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ORIGINAL PAPER

Processability enhancement of poly(lactic acid-*co*-ethylene terephthalate) by blending with poly(ethylene-*co*-vinyl acetate), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), and poly(butylene succinate)

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Abstract Processability enhancement feasibility of an in-house synthesized poly(lactic acid-*co*-ethylene terephthalate), PLET, is investigated by blending with commercial poly(ethylene-*co*-vinyl acetate), EVA, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), PHBV, and poly(butylene succinate), PBS. The three blend systems are prepared by varying PLET contents, and their properties are characterized. DSC, SEM, and FTIR results indicate that PLET/EVA blends are immiscible, while the corresponding PLET/PBS and PLET/PHBV blends are miscible and partially miscible, respectively. DMA results show that the three blend systems have storage modulus comparable to those of commercial EVA, PHBV, and PBS, when PLET content is kept lower than 50, 25, and 25 wt%, respectively. PLET/EVA blends show higher thermal stability, compared to those of the other two blend systems. Results on degradability tests indicate that PLET/PBS blends show highest hydrolytic degradability, compared to the other two blends, as both blend constituents are associated in the hydrolytic degradation.

Keywords Poly(lactic acid) · Poly(ethylene terephthalate) · Degradable polymers · Aliphatic aromatic copolyester · Blends · PHBV · PBS · EVA

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Introduction

Degradable polymers have recently drawn attention from many research groups. Polylactic acid (PLA), aliphatic polyester, is among the most popular degradable polymers, due to its environmental-friendly characteristics, i.e., monomer from renewable resources and biocompatibility. Although aliphatic polyesters are distinguished for their good hydrolytic degradability, their physical properties are not comparable to those of aromatic polyesters. Therefore, development of aliphatic–aromatic copolyesters which combine degradability and good mechanical and physical properties of the corresponding component has been researched. It was reported that degradability of various aromatic polyesters, i.e., PET, PPT, PBT, and PPP, is possibly improved by incorporating diols and/or diacids into their main chains [1–8]. Commercially, Ecoflex®, a material derived from butanediol, adipic acid, and terephthalic acid, is claimed to have good mechanical properties and full biodegradability with negligible toxicological effect on the environment [9].

In this research group, we have focused on the development of aliphatic–aromatic copolyesters from lactic acid and monomers of PET, an aromatic polyester that is extensively used in textile and beverage packaging industries. In our previous study [10, 11], we observed that it was challenging to synthesize high molecular weight copolyesters of lactic acid/ethylene terephthalate to achieve suitable mechanical strength for applications by a typical polycondensation, due to a limitation in the reaction mechanism. As the resulting medium-MW copolymer was brittle in nature, its application as film products was therefore challenging.

The objective of this study is to improve processability of the resulting poly(lactic acid-*co*-ethylene terephthalate) (PLET) by blending with other commercial polymers, i.e., ethylene-*co*-vinyl acetate polymer (EVA), poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), and poly(butylene succinate) (PBS). These are employed, as EVA is well known for its flexibility, while PHBV and PBS are known for their degradability. In addition, PHBV is synthesized by microbes, while PBS has attracted great interest as its monomers are derived from renewable resources. Although some work on EVA [12, 13], PHBV [13], and PBS blends have been reported in the literature, a study on blending of these polymers and PLET is rarely found. Reports related to this copolyester in the literature have been limited to its synthesis, microstructures, and degradability [14–17]. In this communication, effects of polymer type and blend composition on miscibility, thermal and mechanical properties, and hydrolytic degradability of PLET blends will be discussed.

Experimental

Materials

PLET copolyester was synthesized by the procedure previously described [10, 11]. EVA with vinyl acetate 18% by weight (grade N8038F) was kindly supplied by TPI Polene Public Co. PHBV (Enmat Y1000P) and PBS (bionolle 1000) were purchased from Ningbo Tianan Biologic Material Co. and Showa High Polymer Inc., respectively.

Blending and film preparation

EVA, PHBV, and PBS were separately melt-blended with PLET at 180 °C in a Brabender (PLASTI-CORDER® LAB-STATION +W50EHT). The mixing process was carried out at 50 rpm until constant torque was reached. Sample films of the blends were prepared by compression molding (Lab Tech, LP-S-50) at 50 psi.

Characterizations

Differential scanning calorimetry (DSC)

Glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c) were determined using a Mettler Toledo DSC822e. Approximately 5 mg of sample sealed in an aluminum pan was heated to melt for 3 min to erase its thermal history and cooled to −60 °C. The sample was then reheated and its thermogram was recorded to the temperature above its T_m. Heating and cooling rates of 20 °C/min were employed.

Scanning electron microscopy (SEM)

The phase morphology of the blends was analyzed using a scanning electron microscope (HITASHI S3400N, Japan). The samples for the SEM measurements were prepared by cryogenically fracturing in liquid nitrogen.

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of samples were characterized in tension mode by a Mettler Toledo DMA/SDTA861e. Dimensions of film specimens were approximately 5.8 × 10.5 × 0.1 mm. The experiment was performed at 1 Hz, scanning from −70 to 230 °C with a heating rate of 3 °C/min.

Thermogravimetric analysis (TGA)

Thermal stability of blend samples was examined by a Mettler Toledo SDTA/TGA851e. Approximately 10 mg of sample was heated from 50 to 1000 °C at a heating rate of 20 °C/min under nitrogen atmosphere.

Hydrolysis test

Approximately 0.2 g of sample sheet with thickness ~0.1 mm was utilized in hydrolytic degradability tests. The sample sheets were immersed individually in a bottle containing 25 mL phosphate buffer solution (pH 7.4) at ambient temperature and at 60 °C for 16 weeks. Each sample sheet was removed from the medium in a weekly interval to record its dried weight remaining. Excess medium on the sample was wiped clean, and the film was then kept in a desiccator until a constant weight was observed. The percentage weight remaining of the sample was finally calculated.

FTIR spectra

FTIR spectra of film samples were recorded in ATR mode on a Thermo Nicolet 6700 model spectrometer. A ZnSe ATR crystal with 45° face angle was employed. Each spectrum was recorded at 16 scans with 2 cm^{-1} resolution. The neat polymer films and blended sample films were prepared from compression techniques. FTIR spectra of sample films as a function of hydrolytic degradation time were recorded at 1 week intervals. The film samples submersed in a buffer solution were taken from the solution, wiped with tissue paper, and air-dried for 1 h.

Results and discussion

Properties of pristine EVA, PHBV, PBS, PLET, and PLET-based blends with the three respective polymers are characterized by DSC, TGA, DMA, SEM, and FTIR techniques, and hydrolysis tests. Characterization results are discussed in terms of miscibility, dynamic mechanical properties, thermal stability, and degradability.

Miscibility

Miscibility of blends of PLET with EVA, PHBV, and PBS was examined by monitoring changes in their T_gs as a function of the blend composition. Figure 1 presents DSC thermograms recorded during the cooling run from a molten sample. Both T_g and T_c are observed in thermograms of EVA (Fig. 1a), PHBV (Fig. 1b), and PBS (Fig. 1c), while only T_g is observed in PLET thermogram. It is clearly seen in Fig. 1a that T_g of PLET/EVA blends remain unchanged at approx. −24 °C for all blend compositions. Moreover, the crystallization peak of EVA domain tends to decrease in intensity with increasing PLET content. However, the normalized area of the peak is rather similar in all blends, reflecting that crystallization behavior of EVA is undisturbed even in the blend with PLET content as high as 75 wt%. Since the exothermic crystallization peaks of EVA and T_g of PLET occur in the same temperature range, it is not plausible to examine the blend's T_g as a function of the blend composition from this cooling step. However, DSC thermograms recorded from the 2nd heating cycle of the blends, as shown in Fig. 2a, indicate that T_g of PLET component occurs at the same temperature ($\sim$64 °C) irrespective of the blend composition, indicating immiscible blends.

In PLET/PHBV blends, crystallization of PHBV is not observed during the cooling step (Fig. 1b), but is clearly evidenced in the 2nd heating thermogram (Fig. 2b). This reflects that an addition of PLET significantly retards the crystallization of PHBV in the blends. Similar incidents are also observed in PLET/PBS blends (Figs. 1c, 2c). A closer examination indicates that an inclusion of

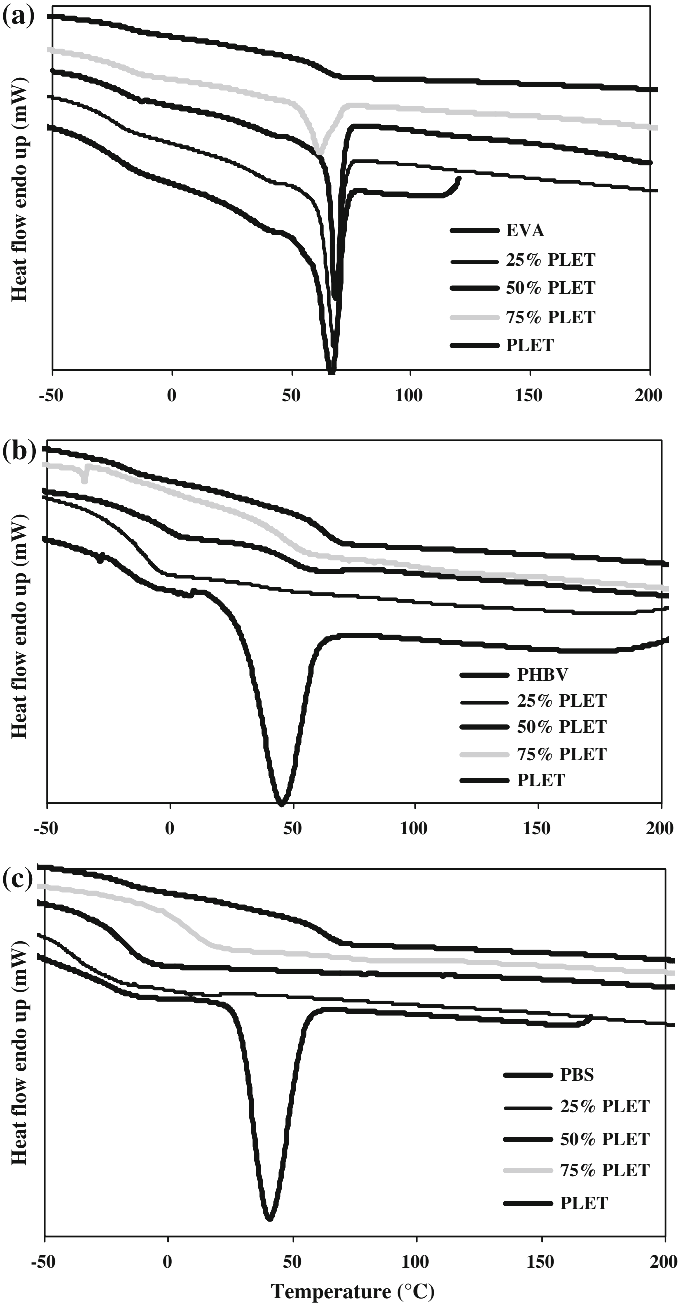


Fig. 1 DSC thermograms recorded from the 1st cooling cycle of: **a** PLET/EVA, **b** PLET/PHBV, and **c** PLET/PBS blends

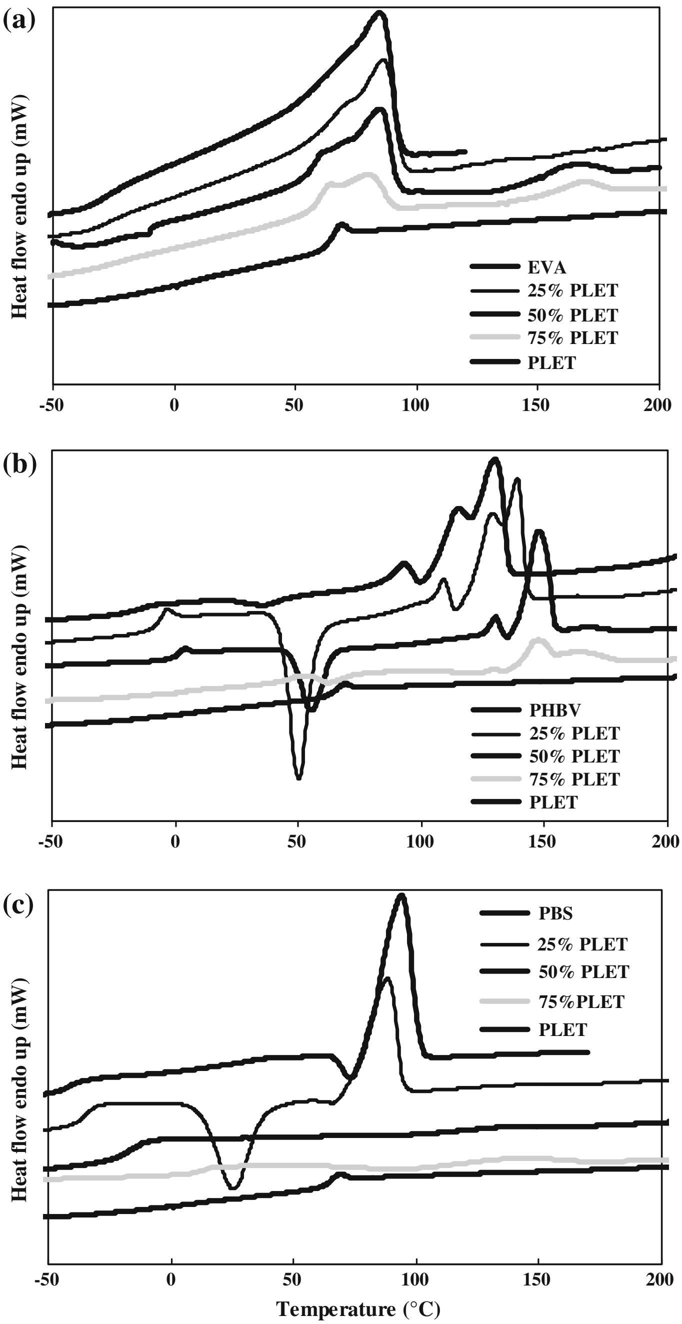


Fig. 2 DSC thermograms recorded from the 2nd heating cycle of: **a** PLET/EVA, **b** PLET/PHBV, and **c** PLET/PBS

PLET impedes crystallization of PBS more severely than that of PHBV. In the blend with 50% PLET, the crystallization of PBS component was further hindered even in the 2nd heating step. Nevertheless, it is evident from Fig. 2b and c that T_gs of PLET/PHBV and PLET/PBS blend shift to higher temperatures with an increase in PLET content. These distinct characteristics, compared to that observed in PLET/EVA blends, clearly indicate that PLET is partially miscible with PHBV and PBS. In addition, it is observed that at 50 and 75 wt% PLET compositions, two T_gs are observed in PHBV blends, while a single T_g is seen in the PBS blend counterparts. This implies a higher degree of miscibility of PLET/PBS, compared to that of PLET/PHBV blends.

Although endothermic melting peaks (T_m) of EVA (Fig. 2a) in blends are located in the same temperature range of that of pure EVA, it is found that T_ms of PHBV (Fig. 2b) and PBS (Fig. 2c) in the corresponding blends are located at different temperatures from that of the pristine polymers. Surprisingly, T_ms of PHBV component in blends shifts to higher temperature, while those of the PBS component in the corresponding blends slightly shift to lower temperature. As mentioned earlier, the presence of PLET has a notable impact on crystallization behaviors of PHBV and PBS. The crystallization process of PLET is also influenced by PHBV and EVA. This is implied from the presence of endothermic melting peaks, located in the range of 150–180 °C, especially in blends with $\geq$50 wt% PLET composition (Fig. 2a, b). Since this T_m is observed at temperatures much higher than T_m of EVA and PHBV, it is confidently believed that this is originated from the crystallite domain of PLET. This indicates an enhancement of PLET crystallization by the presence of EVA and PHBV.

Phase morphology of the three blend systems was characterized by SEM microscope. SEM images of PLET/EVA blends (Fig. 3c, d) indicate that dispersed phase of PLET domains clearly present in the matrix of EVA (smooth area) when 25 or 50% PLET are introduced. This indicates that PLET is totally immiscible with EVA as previously discussed. In contrast, noticeable difference in features is not detected in SEM micrographs of PHBV and the PLET/PHBV blend containing 25% PLET (Fig. 4a, b). When PLET content is increased to 50%, however, it is observed that some PLET-rich phase domains (marked area) are dispersed in the blend matrix (Fig. 4c). This supports the partial miscibility behavior, where the degree of miscibility is dependent on the blend compositions. Unlike the other two blend systems, SEM micrographs of PLET/PBS blends show similar features irrespective of the blend compositions (Fig. 4e, f). Hence, miscibility between PLET and PBS is proven. These are in good accord with those observed from DSC experiments.

Dynamic mechanical properties

Effects of types of the constituent polymers and blend compositions on storage modulus of the blends are shown in Fig. 5. Although DMA measurement on PLET film cannot be performed due to its brittleness, corresponding results from its blends indicate that PLET has poor strength. Nevertheless, it is obviously seen from Fig. 5a that modulus of PLET/EVA blends is not deteriorated by adding of the copolymer, as much as 50%. This implies that it is practical to enhance processability of our

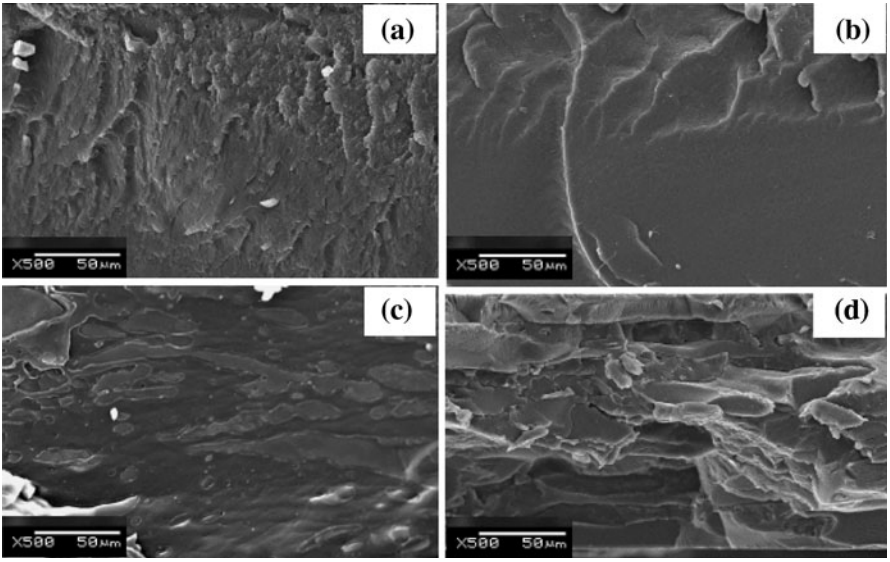


Fig. 3 SEM micrographs of **a** PLET, **b** EVA, and PLET/EVA blends with: **c** 25% and **d** 50% PLET compositions

in-house synthesized PLET copolymer (with moderate molecular weight) by blending with flexible EVA polymer. Moreover, results from Fig. 5b and c indicate that blending of PLET with other environmental-friendly polymers, such as PHBV and PBS, is also feasible. It is clearly seen that blends of PLET with these polymers, by employing PLET composition of up to 25%, essentially maintain good modulus of the materials.

When different blends with the same PLET composition are compared, the poor strength of the copolymer orderly imposes stronger influence on PBS, PHBV, and EVA blends. This is in good accord with DSC results, where the crystallization of PBS is considerably poorer than those of PHBV and EVA in their respective blends. It is therefore concluded that effectiveness of PLET in hindering the crystal microstructure of its blending counterpart has a major role in the determination of the maximum PLET content to retain mechanical properties of the blends.

Thermal stability

TGA thermograms of the three blend systems are presented in Fig. 6. The results indicate that EVA, among the constituent polymers, is the least sensitive to heat. As a result, it is observed that an increase in PLET content leads to a reduction in thermal stability of PLET/EVA blends. Figure 6b and c also indicates that our in-house synthesized PLET exhibits better thermal stability than commercial aliphatic polyesters, i.e., PHBV and PBS. This excellent heat stability is probably due to an inclusion of aromatic components into the chain structure. Given these results, it is concluded that thermal stability of PHBV and PBS can be enhanced by blending

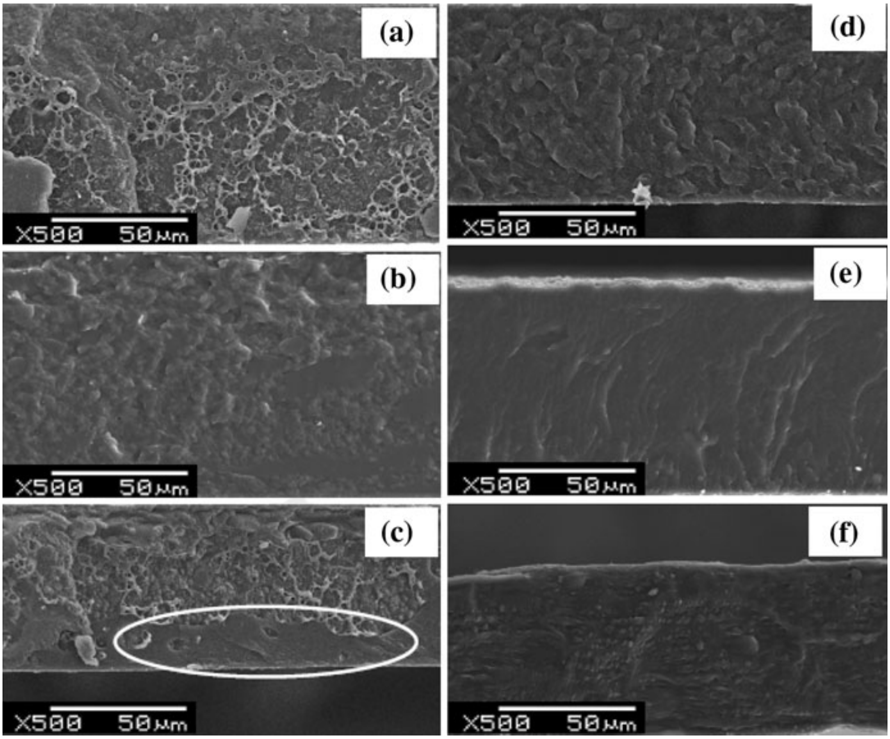


Fig. 4 SEM micrographs of **a** PHBV, PLET/PHBV blends with: **b** 25% and **c** 50% PLET compositions, **d** PBS, PLET/PBS blends with: **e** 25% and **f** 50% PLET compositions

with PLET, where the degree of enhancement is strongly dependent on the PLET content.

Hydrolytic degradability

Hydrolysis testing is conducted by monitoring percentage weight remaining of sample films after immersing in a phosphate buffer solution of pH 7.4 at 60 °C, as a function of time. Figure 7 shows hydrolytic degradability of neat PLET, EVA, PHBV, and PBS polymers, where that of a common degradable polylactic acid (PLA) (NatureWorks® 4042D) is also compared. The results demonstrate that the commercial PLA is the most sensitive to hydrolysis, compared to the other two degradable polymers, i.e., PHBV and PBS. As expected, PLET copolymer, which consists of PLA segments in the chain structure, possesses good hydrolysability comparable to that of PBS. On the other hand, PHBV shows good tolerance to hydrolysis at 60 °C throughout 16 weeks of measurement. This is because the polymer is highly susceptible to microbial or enzyme degradation rather than hydrolysis [18] and is partly due to its high molecular weight. In addition, it is also clearly evidenced that the remaining weight of EVA film remains significantly unchanged, indicating poor hydrolytic degradability of the polymer.

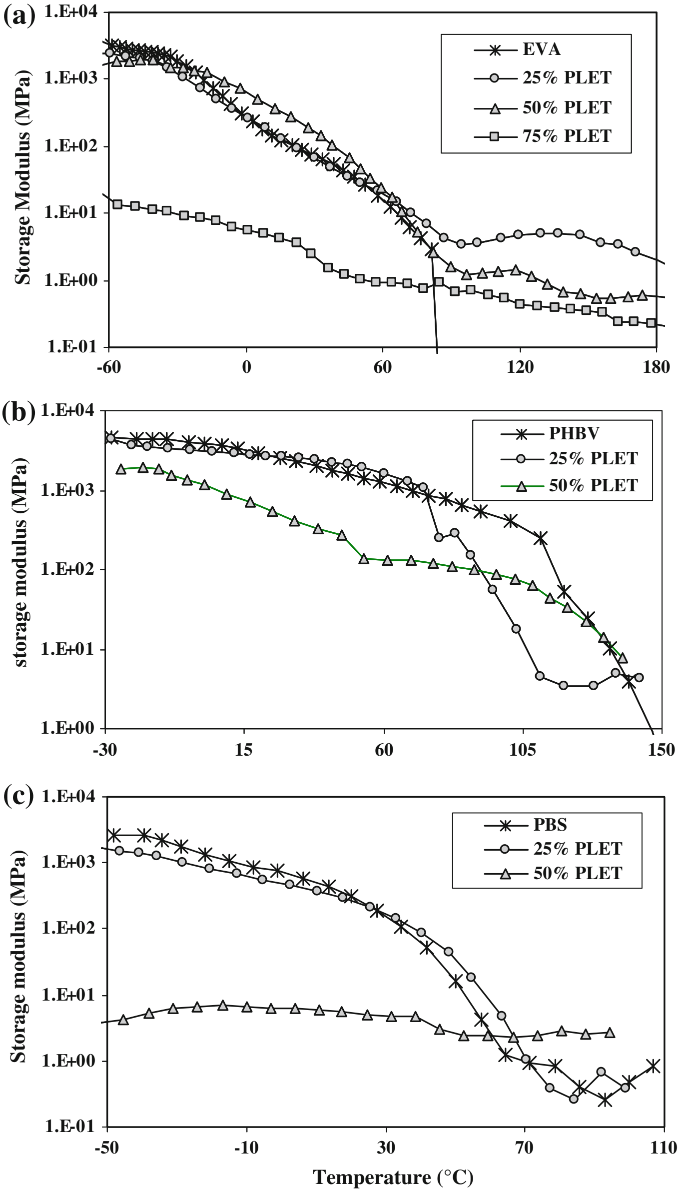


Fig. 5 Storage modulus at 1 Hz of: **a** PLET/EVA, **b** PLET/PHBV, and **c** PLET/PBS blends

Hydrolytic degradability of blend samples, consisting of 50 wt% PLET, is compared with those of their constituent polymers. Figure 8a and b demonstrates that the percentage weight remaining of the corresponding EVA and PHBV blends resembles that of PLET copolymer. Hydrolysis of these blend samples occurs at higher rates during the first 8 weeks and remains nearly constant during the latter

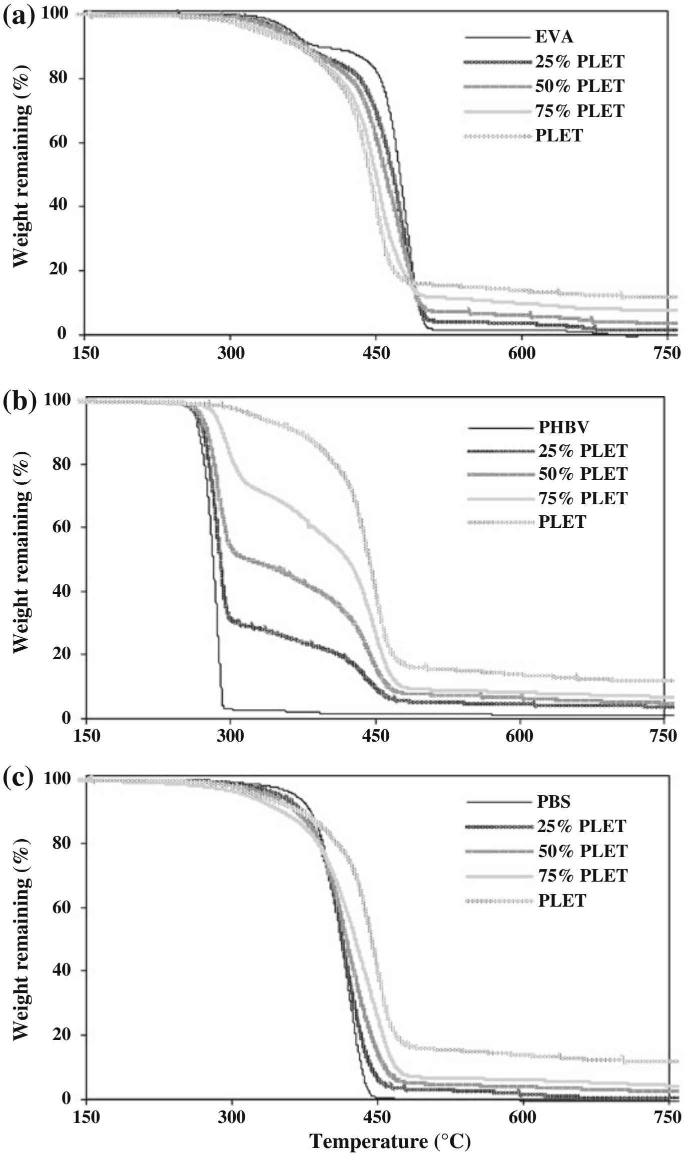


Fig. 6 TGA thermograms of: **a** PLET/EVA, **b** PLET/PHBV, and **c** PLET/PBS blends

8 weeks. This indicates that the degradability of the blends is largely associated with the PLET copolymer constituent. On the other hand, Fig. 8c indicates that the hydrolysis of the 1:1 PLET/PBS blend is similar to that of neat PBS, not the copolymer. Given these results, it is concluded that the PLET/PBS blend system is possibly the most suitable for use as polymeric films with excellent degradability.

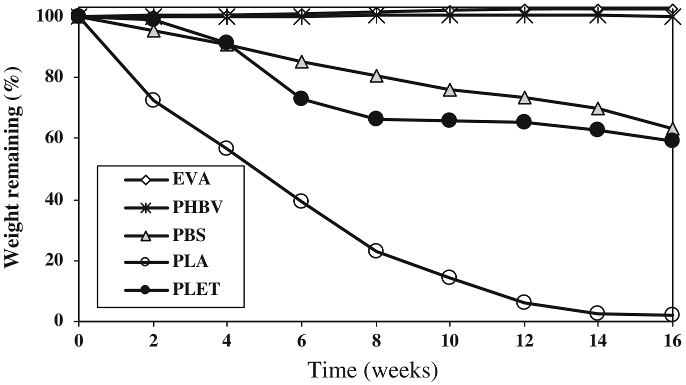


Fig. 7 Percentage weight remaining of samples during hydrolysis tests in a phosphate buffer solution pH 7.4 at 60 °C as a function of time: EVA (*diamond*), PHBV (*asterisk*), PBS (*filled triangle*), PLA (*open circle*), and PLET copolymer (*filled circle*)

FTIR spectra

FTIR spectra in the carbonyl stretching region of neat PLET copolymer, EVA, PHBV, and PBS are shown in Fig. 9. The spectra show that aliphatic and aromatic C=O stretching modes of PLET are located at 1760 and 1716 cm^{-1}, respectively. The C=O mode of ester groups of EVA is observed at 1735 cm^{-1}, while the corresponding band of PHBV is located at 1713 cm^{-1}, with a weak shoulder at 1745 cm^{-1}. In addition, three C=O stretching bands are observed in the spectrum of PBS at 1735, 1720, and 1713 cm^{-1} [19, 20]. Infrared spectra of the three PLET-based blends and the blend samples after hydrolytic degradation are recorded as a function of hydrolysis time (at 1 week intervals), as shown in Fig. 10. FTIR spectra and the 2nd derivative spectra of PLET/EVA blends (Fig. 10a) show bands due to carbonyl stretching modes of L and T units in the copolymer chain at 1760 and 1715 cm^{-1}, respectively. It is clearly seen that band position of these vibrational modes remains significantly unchanged, indicating that no specific interaction formed between the two blend components. This agrees with those observed earlier from DSC and SEM experiments that the blend is immiscible. In contrast, the corresponding spectra of PLET/PHBV (Fig. 10b) and PLET/PBS (Fig. 10c) blends show a shift in band position of the aromatic C=O of PLET to 1723 cm^{-1}. Bands due to C=O of PHBV and PBS in their corresponding blends also slightly shift from original positions at 1750 and 1740 cm^{-1}, respectively. This indicates a formation of specific interaction, which largely results in formation of miscible blends systems [20, 21]. Nevertheless, the aliphatic C=O band from PLET remains at the same position (1760 cm^{-1}) for all blends.

FTIR spectra as a function of hydrolysis time of PLET/EVA (Fig. 10a) and PLET/PHBV (Fig. 10b) blends show a decrease in band intensity of the aliphatic C=O mode at 1760 cm^{-1}, while that of other bands remain significantly unchanged. This implies that bond scissions at L sequences in PLET copolymer are largely

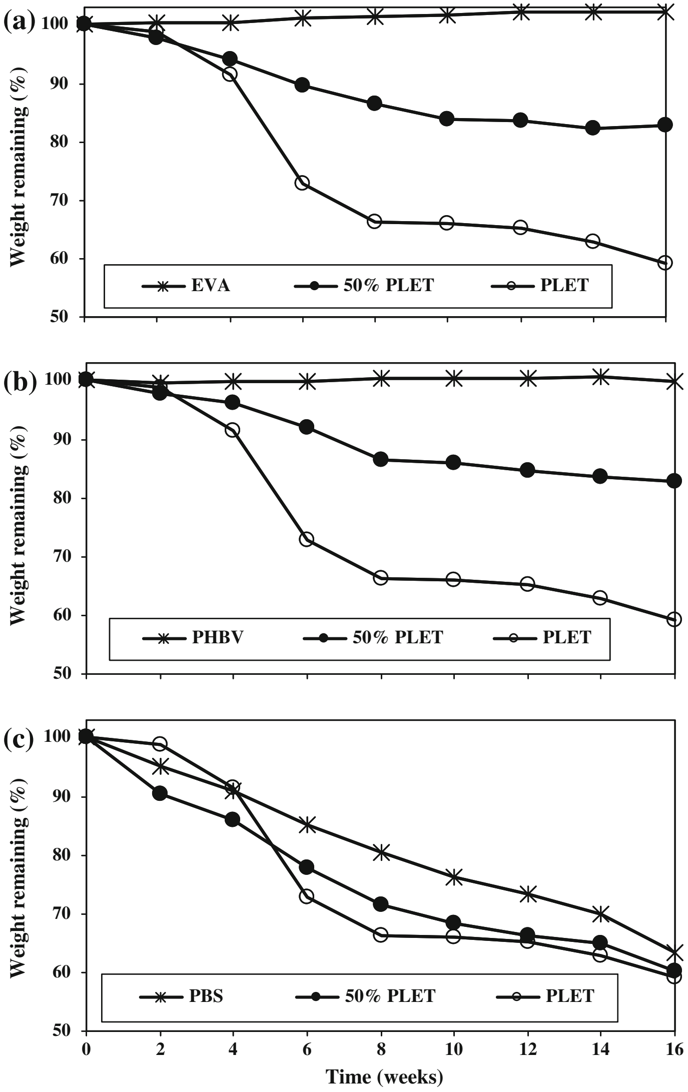
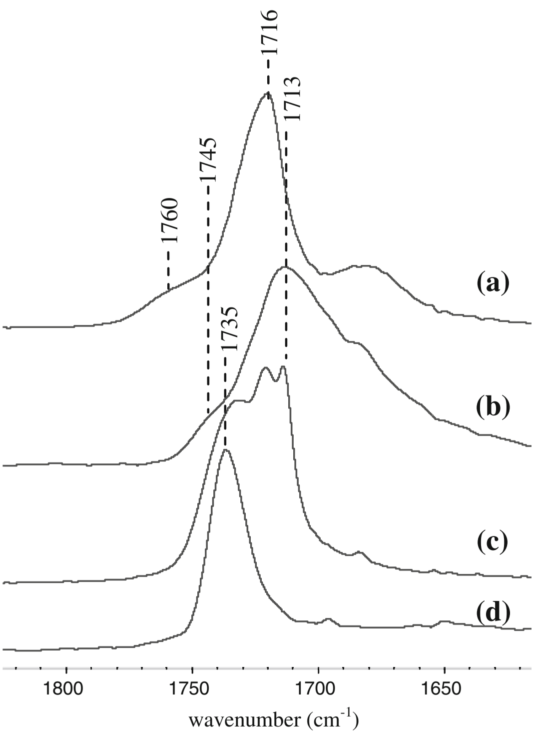


Fig. 8 Percentage weight remaining of 50:50 blended sample films during hydrolysis tests in a phosphate buffer solution pH 7.4 at 60 °C as a function of time: **a** PLET/EVA, **b** PLET/PHBV, and **c** PLET/PBS blends, in comparison with their constituent polymers

responsible for hydrolytic degradation of these blends. On the other hand, a decrease in intensities of C=O stretching modes of L in PLET (1760 cm^{-1}), and PBS (1740 cm^{-1}), is observed, as shown in Fig. 10c. This reflects an involvement of the two blend components in hydrolytic degradation of the blend samples. These observations are in good accord with those observed earlier from weight loss measurements.

Fig. 9 FTIR spectra in the carbonyl stretching region of (*a*) PLET, (*b*) PHBV, (*c*) PBS, and (*d*) EVA



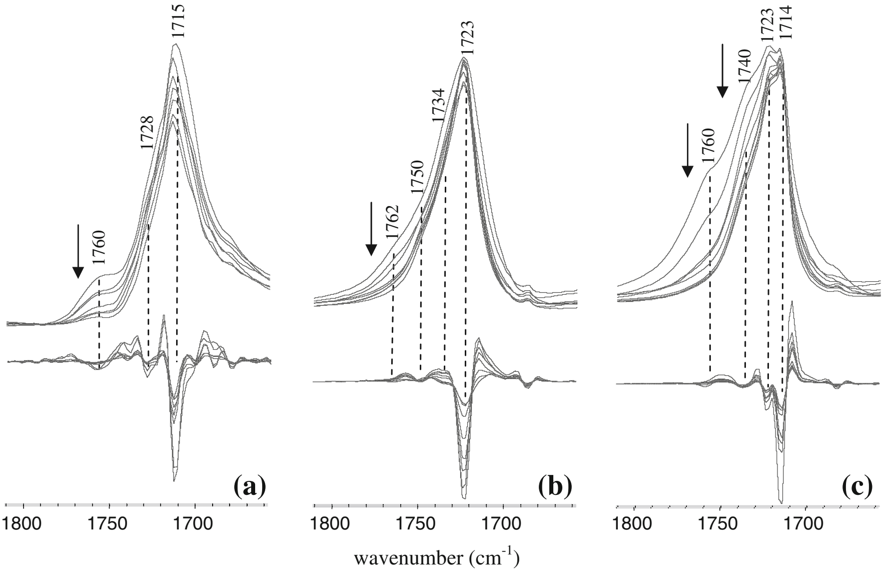


Fig. 10 FTIR spectra in the carbonyl stretching region and their 2nd derivative spectra as a function of hydrolysis time (1 week intervals) of: **a** PLET/EVA, **b** PLET/PHBV, and **c** PLET/PBS blends. (*Arrows* indicate bands that show a decrease in intensity as a function of hydrolytic degradation time)

Conclusions

Feasibility of employing an in-house synthesized poly(lactic acid-*co*-ethylene terephthalate), PLET, with moderate molecular weight and low mechanical properties, in film applications is demonstrated by blending the copolymer with commercial EVA, PHBV, and PBS. Results from DSC and SEM experiments indicate that immiscible blends are obtained from a mixture of EVA and PLET. On the other hand, miscible and partially miscible blends are achieved when PLET is mixed with PBS and PHBV, respectively. This results in crystallization retardation of PHBV and PBS components in their respective blends. Similar miscibility behaviors of the three blends are also observed from FTIR study, where band positions of C=O stretching modes of blend components in blends are compared with those of single component polymers. As storage modulus of these PLET-based blends decreases with an increase in PLET copolymer content, the maximum PLET content to retain appreciable mechanical properties of the blends is investigated. The results indicate that PLET content of up to 50 wt% is suitable for PLET/EVA system, while the corresponding value for PLET/PHBV and PLET/PBS blends is 25 wt%. At these PLET blend compositions or less, the storage modulus of blends is comparable to that of neat commercial polymer counterparts.

TGA results on PLET/EVA blends show that blends consisting of higher EVA content significantly exhibit higher heat stability, as EVA is more thermally stable than polyesters. On the other hand, an addition of PLET copolymer to PHBV and PBS results in an improvement in the blend's thermal stability, where the degree of improvement depends strongly on the copolymer content. Results from hydrolysis tests indicate that the PLET/PBS blend is the most susceptible to hydrolytic degradation, compared to other blend systems. Corresponding results are also observed from FTIR spectra of the blends as a function of hydrolysis time. The change in intensities of specific C=O bands with hydrolysis time indicates functional groups that are responsible for hydrolytic degradation of blends.

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