PREPARATION AND CHARACTERIZATION OF POLYLACTIDE/POLYCAPROLACTONE/FATTY HYDRAZIDE AND OCTADECYLAMINE-MODIFIED CLAY NANOCOMPOSITE

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MASTER OF SCIENCE
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By

SITI ZULAIHA BINTI HAIRALDIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in fulfilment of the Requirement for degree of Master of Science

December 2012
This thesis is especially dedicated to:

My mother Saadiah Brahim, My father Hairaldin Senawi, and My siblings, who are infinitely precious to me,

&

My husband Shaiful Amri Mohd Som, My daughter Nuradryana Amani, who has filled my life with joy and happiness,

&

My friends, who were there for me
Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

PREPARATION AND CHARACTERIZATION OF POLYLACTIDE/POLYCAPROLACTONE/FATTY HYDRAZIDE AND OCTADECYLAMINE-MODIFIED CLAY NANOCOMPOSITE

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December 2012

Chairman : Nor Azowa Ibrahim, PhD
Faculty : Science

In this study, two organically modified montmorillonite (OMMT) clay were prepared via ion exchange reaction. One was fatty hydrazides synthesized from palm oil functions was use to modify the nature of montmorillonite (Na-MMT). The other was ODA which is obtained from the industry. FH-MMT and ODA-MMT organoclay were successfully prepared by intercalation of the alkylammonium chains into the gallery of MMT via ion exchanged reaction. The basal spacing of FH-MMT and ODA-MMT has increased from the original Na-MMT of 11.62Å to 13.10 Å 29.90 Å respectively. The shifting of the basal peak position indicates successfully intercalation of alkylammonium ion into the modified clay. Fourier Transform Infrared (FTIR) spectra of the FH-MMT and ODA-MMT organoclay indicated that the presence of alkylammonium ion group resulting from modification reaction.
The 90/10 of PLA/PCL ratio nanocomposites was chosen to produce PLA/PCL nanocomposite in the internal mixer. This was chosen due to the highest tensile strength among PLA/PCL blends besides severe loss in elongation at break. Furthermore, TGA result indicated ratio 90/10 increase about 27 °C and 72 °C of maximum thermal degradation temperature \( (T_{\text{max}}) \) and decomposition temperature \( (T_d) \) compared to neat PLA. Two types of nanocomposites were prepared by melt blending technique and characterized. The X-ray diffraction (XRD) technique was used to analyze the degree of expansion of the prepared clays. XRD analysis indicated that PLA/PCL containing 1, 3, 5, 7, and 10% FH-MMT exhibits interlayer distance of 13.26, 13.80, 13.93, 14.31, and 14.06 Å respectively. Meanwhile, the \( d_{001} \) diffraction for PLA/PCL containing 1, 3, 5, 7% ODA-MMT exhibits interlayer distance of 30.87, 31.14, 32.24 and 32.34 Å respectively.

The transmission electron microscopy (TEM) was used to confirm the presence of the clay. The presence of intercalated and partially exfoliated structure for nanocomposites was observed. The clay was dispersed however the agglomeration in the TEM micrograph was still exist. The thermal stability of PLA/PCL improved after addition of FH-MMT and ODA-MMT. Presence of 1% of FH-MMT in PLA/PCL improved about 24 °C and 17 °C compared to neat PLA/PCL in term of the maximum thermal degradation temperature \( (T_{\text{max}}) \) and initial degradation temperature \( (T_{\text{on}}) \) respectively.
Tensile test showed different effects on the strength, modulus and elongation of the PLA/PCL nanocomposites. The morphology of etched samples was investigated by scanning electron microscopy (SEM), which showed addition of OMMT reduces the diameter of black hole of PLA/PCL. The diameter of spherulites which indicated phase separation in fractured surface samples also reduced after addition of FH-MMT and ODA-MMT. TEM analysis confirmed that the prepared PLA/PCL/FH-MMT and PLA/PCL/ODA-MMT nanocomposites are intercalated and exfoliated types.
Dalam kajian ini, dua tanah liat organik terubahsuai montmorilonit (OMMT) telah disediakan melalui tindak balas pertukaran ion. OMMT yang pertama disediakan menggunakan hydrazides lemak yang disintesis daripada minyak sawit untuk mengubahsuai sifat montmorilonit (Na-MMT). OMM kedua pula menggunakan ODA yang diperolehi daripada industri. Tanah liat Organo FH-MMT dan ODA-MMT telah berjaya disediakan melalui interkalasi rantaian alkylammonium ke dalam galeri MMT melalui tindakbalas pertukaran ion. Hasilnya, jarak basal FH-MMT dan ODA-MMT telah meningkat dari jarak asal Na-MMT iaitu 11.62Å kepada 13.10 Å 29.90 Å. Peralihan kedudukan puncak basal menunjukkan interkalasi OMMT ke dalam tanah liat yang diubahsuai telah berjaya. Spectrum IR (FTIR) FH-MMT dan ODA-MMT menunjukkan kehadiran kumpulan ion alkilammonia selepas tindakbalas pengubahsuai.
Nisbah 90/10 daripada PLA/PCL telah dipilih untuk menghasilkan nanokomposit PLA/PCL dalam pencampur dalaman. Nisbah ini telah dipilih kerana menghasilkan kekuatan tegangan tertinggi di antara nisbah campuran PLA/PCL tanpa kerugian teruk dalam sifat pemanjangan. Tambahan pula, keputusan TGA menunjukkan nisbah campuran 90/10 menghasilkan peningkatan masing-masing sebanyak 27 °C dan 72 °C bagi suhu degradasi terma maksimum ($T_{\text{max}}$) dan suhu penguraian ($T_d$) berbanding PLA. Dua jenis nanokomposit telah disediakan oleh teknik pengadunan leburan dan dicirikan. Pembelauan sinar-X (XRD) teknik telah digunakan untuk menganalisis tahap pengembangan tanah liat yang disediakan. XRD analisis menunjukkan bahawa PLA/PCL yang mengandungi 1, 3, 5, 7, dan 10% FH-MMT memberi jarak antara lapisan masing-masing sebanyak 13.26, 13.80, 13.93, 14.31, dan 14.06 Å. Sementara itu, pembelauan $d_{001}$ untuk PLA/PCL yang mengandungi 1, 3, 5, 7% ODA-MMT pula menghasilkan jarak antara lapisan masing-masing sebanyak 30.87, 31.14, 32.24 dan 32.34 Å.

Transmisi mikroskopi elektron (TEM) telah digunakan untuk mengesahkan kehadiran tanah liat. Kehadiran struktur interkalasi dan sebahagianya exfoliasi nanokomposit telah diperhatikan. Walaupun tanah liat telah tersebar, namun masih terdapat agglomerasi di dalam sempel. Kestabilan terma PLA/PCL telah ditambah baik selepas penambahan FH-MMT dan ODA-MMT. Dengan Kehadiran 1% FH-MMT sahaja, suhu degradasi maksimum haba ($T_{\text{max}}$) dan suhu degradasi awal ($T_{\text{on}}$) nanokomposit PLA/PCL masing-masing telah meningkat sebanyak 24 °C dan 17 °C berbanding dengan PLA/PCL.
Ujian tegangan menunjukkan kesan yang berbeza terhadap modulus kekuatan dan pemanjangan nanokomposit PLA/PCL. Keadaan morfologi sampel terukir telah disiasat oleh imbasan mikroskop elektron (SEM), yang menunjukkan dengan penambahan OMMT telah mengurangkan diameter lubang hitam yang hadir dalam sampel PLA/PCL. Diameter spherulite yang menunjukkan pemisahan fasa antara polimer PLA dan PCL dalam sampel permukaan patah menjadi lebih kecil selepas penambahan FH-MMT dan ODA-MMT. Analisis TEM mengesahkan bahawa nanokomposit PLA/PCL/FH-MMT dan PLA/PCL/ODA-MMT adalah dari jenis interkalasi dan jenis ekfoliasi.
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I certify that an Examination Committee has met on 18 December 2013 to conduct the final examination of Siti Zulaiha Hairaldin on her Master Degree of Science thesis entitled “Preparation and Characterization of Polylactide/Polycaprolactone/Fatty Hydrazide and Octadecylamine-Modified Clay Nanocomposite” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the Master of Science. Members of the Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment for the requirement for the Master Degree of science. The members of the Supervisory Committee were as follows:

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Date:
DECLARATION

I declare that the thesis is my original work expert for quotations and citations which have been fully acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia.

________________________________________

SITI ZULAIHA HAIRALDIN

Date: 18 December 2012
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