

PREPARATION AND CHARACTERIZATION OF  
NATURAL RUBBER-, POLYETHYLENE-AND  
NATURAL RUBBER/POLYETHYLENE-CLAY  
NANOCOMPOSITES

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**By**

**MOHD AIDIL ADHHA BIN ABDULLAH**

**Thesis Submitted to the School of Graduates Studies,  
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for the Degree of Doctor of Philosophy**

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## DEDICATION

PREPARATION AND CHARACTERIZATION OF NATURAL RUBBER,  
POLYETHYLENE AND NATURAL RUBBER/POLYETHYLENE/CLAY  
NANOCOMPOSITES

MOHD ARIFF BIN MOHAMMAD

December 2011

While this dissertation was in preparation, my beloved father, Abdullah bin Chik passed away after a lengthy illness. I dedicate this thesis special to him. I also dedicate this dissertation to my beloved family for their prayers and moral support

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of requirement for the Degree of Doctor of Philosophy

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**Chairman: Associate Professor Mansor Hj Ahmad @ Ayob, PhD**

**Faculty: Science**

The present research aims at studying the influence of organoclay on the properties of natural rubber (NR), low density polyethylene (LDPE) and NR/LDPE blend. Two types of clays, namely montmorillonite, (MMT) (cationic clay) and layered double hydroxide (LDH) (anionic clay) were used in this study. Secondly, to identify the influence of the organoclay on the thermal and mechanical properties effectively, a thoroughly investigation of the NR-clay and LDPE-clay single-phase and NR/LDPE-clay blend were performed. These nanocomposites were evaluated by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and mechanical properties.

The organo-montmorillonite (OMMT) and organo-LDH (OLDH) samples were prepared via ion exchange reaction using organic surfactants;

cetyltrimethylammonium (CTA), n-dodecyl trimethylammonium (DDT), protonated octadecylamines (ODA) and dodecylamines (DDA) as well as dodecylsulphate (DS). The characterization of organoclay were carried out by the Fourier Transform Infrared spectroscopy (FTIR) and the Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) elemental analysis, Scanning Electron Microscopy (SEM) as well as Surface Area and Porosity Analysis (ASAP).

The preparation of a NR nanocomposite may be accomplished either by solvent method or by melt-blending technique. However, the melt-blending technique was applied in this study which is the industrially preferred process. The expansion of the interlayer spacing of the clay indicates the formation of intercalated as well as exfoliated types of nanocomposites which supported by TEM images and XRD diffractograms. Both the tensile strength and the modulus of the nanocomposite increased while elongation at break decreased with the addition of the clay. The Dynamic Mechanical Analysis (DMA) of nanocomposites exhibited enhancement of the storage modulus indicated that the elastic responses of pure NR towards deformation were strongly influenced by the presence of nanodispersed nano-layered material. The thermogravimetric analysis that showed the presence of clay layers in NR matrix gave insignificant improvement in thermal stability of NR-clay nanocomposites.

LDPE-clay nanocomposites were prepared by in-situ grafting-intercalating in melt. The organoclay was first modified with maleic anhydride (MAH). It was then blended with LDPE in melt. The grafting MAH onto LDPE chain favors the exfoliation and intercalation of the organoclay, hence resulting better dispersion of



clay layers in the LDPE matrix. Tensile properties revealed that the tensile strength increased up to 3 parts per hundred polymer by weight (php) while elongation at break decreased with the addition of the clay. Enhancement in storage modulus observed were the characteristic of reinforcing fillers. Thermally stable LDPE-clay nanocomposites were obtained with the increase of the clay content at higher temperature ( $\geq 400$  °C).

Polymer blends with ratio 70/30 amount of LDPE and NR with N, N-m-phenylenebismaleimide (HVA-2) as a compatibilizer was developed. The introduction of cross-links into the elastomer phase has contributed to the improvement of the tensile properties of dynamically vulcanized LDPE/NR blends. These results are supported by scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM) images of extracted surfaces of the blends.

Finally, NR/LDPE-clay nanocomposites were successfully prepared by melt intercalation technique. XRD results revealed the formation of both intercalated and exfoliated nanocomposites. The tensile properties enhanced resulted from melt compounding of NR/LDPE with 3 php or less modified organoclay. All nanocomposites formed in this investigation showed enhancement in the mechanical properties which are the characteristic of reinforcing fillers. The TEM micrograph revealed the clay layers was dominantly distributed in NR domain and manifested by insignificant improvement in thermal stability of the nanocomposites.

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

**PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT GETAH ASLI-,  
POLIETILENA- DAN GETAH ASLI/ POLIETILENA -TANAH LIAT**

Oleh

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**Disember 2007**

**Pengerusi : Profesor Madya Mansor bin Hj Ahmad @Ayob, PhD**

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Matlamat kajian ini adalah untuk mengetahui kesan penggunaan organo-tanah liat ke atas sifat adunan getah asli (NR), polietilena berketumpatan rendah (LDPE) dan adunan NR/LDPE. Dua jenis tanah liat, iaitu montmorilonit (MMT) (tanah liat bercas positif) dan hidroksida berlapis ganda (LDH) (tanah liat bercas negatif), telah digunakan bagi kajian ini. Keduanya, bagi menentukan kesan organo-tanah liat terhadap sifat termal dan mekanikal secara berkesan, penyiasatan keseluruhan terhadap NR-tanah liat dan LDPE-tanah liat fasa-tunggal dan adunan LDPE/NR-tanah liat dijalankan. Nanokomposit ini kemudiannya dinilai menggunakan pembelauan sinar-X (XRD), mikroskop transmisi elektron (TEM), analisis termogravimetrik (TGA) dan sifat mekanikal.

Sampel organo-montmorillonit (OMMT) dan organo-LDH (OLDH) disediakan melalui tindak balas penukar ion menggunakan surfaktan; setiltrimetilammonium



(CTA), n-dodesiltrimetil ammonium (DDT), oktadesilamina (ODA) dan dodesilamina (DDA) terproton dan juga dodesil sulfat (DS). Pencirian organo-tanah liat dijalankan menggunakan spektroskopi penukar Fourier infra-merah (FTIR), analisis unsur Karbon, Hidrogen, Nitrogen dan Sulfur (CHNS), mikroskop imbasan elektron (SEM) dan juga analisis luas permukaan dan keliangan (ASAP).

Nanokomposit NR boleh disediakan samada dengan menggunakan kaedah pelarut atau kaedah pengadunan leburan. Walau bagaimanapun, kaedah pengadunan leburan diaplikasikan dalam kajian ini kerana ianya merupakan kaedah yang biasa digunakan oleh industri. Pengembangan ruang antara lapisan tanah liat menunjukkan pembentukan nanokomposit jenis interkalasi dan terkelupas yang mana ianya disokong oleh imej TEM dan difraktogram XRD. Kedua-dua kekuatan tegasan dan modulus bagi nanokomposit meningkat manakala pemanjangan pada takat putus menurun dengan pertambahan tanah liat. Analisis Mekanikal Dinamik bagi nanokomposit menunjukkan peningkatan modulus simpanan yang membuktikan tindak balas kekenyalan NR tulen terhadap canggaan sangat dipengaruhi oleh kehadiran sebaran bahan nano-lapisan. Analisis termogravimetrik menunjukkan kehadiran lapisan tanah liat memberikan peningkatan yang tidak signifikan terhadap kestabilan termal bagi nanokomposit NR-tanah liat.

Nanokomposit LDPE-tanah liat disediakan melalui kaedah *in-situ* cangkukan-interkalasi di dalam leburan. Organo-tanah liat mulanya diubahsuai menggunakan maleik anhidrida (MAH). Ia kemudiannya diadunkan dengan LDPE dalam keadaan lebur. Cangkukan MAH pada rangkaian LDPE menghasilkan organo-tanah liat pengelupasan dan interkalasi dan seterusnya menjadikan sebaran lapisan tanah liat

dalam matrik LDPE lebih baik. Sifat tegasan menunjukkan kekuatan tegasan meningkat sehingga 3 bahagian bagi seratus polimer mengikut berat (php) sementara pemanjangan pada takat putus menurun dengan penambahan tanah liat. Peningkatan modulus simpanan yang diperhatikan menunjukkan ciri-ciri bagi pengisi penguat. Nanokomposit LDPE-tanah liat berkestabilan termal diperolehi dengan peningkatan kandungan tanah liat pada suhu yang lebih tinggi ( $\geq 400$  °C ).

Adunan polimer dengan nisbah kandungan 70/30 LDPE dan NR bersama N, N-m-fenilinbismaleimida (HVA-2) sebagai pengserasi telah dibangunkan. Pengenalalan rangkai silang kepada fasa elastomer telah menyumbang kepada peningkatan sifat tegangan bagi komposit adunan pemvulkanan dinamik NR/LDPE. Keputusan ini disokong oleh imej yang diperolehi dengan mikroskop pengimbasan elektron (SEM) dan mikroskop daya pengatoman (AFM) bagi sampel adunan setelah pengestrakan permukaan dilakukan.

Akhirnya, nanokomposit NR/LDPE-tanah liat telah berjaya disediakan melalui keadah pengadunan leburan. Keputusan XRD menunjukkan pembentukan kedua-dua jenis nanokomposit interkalasi dan terkelupas. Sifat tegasan meningkat hasil daripada pengadunan leburan bagi NR/LDPE dengan 3 php atau kurang organo-tanah liat. Kesemua nanokomposit yang terhasil dalam ujikaji ini menunjukkan peningkatan sifat mekanikal yang mana ia merupakan ciri bagi pengisi penguat. Mikrograf TEM menunjukkan lapisan tanah liat mendominasi fasa NR merupakan punca kepada peningkatan yang tidak signifikan terhadap kestabilan termal bagi nanokomposit.