



UNIVERSITI PUTRA MALAYSIA

**MICROWAVE-ASSISTED PREPARATION AND CHARACTERIZATION
OF NATURAL RUBBER-MODIFIED SODIUM MONTMORILLONITE-
POLY(METHYLMETHACRYLATE) INTERPENETRATING POLYMER
NETWORK NANOCOMPOSITES**

SHARIL FADLI BIN MOHAMAD ZAMRI

FS 2008 3



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**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

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By

SHARIL FADLI BIN MOHAMAD ZAMRI

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

June 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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June 2008

Chairman : Professor Dato' Wan Md Zin Bin Wan Yunus, PhD

Faculty : Science

In this study, sodium montmorillonite (Na-MMt) was modified by dodecylamine (DDA) to produce dodecylamine montmorillonite (DDA-MMt). Elemental analysis result shows the amount of the surfactant intercalated in the DDA-MMt based on Carbon and Nitrogen content are 1.45 mmole/g and 1.38 mmole/g, respectively. The presence of alkyl ammonium in the DDA-MMt was analyzed by Fourier transform infrared (FTIR) analysis spectroscopy. X-ray Diffraction (XRD) pattern of DDA-MMt shows that the basal spacing of Montmorillonite (MMt) was expanded from 12.9 Å for the Na-MMt to 17.8 Å. The thermogravimetry analysis (TGA) shows that DDA-MMt has an organic content which is equivalent to the mass of the intercalated DDA.

Dicumyl peroxide (DCP) was used as curing agent for the natural rubber (NR). The scorch time of cured NR decreases when the DCP content is increased from 1.0 to 2.5 phr then levels off for further increase of the DCP content. Meanwhile, the torque difference



and the curing time increase with the increase of the DCP concentration of from 1.0 to 3.5 phr. The tensile strength increases with increase of the DCP concentration from 1.0 up to 2.5 phr. However, addition of DCP beyond 2.5 phr decreases the tensile strength drastically. The percentage of gel content of the cured NR increases with the increase of the DCP content from 0.0 to 1.0 phr and slightly enhances with further addition of peroxide until 3.5 phr. TGA shows that the thermal stability of the cured NR improves with the increase of the DCP concentration. Dynamic mechanical analysis (DMA) indicates that the glass transition temperature (T_g) and the storage modulus (E') of cured NR increase with DCP concentration increased.

Preparation of the nanocomposites was carried out by melt blending of DDA-MMt and NR in a two-roll-mill internal mixer. The compounded natural rubber was then blended again with DCP and cured using an electric hydraulic hot press. Preparation of macrocomposites was also carried out using the same process but Na-MMt was used as the filler. The study shows that the scorch time of nanocomposites containing 1.0 to 7.0 phr DDA-MMt is higher than that of the macrocomposites. Increase the DDA-MMt concentration beyond to 7.0 phr lowers scorch time. Meanwhile, the different torque of the nanocomposites is higher than that of the macrocomposites. However, the curing time of the nanocomposites is lower than curing time of the macrocomposites. The FT-IR spectra reveal that the existence of DDA-MMt in the nanocomposites. The tensile strength, percentage of elongation at break and thermal degradation of the nanocomposites vary with the DDA-MMt content. DMA shows that T_g of the nanocomposites is lower than that of the cured NR and macrocomposites. It also found



that their glass temperature decreases while storage modulus increases with increase of the clay content for both nanocomposites and macrocomposites. The percentage of gel content of the nanocomposites are higher than that of the macrocomposites at 1.0 phr DDA-MMt loading but decreases with addition of DDA-MMt up to 15.0 phr. Analysis of DDA-MMt dispersion by XRD and Transmission Electron Micrograph (TEM) shows that the DDA-MMt was intercalated and exfoliated in the NR matrix.

The interpenetrating polymer network (IPN) nanocomposites were prepared by *in situ* microwave polymerization of methyl methacrylate (MMA) containing benzoyl peroxide (BPO) as initiator soaked in the cured NR/7phrDDA-MMt nanocomposite. The optimum conditions for the preparation of the IPN nanocomposites can be summarized as followed: 1% (w/w) of initiator concentration, 20 minutes polymerization and 1.5 hours soaking period. The FT-IR spectra of the IPN nanocomposites confirm that both nanocomposites and PMMA are exist in the IPN nanocomposites. The highest tensile strength of the IPN nanocomposites was observed when it is incorporated with 40 % (w/w) of PMMA. The percentage of the gel content of the IPN nanocomposites decreases with increase of the PMMA composition. The thermal stability of the IPN nanocomposites was determined and is in between thermal stability of PMMA and the nanocomposites. TGA also confirms that the thermal stability of the IPN nanocomposites is PMMA composition dependence. The $\tan \delta$ against temperature curve of the IPN nanocomposites shows 2 T_g s which are around -46.90 to -39.88 °C and 147.88 to 149.03 °C which correspond to T_g of NR and PMMA, respectively. The storage modulus of the IPN nanocomposites increases with the increase of the PMMA composition. The XRD



pattern of the IPN nanocomposites at 52, 35 and 7 % (w/w) of PMMA composition shows no diffractions peaks appeared in range of 2θ from 2 to 10° . TEM micrograph of IPN nanocomposites for both PMMA compositions shows that the DDA-MMt was exfoliated by which most of DDA-MMt platelets are distributed as a individual layer in the IPN nanocomposites matrix.



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

**PENYEDIAAN DAN PENCIRIAN GETAH ASLI-NATRIUM
MONTMORILLONITE TERUBAH-POLI(METHYLMETHACRYLATE)
INTERPENETRATING POLYMER NETWORK NANOKOMPOSIT TERBANTU
GELOMBANG MIKRO**

Oleh

SHARIL FADLI BIN MOHAMAD ZAMRI

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Dalam kajian ini, natrium montmorillonite (Na-MMt) telah diubahsuai dengan menggunakan dodesilamin (DDA) untuk menghasilkan dodesilamin montmorillonite (DDA-MMt). Analisis unsur menunjukkan bilangan surfaktan yang telah diinterkalasi ke dalam DDA-MMt berdasarkan kepada kandungan Karbon dan Nitrogen adalah masing-masing 1.45 mmol/g dan 1.38 mmol/g. Kehadiran alkil ammonium di dalam DDA-MMt telah dianalisa dengan menggunakan Fourier transform infra merah (FTIR) spektroskopi analisis. Corak pembelauan sinar-X (XRD) DDA-MMt menunjukkan bahawa ruang jarak antara lapisan dalam montmorillonite (MMt) telah ditingkatkan daripada 12.9 Å untuk Na-MMt kepada 17.8 Å. Analisis termogravimetri (TGA) menunjukkan bahawa DDA-MMt mempunyai kandungan organik yang sama dengan jisim DDA terinterkalasi.



Dikumul peroksida (DCP) telah digunakan sebagai agen pematangan untuk getah asli (NR). Masa skorj getah termatang menurun apabila kandungan DCP ditingkatkan dari 1.0 ke 2.5 phr kemudian malar untuk peningkatan kandungan DCP seterusnya. Sementara itu, perbezaan tork dan masa pematangan meningkat dengan peningkatan kepekatan DCP dari 1.0 hingga 3.5 phr. Kekuatan tensil meningkat dengan peningkatan kepekatan DCP dari 1.0 hingga 2.5 phr. Walaubagaimanapun, penambahan DCP melebihi 2.5 phr menurunkan kekuatan tensil dengan ketara. Peratusan kandungan gel NR termatang meningkat dengan peningkatan kandungan DCP dari 0.0 ke 1.0 phr dan semakin meningkat dengan penambahan peroksida sehingga 3.5 phr. TGA menunjukkan bahawa kestabilan terma NR termatang meningkat dengan peningkatan kepekatan DCP. Analisis mekanikal dinamik (DMA) menunjukkan bahawa suhu peralihan kaca (T_g) dan moduli tersimpan (E') NR termatang meningkat dengan peningkatan kepekatan DCP.

Penyediaan nanokomposit telah dilakukan melalui adunan lembut DDA-MMt dan NR di dalam dua-pengisar-berputar pencampur dalaman. Adunan getah asli kemudian diadun semula bersama DCP dan dimatangkan menggunakan hidrolis elektrik tekan panas. Penyediaan makrokomposit juga dilakukan menggunakan proses yang sama tetapi Na-MMt digunakan sebagai pengisi. Kajian tersebut menunjukkan bahawa masa skorj nanokomposit yang mengandungi 1.0 ke 7.0 phr adalah tinggi berbanding makrokomposit. Peningkatan kepekatan DDA-MMt melebihi 7.0 phr menurunkan masa skorj. Sementara itu, perbezaan tork nanokomposit adalah tinggi berbanding makrokomposit. Walau bagaimanapun, masa pematangan nanokomposit adalah rendah berbanding masa pematangan makrokomposit. Spectra FT-IR menunjukkan bahawa

DDA-MMt hadir di dalam nanokomposit. Kekuatan tensil, peratusan pemanjangan pada takat putus dan degradasi terma nanokomposit adalah boleh ubah terhadap kandungan DDA-MMt. DMA menunjukkan T_g nanokomposit adalah rendah berbanding NR termatang dan makrokomposit. Didapati juga bahawa T_g menurun sementara moduli tersimpan meningkat dengan peningkatan kandungan tanah liat bagi kesemua nanokomposit dan makrokomposit. Peratusan kandungan gel nanokomposit adalah tinggi berbanding makrokomposit pada penambahan 1.0 phr DDA-MMt tetapi menurun dengan penambahan DDA-MMt sehingga 15.0 phr. Analisis serakan DDA-MMt oleh XRD dan Transmisi elektron mikroskopi (TEM) menunjukkan bahawa DDA-MMt telah diinterkalasi dan terkupas di dalam matrik NR.

Interpenetrating polymer network (IPN) nanokomposit telah disediakan melalui pempolimeran gelombang micro *in situ* methyl methacrylate (MMA) yang mengandungi benzoil peroksida sebagai pemula yang direndam di dalam NR/7phrDDA-MMt nanokomposit termatang. Keadaan optimum untuk penyediaan IPN nanokomposit boleh diringkaskan sebagai berikut: 1 % (w/w) kepekatan pemula, 20 minit masa pempolimeran dan 1.5 jam masa rendaman. Spektrum FT-IR IPN nanokomposit mengesahkan bahawa kesemua NR/DDA-MMt nanokomposit dan PMMA adalah wujud di dalam IPN nanokomposit. Kekuatan tensil tertinggi IPN nanokomposit telah diperhatikan apabila ia ditambah dengan 40 % (w/w) PMMA. Peratusan kandungan gel IPN nanokomposit menurun dengan peningkatan kandungan PMMA. Kestabilan terma IPN nanokomposit telah ditentukan dan ia berada di antara kestabilan terma PMMA dan nanokomposit. TGA juga mengesahkan bahawa kestabilan terma IPN nanokomposit bergantung kepada

kandungan PMMA. Lengkuk $\tan \delta$ terhadap suhu IPN nanokomposit menunjukkan 2 T_g dimana berada diantara -46.90 ke -39.88 °C dan 147.88 ke 149.03 °C dimana masing-masing menepati T_g NR dan PMMA. Moduli tersimpan IPN nanokomposit meningkat dengan peningkatan kandungan PMMA. Corak XRD IPN nanokomposit pada 52, 35 dan 7 % (w/w) komposisi PMMA menunjukkan tiada jalur pembelauan kelihatan di dalam julat 2θ dari 2 ke 10 °. TEM mikrograf IPN nanokomposit bagi kesemua komposisi PMMA menunjukkan bahawa DDA-MMt telah terkupas di mana kesemua platlet DDA-MMt ditaburkan sebagai lapisan individu di dalam matrik IPN nanokomposit.



ACKNOWLEDGEMENT

I would like to express my appreciation to all who contribute to this project, especially to the chairman of my Supervisory Committee, Professor Dato' Dr. Wan Md Zin bin Wan Yunus, for his guidance, constructive comments, continuous support and advices throughout the duration of this study. I extent my sincere thanks to my co-supervisors, Associate Professor Dr. Mansor Hj. Ahmad and Dr. Azowa Ibrahim for their supervision, support and suggestion.

I also wish to express my appreciation to all staff of Electron Microscopy Unit, UPM especially Mr. Ho Oi Kuan. Sincere thanks are also extended to all Laboratory Assistance in the Chemistry Department, UPM especially Mr. Kamal, Mrs. Ros, Mr. Ismail and Mrs. Yusmawati from Physic Department, UPM for their dedication in delivering technical assistance and contribution towards these departments. My appreciation is further extended to all my senior and junior lab mates in Lab G30, 255 and 407 for their endless support and also providing me with laughter, joy and friendship all the way through.

Last but not least, my deepest affection and gratitude goes to my beloved family member for their continuous understanding and moral support throughout the period of my study. Special thanks to Universiti Putra Malaysia and Ministry of Science, Technology and Innovation for the financial support under PASCA and the IRPA grant.



I certify that an Examination Committee has met on August 2007 to conduct the final examination of Sharil Fadli Bin Mohamad Zamri on his Master of Science thesis entitled **“MICROWAVE ASSISTED PREPARATION AND CHARACTERIZATION OF POLY (METHYL METHACRYLATE)/NATURAL RUBBER/DODECYLAMINE MONTMORILLONITE INTERPENETRATING POLYMER NETWORK NANOCOMPOSITES”** in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia Regulations (Higher Degree) 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 14 August 2008



DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at UPM or other institutions.

SHARIL FADLI BIN MOHAMAD ZAMRI

Date: 19 June 2008



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