



UNIVERSITI PUTRA MALAYSIA

**PREPARATION AND CHARACTERIZATION OF TAPIOCA
STARCH/POLYCAPROLACTONE/CLAY COMPOSITES**

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**PREPARATION AND CHARACTERIZATION OF TAPIOCA
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By

THEN YOON YEE

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

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of the requirement for the degree of Master of Science

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Chairman : Yg. Bhg. Professor Dato' Wan Md Zin Wan Yunus, PhD

Faculty : Science

In this work, plasticized tapioca starches (PTSs), blends of PTS and polycaprolactone (PCL), and composites of PTS/clay and PCL/PTS/clay were prepared by melt blending. Both natural clay (MMT) and octadecylamine modified clay (OMMT) were used in this study. OMMT was prepared by cation exchange reaction of Na⁺ cation in the interlayer of MMT with octadecylammonium cation from octadecylammonium chloride. X-ray diffraction (XRD) results showed that the OMMT has bigger d-spacing than that of original MMT indicating octadecylammonium cation has successfully intercalated into the clay interlayer. Thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and elemental analysis also indicated the presence of octadecylammonium cation in the OMMT.



PTSs were prepared by gelatinizing and plasticizing tapioca starch with water and glycerol, respectively in a Thermo Haake Polydrive internal mixer. Scanning electron micrographs showed that the tapioca starch formed a continuous phase after it was gelatinized and plasticized with water and glycerol. The study indicated that the tensile, thermal and water absorption properties of PTSs were strongly influenced by the contents of water and glycerol. The PTSs were water sensitive and exhibited low tensile properties. The formulation of tapioca starch, glycerol and water in the weight ratio of 5:1:4 was selected to study the effect of MMT, OMMT or PCL addition on its properties.

The composites of PTS/clay were prepared by melt blending of PTS with various amount of MMT or OMMT also in a Thermo Haake Polydrive internal mixer. The XRD and TEM results showed that the composites produced are of intercalated types. Transmission electron micrographs revealed that MMT was better dispersed than that of OMMT in the PTS matrix due to the strong polar interaction between the hydrophilic MMT and PTS. Consequently, higher tensile strength, modulus, thermal stability and storage modulus were observed in PTS/MMT composites compared to those of PTS/OMMT composites as well as neat PTS. However the water resistance property of PTS was improved by the presence of OMMT.

The blends of PCL and PTS were prepared by melt blending of PCL and PTS of different compositions also in a Thermo Haake Polydrive internal mixer. The presence of PCL improved the tensile strength, elongation at break, thermal stability and water resistance property of PTS.



PCL/PTS/clay composites were also prepared by melt blending the blend and clays. XRD results showed that the composites produced are of intercalated types. Transmission electron micrographs revealed that OMMT was better dispersed than that of MMT in the matrix. Significant improvements in tensile strength (> 60%) and elongation at break (> 1000%) were observed by the addition of 1 phr of OMMT. Improvement in water resistance property was also observed in PCL/PTS/OMMT composites. In contrast, no obvious properties improvements were observed for PCL/PTS/MMT composites.



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

**PENYEDIAAN DAN PENCIRIAN KOMPOSIT KANJI UBI
KAYU/POLIKAPROLAKTON/TANAH LIAT**

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Dalam kajian ini, kanji ubi kayu terplastik (PTSs), adunan PTS dan polikaprolakton (PCL) dan komposit PTS/tanah liat dan PCL/PTS/tanah liat telah disediakan melalui proses pengadunan lebur. Kedua-dua tanah liat semula jadi (MMT) dan tanah liat oktadesilamina terubahsuai (OMMT) telah digunakan dalam kajian ini. OMMT telah disediakan melalui kaedah penukaran kation di antara kation Na^+ dalam ruang antara lapisan MMT dengan kation oktadesilammonium dari oktadesilammonium klorida. Keputusan belauan x-ray (XRD) mendapati OMMT mempunyai jarak-d yang lebih besar daripada MMT asal menunjukkan kation oktadesilammonium telah berjaya interkalasi ke dalam ruang antara lapisan tanah liat. Analisis termogravimetrik (TGA), spektroskopi infra-merah jelmaan Fourier (FTIR), dan analisis unsur juga menunjukkan kehadiran kation oktadesilammonium dalam OMMT.



PTSs telah disediakan melalui proses penggelatinan dan pemplastikan kanji ubi kayu dengan menggunakan air dan gliserol, dalam mesin pencampur dalaman *Thermo Haake Polydrive*. Mikrograf imbasan elektron menunjukkan bahawa butiran kanji ubi kayu menjadi fasa berterusan selepas proses penggelatinan dan pemplastikan. Keputusan kajian menunjukkan bahawa kandungan air and gliserol mempunyai pengaruh yang kuat terhadap sifat-sifat ketegangan, terma dan penyerapan air bagi PTSs. PTSs adalah peka terhadap air dan mempunyai sifat tegangan yang rendah. Formulasi kanji ubi kayu, gliserol dan air dalam nisbah 5:1:4 telah dipilih untuk mengkaji kesan penambahan MMT, OMMT atau PCL ke atas sifat-sifat komposit yang dihasilkan.

Komposit PTS/tanah liat telah disediakan dengan mengadun leburan PTS dengan pelbagai kandungan MMT atau OMMT, juga dalam mesin pencampur dalaman *Thermo Haake Polydrive*. Keputusan XRD dan TEM menunjukkan komposit yang terhasil adalah jenis interkalasi. Mikrograf elektron transmisi mendedahkan bahawa MMT menyerak lebih baik daripada OMMT dalam matrik PTS kerana interaksi kutub lebih kuat antara hidrofilik MMT dan PTS. Ini menyebabkan kekuatan tegangan, modulus, kestabilan haba dan modulus simpanan yang lebih tinggi diperhatikan dalam komposit PTS/MMT berbanding dengan komposit PTS/OMMT serta PTS. Tetapi, sifat ketahanan terhadap penyerapan air pada PTS juga telah ditingkatkan dengan kehadiran OMMT.

Adunan PCL dan PTS telah disediakan dengan mengadun leburan PCL dan PTS dalam pelbagai komposisi, juga dalam mesin pencampur dalaman *Thermo Haake Polydrive*. Kekuatan tegangan, pemanjangan takat putus, kestabilan terma dan

ketahanan terhadap penyerapan air bagi PTS telah ditingkatkan dengan kehadiran PCL.

Komposit PCL/PTS/tanah liat juga disediakan dengan mengadun leburan adunan dengan tanah liat. Keputusan XRD menunjukkan komposit yang terhasil adalah jenis interkalasi. Mikrograf elektron transmisi mendedahkan bahawa OMMT menyerakan lebih baik berbanding dengan MMT dalam matrik. Peningkatan ketara dalam kekuatan tegangan ($> 60\%$) dan pemanjangan takat putus ($> 1000\%$) diperhatikan dengan penambahan 1 php OMMT. Peningkatan sifat terhadap ketahanan penyerapan air juga diperhatikan dalam komposit PCL/PTS/OMMT. Sebaliknya, tiada peningkatan sifat yang ketara diperhatikan bagi komposit PCL/PTS/MMT.

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I certify that a Thesis Examination Committee has met on 4 March 2011 to conduct the final examination of Then Yoon Yee on his thesis entitled “Preparation and Characterization of Tapioca Starch/Polycaprolactone/Clay Composites” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

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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 Universiti Putra Malaysia or at any other institution.

THEN YOON YEE

Date: 4 March 2011



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