

Analysis of Mechanical, Thermal, and Morphological Behavior of Polycaprolactone/Wood Flour Blends

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ABSTRACT: In the present study, the properties of polycaprolactone (PCL) and wood flour (WF) blends were examined by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), Instron mechanical tester, and scanning electron microscopy (SEM). As for results, the mechanical properties of PCL were lowered obviously, due to the poor compatibility between the two phases, when it was blended with wood flours. A fine dispersion and homogeneity of wood flour in the polymer matrix could be obtained when the acrylic acid grafted PCL (PCL-g-AA) was used to replace PCL for manufacture of blends. This better dispersion is due to the formation of branched and

crosslinked macromolecules since the PCL-g-AA copolymer had carboxyl groups to react with the hydroxyls. This is reflected in the mechanical and thermal properties of the blends. In comparison with pure PCL/WF blend, the increase in tensile strength at break was remarkable for PCL-g-AA/WF blend. The PCL-g-AA/WF blends are more easily processed than the PCL/WF ones since the former had lower melt viscosity than the latter. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1000–1006, 2004

Key words: blends; FTIR; graft copolymers; mechanical properties

INTRODUCTION

In the past decades, blending of plastic materials with organic fillers, such as wood flour (WF), has received considerable industrial and academic interest in developing new materials with desired combinations of properties.^{1–8} This is due to the advantage that WF is an abundant, inexpensive, renewable, and fully biodegradable natural raw material. However, WF and hydrophobic polymers blends have poor mechanical properties because the hydrophilic character of WF leads to poor adhesion with the synthetic polymer. It requires a compatibilizer and/or a toughener, which can be produced by introducing a reactive functional group into the synthetic polymer, to enhance the compatibility between two immiscible polymers and to improve the mechanical properties of the blends.^{9–10} Previous work on the polyethylene and wood flour (PE/WF) composites showed that the styrene-butadiene-styrene block copolymer, which is located at the interfacial region between WF surfaces and the PE matrix, can be used as a compatibilizer to give a positive effect on the composite's properties.¹¹ In a polypropylene and cellulose fiber (PP/CF) composite system, a maleated polypropylene was chosen as a compatibilizer to increase the compatibility between

the CF and the PP matrix.¹² In spite of its relative weakness and an about 60°C melting point that is too low for many applications,¹³ polycaprolactone (PCL) has recently received much attention due to its flexibility and biodegradability. Additionally, similar to other aliphatic polyesters, such as polylactide (PLA), polyglycolide (PGA), PCL, and their copolymers are the group of biomaterials that have commercially successful applications, because of their biocompatibility.^{14,15} PCL is, however, more expensive. Hence, 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.^{16,17}

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/WF composites. The main reason for using WF in the present work is that some papers showed higher amounts of WF can be incorporated with LDPE.^{18,19} Fourier transform infrared (FTIR) spectroscopy is used to characterize the composites, while 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.

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EXPERIMENTAL

Materials

PCL, with a molar mass of 80,000 g/mol, was supplied by Solvay (Warrington, United Kingdom). Acrylic acid (AA), a commercial product of Aldrich (Milwaukee, WI), was purified by re-crystallization from chloroform before use. The initiator used in this study was benzoyl peroxide (BPO) that was purified by dissolving it in chloroform and reprecipitating with methanol. The wood flours, supplied by Zell Wildshausen GMBH (Steinheim, Germany), were Celluflex. The grain size distribution of WF is 100% finer than 250 μm , 87% finer than 100 μm , and 37% finer than 50 μm . The moisture content and apparent density of the wood flours are $8 \pm 2\%$ and $\sim 0.10\text{--}0.12 \text{ g/cm}^3$, respectively. The PCL-g-AA copolymer was constructed in our laboratory as described below.

Sample preparation

PCL-g-AA copolymer

The grafting of AA onto molten PCL was performed by using xylene as an interface agent and BPO as an initiator under a nitrogen atmosphere at $85 \pm 2^\circ\text{C}$. The reaction lasted for 6 h with a rotor speed of 60 rpm. The grafting product (4g) was dissolved in 200 mL refluxing xylene at 85°C and then the solution was extracted five times by using 600 mL cold acetone for each extraction operation. The acetone insoluble polymer, which was dried at 80°C overnight, was used to measure the grafting percentage by a titration method.²⁰ The result showed that the grafting percentage of graft reaction product was about 6.05 wt % when BPO loading and AA loading were kept at 0.3 wt % and 10 wt %, respectively.

Blend preparation

Blends were prepared by a BRABENDER "PLATOGRAPH" 200Nm MIXER W50EHT instrument (Duisburg, Germany) with blade type rotor for 15 min under the conditions that rotor speed and blending temperature were kept at 50 rpm and $\sim 100\text{--}110^\circ\text{C}$, respectively. The WF was cleaned with acetone and then dried in an oven at 105°C for 24 h prior to blending. The mass ratios of WF to PCL or to PCL-g-AA were chosen as 10/90, 20/80, 30/70, 40/60, and 50/50. To eliminate the effect of unreacted AA on PCL-g-AA/WF blends, it was removed from the grafting product by acetone extraction before preparation of PCL-g-AA/WF ones. After blending, the blends were pressed into thin plates by a hot presser and then they were put into a dryer for cooling. Next, the thin plates were made into standard specimens for characterizations.

Characterizations of blends

FTIR/XRD/DSC analyses of pcl and pcl-g-aa

Infrared spectra of samples were obtained using a Bio-Rad FTS-7PC type FTIR spectrophotometer (Madison, WI). The X-ray diffraction intensity curves, recorded using a Rigaku D/max 3V X-ray diffractometer (Tokyo, Japan) with a Co target and $K\alpha$ 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 (ΔH_f) were determined using a TA instrument 2010 DSC system. For the DSC tests (New Castle, DE), sample amounts were between 4 to 6 mg, and the melting curves were recorded from -30°C to $+120^\circ\text{C}$, heated at a rate of $10^\circ\text{C}/\text{min}$.

Mechanical testing

According to the ASTM D638 method, the Instron mechanical tester (Model LLOYD, LR5K type) was used to measure the tensile strength and the elongation at break. The testing films, which were conditioned at $50 \pm 5\%$ relative humidity for 24 h prior to the measurements, were prepared in a hydrolytic press at 140°C and then the measurements were done using a 20 mm/min crosshead speed. Five measurements were conducted for each sample and the results were averaged to obtain a mean value.

Blend morphology

A scanning electron microscope (HITACHI microscopy Model S-1400; Fareham hants, United Kingdom) was used to study the morphology of blends. Before test, blend was prepared in a thin film by a hydrolytic press and then the film was treated with hot water in 80°C for 24 h. Afterwards, the films were coated with gold and observed by SEM (Tokyo, Japan).

RESULTS AND DISCUSSION

Infrared spectroscopy

FTIR spectroscopy was used to investigate the grafting of AA onto PCL. The FTIR spectra of unmodified PCL and PCL-g-AA are shown in Figures 1(A) and (B), respectively. While the characteristic peaks of PCL ($\sim 3300\text{--}3700$, 1737, 1725, $\sim 850\text{--}1480$, and 720 cm^{-1})^{21,22} all appear in both polymers, an extra peak was observed for the modified PCL at 1710 cm^{-1} (also seen in Fig. 1(B)), characteristic of $\text{C}=\text{O}$, as well as a broad O-H stretching absorbance at $\sim 3200\text{--}3700 \text{ cm}^{-1}$. Similar results have been reported elsewhere.^{23,24} This pattern of peaks demonstrates that AA had been grafted onto PCL because the discernible shoulder near 1710 cm^{-1} is a product of free acid from the modified polymer.

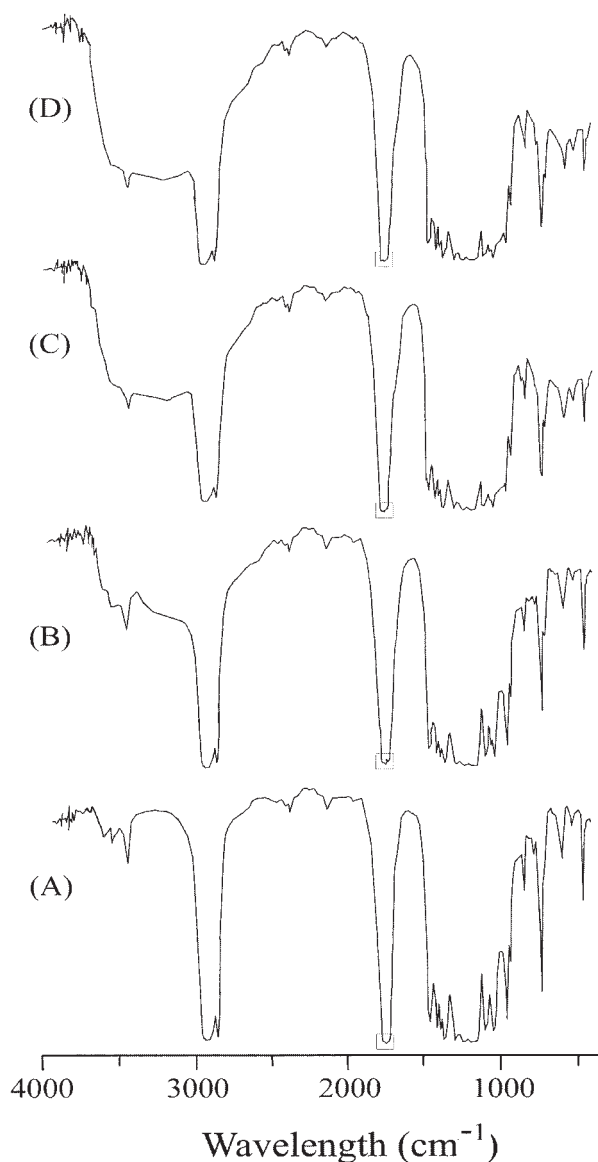


Figure 1 FTIR spectra of (A) PCL, (B) PCL-g-AA, (C) PCL/WF (30 wt %), and (D) PCL-g-AA/WF (30 wt %)

Expansion of the FTIR spectra in the limited range of $\sim 1700\text{--}1750\text{ cm}^{-1}$ (Fig. 2) more clearly illustrates the difference between the spectra of PCL/WF and PCL-g-AA/WF (30 wt %). Figure 2(A) shows the $\text{C}=\text{O}$ stretching vibration as a strong broad band at $1725\text{--}1736\text{ cm}^{-1}$ in the PCL spectrum, a similar result to that of Wang et al.²² Comparing this with the PCL-g-AA spectrum (Fig. 2(B)), an extra peak is seen at 1710 cm^{-1} , caused by the grafting of AA onto PCL. The PCL/WF (30 wt %) spectrum in Figure 2(C), like that in 2(A), shows a broad absorption band at $1725\text{--}1736\text{ cm}^{-1}$; the new absorption peak at about 1735 cm^{-1} , which appeared in the FTIR spectrum of PCL/WF blend, is assigned to the characteristic peak of WF.^{11,12} The spectra of PCL-g-AA/WF (30 wt %) (Fig. 2(D)) exhibits a fourth peak newly formed at 1746

cm^{-1} . Comparison between the FTIR spectra of pure PCL and PCL/WF (30 wt %), and PCL-g-AA/WF (30 wt %) blends, Figures 2(C) and 2(D), it is seen that the peak at 1735 cm^{-1} shifted to 1746 cm^{-1} nearly disappeared when the PCL-g-AA was used to replace PCL. This phenomenon may probably be due to the formation of ester carbonyl functional group from reaction between -OH group of WF and -COOH group of PCL-g-AA. This result is similar to that of Oksman et al.,¹¹ in which LDPE/WF blends were studied and the FTIR spectrum of ester carbonyl showed its functional group appeared at 1746 cm^{-1} . As the result of Figure 2(D), one can infer that branched and crosslinked macromolecules may be produced because PCL-g-AA copolymer has carboxyl groups to react with the hydroxyls.

X-ray diffraction

The XRD spectra of pure PCL, PCL/WF (30 wt %) composite, and PCL-g-AA/WF (30 wt %) composite are shown in Figures 3(A–C), respectively. Showing similarity to the results of Ha et al.,²⁵ pure PCL produced two peaks at about 23.8° and 21.3° (2θ , designated as "1" and "2"). For the two PCL/starch composites, it was found that there were two other peaks at about 15.1° (2θ , designated as "3"). The peaks at 3 may be due to the change in coordinate property of PCL molecules when WF was blended with it.^{5,26} The spectra of the PCL/WF (30 wt %) composites, therefore, show that starch was dispersed physically in the PCL matrix.

Figure 3(C) shows a new peak at 18.1° (2θ , designated as "4") for the PCL-g-AA/WF (30 wt %) com-

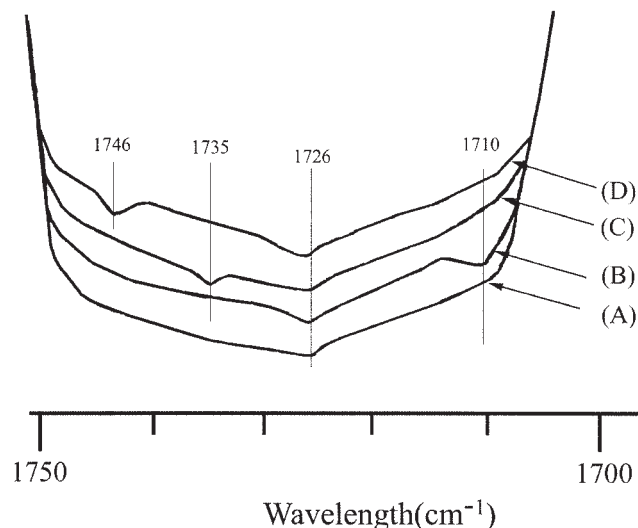


Figure 2 FTIR spectra in the vicinity of the peaks C-O and C = O bending deformation for pure PCL and composites with different starch content: (A) pure PCL, (B) PCL-g-AA, (C) PCL/WF (30 wt %), and (D) PCL-g-AA/starch (30 wt %).

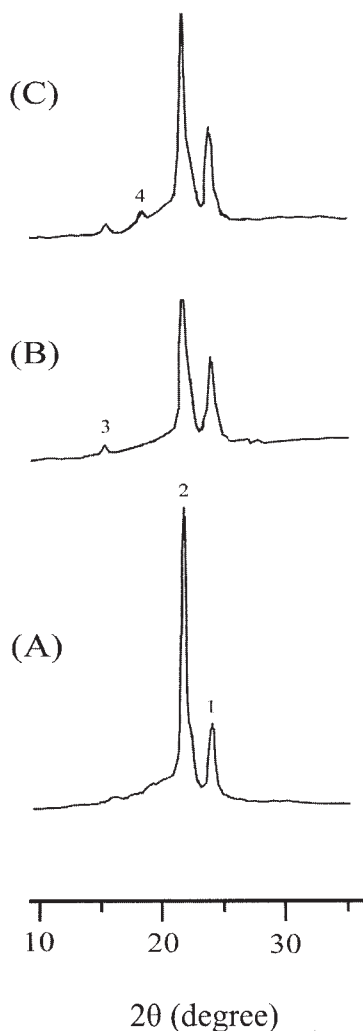


Figure 3 X-ray diffraction spectra of pure PCL and composites: (A) pure PCL, (B) PCL/WF (30 wt %), and (C) PCL-g-AA/WF (30 wt %).

posite. This new peak, also identified by Shogren et al.,²⁷ 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/WF composite is altered when PCL-g-AA is used in it.

Torque measurements

The curves of torque versus mixing time for PCL/WF and PCL-g-AA/WF blends with different amounts of WF are presented in Figure 4. It was observed that the torque value of each blend decreased with increasing WF content and mixing time, and it approached a stable value when the mixing time is greater than 10 min. One can suggest that good mixing has occurred with mixing time of 15 min. The reason that final torque decreased with increasing WF content is due to the lower viscosity of the WF melt as compared to PCL

and to PCL-g-AA. This caused a decrease in the melt viscosity of the blend as the WF concentration was increased. Comparing the torque responses of PCL-g-AA/WF and PCL/WF blends having the same WF content (30 wt % and 50 wt %), we can observe that the melt torque values of the former are significantly lower than those of the latter. This improved rheological behavior is due to the formation of ester carbonyl functional group (as discussed in FTIR), as this functional group leads to conformation changes in the WF molecule.²⁸ In a previous study,²⁹ it has been shown that the melt viscosity of esterified starches decreased with increasing molecular weight of the ester group.

DSC test

DSC was used to study the thermal properties of blends. The variations of fusion heat (ΔH_f) and melt temperature (T_m) with WF contents for PCL/WF and PCL-g-AA/WF blends were determined from the DSC heating thermograms (not shown here), and the results are given in Figure 5 and Table I. In Figure 5, it can be seen that a decrease in melt temperature was observed with increasing WF content for both the PCL/WF and PCL-g-AA/WF blends. This result is due to the fact, as discussed in torque study, that WF could lower the melt viscosity of PCL and PCL-g-AA copolymers. This decrease is almost linear for starch contents up to 30 wt %. With the same starch content, it can be seen from Figure 5 that the PCL/WF blends show a higher melt temperature compared to the PCL-g-AA/WF blends. This observation was in accordance with the corresponding torque measurements, which showed that PCL-g-AA/WF blends have a lower melt

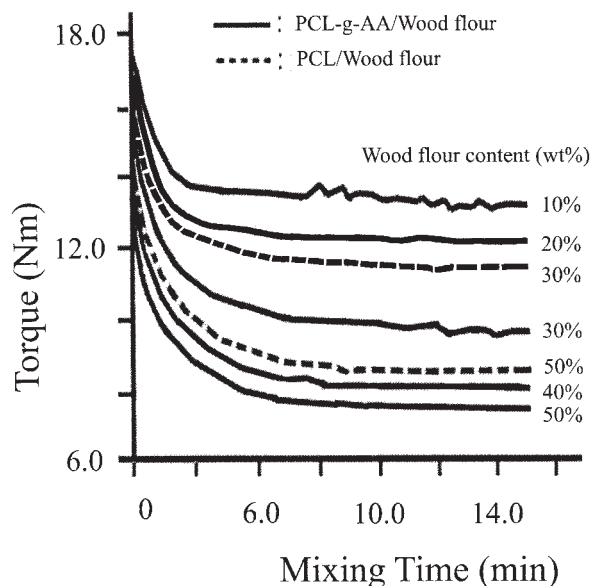


Figure 4 Torque diagrams versus mixing for PCL/WF and PCL-g-AA/WF blends.

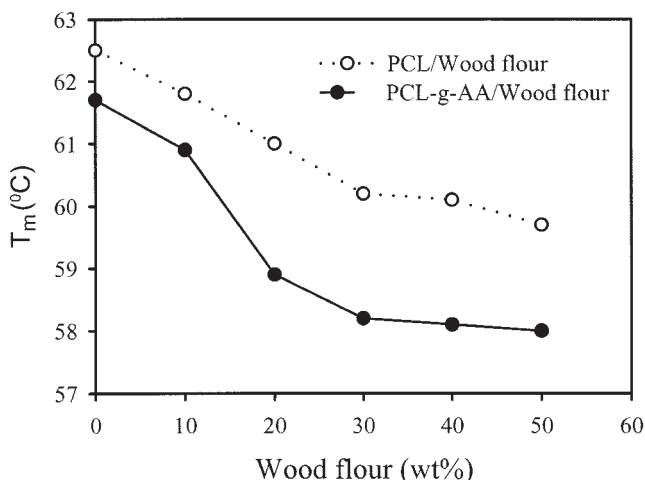


Figure 5 Melt temperature versus WF content for PCL/WF and PCL-g-AA/WF blends.

torque than PCL/WF blends for the same WF content (Fig. 4). These two observations (lower values of melt temperature and torque) for PCL-g-AA/WF blends agreed with the fact that they also present a lower melt viscosity compared to PCL/WF blends. The low melt viscosity of PCL-g-AA/WF blends means that they are more easily processed than the PCL/WF blends.

Table I shows that the values of fusion heat (ΔH_f) of pure PCL and PCL-g-AA are 72.5 J/g and 52.1 J/g, respectively. The lower fusion heat for PCL-g-AA, compared to pure PCL, was probably due to the grafted branches that disrupted the regularity of the chain structures in PCL and increased the spacing between the chains.²⁸ It can be seen from the dotted line of Table I that the corresponding ΔH_f values of PCL/WF blends having starch contents of 10 wt %, 20 wt %, 30 wt %, 40 wt %, and 50 wt % are 46.8 J/g, 36.2 J/g, 31.3 J/g, 27.8 J/g, and 23.2 J/g. For the PCL-g-AAH/WF blends with 10 wt %, 20 wt %, 30 wt %, 40 wt %, and 50 wt % WF, the corresponding values of ΔH_f are 51.9 J/g, 45.5 J/g, 39.8 J/g, 33.2 J/g, and 29.5 J/g (Table I). It is clear that the ΔH_f values of PCL/WF and PCL-g-AA/WF, which indicate percent crystallinity of blends, both decreased as the extent of WF was increased. These phenomena are similar to the result of Aburto et al.,²⁸ who studied the properties of octanoated starch and its blends with polyethylene. The marked decrease in crystallinity for PCL/WF blends was probably caused by the increase in difficulty of polymer chain arrangements as the WF prohibited the movements of the polymer segments and was also due to the steric effect because the hydrophilic character of WF leads to poor adhesion with the hydrophobic PCL.^{28,30} Comparison between the results of PCL/WF and PCL-g-AA/WF found that the latter gave higher ΔH_f values than the former and the increment was about ~5–9 J/g. The increase of ΔH_f is due to the

generation of ester carbonyl functional group from the reaction between -OH group of WF and -COOH group of PCL-g-AA.

Blend morphology

It is necessary to study the morphology of the polymer blends since the mechanical properties depend on it. In general, the good dispersion of WF in the matrix, effective wetting of WF by matrix, and the strong interfacial adhesion between two phases are required to obtain a composite material with satisfactory mechanical properties. SEM was used to study the tensile fracture surfaces of composite samples based on PCL/WF (30 wt %) and PCL-g-AA/WF (30 wt %) blends, and the SEM microphotographs of the fracture surfaces are shown in Figure 6. For the blends studied in this article, the major component (PCL or PCL-g-AA) forms the matrix whereas the minor component (WF) is the dispersed phase. The SEM microphotograph of PCL/WF (30 wt %) blend, Figure 6(A), shows that it tends to agglomerate into bundles and becomes unevenly distributed throughout the matrix. The bad dispersion of WF in the PCL matrix is due to the formation hydrogen bonds and the wide difference in character between PCL and wood flours. The markers in Figure 6(A) also show the poor wetting of WF when PCL/WF was used. The reason for this is the large difference in surface energy between WF and PCL matrix.¹² For the PCL-g-AA/WF (30 wt %) blend, as shown in Figure 6(B), there is a better dispersion and homogeneity of WF in the PCL-g-AA matrix. It can also be seen from Figure 6(B) that better wetting is obtained since layers of the matrix material have been pulled out together with the WF covering the entire WF. The reason for this result is that the properties of WF surfaces and PCL-g-AA matrix become more similar because the PCL-g-AA/WF blend can produce branched and crosslinked macromolecules and prevent hydrogen bonds from being formed.

Mechanical properties

Figure 7 shows the variations of tensile strength and elongation at break with WF content for PCL/WF and

TABLE I
Effect of Wood Flour Content on the Fusion Heat of PCL and PCL-g-AA Composites

Wood flour (wt %)	PCL	PCL-g-AA
	ΔH (J/g)	
0	72.5	52.6
10	46.8	51.9
20	36.2	45.5
30	31.3	39.8
40	27.8	33.2
50	23.2	29.5

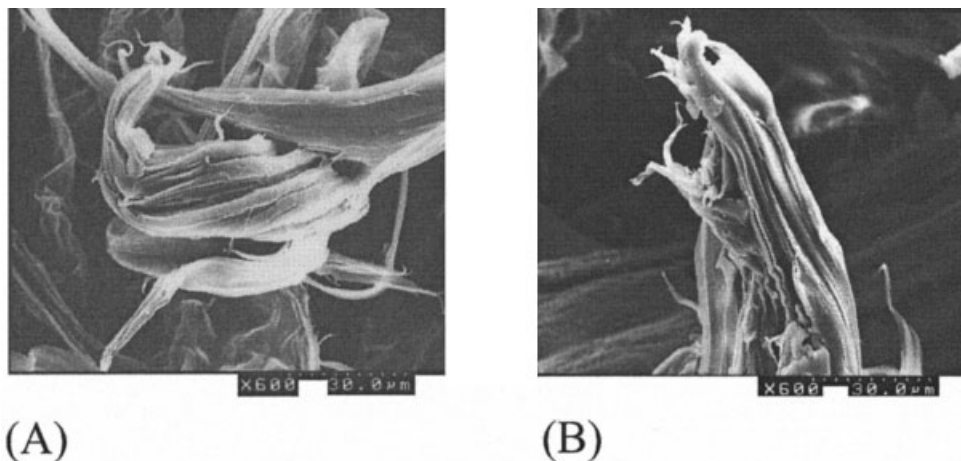


Figure 6 SEM micrographs of PCL/WF (30 wt %) and PCL-g-AA/WF (30 wt %) blends.

PCL-g-AA/WF blends. It could be seen that the tensile strength and elongation of pure PCL were both decreased when it was grafted with AA. For PCL/WF blends, as shown in the dotted line of Figure 7, tensile strength at break decreased markedly and continuously as WF content was increased. This behavior can be explained from the result of SEM micrograph of PCL/WF blend, Figure 6(A), because the dispersion of WF in the PCL matrix is bad. As a result, it is certain that effect of the incompatibility between the two polymers on the mechanical properties is great. For PCL-g-AA/WF blends, the solid line of Figure 7, a quite different behavior about tensile strength at break was obtained, namely, the tensile strength of PCL-g-AA/WF blends increased obviously with increasing of WF content though the PCL-g-AA had a lower value of tensile strength than the pure PCL. It was also found that the PCL-g-AA/WF blends not only gave larger values of tensile strength than the PCL/WF ones, but also provided stable values of tensile strength while the WF content is beyond 30 wt %. A

contribution to this behavior may be the better dispersion, coming from the formation of branched or crosslinked macromolecules, of WF in the PCL-g-AA matrix.

Figure 7 gives the variation of elongation at break with WF content for PCL/WF and PCL-g-AA/WF blends and shows that the former exhibited lower values in elongation at break compared to the latter. The decrease in elongation for PCL/WF blend was marked since the addition of WF caused the blend to tend to agglomerate into bundles and gave the poor compatibility between the two phases. In the PCL-g-AA/WF blends, as shown in the solid line of Figure 7, the elongation at break also decreased with an increasing content of WF but they had larger values of elongation than those of PCL/WF ones. However, the elongation at break still remains lower compared to that of pure PCL. The result of mechanical properties in our work is similar to that of Bikiaris.¹⁸ As a result of Figure 7, one can conclude that the PCL-g-AA/WF blends can improve the tensile strength and elongation of PCL/WF ones but the increment of elongation is smaller than that of tensile strength.

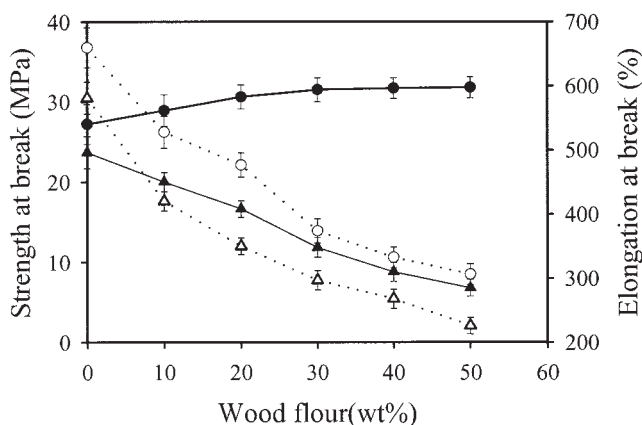


Figure 7 Tensile strength and elongation at break versus WF content for PCL/WF and PCL-g-AA/WF blends.

CONCLUSION

To improve compatibility and mechanical properties of PCL/starch blends, PCL-g-AA copolymer produced in our laboratory was taken to replace the pure PCL for preparation of blends. We investigated systematically the properties of PCL/WF and PCL-g-AA/WF blends. According to the results of FTIR, due to the generation of ester carbonyl functional group from reaction between -OH group of WF and -COOH group of PCL-g-AA copolymer, the crystalline structure of PCL/WF blend was changed when PCL-g-AA was used in the blending system. The DSC tests showed that melt temperatures of PCL/WF and PCL-

g-AA/WF both decreased as the content of WF was increased. It was also found that the PCL-g-AA/WF blends have easy processing property due to the low values of melt temperature and torque compared to PCL/WF blends. The morphology of PCL-g-AA/WF blends confirmed a good adhesion between WF and PCL-g-AA matrix. As a result of mechanical test, compared to PCL/WF blends, PCL-g-AA/WF blends can enhance the mechanical properties of the blends especially in tensile strength. Finally, we can conclude that PCL-g-AA copolymer produced in our laboratory can be used to lower the cost and to improve the properties of PCL/WF blends.

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