ABSTRAK

Pengajian ini melibatkan sintesis dan pencirian tiga makromer berbeza berasaskan asid oleik sawit. Makromer ini dibuat daripada asid oleik, bersama-sama dengan fthalat anhidrida dan gliserol. Struktur molekul makromer ini diubah dengan menggunakan 28, 40 dan 65% berat asid oleik dalam rumusan keseluruhan dan dilabel sebagai AlkOA28, AlkOA40 dan AlkOA65 masing-masing. Tahap tindak balas pada akhir tindak balas polikondensasi dalam pembuatan setiap makromer melebihi dari 95%. Kajian degradasi terma bagi tiga makromer ini menunjukkan bahawa makromer AlkOA28 mempunyai kestabilan terma yang secara relatif adalah tinggi diikuti dengan AlkOA40 dan AlkOA65. Dari kaedah Kissinger, tenaga pengaktifan degradasi terma bagi makromer AlkOA28, AlkOA40dan AlkOA65 didapati ialah masing-masing 229,0, 183,0 dan 134,0 kJ mol^{-1}. Juga kaedah Ozawa, Flynn dan Wall (OFW) menunjukkan bahawa tindak balas degradasi menjadi lebih rumit dengan peningkatan kandungan asid oleik. Struktur makromer ini telah diciri menggunakan FTIR dan ^{1}H-NMR.

Kopolimer dengan nisbah macromer-metil metakrilat (MMA) berbeza telah disintesis melalui pempolimeran radikal bebas dengan kehadiran benzoil peroksida (BPO) sebagai pemula pada 95-100°C. Kadar kopempolimeran bergantung pada nisbah makromer/MMA. . Nisbah makromer/MMA tinggi menyebabkan kadar tindak balas lebih rendah dan juga penukaran lebih rendah selepas masa tindak balas yang sama. Membandingkan spektrum ^{1}H-NMR makromer dan kopolimer berkaitan, adalah didapati bahawa nisbah luas puncak bagi kumpulan vinil ke kumpulan metil terminal bagi cabang oleate berkurang, memberi sokongan bahawa ikatan dubel bagi kumpulan oleate telah bertindak balas.

Selain itu, kumpulan metoksi (-OCH_3) dari bahagian MMA boleh dilihat jelas pada spektrum ^{1}H-NMR kopolimer. Keputusan DSC menunjukkan bahawa kopolimer mempamerkan T_g tunggal yang luas tanpa puncak peleburan, menunjukkan bahawa makromer dan MMA adalah serasi dan sebahagian besar kopolimernya bersifat amorfus. Mengurangkan nisbah makromer/MMA tinggi telah menyebabkan T_g dan berat molekul yang lebih tinggi. Kepelbagaian T_g pada nisbah makromer/MMA yang berbeza boleh dijelaskan melalui persamaan Gordon-Tailor. Analisis TGA menunjukkan bahawa kestabilan terma kopolimer meningkat dengan nisbah makromer/MMA. Keputusan DMA juga telah menunjukkan bahawa nisbah makromer/MMA telah menyebabkan T_g lebih rendah modulus hilang dan akibatnya meningkatkan kekenyalan. Kopolimer dari AlkOA28 menunjukkan T_g lebih tinggi pada modulus hilang dan kekenyalan yang lebih rendah.

Kopolimer ini telah dinilai prestasinya sebagai bahan pelindung. Makromer dengan berat molekul rendah tidak dapat mengering di udara. Memasukkan MMA telah menghasilkan kopolimer yang mempunyai masa pengeringan fizik yang pendek, serta lebih tahan terhadap hidrolisis. Secara keseluruhan mengurangkan nisbah makromer/ MMA, telah mengakibatkan ketahanan kimia yang lebih tinggi tetapi lekatan mengalami penurunan.

Sebagai sambungan kepada projek, sifat kopolimer boleh diubahsuai dengan memperkenalkan monomer butil akrilat (BA) untuk menggantikan sebahagian daripada MMA. Keputusan kajian menunjukkan bahawa kadar pempolimeran meningkat ketika nisbah makromer/akrilat menurun (tren yang sama dengan kadar kopempolimeran sebelum menggunakan BA). Selanjutnya, penukaran lebih besar berbanding dengan penukaran diperolehi kopempolimeran makromers dengan MMA sahaja. Struktur kopolimer diubahsuai telah dicirikan menggunakan ^{1}H-NMR. Kemasukan BA dalam kopolimer telah meningkatkan berat molekul, kestabilan terma, sementara nilai T_g dari pengukuran DSC dan

T_g pada puncak tan δ_{max}, dan modulus hilang dari keputusan DMA menunjukkan penurunan. Selain itu, sebahagian besar sampel menunjukkan peralihan β antara -50˚C dan suhu bilik.

Secara keseluruhan, keputusan terbaik bagi persembahan pelindung dicerap selepas kemasukan 5% BA dalam kopolimer yang disintesis dari AlkOA28. Siri ini menunjukkan lekatan, kekerasan goresan, ketahanan air dan garam yang terbaik. Selanjutnya mengurangkan nisbah makromer/akrilat, telah menyebabkan peningkatan ketahanan asid dan alkali. Sampel kopolimer selepas pengubahsuaian dengan BA dikeringkan dalam masa yang lebih lama dibandingkan dengan kopolimer tanpa diubahsuai. Untuk siri kopolimer yang diubahsuai ini, penukaran dan kandungan pepejal (dengan nisbah makromer/akrilat = 0,25) ialah masing-masing 90,7% dan 31,1%. Memahami perubahan dalam sifat tipisan disebabkan oleh kepelbagaian nisbah AlkOA/akrilat, adalah berguna untuk mereka-bentuk bahan pelindung dengan prestasi yang dikehendaki.

ASTRACT

This study concerns the synthesis and characterization of three different palm oleic acid-based macromers made from oleic acid, together with phthalic anhydride and glycerol. The molecular structure of the macromers had been varied by using 28, 40 and 65 wt% of oleic acid in the overall formulation and labeled as AlkOA28, AlkOA40 and AlkOA65 respectively. The extent of reaction at the end of polycondensation reaction in making each macromer was more than 95%. Thermal degradation studies of three macromers revealed that AlkOA28 macromer has a relatively higher thermal stability and followed by AlkOA40 and AlkOA65. From Kissinger method, activation energy of the thermal degradation for the macromers AlkOA28, AlkOA40 and AlkOA65 are found to be 229.0, 183.0 and 134.0 kJ mol^{-1} respectively. Further, Ozawa, Flynn and Wall (OFW) method revealed that degradation reaction become more complex with increase in oleic acid content. The macromer structures were characterized using FTIR and ^{1}H-NMR.

Copolymers with different macromer-methyl methacrylate (MMA) ratios were synthesized via free radical polymerization in the presence of benzoyl peroxide (BPO) as initiator at 95-100°C. The copolymerization rate is dependent on macromer/MMA ratio. The higher ratio of macromer/MMA has led to the lower reaction rate and lower conversion after the same reaction time. Comparing ^{1}H-NMR spectra of macromer and related copolymer, it was found that ratio of peak areas of vinyl group to terminal methyl group of oleate branches has decreased, providing support that the double bonds of the oleate moiety have reacted. Besides, the methoxy ($-OCH_3$) group from MMA moiety could be clearly seen in ^{1}H-NMR spectra of copolymers. DSC results have shown that the copolymers exhibited a single broad T_g without any melting peak, indicating that the macromer and MMA were compatible and their copolymers were largely amorphous in nature. Reducing the

macromer/MMA ratio has led to higher molecular weight and T_g of the copolymers. The variation in T_g at different macromer/MMA ratio could be described by the Gordon-Tailor equation. TGA analysis showed that the thermal stability of copolymer increases with increasing the macromer/MMA ratio. DMA results have also shown that higher macromer/MMA ratio has led to lower T_g at loss modulus and consequently increase elasticity. Copolymers from AlkOA28 showed higher T_g at loss modulus and lower elasticity.

The copolymers were evaluated as coatings materials. The low molecular weight macromers are unable to air drying. Incorporation of MMA has resulted in copolymers that have short physical drying time, as well as better resistant toward hydrolysis. Overall decreasing the macromer/MMA ratio, has led to higher chemical resistance but adhesion has decreased.

As an extension to the project, some of the properties of copolymers could be modified by introducing butyl acrylate (BA) monomer to replace part of MMA. The results demonstrated that polymerization rate increased when the macromer/acrylate ratio decreased (the same trend with the copolymerization rate before using BA). Furthermore, conversion was greater compared to the conversion obtained for copolymerization of macromers with only MMA. The structure of modified copolymers was characterized using ^{1}H-NMR and FTIR. The incorporation of BA into the copolymers have increased the molecular weight, thermal stability, while T_g values from DSC measurements and T_g at loss modulus from DMA results showed a decrease. In addition, most of the samples showed β transitions between -50°C and room temperature.

Overall, the best results for coating performances were observed after incorporation of 5% BA in copolymers synthesized from AlkOA28. This series demonstrated the best adhesion, scratch hardness, water and salt resistances. Furthermore decreasing the macromer/acrylate ratio, has led to improve acid and alkali resistances. Copolymer samples after modification with BA dried in longer time compared to the unmodified copolymers. For this series of modified copolymers (maromer/acrylate ratio = 0.25), conversion and solid content were 90.7 % and 31.1% respectively. Understanding the changes in film properties due to the variation of AlkOA/acrylate ratio, could be useful for designing coating of the desired performance.

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