UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLY(LACTIC ACID)/POLY(BUTYLENE ADIPATE-CO-TEREPTHALATE)/CLAY NANOCOMPOSITES

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By

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Faculty: Science

Poly(lactic acid) (PLA) is a biodegradable plastic that is brittle. Because of this nature, PLA has a limitation in its usage. The toughness of PLA can be improved by adding plasticizer. In this study, poly(butylenes adipate-co-terepthalate) was added to act as a plasticizer for PLA. The new biodegradable plastic, poly(lactic acid)/poly(butylene adipate-co-terepththalate) (PLA/PBAT), PLA/PBAT/sodium montmorillonite (PLA/PBAT/Na-MMT) and PLA/PBAT/organomodified montmorillonite (PLA/PBAT/OMMT) nanocomposites were prepared by using melt blending technique. This thesis describes the preparation and characterization of PLA/PBAT blends, PLA/PBAT/MMT composites and PLA/PBAT/OMMT nanocomposites.

In order to improve the compatibility of polymer and clay, the clay was first modified to become organoclay (OMMT). The organoclays were prepared from sodium montmorillonite (Na-MMT) through cation exchange technique using two types of organic surfactants; octadecyl amine (ODA) and dimethyl

dioctadecyl amine bromide (DDOAB). Cloisite 20A (C 20A) commercialize organoclay also used to compare the effect of this organoclay to PLA/PBAT blends. The increase in interlayer spacing of OMMT was characterized using X-Ray Diffraction (XRD) analysis. The presence of alkylammonium ions in organoclay was also studied by Fourier Transform Infrared (FTIR). Thermal behaviour and amount of surfactant intercalate into the clay galleries of OMMT was study by Thermogravimetric analysis (TGA) and elemental analysis respectively.

In studying properties of PLA/PBAT blends, the interaction between these two polymers will affect the tensile and mechanical properties of PLA/PBAT blends. In this study, PBAT acts as a plasticizer of PLA whereas the addition of PBAT decreased the tensile strength and tensile modulus of PLA however increased the elongation at break. The interaction between PLA and PBAT was examined by FTIR. From the dynamic mechanical analysis, PLA and PBAT form immiscible blends as there is two peaks at loss modulus curve represented the T_g for PLA and PBAT. This was supported by SEM observation. Water absorption of sample was found have the same trends as the biodegradation rate of the sample. With greater amounts of PBAT, water absorption and biodegradation rate of the sample increase.

Since blending PLA and PBAT will result immiscible blends, OMMT is introduce into PLA/PBAT blends system to improve the compatibility between PLA/PBAT and OMMT. The type of modifier plays a significant role to influence the tensile properties of PLA/PBAT/OMMT nanocomposites.

Generally, OMMT with more polar modifier give higher tensile properties of PLA/PBAT/OMMT nanocomposites. This was expected due to the hydrogen bonding between PLA/PBAT blends and the hydroxyl group inside the clay galleries. As a result, shifting for C - O group detected on FTIR spectra. Dynamic mechanical studies revealed the same result as the tensile properties. The addition of OMMT into PLA/PBAT blends increased the thermal degradation as shown in TGA. SEM images show the improvement on continuity and compatibility of PLA/PBAT/OMMT nanocomposites as the reduction of cavity and smoother surface. Transmission electron microscopy (TEM) was used to observe the distribution of OMMT and study the type of nanocomposite formed. The addition of OMMT also enhances the barrier properties in term of water absorption of PLA/PBAT/OMMT nanocomposites, which due to increasing of tortousity. The sample was confirmed as biodegradable as it degraded (loss in weight) after 3 weeks of biodegradable test.

The effect of clay loading on tensile properties, mechanical properties, thermal properties, water uptake and biodegradability of PLA/PBAT blends, PLA/PBAT/MMT composites and PLA/PBAT/OMMT nanocomposites were discuss in term of clay loading. The optimum clay loading for PLA/PBAT blends is 1%. The tensile strength and tensile modulus increase until 1 % clay loading and start to decrease with increasing clay loading due to the tactoid structure at high clay loading. The mechanical properties and thermal properties increased with increasing clay content due to the enhancement reinforcing action between clay and polymer and the barrier properties of the clay. The tortuous path created

after addition of clay influenced the water uptake and biodegradability of PLA/PBAT/OMMT nanocomposites and PLA/PBAT/MMT composites.

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

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT POLI(ASID LAKTIK)/POLI(BUTILENA ADIPAT-KO-TEREFTALAT)/TANAH LIAT

Oleh

MOHD JUNAEDY BIN OSMAN

Februari 2011

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Poli(asid laktik) (PLA) adalah salah satu plastik terbiodegradasi yang rapuh. Disebabkan sifat ini, PLA penggunaannya terbatas. Kekerasan PLA boleh ditambahbaikkan dengan menambahkan pemplastik. Dalam kajian ini, poli(butilena adipat-ko-tereftalat) (PBAT) telah ditambah untuk bertindak sebagai pemplastik bagi PLA. Plastik terbiodegradasi baru, Poli(asid laktik)/poli(butilena adipat-ko-tereftalat) (PLA/PBAT), PLA/PBAT/natrium montmorillonit (PLA/PBAT/Na-MMT) dan PLA/PBAT/organik terubahsuai montmorillonit (PLA/PBAT/OMMT) telah disediakan menggunakan teknik pengadunan lebur. Tesis ini menghuraikan tentang penyediaan dan pencirian adunan PLA/PBAT, PLA/PBAT/Na-MMT komposit dan PLA/PBAT/OMMT nanokomposit.

Untuk menambahbaikkan keserasian polimer dan tanah liat, tanah liat telah diubahsuai menjadi organo-tanah liat (OMMT). Organo-tanah liat telah disediakan dari natrium montmorillonit (Na-MMT) melalui teknik pertukaran kation menggunakan dua jenis surfaktan organik; oktadesil amino (ODA) dan dimetil dioktadesil amino bromida (DDOA). Cloisit 20A (C 20A) organo-tanah

liat komersil juga digunakan untuk membandingkan kesan organo-tanah liat ini kepada adunan PLA/PBAT. Penambahan pada jarak antara lapisan OMMT telah ditentukan menggunakan analisis belauan sinar X (XRD). Kehadiran ion alkilammonium dalam organo-tanah liat telah ditentukan menggunakan spektroskopi infra-merah pengubah Fourier (FTIR). Kelakuan terma dan jumlah surfaktan yang masuk ke dalam lapisan tanah liat OMMT ditentukan menggunakan analisis termogravimetri (TGA) dan analisis unsur.

Dalam mempelajari sifat-sifat adunan PLA/PBAT, interaksi antara kedua-dua polimer ini dipercayai mempengaruhi regangan dan sifat-sifat mekanikal adunan PLA/PBAT. PBAT telah diketahui bertindak sebagai pemplastik kepada PLA dimana penambahan PBAT, menurunkan kekuatan regangan dan modulus regangan PLA namun meningkatkan nilai pemanjangan putus. Interaksi antara PLA dan PBAT telah disiasat menggunakan FTIR. Dari analisis mekanikal dinamik, PLA dan PBAT membentuk adunan tidak berpadu kerana wujud dua puncak pada modulus hilang mewakili Tg untuk PLA dan PBAT. Ini disokong dengan pemerhatian SEM. Penyerapan air oleh sampel ditemui mempunyai kecenderungan yang sama dengan kadar biodegradasi sampel. Dengan penambahan jumlah PBAT, penyerapan air dan kadar biodegradasi sampel juga bertambah.

Oleh kerana mengadun PLA dan PBAT akan menghasilkan adunan tidak berpadu, OMMT diperkenalkan ke dalam adunan PLA/PBAT untuk menambahbaikkan keserasian antara PLA/PBAT dan OMMT. Jenis pengubahsuai memainkan peranan yang penting dalam mempengaruhi sifat

regangan PLA/PBAT/OMMT nanokomposit. Amnya OMMT dengan pengubahsuai yang lebih polar menghasilkan PLA/PBAT/OMMT nanokomposit bersifat regangan tinggi. Ini sudah dijangka kerana ikatan hidrogen antara adunan PLA/PBAT dan kumpulan hidroksil di dalam lapisan tanah liat. Ini disahkan dengan penganjakkan untuk kumpulan C - O dikesan pada spektra FTIR. Kajian mekanikal dinamik membuktikan keputusan yang sama dengan keputusan sifat regangan. Penambahan OMMT ke dalam adunan PLA/PBAT meningkatkan degradasi termal seperti yang ditunjukkan dalam TGA. Imej SEM menunjukkan penambahbaikkan dalam kesinambungan dan keserasian PLA/PBAT/OMMT nanokomposit dari pengurangan jumlah lubang dan permukaan yang rata. Mikroskop transmisi elektron (TEM) digunakan bagi memerhatikan pengagihan OMMT dan mengkaji jenis nanokomposit terhasil. Penambahan OMMT juga meningkatkan sifat rintangan dari sudut penyerapan air PLA/PBAT/OMMT nanokomposit adalah kerana peningkatan keluk-keluk dalam polimer. Sampel disahkan terdegradasi kerana terdapat penyusutan berat selepas 3 minggu dalam ujian terbiodegradasi.

Kesan pengisian tanah liat terhadap sifat regangan, sifat mekanikal, sifat terma, pengambilan air dan sifat biodegradasi adunan PLA/PBAT, PLA/PBAT/MMT komposit dan PLA/PBAT/OMMT nanokomposit dibincangkan dari sudut jumlah pengisian tanah liat. Pengisian tanah liat yang optimum untuk adunan PLA/PBAT adalah 1%. Kekuatan regangan dan modulus regangan bertambah sehingga 1% kandungan tanah liat dan mula berkurang dengan penambahan kandungan tanah liat kerana struktur taktoid dalam kandungan tanah liat yang tinggi. Sifat mekanikal dan sifat termal meningkat dengan penambahan tanah liat

termuat disebabkan peningkatan kesan peneguhan antara tanah liat dan polimer juga sifat rintangan tanah liat. Laluan berkelok-kelok terhasil setelah penambahan tanah liat mempengaruhi pengambilan air dan biodegradasi PLA/PBAT/OMMT nanokomposit dan PLA/PBAT/MMT komposit.

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APPROVAL

I certify that an Examination committee has met on 17 February 2011 to conduct the final examination of Mohd Junaedy Bin Osman on his degree thesis entitled "Preparation and characterization of poly(lactic acid)/poly(butylenes adipate-co-terepththalate) clay nanocomposites" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and University Pertanian Malaysia (Higher Degree) Regulation 1981. The committee recommended that the student awarded the degree of Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the Master of Science. The members of the Supervisory Committee were as below:

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DECLARATION

I declare that the thesis is my original work except for quotation and citation, which have been duly acknowledged. I also declare that this thesis has not been previously and is not concurrently submitted for any other degree at Universiti Putra Malaysia or any other institution.

MOHD JUNAEDY BIN OSMAN
Date: 17 February 2011

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