

Effect of PEG Molecular Weight on the Tensile Toughness of Starch/PCL/PEG Blends

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ABSTRACT: The blend of a gelatinized starch and poly(ϵ -caprolactone) (PCL) was prepared and the effect of starch gelatinization on the mechanical properties of the blend was studied. The gelatinization of starch resulted in good dispersion of the starch in the PCL matrix and a higher modulus and strength of the blend. The mechanical properties of the starch/PCL/poly(ethylene glycol) (PEG) blends were also investigated. From the change of the toughness of the blends with the PEG molecular weight, it was found that the blend containing PEG of molecular weight 3400 shows the highest tensile toughness. It was also found from the SEM images that the blend containing PEG of molecular weight 3400 had the smallest domain size of the starch dispersion phases, which implies that PEG of the proper molecular weight could effectively stabilize the interface of the starch/PCL blend. The PEG of the proper molecular weight seems to locate mainly at the interface between the starch and PCL phases and to interact with both the starch phase and the PCL phase. The interactions between starch and PEG and between PCL and PEG in the blend were studied using DSC and FTIR techniques. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2049–2056, 2000

Key words: starch/PCL blend; poly(ethylene glycol) (PEG); tensile toughness; interface; compatibilizer

INTRODUCTION

Synthetic polymers, natural polymers, and modified natural polymers are now widely used as commodity plastics in such diverse applications as packaging, personal hygiene products, computers, houses, and clothing. In spite of all these enormous benefits for human life, synthetic polymers have an overriding connotation of being harmful to the environment. Especially, the current synthetic polymers that were developed for their durability and resistance properties are visible as litter in the environment and they contrib-

ute to landfill overcapacity. This problem was acknowledged by the polymer industries and attempts were made to develop environmentally degradable polymers that on disposal and after use degrade harmlessly and return to their natural state.

As a result, many kinds of plastics that degrade in landfills have been reported. Among them, there are aliphatic polyesters such as polycaprolactone (PCL), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(ethylene succinate), and these materials have been shown to undergo microbial degradation.^{1,2} Starch and its derivatives, both in granular and destructured forms, have been blended with various plastics, including polyethylene, poly(vinyl alcohol), and poly(ethylene-co-acrylic acid).^{3–7} Also, the aliphatic polyesters have been blended with polyeth-

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ylene, the styrene-acrylonitrile copolymer, etc.⁸ However, they cannot be degraded completely due to the presence of synthetic plastics which are not biodegradable in the blend, even though starch or aliphatic polyesters have biodegradable characteristics.

The blends of starch and aliphatic polyester, especially PCL, have been considered as completely biodegradable plastics⁹⁻¹² because both components in the blends are biodegradable. PCL was used as the matrix material, and starch, as a modulus-modifier for these blends. PCL was chosen because of its good mechanical properties such as tensile strength and elongation and also its good compatibility with many types of polymers. Starch helps to lower the cost of the final product as well as giving a good mechanical property such as the tensile modulus. However, the poor miscibility between PCL and starch is still a problem to be overcome for enhancement of the properties of the blends. Previous works have reported^{9,10,12} on the simple blend of starch granules and PCL that were not miscible with each other. They showed that there is a significant decrease in tensile strength at a higher percentage of starch granules over 30 wt % because the starch coalesces into larger aggregates of about 30–40 μm in diameter and is not uniformly distributed within the PCL matrix. It is thus necessary to obtain small and well-dispersed starch domains within the PCL matrix for good mechanical properties of the starch/PCL blends.

In this work, we prepared a blend of a gelatinized starch and PCL and studied the effect of starch gelatinization on the mechanical properties of starch/PCL blends. Poly(ethylene glycol) (PEG) is known to be a starch plasticizer and to reduce the brittleness of the starch.^{3,13,14} In the present study, PEGs of various molecular weights were used in starch/PCL blends and the effect of the PEG molecular weight on the mechanical properties of the blend system was also investigated.

EXPERIMENTAL

Materials and Blends Preparation

The PCL used in this study, Tone[®], was purchased from Union Carbide (Danbury, CT). The granular corn starch and four kinds of PEGs were obtained from Sigma Chemical (St. Louis, MO) and Aldrich (Milwaukee, WI), respectively. The

number-average molecular weights of the PEGs used in this work are 400, 3400, 8000, and 100,000.

The simple blend of corn starch granules/PCL (CS/PCL) was prepared by mixing the starch granules which were not destructured and the PCL pellets in a Brabender mixing head at 90°C and 80 rpm. The gelatinized starch/PCL (GS/PCL) blend was prepared from gelatinized starch and PCL pellets by melt mixing with a Brabender mixing head at 90°C and 80 rpm: A mixture of corn starch and enough water was blended for 3 min at 90°C in a Brabender mixer to gelatinize the starch. After that, the PCL pellets were added, while heating and mixing were continued. The resulting product, which looks like a gum, was dried under a vacuum at 40°C for 7 days to remove the water used in the starch gelatinization. The compositions of the CS/PCL and GS/PCL blends (40/60 by weight percent) were the same.

The starch/PCL/PEG blends in which PEG acts as a starch plasticizer were also prepared by melt mixing with the same mixing and drying conditions as for the GS/PCL blend. The relative amounts of PCL, starch, and PEG for all the blends studied were fixed at the ratio of 60/40/10 by weight.

Mechanical Property Measurements

All the blend samples were molded by hot-pressing at 150°C to make sheets of 1 mm thickness and then the specimens for tensile measurements were cut from the sheets and shaped into dog-bone-type bars (1 mm thickness, 5 mm width, and 20 mm length) using a cutter. All tensile measurements were performed using an Instron Model 4204 tester at room temperature. Experiments were performed at a constant crosshead speed of 10 mm/min. A minimum of five samples was tested under the same conditions for each blend to give an average value of the experimental data.

Electron Microscopy

The morphologies of the blends were investigated using a scanning electron microscope (Phillips SEM 535M). To observe the domain structure of the starch phase, the surface of the compression-molded blend specimen was etched physically for 1 h in a water medium by the irradiation of ultrasonic waves (Branson 2210). The ultrasonication was performed at 40°C for all the samples.

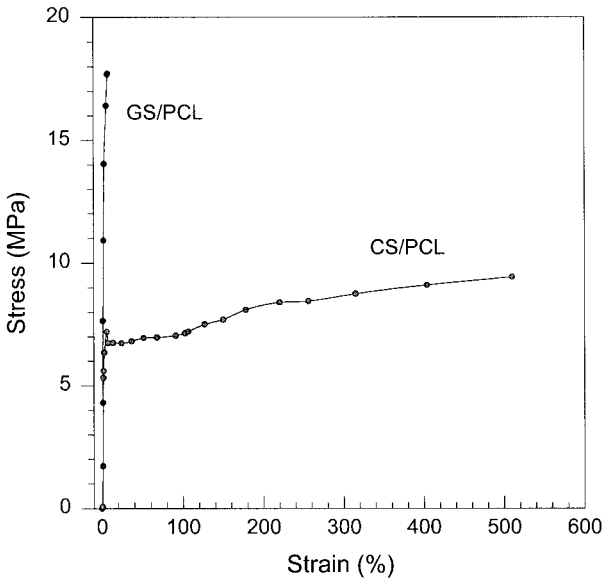


Figure 1 Tensile s-s curves for CS/PCL and GS/PCL at room temperature.

Thermal Measurements

Differential scanning calorimetric studies were carried out using a DuPont 9900 instrument with a heating rate of $10^{\circ}\text{C}/\text{min}$. Each sample was rapidly quenched from room temperature to -50°C and then heated to 250°C under a nitrogen atmosphere. Thermal transition behavior was recorded during the first heating because of the thermal degradation of the starch above 200°C .

FTIR Measurements

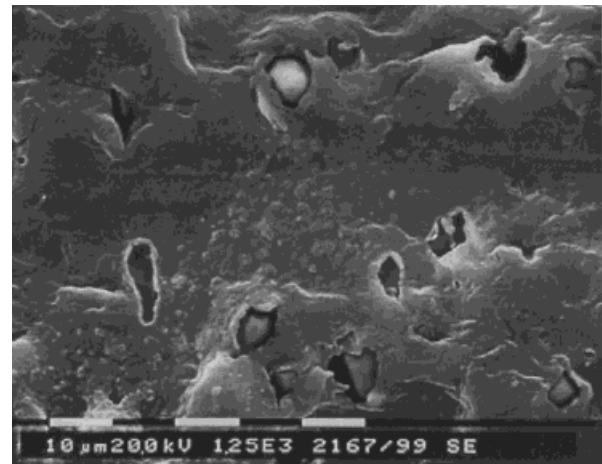
All the FTIR spectra were obtained on a Bomem 102 spectrometer at a resolution of 2 cm^{-1} . Measurements were carried out using a deuterated triglycine sulfate detector (DTGS). For IR measurements, all the blend samples were molded for the film formation by hot-pressing at 150°C under 12,000 psi. The thickness of all the samples for IR measurements was about $10\ \mu\text{m}$.

RESULTS AND DISCUSSION

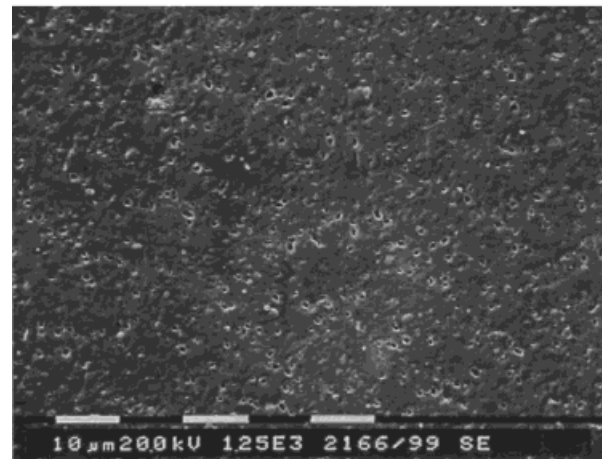
Effect of Starch Gelatinization on the Mechanical Properties of the Starch/PCL Blend

Figure 1 shows the stress-strain (s-s) curves of the GS/PCL and CS/PCL blends. It is found that the mechanical properties of the GS/PCL blend are significantly different from those of the CS/PCL blend: The higher the modulus and strength,

the lower percentage of the elongation at break and tensile toughness of the GS/PCL blend. To investigate the origin of the differences in the mechanical properties of the above two blends, SEM images of the blends were taken and are shown in Figure 2. Figure 2(a) shows the SEM image of the CS/PCL blend and it is found that the starch granules dispersed in the PCL matrix



(a)



(b)

Figure 2 SEM images of the (a) CS/PCL ($\times 1250$) and (b) GS/PCL ($\times 1250$).

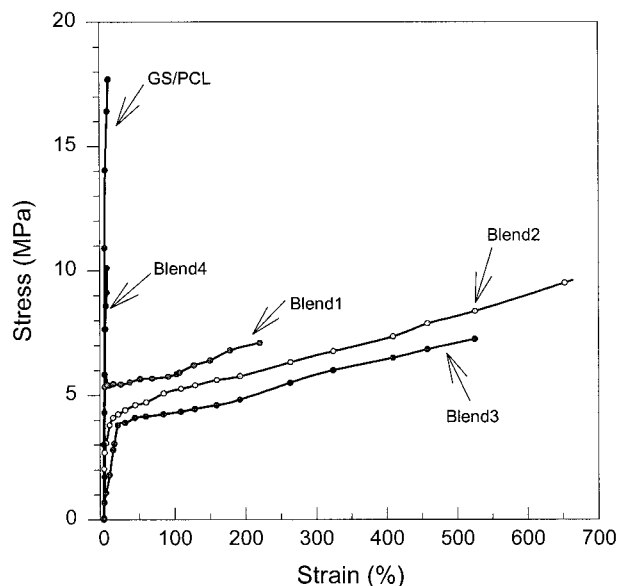


Figure 3 Tensile σ - ϵ curves for gelatinized starch/PCL/PEG (40/60/10 wt ratio) blends with different PEG molecular weights.

are not effectively disrupted during the blend process. Thus, the CS/PCL blend could exhibit a shear-yielding deformation as shown in Figure 1, just as in the case of pure PCL.¹² On the other hand, in the case of the GS/PCL blend, as shown in Figure 2(b), the starch granules are well gelatinized, which results in good dispersion of the starch in the PCL matrix. The GS/PCL blend shows a brittle deformation pattern instead of shear-yielding deformation as shown in Figure 1.

Effect of PEG on the Mechanical Properties of the Starch/PCL Blend

Figure 3 shows the σ - ϵ curves of the starch/PCL/PEG blends with different molecular weights of PEG at the given composition. Four different molecular weight PEGs are used and the starch/PCL blends containing PEGs are named blend 1 for PEG400, blend 2 for PEG3400, blend 3 for PEG8000, and blend 4 for PEG100,000. Unlike blends 1, 2, and 3, blend 4 showed a brittle deformation behavior. It is due to that PEG100,000 is not miscible with starch, and, thus, it cannot effectively reduce the brittleness of the starch. The DSC studies on determination of the miscibility of PEG100,000 and starch will be presented in the latter part of this section.

Figure 4 shows the tensile toughness of the blends as a function of PEG molecular weight at

the given composition. From Figure 4, it is found that the addition of PEG to the GS/PCL blend could lead to the enhancement of toughness if the molecular weight of PEG is not very high. It seems that the lower molecular weight PEG reduces the brittleness of rigid starch and makes the mobility of starch chains increase. However, for blend 4, which showed a brittle deformation behavior, the toughness was not different from that of the GS/PCL. This is because PEG100,000 could not reduce the brittleness of the starch. The starch is too hydrophilic to be miscible with PEG100,000 in that it has a significantly lower number of hydroxyl groups per unit mass compared with the low molecular weight PEG. It is also found from Figure 4 that the toughness of the blend shows a maximum at a certain molecular weight of PEG. To enhance toughness of the blends, it is usually necessary to ensure that the adhesion between the dispersion phase and the matrix is good, and the choice of the dispersed particle size for higher tensile toughness depends upon the relative positions of the shear-yielding envelope and the critical crazing stress. Bucknall¹⁵ reported that in polycarbonate (PC), which is relatively resistant to crazing and shows shear-yield deformation, the smaller dispersion phase could lead to the higher tensile toughness. The smaller dispersed particle size ensures that both cavitation and debonding at interfaces are post-

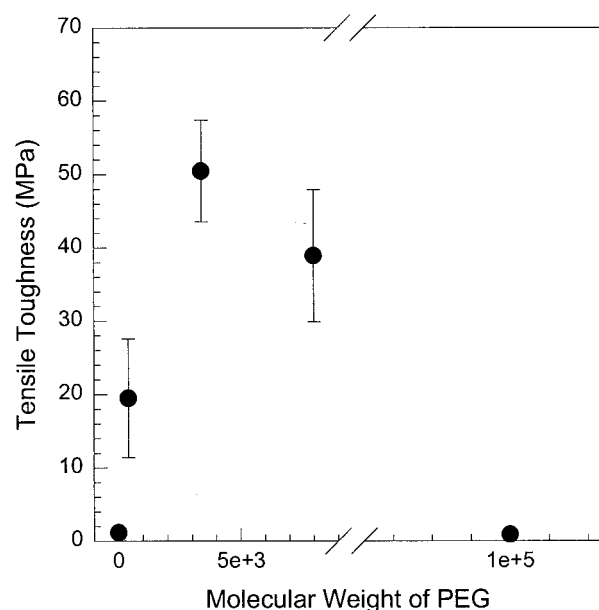


Figure 4 Tensile toughness of GS/PCL/PEG (40/60/10 wt ratio) blends as a function of PEG molecular weight.

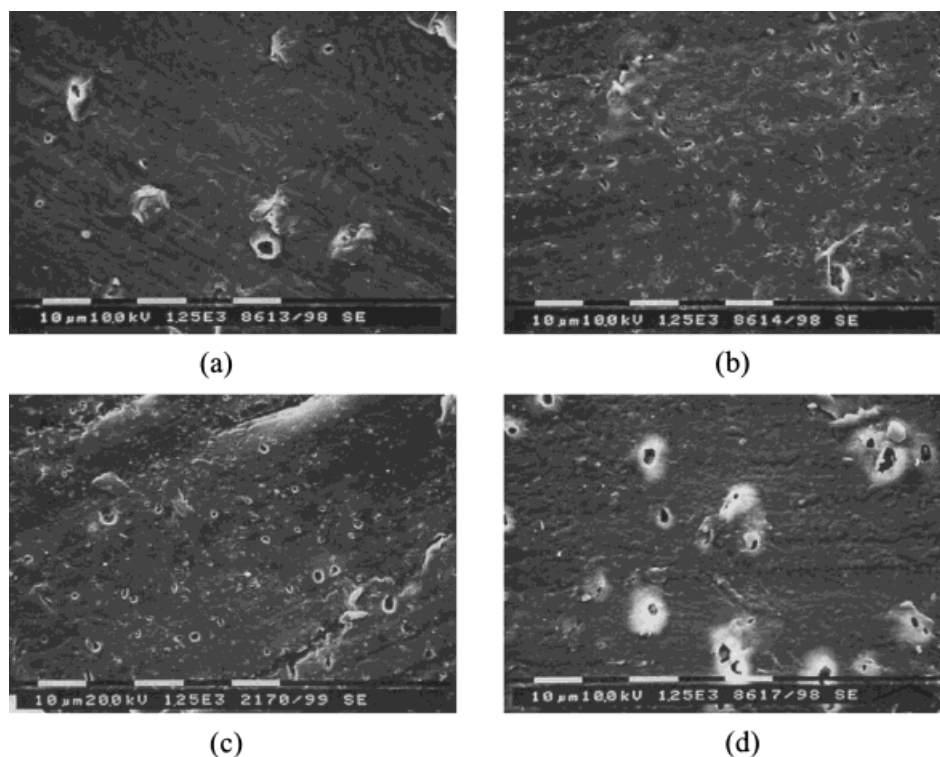


Figure 5 SEM images of the starch/PCL blends containing (a) PEG400 ($\times 1250$), (b) PEG3400 ($\times 1250$), (c) PEG8000 ($\times 1250$), or (d) PEG100,000 ($\times 1250$).

poned until they can initiate immediate dilatational shear yielding. PCL is a typical polymeric material which exhibits shear-yield deformation. Thus, the toughness of the starch/PCL blend in this study will become higher when the domain size of the starch phase is smaller. In a previous study on the PCL/starch blend,¹² the blend with the smaller starch granules showed a higher tensile toughness than that with the larger starch granules.

Figure 5 shows SEM images of the starch domains dispersed in the PCL matrix in the blends. The mean diameters of the starch domain measured using an image analyzer are $9.73 \mu\text{m}$ for PEG400, $2.34 \mu\text{m}$ for PEG3400, $3.60 \mu\text{m}$ for PEG8000, and $7.34 \mu\text{m}$ for PEG100,000. The starch domain size of the blend containing PEG3400 is smaller than those of the others and thus higher tensile toughness of the blend was observed. The smaller starch domain and higher tensile toughness of the blend containing PEG3400 may result from the most effective compatibilizing effect of PEG3400 for the blend. We thus tried to investigate the interactions between PEG and starch and between PEG and PCL in the blend by DSC and FTIR, respectively.

Previous studies showed that the mechanical properties of the starch/PCL blend are poor due to the poor miscibility between starch and PCL.^{9–12} We confirmed that there was no interaction between starch and PCL in the GS/PCL blend from the FTIR studies, the result of which is shown in Table I and will be discussed in detail in the latter part of this discussion. Thus, the change of the melting transition of starch will originate from the interaction degree of starch and PEG in the blend. Figure 6 shows the thermal behavior of the

Table I Relative Peak Area of the Carbonyl Stretching Band of PCLs Having Different Structures and Interactions

Sample	Amorphous (1737 cm^{-1})	Interacted (1730 cm^{-1})	Crystalline (1724 cm^{-1})
PCL	74.0	0.0	26.0
GS/PCL	74.1	0.0	25.9
Blend 1	68.5	14.3	17.2
Blend 2	68.5	21.5	10.0
Blend 3	66.8	27.4	5.8
Blend 4	65.2	28.7	6.1

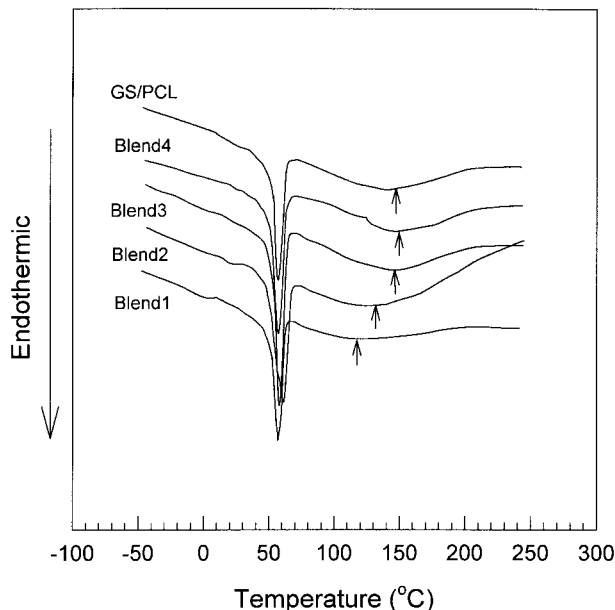


Figure 6 DSC heating thermograms of GS/PCL/PEG (40/60/10 wt ratio) blends with various PEG molecular weights. Heating rate: 10°C/min.

starch/PCL/PEG blends with different PEG molecular weights. The melting temperature of the starch in the GS/PCL blend not containing PEG was about 150°C. As shown in Figure 6, the melting temperature of the starch in each blend increased gradually with increase of the PEG molecular weight for blends 1–3. For blend 4, the melting temperature of the starch was almost same as that in the GS/PCL blend not containing PEG. The starch has three hydroxyl groups in each monomeric unit, and thus it is very hydrophilic and will effectively interact with other polar groups. The number of hydroxyl group per unit mass of the low molecular weight PEG is higher than that of the high molecular weight PEG, indicating that the low molecular weight PEG is more hydrophilic than is the high molecular weight PEG. PEG400 is thus the most miscible with starch and it can lower the starch melting temperature more effectively than can the other PEGs, as shown in Figure 6. The low molecular weight PEG will make the starch chains more mobile, which might contribute to the enhancement of toughness.

For better understanding of the results as shown in Figures 4 and 5, the interaction between PCL and PEG was also considered. To obtain information on the interaction between PCL and PEG as a function of the PEG molecular weight,

we took the FTIR spectra of the pure PCL and the PCL/PEG400 blend and focused on the carbonyl stretching vibration observed in the region of 1600–1800 cm^{-1} . As shown in Figure 7(a), which is the FTIR spectrum for the pure PCL, the carbonyl stretching frequencies, $\nu_s(\text{C}=\text{O})$, were observed at 1724 and 1737 cm^{-1} , which correspond to the crystalline and amorphous components.¹⁶ Figure 7(b) shows the FTIR spectra of the PCL/PEG400 blend in the region of 1600–1800 cm^{-1} . From Figure 7(b), the new peak, which was not observed from the FTIR spectrum of the pure PCL, appeared at about 1730 cm^{-1} . In the previous reports of Coleman and Zarian¹⁶ and Hubbell and Cooper,¹⁷ the carbonyl stretching of the PCL having a specific interaction in the PVC/PCL blend was observed around 1730 cm^{-1} . Liberman et al.¹⁸ also reported that the PEO/PMMA blend system was compatible and might form thermodynamically stable mixtures because of the specific interaction between the carbonyl groups of PMMA and the ether groups of PEG. Thus, it can be concluded that the carbonyl stretching of the PCL amorphous region having a specific interaction between the carbonyl groups of PCL and the ether groups of PEG is observed at 1730 cm^{-1} in the PCL/PEG blend.

For the starch/PCL/PEG blend systems, we tried to obtain qualitative information on the rel-

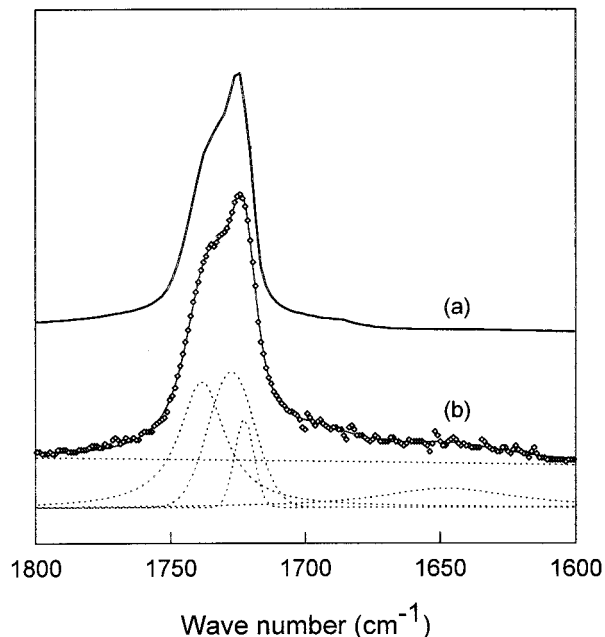


Figure 7 FTIR spectrum of (a) pure PCL and (b) PCL/PEG400 (5/5 wt ratio) blend in the range of 1600–1800 cm^{-1} .

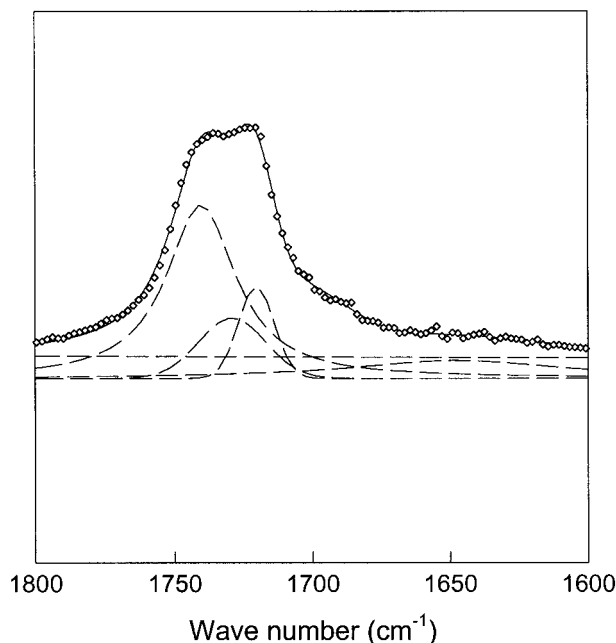


Figure 8 FTIR spectrum of GS/PCL/PEG3400 (40/60/10 wt ratio) blend in the range of 1600–1800 cm^{-1} .

ative amount of the interacting carbonyl groups of PCL with PEG by deconvolution of the carbonyl stretching band of the PCL in the blend. A typical result for the deconvolution is shown in Figure 8. The carbonyl stretching band of the PCL in the starch/PCL/PEG blend was also resolved into three components: The crystalline component was observed at 1724 cm^{-1} ; the amorphous component interacting with PEG, at 1730 cm^{-1} ; and the amorphous component without interaction with PEG, at 1737 cm^{-1} . From each resolved peak area, we could calculate the relative fraction of the carbonyl groups interacting with PEG. The interacting carbonyl band was not observed in either the pure PCL or the GS/PCL blend. Their carbonyl bands were resolved into only two peaks corresponding to the crystalline and amorphous components. By addition of PEG to the blend, the interacting carbonyl band of the PCL in the blend was generated in the FTIR spectra.

The relative peak area of the components in the blend is summarized in Table I. As seen from Table I, it is found that there is no interaction between the gelatinized starch and PCL. As the PEG molecular weight becomes higher, the relative fraction of the interacting carbonyl groups is found to increase. As already shown in Figure 6, the miscibility of PEG with starch increased with decrease of PEG molecular weight owing to the

increase of the hydrophilicity of the PEG with decrease of the PEG molecular weight. Therefore, the low molecular weight PEG (PEG400) is expected to be distributed mainly in the starch phase instead of the PCL phase, which resulted in that the low molecular weight PEG could not interact with the PCL. However, as the molecular weight of PEG increases, the miscibility between starch and PEG becomes poorer and the higher molecular weight PEG began to diffuse out from the starch phase.

When the PEG molecular weight is 100,000, PEG is not miscible with starch any more and phase separation occurs, which is evidenced from Figure 6: The melting temperature of the starch in the GS/PCL blend was almost the same as that in blend 4. In this case, PEG100,000 would be distributed mainly in the PCL phase and interacts with PCL instead of starch. Thus, blend 4 could show a brittle deformation behavior which was similar to the one for the GS/PCL. From these results, it is found that, in the case of low or high molecular weight PEG, PEG could not act effectively as a compatibilizer for the gelatinized starch/PCL blend, resulting in the poor adhesion between the two phases. The poor adhesion leads to a very weak and brittle mechanical behavior.

However, PEG3400 is expected to effectively interact with both starch and PCL in the blend. Only the PEG which has a proper molecular weight could act as an effective compatibilizer for the gelatinized starch/PCL blend.

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