

# Performance of an Acrylic Acid Grafted Polycaprolactone/Starch Composite: Characterization and Mechanical Properties

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**ABSTRACT:** In this article, the properties of a polycaprolactone and starch composite (PCL/starch) and an acrylic acid grafted polycaprolactone and starch composite (PCL-g-AA/starch) were examined by Fourier transform infrared spectroscopy, nuclear magnetic resonance, differential scanning calorimetry, Instron mechanical testing, and scanning electron microscopy. Mechanical properties of PCL became significantly worse when it was blended with starch, due to the poor compatibility between the two phases. Much better dispersion and homogeneity of starch in the polymer matrix was obtained when PCL-g-AA was used in place of PCL in

the composite. Improved mechanical and thermal properties of the PCL-g-AA/starch composite, notably an increase in tensile strength at breakpoint, evidenced its superiority to the PCL/starch one. Furthermore, PCL-g-AA/starch was more easily processed than PCL/starch because the former had lower melt viscosity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2888–2895, 2003

**Key words:** polycaprolactone/starch composite; acrylic acid grafted polycaprolactone/starch composite; mechanical and thermal properties; characterization

## INTRODUCTION

In the past few decades, blending of plastic polymer materials with organic fillers such as starch, with a view to developing new materials with desired properties,<sup>1–8</sup> has received considerable industrial and academic interest. Although starch is an abundant, inexpensive, renewable, and fully biodegradable natural raw material, the hydrophilic character of starch leads to poor adhesion with the hydrophobic polymer in starch/polymer blends. Such blends therefore require a compatibilizer and/or a toughener, a reactive functional group introduced into the synthetic polymer, to enhance the compatibility between the two immiscible phases and hence to improve the mechanical properties of the composite.<sup>9,10</sup> Bikiaris and Panayiotou<sup>11</sup> showed that maleic anhydride (MAH) grafted onto low-density polyethylene (LDPE) increased the compatibility between the polyethylene and starch. This was reflected in the mechanical properties of the composite, especially in the tensile strength. In spite of its relative weakness and a about 60°C melting point that is too low for many applications,<sup>2,12</sup> polycaprolactone (PCL) has recently received much attention due to its flexibility and biodegradability. Additionally, similar to other aliphatic polyesters, such as polylactide (PLA) and polyglycolide (PGA), PCL and its copolymers are the group of biomaterials that have commercially suc-

cessful applications, because their biocompatibility.<sup>13,14</sup> However, PCL is more expensive. Therefore, a blend of PCL with the cheaper material starch, with a reactive functional group grafted onto PCL to improve adhesion and dispersion of the two immiscible phases, would appear to offer the best of both worlds.<sup>15,16</sup> In this article we will systematically investigate the effect of replacing pure PCL with acrylic acid grafted PCL (PCL-g-AA), synthesized in our laboratory, on the structure and properties of PCL/starch composites. The main reason for using starch is that some investigations have shown that higher amounts of starch can be incorporated into LDPE.<sup>10,11</sup> Based on the results of refs. 10 and 11, where the starch contents can be as high as about 20–30 wt %, in this work we will add starch up to an amount of 50 wt % to find an optimal starch content. Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) are used to characterize the composites, while X-ray diffraction (XRD) spectroscopy and differential scanning calorimetry (DSC) are applied to understand the structural change that occurs with the acrylic acid graft. Meanwhile, scanning electron microscopy (SEM) and an Instron mechanical tester are used to examine morphology and mechanical properties of the blends.

## EXPERIMENTAL

### Materials

PCL, with a molar mass of 80,000g/mol, was supplied by Solvay. (Warrington, England). Acrylic acid (AA),

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supplied by Aldrich (Milwaukee, WI), was purified by re-crystallization from chloroform before use. Benzoyl peroxide (BPO), used as an initiator, was purified by dissolution in chloroform and reprecipitation with methanol. Starch, composed of 27% amylose and 73% amylopectine, was obtained from the Sigma Chemical Corporation. The PCL-g-AA copolymer was constructed in our laboratory as described below.

### Sample preparation

#### Graft reaction and sample preparation

A mixture of AA and BPO was added in four equal portions at 2-min intervals to molten PCL to allow grafting to take place. The reactions were carried out under nitrogen at  $85 \pm 2^\circ\text{C}$ . Preliminary experiments showed that reaction equilibrium was attained in less than 6 h, and reactions were therefore allowed to progress for 6 h, at a rotor speed of 60 rpm. The product (4 g) was dissolved in 200 mL of refluxing xylene at  $85^\circ\text{C}$  and the solution was then filtered through several layers of cheesecloth. The xylene-insoluble product remaining on the cheesecloth was washed using acetone to remove the unreacted acrylic acid and was then dried in a vacuum oven at  $80^\circ\text{C}$  for 24 h. The xylene-soluble product in the filtrate was extracted five times, using 600 mL of cold acetone for each extraction. Using a titration method,<sup>17</sup> the percentage grafting was determined as being about 6.05 wt % when BPO loading and AA loading were kept at 0.3 and 10 wt %, respectively.

#### Determination of grafting percentage

The acrylic acid loading of the xylene-soluble polymer was calculated from the acid number and the result was expressed as the grafting percentage.

About 2 g of copolymer was heated for 2 h in 200 mL of refluxing xylene. This solution was then titrated immediately with a 0.03N ethanolic KOH solution, which had been standardized against a solution of potassium hydrogen phthalate, while phenolphthalein was used as an indicator. The acid number and the grafting percentage could then be calculated using the following equations<sup>17</sup>:

Acid number (mg KOH/g)

$$= \frac{V_{\text{KOH}}(\text{mL}) \times C_{\text{KOH}}(N) \times 56.1}{\text{polymer (g)}} \quad (1)$$

Grafting percentage(%)

$$= \frac{\text{Acid number} \times 72}{2 \times 561} \times 100\% \quad (2)$$

### Composite preparation

The composites were prepared using a Brabender "Platograph" 200Nm mixer W50EHT instrument with a blade-type rotor, with rotor speed maintained at 50 rpm and blending temperature at  $100^\circ\text{C}$ , and a reaction time of 15 min. The starch was dried in an oven at  $105^\circ\text{C}$  for 24 h prior to blending. Mass ratios of starch to PCL were fixed at 10/90, 20/80, 30/70, 40/60, and 50/50. After blending, the composites were pressed into thin plates by a hot press at  $140^\circ\text{C}$  and then put into a dryer for cooling. The relative humidity of dryer was set at  $50 \pm 5\%$  and the samples were conditioned for 24 h. We find 24 h conditioning time is enough for dehydrating samples to appropriate water content and longer storage time does not show appreciable effect on the property of composites.

### Characterization of composites

NMR, FTIR, XRD, and DSC analyses of PCL and PCL-g-AA

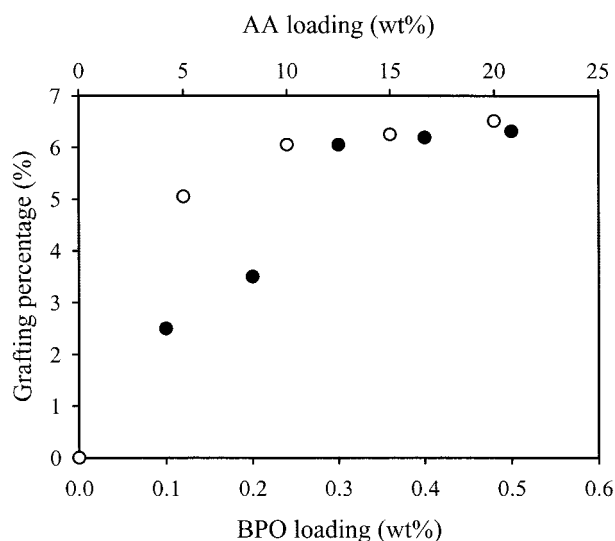
For NMR analysis, using a Bruker AMX400  $^{13}\text{C}$ -NMR spectrometer, the sample was dissolved in  $\text{CDCl}_3$  and sealed in a NMR tube (10 mm). After being degassed, analysis was performed at 100 MHz, using a  $30^\circ$  pulse and a 4 s cycle time. Infrared spectra of samples were obtained using a Bio-Rad FTS-7PC type FTIR spectrophotometer. The XRD intensity curves, recorded using a Rigaku D/max 3V X-ray diffractometer with a Cu target and  $\text{K}\alpha$  radiation at a scanning rate of  $2^\circ/\text{min}$ , enabled changes in the crystal structure to be studied. The melting temperature ( $T_m$ ) and fusion heat ( $\Delta H_f$ ) were determined using a TA instrument 2010 DSC system. For the DSC tests, sample amounts were between 4 and 6 mg, and the melting curves were recorded from  $-30$  to  $+120^\circ\text{C}$ , heated at a rate of  $10^\circ\text{C}/\text{min}$ .

### Mechanical properties

Following the ASTM D638 method, the Instron mechanical tester (Model Lloyd, LR5K type) was used to measure the tensile strength and elongation at break-point. By using thin plates, about 1 mm, of the previous conditioned samples, the measurements were conducted at a 20 mm/min crosshead speed. Five measurements were taken for each sample and the data were averaged to obtain a mean value.

### Composite morphology

A Hitachi Microscopy Model S-1400 scanning electron microscope was used to study the morphology of the composites. Films from the mechanical analysis were treated with hot water at  $80^\circ$  for 24 h, thereafter coated with gold, and observed using SEM.



**Figure 1** Effect of BPO and acrylic acid loading on the grafting percentage of PCL. (Solid symbols: BPO; open symbols: acrylic acid.)

## RESULTS AND DISCUSSION

### Effects of loading on percentage grafting

#### Effect of peroxide loading

Figure 1 shows the effect of BPO loading on percentage grafting of PCL with acrylic acid loading maintained at 10 wt %. It was found that percentage grafting increased steadily with the BPO loading until 0.3 wt %, while at BPO loading above 0.3 wt %, percentage grafting approximated to a maximum value. The above findings are similar to those of Gaylord et al.<sup>17,18</sup>

#### Effect of acrylic acid loading

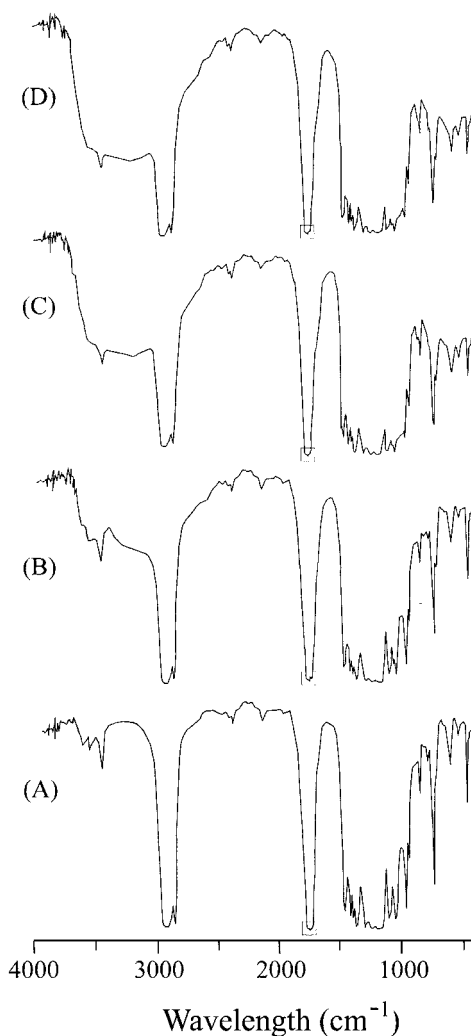
Figure 1 also illustrates the effect of acrylic acid loading on percentage grafting with BPO loading maintained at 0.3 wt %. A noticeable increase in percentage grafting occurred as the loading was increased from 0 to 5 wt %, with only a slight increase thereafter. It is probable, therefore, that 5 wt % represents the approximate point at which AA is replaced as the rate-limiting factor by availability of free radical sites on the PCL backbone.<sup>19</sup>

### Characterization of PCL-g-AA/starch

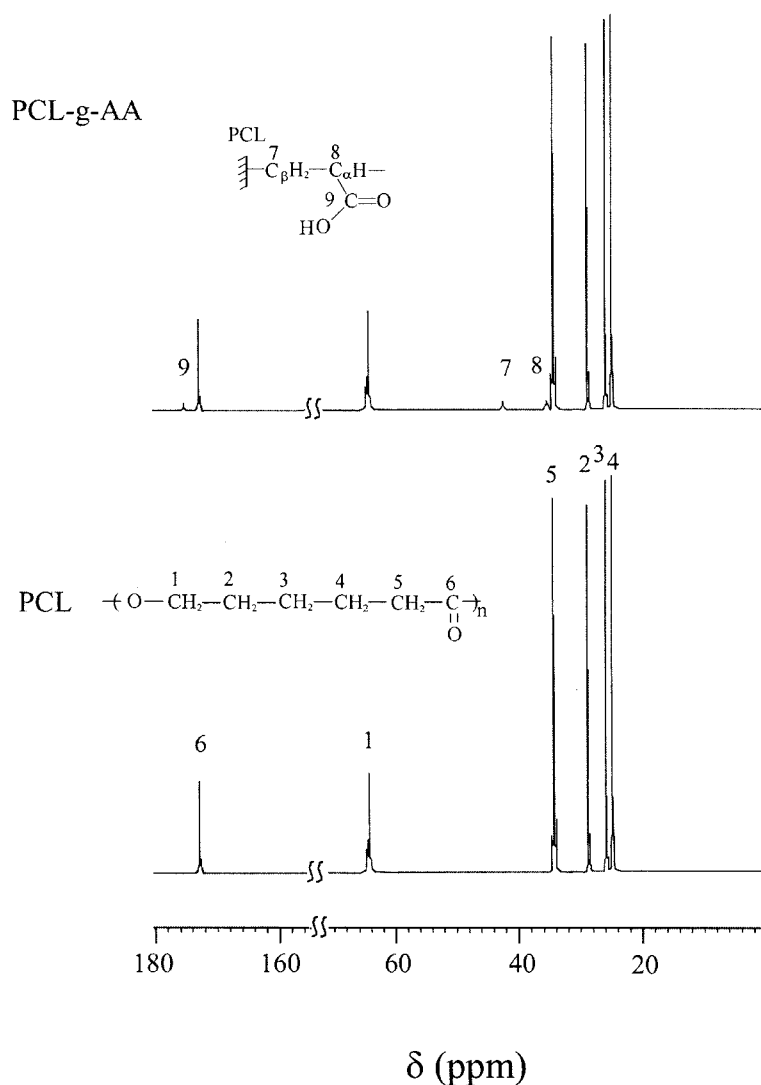
FTIR spectroscopy was used to investigate the grafting of acrylic acid onto PCL. The FTIR spectra of unmodified PCL and PCL-g-AA are shown in Figures 2(A) and 2(B), respectively. While the characteristic peaks of PCL,<sup>4,20</sup> (3300–3700, 1737, 1725, 850–1480, and 720)  $\text{cm}^{-1}$ , all appear in both polymers, an extra peak was observed for the modified PCL at 1710  $\text{cm}^{-1}$  [also seen

in Fig. 4(B)], characteristic of  $\text{—C=O}$ , as well as a broad O—H stretching absorbance at 3200–3700  $\text{cm}^{-1}$ . Similar results have been reported elsewhere.<sup>1,22</sup> This pattern of peaks demonstrates that acrylic acid had been grafted onto PCL because the discernible shoulder near 1710  $\text{m}^{-1}$  is a product of free acid from the modified polymer.

To confirm the grafting of AA,  $^{13}\text{C}$ -NMR was used to compare the structure of PCL and PCL-g-AA. Figures 3(A) and 3(B) contain the  $^{13}\text{C}$ -NMR spectra of PCL and PCL-g-AA, respectively. Carbon peaks occurred in six places for unmodified PCL (1:  $\delta = 64.21$  ppm; 2:  $\delta = 28.88$  ppm; 3:  $\delta = 25.93$  ppm; 4:  $\delta = 25.01$  ppm; 5:  $\delta = 34.26$  ppm; 6:  $\delta = 173.11$  ppm), a result similar to that reported by Kesel et al.,<sup>23</sup> in which a polycaprolactone polyvinylalcohol composite was studied. The  $^{13}\text{C}$ -NMR spectrum of PCL-g-AA shows some extra peaks (7:  $\text{C}_\beta$   $\delta = 35.63$  ppm; 8:  $\text{C}_\alpha$   $\delta = 42.19$  ppm; 9:  $\text{—C=O}$   $\delta = 175.05$  ppm). The extra peaks,  $\text{C}_\alpha$ ,



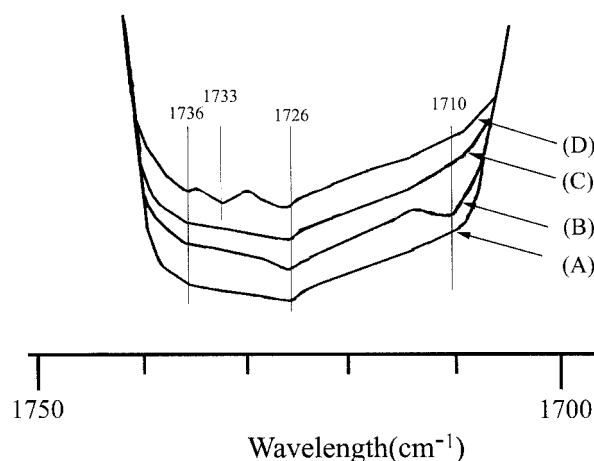
**Figure 2** FTIR spectra of pure PCL and composites. [(A): pure PCL; (B): PCL-g-AA; (C): PCL/starch (20 wt %); and (D): PCL-g-AA /starch (20 wt %).]



**Figure 3**  $^{13}\text{C}$ -NMR spectra of unmodified PCL and PCL-g-AA prepared with 10 wt % AA and 0.3 wt % BPO.

$\text{C}_\beta$ , and  $-\text{C}=\text{O}$ , do indeed confirm that AA had been grafted onto PCL, and the corresponding structure is illustrated in Figure 3(B). The appearance of these three extra peaks is in agreement with the results of Pham et al.<sup>24</sup>

Furthermore, the FTIR spectra of PCL/starch (20 wt %) [Figure 2(C)] shows a much more intense peak, assigned to O—H bond stretching vibration, at  $3200\text{--}3700\text{ cm}^{-1}$ , compared with those of PCL and PCL-g-AA. This is because the —OH group of starch adds to the bond stretching vibration.<sup>11,22,24</sup> In addition, a comparison between the FTIR spectra of PCL/starch (20 wt %) and that of PCL-g-AA/starch (20 wt %) [Fig. 2(D)] reveals a new absorption peak at  $1733\text{ cm}^{-1}$  in the latter, which is assigned to the ester carbonyl stretching vibration in the copolymer. Expansion of the FTIR spectra in the limited range of  $1700\text{--}1750\text{ cm}^{-1}$  (Fig. 4) more clearly illustrates the difference between the spectra of PCL/starch and PCL-g-AA/starch. Figure 4(A) shows the  $-\text{C}=\text{O}$  stretching vibration as a

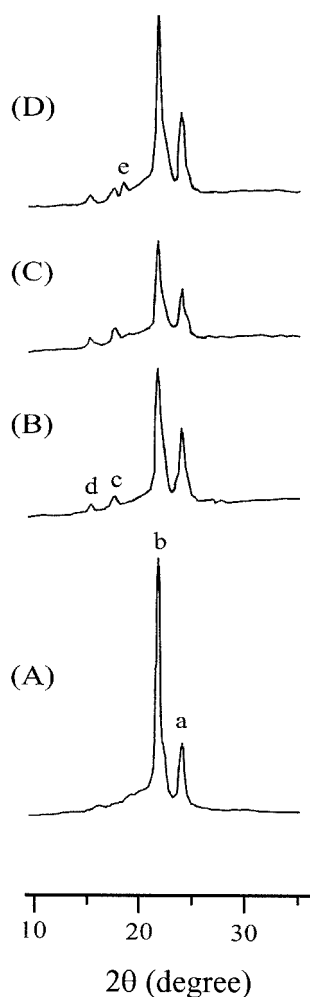


**Figure 4** FTIR spectra in the vicinity of the peaks C—O and C=O bending deformation for pure PCL and composites with different starch content. [(A): pure PCL; (B): PCL-g-AA; (C): PCL/starch (20 wt %); and (D): PCL-g-AA/starch (20 wt %).]

strong broad band at  $1725\text{--}1736\text{ cm}^{-1}$  in the PCL/starch spectrum, a similar result to that of Wang et al.<sup>20</sup> Comparing this with the PCL-g-AA spectrum [Fig. 4(B)], an extra peak is seen at  $1710\text{ cm}^{-1}$ , caused by the grafting of AA onto PCL. The PCL/starch spectrum in Figure 4(C), like that in 4(A), shows a broad absorption band at  $1725\text{--}1736\text{ cm}^{-1}$ , while the spectra of PCL-g-AA/starch [Fig. 4(D)] exhibits a fourth peak newly formed at  $1733\text{ cm}^{-1}$ . The work of Bikiaris et al.,<sup>25</sup> in which an LDPE/starch composite was studied, indicated an absorbency at a near identical  $1735\text{ cm}^{-1}$ . The appearance of this new absorption peak may be due to the formation of an ester carbonyl functional group via the reaction between  $\text{—OH}$  of starch and  $\beta\text{od}\delta\delta\text{;COOH}$  of PCL-g-AA.

### X-ray diffraction

The XRD spectra of pure PCL, PCL/starch (20 wt %) composite, PCL/starch (40 wt %) composite, and PCL-



**Figure 5** X-ray diffraction spectra of pure PCL and composites. [(A): pure PCL; (B): PCL/starch (20 wt %); (C): PCL/starch (40 wt %); and (D): PCL-g-AA/starch (20 wt %).]

**TABLE I**  
Effect of Starch Content on the Thermal Properties of PCL and PCL-g-AA Composites

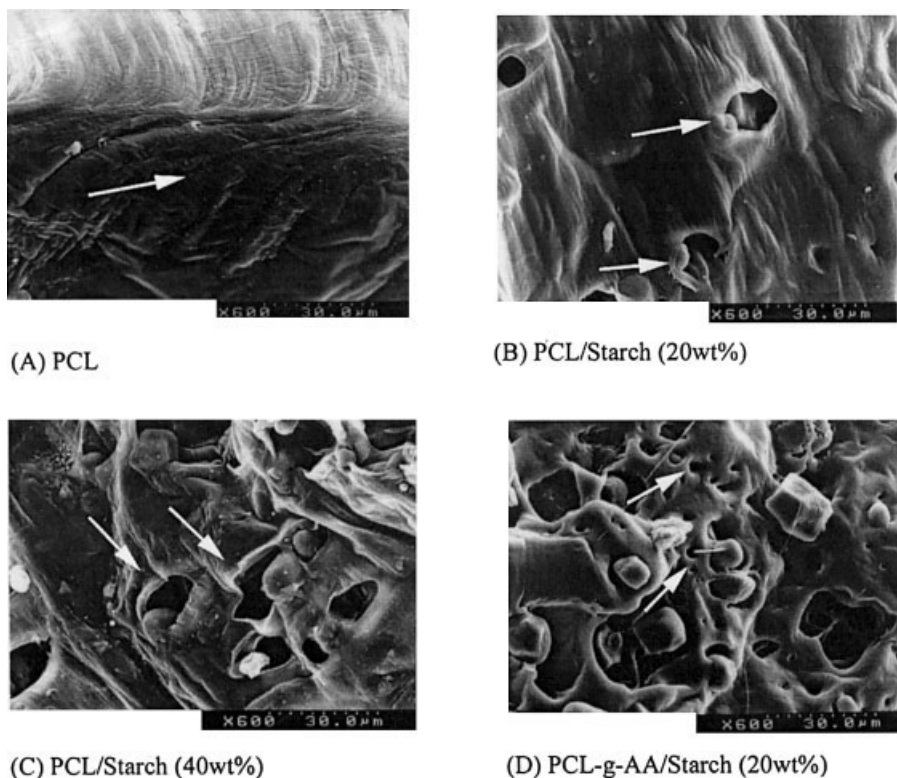
Starch (wt %)	PCL		PCL-g-AA	
	$T_m$ (°C)	$\Delta H$ (J/g)	$T_m$ (°C)	$\Delta H$ (J/g)
0	62.5	72.5	61.3	50.6
10	61.6	48.6	60.9	53.7
20	60.8	38.2	59.5	47.5
30	60.5	33.8	58.8	39.9
40	60.1	29.6	57.9	36.2

g-AA/starch (20 wt %) composite are shown in Figures 5(A–D), respectively. Showing similarity to the results of Ha et al.,<sup>26</sup> pure PCL produced two peaks at about  $23.8^\circ$  and  $21.3^\circ$  ( $2\theta$ , designated as “a” and “b”). For the two PCL/starch composites, it was found that there were two other peaks at about  $17.3^\circ$  and  $15.1^\circ$  ( $2\theta$ , designated as “c” and “d”). The peaks at c and d may be due to the change in coordinate property of PCL molecules when starch was blended with it.<sup>27</sup> Further, we found that the higher starch content (40 wt %) gave a more intensive peak at  $17.3^\circ$ . This is in agreement with the results of Arvanitoyannis et al.,<sup>27</sup> and the peaks at  $15.1^\circ$  and  $17.3^\circ$  are assigned to amylose and amylopectine of starch, respectively. The spectra of the PCL/starch composites therefore show that starch was dispersed physically in the PCL matrix.

Figure 5(D) shows a new peak at  $18.1^\circ$  ( $2\theta$ , designated as “e”) for the PCL-g-AA/starch (20 wt %) composite. This new peak, also identified by Shogren et al.,<sup>28</sup> may be caused by the formation of an ester carbonyl group, as described in the FTIR spectroscopy analysis, and provides evidence that the crystalline structure of the PCL/starch composite is altered when PCL-g-AA is used in it.

### DSC analysis

Thermal properties of pure PCL, PCL/starch, and PCL-g-AA/starch, obtained via DSC, are given in Table I. The melting temperature ( $T_m$ ) and fusion heat ( $\Delta H_f$ ) of pure PCL were  $62.5^\circ\text{C}$  and  $72.3\text{ J/g}$ , respectively. The values of both these parameters, increases that indicate increased crystal formation, decreased as the starch content increased. The decrease in crystallization was probably caused by the increased difficulty in arranging the polymer chain, due to starch prohibiting movement of the polymer segments. Another potential cause is the hydrophilic character of starch, which would lead to poor adhesion with the hydrophobic PCL. Similar phenomena were reported by Averous et al.,<sup>29</sup> who studied the properties of thermoplastic starch and its blends with polycaprolactone. Table I also shows that  $T_m$  and  $\Delta H_f$  decreased with increased starch content for both PCL/starch and



**Figure 6** SEM micrographs of pure PCL and composites. [(A): pure PCL; (B): PCL /starch (20 wt %); (C): PCL/starch (40 wt %); and (D): PCL-g-AA/starch (20 wt %).]

PCL-g-AA/starch. The decrease in  $T_m$  is due to the lower melt viscosity of starch compared to that of PCL.<sup>30</sup> We also found that when PCL was replaced with PCL-g-AA in the composite,  $T_m$  decreased (by about 1–4°C) and  $\Delta H_f$  increased (by about 5–10 J/g). Moreover, because the PCL-g-AA/starch had lower melt viscosity than the PCL/starch, it could be processed more easily.

### Composite morphology

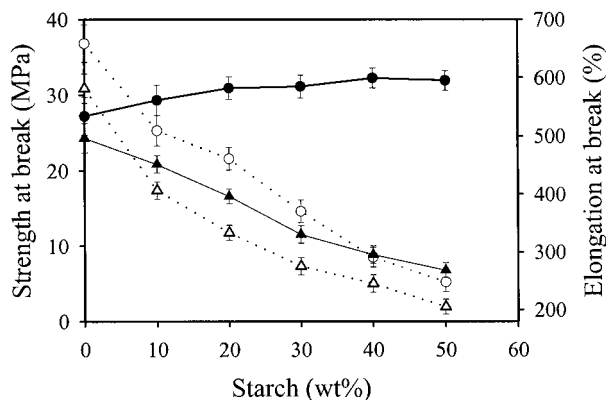
Because mechanical properties of the composites were affected by their morphology, the morphology of the polymer was investigated via SEM. In the PCL/starch composites, the major component (PCL) forms the matrix and the minor component (starch) forms the dispersed phase. SEM micrographs of pure PCL, PCL/starch (20 wt %) composite, PCL/starch (40 wt %) composite, and PCL-g-AA/starch (20 wt %) composite are presented in Figure 6, while the starch phase size (the average pore diameter) of composites is tabulated in Table II. It was found that the average pore diameter of the PCL/starch composite containing 20 wt % starch [Fig. 6(B)] was about 12  $\mu\text{m}$ , smaller than the average 18  $\mu\text{m}$  of the PCL/starch composite containing 40 wt % starch [Fig. 6(C)]. In addition, by examining the morphology of the PCL/starch composites, it was seen that the size of the starch phase

increased with starch content (Table II). However, when the starch loading was less than 10 wt %, there was a fine dispersion and homogeneity of starch in the PCL/starch matrix. The large starch phase size, especially that formed in the composite containing 40 wt % starch, suggests that the adhesion between starch and PCL is very poor and that the two polymers are strongly incompatible.<sup>11</sup>

When the AA graft was added to PCL as compatibilizer, the size of the starch phase was much decreased compared with the ungrafted equivalent [Fig. 6(D) and Table II]. Table II also shows that there is a fine dispersion and homogeneity of starch in the PCL matrix for all PCL-g-AA/starch composites shown, as the phase size is never greater than 4  $\mu\text{m}$ , and is detectable only in higher magnification. This better dispersion arises from the formation of branched and

**TABLE II**  
The Starch Phase Size of PCL-g-AA and PCL Composites at Different Starch Content

Starch (wt%)	Phase size ( $\mu\text{m}$ )	
	PCL	PCL-g-AA
10	6.5 $\pm$ 2	2.0 $\pm$ 0.2
20	12.0 $\pm$ 3	2.5 $\pm$ 0.3
30	15.5 $\pm$ 3	3.5 $\pm$ 0.3
40	18.0 $\pm$ 5	4.0 $\pm$ 0.3



**Figure 7** Tensile strength and elongation at breakpoint vs starch content for PCL-g-AA and PCL composites. (The solid and dotted lines indicate PCL-g-AA and PCL, respectively.)

crosslinked macromolecules, since this PCL-g-AA copolymer has anhydride groups to react with the hydroxyl groups of starch. Because the different parts of the branched and crosslinked macromolecules are all compatible with the polymer phases, this gives them the ability to place themselves in the interface of PCL/starch during melt blending. The result is a reduction in the interfacial tension between the two polymers and a finer distribution of starch in all the grafted composites. Such a scenario was also proposed by Bikiaris,<sup>11</sup> who found that a compatibilized LDPE (LDPE-g-MAH)/starch composite produced smaller pore sizes under tensile disruption.

### Mechanical properties

Figure 7 shows the effect of starch content on tensile strength and elongation at breakpoint for PCL/starch and PCL-g-AA/starch composites. For PCL composites, the tensile strength at breakpoint decreased continuously as starch content increased. The composite containing 50 wt % starch gave the lowest tensile strength at breakpoint because the higher starch content increased the phase size. It is thus clear that mechanical incompatibility of the two polymers is great. For PCL-g-AA composites, though a decrease in tensile strength at breakpoint compared to the equivalent pure PCL was observed, this decrease was smaller than that of the equivalent uncompatibilized composites. The absolute value of tensile strength at breakpoint for all compatibilized composites was, indeed, evidently higher than that of their uncompatibilized counterparts. It was also found that the PCL-g-AA composites provided more stable values of tensile strength when the starch content was above 10 wt %.

Figure 7 also shows that the PCL-g-AA composites exhibited a higher elongation at breakpoint compared

with the uncompatibilized composites, and the difference increased with increasing starch content. However, elongation at breakpoint of the PCL composites, compared with the equivalent pure PCL, decreased with increasing starch content. Findings of Bikiaris and Panayiotou<sup>11</sup> regarding mechanical properties are similar to those discussed here. It is evident that the mechanical properties strongly depend on the dispersion and phase size of starch in the PCL matrix. With a smaller dispersed phase, an increase in mechanical properties, especially in tensile strength, was observed.

### CONCLUSIONS

By using PCL-g-AA in place of PCL, the compatibility and mechanical properties of a PCL/starch-type composite can be improved. The crystalline structure of PCL-g-AA/starch differs from that of PCL/starch, due to the formation of an ester carbonyl functional group from the reaction between the —OH of starch and the —COOH of PCL-g-AA. For PCL/starch, the melting temperature ( $T_m$ ) and fusion heat ( $\Delta H_f$ ) both decrease with increasing starch content. When PCL is replaced with PCL-g-AA,  $T_m$  is decreased and  $\Delta H_f$  is increased, though the difference between these two composites is somewhat insignificant. Morphology of PCL/starch composites indicates that the starch phase size increases with increasing starch content, suggesting that the compatibility between PCL and starch is very poor. For PCL-g-AA/starch composites, the size of the starch phase is noticeably reduced and, being always less than 4.5  $\mu\text{m}$ , is detectable only under higher magnification. Tensile strength and elongation at breakpoint of PCL/starch composites decreases noticeably and continuously as starch content is increased. The composite containing PCL-g-AA exhibits enhanced mechanical properties compared with that containing PCL, especially regarding tensile strength at breakpoint. Finally, we can conclude that the PCL-g-AA copolymer effectively compatibilizes PCL and starch in the composite since only a small amount of it is required to improve the properties of the composite.

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