

Research Article

Improvements in the Rheological Properties, Impact Strength, and the Biodegradability of PLA/PCL Blend Compatibilized by Electron-Beam Irradiation in the Presence of a Reactive Agent

Jae Sung Jeon,^{1,2} Do Hung Han,¹ and Boo Young Shin ¹

¹School of Chemical Engineering, Yeungnam University, 280 Daehak-Ro, Gyeongsan 38541, Republic of Korea

²Technical Team, Poongsan Corporation, 2606-10, Hoguk-Ro, Gyeongju 38026, Republic of Korea

Correspondence should be addressed to Boo Young Shin; byshin@ynu.ac.kr

Received 27 August 2018; Revised 2 October 2018; Accepted 16 October 2018; Published 4 November 2018

Academic Editor: Yuanshi Li

Copyright © 2018 Jae Sung Jeon et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this study, we blended poly(ϵ -caprolactone) (PCL) into poly(lactic acid) (PLA) and compatibilized these PLA/PCL blends by electron-beam irradiation in the presence of a reactive agent to overcome drawbacks of PLA. To produce compatibilized blends, mixtures of the PLA/PCL/reactive agent were prepared using a twin-screw extruder and exposed to electron-beam radiation at room temperature. Glycidyl methacrylate (GMA) was chosen as the reactive agent to achieve interfacial cross-copolymerization between PLA and PCL phases. Morphological, rheological, and mechanical properties and biodegradabilities of blends were investigated. The morphological study showed significantly improved interfacial adhesion for compatibilized blends, and this was supported by FTIR analysis and a rheological study. Impact strengths, thermal stabilities, and rheological properties of PLA/PCL blends were improved by compatibilization, and the biodegradabilities of compatibilized PLA/PCL blends were greater than that of pure PLA.

1. Introduction

Poly lactic acid (PLA) is an important bio-based and biodegradable polymer of high tensile strength and modulus, which now can be found in various industrial items, and is produced from nonfossil renewable resources by fermentation of polysaccharide [1]. However, PLA has some drawbacks, which include low melt viscosity, low thermal stability, and brittleness, which limits its potential applications. Furthermore, although PLA is biodegradable, it degrades at a relatively low rate, and this leaves scope for improvement for industrial composting solid waste treatment. To overcome these shortcomings of PLA, we considered blending it with poly(ϵ -caprolactone) (PCL), which is a soft biodegradable polymer. However, as is the case for most polymer blends, PLA and PCL are immiscible and incompatible, and considerable efforts have been made to enhance compatibility between these two polymers to achieve acceptable PLA/PCL

blends. As a result, many compatibilization strategies have been devised, such as reactive compatibilization or methods based on the addition of a polymeric compatibilizer [2–14].

The addition of poly(L-lactide-co-caprolactone) (PLLA-CL) as a polymeric compatibilizer [3, 4] is one of the common ways to increase compatibility of the PLA/PCL blend [3, 4]. The enzymatic hydrolyzability of PLA/PCL blend compatibilized by the addition of PLLA-CL decreased with increasing PLLA-CL content; however, tensile strength, Young's modulus, and elongation at break were increased by compatibilization. For the reactive compatibilized PLA/PCL blends, Semba et al. and Wang et al. [5, 6] reported that the biodegradability and mechanical properties such as tensile strength, Young's modulus, elongation at break, and impact strength of blends were increased by reactive compatibilization.

Recently, exposure of polymer blends to high-energy radiation at room temperature has also been introduced to

improve PLA/PCL compatibility [15–18]. High-energy radiation has several advantages; for example, it provides continuous operation, requires little time, and causes less atmospheric pollution; curing is performed at ambient temperature, and because it enables process control, it offers design flexibility [19].

In this work, we blended PCL and PLA and compatibilized mixtures by exposing them to electron-beam irradiation (20 kGy) in the presence of glycidyl methacrylate (GMA) with the aim of reducing brittleness and increasing thermal stability, melt viscosity, and biodegradability of PLA. Morphological, rheological, and mechanical properties of compatibilized PLA/PCL blends were measured and compared with those of uncompatibilized blends. In addition, the biodegradabilities of compatibilized PLA/PCL (90/10) and (70/30) blends were determined under specific composting conditions [20].

2. Materials and Methods

2.1. Materials. PLA (NatureWorks® PLA Polymer 4032D) of density 1.24 g/cm^3 and a melt flow index of 6.5 g/10 min (measured at 190°C at a load of 2.16 kg) was purchased from NatureWorks LLC, and PCL (TONE-787) of the melt flow index 0.5 g/10 min was obtained from Dow/Union Carbide. Glycidyl methacrylate (GMA) and *N,N*-dimethyl formamide (DMF) were supplied by Sigma-Aldrich (WI, USA).

2.2. Preparation of PLA/PCL/GMA Mixtures. The blend ratios of PLA to PCL of 90/10 and 70/30 (weight percent) were used in the study, and the amount of GMA content was fixed to 3 parts per hundred parts of resin (phr) based on the total mass of PLA and PCL. PLA, PCL, and GMA were mixed in a plastic bag before being extruded in a twin-screw corotating extruder (Ikegai, PCM-45, Japan). The extruder was operated at 200 rpm at a constant feed rate of 5 kg/h , and barrel and die temperatures were controlled at 190°C and 185°C , respectively. The extrudate was cooled in chilled water and cut into pellets of $\sim 1\text{ mm}$ diameter. The pellets were then dried for 24 hours at 50°C prior to electron-beam treatment. PLA/PCL blends without GMA (uncompatibilized PLA/PCL blends) were also prepared for comparison purposes [21].

2.3. Electron-Beam Irradiation. The pellets of PLA/PCL/GMA mixtures were irradiated using a commercial electron-beam accelerator (ELV-0.5, BINP, Russia, at a maximum beam current of 40 mA and beam energy of $0.5\text{--}0.7\text{ MeV}$) under a nitrogen atmosphere. The irradiation dose was controlled by varying beam currents from 0.5 to 10 mA and conveyor speeds from 1 to 2 m/min . Radiation doses were measured by dosimetry (GENESYS 20, Thermo SCIENTIFIC Co.) using dosimetry film (B3 WINdose Dosimetry, GEX Co.). The acceleration energy used was 0.7 MeV , and the effective penetration depth was $\sim 2\text{ mm}$ for a substrate of density 1 g/cm^3 [16, 21, 22]. The compatibilized blends produced were dried in an oven at 50°C for 12 hours to eliminate residual radicals.

2.4. Separation of Blends. For FTIR analysis, compatibilized and uncompatibilized PLA/PCL (70/30) blends were separated into components using *N,N*-dimethyl formamide (DMF), which dissolves PLA but not PCL [6, 23]. The separation and purification was carried out as follows; first, a blend was immersed in DMF for 24 hours at room temperature. The solution was then filtered, and the dissolved polymer was precipitated by adding water. To obtain high-purity precipitate, the process was repeated a second time. Unreacted GMA was removed because it is soluble in water. The precipitate so obtained was vacuum dried at 50°C for 24 hours.

2.5. Characterization. Morphological analysis was carried out by scanning electron microscopy (SEM, Hitachi model s-4200, Japan) on cryofractured surfaces of blends. Infrared spectra were obtained by Fourier transform infrared spectroscopy (FTIR; Excalibur Spectrometer FTS 3000MX, Bio-Rad, USA) by grinding a constant weight of the dry sample with KBr and then pressing the powder mix to form transparent discs. Rheological properties were measured using a rotational rheometer (Physica MCR 30; Anton Paar GmbH, Germany). The equipment was run in parallel plate geometry with a plate of diameter 25 mm and a gap of 1.5 mm at 190°C . Dynamic frequency sweep testing was performed at a strain of 2% in the angular frequency range 0.5 to 500 rad/s . Dynamic time sweep testing was also used to examine the thermal stabilities of blends at an angular frequency of 1.0 rad/s and a strain of 2% [24]. The mechanical properties of pure PLA and blends were determined using a tensile tester (Instron 4464; Instron, USA), and impact strengths were measured using an impact tester (Model 43-76; TMI Test Machines Inc., USA). The tensile and impact strength test specimens were prepared by injection molding (Nissei 35-oz, Japan) at a cylinder temperature of 200°C and mold temperature of 40°C . Tensile testing was performed at room temperature with a gauge speed of 10 mm/min and a gauge length of 25 mm . The tensile and impact strengths mentioned are the mean values of four independent tests. Biodegradability studies were performed as per ISO 14855 under aerobic controlled composting conditions [20, 25]. Biodegradability was defined as the percentage of carbon from test materials mineralized to carbon dioxide during composting. Three 3 liter vessels were used for each test material. Each vessel contained 30 g of the test material in a 300 g mature compost inoculum (Biocom, Kanglim Organic Company, Korea). The entire apparatus was placed in a dark incubator and maintained at $58 \pm 2^\circ\text{C}$ for 45 days. Amounts of carbon dioxide produced from test materials were calculated by subtracting the total amount evolved in blank vessels containing only compost inoculum.

3. Results and Discussion

3.1. Morphologies of Blends. The morphologies of PLA/PCL blends compatibilized or not by electron-beam treatment in the presence of GMA were compared. Figure 1 shows the

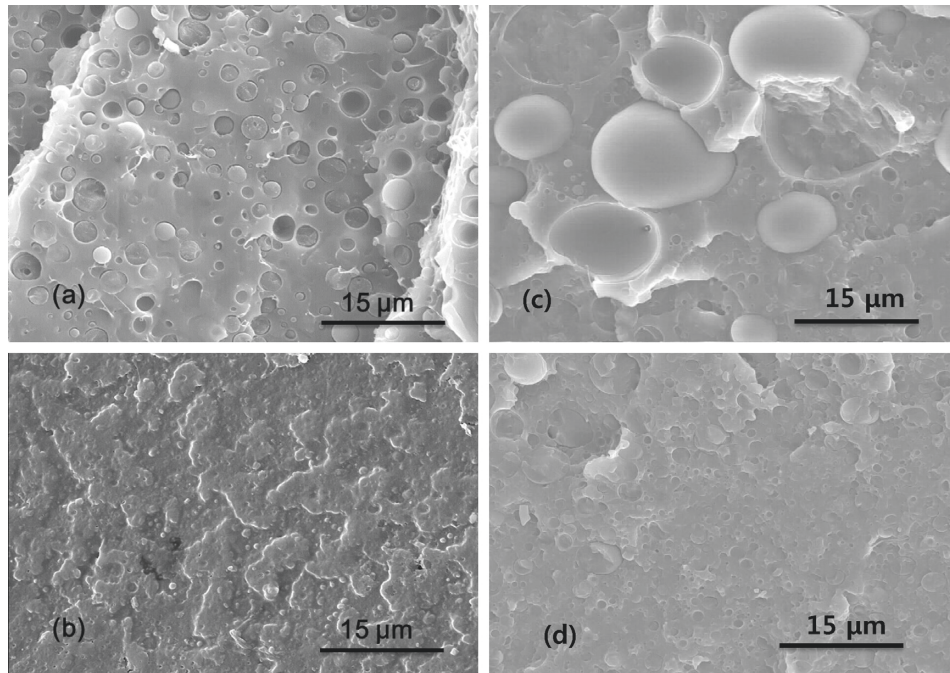


FIGURE 1: SEM images of cryofractured surfaces of uncompatibilized (a) and compatibilized (b) PLA/PCL (90/10) blends and uncompatibilized (c) and compatibilized (d) PLA/PCL (70/30) blends.

SEM images of cryofractured surfaces of compatibilized and uncompatibilized PLA/PCL (90/10) and (70/30) blends. The SEM images of uncompatibilized blends (Figures 1(a) and 1(c)) showed voids between the dispersion phase (PCL) and the continuous phase (PLA) and the removal of some particles from the PLA matrix. On the contrary, no voids or PCL dislodgement was observed in compatibilized blends (Figures 1(b) and 1(d)). In addition, the diameters of dispersed PCL particles were smaller in compatibilized blends, which were attributed to reduced interfacial tension difference between the two phases. These morphological results indicate that interfacial adhesion between the PLA matrix and the PCL dispersion was substantially enhanced by electron-beam treatment, presumably caused by electron-beam initiated cross-copolymerization between PLA and PCL at PLA/PCL interfaces [21, 26].

3.2. FTIR Analysis. The FTIR analysis was performed to support the results of the morphology study, that is, to provide evidence of increased compatibility due to cross-copolymerization by electron-beam irradiation. Figure 2 presents the FTIR spectra (3200–650 cm^{-1}) of pure PLA, pure PCL, and the separated substances from uncompatibilized and compatibilized PLA/PCL (70/30) blends. The spectrum of pure PLA (Figure 2(a)) showed absorption bands corresponding to C=O stretching vibration at 1745 cm^{-1} , CH₃ stretching at 2994 and 2947 cm^{-1} , asymmetric bending absorption of CH₃ at 1453 cm^{-1} , and C-O-C stretching at 1181, 1084, and 1043 cm^{-1} [27]. On the contrary, the spectrum of pure PCL (Figure 2(b)) showed absorption bands corresponding to C=O stretching vibration at 1723 cm^{-1} , the CH₂ stretching at 2942 and 2864 cm^{-1} , and

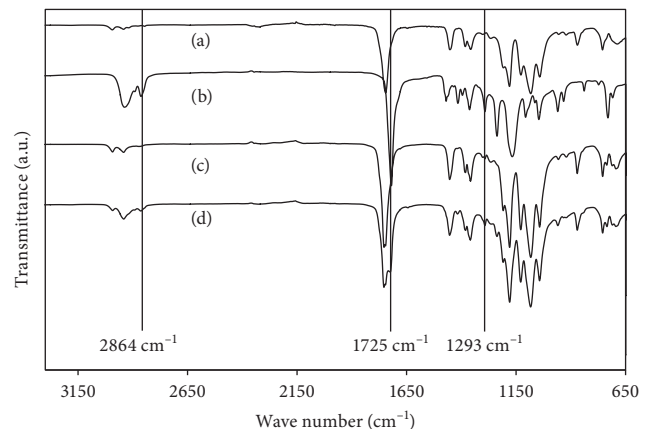


FIGURE 2: FTIR spectra (3200–650 cm^{-1}) of pure PLA (a), pure PCL (b), and the separated substances from uncompatibilized (c) and compatibilized (d) PLA/PCL (70/30) blends.

C-O and C-C (crystal phase) stretching absorption at 1293 cm^{-1} [27]. The spectrum (Figure 2(c)) of the separated substance from the uncompatibilized blend was similar to that of the pure PLA (Figure 2(a)) and showed characteristic PLA bands, such as C=O stretching vibration at 1745 cm^{-1} and CH₃ stretching at 2994 and 2947 cm^{-1} . However, C=O stretching vibration of PCL at 1723 cm^{-1} and CH₂ stretching at 2864 cm^{-1} were absent. These results indicate the absence of an interfacial reaction between PLA and PCL. On the contrary, the spectrum (Figure 2(d)) of the separated component from the compatibilized blend displayed strong absorption bands corresponding to C=O stretching of both PLA and PCL at 1746 and 1725 cm^{-1} , respectively, which were shifted a little to higher wave numbers compared to

those of pure PLA (1745 cm^{-1}) and PCL (1723 cm^{-1}). In addition, we also observed CH_2 and C-C (crystal phase) of PCL at 2864 cm^{-1} and 1293 cm^{-1} of PCL. These FTIR results support that electron-beam-initiated cross-copolymerization had occurred in the presence of GMA at the PLA/PCL interface [21].

3.3. Rheological Properties. Dynamic rheological properties of polymers and their blends are highly dependent on polymer molecular weight and blend structure and compatibility [2, 7, 10, 28]. In the present study, we first determined the optimum radiation dose required to compatibilize PLA/PCL blends and then investigated the storage moduli and complex viscosities of the compatibilized blends prepared at optimum dosage. For this purpose, we prepared compatibilized PLA/PCL (90/10) blends irradiated at various doses (5–200 kGy) in the presence of GMA and then measured their complex viscosities in the angular frequency range 0.5–100 rad/s. Change in qualitative behaviors with radiation dose indicated that some chemical reactions, such as grafting, crosslinking, and chain scission, had been induced. As shown in Figure 3, the complex viscosity of the compatibilized PLA/PCL blend increased on increasing dosage to 20 kGy. However, blend complex viscosity decreased when the radiation dose was increased over 20 kGy, which was considered to have been caused by chain scission [19, 29]. In addition, complex viscosities of all compatibilized blends were higher than those of the uncompatibilized blend. Exceptionally, the compatibilized blend irradiated at 200 kGy had lower complex viscosity than uncompatibilized PLA/PCL blend in the high-frequency range due to decreased molecular weight and increased molecular weight distribution, which were caused by chain scission. Based on these results, we chose 20 kGy as the optimum dosage for preparing compatibilized PLA/PCL blends.

Figure 4 shows changes in the storage moduli of pure PLA, pure PCL, uncompatibilized blends, and blends compatibilized by electron-beam irradiation at 20 kGy. In the absence of increased interfacial adhesion, the storage moduli of PLA/PCL blends would be expected to lie between the values of the pure PLA and PCL. As shown in Figure 4, the storage moduli of uncompatibilized PLA/PCL (90/10) and (70/30) blends lay between those of pure PLA and PCL over the frequency ranges of 20–500 rad/s and 7–500 rad/s, respectively, but were higher than pure PLA and PCL below 20 rad/s (PLA/PCL (90/10) blend) and 7 rad/s (PLA/PCL (70/30) blend), respectively (arrows in Figure 4). This increase in the storage moduli of uncompatibilized blends might be caused by hydrogen bonding interaction between ester carbonyls and hydroxyls of PCL and PLA at the interface [30]. However, modulus values between those of pure PLA and PCL at higher frequencies indicate that hydrogen bonding forces were negligible compared with dynamic shear force portion required for deformation [30]. This suggests that interfacial adhesion induced by hydrogen bonding was not enough to transfer exerted stress at the interface between PLA and PCL phases. Interestingly, below 2 rad/s, the modulus of the uncompatibilized PLA/PCL

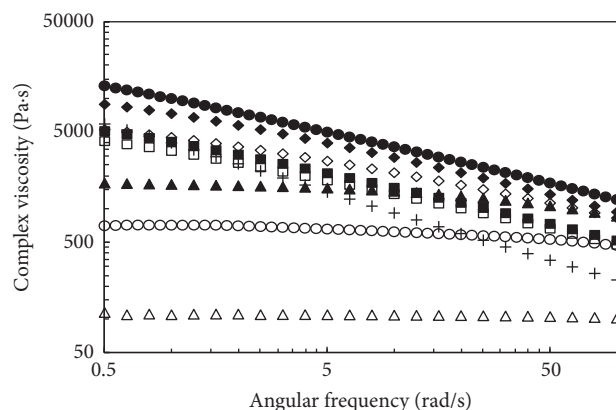


FIGURE 3: Complex viscosities (measured at 190°C) of pure PLA (\blacktriangle), pure PCL (\triangle), uncompatibilized PLA/PCL (90/10) (\circ), and compatibilized PLA/PCL (90/10) blends irradiated at 5 kGy (\diamond), 10 kGy (\blacklozenge), 20 kGy (\bullet), 50 kGy (\square), 100 kGy (\blacksquare), and 200 kGy (\oplus).

(70/30) blend was higher than that of the uncompatibilized PLA/PCL (90/10) blend despite a higher PCL content, presumably because total interfacial area had been increased, and thus, the amount of interfacial hydrogen bonding force had been increased.

In contrast to uncompatibilized blends, the storage moduli of all compatibilized blends were higher than those of pure PLA and PCL over the entire frequency range tested, indicating that compatibility of the PLA/PCL blend has been increased by electron-beam irradiation. In addition, high interfacial adhesion between continuous and dispersed phases can induce morphological stability by acting as a morphological network structure and thus increase blend moduli as is observed for cross-linked polymers. Moreover, the storage moduli of compatibilized PLA/PCL (90/10) and (70/30) blends were about 900 and 640 times higher, respectively, than those of pure PLA at an angular frequency of 0.5 rad/s.

Changes in the complex viscosities of pure PLA and PCL and of all blends as a function of angular frequency are shown in Figure 5. Pure PLA and PCL exhibited a long Newtonian viscosity plateau region and uncompatibilized PLA/PCL (90/10) and (70/30) blends showed weak shear thinning behavior. Complex viscosity of the uncompatibilized PLA/PCL (70/30) blend lays between those of pure PLA and PCL due to lack of compatibility, whereas that of the uncompatibilized PLA/PCL (90/10) blend was higher than pure PLA below an angular frequency 1 rad/s due to the effect of hydrogen bonding, as mentioned above.

For compatibilized blends, however, complex viscosities were much higher than those of pure PLA or pure PCL and showed strong shear thinning behavior over the whole frequency range. In fact, complex viscosities of compatibilized PLA/PCL (90/10) and (70/30) blends were 18 and 11 times higher than that of pure PLA at 0.5 rad/s, respectively. These rheological results provide additional evidence of enhanced compatibility due to electron-beam-induced cross-copolymerization between PLA and PCL [21]. In addition, the enhanced melt complex viscosities and storage moduli of electron-beam-treated PLA/PCL blends would

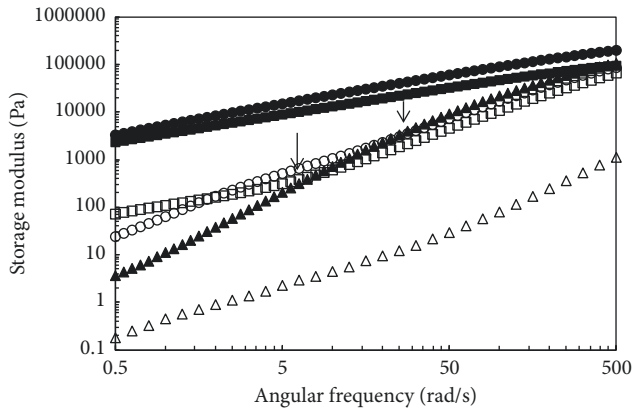


FIGURE 4: Storage modulus curves (measured at 190°C) of pure PLA (▲), pure PCL (△), compatibilized PLA/PCL (90/10) (○), uncompatibilized PLA/PCL (90/10) (○), compatibilized PLA/PCL (70/30) (■), and uncompatibilized PLA/PCL (70/30) (□) blends.

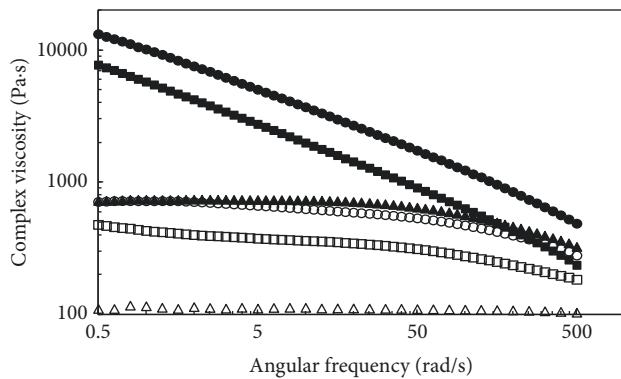


FIGURE 5: Complex viscosity curves of pure PLA (▲), pure PCL (△), compatibilized PLA/PCL (90/10) (○), uncompatibilized PLA/PCL (90/10) (○), compatibilized PLA/PCL (70/30) (■), and uncompatibilized PLA/PCL (70/30) (□) blends at 190°C.

make them suitable for applications, such as thermoforming, blow molding, and foaming, which require high melt viscosity and elasticity.

3.4. Thermal Stability Investigation. It is well known that thermal degradation reaction occurs during the melt processing of polymers and that this affects their final properties and those of their blends [2]. Thus, the thermal stability of polymers is important for long-term melt processing, such as that required for extrusion processes. To investigate thermal stabilities of pure PLA and PCL, and of PLA/PCL blends, oscillatory complex viscosities were measured as a function of time at a strain of 2% and an angular frequency of 1 rad/s at 190°C. Complex viscosities (η^*), normalized by their initial complex viscosities at $t = 0$ (η^{*o}), are presented as a function of time for pure PLA and PCL and uncompatibilized PLA/PCL blends in Figure 6. The normalized complex viscosities ($\eta^*(t)/\eta^{*o}$) of pure PLA and PCL decreased to 0.62 and 0.83, respectively, after 30 min indicating PCL was more stable than PLA during melt processing. These decreases corresponded to a loss in molecular weight

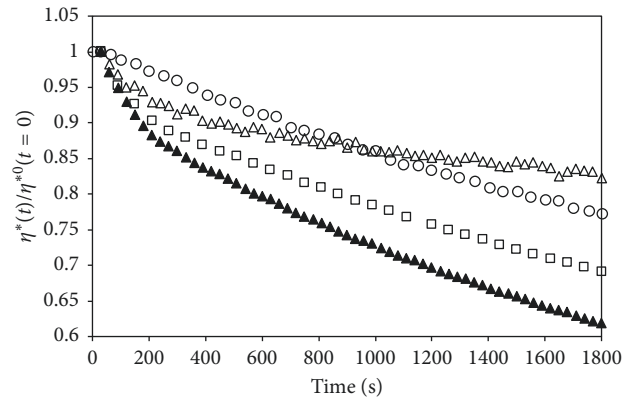


FIGURE 6: Evolution of $\eta^*(t)/\eta^{*o}(t=0)$ versus time of pure PLA (▲), pure PCL (△), uncompatibilized PLA/PCL (90/10) (○), and uncompatibilized PLA/PCL (70/30) (□) blends at 190°C.

caused by thermal degradation in the rheometer. Furthermore, the normalized complex viscosities of uncompatibilized PLA/PCL (90/10) and (70/30) blends were higher than that of pure PLA due to the blending of PCL.

To observe the effect of compatibilization on the thermal stability of blends, we also normalized complex viscosities of compatibilized PLA/PCL (90/10) and (70/30) blends and compared them with those of uncompatibilized blends (Figure 7). The normalized complex viscosities of uncompatibilized PLA/PCL (90/10) and (70/30) decreased to 0.77 and 0.69, respectively, after 30 min at 190°C, whereas those of compatibilized PLA/PCL (90/10) and (70/30) increased to 1.44 and 1.60, respectively. This increase in the normalized complex viscosities of compatibilized blends indicates improved thermal stability. Interestingly, the normalized complex viscosities of compatibilized blends were higher than 1. A similar result for the normalized complex viscosity of a compatibilized blend was reported by Al-Itry et al. [2]. From these results, we conclude the thermal stability of PLA is improved by the addition of PCL and by the compatibilization treatment, which would provide more stable melt processing for industrial manufacturing operations.

3.5. Mechanical Properties. Figure 8 presents the impact strengths of pure PLA and PLA/PCL blends as determined by the notched Izod impact test. The impact strength of pure PLA was relatively low (28.8 J/m) due to its brittleness [31]. The impact strength of uncompatibilized PLA/PCL (90/10) blend was 1.8 times higher (51.9 J/m) than that of pure PLA, whereas that of the uncompatibilized PLA/PCL (70/30) blend (31.9 J/m) was similar despite a higher content of soft PCL, which was probably due to the greater particle size of PCL than that of the uncompatibilized PLA/PCL (90/10) blend. As shown in Figure 1(c), the uncompatibilized PLA/PCL (70/30) blend had much larger PCL particles than the PLA/PCL (90/10) blend (Figure 1(a)) and had voids at interfaces between the PLA matrix and the PCL particles, which result in local stress concentration in a broader region, and this caused more rapid fracture progress [32]. Interestingly, the impact strengths of compatibilized blends

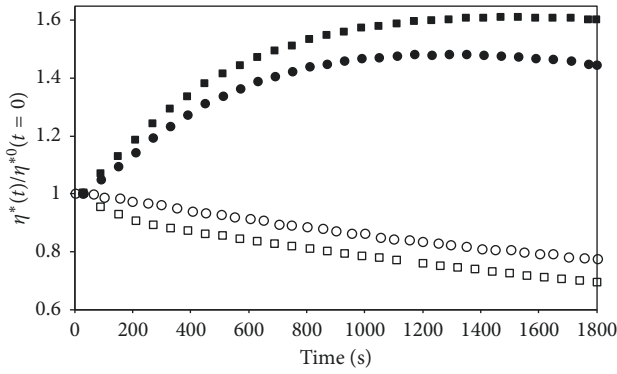


FIGURE 7: Evolution of $\eta^*(t)/\eta^{*o}(t=0)$ versus time for compatibilized PLA/PCL (90/10) (○), uncompatibilized PLA/PCL (90/10) (○), compatibilized PLA/PCL (70/30) (■), and uncompatibilized PLA/PCL (70/30) (□) blends at 190°C.

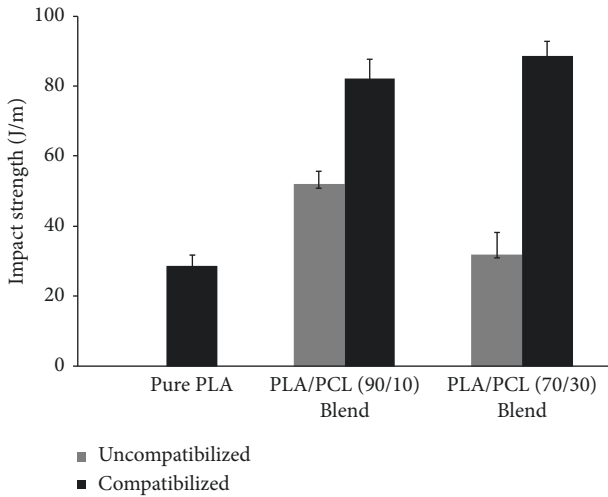


FIGURE 8: Impact strengths of pure PLA, compatibilized PLA/PCL blends, and uncompatibilized PLA/PCL blends.

were markedly higher than those of uncompatibilized blends. More specifically, the impact strengths of compatibilized PLA/PCL (90/10) and (70/30) were 2.9 and 3.1 times higher, respectively, than that of pure PLA.

Figure 9 shows the tensile moduli of pure PLA and compatibilized and uncompatibilized PLA/PCL blends. For uncompatibilized blends, tensile moduli decreased as PCL content increased and were lower than that of pure PLA, whereas compatibilized blends had tensile moduli similar to that of pure PLA due to increased compatibility.

3.6. Biodegradability. The ASTM defines “biodegradable” as being “capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass, predominantly due to the enzymatic actions of microorganisms” [20]. Figures 10 and 11 show the results of our biodegradability studies on pure PLA and PCL and compatibilized PLA/PCL (90/10) and (70/30) blends. The test apparatus was calibrated using cellulose as the reference material and was found to biodegrade by 91% after 45 days.

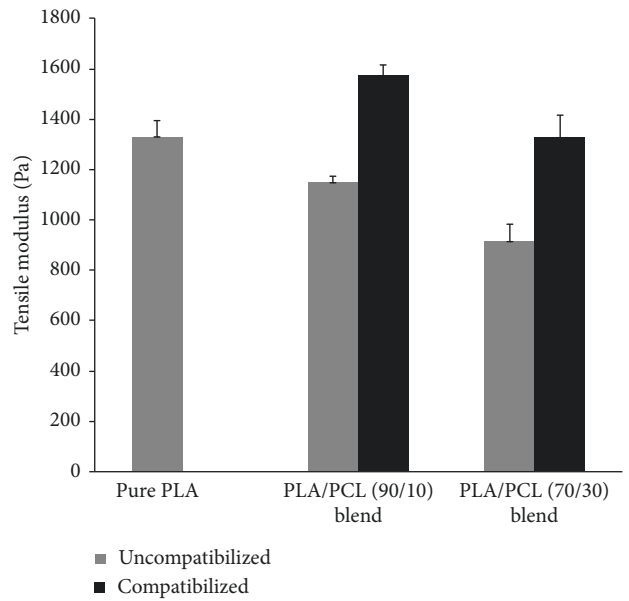


FIGURE 9: Initial tensile moduli of pure PLA, compatibilized PLA/PCL blends, and uncompatibilized PLA/PCL blends.

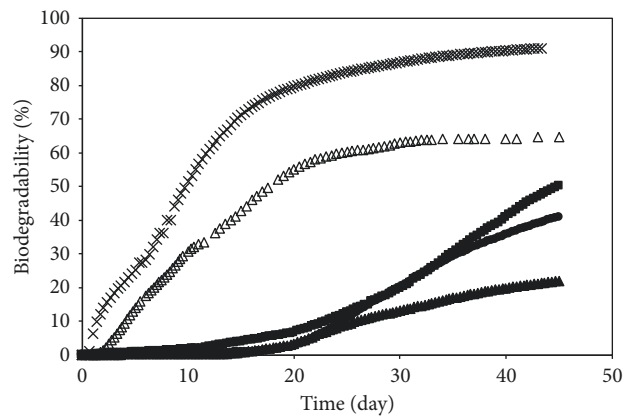


FIGURE 10: Cumulative biodegradation of cellulose (x), pure PLA (▲), pure PCL (△), and compatibilized PLA/PCL (90/10) (●) and (70/30) (■) blends.

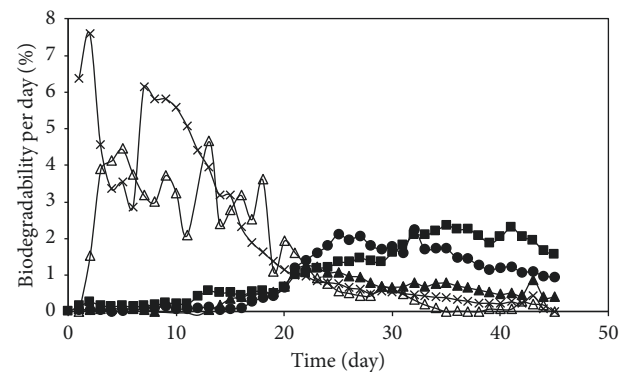


FIGURE 11: Rate of biodegradation of cellulose (x), pure PLA (▲), pure PCL (△), and compatibilized PLA/PCL (90/10) (●) and (70/30) (■) blends.

The biodegradabilities of pure PLA and PCL were 22 and 65%, respectively, after the same period (Figure 10). Initial time lags (time required for the hydrolysis of polymer into diffusible oligomers before the onset polymer mass loss or microbial utilization) of pure PLA and PCL were approximately 14 and 2 days, respectively [20]. The lower biodegradability and longer initial time lag of pure PLA might be problematic when PLA is composted with easy compostable waste under industrial composting conditions [20, 33]. The biodegradabilities of compatibilized PLA/PCL (90/10) and (70/30) were increased to 41 and 50%, respectively, and initial time lags were 12 and 7 days, respectively. Cellulose and PCL had very high biodegradation rate at the earlier composting period, whereas PLA had very low biodegradation rate over the entire test period. Compatibilized PLA/PCL blends had high biodegradation rate after 20 composting days, presumably due to the fact that, in PLA/PCL blends, PCL degraded first to create holes which accelerated the degradation of PLA [34, 35].

4. Conclusions

In this work, PCL was blended into PLA at the loading of 10 or 30% by weight to try to overcome the limitations (brittleness, low melt viscosity, thermal stability, and relatively poor biodegradability) of PLA. PLA/PCL blends were compatibilized by electron-beam irradiation in the presence of GMA. Morphology study showed that compatibilization diminished PCL (dispersed phase) particle sizes in blends and markedly reduced voids at PLA/PCL interface. FTIR analysis provided supporting evidence of an interfacial reaction between PLA and PCL. Furthermore, the storage modulus and complex viscosity of the compatibilized PLA/PCL (90/10) blend were about 900 and 18 times higher, respectively, than those of pure PLA at an angular frequency of 0.5 rad/s. Compatibilization increased the normalized complex viscosities $\{\eta^*(t)/\eta^{*o}(t=0)\}$ of uncompatibilized PLA/PCL (90/10) and (70/30) from 0.77 to 0.69 to 1.44 and 1.60, respectively, and impact strengths of these compatibilized blends were 2.9- and 3.1-fold higher, respectively, than that of pure PLA. The biodegradability of the compatibilized PLA/PCL 70/30 blend was more than twice that of PLA (50% vs. 22%) after composting for 45 days. From these results, it can be concluded that blending PCL with PLA and electron-beam compatibilization in the presence of GMA reduced the brittleness of PLA and enhanced the storage modulus, melt viscosity, and thermal stability. In addition, the biodegradability of PLA was also increased by blending of PCL. It is believed these enhancements substantially increase the utilities of PLA/PCL blends.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors have no conflicts of interest to declare.

Acknowledgments

This research was supported by the Yeungnam University research grants in 2018.

References

- [1] R. Narayan, "Biobased and biodegradable polymer materials; rationale, drivers, and technology exemplars," in *Degradable Polymers and Materials*, K. C. Khemani and C. Scholz, Eds., pp. 281–306, American Chemical Society, Washington, DC, USA, 2006.
- [2] R. Al-Itry, K. Lamnawar, and A. Maazouz, "Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy," *Polymer Degradation and Stability*, vol. 97, no. 10, pp. 1898–1914, 2012.
- [3] H. Tsuji and T. Yamada, "Blends of aliphatic polyesters. VIII. Effects of poly(L-lactide-co- ϵ -caprolactone) on enzymatic hydrolysis of poly(L-lactide), poly(ϵ -caprolactone), and their blend films," *Journal of Applied Polymer Science*, vol. 87, pp. 412–419, 2003.
- [4] H. Tsuji, T. Yamada, M. Suzuki, and S. Itsuno, "Blends of aliphatic polyesters. Part 7. Effects of poly(L-lactide-co- ϵ -caprolactone) on morphology, structure, crystallization, and physical properties of blends of poly(L-lactide) and poly(ϵ -caprolactone)," *Polymer International*, vol. 52, no. 2, pp. 269–275, 2003.
- [5] T. Semba, K. Kidakawa, U. S. Ishiaku, and H. Hamada, "The effect of crosslinking on the mechanical properties of polylactic acid/polycaprolactone blends," *Journal of Applied Polymer Science*, vol. 101, no. 3, pp. 1816–1825, 2006.
- [6] L. Wang, W. Ma, R. A. Gross, and S. P. McCarthy, "Reactive compatibilization biodegradable blends of poly(lactic acid) and poly(ϵ -caprolactone)," *Polymer Degradation and Stability*, vol. 59, no. 1–3, pp. 161–168, 1998.
- [7] D. Wu, Y. Zhang, M. Zhang, and W. Zhou, "Phase behavior and its viscoelastic response of poly(lactide)/poly(ϵ -caprolactone) blend," *European Polymer Journal*, vol. 44, no. 7, pp. 2171–2183, 2008.
- [8] R. Dell'Erba, G. Groeninckx, G. Maglio, M. Malinconico, and A. Migliozi, "Immiscible polymer blends of semicrystalline biocompatible components: thermal properties and phase morphology analysis of PLLA/PCL blends," *Polymer*, vol. 42, no. 18, pp. 7831–7840, 2001.
- [9] G. Maglio, M. Malinconico, A. Migliozi, and G. Groeninckx, "Immiscible poly(lactide)/poly(ϵ -caprolactone) blends: influence of the addition of a poly(L-lactide)-poly(oxyethylene) copolymer on thermal behavior and morphology," *Macromolecular Chemistry and Physics*, vol. 205, no. 7, pp. 946–950, 2004.
- [10] W. Baker, C. Scott, and G. H. Gu, *Reactive Polymer Blending*, Hanser, Munich, Germany, 2001.
- [11] M. Harada, K. Lida, K. Okamoto, H. Hayashi, and K. Hirano, "Reactive compatibilization of biodegradable poly(lactide)/poly(ϵ -caprolactone) blends with reactive processing agents," *Polymer Engineering and Science*, vol. 48, no. 7, pp. 1359–1368, 2008.
- [12] C. L. Simões, J. C. Viana, and A. M. Cunha, "Mechanical properties of poly(ϵ -caprolactone) and poly(lactic acid) blends," *Journal of Applied Polymer Science*, vol. 112, no. 1, pp. 345–352, 2009.
- [13] C. C. Chen, J. Y. Chueh, H. Tseng, H. M. Huang, and S. Y. Lee, "Preparation and characterization of biodegradable PLA

- polymeric blends,” *Biomaterials*, vol. 24, no. 7, pp. 1167–1173, 2003.
- [14] T. Takayama and M. Todo, “Improvement of impact fracture properties of PLA/PCL polymer blend due to LTI addition,” *Journal of Materials and Science*, vol. 41, no. 15, pp. 4989–4992, 2006.
- [15] A. Singh and K. Bahari, “Use of high-energy radiation in polymer blends,” in *Polymer Blends Handbook*, L. A. Utracki, Ed., Vol. 2, Kluwer Academic Publishers, Dordrecht, Netherlands, 2003.
- [16] R. J. Woods and A. K. Pikaev, *Applied Radiation Chemistry: Radiation Processing*, John Wiley & Sons, Hoboken, NJ, USA, 1994.
- [17] Y. Komada, L. D. B. Machado, C. Giovedi, and K. Nakayama, “Gamma radiation effect on structural properties of PLLA/PCL blends,” *Nuclear Instruments and Methods in Physics Research Section B*, vol. 265, no. 1, pp. 294–299, 2007.
- [18] A. Kondyurin and M. Bilek, *Ion Beam Treatment of Polymers*, Elsevier, Amsterdam, The Netherlands, 2008.
- [19] R. A. Khan, D. Dussault, S. Salmieri, A. Safrany, and M. Lacroix, “Improvement of the mechanical and barrier properties of methylcellulose-based films by treatment with HEMA and silane monomers,” *Radiation Physics and Chemistry*, vol. 81, no. 8, pp. 927–931, 2012.
- [20] J. B. Snook, “Biodegradability of polylactide film in simulated composting environments,” M. S. thesis, Michigan State University, Lansing, MI, USA, 1994.
- [21] B. Y. Shin and D. H. Han, “Compatibilization of immiscible poly (lactic acid)/poly (ϵ -caprolactone) blend through electron-beam irradiation with the addition of a compatibilizing agent,” *Radiation Physics and Chemistry*, vol. 83, pp. 98–104, 2013.
- [22] D. Han, J. Jang, B. Kim, and B. Shin, “Manufacturing and foaming of high melt viscosity of polypropylene by using electron beam radiation technology,” *Polymer Engineering and Science*, vol. 46, no. 4, pp. 431–437, 2006.
- [23] C. Han, X. Ran, K. Zhang, Y. Zhuang, and L. Dong, “Thermal and mechanical properties of poly(ϵ -caprolactone) cross-linked with γ radiation in the presence of isocyanurate,” *Journal of Applied Polymer Science*, vol. 103, no. 4, pp. 2676–2681, 2007.
- [24] B. Y. Shin and D. H. Han, “Viscoelastic properties of PLA/PCL blends compatibilized with different methods,” *Korea-Australia Rheology Journal*, vol. 29, no. 4, pp. 295–302, 2017.
- [25] B. Y. Shin, S. I. Lee, Y. S. Shin, S. Balakrishnan, and R. Narayan, “Rheological, mechanical and biodegradation studies on blends of thermoplastic starch and polycaprolactone,” *Polymer Engineering and Science*, vol. 44, no. 8, pp. 1429–1438, 2004.
- [26] A. Bhattacharya and P. Ray, “Basic features and technique,” in *Polymer Grafting and Crosslinking*, A. Bhattacharya, J. W. Rawlins, and P. Ray, Eds., John Wiley & Sons, Hoboken, NJ, USA, 2008.
- [27] Y. Cai, J. Lv, and J. Feng, “Spectral characterization of four kinds of biodegradable plastics: poly(lactic acid), poly(butylene adipate-co-terephthalate), poly(hydroxybutyrate-co-hydroxyvalerate) and poly(butylene succinate) with FTIR and Raman Spectroscopy,” *Journal of Polymers and the Environment*, vol. 21, no. 1, pp. 108–114, 2013.
- [28] S. B. Brown, “Reactive compatibilization of polymer blends,” in *Polymer Blends Handbook*, L. A. Utracki, Ed., vol. 1, pp. 339–415, Kluwer Academic Publishers, Dordrecht, Netherlands, 2002.
- [29] B. Y. Shin, D. H. Han, and R. Narayan, “Rheological and thermal properties of the PLA modified by electron beam irradiation in the presence of functional monomer,” *Journal of Polymers and the Environment*, vol. 18, no. 4, pp. 558–566, 2010.
- [30] T. Yokohara and M. Yamaguchi, “Structure and properties for biomass-based polyester blend of PLA and PBS,” *European Polymer Journal*, vol. 44, no. 3, pp. 677–685, 2008.
- [31] W. K. Chee, N. A. Ibrahim, N. Zainuddin, M. F. A. Rahman, and B. W. Chieng, “Impact toughness and ductility enhancement of biodegradable poly(lactide)/poly(ϵ -caprolactone) blends via addition of glycidyl methacrylate,” *Advances in Materials Science and Engineering*, vol. 2013, Article ID 976373, 8 pages, 2013.
- [32] M. Todo, K. Arakawa, H. Tsuji, and Y. Takenoshita, “Toughening mechanism of bioabsorbable PLA/PCL polymer blend,” in *Proceedings of SEM X International Congress and Exposition on Experimental and Applied Mechanics*, Costa Mesa, CA, USA, June 2004.
- [33] F. Lefebvre, C. David, and C. Vander Wauven, “Biodegradation of polycaprolactone by micro-organisms from an industrial compost of household refuse,” *Polymer Degradation and Stability*, vol. 45, no. 3, pp. 347–353, 1994.
- [34] J. W. Park, S. S. Im, S. H. Kim, and Y. H. Kim, “Biodegradable polymer blends of poly(L-lactic acid) and gelatinized starch,” *Polymer Engineering and Science*, vol. 40, no. 12, pp. 2539–2550, 2000.
- [35] H. Pranamuda, Y. Tokiwa, and H. Tanaka, “Physical properties and biodegradability of blends containing poly(ϵ -caprolactone) and tropical starches,” *Journal of Polymers and the Environment*, vol. 4, no. 1, pp. 1–7, 1996.

