

A comparison of the structure, thermal properties, and biodegradability of polycaprolactone/chitosan and acrylic acid grafted polycaprolactone/chitosan

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Abstract

The effects of replacing PCL with acrylic acid grafted PCL (PCL-*g*-AA) on the structure and properties of a PCL/chitosan composite were investigated. The properties of both PCL-*g*-AA/chitosan and PCL/chitosan were examined and compared using FTIR, ¹H and ¹³C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and a biodegradation test. With PCL-*g*-AA in the composite, compatibility with chitosan and, consequently, the properties of the blend were both much improved due to the formation of ester and imide groups that conferred better dispersion and homogeneity of chitosan in the matrix. Moreover, PCL-*g*-AA/chitosan had a lower melt temperature and was, therefore, more easily processed than PCL/chitosan. Resistance to water was higher in the PCL-*g*-AA/chitosan blend, and consequently so was its resistance to biodegradation in soil and in an enzymatic environment. Nevertheless, weight loss of blends buried in soil or exposed to an enzymatic environment indicates that both blends were biodegradable, especially at high levels of chitosan content. Both blends suffered deterioration in tensile strength and elongation at break after exposure to soil or enzymatic environments.

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1. Introduction

Some plastics are recyclable, but most are irrecoverable and end up in landfill burial sites. Not only is it increasingly difficult to find such sites, but there are also many environmental problems associated with this method of disposal of plastics. For these reasons, the development of biodegradable polymers for use in plastics has received much attention. One such polymer is polycaprolactone (PCL). It is expensive, but has been noted for its flexibility and biodegradability [1–3]. Fortunately, it is possible to blend PCL with cheaper copolymers, so reducing the cost of the final product and leading to commercially successful applications, just as with some other aliphatic polyesters (polylactide acid and polyglycolide acid) [4–7]. It has been blended with copolymers for use as a packaging material,

and has been proposed for use in biomedical applications including catheters, blood bags and packaging [8,9].

In the past, many attempts have been made at blending plastic materials such as PCL with cheaper, biodegradable natural biopolymers such as starch, cellulose and chitin [10–13], and interest in the production of biodegradable polymers using these renewable resources is now growing [14]. Chitosan, the product of *N*-deacetylation of chitin, has received particular attention, not least because it is produced as a waste product in crustacean (shrimp and crabs) processing. It can also be obtained from the chitin component of fungal cell walls. In addition to being derived from renewable resources, chitosan offers unique physical, chemical, and biological properties, which have been studied for various applications [15]. One such feature, the high content of primary amino groups, confers two important characteristics on this biopolymer. First, because the amino groups are basic, it can be protonated at moderately low pH (<6.3), and the resulting cationic

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polyelectrolyte is water-soluble. Second, the amino groups' nucleophilicity means that at higher pH values (>7) they are deprotonated, and the unshared electron pair can undergo a variety of reactions. The reactivity of these amino groups allows chemical modification of chitosan under mild conditions, and because of the mild conditions modification is typically confined to the amino group [16, 17]. This suggests that there is good potential for controlled modification of the functional properties of chitosan.

Despite the apparent advantages of PCL/chitosan blends, their utility is limited because of their susceptibility to water absorption and their inferior mechanical properties, due to poor adhesion between the hydrophobic PCL polymer and the hydrophilic chitosan biopolymer. Adhesion of the two polymers can be aided by using a compatibilizer and/or a toughener to improve the compatibility between the two immiscible phases, thereby improving the mechanical properties of the composite [18]. Avella et al. [19] showed that by using pyromellitic anhydride as a compatibilizer, modification of PCL on its terminal groups increased its compatibility with plasticized starch. This suggests that grafting a reactive functional group onto PCL in a PCL/chitosan blend is likely to produce a blend that offers the best combination of low cost and good mechanical properties [20].

In this study, the effect of grafting acrylic acid onto PCL in a PCL/chitosan blend on the structure and thermal properties of the blend was investigated. The composites were characterized using FTIR spectroscopy, ^{13}C nuclear magnetic resonance, and differential scanning calorimetry (DSC) to identify the structural changes caused by the grafting of acrylic acid. Additionally, water absorption of synthesized blends and weight loss of blends buried in soil or exposed to an enzymatic environment was estimated in order to assess water resistance and biodegradability.

2. Experimental

2.1. Materials

PCL (molar mass 80,000 g/mol) was used as supplied by Solvay, while acrylic acid (AA), supplied by Aldrich, was purified by re-crystallization with chloroform before use. PCL-g-AA was synthesized from these constituents in our laboratory. Benzoyl peroxide (BPO), initiator in the grafting reaction was purified by dissolving in chloroform and reprecipitating with methanol. Chitosan (degree of deacetylation 83.8%), supplied by Tokyo Kasei Kogyo Co. Ltd, was purified before use. It was first dissolved into a 1% acetic acid solution, and then precipitated out by the addition of a concentrated 1 M NaOH solution. The precipitate was washed several times with deionized water until it became neutral. Scanning electron microscopy analysis revealed the particle size of the resultant chitosan powder to be 30–90 μm . For the enzymatic exposure test, *p*-

cresol and mushroom tyrosinase were obtained from Sigma Chemical Co. Mushroom tyrosinase was reported by the manufacturer to have a specific activity of 208 U/mg.

2.2. Sample preparation

2.2.1. Graft reaction and sample preparation

A mixture of AA and BPO was added in four equal portions at 2-minute intervals to molten PCL to allow grafting to take place. The reactions were carried out under a nitrogen atmosphere at 85 ± 2 °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 was dissolved in refluxing xylene (4 g in 200 ml) at 85 °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 °C for 24 h. The xylene-soluble product in the filtrate was extracted five times, using 600 ml of cold acetone for each extraction.

2.2.2. Determination of 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 0.03 N ethanolic KOH solution, which had been standardized against a solution of potassium hydrogen phthalate, with phenolphthalein used as an indicator. The acid number and the grafting percentage were then calculated using the following equations [21]:

$$\begin{aligned} \text{Acid number (mg KOH/g)} \\ &= \frac{V_{\text{KOH}} \text{ (ml)} C_{\text{KOH}} \text{ (N)} 56.1}{\text{polymer (g)}} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Grafting percentage (\%)} \\ &= \frac{\text{Acid number} \times 72}{2 \times 561} \times 100\% \end{aligned} \quad (2)$$

With BPO loading and AA loading maintained at 0.3 and 10 wt%, respectively, the grafting percentage was determined as 6.05 wt%.

2.2.3. Composite preparation

The chitosan was dried in an oven at 50 °C for 3 days prior to blending. Mass ratios of chitosan to PCL were fixed at 5/95, 10/90, 15/85 and 20/80, and composites were prepared using a Brabender 'Platograph' 200 Nm mixer W50EHT instrument with a blade-type rotor, with rotor speed maintained at 50 rpm and temperature at 100 °C, and a reaction time of 15 min. After blending, the composites were pressed into 1 mm-thick plates using a hot press at 100 °C, then put into a desiccator for cooling. The cooled plates were then made into standard samples for characterization.

2.3. Characterization of composites

2.3.1. NMR/FTIR/XRD/DSC analyses

In preparation for NMR analysis, the sample was dissolved in CDCl_3 and sealed in an NMR tube (10 mm O.D.). After being degassed, samples were analyzed using a Bruker AMX400 ^{13}C NMR spectrometer at 100 MHz, with a 30° pulse and a 4 s cycle time. Additionally, solid-state samples were analyzed at 50 MHz, and the spectra were observed under cross-polarization, magic angle sample spinning and power decoupling conditions with a 90° pulse and 4 s cycle time. Infrared spectra of samples were obtained using a Bio-Rad FTS-7PC type FTIR spectrophotometer. The X-ray diffraction intensity curves, recorded using a Rigaku D/max 3V X-ray diffractometer with a Cu target and $K\alpha$ radiation at a scanning rate of 2° min^{-1} , enabled changes in the crystalline structure to be studied. The melt temperature (T_m) and enthalpy of melting (ΔH_m) 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 -100 to $+120^\circ\text{C}$, heated at a rate of $10^\circ\text{C}/\text{min}$.

2.4. Water absorption

Samples for measuring water absorption were prepared in the form of $150 \pm 5 \mu\text{m}$ thick, $75 \times 25 \text{ mm}$ film strips, following the ASTM D570-81 method. The samples were dried in a vacuum oven at $50 \pm 2^\circ\text{C}$ for 8 h, cooled in a desiccator, and then immediately weighed to the nearest 0.001 g (this weight designated as W_c). Samples were then immersed in distilled water, maintained at $25 \pm 2^\circ\text{C}$, for the 6-week test period. During this period, they were removed from the water at one-week intervals, gently blotted with tissue paper to remove excess water on the surface, immediately weighed to the nearest 0.001 g (designated as W_w), and returned to the water. Each W_w was an average value obtained from three measurements. The percentage increase in weight from water uptake was calculated to the nearest 0.01% as follows

$$\%W_f = \frac{W_w - W_c}{W_c} \times 100$$

where $\%W_f$ is the final percentage increase in weight of the tested samples.

2.5. Biodegradation studies

2.5.1. Exposure to soil environment

Biodegradability of the samples was studied by evaluating weight loss of blends over time in a soil environment. Samples ($30 \times 30 \times 1 \text{ mm}^3$) were weighed and then buried in boxes of alluvial-type soil, obtained in March 2001 from farmland topsoil before planting. The soil was sifted to remove large clumps and plant debris. Procedures used for

soil burial were as those described by Chandra and Rustgi [22]. Soil was maintained at approximately 20% moisture in weight and samples were buried at a depth of 15 cm. A control box was also prepared for comparison, consisting of only samples and no soil. The buried samples were dug out once a month, washed in distilled water, dried in a vacuum oven at $50 \pm 2^\circ\text{C}$ for 24 h, and equilibrated in a desiccator for at least a day. The samples were then weighed before returning them to the soil.

2.5.2. Exposure to enzymatic environment

Samples were cast into films using a $50 \times 50 \text{ mm}$ plastic mold. Films were removed from the mold and then rinsed several times with distilled water until the waste water from rinsing was of neutral pH. They were then clamped to a glass sheet and dried in a vacuum oven ($50 \pm 2^\circ\text{C}$, 0.5 mmHg , 24 h), after which their thickness was measured as $0.05 \pm 0.02 \text{ mm}$.

Films were then placed in Petri dishes containing a compost of 30 ml phosphate buffer (100 mM; pH 6.3) with *p*-cresol (1.8 mM) and tyrosinase (20 U/ml), incubated at $35 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. The films were subsequently washed extensively with deionized water and then dried. In this work, the studies were conducted using three replicate incubators and three replicate samples in each incubator for each exposure time, meaning that each result was based on nine samples.

2.6. Composite morphology

To analyze composite morphology, samples were treated with hot water at 80°C for 24 h, coated with gold, and then analyzed using a Hitachi Microscopy Model S-1400 scanning electron microscope.

3. Results and discussion

3.1. Characterization of PCL-g-AA/chitosan

Grafting of AA onto PCL was investigated via FTIR. Fig. 1(A) and (B) show the FTIR spectra of PCL and PCL-g-AA. In addition to the characteristic peaks ($3300\text{--}3700$, 1725 , $852\text{--}1480$ and 720 cm^{-1}) observed in both polymers [19, 23], there exists an obvious extra peak at 1710 cm^{-1} for the modified PCL. This extra peak is characteristic of $\text{C}=\text{O}$ and represents the free acid in the modified polymer. This peak at 1710 cm^{-1} , as well as a broad OH stretching absorbance at $3200\text{--}3700 \text{ cm}^{-1}$, also reported elsewhere [13,24], demonstrates that AA had been grafted onto PCL.

Furthermore, the FTIR spectra of PCL/chitosan (10 wt%) (Fig. 2(A)) and PCL-g-AA/chitosan (10 wt%) (Fig. 2(B)) show peaks between 3200 and 3700 cm^{-1} that are much more intense than the stretching absorbance at $3000\text{--}3600 \text{ cm}^{-1}$ observed in the absence of chitosan (Fig. 1). These more intense peaks are caused by the NH group of

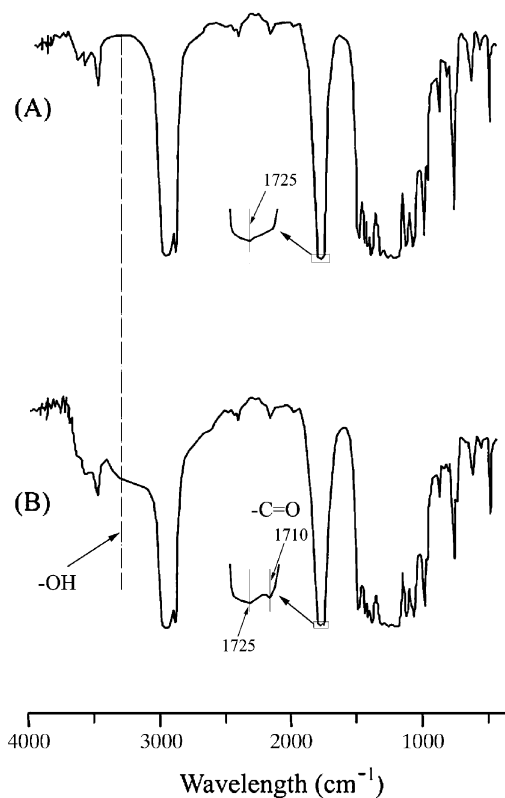


Fig. 1. FTIR spectra of pure PCL and PCL-g-AA. [(A) PCL; (B) PCL-g-AA].

chitosan [7]. The spectra of PCL-g-AA/chitosan (10 wt%) shows additional unique absorption peaks at 1717 and 1745 cm^{-1} . The peak at 1717 cm^{-1} is assigned to $-\text{C}=\text{O}$ of N (COR)₂ while the peaks at 1745 cm^{-1} are assigned to absorption of $-\text{C}=\text{O}$ in OCOR. These ester and imide functional groups are formed via the reaction between $-\text{OH}$ of PCL-g-AA and $-\text{NH}$ of chitosan when the two polymers are blended. Zong et al. [25] studied acylated chitosan copolymers, with similar results. Additionally, the spectra in Fig. 2 identify differences in absorbance intensity at 1650 cm^{-1} (amide I, secondary amide) and 1590 cm^{-1} (non-acylated primary amide). The absorbance at 1590 cm^{-1} in PCL/chitosan is much greater than at 1650 cm^{-1} , while it is less marked in PCL-g-AA/chitosan. This result, similar to that obtained by Nge et al. [26], indicates that in the blending of PCL-g-AA with chitosan, part of the primary amide of chitosan reacts with the carboxyl group of PCL-g-AA.

To further confirm the grafting of AA, the structure of PCL and PCL-g-AA was compared using ^{13}C NMR, and the spectra are shown in Fig. 3(A) (PCL) and Fig. 3(B) (PCL-g-AA). The spectra for unmodified PCL shows six carbon peaks (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), an outcome also reported by Kesel et al. [27] in their study of a polycaprolactone polyvinylalcohol composite. Three extra peaks in the spectra of PCL-g-AA

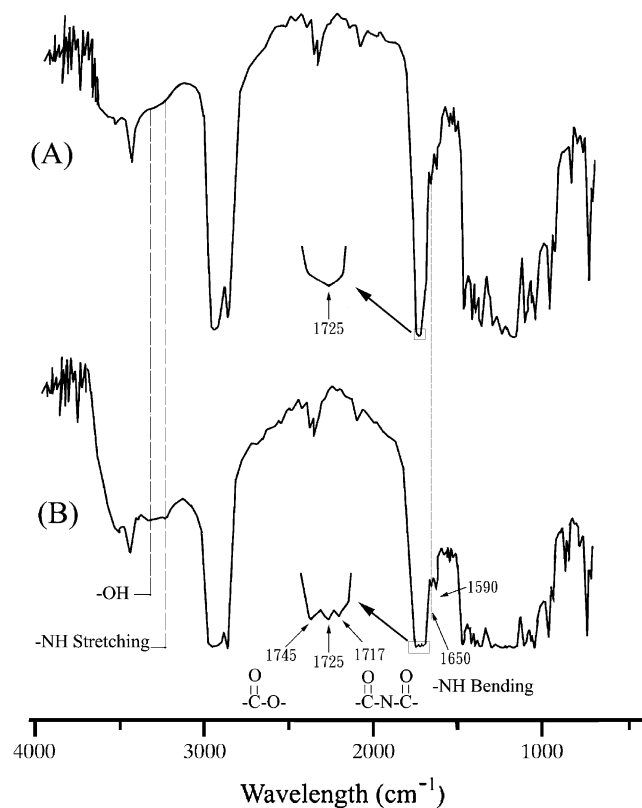


Fig. 2. FTIR spectra for PCL/chitosan (10 wt%) and PCL-g-AA/chitosan (10 wt%). [(A) PCL/chitosan (10 wt%); (B) PCL-g-AA/chitosan (10 wt%)].

(7: C_β $\delta=35.63$ ppm; 8: C_α $\delta=42.19$ ppm; 9: $-\text{C}=\text{O}$ $\delta=175.05$ ppm) confirm the grafting of AA onto PCL.

The solid-state ^{13}C NMR spectra of original chitosan, PCL/chitosan (10 wt%), and PCL-g-AA/chitosan (10 wt%) are shown in Fig. 4(A)–(C). The spectrum of original chitosan is the same as that reported by Zong et al. [25]. Moreover, the PCL-g-AA/chitosan (10 wt%) spectrum, in Fig. 4(C), coincides with Zong et al.'s [25] ^{13}C NMR results for acylated chitosan. Comparing the spectra of PCL/chitosan (10 wt%) and PCL-g-AA/chitosan (10 wt%), we found that there were extra peaks at $\delta=42.19$ ppm (C_α) and $\delta=35.63$ ppm (C_β) in the latter. These peaks were also observed in our previous reports [13,28] on the ^{13}C NMR of POE-g-AA/chitosan. As already indicated, the appearance of peaks at $\text{C}_{\alpha\alpha}$ and C_β in PCL-g-AA is due to grafting of AA onto PCL. However, the peak at $\delta=175.05$ ppm ($\text{C}=\text{O}$) (shown in Fig. 3(B)), also characterizing the grafting of AA onto PCL, is absent in the solid state spectrum of PCL-g-AA/chitosan (10 wt%) (Fig. 4(C)). This is because the reaction between $-\text{COOH}$ of AA and $-\text{OH}$ or $-\text{NH}$ of chitosan shifted the peak at $\delta=175.05$ ppm to the duplicates at b, c, d, e and f ($\delta=178.7, 177.1, 171.7, 170.3$ and 168.9 ppm). This is evidence of a condensation reaction between PCL-g-AA and chitosan, via which the original chitosan was fully acylated and the amino and amide groups were converted to imides (represented by peaks d, e and f in

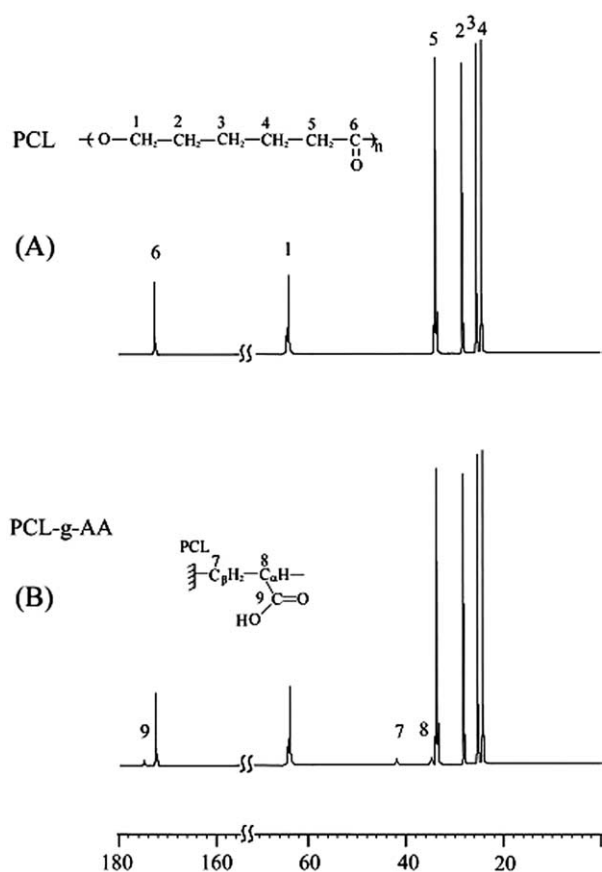


Fig. 3. ^{13}C NMR spectra of pure PCL and PCL-g-AA.

Fig. 4(C)). This reaction does not occur between PCL and chitosan, a point illustrated by the absence of corresponding peaks in the PCL/chitosan (10 wt%) spectrum (Fig. 4(B)). Formation of imide and ester functional groups noticeably affected the thermal, mechanical and biodegradation properties of PCL-g-AA/chitosan, as discussed in the following sections.

3.2. X-ray diffraction

The X-ray diffraction spectra of pure PCL, PCL/chitosan (10 wt%), PCL-g-AA/chitosan (10 wt%), and pure chitosan are shown in Fig. 5(A)–(D), respectively. Pure PCL produced two peaks at about 23.8° and 21.3° (Fig. 5(A)), as previously reported by Ha et al. [29]. The two blends, meanwhile, produced two extra peaks, at about 15.0° and 10.3° (Fig. 5(B) and (C)). These peaks were also found in the spectrum of pure chitosan (Fig. 5(D)), and are caused by the blending of chitosan with PCL or PCL-g-AA. Furthermore, the intensity of another peak at 19.5° in the PCL/chitosan (10 wt%) spectrum (Fig. 5(B)) is much less than that in the pure chitosan spectrum. This is perhaps caused by the change in coordinate property of the molecules of PCL when it is blended with chitosan [30]. Two peaks present in the PCL-g-AA/chitosan spectrum but not in the PCL/chitosan spectrum, at $2\theta = 18.1^\circ$ and 19.0° , may be caused by

the generation of an ester and amide carbonyl functional group, as described in the discussion of FTIR and NMR analysis. Muzzarelli et al. [31] reported similar results. This functional group changes the crystalline structure of the blend.

3.3. Differential scanning calorimetry analysis

Thermal properties of pure PCL, PCL/chitosan, and PCL-g-AA/chitosan, obtained via DSC, are given in Table 1. PCL recorded the highest melt temperature (T_m) and the highest enthalpy of melting (ΔH_m), at 62.5°C and 72.5 J/g , respectively. The lower T_m recorded for PCL/chitosan and PCL-g-AA/chitosan is due to the lower melt viscosity of chitosan while the lower ΔH_m is caused by the lower crystallinity of the blends. Moreover, the values of both parameters in the blends decreased as the chitosan content increased. This implies a decrease in crystallinity with chitosan content, probably caused by chitosan prohibiting movement of the polymer segments and thereby making it more difficult to arrange the polymer chain. Additionally, the hydrophilic character of chitosan likely leads to poor adhesion with the hydrophobic PCL. Averous et al. [32] drew similar conclusions in their study of PCL blended with thermoplastic starch. We also found that when PCL was replaced with PCL-g-AA in the composite, T_m decreased (by about $1\text{--}3^\circ\text{C}$) and ΔH_m increased (by about $7\text{--}15\text{ J/g}$). The lower melt viscosity of PCL-g-AA/chitosan, which suggests that it is more crystalline than PCL/chitosan, makes it easier to process. The glass temperature (T_g), shown in Table 1, increased with increasing chitosan content for both PCL/chitosan and PCL-g-AA/chitosan. The increase in T_g is a result of the decrease in the space available for molecular motion with increasing chitosan content. Furthermore, we found that T_g was higher with PCL-g-AA in the composite (by about $0.7\text{--}3.5^\circ\text{C}$). It is proposed that this is also a result of less space available for molecular motion within this composite.

3.4. Water absorption

PCL-g-AA/chitosan blends exhibited moderately good water resistance, while water resistance of the equivalent PCL/chitosan blends was always inferior (Fig. 6). The increment of water absorption for PCL/chitosan was about 2–8% higher than that of PCL-g-AA/chitosan. Percentage water gain increased with chitosan content in both blends. Bikiaris and Panayiotou [33] also noted increases in water absorption with chitosan content in their study of chitosan-polyethylene blends. They deduced that the marked increase in water absorption was probably caused by increased difficulty in forming polymer chain arrangements as the chitosan prohibited the movements of the polymer segments, and also that the hydrophilic character of chitosan led to poor adhesion with the hydrophobic polyethylene (a steric effect). In this study, the difficulty in forming polymer

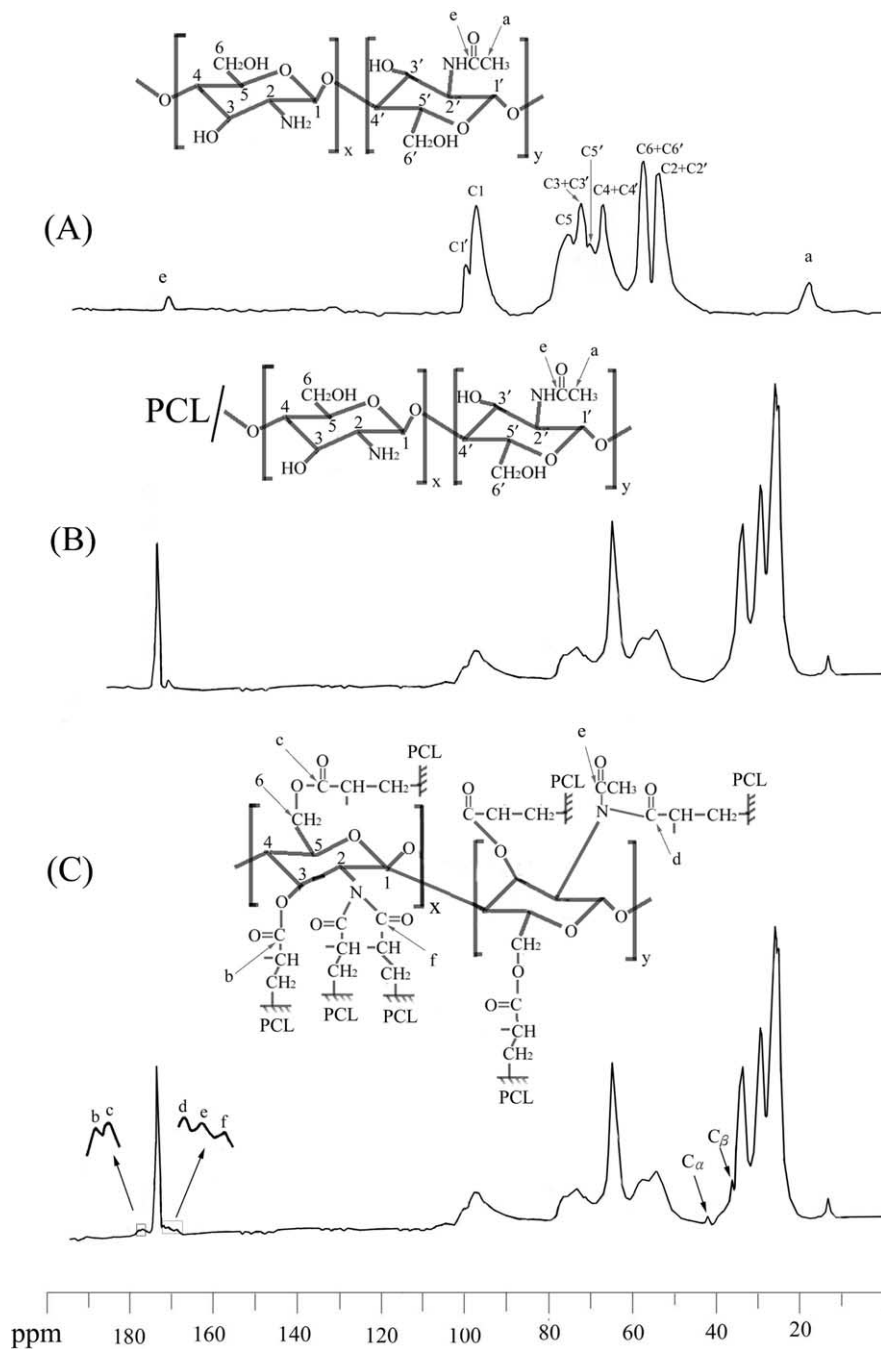


Fig. 4. Solid state ^{13}C NMR spectra for original chitosan, PCL/chitosan (10 wt%) and PCL-g-AA/chitosan (10 wt%). [(A) Pure chitosan; (B) PCL/chitosan (10 wt%); (C) PCL-g-AA/chitosan (10 wt%)].

Table 1

Effect of chitosan content on the thermal properties of PCL/chitosan and PCL-g-AA/chitosan composites

Chitosan (wt%)	PCL/chitosan			PCL-g-AA/chitosan			
	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	
0	-59.6	62.5	72.5	-58.6	61.3	50.6	
05	-58.7	61.3	45.2	-57.5	60.2	47.9	
10	-57.3	60.2	35.3	-54.8	58.9	40.8	
15	-56.9	59.5	27.8	-53.8	58.2	36.6	
20	-56.3	59.1	20.6	-52.9	57.3	32.6	

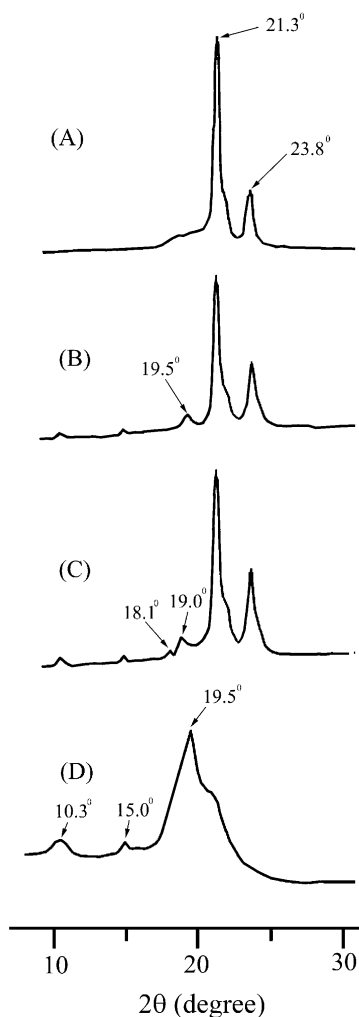


Fig. 5. X-Ray spectra for pure PCL, pure chitosan, PCL/chitosan and PCL-g-AA/chitosan (10 wt%). [(A) Pure PCL; (B) PCL/chitosan (10 wt%); (C) PCL-g-AA/chitosan (10 wt%); (D) pure chitosan].

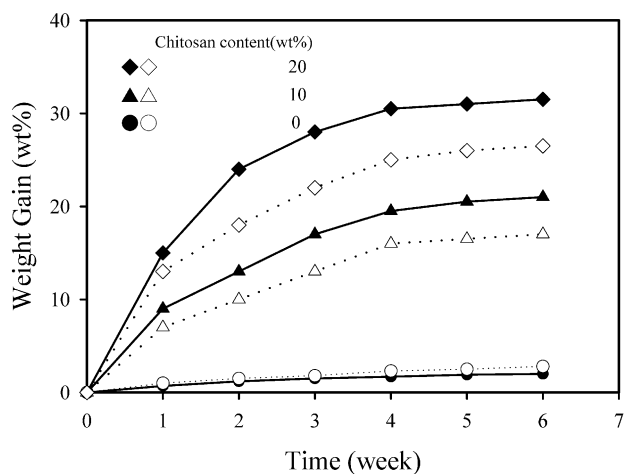


Fig. 6. Percentage weight gain of PCL/chitosan and PCL-g-AA/chitosan blends during water absorption tests. [The dotted and solid lines indicate the PCL-g-AA and PCL composites with various chitosan contents].

chain arrangements and the steric effect of PCL-g-AA/chitosan was caused by the ester carbonyl and amide functional group on that blend. Also a factor in the less effective water absorption of PCL-g-AA/chitosan is the reduction of the hydrolytic functional groups of PCL-g-AA and chitosan during blending.

3.5. Biodegradation

3.5.1. Exposure to soil environment

Fig. 7 shows changes in weight ratio (degraded sample/initial sample) with time for PCL/chitosan and PCL-g-AA/chitosan buried in soil. In the soil, water diffused into the polymer sample, causing swelling and enhancing biodegradation. The blends containing a higher percentage of chitosan (20%) degraded rapidly in the initial 10 weeks, equivalent to their approximate chitosan content, followed by a gradual decrease in weight during the next 6 weeks. For both PCL/chitosan and PCL-g-AA/chitosan, the weight loss, which indicated the extent of biodegradation of the blends, increased as the content of chitosan increased. Further comparison of the two copolymers revealed that PCL-g-AA/chitosan had a higher weight ratio, with an increment of about 0.01–0.05, and had, therefore, suffered less degradation. The greater biodegradation of PCL/chitosan may be caused by the same factors that lead to its higher absorption of water. Exposure to a soil environment also caused deterioration in tensile strength and elongation at break in both blends.

3.5.2. Exposure to enzymatic environment

Fig. 8 shows that the changes in weight ratio (degraded sample/initial sample) with time for PCL/chitosan and PCL-g-AA/chitosan exposed to incubated tyrosinase followed a similar pattern to the weight loss on exposure to a soil environment. The extent of biodegradation was assessed by

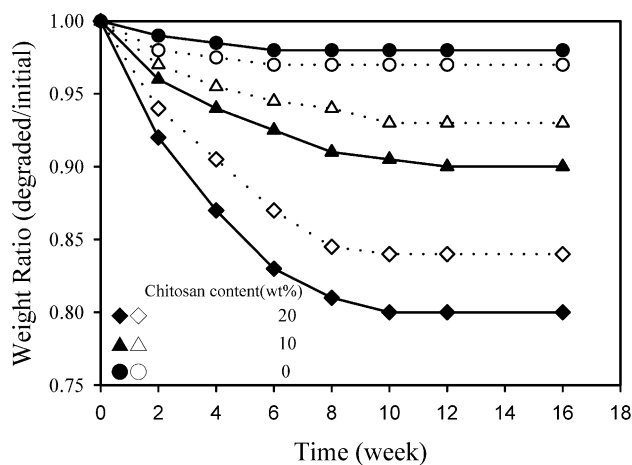


Fig. 7. Weight ratio of PCL/chitosan and PCL-g-AA/chitosan blends exposed to soil environment. [The dotted and solid lines indicate the PCL-g-AA and PCL composites with various chitosan contents].

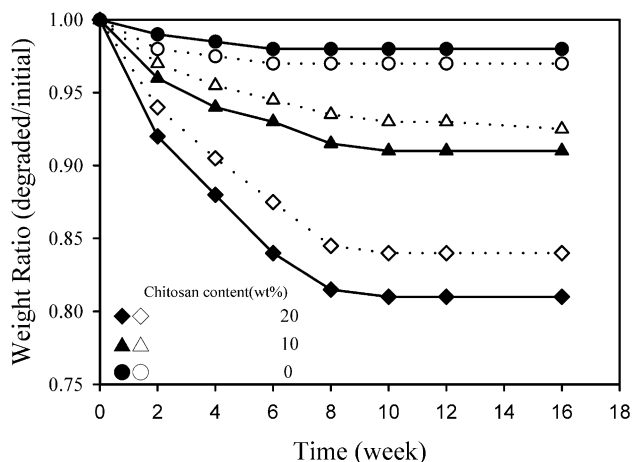
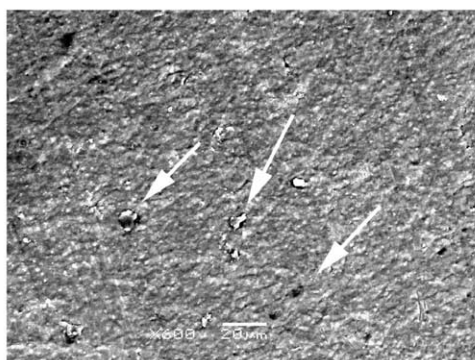


Fig. 8. Weight ratio of PCL/chitosan and PCL-g-AA/chitosan blends exposed to tyrosinase environment. [The dotted and solid lines indicate the PCL-g-AA and PCL composites with various chitosan contents].

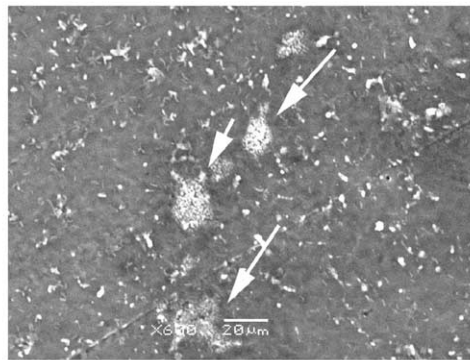
studying SEM microphotographs, taken after 2 and 8 weeks exposure to incubated tyrosinase, showing the morphology of the PCL/chitosan (10 wt%) and PCL-g-AA/chitosan (10 wt%) blends (Fig. 9). There were bigger and deeper holes/pits in PCL/chitosan (Fig. 9(A)) after 2 weeks, which

were also more random in distribution than those in the PCL-g-AA/chitosan blend (Fig. 9(B)). Moreover, the extent of phase biodegradation was less than 20% in all compatibilized blends and was detectable only at higher magnifications. It was also noted that biodegradation of the chitosan phase of PCL/chitosan blends increased with time, confirming the results presented in Fig. 8.

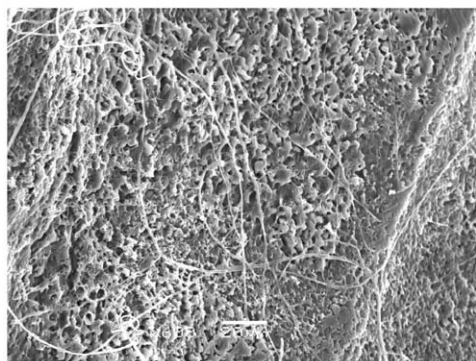
In the PCL-g-AA/chitosan blend, there was fine dispersion and homogeneity of chitosan in the PCL-g-AA matrix (Fig. 9(D)). This was not true of the PCL/chitosan blend. This better dispersion arises from the formation of branched and crosslinked macromolecules created from hydroxyls (of chitosan) reacting with free acid groups (of PCL-g-AA). These macromolecules contain two different parts, one of which is compatible with PCL-g-AA and one with chitosan, giving them the ability to place themselves in the interface of PCL-g-AA/chitosan during melt blending. The result is a reduction in the interfacial tension between the two polymers and a finer distribution of chitosan in all the compatibilized blends. In a paper on the compatibility of starch particles in LDPE/starch blends, Bikiaris [20], using PE-g-MAH as a compatibilizer, proposed a similar explanation for low biodegradation of compatibilized blends under tensile disruption.



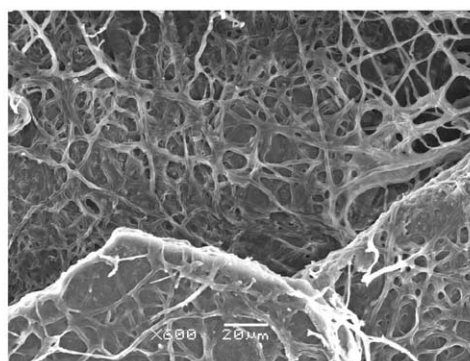
(A) 2 week



(B) 2 week



(C) 8 week



(D) 8 week

Fig. 9. SEM micrographs of PCL/chitosan and PCL-g-AA/chitosan blends exposed to incubated tyrosinase after 2 and 8 weeks. [(A), (C) PCL/chitosan (10 wt%); (B), (D) PCL-g-AA/chitosan (10 wt%)].

4. Conclusions

Compatibility and mechanical properties of a PCL/chitosan composite were improved by using PCL-*g*-AA in place of PCL. The blending of PCL-*g*-AA with chitosan leads to the formation of ester carbonyl and amide functional groups not present in PCL/chitosan. These groups are responsible for many of the differences in mechanical properties between the two copolymers. The melt temperature (T_m) of both composites decreased with increasing chitosan content, making such composites easier to process. The enthalpy of melting (ΔH_m) of PCL/chitosan and PCL-*g*-AA/chitosan also decreased with increasing chitosan content. Nevertheless, ΔH_m was higher for PCL-*g*-AA/chitosan, implying that it has a more crystalline structure. The glass transition temperature of PCL-*g*-AA/chitosan was also higher than that of PCL/chitosan, indicating a smaller space for molecular motion. PCL-*g*-AA/chitosan was more resistant to water than PCL/chitosan, although it showed only a slightly higher resistance to biodegradation when exposed to soil and enzymatic environments.

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