



**UNIVERSITI PUTRA MALAYSIA**

**PREPARATION AND CHARACTERIZATION OF NATURAL  
RUBBER/POLYPROPYLENE/FATTY HYRAZIDE-OCTADECYL  
AMMONIUM MODIFIED CLAY NANOCOMPOSITES**

**EID MONEER ALOSIME**

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**By**

**EID MONEER ALOSIME**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfillment of the Requirement for the Degree of Master of Science**

**August 2008**



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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**August 2008**

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

**Faculty : Science**

Fatty hydrazides (FH) which were synthesized from palm oil were used as one of the organic compounds to modify a natural clay (sodium montmorillonite). The clay modification was carried out by stirring the clay particles in an aqueous solution of a mixture of FH and octadecylammonium (ODA) by which the clay layer distance increases from 1.27 nm to 2.60 nm. The modified clay was then used in the preparation of the natural rubber/polypropylene (NR/PP) blend nanocomposites. The intercalation of the modifier in the clay layer was characterized by X-ray diffraction (XRD) and Fourier Transform Infrared (FT-IR). Elemental analysis was used to estimate the presence of FH and ODA in the clay.

In the first part of the preparation, the nanocomposites were synthesized by melt mixing of the modified clay and a natural rubber (SMR CV60) using a two-roll-mill internal mixer. The compounded natural rubber was then mixed with organic peroxide-Luperox F-40P at 60 °C and cured at 130 °C using an electrical hydraulic hot press. Mechanical properties of the produced composites were then



characterized. The results indicate that the presence of the modified clay has dramatically improved these properties. The crosslinked NR/clay nanocomposites were further characterized by XRD, Transmission Electron Microscopy (TEM) and Thermogravimetric Analysis (TGA).

In the final part of the study, preparation of the nanocomposites was carried out by melt mixing of the modified clay with NR/PP in the ratio of 50:50 using the internal mixer. The study of mixing temperature, rotor speed and mixing time shows that under the following mixing conditions: temperature of 170 °C, 75 rpm of rotor speed and 10 minutes of mixing time, the composites with maximum tensile strength and elongation at break were obtained. The modified clay content to give maximum tensile strength is 1 php. The crosslinking of NR/PP, using Luperox F-40P to crosslink the rubber phase was also investigated. The compound was then cured in a hot press at 185 °C. The optimum concentration of Luperox F-40P to give maximum strength and elongation at break is 2.0 php. The tensile strength of Luperox F-40P crosslinked NR/PP/clay is higher compared to those of the unfilled crosslinked NR/PP/clay. The presence of 1 or 3 php of the modified clay into the Luperox F-40P crosslinked NR/PP increases its tensile strength. TGA study shows that crosslinked NR/PP/clay nanocomposites have higher decomposition temperatures in comparison with those of the crosslinked NR/PP/clay composites.



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

**PENYEDIAAN DAN PENCIRIAN GETAH ASLI/POLIPROPILENA/TANAH LIAT TERUBAHSUAI HIDRAZIDA LEMAK-OKTADESIL AMMONIUM NANOKOMPOSIT**

Oleh

**EID MONEER ALOSIME**

**Ogos 2008**

**Penerusi: Profesor Wan Md. Zin bin Wan Yunus, PhD**

**Fakulti : Sains**

Hidrazida lemak (FH) yang telah disintesis dari minyak kelapa sawit telah digunakan sebagai salah satu bahan organik untuk mengubahsuai tanah liat semulajadi (sodium montmorillonite). Pengubahsuaian tanah liat telah dilakukan dengan mengacau partikel tanah liat di dalam larutan akues campuran FH dan oktadesilammonium (ODA) yang berjaya mengubah jarak lapisan tanah liat dari 1.27 nm kepada 2.60 nm. Tanah liat terubahsuai kemudian digunakan dalam penyediaan campuran antara getah asli/polipropilina nanokomposit. Lapisan tanah liat terubahsuai telah dicirikan menggunakan corak pembelauan sinar-X (XRD), dan analisis Fourier transform infra merah (FTIR). Analisis unsur telah digunakan untuk menganggar kehadiran FH dan ODA di dalam tanah liat.

Pada peringkat awal penyediaan, nanokomposit disintesis dengan adunan lebur di antara tanah liat terubahsuai dan getah asli (SMR CV60) menggunakan dua-pengisar-berputar pencampur dalaman. Adunan getah asli kemudian telah dicampur dengan peroksida organik-Luperox F-40P pada suhu 60 °C dan dimatangkan pada



suhu 130 °C menggunakan hidrolis elektrik tekan panas. Sifat-sifat mekanikal komposit yang dihasilkan kemudian dicirikan. Keputusan menunjukkan bahawa kehadiran tanah liat terubahsuai memberi peningkatan dramatik terhadap sifat-sifat ini. Getah asli/tanah liat nanokomposit tautsilang kemudian telah dicirikan oleh XRD, mikroskopi transmisi elektron (TEM) dan analisis termogravimetri (TGA).

Pada bahagian akhir kajian, penyediaan nanokomposit telah dilakukan dengan adunan lembut tanah liat terubahsuai dengan NR/PP dalam nisbah 50:50 menggunakan pencampur dalaman. Kajian mengenai suhu campuran, kelajuan rotor dan masa campuran menunjukkan bahawa di dalam keadaan campuran berikut: suhu 170 °C, 75 rpm kelajuan rotor dan 10 minit masa campuran, komposit dengan kekuatan tensil dan pemanjangan pada takat putus maksimum didapati. Kandungan tanah liat terubahsuai memberikan kekuatan tensil yang maksimum pada 1 php. Tautsilang NR/PP menggunakan Luperox F-40P untuk mentautsilang fasa getah juga dikaji. Adunan tersebut kemudian dimatangkan menggunakan pemampat-panas pada suhu 185 °C. Kepekatan optimum Luperox F-40P yang memberi kekuatan tensil dan pemanjangan pada takat putus maksimum adalah pada 2.0 php. Kekuatan tensil Luperox F-40P tautsilang getah asli/PP/tanah liat adalah lebih tinggi berbanding tanpa tautsilang getah asli/PP/tanah liat. Kehadiran 1 atau 3 php daripada tanah liat terubahsuai di dalam getah asli/PP ditautsilang oleh Luperox F-40P telah meningkatkan kekuatan tensilnya. Keputusan TGA menunjukkan bahawa nanokomposit tautsilang getah asli/PP/tanah liat mempunyai suhu penguraian yang tinggi berbanding komposit tautsilang getah asli/PP/tanah liat.

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I certify that an Examination Committee met on 1<sup>st</sup> August to conduct the final examination of Eid Moneer Alosime on his Master of Science thesis entitled "Preparation and Characterization of Natural Rubber/Polypropylene/Fatty Hydrzazide-Octadecyl Ammonium Modified 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 Hussien, Ph.D.**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Anuar Kassim, Ph.D.**

Professor  
Faculty of Science  
Universiti Purta Malaysia  
(Member)

**Nor Azowa Ibrahim, Ph.D.**

Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Rusli Daik, Ph.D.**

Associate Professor  
Faculty of Science and Technology  
Universiti Kebangsaan Malaysia  
(Independent Examiner)

---

**HASANAH MOHD GHAZALI, Ph.D.**

Professor/ Deputy Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date:





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

**Dato' Wan Md Zin Wan Yunus, PhD**

Professor  
Faculty of Science  
Universiti Purta Malaysia  
(Chairman)

**Mansor Hj. Ahmad, PhD**

Associate Professor  
Faculty of Science  
Universiti Purta Malaysia  
(Member)

**Mohamad Zaki Abdrhman, PhD**

Associate Professor  
Faculty of Science  
Universiti Purta Malaysia  
(Member)

---

**AINI IDERIS, PhD**

Professor And Dean  
School of Graduate Studies  
Universiti Purta Malaysia

Date: 11 September 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 UPM or other institutions

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**EID MONEER ALOSIME**

Date: 15 August 2008



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## LIST OF ABBREVIATIONS

DTG	Derivative thermal gravimetry
ENR	Epoxidized natural rubber
EPDM	Ethylene-propylene-diene terpolymer
FH	Fatty hydrazide
FH-MMT	Fatty hydrazide modified montmorillonite
20FH5ODA-MMT	20mmol Fatty hydrazide-5mmol Octadecylamine modified Montmorillonite
15FH10ODA-MMT	15mmol Fatty hydrazide-10mmol Octadecylamine modified Montmorillonite
10FH15ODA-MMT	10mmol Fatty hydrazide-15mmol Octadecylamine modified Montmorillonite
FTIR	Fourier transform infrared
Luperox F-40P	1,3-1,4bis (tert-butylperoxyisopropyl) benzene
N6	Nylon-6
Na-MMT	Sodium montmorillonite
NR	Natural rubber
NR/PP	Natural rubber/Polypropylene
ODA	Octadecylamine
ODA-MMT	Octadecylamine modified montmorillonite
OMLS	Organically modified layered silicate
PCL	Poly( $\epsilon$ -caprolactone)
PCN	Polymer-clay nanocomposites
PEI	poly(etherimide)
PEO	Poly(ethylene oxide)
php	parts per hundred polymer
phr	parts per hundred rubber
PLS	Polymer layered silicate
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PP-MA	Maleic anhydride modified propylene oligomers
PS	Poly styrene
SBR	Styrene butadiene rubber
SMR CV	Standard Malaysian Rubber constant viscosity



TEM	Transmission electron microscopy
T <sub>g</sub>	Glass transition temperature
TGA	Thermogravimetric analysis
T <sub>max</sub>	Temperature at maximum decomposition
TPE	Thermoplastic elastomers
TPNR	Thermoplastic natural rubber
TPO	Thermoplastic polyolefin
TPV	Thermoplastic vulcanisates
WAXD	Wide angle X-ray diffraction
XRD	X-ray diffraction

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

Polymer blends are a popular form of new thermoplastic engineering materials which constitute a rapidly changing field. Their growth rate is very significant and exceeds more than 10% which is a few times that of the plastics industry on the whole (Ibrahim and Dahlan, 1998).

Preparation of a polymer blend is an effective way to achieve desirable combination properties from parent polymer pairs. However, most polymer pairs in blends are thermodynamically incompatible which gives poor mechanical properties. This is because of the lack of interaction at the interface, which leads to poor interfacial adhesion. Compatibilization of polymer blends is becoming a rapidly growing field since it provides a convenient procedure to change the mechanical, thermal or chemical properties of existing materials without the expense of synthesis of new polymers (Datta and Lohse, 1996). There are two important routes to improve the blend compatibility of different polymers. One is the application of a third component (i.e. a blend compatibilizer), typically a block or graft copolymer or a polymer with reactive functional groups (George *et al.*, 1999; Oommen *et al.*, 1997; Braun *et al.*, 1996). The compatibilizers consist of segments that are chemically identical to their respective counterparts in the polymer pairs and are thought to be located preferentially at the interface (Oh *et al.*, 2003). The other is to perform a chemical reaction between the blend component and modification of interfaces, i.e. reactive blending (Mohanty *et al.*, 1996; Nakason *et al.*, 2001).



Thermoplastic elastomers (TPE) are a class of polymers or polymer blends that have rubber-like behaviour, but can be melt processed like thermoplastic polymers (Holden and legge, 1996; Bohmick *et al.*, 2001). The most spectacular results in the search for TPE have been achieved by blending rubbers and plastics. Among the various rubber-plastic blends (Coran, 1988), thermoplastic natural rubber is the most useful for natural-rubber-producing countries. Several studies have been made in this field regarding processability and rheological behaviour (Akhtar *et al.*, 1986; Tinker, 1987), mechanical properties, strength and failure behaviour (Roy *et al.*, 1990), adhesion between the components of the blends (Roy *et al.*, 1988), ageing behaviour (Roy *et al.*, 2002), etc.

There are many methods to combine the desired features of each component of the blend. One method is to prepare the blend in an intensive internal mixer such as a Brabender plasticorder. These materials are phase-separated systems in which one phase is rubbery at room temperature and the other is hard and solid. They possess the elasticity of a rubber and the thermoplastic nature of a plastic (Ismail *et al.*, 2001). TPE give better material utilization because scraps and rejects can be recycled (Lopez-Manchado and Arroyo, 2000). Furthermore, productivity is high because no compounding or vulcanization is required and they are easily processed by internal mixers or extrusion.

As the composition of blends varies, materials with a wide range of properties are obtained (Norzalia *et al.*, 1993). Because of its excellence in molding processability and good mechanical properties, polypropylene (PP) has been widely used in the form of molded articles, films or sheets. Toughening of PP can be enhanced while

maintaining stiffness, strength and processability by addition of some elastomers. Polypropylene is considered to be the best choice for blending with natural rubber (NR) due to its high softening temperature of about 150 °C and low glass transition temperature of about -60 °C for the blend (Ibrahim and Dahlan, 1998). Early studies of blending elastomer with PP were aimed to overcome the inherent brittleness of PP at low temperature by the addition of relatively small proportions of an elastomer (Elliott, 1990).

The blending of various rubbers with PP to provide improvements in impact resistance has been widely studied (Speri and Patrick, 1975; Danesi and Porter, 1978; Karger-Kocsis *et al.*, 1979). The ethylene-propylene copolymer (EPM) and the ethylene-propylene-diene terpolymer (EPDM) are often used as impact modifiers for PP. Typical rubber-modified PP resins contain about 15% modifiers, and effective impact toughening is obtained when small rubber particles ( $< 0.5 \mu\text{m}$  in diameter) are distributed homogeneously in the PP matrix. Physical blends of NR and PP, which form a TPNR, have also been developed into a semi-rigid and impact-resistant plastic. These hard grades of impact modified PP have a flexural modulus in the range 300–1000 MPa. These materials have been put to rather modest uses like automotive applications, wires and cables, footwear, hoses, tubes, flexible couplings, and sports goods.

The use of fine particle silica at lower loading has been reported to improve the physical properties and reduce the shrinkage of TPE blends containing a higher proportion of elastomer phase (Elliott, 1982). In the past, where reinforcement of the polymer was not the main factor, different types of clay minerals have been used as

fillers to reduce the cost of the host polymer and provide certain properties useful in rubber compounding. The term “reinforcement” refers to an improvement in end use performance of the rubber compound associated with an increase in modulus and in the so called ultimate properties including tensile strength, tear resistance and abrasion resistance.

It has been well known that particle size, structure, and surface characteristics of reinforcing materials were three factors that influence and help decide their reinforcing ability, and of these factors particle size of the filler has the most significant influence (Bissot, 1990; Maine and Shephed, 1974; Haplin, 1969). Fillers are incorporated in order to modify certain properties to an acceptable level.

Clay is one of the most widely used nonblack fillers for rubber. It is an inexpensive natural mineral which has been an important part of the rubber industry. In this type of industry, it is used as economical filler to modify processing and performance of natural and synthetic rubbers but the reinforcing ability of clay is poor due to its large particle size and low surface activity. The clay particles could only be dispersed on the microscale in the polymer matrix even though the clay comprised of silicate layers having a 1 nm thick planar structure. The layers cannot be separated from each other through general polymer processing methods. The recent way of improving the reinforcing ability of clay is done by changing the hydrophilic nature of clay to organophilic. This is done by ion exchange of the clay interlayer cations with organic cations such as alkylammonium or alkylphosphonium. By using the modified clay, many researchers have succeeded in intercalating various polymers in the clay interlayer to prepare polymer/clay nanocomposites. The first such clay-based

nanocomposites were synthesized by a Toyota research group (Kojima *et al.*, 1993; Usuki *et al.*, 1995) using a polyamide as the polymer matrix.

## **1.2 Nanocomposites**

### **1.2.1 Structure and Properties of Layered Silicates**

Clay minerals are hydrous aluminum silicates which are classified either as phyllosilicates, or as layer silicates. The silicates commonly used in nanocomposites belong to the structural family of 2:1 phyllosilicates. All layer silicates can be imagined as constructed from two modular units (Moore and Reynolds, 1997), a sheet of corner-linked tetrahedra and a sheet of edgeshared octahedra. The 2:1 type layer structure is made up of two tetrahedral sheets of silica fused to an octahedral sheet of either aluminum (gibbsite) or magnesium (brucite) hydroxide as illustrated in Figure 1.1. The layer thickness is approximately 1 nm and the lateral dimension of these layers may vary from 300 Å to several microns and even larger depending on the particular silicate. These layers organize themselves to form stacks with a regular electrostatic and van der Waals bonded gap between them is called the interlayer or gallery.

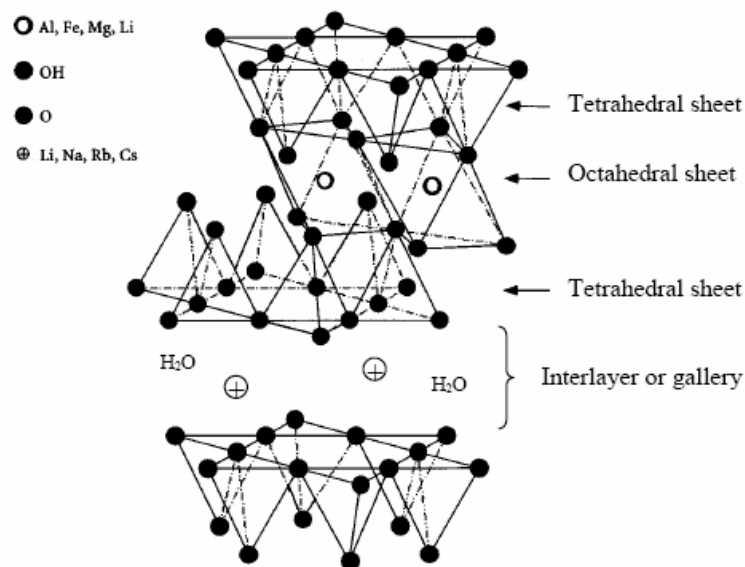
Various layer silicates are classified either as dioctahedral or trioctahedral. In clay minerals, the smallest structural unit contains three octahedral sites. If all three octahedral sites are occupied, i.e. have octahedral cations at their centers, the sheet is classified as trioctahedral. If only two octahedral sites are occupied and the third octahedron is vacant, the sheet is classified as dioctahedral. The 2:1 type layer silicates have various cation substitutions in both the tetrahedral and octahedral positions. Substitutions within the layers by ions of lesser charge, notably  $\text{Si}^{4+}$  by



$\text{Al}^{3+}$  in tetrahedral positions and  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  by  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  in octahedral positions, result in negative charges on the layers. These are normally interlayer counterbalanced by alkali or alkali earth cations situated in the interlayer space. In pristine layer silicates the interlayer cations are usually hydrated  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, but a wide range of other cations, including organic ions, can be introduced by exchange reactions (Newman, 1987).

The replacement of inorganic exchange cations in the galleries of the native clay by cationic surfactants such as alkylammonium ions is known to help compatibilize the surface chemistry of the clay and the hydrophobic polymer matrix.

Montmorillonite, hectorite and saponite are the most commonly used layered silicates. Their structure is given in Figure 1.1 and their chemical formula are shown in Table 1.1.



**Figure 1.1: Structure of 2:1 phyllosilicates (Giannelis *et al.*, 1999).**