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Modification of cassava starch by using propionic anhydride and properties of the starch-blended polyester polyurethane

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Abstract

Chemical modification of the cassava starch was conducted through acylation by using propionic anhydride as an esterifying reagent. The reaction was carried out in the presence of a pyridine catalyst and the effects of reaction variables such as the anhydride content, reaction time and reaction temperature on the degree of acylation were investigated. Results from Fourier transform infrared spectroscopy suggested that the hydroxyl groups in the starch molecules were converted into ester groups, accompanied by an increase in water stability of the starch. The propionyl content was found to be non-linearly dependent with the reaction variables. Scanning electron micrographs of the modified starch-blended polyurethane showed a better interfacial adhesion than the normal starch-blended polyurethane. However, results from the soil burial test showed that the modified starch experienced a slower biodegradation than the normal starch. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Cassava starch; Acylation; Blends; Compatibilization; Biodegradation

1. Introduction

Starch is a potentially useful polymer for thermoplastic biodegradable materials because of its low cost, availability and production from annually renewable resources. However, the use of starch as a material has been challenged by some limitations, including the low moisture resistance, poor process-ability (high viscosity), high brittleness, and incompatibility with some hydrophobic polymers. Consequently, several strategies have been created to cope with these problems. The moisture resistance of starch was improved by performing hydrophobic coating using various chemicals such as waxes, oils, varnishes, and alkyd resins (Lowell, 1985). These coating materials are, however, non-biodegradable and thus waste disposal problem of the coated materials still exist. Alternatively, some biodegradable polymers such as poly(3-hydroxy butyrate) polyurethane (Oertel, 1985), polyester based-polyurethane and polycaprolactone (PCL) (Koenig & Huang, 1994; Koleske, 1978) were used as the coating materials.

The toughness of starch was improved by blending with non-biodegradable plastics such as polyolefins (Goheen & Wool, 1991; Prinos, Bikiaris, Theologidis, & Panayiotou, 1991). It was found that the toughness of starch increased at the expense of its complete biodegradability and thus it is sometimes preferable to blend the starch with biodegradable plastics such as PCL, polylactic acid (PLLA), poly(vinyl alcohol) (PVOH), polyethylene glycol (PEG), and other aliphatic polyesters. The PCL has been extensively studied probably because of the superior toughness, water stability, and biodegradability of the material (Mayer & Kaplan, 1994). The blends of starch and PCL are known to be completely biodegradable (Choi, Kim, & Park, 1999; Koenig & Haung, 1995), however, mechanical properties of the blends become poorer with increase of the starch content in the blend. This is due to an incompatibility between the hydrophilic starch and the hydrophobic PCL (Koenig & Haung, 1995). From an economic point of view, it is preferable that the blend contains as much starch as possible, taking into account the fact that the PCL is more expensive. Several techniques were used to enhance the compatibility. For example, by grafting the PCL with glycidyl methacrylate (Kim, Cho, & Park, 2001), by using PEG as a compatibilizer (Kim, Choi, & Park, 2000), by using polylactide-*co*-e-caprolactone as a compatibilizer (Kim, Cho, Choi, & Park, 2000), and by modifying the PCL with pyromellitic anhydride (Avella et al., 2000).

Our research lies its interest on blending of a cassava

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starch with aliphatic polyester to create a biodegradable material with good mechanical properties and water stability. To improve water stability of the starch and to enhance compatibility between the starch and polyester, chemical structure of the cassava starch was modified by conducting an acylation, which changes a functional group of the starch molecules from the highly hydrophilic hydroxyl group to a more hydrophobic ester group. In term of blending, a thermoplastic polyurethane (TPU) was used as a representative of the polyester, taking into account that it contains aliphatic polyester in the soft block. In addition, mechanical properties and price of the TPU are reasonable for this purpose.

Conventionally, acylation of a starch can be carried out by pre-activating the starch with pyridine to open up the crystalline zone (amylose phase), improving accessibility of esterifying reagents and ensuring more uniform substitution. After that acetic anhydride was added to complete the acylation (Beck, Fitton, & Krichedorf, 1992; Parandoosh & Hudson, 1993). From our experience, however, the acetic anhydride is not available in Thailand. Due to its similar functionality, an analogue acid anhydride such as a propionic anhydride was considered to be a substitution for the acetic anhydride. The aim of this work is to study an acylation of cassava starch with propionic anhydride as a function of reaction variables. In addition, water stability, mechanical properties, morphology, and biodegradability of the modified starch-blended TPU are of interest.

2. Experimental

2.1. Materials

The cassava starch, which contained 17% of amylose and 83% of amylopectin, was obtained from The Thai Quality Starch Co. Ltd. Thermoplastic polyurethane (TPU) (S385A grade, comprising of 1,4-butanediol in the hard segment and a polyester–polyol in the soft segment) was supplied from SK Chemicals Co. Ltd. It has an average molecular weight of 250,000.

2.2. Preparation of starch propionate

To a reaction flask, 2.5 g of a dried starch was added followed by 20 ml of pyridine (AR grade from Carlo Erba) and then the flask was heated to 90 °C for 2 h to pre-activate the starch, under nitrogen flushing. A reflux-condenser was also used to prevent the loss of organic liquid. After the pre-activation for 2 h, the temperature was decreased to 75 °C and 8.2 ml of propionic anhydride (AR grade from Fluka) was added drop-wise, and then the reaction was continued for a further 22 h to ensure an equilibrium between the starch and the propionic anhydride. After carrying out the reaction for the given time, the content in the reaction flask was coagulated by adding 100 ml of isopropanol (AR grade from Analar) and stirring. The product was filtered off and washed with methanol. Finally, it was dried in an oven at 70 °C for 24 h. Percentage moisture absorption of the starch was evaluated by calculating the change in weight of the starch after drying in the oven at 70 °C.

2.3. Determination of propionyl content

A sample (0.5 g) of starch propionate was dissolved in 10 ml of methanol in a conical flask and then 10 ml of 1 M sodium hydroxide was added to the solution to saponify the ester. The excess base was determined by titration with 1 M HCl and a phenolphthalein indicator. The following equation was used to determine the propionyl content:

$$\%\text{Propionyl} = [(\text{mole of 1 M NaOH}) - (\text{mole of 1 M HCl})] \times 57(\text{g/mole}) \times 100/[\text{Starch(g)}] \quad (1)$$

2.4. Characterization

Change in chemical structure of the starch was qualitatively analyzed by using a Fourier transform infrared spectrophotometer (FTIR) (Bio-Rad, FTS 175). Sample was prepared by mixing the starch with nujol before casting onto a ZnSe window cell. The spectrum was recorded over the wavenumber ranging between 600 and 4000 cm^{-1}.

2.5. Blending and fabrication

Three different compositions of the starch-blended polyurethane were prepared (20/80, 40/60, and 60/40 w/w% of starch/TPU) by using a two-roll mill (LRM 110 from Labtech Engineering Co. Ltd). The polyurethane pellet was initially milled at 170 °C, after which the starch was gradually added and the blending was continued for 15 min. The blend was then converted into a sheet (3 mm thick), using a hydraulic hot press (LP20 from Labtech Engineering Co. Ltd) at 180 °C for 5 min.

2.6. Mechanical testing

The mechanical properties of the blends were evaluated by tensile testing. Dumbbell-shaped specimens were prepared by stamping the sheet with a standard die in accordance with ASTM D638-Type IV. The tensile test was performed at a cross-head speed of 100 mm/min, using an initial gauge length of 25 mm. Tensile strength, elongation, and toughness of each specimen were averaged from five tests.

2.7. Morphology

Morphology of various blends was examined by using a scanning electron microscope (SEM), (JEOL-JSM 5800) equipped with a secondary electron detector. Specimens

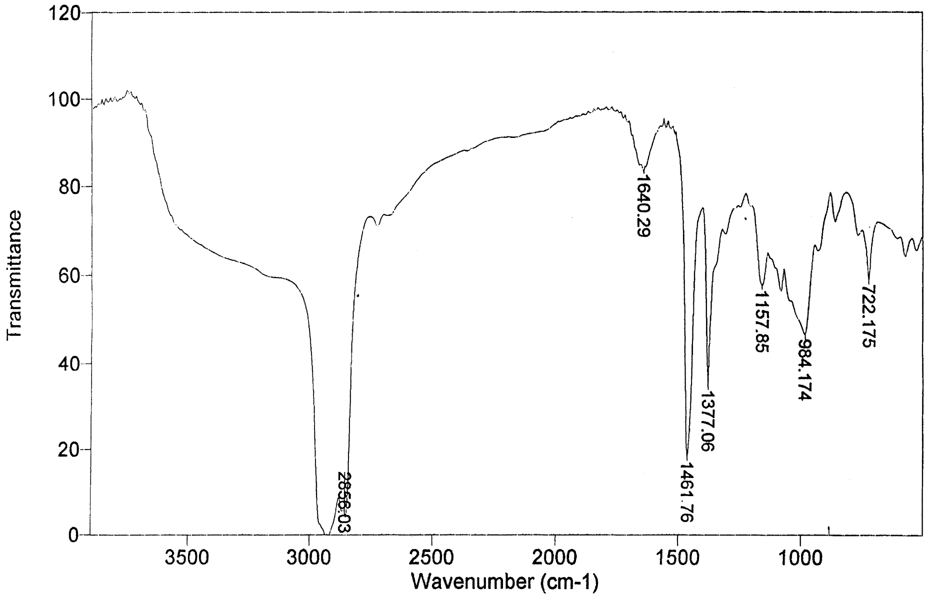

Fig. 1. FTIR spectrum of the normal starch.

were prepared by cryogenically fracturing the blends using liquid nitrogen. After that the fracture surface was coated with carbon using a vacuum coating unit (JEOL-JEE400). The accelerating voltage of the primary electron beam was 15 keV. To enhance a compositional contrast, the starch phase may be selectively etched from the blend, using suitable solvents (water and acetone for the normal and starch propionate, respectively).

2.8. Soil burial test

The fabricated sample (3 mm thick sheet) were cut into 30 mm × 30 mm squares and buried in soil at a depth of 15 cm, in Bangkok, Thailand from February to May 2001. After 1 and 3 months, the samples were collected and weighed.

3. Results and discussion

Figs. 1 and 2 show the FTIR spectra of normal starch and the modified starch, respectively. It can be seen that the broad peak at the wavenumber ranging between 3400 and 3600 cm^{-1} disappeared and a new peak at 1740 cm^{-1} was created after the acylation, which suggested that the hydroxyl groups were converted to propionate groups. The degree of substitution was quantitatively determined by titration and the results are summarized in Table 1. The

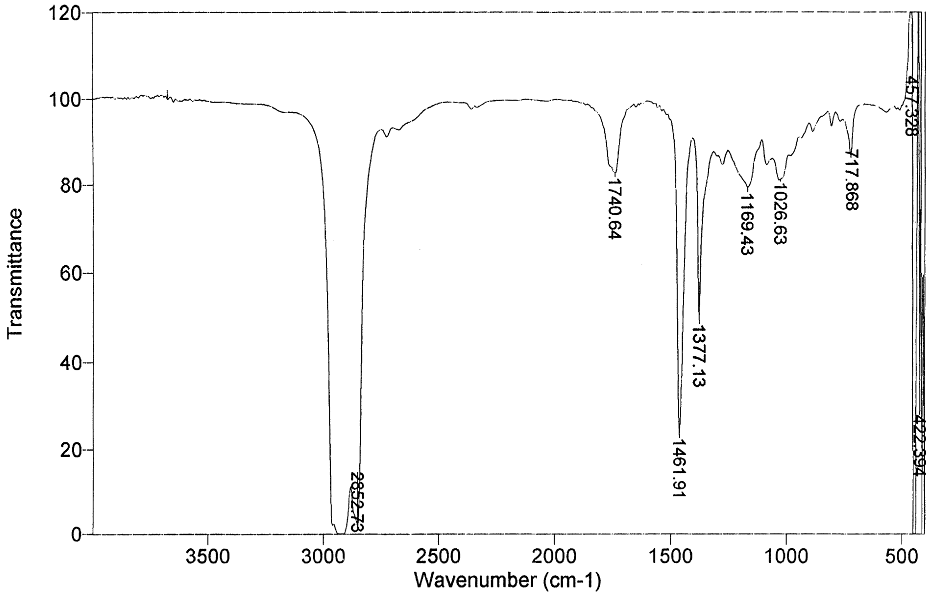

Fig. 2. FTIR spectrum of the modified starch.

Table 1
Propionyl content as a function of reaction parameters

Pyridine (ml)	Pre-activation time (h)	Pre-activation temperature (°C)	Propionic anhydride (ml)	Acylation temperature (°C)	Propionyl content (%)
20	2	95	8.2	75	12.5
25	2	95	8.2	75	17.6
30	2	95	8.2	75	47.2
35	2	95	8.2	75	24.6
20	3	95	8.2	75	27.7
20	4	95	8.2	75	48.5
20	5	95	8.2	75	44.8
20	2	80	8.2	75	11.2
20	2	85	8.2	75	35.2
20	2	90	8.2	75	33.3
20	2	95	6.2	75	8.6
20	2	95	10.2	75	51.1
20	2	95	14.2	75	43.8
20	2	95	18.2	75	15.9
20	2	95	8.2	55	35.4
20	2	95	8.2	65	42.5
20	2	95	8.2	85	6.8

Table 2
Tensile properties of various blends

Sample	Starch content (wt%)	Tensile strength (MPa)	Elongation (%)	Toughness (MPa)
Normal starch/TPU	20	27.3 ± 2.3	1150 ± 50	138.0 ± 18.0
	40	15.5 ± 0.2	864 ± 6	76.0 ± 7.3
	60	9.6 ± 1.3	75 ± 14	2.8 ± 1.5
Modified starch/TPU	20	30.8 ± 0.4	1376 ± 63	176.0 ± 8.5
	40	17.3 ± 0.9	937 ± 54	97.0 ± 18.0
	60	10.2 ± 1.1	36 ± 7	3.7 ± 0.5

Note: The propionyl content of the modified starch = 51%.

propionyl content is significantly affected by reaction parameters such as pyridine concentration, pre-activation temperature, pre-activation time, propionic anhydride concentration, and acylation temperature. Interestingly, the propionyl content is non-linearly related to the reaction parameters, i.e. there was an optimum value for each of the reaction parameters, corresponding to the maximum propionyl content. The optimum pyridine content was 30 ml (per 2.5 g of the normal starch) while the optimum pre-activation temperature and time was 85 °C and 4 h, respectively. It is also worth noting that these values were verified by repeating the experiments. It is believed that the reduction of propionyl content beyond the optimum value is attributed to the presence of water fraction, which is a by-product from the reaction between the hydroxyl group of the starch and propionic acid. The acid could be generated from the reaction between propionic anhydride and the starch as well as from the hydrolysis of the propionic anhydride (Pine, Hendrickson, Cram, & Hammond, 1985). The presence of water fraction and the pyridine catalyst might induce an ester hydrolysis of the modified starch (Pine et al., 1985), which decreased the degree of acylation. This effect can be dominant once the amount of water fraction, the degree of substitution (propionyl content) and the activation energy for the ester hydrolysis are sufficiently high. It seems that these factors are attributed to the increase in pyridine content, propionic anhydride content, pre-activation time, pre-activation temperature, and the acylation temperature.

Fig. 3 shows the relationship between propionyl content and percentage moisture absorption of various modified

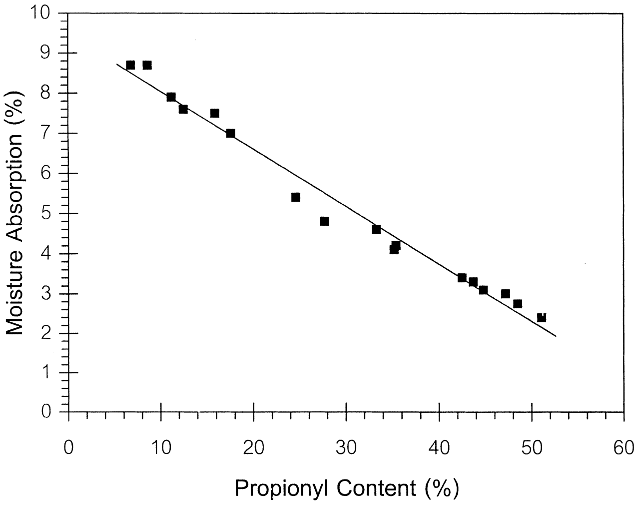

Fig. 3. Percentage moisture absorption as a function of propionyl content.

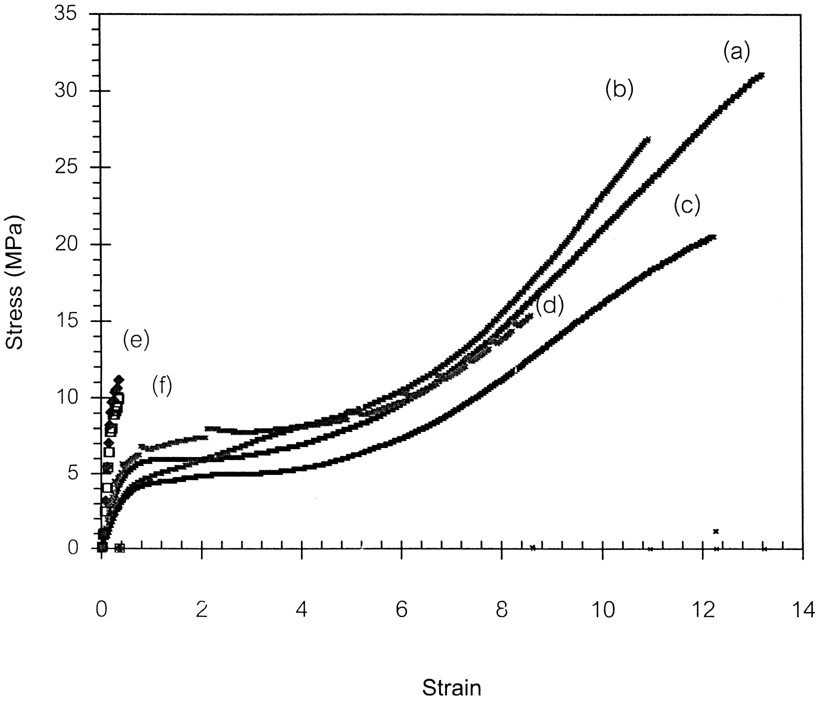

Fig. 4. Typical tensile force–displacement traces of: (a) modified starch/TPU (20/80); (b) normal starch/TPU (20/80); (c) modified starch/TPU (40/60); (d) normal starch/TPU (40/60); (e) modified starch/TPU (60/40); (f) normal starch/TPU (60/40). The propionyl content of modified starch = 51%.

starches. It can be seen that the moisture absorption linearly decreases with the propionyl content to the minimum value of 2.4%. In addition, it was observed that the modified starch (51% of propionyl content) was rarely soluble in water after stirring overnight. On the other hand, the normal starch was rapidly soluble in water as expected. The above results indicate that water stability of the normal starch can be improved by the acylation. Moreover, considering the results shown in Table 1, the linear trend in Fig. 3 implies that moisture resistance of the modified starch was also non-linear with the reaction parameters.

Fig. 4 shows typical tensile force–displacement traces of various blends. It was found that the blends containing less than 40 wt% of the starch, extended up to 10 times compared to the initial gauge length which means that an impact testing for these blends could not be conducted. However, by integrating the area under the stress–strain curves, the tensile toughness of various blends can be considered as shown in Table 2. It can be seen that the blends containing 20 and 40 wt% of the modified starch had higher tensile toughness than those containing the same amount of the normal starch. However, the differences are not too great taking into account the standard deviation, which means that the amount of propionyl content in the modified starch should be further increased for the purpose of improving the toughness. For the blend containing a

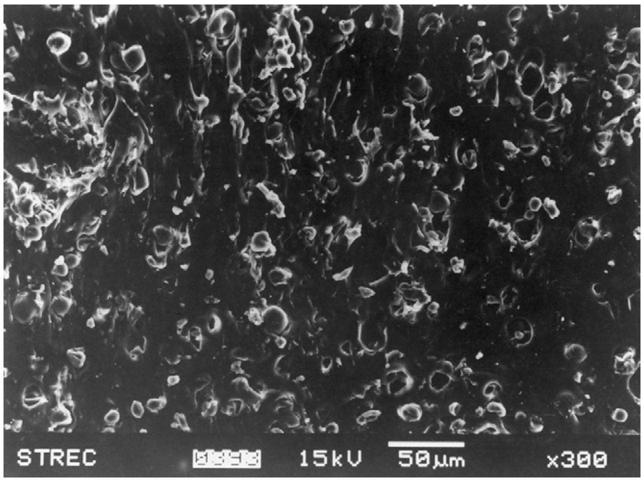

Fig. 5. Scanning electron micrograph of the normal starch/TPU blend (20/80).

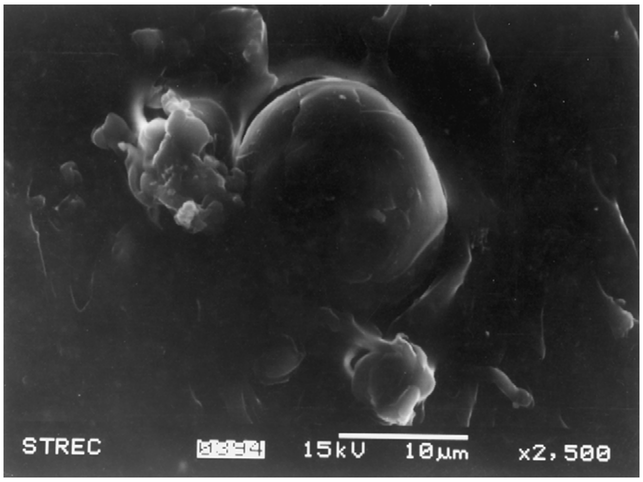

Fig. 6. Scanning electron micrograph of the normal starch/TPU blend (20/80).

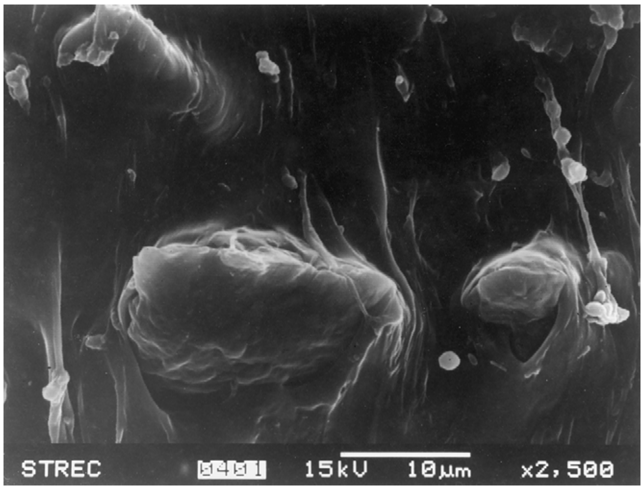

Fig. 7. Scanning electron micrograph of the modified starch/TPU blend (20/80).

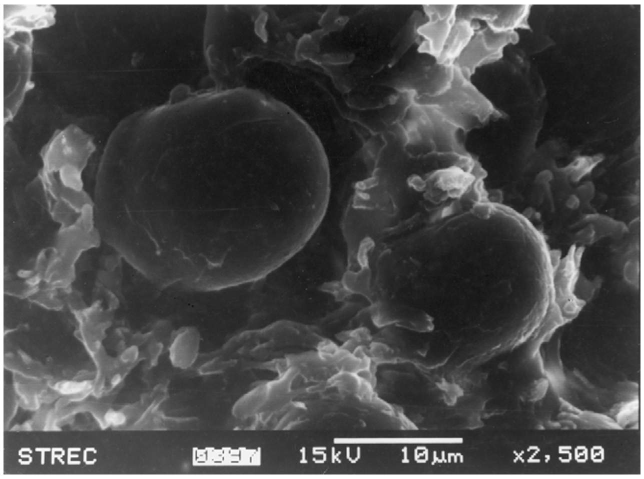

Fig. 8. Scanning electron micrograph of the normal starch/TPU blend (60/40).

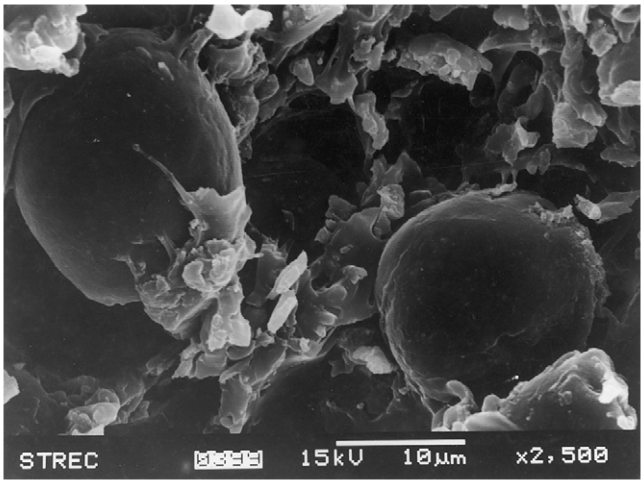

Fig. 9. Scanning electron micrograph of the modified starch/TPU blend (60/40).

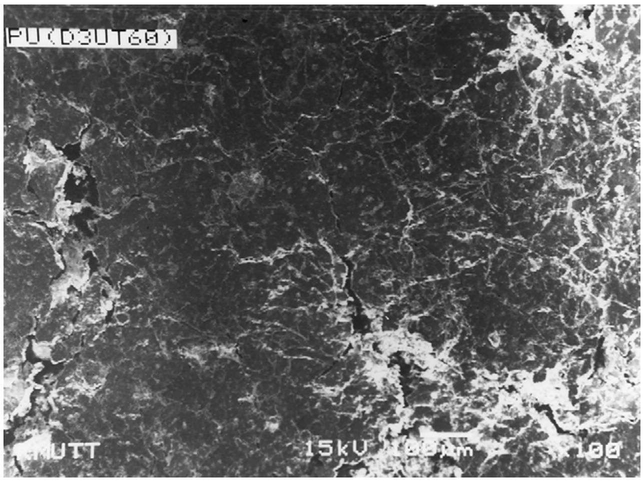

Fig. 10. Scanning electron micrograph of the surface of normal starch/TPU blend (40/60) after performing the soil burial test for 3 months.

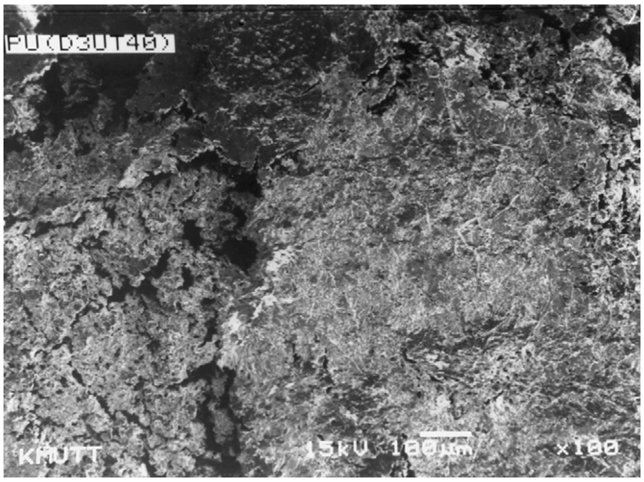

Fig. 11. Scanning electron micrograph of the surface of normal starch/TPU blend (60/40) after performing the soil burial test for 3 months.

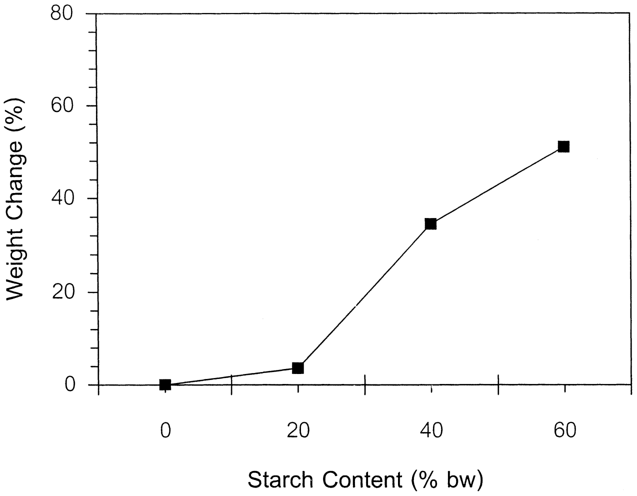

Fig. 12. Change in weight of the blends as a function of starch content after performing the soil burial test for 3 months.

higher amount of starch (60 wt%), the effect of chemical modification is not significant.

SEM micrographs of the blend containing 20 wt% of the normal starch (Fig. 5) revealed a dispersion of the starch particles in a TPU matrix. This was confirmed by conducting control experiments, in which the starch phase was removed by etching with a selective solvent (water). However, for the purpose of examining an interfacial adhesion of the blends, all of the samples were analyzed by the SEM technique without etching with selective solvents. From Fig. 6, it can be seen that normal starch particles with an average particle size of 10 μm were poorly bonded to the TPU matrix. On the other hand, the modified starch particle seems to be embedded in the TPU matrix (Fig. 7), indicating a good interfacial adhesion, which could be attributed to the chemical modification of the cassava starch. For the blends containing more starch (60 wt%), particulate characteristic of the starch phase was retained (Fig. 8) without forming a continuous phase, even though it had a higher blending ratio. This is probably because of the very high melting temperature of the starch (275 °C), which inhibited a fusion of the starch particles at the blending temperature used here. In addition, poor interfacial adhesion was observed in this case, which can account for the poor tensile toughness of the blend. An SEM micrograph of the blend containing modified starch (Fig. 9) also shows similar characteristics in terms of morphology and adhesion, which are probably the reasons why tensile properties of the modified starch-blended TPU were very close to those of the normal starch-blended TPU. It seems that compatibility between the two phases in the blend is dependent on the content of the starch particles.

Finally, degradability of the blends was investigated. Figs. 10 and 11 show the surfaces of the blends (40 and 60 wt% of the normal starch, respectively) which experienced the soil burial test for 3 months. It can be seen that the samples disintegrated indicating a biodegradation in the starch phase. It is worth noting that the disintegration was accompanied by the formation of white lines, which were believed to be precursors for cracking and the disintegration. Fig. 12 shows that weight loss of the soil burial tested samples increased with the starch content, which is in a good agreement with morphological changes. On the other hand, the weight of the blends containing the modified starch rarely changed (less than 3%) after the soil burial test. However, the white lines, which were believed to be a precursor for the cracking and the disintegration could be observed (Fig. 13), suggesting that the blend might be degraded at a slower rate than the normal starch-blended polyurethane. The retardation of the biodegradation here could be attributed to the fact that hydrolysis of chemical bonds in the starch molecules is a prerequisite for the biodegradation (Goldberg, 1995; Mayer & Kaplan, 1994). Therefore, the lower the hydrophilicity of the starch, the slower the enzymatic degradation. It seems that the propionyl content in the modified starch here (51%) was too high to permit the biodegradation within the period of 3 months. In comparison, Parandoosh and Hudson (1993) showed that the optimum acetyl content for the modified cornstarch was 22%. Relative to this work, the optimum propionyl content for the cassava starch with respect to the biodegradability, compatibility, and water stability of the modified starch blend has yet to be determined.

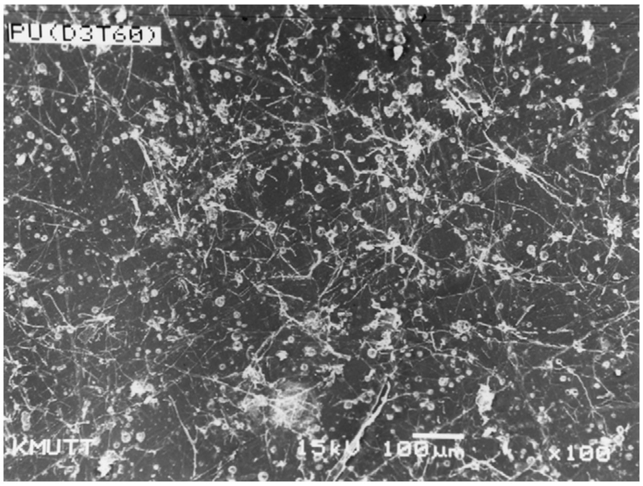

Fig. 13. Scanning electron micrograph of the surface of modified starch/TPU blend (40/60) after performing the soil burial test for 3 months.

4. Conclusions

The cassava starch was chemically modified via an acylation through the use of a propionic anhydride/pyridine mixture. The propionyl content was found to be non-linearly related to the reaction variables such as pyridine content, propionic anhydride content, pre-activation time, pre-activation temperature and the acylation temperature. As a result of the modification, the moisture resistance of the starch and its compatibility with polyester–polyurethane were improved at the expense of the rate of biodegradation.

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