

# Effects of Propionyl Content on the Morphology, Mechanical Properties, and Biodegradability of Esterified Cassava Starch/Polycaprolactone Blends

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**ABSTRACT:** The chemical structure of cassava starch was modified via an acylation with two different reaction systems: propionic anhydride in an aqueous sodium hydroxide solution and propionic anhydride in dimethyl sulfoxide/triethylamine mixtures. The acylation was carried out by the variation of reaction parameters to generate modified starches with a variety of propionyl contents. After that, the modified starch was blended with polycaprolactone (PCL) at a 30/70 weight composition in a twin-screw extruder. The results from the tensile testing of the various modified starch/PCL blends show that the moduli and tensile stresses of the materials were higher than those of the unmodified

starch/PCL blend. The elongation values of the modified starch/PCL blends, however, decreased with the propionyl content. Scanning electron micrographs of the blends containing modified starch with 62 and 80% propionyl were also different from those of blends containing modified starch with 16 and 28% propionyl in term of phase contrast. Finally, the rate of biodegradation of the blends decreased with increasing propionyl content. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2154–2162, 2005

**Key words:** biodegradable; blends; esterification; polyesters; polysaccharides

## INTRODUCTION

In an attempt to develop starch-based biodegradable materials, chemical modification of starch and blending of starch with biodegradable aliphatic polyesters have been widely carried out to change the chemical structure, polarity, and mechanical properties of the material.<sup>1–3</sup> In an earlier study,<sup>4</sup> we showed that by the acylation of cassava starch with propionic anhydride in pyridine, the hydroxyl groups of the starch were converted into ester (propionyl) groups. The moisture resistance of the modified starch was improved at the expense of its biodegradation rate. In addition, results from scanning electron microscopy (SEM) showed that the interfacial adhesion between the modified starch and the polyester plastic were improved. These results suggest that the development of biodegradable materials by the blending of modified starch with polyester plastic blends is promising. However, an optimum value of the degree of acylation with respect to good biodegradability, moisture resis-

tance, and mechanical properties of starch–polyester blends has not been reported and deserves an investigation. In addition, there are some problems with the acylation of starch that have yet to be improved before the commercial production and utilization of the material. For example, the use of pyridine as a catalyst and as a reaction medium (to preactivate the starch) in the acylation of starch is undesirable due to its unpleasant smell and toxicity. It would be more desirable to replace pyridine with some other catalyst and medium. For example, an aqueous sodium hydroxide solution was used to prepare acetylated starch with a low degree of substitution (DS).<sup>5</sup> In that case, sodium hydroxide acted as a catalyst, and the reaction temperature was kept below the gelatinization temperature of the starch to obtain the product in a granular form. Stojanovic et al.<sup>6</sup> prepared starch benzoate with benzoyl chloride and a solution of sodium hydroxide in alcohol–water mixture. The DS of the modified starch initially increased with the reaction time and reached the optimum value at 90 min. After that, the DS tended to decrease with increasing reaction time. It was believed that the result was due to some hydrolysis of starch benzoate at longer reaction times. To achieve a higher degree of acylation, it is necessary to preactivate the starch to open up the structure of a crystalline amylose phase of the starch. This can be achieved by the treatment of the starch with some solvent. In this regard, nonaqueous polar aprotic sol-

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vents, such as dimethyl sulfoxide (DMSO) and dimethylformamide, should be considered. In addition, a basic catalyst, such as triethylamine (TEA), should be used to improve the rate of acylation.<sup>5</sup>

In relation to this work, the acylation of cassava starch and the blending of the modified starch with polycaprolactone (PCL) were studied. The aim of this study was to investigate the effects of the degree of acylation on the morphology, biodegradability, and mechanical properties of the blends.

## EXPERIMENTAL

### Materials

The cassava starch, which contained 17% of amylose and 83% of amylopectin, was obtained from the Thai Quality Starch Co., Ltd. (Bangkok, Thailand) PCL (TONE 767, weight-average molecular weight = 50,000 g/mol) was kindly supplied by Dow Chemical Co., Ltd. (Danbury, CT) Propionic anhydride (purum grade, Fluka, Buchs, Switzerland), DMSO (Gas-chromatography grade, Reidel deHaen, Seelze, Germany), TEA (purum grade, Fluka, Buchs, Switzerland), and sodium hydroxide (analytical-reagent grade, Merck) were used as received.

### Preparation of the starch propionate

Acylation of the starch with propionic anhydride were carried out with two different reaction systems: a reaction in the DMSO medium in the presence of the TEA catalyst and a reaction in an aqueous solution of sodium hydroxide. The reactions were carried out under various conditions to produce modified starches with a variety of degrees of acylation.

#### Reaction in the aqueous medium

To a reaction flask, 3 g of dried starch was added followed by 40 mL of deionized water. Propionic anhydride (analytical-reagent grade, Fluka) was added dropwise to allow the reaction to proceed. Concurrently, sodium hydroxide (5% aqueous solution) was added dropwise to maintain the pH value of the mixture at 8 in the reaction flask. The reagents had to be dropped slowly into the flask to minimize any exothermic heat of reaction, which might have induced a gelatinization of the starch. After the addition of the anhydride was complete, the reaction was allowed to continue for a given time with the pH value kept constant at 8 by the regular addition of the sodium hydroxide solution. After the reaction was carried out for a given time, the content in the reaction flask was allowed to precipitate and was then filtered off and washed with

deionized water. Finally, the purified starch was dried to a constant weight in an oven at 70°C for 12 h.

#### Reaction in the DMSO medium

To a three-necked flask equipped with a reflux condenser and a stirrer, 3 g of dried starch was added, followed by 40 mL of DMSO, and then, the flask was heated to 50°C for 1 h to preactivate the starch under nitrogen flushing. After preactivation, a mixture of propionic anhydride and TEA was added dropwise, and then, the reaction was allowed to continue. After the reaction was carried out for a given time, the contents in the reaction flask was precipitated in deionized water followed by filtering off and washing with deionized water. This purification process was repeated two times to ensure good purity of the product. Finally, the purified starch was dried to a constant weight in an oven at a temperature below 50°C to avoid degradation of the starch.

### Characterization

The change in the chemical structure of the starch was qualitatively analyzed with a Fourier transform infrared (FTIR) spectrophotometer (Bio-Rad, FTS 175, Hertfordshire, UK). The sample was prepared with the KBr method. The spectrum was recorded over the wave number range 600–4000  $\text{cm}^{-1}$ .

### Determination of propionyl content

A sample (0.5 g) of starch propionate was dissolved in 10 mL of ethanol in a conical flask, and then an excess amount (20 mL) of an aqueous sodium hydroxide solution (1M) was added to the solution to saponify ester groups in the starch molecules. The reaction was performed by the refluxing of the starch solution at 85°C for 1 h. After the saponification was complete, the amount of remaining sodium hydroxide was determined by titration with 1M HCl and a phenolphthalein indicator. The following equation was used to determine the propionyl content:

$$\text{Propionyl (\%)} = [1\text{MNaOH (mol)} - 1\text{MHCl (mol)} \times 57 \text{ (g/mol)} \times 100] / [\text{Starch (g)}] \quad (1)$$

### Moisture absorption

The moisture absorption of the modified starch was determined by the drying of the starch in an oven at 75°C to a constant weight. Next, the percentage moisture absorption was calculated with the following equation:

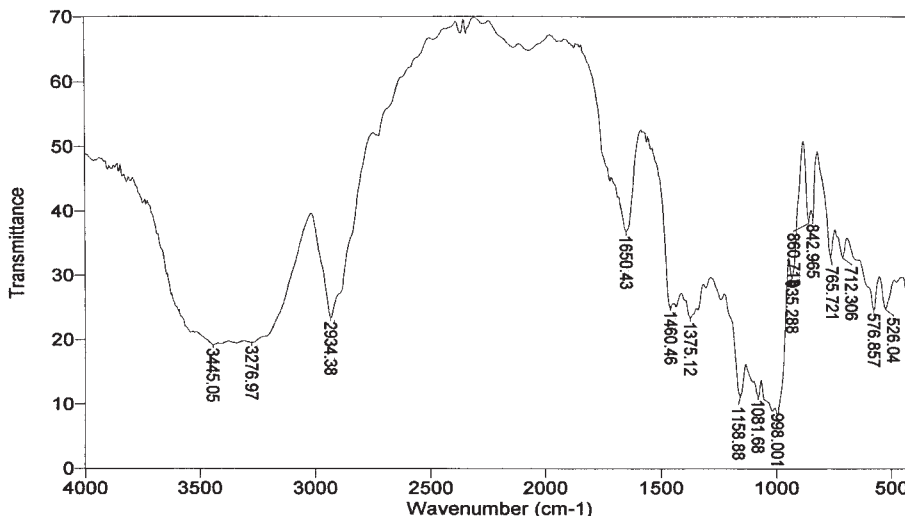


Figure 1 FTIR spectrum of an unmodified starch.

$$\text{Moisture absorption (\%)} = [(W_0 - W)/W_0] \times 100 \quad (2)$$

where  $W_0$  is the weight of the starch before drying and  $W$  is the weight of the dried starch.

### Blending and fabrication

Starch/PCL blends (30/70% w/w) were prepared with a twin-screw extruder (Haake PolyLab CTW100, Karlsruhe, Germany). The PCL pellet was initially premixed with the dried starch at a given composition, followed by the blending of the materials through a twin-screw extruder at barrel temperatures of 80, 85, 90, and 95°C (from the feed zone through the die zone) at a screw-rotation speed of 80 rpm. Strands of the extrudate were solidified by being passed

through a water bath before they were cut in a pelletizing unit. The pelletized material was passed through the extruder again to improve the dispersion and distribution of the blend components.

Next, the blend pellets were homogenized on a two-roll mill (LRM 110 from Labtech Engineering Co., Ltd., Bangkok, Thailand) at temperatures of 75°C (front roll) and 65°C (back roll). Finally, the blend was converted into a sheet 3 mm thick with a hydraulic hot press (LP20 from Labtech Engineering Co.) at 90°C and 600 psi for 1 min and was cooled for 5 min.

### Mechanical testing

The mechanical properties of the blends were evaluated by tensile testing. Dumbbell-shaped specimens were prepared by the stamping of the sheet with a

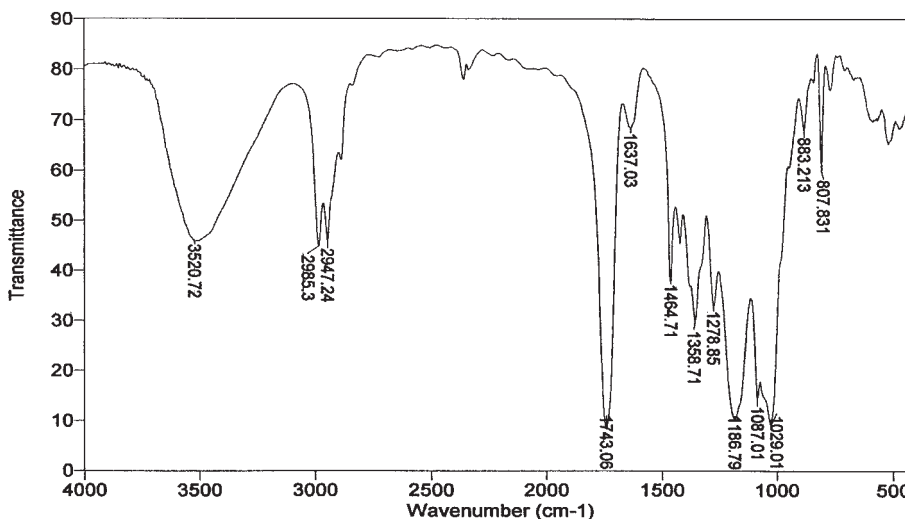


Figure 2 FTIR spectrum of the starch modified in the DMSO medium.

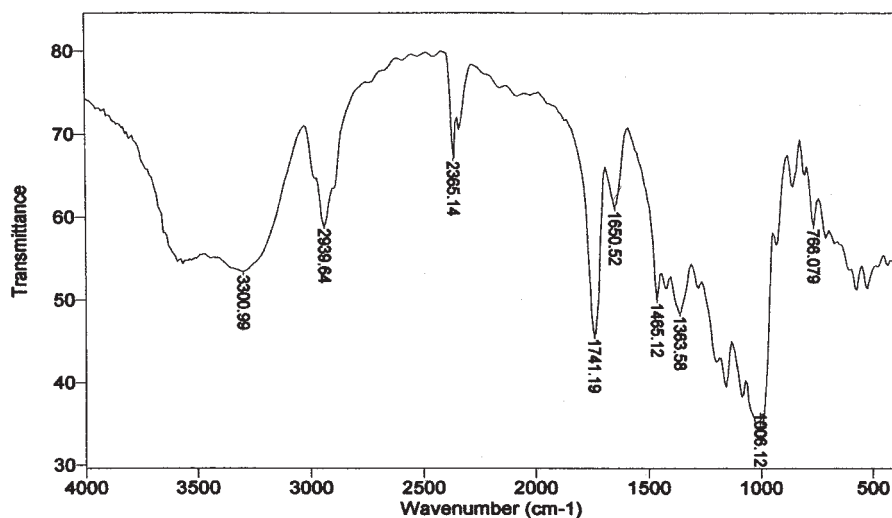


Figure 3 FTIR spectrum of the starch modified in an aqueous sodium hydroxide solution.

standard die in accordance with ASTM D 638-Type IV. The tensile test was performed at a crosshead speed of 100 mm/min with an initial gauge length of 25 mm. The tensile strength, elongation, and toughness of each specimen were averaged from five tests.

### Morphology

The morphology of various blends was examined with a scanning electron microscope (Jeol JSM 5800, Peabody, MA) equipped with a secondary electron detector. Specimens were prepared by the cryogenic fracturing of the blends with liquid nitrogen. Next, the fracture surface was coated with carbon with a vac-

uum coating unit (Jeol JEE400). The accelerating voltage of the primary electron beam was 15 keV.

### Thermal analysis

The thermal characteristics of the modified starch and that of the starch/PCL blends were studied with differential scanning calorimetry (DSC; Netzsch DSC 200). Starch samples were scanned over temperatures ranging from  $-100$  to  $250^{\circ}\text{C}$ , whereas the starch/PCL blends were scanned over temperatures ranging from  $-100$  to  $200^{\circ}\text{C}$  under a nitrogen atmosphere. The heating rate used was  $10^{\circ}\text{C}/\text{min}$ .

TABLE I  
Propionyl Content (%) of the Modified Starch as a Function of Acylation Parameters (DMSO/TEA System)

No.	Reaction parameter				Propionyl content (%)
	Anhydride content (mL)	TEA content (mL)	Acylation temperature ( $^{\circ}\text{C}$ )	Reaction time (min)	
1	10	10	70	240	$81.0 \pm 4.0$
2	10	10	70	120	$79.0 \pm 2.0$
3	10	10	70	60	$80.0 \pm 3.0$
4	10	10	70	30	$76.6 \pm 1.0$
5	10	10	70	15	—
6	10	10	70	60	$80.0 \pm 3.0$
7	10	10	50	60	$72.6 \pm 2.0$
8	10	10	30	60	$16.9 \pm 1.0$
9	20	20	50	60	$83.0 \pm 3.0$
10	15	15	50	60	$82.0 \pm 2.0$
11	10	10	50	60	$72.6 \pm 2.0$
12	5	5	50	60	—
13	20	10	50	60	$79.0 \pm 1.0$
14	10	5	50	60	$75.0 \pm 2.0$
15	10	20	50	60	$62.0 \pm 2.0$

**TABLE II**  
Propionyl Content (%) of Various Starches Modified in a  
Aqueous Sodium Hydroxide Solution

No.	Acylation time (min)	Propionic anhydride content (mL)	Propionyl content (%)
1	30	20	28.8 ± 0.0
2	60	20	27.5 ± 3.0
3	90	20	24.8 ± 0.0
4	60	5	16.0 ± 3.0
5	60	20	27.5 ± 3.0
6	60	25	31.8 ± 3.0
7	60	30	29.0 ± 2.0

### Soil burial test

The fabricated sample (a 3 mm thick sheet) was cut into 10 × 30-mm rectangles and buried in soil at a depth of 20 cm in Bangkok, Thailand, in May 2003. After 3 months, the samples were collected and weighed.

## RESULTS AND DISCUSSION

### Degree of acylation as a function of the reaction parameters

Changes in chemical structure of the starch after the acylation were confirmed by the comparison of the FTIR spectrum of the unmodified starch (Fig. 1) to that of the modified starch. For the starch modified in the DMSO medium, a new peak at about 1740 cm<sup>-1</sup> emerged (Fig. 2). In addition, the magnitude of the peak at wave numbers ranging between 3400 and 3600 cm<sup>-1</sup>, as shown in Figure 2, tended to decrease after

**TABLE III**  
Moisture Absorption of Various Modified Starches as a  
Function of Propionyl Content

Propionyl content (%)	Moisture content (%)
0	19.0
16	12.0
28	11.0
62	9.0
80	6.0

the acylation. These results suggest that some of the hydroxyl groups in the starch molecules were converted into carbonyl groups. Similarly, the FTIR spectrum of the starch modified in the aqueous sodium hydroxide solution (Fig. 3) showed the presence of a carbonyl peak at about 1740 cm<sup>-1</sup>. The peak at 3400–3600 cm<sup>-1</sup> was, however, considerably broad, and that might be attributed to a relatively low degree of acylation of the starch.

Changes in the DS of the modified starch as a function of the reaction parameters are summarized in Tables I and II. For the reaction carried out in DMSO, the content in the reaction flask did not precipitate in water after the reaction was performed for 15 min (no. 5, Table I). It seemed that chemical structure and polarity of the starch rarely changed. However, as the reaction time was increased to 30 min, the starch could be precipitated and isolated. The propionyl content of the modified starch was 76.6%. Further increasing the reaction time from 30 min to 60, 120, and 240 min only slightly increased the propionyl content. The reaction temperature affected the propionyl content considerably. The propionyl content increased with the tem-

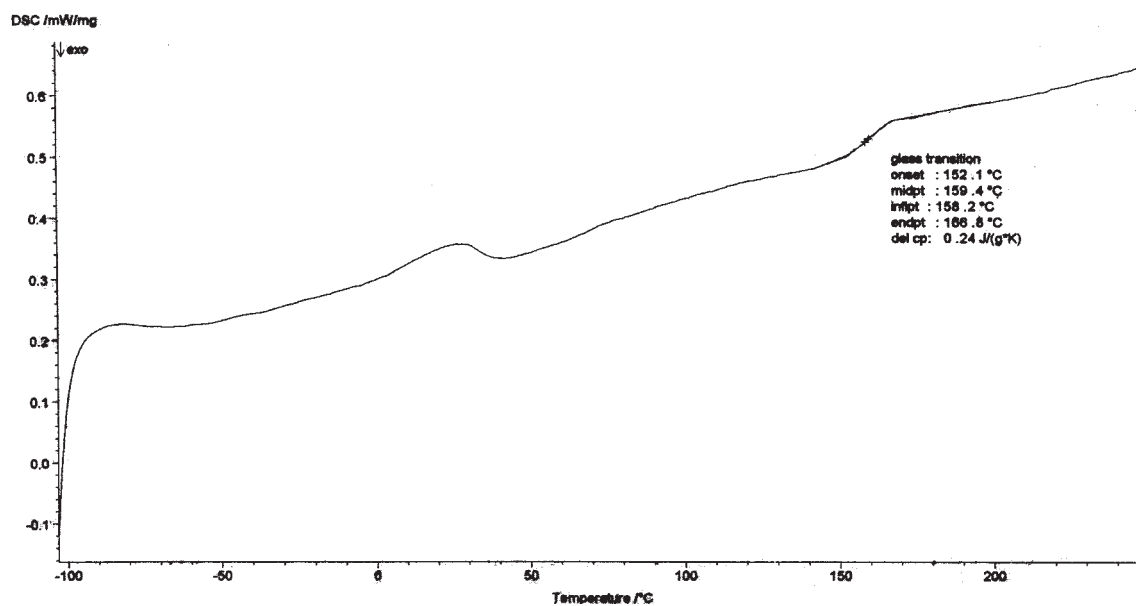


Figure 4 DSC thermogram of the modified starch (62% propionyl).

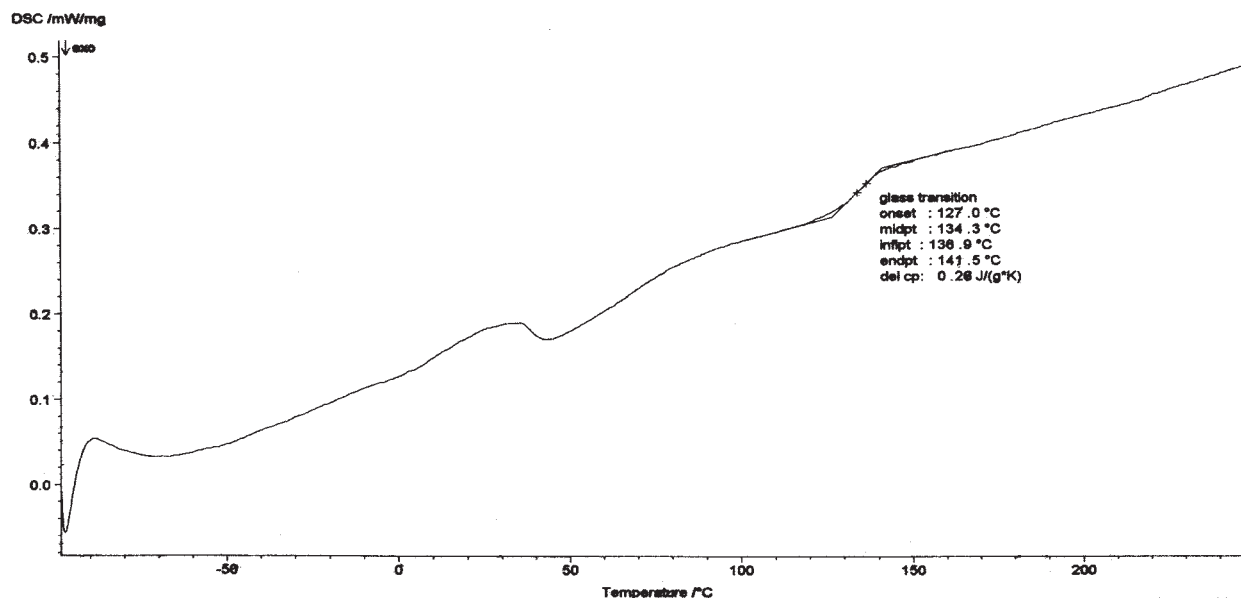


Figure 5 DSC thermogram of the modified starch (80% propionyl).

perature even through the relationship was not linear (nos. 6–8, Table I).

In term of the effects of the amount of esterifying reagents (propionic anhydride and TEA), the use of 5 mL of both reagents to react with 3 g of starch was not sufficiently high to change the polarity of the starch, and thus, the product could not be precipitated in water (no. 12, Table I). As the amount of both reagents were increased from to 10 mL, the propionyl content increased rapidly. Further increases in the content of both reagents only slightly increased the propionyl content. Finally, the volume ratio between anhydride and the TEA catalyst significantly affected the propionyl content of the modified starch. Generally speaking, the higher the ratio was, the greater the propionyl content was.

Notably, the propionyl contents of some of the modified starches reported in Table I were considerably higher than the theoretical value, with the assumption that all of the hydroxyl groups were esterified. In the latter case, the maximum value of propionyl content was about 51%. In this regard, we believed that the

differences might have been due to some degradation of the starch molecules. The propionic acid generated as a byproduct from the acylation might have induced chain scission at the 1,4-glucosidic bonds along the chain of starch molecules. The cleavage of 1,4-glucosidic bonds under acidic conditions is common and is sometime known as an acid thinning process.<sup>7</sup> Consequently, the degraded starch molecule contained more hydroxyl groups at the chain end. Furthermore, these additional hydroxyl groups could also be esterified, and thus, the overall content of propionyl groups of the modified starch increased. However, some further studies need yet to be conducted to verify this hypothesis.

For the starch, which experienced acylation in the aqueous sodium hydroxide solution, the effects of the two reaction parameters, that is, the anhydride con-

TABLE IV  
Tensile Properties of Various Modified Starch/PCL Blends (30/70 % w/w) as a Function of the Propionyl Content of the Starch

Propionyl content (%)	Modulus (MPa)	Elongation at break (%)	Tensile stress at yield (MPa)
0	92.0 ( $\pm 6.2$ )	1011 ( $\pm 102$ )	7.8 ( $\pm 0.1$ )
16	134.5 ( $\pm 14.4$ )	1024 ( $\pm 92$ )	11.9 ( $\pm 0.9$ )
28	117.0 ( $\pm 16.2$ )	998 ( $\pm 67$ )	12.0 ( $\pm 0.4$ )
62	120.5 ( $\pm 10.6$ )	124 ( $\pm 69$ )	14.5 ( $\pm 0.7$ )
80	122.4 ( $\pm 7.5$ )	35 ( $\pm 12$ )	14.1 ( $\pm 1.1$ )

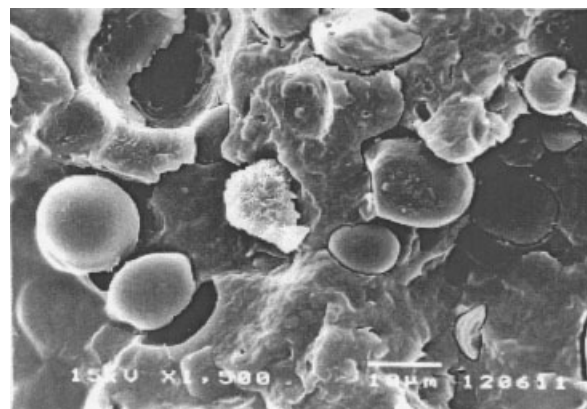
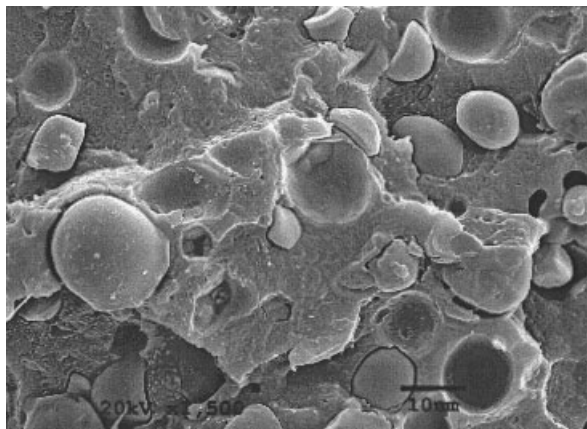
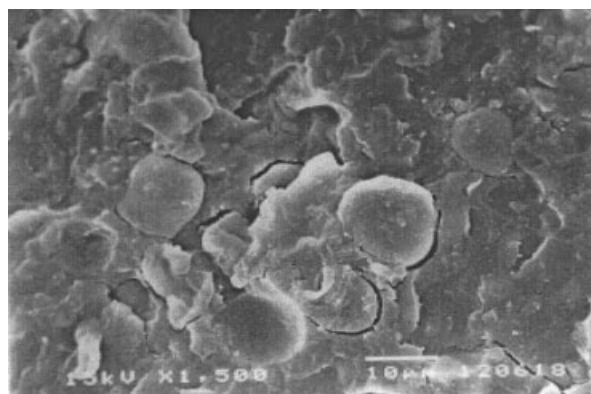


Figure 6 SEM micrograph of the unmodified starch/PCL blend.

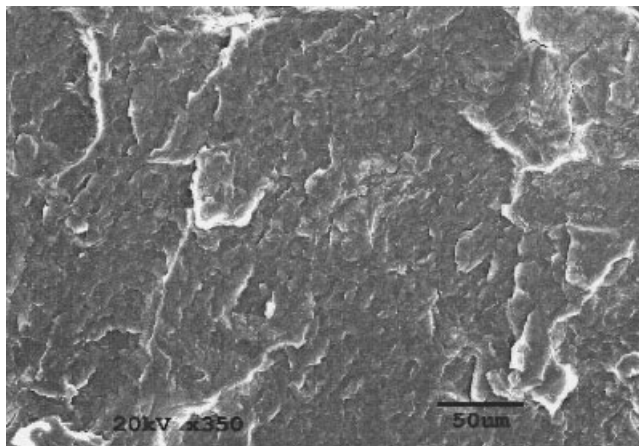


**Figure 7** SEM micrograph of a modified starch (16% propionyl)/PCL blend.

tent and the reaction time, on the DS were investigated. Increasing the time from 30 min to 60 and 90 min did not affect the propionyl content (nos. 1–3, Table II). It seemed that the acylation was almost completed after 30 min, and it was not necessary to extend the reaction time. In addition, work by Stojanovic et al.<sup>6</sup> showed that the degree of acylation might be decreased by a further increase in the reaction time after the optimum reaction time has been reached. Hydrolysis of the modified starch was believed to be responsible for the reduction of the DS of the starch. In terms of the effect of anhydride content, increasing the amount of the anhydride from 5 to 20 mL significantly increased the propionyl content from 16.0 to 27.5%. However, as the amount of the anhydride was further increased from 20 mL to 25 and 30 mL, the propionyl content rarely increased. In this regard, it might be possible that the higher the anhydride content was, the longer the reaction time was needed. This was because the anhydride had to be dropped slowly into the reaction flask to minimize the exothermic heat of reaction. Consequently, the modi-



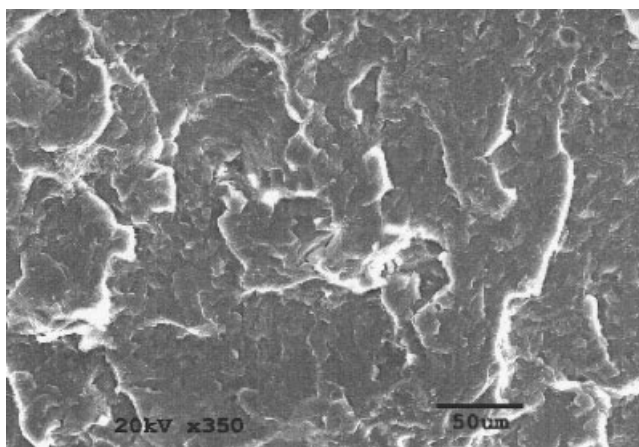
**Figure 8** SEM micrograph of a modified starch (28% propionyl)/PCL blend.



**Figure 9** SEM micrograph of a modified starch (62% propionyl)/PCL blend.

fied starch might have experienced more hydrolysis, leading to the lower propionyl content. As a result, the effect of propionic anhydride content on the DS was counterbalanced. In the other words, there was a competition between acylation and hydrolysis. A similar result was observed by Stojanovic et al.<sup>6</sup> for starch modified with benzoyl chloride in a solution of sodium hydroxide. In that case, the DS initially increased and then reached a maximum value. The results were attributed to some hydrolysis of the starch benzoate at longer reaction times.

To investigate the effects of the degree of acylation on the structure and properties of the starch/PCL blends, four grades of the modified starch with different propionyl contents, that is, 80, 62, 28, and 16% (from nos. 13 and 15, Table I, and nos. 2 and 4, Table II, respectively) were selected for further study. Table III shows the relationship between the propionyl content and the percentage moisture absorption of these modified starches. The moisture absorption decreased



**Figure 10** SEM micrograph of a modified starch (80% propionyl)/PCL blend.

with propionyl content as expected. This result implies that the higher the propionyl content was, the lower the polarity of the starch molecules was.

### Properties of the modified starch

Figure 4 shows the DSC thermogram of the modified starch with 62% propionyl. An endothermic transition at a temperature of about 159°C was observed. This was ascribed to the glass-transition temperature ( $T_g$ ) of the modified starch. Normally, the  $T_g$  of unmodified cassava starch is relatively high ( $\sim 230^\circ\text{C}$ ), and this is very close to the degradation temperature of the starch ( $220^\circ\text{C}$ ).<sup>8</sup> Therefore, the endothermic transition corresponding to the  $T_g$  of the unmodified starch could not be clearly seen in the DSC thermogram. Furthermore, Figure 5 reveals that the transition temperature of the modified starch with 80% propionyl further decreased to  $134^\circ\text{C}$ . It seemed that the higher the degree of acylation was, the lower the  $T_g$  of the starch was. This could be attributed to the presence of bulky propionyl groups, which increased free volume and segmental chain mobility in the amorphous phase of the polymer.

### Effects of propionyl content on the morphology and tensile properties of the starch/pcl blends

The tensile properties of various starch/PCL blends are illustrated in Table IV. Before discussion of the results from Table IV, it is worth mentioning that

molecular weight of the PCL samples before and after extrusion and compression molding were analyzed with gel permeation chromatography to examine whether the tensile properties were affected by the thermal degradation of the PCL. The number-average molecular weight of the PCL did not decrease after processing. The results suggest that differences in the tensile properties of the blends, as shown in Table IV, should be attributed to other factors, including the compatibility between the two polymers.

As shown in Table IV, the tensile stress and modulus of the blends containing modified starch were slightly higher than those of the blend containing the unmodified starch. This was attributed to better compatibility between PCL and the modified starches. More interestingly, the elongation values of the blends containing modified starches with 62 and 80% propionyl were much lower than those of the blend containing the unmodified starch and/or the modified starches with 16 and 28% propionyl. Figures 6–10 show the scanning electron micrographs of various blends. For the blend containing the unmodified starch, a typical dispersed particle morphology showing starch particles in the PCL matrix was observed (Fig. 6). Similar aspects were observed in the micrographs of the blends containing modified starches with 16 and 28% propionyl (Figs. 7 and 8). However, for the blends containing modified starches with 62 and 80% propionyl, no starch particles were observed (Figs. 9 and 10). It seemed that the modified starch was soluble in PCL, and thus, the phase contrast was not

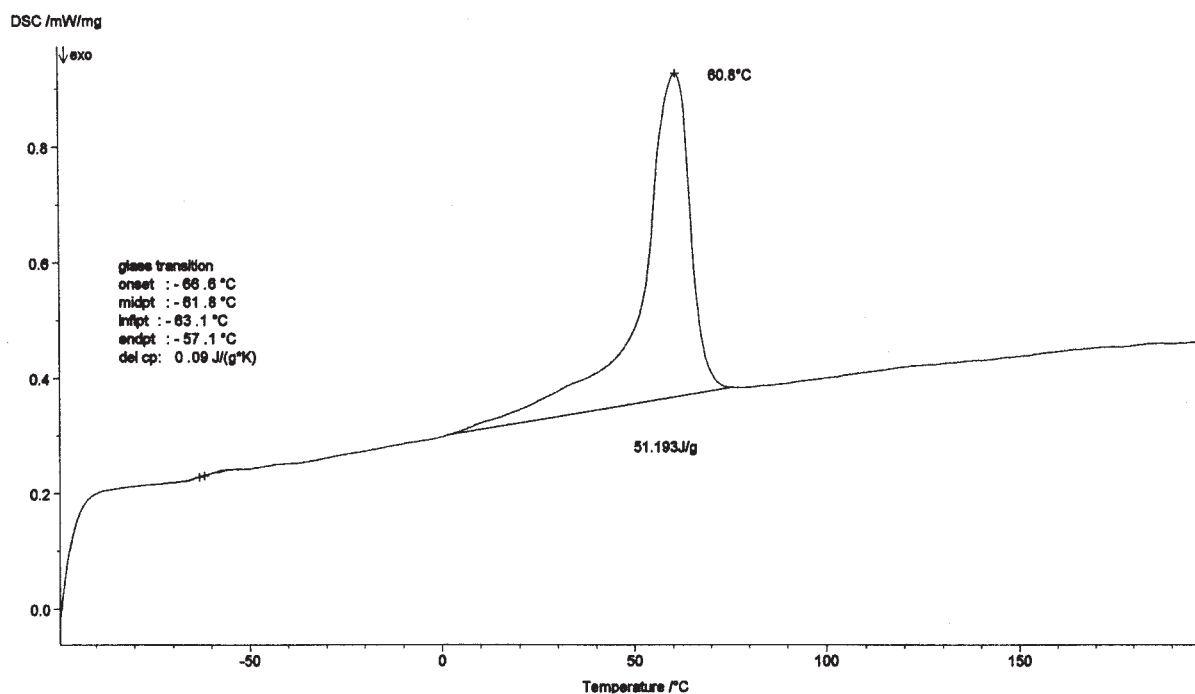


Figure 11 DSC thermogram of a modified starch (62% propionyl)/PCL blend.



TABLE V  
Changes in Weight of Various Starch/PCL Blends as a  
Function of Propionyl Content

Propionyl content (%)	Initial weight (g)	Weight after 3 months (g)	Changes in weight (%)
0	1.619	1.321	18.4
16	1.576	1.495	5.2
28	1.504	1.443	4.1
62	1.413	1.382	2.2
80	1.427	1.392	2.5

visible through the use of a secondary electron detector. However, the lack of phase contrast in the secondary electron image did not mean that the modified starch was miscible with PCL. To confirm the miscibility between the two phases, a backscattering electron detector should be used. Unfortunately, the chemical structures of both polymers were very similar, and thus, the compositional contrast could not be created by any staining agents. Therefore, the SEM images with a backscattering electron detector would not yield any phase contrast. However, consideration of the DSC thermogram of the blend containing modified starch with 62% propionyl (Fig. 11) revealed a  $T_g$  of PCL at  $-62^\circ\text{C}$  along with a melting peak of PCL at  $61^\circ\text{C}$ . A similar result was observed from the DSC thermogram of the blend containing modified starch with 80% propionyl. This result suggests that the PCL phase was separated from the starch phase. In other words, the PCL was immiscible but compatible with the modified starch with a large amount of propionyl. In relation to the elongation values of the blends, it might be possible that the starch particles acted as pseudocrosslinks in the PCL matrix due to a strong interaction between the two phases. This interaction, in turn, restricted some deformation of the PCL matrix phase during the tensile test, which led to a lower elongation value.

Finally, Table V provides some idea about the biodegradability of the blends as a function of DS.

Through the chemical modification of the cassava starch via acylation, the rate of biodegradation of the starch/PCL blends decreased. The blends containing modified starch with a relatively low propionyl content (16 and 28%) seemed to degrade faster than those containing highly modified starches (62 and 80% propionyl). It was apparent that the lower the number of hydroxyl groups in the starch molecules was, the slower the biodegradation of the material was.

## CONCLUSIONS

This study showed that the moisture resistance of modified cassava starch increased with propionyl content at the expense of the biodegradation rate of the material. Also, there was an optimum value of propionyl content corresponding to the maximum tensile properties of the modified starch/PCL blends. In this study, the best composition of the starch/PCL blend (30/70% w/w) with respect to these properties was that of the blend containing modified starch with 28% propionyl.

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