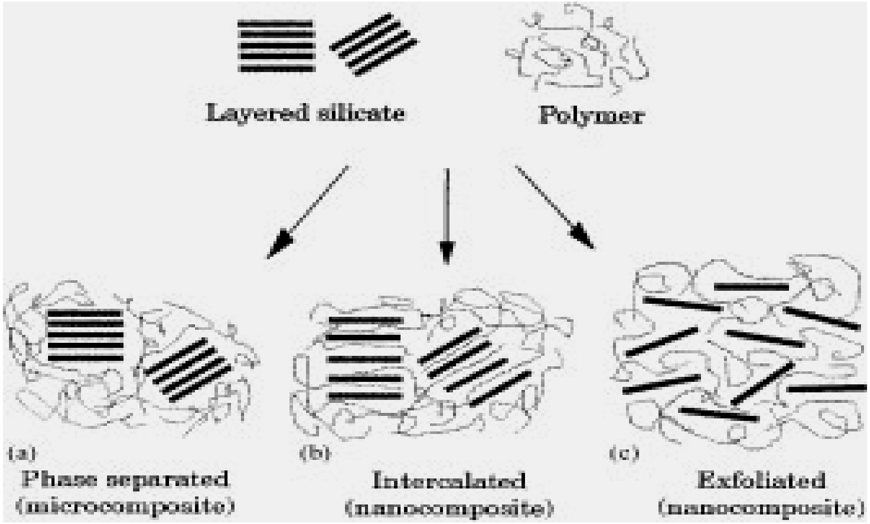


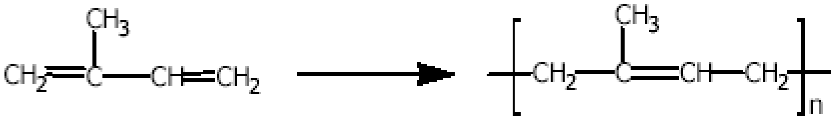
Figure 1: Possible structures for clay polymer composites.

Small amounts well-dispersed natural clay can lead to environmentally friendly and inexpensive plastic composites with improved specialized properties. Due to the nanoscale dispersion, when compared with the conventional fiber or filler-filled composites, nanocomposites exhibit outstanding improvement on properties. These include the increasing of modulus, strength, thermal stability, solvent resistance, decreasing of gas permeability and flammability (Usuki et al., 1993b; Agag and Takeichi, 2000) and increased biodegradability of biodegradable polymers (Sinha et al., 2002a). Adding the clay into a polymer is not a simple process as they are not compatible. However, if the clay is treated with an organic surfactant, the hydrophobicity of the clay can be increased, their compatibility can be improved.

Natural rubber

Rubber is collected in the form of latex that excludes from the bark of the tree when it is cut. The average rubber content of latex may range between 30-45%. This fresh ‘field’ latex is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate the latex, so that the end product is stable and contains 60 % or more of rubber. Latex concentrates are differentiated by the method of concentration, and type of preservative used. Concentration is achieved by centrifugation (most common), by creaming, or by evaporation. Currently, about 50% of all latex concentrate is consumed by the dipped goods industry (medical and household gloves). Other uses of latex are in carpet backing, thread and adhesives (Tantatherdtam, 2003).

Natural rubber is a high molecular weight polymer of isoprene, C_5H_8. The repeating unit is $–CH_2–C(CH_3)=CH–CH_2–$. Hevea rubber which is extracted from the tree *Hevea Brasiliensis* is the major naturally occurring form of cis-1,4-polyisoprene. This rubber contains more than 98% of its double bonds in the cis configuration, which is essential for elasticity in polyisoprene. Over 90% of all cis -1,4-polyisoprene used industrially is natural Hevea rubber (Odian, 1991). 1,4 polymerization of the conjugated diene system of isoprene leads to a polymer structure with a repeating alkene double bond in the polymer chain (Scheme I).



Scheme I. 1,4-Isoprene and 1,4-Polyisoprene.

The double bond in each repeating unit in the polymer chain is a site of steric isomerism since it can have either a cis or a trans configuration. The polymer chain segments on each carbon atom of the double are located on the same side of the double bond in the