PREPARATION AND CHARACTERIZATION OF POLY(METHYL METHACRYLATE)/CLAY AND POLY(METHYL ACRYLATE)/CLAY NANOCOMPOSITES BY MICROWAVE IRRADIATION AND CONVENTIONAL HEATING

By

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

January 2006

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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Faculty : Science

Poly(methyl methacrylate)/clay and poly(methyl acrylate)/clay nanocomposites are prepared by polymerizing the monomers in the presence of modified sodium montmorillonite (Na-MMT). Na-MMT is modified by either cetyltrimethylammonium (CTA^+) or dodecylammonium (DDA^+) ions via a cation exchange process. After the modification, CHN elemental analysis shows that CTA^+ and DDA^+ ions are present in the montmorillonite. Fourier Transform Infrared (FT-IR) spectra of CTA-MMT and DDA-MMT clearly indicate the presence of new absorption bands, i.e. C-H asymmetric and symmetric stretching vibrations. The basal spacing of CTA-MMT and DDA-MMT increases from 11.6Å to 19.3Å and 18.7Å, respectively. Thermal gravimetric analysis (TGA) shows that CTA-MMT and DDA-MMT degrade at higher temperatures as compared to Na-MMT. Conversions of methyl methacrylate (MMA) and methyl acrylate (MA) into the polymers are carried out by either microwave irradiation or conventional heating methods in the presence of benzoyl peroxide as the initiator. The

microwave assisted preparation of PMMA/clay and PMA/clay nanocomposites significantly reduces the reaction period as compared to conventional heating. Gel permeation chromatography (GPC) results show that polydispersity indices of PMMAs prepared at high (650 W) and medium high (530 W) microwave power level and PMAs prepared at high microwave power level are narrower than that of PMMA and PMA prepared by conventional heating. FT-IR spectra of PMMA/clay and PMA/clay clearly indicate the presence of the polymer and clay functional groups. X-ray diffraction analysis (XRD) analysis shows that there are increments in the clay basal spacing of the PMMA/clay and PMA/clay nanocomposites prepared by both methods. This indicates that PMMA or PMA are successfully intercalated into the interlayer galleries of the clay. However, transmission electron microscopy (TEM) shows that the nanocomposites are of intercalated and flocculated type. The TGA thermograms indicate enhancement in thermal stability for PMMA/clay and PMA/clay nanocomposites and microcomposites as compared to that of the pure PMMA or PMA prepared by both microwave irradiation and conventional heating. The remarkable improvement in storage modulus of PMMA/clay and PMA/clay nanocomposites compared to that of the pure PMMA and PMA indicates there is a strong interaction between the matrix and the organoclay. The glass transition temperatures (T_g) of PMMA/CTA-MMT nanocomposites increase by around 10-20 ^{o}C as compared to that of the pure PMMA. PMMA/DDA-MMT nanocomposite with 1 wt% of DDA-MMT filled PMMA gives a higher T_g compared to the other DDA-MMT filled PMMA. However, the T_g for PMA/CTA-MMT and PMA/DDA-MMT nanocomposites is similar to that of the pure PMA.

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

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT POLI(METIL METAKRILAT)/TANAH LIAT DAN POLI(METIL AKRILAT)/TANAH LIAT MELALUI PENYINARAN GELOMBANG MIKRO DAN PEMANASAN KONVENSIONAL

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Nanokomposit poli(metil metakrilat)/tanah liat dan poli(metil akrilat)/tanah liat disediakan melalui pempolimeran monomernya dengan kehadiran natrium montmorillonit (Na-MMT) yang terubahsuai. Na-MMT diubahsuai dengan menggunakan ion setiltrimetilammonium (CTA^+) dan ion dodesilammonium (DDA^+) melalui proses penukaran kation. Analisis unsur CHN yang dilakukan selepas pengubahsuaian menunjukkan bahawa ion-ion CTA^+ dan DDA^+ hadir dalam montmorillonit tersebut. Spektra infra-merah terubah Fourier (FT-IR) bagi CTA-MMT dan DDA-MMT jelas menunjukkan kehadiran jalur serapan baru, iaitu getaran regangan asimetrik dan simetrik C-H. Ruang jarak antara lapisan dalam CTA-MMT dan DDA-MMT meningkat daripada 11.6Å ke 19.3Å dan 18.7Å. Analisis termogravimetrik (TGA) menunjukkan bahawa CTA-MMT dan DDA-MMT diurai pada suhu yang lebih tinggi berbanding dengan Na-MMT. Penukaran metil metakrilat (MMA) dan metil akrilat (MA) kepada polimer masing-masing dilakukan melalui kaedah penyinaran gelombang

mikro atau pemanasan konvensional dengan kehadiran benzoil peroksida sebagai pemula. Jangka masa penyediaan nanokomposit PMMA/tanah liat dan PMA/tanah liat melalui penyinaran gelombang mikro adalah pendek berbanding dengan penyediaan melalui pemanasan konvensional. Keputusan kromatografi penelapan jel (GPC) menunjukkan bahawa indeks poliserakan bagi PMMA yang disediakan pada tahap gelombang mikro kuasa tinggi (650W) dan sederhana tinggi (530W) dan PMA yang disediakan pada tahap gelombang mikro kuasa tinggi adalah lebih sempit berbanding dengan penyediaan melalui kaedah pemanasan konvensional. Spektra FT-IR nanokomposit PMMA/tanah liat dan PMA/tanah liat jelas menunjukkan kehadiran kumpulan-kumpulan berfungsi polimer dan tanah liat. Analisis pembelauan sinaran-X (XRD) menunjukkan bahawa terdapat peningkatan ruang jarak antara lapisan nanokomposit PMMA/tanah liat dan PMA/tanah liat yang disediakan melalui kedua-dua kaedah. Ini menunjukkan bahawa PMMA atau PMA telah berjaya diinterkalasi ke dalam galeri ruang antara lapisan tanah liat. Walau bagaimanapun, mikroskopi elektron penghantaran (TEM) menunjukkan bahawa nanokomposit yang dihasilkan adalah jenis interkalasi dan penggumpalan. Termogram TGA menunjukkan peningkatan kestabilan terma bagi nanokomposit dan mikrokomposit PMMA/tanah liat dan PMA/ tanah liat berbanding dengan PMMA atau PMA tulen yang disediakan melalui kedua-dua kaedah. Peningkatan modulus bagi nanokomposit PMMA/tanah liat dan PMA/tanah liat berbanding dengan PMMA dan PMA tulen menunjukkan interaksi yang kuat antara matriks dengan tanah liat. Suhu peralihan kaca (T_g) bagi nanokomposit PMMA/CTA-MMT meningkat sebanyak 10-20 ^{o}C berbanding dengan PMMA tulen. T_g bagi PMMA/DDA-MMT di mana 1 wt% DDA-MMT terisi dalam PMMA adalah lebih

tinggi berbanding dengan PMMA yang diisi dengan kandungan DDA-MMT yang berlainan. Walau bagaimanapun, T_g bagi nanokomposit PMA/tanah liat adalah hampir sama dengan PMA tulen.

ACKNOWLEDGEMENTS

I would like to express my appreciation to all of the individuals who contributed to this project, in particular, the chairman of my Supervisory Committee, Professor Dr. Wan Md. Zin bin Wan Yunus, for his guidance, constructive comments, continuous support and advice throughout the duration of this study. I extend my sincere thank to my co-supervisors, Professor Dr. Kaida Khalid and Associate Professor Dr. Mohammad Zaki Abd. Rahman for their supervision, support and suggestions.

I also wish to express my appreciation to all the staff in Electron Microscopy Unit, UPM especially Mr. Ho Oi Kuan. Sincere thanks are also extended to all the Laboratory Assistants in the Chemistry Department UPM especially Mr. Zulhisham, Mrs Ros, Mr. Kamal and Mr. Ismail as well as Miss Wan Yusmawati bt Wan Yussof in the Physics Department UPM for their dedication in delivering technical assistance and contribution towards these departments. My appreciation is further extended to Mr Yussof and Mr. Mohamad Nor in the Chemistry and Food Technology Department UKM for delivering technical assistance. My special appreciation also goes to all my senior and junior lab mates in Lab 407 and 255 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 members for their continuous understanding and moral support throughout the period of study. Special thanks to Ministry of Science, Technology and Environment for the financial support under the IRPA grant.

I certify that an Examination Committee met on 26 January 2006 to conduct the final examination of Yeoh Ean Nee on his Master of Science thesis entitled "Preparation and Characterization of Poly(methyl methacrylate)/Clay and Poly(methyl acrylate)/Clay Nanocomposites by Microwave Irradiation and Conventional Heating" in accordance with Universiti Pertanian (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (higher Degree) Regulation 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 of Science. 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 the citations which have been duly acknowledged. I also declare that is has not been previously or concurrently submitted for any other degree at UPM.

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YEOH EAN NEE

Date: 10 March 2006

TABLE OF CONTENTS