



Miscibility and thermal behavior of poly (ϵ -caprolactone)/long-chain ester of cellulose blends

Yuzhi Xu^{a,1}, Chunpeng Wang^a, Nicole M. Stark^b, Zhiyong Cai^b, Fuxiang Chu^{c,*}

^a Institute of Chemical Industry of Forest Products, CAF, Nanjing 210042, China

^b Forest Products Laboratory, USDA Forest Service, Madison, WI 53726-2398, USA

^c Institute of New Technology, Chinese Academy of Forestry, Beijing 100091, China

ARTICLE INFO

Article history:

Received 25 October 2011

Received in revised form

23 November 2011

Accepted 25 November 2011

Available online 6 December 2011

Keywords:

Cellulose laurate

Poly (ϵ -caprolactone)

Blends

Thermal behaviors

Miscibility

ABSTRACT

The long-chain cellulose ester (LCCE) cellulose laurate, poly(ϵ -caprolactone) (PCL) and their blends were characterized by tensile strength, Fourier transform infrared spectroscopy (FTIR), dynamic mechanical thermal analysis, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). The compatibility of the blends was investigated and the TEM results showed that PCL tended to disperse as discrete particles in LCCE. FTIR revealed that there were several specific interactions between the chains of PCL and LCCE: the interaction between C—H and O=C—, —C=O...O=C— or —C=O...O—C dipole–dipole interactions. The addition of PCL into LCCE increased slightly the tensile stress at break and the elongation up to 90/10 LCCE/PCL (w/w), which suggested partial compatibility between the polymers. In agreement with this, TGA showed that the compatibility of PCL and LCCE enhanced the thermal stability of LCCE in the blends. Together, these results indicated the existence of intermolecular interactions between the two polymers.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Among strategies to reduce pollution and to decrease the expenditure in natural resources such as petroleum, numerous studies have investigated the development of biodegradable materials and renewable polymer derivatives. The development of polymer blends is an alternative to reduce costs and, in some cases, to improve the properties of pure components (Vařquez-Torres & Cruz-Ramos, 1994). The difficulty in producing blends lies in the choice of materials that are compatible and can provide desirable properties (Braganca & Rosa, 2003).

By varying their substitution, cellulose esters can be either melt processed or readily dissolved into organic solvent, and then made into different products (Buchanan et al., 2003; Meireles et al., 2010; Muller & Leuschke, 1996; Wang, Sun, & Yu, 2011). To eliminate fugitive plasticizers, the preparation of long-chain cellulose esters (LCCEs) has afforded promising results. Cellulose laurate, one of the LCCEs, has promise as an internally plasticized cellulose ester, and is identified as a potentially biodegradable plastic because of the enzymatically labile ester bond and the O-glucosidic bond of cellulose (Edgar et al., 2001).

Poly(ϵ -caprolactone) (PCL) is a partially crystalline, synthetic aliphatic polyester with low melting point and glass transition temperature, which can be processed by injection molding or extrusion (Braganca & Rosa, 2003). PCL also has good biocompatibility and degradability (De Kesel, Wauven, & David, 1997; Li, Wu, Liu, & Esker, 2006; Miola, Hamaide, & Spitz, 1997; Oishi, Zhang, Nakayama, Masuda, & Taguchi, 2006; Yamashita, Kikkawa, Kurokawa, & Doi, 2005). According to Muller, Kleeberg, and Deckwer (2001), PCL can be blended with other biodegradable polymers to produce new biodegradable materials with properties better than those of respective individual components. Previous studies have shown that PCL is miscible with cellulose nitrate (Olhoft et al., 1972), cellulose butyric ester (Kusumi, Inoue, Shirakawa, Miyashita, & Nishio, 2008; Nishio, Matsuda, Miyashita, Kimura, & Suzuki, 1997), cellulose acetate–butyrate (Braganca & Rosa, 2003; Hubbell & Cooper, 1977), cellulose acetate (Braganca & Rosa, 2003; Hatakeyama, Yoshida, & Hatakeyama, 2000; Rosa, Guedes, & Bardi, 2007) and other polymers such as ethylcyanoethyl cellulose (Zhou & Huang, 2004), chitin or its derivative (Yang, Wu, & Zhu, 2001) and poly(3-hydroxybutyrate) (Gassner & Owen, 1994; Suave, Dall'Agnol, Pezzin, Meier, & Silva, 2010). Numerous PCL blends in the literature support the notion “the art of tailoring polymers has emerged which relies on the mixing of two or more homopolymers with differing properties to obtain some synergistic effect” described by Kaplan in 1976.

Blends of LCCE and PCL were desirable because PCL has been proved as an effectively polymeric plasticizer to facilitate cellulosic

* Corresponding author. Tel.: +86 10 62889300; fax: +86 10 62889013.

E-mail addresses: chufuxiang@forestry.ac.cn, xuyzz@hotmail.com (F. Chu).

¹ Tel.: +86 25 85482519; fax: +86 25 85410452.

blends to be better processed and to be more flexible than the pure LCCE. In this work, blends containing different proportions of cellulose laurate and PCL were prepared, and their tensile strength, thermal properties (by thermogravimetric analysis, TGA and dynamic mechanical thermal analysis, DMA), crystallinity and morphology (by transmission electron microscopy, TEM) were evaluated.

2. Experimental

2.1. Materials

Cellulose laurate was prepared as the following (Satge et al., 2002): Ts-Cl was added in cellulose solution followed by lauric acid with DMAP. Then, the mixture was subjected to microwave reactor and irradiated for 60–120 s. The reaction mixture was precipitated in distilled water and purified with NaHCO_3 solution (0.2 M) and ethanol, respectively. The product was vacuum dried at 50 °C to constant weight. The average degree of substitution was 2.6, and the weight average molecular weight was about 56,000 g/mol (weight average molecular weight/number average molecular weight = 1.96). PCL was supplied in pellet form by YouLi Materials Science Ltd. (Suzhou, Jiangsu, China). The weight average molecular weight was 100,000 g/mol.

2.2. Methods

2.2.1. Film preparation

All samples were prepared by dissolving the materials in chloroform. A typical casting procedure was carried out as follows: Cellulose laurate (~1.25 g) was dissolved in 15 mL chloroform, and the solution was stirred at ambient temperature and then poured into a culture dish, after which the solvent was allowed to evaporate thoroughly in a fume hood. For the preparation of blends, 1.25 g mixture of LCCE/PCL with the proportions (w/w) of 95/5, 90/10, 85/15 and 75/25% were dissolved in chloroform. Pure materials were represented by 100/0 and 0/100 for LCCE and PCL, respectively.

2.2.2. Film characterization

Specimens of 5 mm × 25 mm were prepared. The film thickness of blends, which was measured with a digital caliper, was in the range of 0.12–0.2 mm. The mechanical tests were done at room temperature using an INSTRON 4466 universal testing machine (Instron, Euclid, OH, USA). The load cell used had a capacity of 500 N and the crosshead speed was 5 mm/min. The test was run according to ISO 527-3.

FTIR spectra were obtained at a 4 cm^{-1} resolution with 64 scans. The sample was casted as transparent thin films on a KBr plate and measured using a Nicolet MAGNA550 FTIR spectrophotometer (ThermoScientific, Verona, WI, USA).

Dynamic mechanical thermal analysis was carried out with a TA instrument (DMA Q 800) in tension mode. The samples were tested over a temperature range from –110 °C to 260 °C at a heating rate of 3 °C/min. The oscillation frequency was 10 Hz and the strain amplitude was 0.250%.

TGA of the pure polymers and blends was measured with a STA 409 PC thermal analyzer (Netzsch Instruments, Burlington, MA, USA). The sample weight varied from 5 to 10 mg. The samples were scanned from 30 °C to 800 °C at a heating rate of 20 °C/min.

The crystallinity of samples for different blends was examined by wide-angle X-ray diffraction (WAXD) technique, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), equipped with computerized data collection and analytical tools. The X-ray source was operated at a voltage of 40 kV and a filament current of 40 mA. All samples were scanned in 2θ ranging from 10 to 30° at a step size of 0.01°. In addition, these

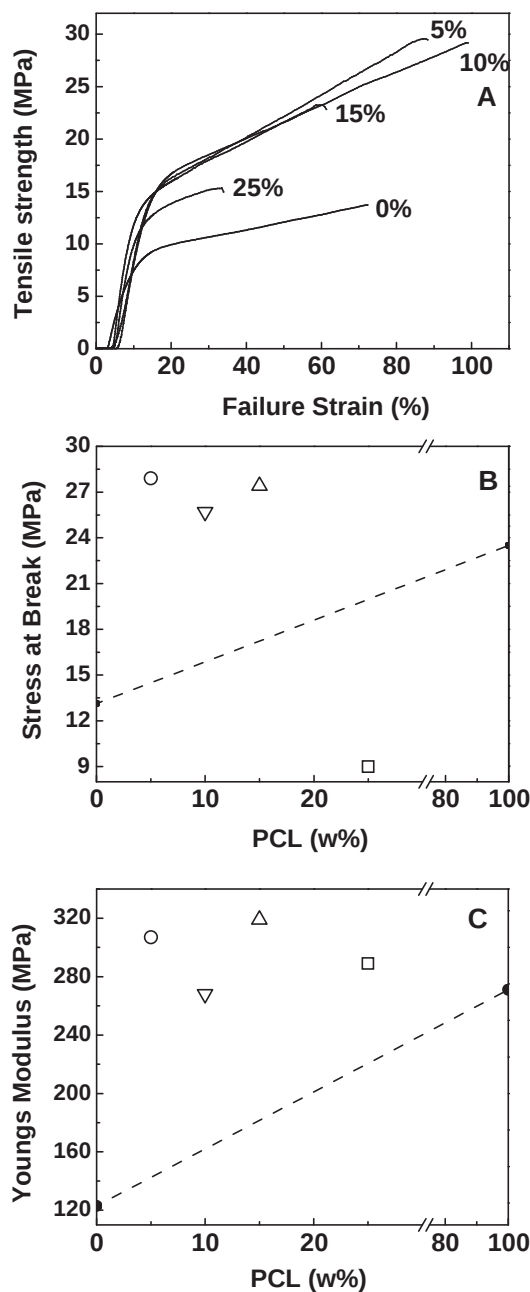


Fig. 1. Tensile properties: (A) strength-strain behavior versus %PCL for LCCE/PCL blends, (B) break strength versus %PCL for LCCE/PCL blends and (C) Young's modulus versus %PCL for LCCE/PCL blends. The dash line indicated the weight average values for LCCE and PCL in (B) and (C).

samples were also characterized using HITACHI H-600 transmission electron microscope.

3. Results and discussion

3.1. Tensile strength

Tensile strength curves including stress at break and Young's modulus are shown in Fig. 1A–C, for the pure polymers and their blends. The tensile strength values of the blends were higher than the pure LCCE value while the blends of LCCE/PCL with 5% and 10% PCL showed elongations larger than pure LCCE. These results suggested a partial compatibility between LCCE and PCL. Miscibility

was favored through physical interactions such as hydrogen bonding, when there is a minimum number of proton donor or acceptor group in the polymers of the blends (Braganca & Rosa, 2003). LCCE has hydroxyl group, which acted as proton donors and was involved in hydrogen bonding with the carbonyl groups of PCL. These results indicated the existence of partial physical interaction between these polymers. However, further increase of PCL to 25% resulted in a much lower elongation. This indicated that the miscibility was poor with high fraction of PCL, suggesting macrophase separation was dominant.

Tensile strength at break (Fig. 1B) and Young's modulus (Fig. 1C) versus %PCL were presented. Because the mechanical properties primarily depended on the properties of each component, a dash line connected the value for 0% PCL to 100% PCL. This dash line represented the weighted average. The strength at break of PCL was higher than that of LCCE, so the continuous LCCE phase was reinforced by PCL efficiently only with high interfacial adhesion. Efficient interfacial adhesion could be accounted for the observed higher stress at break for blends except the one with 25% PCL (Fig. 1B). This result was consistent with the tensile strength measurement. Young's modulus was also affected by the interfacial interactions. The Young's modulus of the blends showed an increase in the modulus in blends when compared with the weight average values (dash line). This confirmed efficient interfacial adhesion between the two polymers in the LCCE/PCL blends (Fig. 1C). It is not clear why the blend with 25% PCL also showed increase of Young's modulus.

3.2. FTIR

The molecular interaction of polymer blends can be confirmed by FTIR spectra (Ma, Yu, & Wang, 2006). If two polymers form completely immiscible blends, there are no appreciable changes in the FTIR spectra of the blends with respect to the co-addition of each component (Zhang, Zhang, Zhou, & Shen, 2003). However, if two polymers are compatible, a distinct interaction (a hydrogen-bonding or dipolar interaction) exists between the chains of one polymer and those of the other, causing the IR spectra for the blend to change (e.g., band shifts or broadening) (Peng, Wang, & Dong, 2005). In this way FTIR can identify segment interactions and provide information about the miscibility of polymer blends (Ma et al., 2006).

Fig. 2 shows the FTIR spectra of LCCE/PCL blends at room temperature. As observed in Fig. 2A, the peak at 2920 cm^{-1} and 2860 cm^{-1} of LCCE ascribed to the $-\text{CH}_2-$ stretching vibrations respectively, changed slightly when the PCL concentration varied from 0 to 100%.

Both LCCE and PCL had a strong carbonyl stretching absorption (Fig. 2B). The $\text{C}=\text{O}$ peak of LCCE shifted to a higher wavenumber with the addition of PCL. This indicated that the interaction reduced the stretching vibration frequency of the carbonyl bond and gave rise to a shift to a lower frequency. This was consistent with other reports on poly(vinylphenol)/PCL blends and PCL/chlorinated polypropylene blends (Allard & Prudhomme, 1982; Kuo, Huang, & Chang, 2001). There are two possible reasons for the shift. The first is the interaction between $\text{C}-\text{H}$ and $\text{O}=\text{C}-$, as mentioned previously. The second is $\text{C}=\text{O}\cdots\text{O}=\text{C}$ or $\text{C}=\text{O}\cdots\text{O}-\text{C}$ dipole-dipole interactions, similar to the dipole-dipole $\text{C}=\text{O}\cdots\text{Cl}-\text{C}$ interaction reported for PCL/chlorinated polypropylene blends (Allard & Prudhomme, 1982).

3.3. DMA

Fig. 3 shows representative dynamic mechanical measurements for LCCE/PCL blends. Fig. 3A–C corresponds to pure LCCE, 90/10 and 75/25 blends, respectively. Pure LCCE exhibited two peaks on the tan delta curve in the range of temperatures at -45 to -35°C

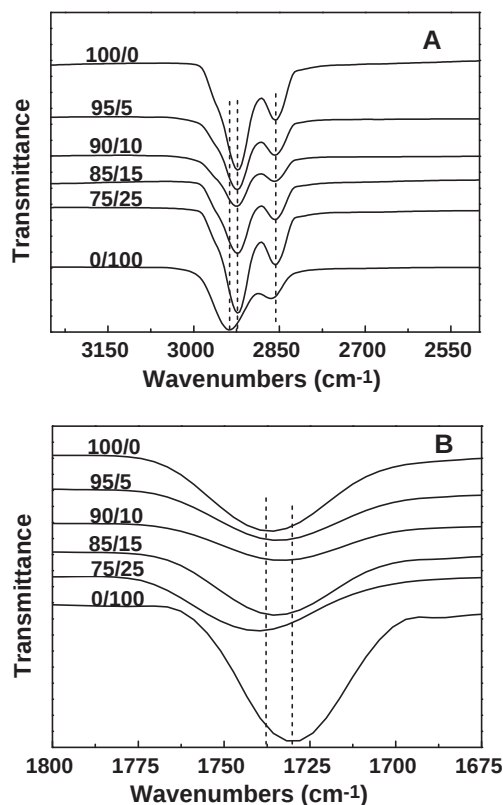


Fig. 2. Selected regions of FTIR spectra showing (A) $-\text{CH}_2-$ absorptions, and (B), $\text{C}=\text{O}$ absorptions for LCCE (100/0) PCL (0/100) and blends.

and 155 – 145°C respectively (Fig. 3A). The peak at the lower temperature corresponded to the β -transition, accompanying a lateral substituent melting in the vicinity of -30°C . The relaxation at the higher temperature (α -transition) corresponded to the glass transition of the polymer. When the blend contained 10% PCL three peaks were present on the tan delta curve (Fig. 3B). The peaks appeared in the range of temperatures at -45 to -35°C , 155 – 145°C and 220 – 240°C . For the 75/25 LCCE/PCL blends (Fig. 3C) two peaks were present on the tan delta curve in the temperature ranges -45 to -35°C and 155 – 145°C , but no data was recorded beyond 220°C due to sample degradation. From these observations, it could be inferred that the peak at about -40°C , which was broader for LCCE/PCL blends than that for pure LCCE, might correspond to crystalline interaction (Muller et al., 2001), while the peak

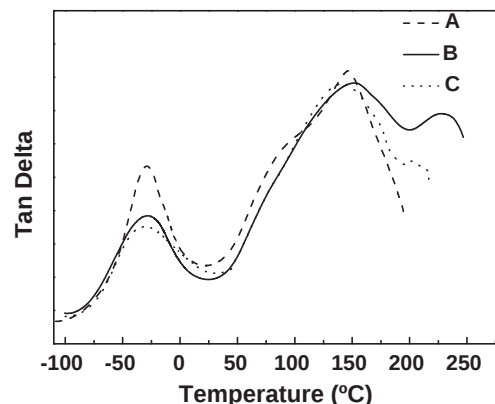
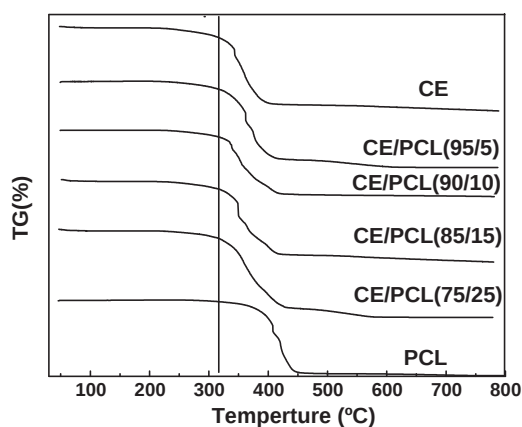


Fig. 3. DMA curves of (A) LCCE, (B) LCCE/PCL 90/10 and (C) LCCE/PCL 75/25.

Table 1

Thermo gravimetric parameters of cellulose laurate and PCL blend.

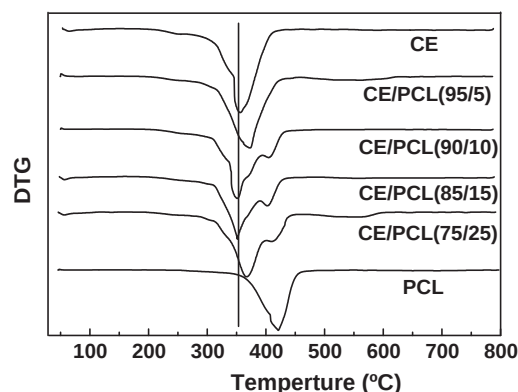
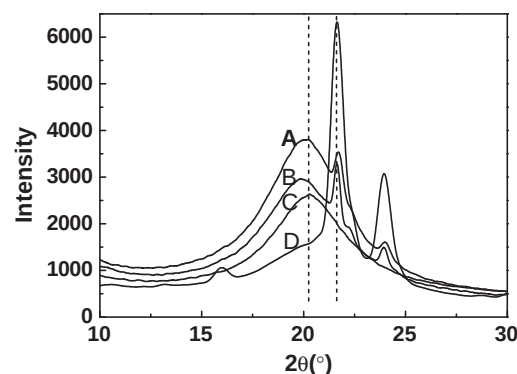
LCCE/PCL (w/w)	LCCE $T_{\max}$ (K)	PCL $T_{\max}$ (K)	Slope of Eq	LCCE E_t (kJ mol ⁻¹)	PCL E_t (kJ mol ⁻¹)
100/0	621.65	–	0.0244	78.4	–
95/5	623.90	638.40	0.0273	88.2	92.3
90/10	626.05	678.05	0.0356	116.0	136.1
85/15	624.15	673.15	0.0202	65.2	75.9
75/25	636.65	683.15	0.0277	93.3	107.4
0/100	–	693.85	0.0407	–	162.7

**Fig. 4.** Thermogravimetric curves for LCCE/PCL blends at a heating rate of 20 °C/min.

at 220–240 °C might be attributed to transesterification reactions between components in polyester blends at such high temperature. This clearly indicated that the LCCE/PCL system was partially compatible which supported the FTIR results. The DMA results also agreed with the tensile strength and TGA, as discussed below.

3.4. TGA

TGA was performed for the blends (Ma et al., 2006), and the weight loss due to the decomposition of products was monitored as a function of temperature, as shown in Fig. 4. The addition of PCL improved the thermal stability of LCCE. The $T_{\max}$, which was the temperature at the maximum rate of weight loss determined by the derivative thermogravimetry (DTG) curve for LCCE and PCL blend as shown in Fig. 5, is summarized in Table 1. $T_{\max}$ of LCCE

**Fig. 5.** DTG curves for LCCE/PCL blends at a heating rate of 20 °C/min.**Fig. 6.** X-ray diffraction patterns of (A) LCCE/PCL 90/10, (B) LCCE/PCL 75/25, (C) LCCE and (D) PCL.

and PCL in blends was located between those of pure LCCE and PCL. The $T_{\max}$ increase of LCCE suggested partial compatibility of LCCE and PCL. However, $T_{\max}$ of PCL in the blends decreased compared to that of pure PCL.

3.5. Crystallinity

The wide-angle X-ray diffraction patterns of blends are shown in Fig. 6. It could be seen from Fig. 6C that spectra of pure cellulose laurate film showed a broader peak at $2\theta = 20.5^\circ$. The origin of this broad peak might come from appearance of side-chain crystallization of cellulose ester as reported in a previous study (Sealey, Samaranayake, Todd, & Glasser, 1996). The part of the side chains that overlapped became larger with increasing degree of substitution, and the crystallinity of polymer correlated directly with side chain's thickness. The large breadth of the cellulose esters at angles around 18–22° was therefore attributed to a broad distribution of side-chain crystal thicknesses due to differences in substituent overlap arising from local differences in main-chain spacing and orientation. In contrast, Pure PCL film had a strong diffraction peak at about 21°. The 2θ of blends shifted to a lower value with the addition of PCL. This indicated that the interaction occurred between cellulose laurate and PCL, in good agreement with the FTIR and DMA results.

Films of pure LCCE, PCL and their blends were analyzed by TEM. As shown in Fig. 7, the blends with a lower fraction of PCL (e.g. LCCE/PCL 95/5) exhibited quite homogeneous morphology. The presence of PCL was more evident in LCCE/PCL blends (75/25) (Fig. 7D), which showed more heterogeneous macrophased separated morphology. The phase morphology indicated lower anchorage of PCL in LCCE. The macrophased separated behavior of the blends with high loading of PCL should favor the biodegradation of the new material because of the weak interaction between the two polymers.

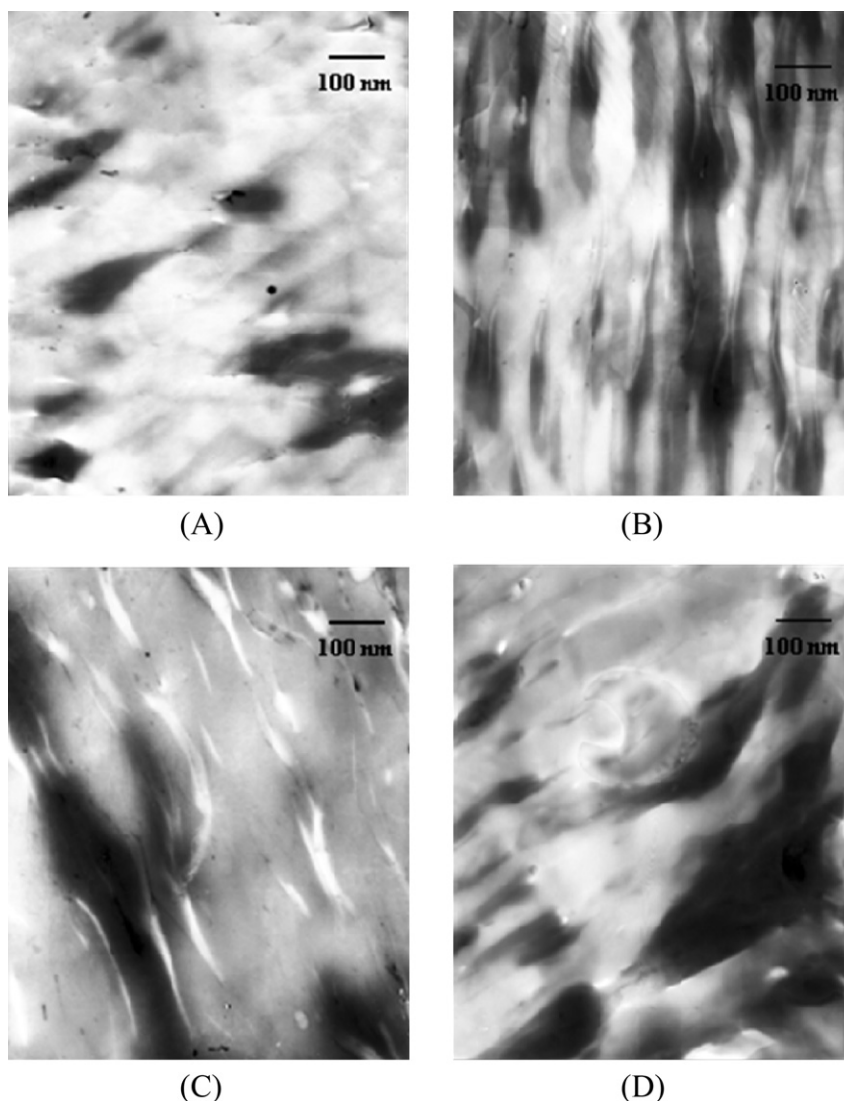


Fig. 7. TEM images of (A) LCCE/PCL 95/5, (B) LCCE/PCL 90/10, (C) LCCE/PCL 85/15 and (D) LCCE/PCL 75/25.

4. Conclusions

FTIR, DMA, TGA, and TEM characterization indicated that the LCCE/PCL blends studied in this work were partially compatible with low loading of PCL because of potential physical interactions such as hydrogen bonding and dipole–dipole interactions. According to Muller's considerations, three possible blends might result when PCL was blended with other polymers, namely true compatibility, mechanical compatibility and crystalline interaction. Consequently, these latter kinds of blends were observed in this work. The partial compatibility of LCCE and PCL enhanced $T_{\max}$ of LCCE in blends. This was further confirmed that the tensile strength at break increased in blends when compared to LCCE when PCL loading was low. This property should make biodegradable bio-based blends more attractive than single component polymers.

Acknowledgements

The authors gratefully acknowledge the financial support from Technology Division of the State Forestry Bureau (201104004) and Chinese Academy of Forestry (CAFIN2009C03).

References

- Allard, D., & Prud'homme, R. E. (1982). Miscibility of poly(caprolactone)/chlorinated polypropylene and poly(caprolactone)/poly(chlorostyrene) blends. *Journal of Applied Polymer Science*, 27, 559–568.
- Braganca, F. C., & Rasa, D. S. (2003). Thermal, mechanical and morphological analysis of poly(ϵ -caprolactone), cellulose acetate and their blends. *Polymers for Advanced Technologies*, 14, 669–675.
- Buchanan, M. C., Buchanan, L. N., Debenham, S. J., Gatenholm, P., Jacobsson, M., Shelton, C. M., et al. (2003). Preparation and characterization of arabinoxylan esters and arabinoxylan ester/cellulose ester polymer blends. *Carbohydrate Polymers*, 52, 345–357.
- De Kesel, C., Wauven, C. V., & David, C. (1997). Biodegradation of polycaprolactone and its blends with poly(vinylalcohol) by micro-organisms from a compost of house-hold refuse. *Polymer Degradation and Stability*, 55, 107–113.
- Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A., Seiler, B. D., Shelton, M. C., et al. (2001). Advances in cellulose ester performance and application. *Progress in Polymer Science*, 26, 1605–1688.
- Gassner, F., & Owen, A. J. (1994). Physical properties of poly (β -hydroxybutyrate)–poly(ϵ -caprolactone) blends. *Polymer*, 35, 2233–2236.
- Hatakeyama, H., Yoshida, T., & Hatakeyama, T. (2000). The effect of side chain association on thermal and viscoelastic properties: Cellulose acetate based polycaprolactones. *Journal of Thermal Analysis and Calorimetry*, 59, 157–168.
- Hubbell, D. S., & Cooper, S. L. (1977). The physical properties and morphology of poly- ϵ -caprolactone polymer blends. *Journal of Applied Polymer Science*, 21, 3035–3061.
- Kaplan, D. S. (1976). Structure–property relationships in copolymers to composites: Molecular interpretation of the glass transition phenomenon. *Journal of Applied Polymer Science*, 20, 2615–2629.

- Kuo, S. W., Huang, C. F., & Chang, F. C. (2001). Study of hydrogen-bonding strength in poly(ϵ -caprolactone) blends by DSC and FTIR. *Journal of Polymer Science Part B: Polymer Physics*, 39, 1348–1359.
- Kusumi, R., Inoue, Y., Shirakawa, M., Miyashita, Y., & Nishio, Y. (2008). Cellulose alkyl ester/poly(ϵ -caprolactone) blends: Characterization of miscibility and crystallization behavior. *Cellulose*, 15, 1–16.
- Li, B. B., Wu, Y. T., Liu, M. H., & Esker, A. R. (2006). Brewster angle microscopy study of poly(ϵ -caprolactone) crystal growth in Langmuir films at the air/water interface. *Langmuir*, 22, 4902–4905.
- Ma, X. F., Yu, J. G., & Wang, N. (2006). Compatibility characterization of poly(lactic acid)/poly(propylene carbonate) blends. *Journal of Polymer Science Part B: Polymer Physics*, 44, 94–101.
- Meireles, C. S., Filho, G. R., Ferreira, M. F., Jr., Cerqueira, D. A., Assuncao, R. M. N., Ribeiro, E. A. M., et al. (2010). Characterization of asymmetric membranes of cellulose acetate from biomass: Newspaper and mango seed. *Carbohydrate Polymers*, 80, 954–961.
- Miola, C., Hamaide, T., & Spitz, R. (1997). End-functionalized poly(ϵ -caprolactone) oligomers through heterogeneous catalysis in protic conditions: A mechanistic approach. *Polymer*, 38, 5667–5676.
- Muller, F., & Leuschke, Ch. (1996). Organic cellulose esters, thermoplastic molding compounds. In L. Bottenbruch, & A. Siegfried (Eds.), *Engineering thermoplastics: Polycarbonates, polyacetals, polyesters and cellulose esters* (pp. 385–441). Hunser: Ohio.
- Muller, R. J., Kleeberg, I., & Deckwer, W. D. (2001). Biodegradation of polyesters containing aromatic constituents. *Journal of Biotechnology*, 86, 87–95.
- Nishio, Y., Matsuda, K., Miyashita, Y., Kimura, N., & Suzuki, H. (1997). Blends of poly(ϵ -caprolactone) with cellulose alkyl esters: Effect of the alkyl side-chain length and degree of substitution on miscibility. *Cellulose*, 4, 131–145.
- Oishi, A., Zhang, M., Nakayama, K., Masuda, T., & Taguchi, Y. (2006). Synthesis of poly(butylene succinate) and poly(ethylene succinate) including diglycollate moiety. *Polymer Journal*, 38, 710–715.
- Olthoff, G. V., Eldred, N. R., & Koleske, J. V. (1972). *Compositions of nitrocellulose and cyclic ester polymers*. US Patent 3,642,507.
- Peng, S. W., Wang, X. Y., & Dong, L. S. (2005). Special interaction between poly(propylene carbonate) and corn starch. *Polymer Composites*, 26, 37–41.
- Rosa, D. S., Guedes, C. G. F., & Bardi, M. A. G. (2007). Evaluation of thermal, mechanical and morphological properties of PCL/CA and PCL/CA/PE-g-GMA blends. *Polymer Testing*, 26, 209–215.
- Satge, C., Verneuil, B., Branland, P., Granet, R., Krausz, P., Rozier, J., et al. (2002). Rapid homogeneous esterification of cellulose induced by microwave irradiation. *Carbohydrate Polymers*, 49, 373–376.
- Sealey, J. E., Samaranayake, G., Todd, J. G., & Glasser, W. G. (1996). Novel cellulose derivatives. IV. Preparation and thermal analysis of waxy esters of cellulose. *Journal of Polymer Science Part B: Polymer Physics*, 34, 1613–1620.
- Suave, J., Dall'Agnol, E. C., Pezzin, A. P. T., Meier, M. M., & Silva, D. A. K. (2010). Biodegradable microspheres of poly(3-hydroxybutyrate)/poly(ϵ -caprolactone) loaded with malathion pesticide: Preparation, characterization, and in vitro controlled release testing. *Journal of Applied Polymer Science*, 117, 3419–3427.
- Vázquez-Torres, H., & Cruz-Ramos, C. A. (1994). Blends of cellulosic esters with poly(caprolactone): Characterization by DSC, DMA, and WAXS. *Journal of Applied Polymer Science*, 54, 1141–1159.
- Wang, D., Sun, G., & Yu, L. W. (2011). Recyclability of cellulose acetate butyrate (CAB) matrix for controllable and productive fabrication of thermoplastic nanofibers. *Carbohydrate Polymers*, 83, 1095–1100.
- Yamashita, K., Kikkawa, Y., Kurokawa, K., & Doi, Y. (2005). Enzymatic degradation of poly(L-lactide) film by proteinase K: Quartz crystal microbalance and atomic force microscopy study. *Biomacromolecules*, 6, 850–857.
- Yang, A. L., Wu, R. J., & Zhu, P. F. (2001). Thermal analysis and miscibility of chitin/polycaprolactone blends. *Journal of Applied Polymer Science*, 81, 3117–3123.
- Zhang, G. B., Zhang, J. M., Zhou, X. S., & Shen, D. Y. (2003). Miscibility and phase structure of binary blends of polylactide and poly(vinylpyrrolidone). *Journal of Applied Polymer Science*, 88, 973–979.
- Zhou, X. S., & Huang, Y. (2004). Formation and morphologies of ethylcyanoethyl cellulose/poly(ϵ -caprolactone) blending films. *Journal of Applied Polymer Science*, 93, 550–554.