



Miscibility and Hydrolytic Degradability of Polylactic acid/Poly (ethylene terephthalate-co-lactic acid) Blends

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ABSTRACT

Poly(ethylene terephthalate-co-lactic acid) (PET-co-PLA) copolymer with medium molecular weight was synthesized and blended with commercial polylactic acid (PLLA) by solution and mechanical blending methods to optimize its mechanical properties. Miscibility and properties of the blends were characterized. Miscible blends are achieved at all compositions. A decrease in storage modulus and T_g of the blends, compared to neat PLLA, indicates a plasticizing effect of the copolymer in the blends. Hydrolytic degradability of the samples is examined in phosphate buffer solution (pH 7.2) at 60°C. Appreciable degradability of the blends is retained despite the incorporation of aromatic esters. Anomalous degradation behavior of the samples in buffer medium is examined. Negative weight loss values and flocculation of the samples are clearly apparent at a specific hydrolysis time. This is due to the re-precipitation of degraded species onto the remaining solid sample. The copolymer and its blends show high potential for use in various applications, especially in packaging and agricultural fields.

Keywords: aliphatic-aromatic copolyester, degradable, hydrolysis, blend, miscibility

1. INTRODUCTION

Polymeric materials are widely used because of their versatility, low cost, light weight, and durability, leading to a rapid increase in the material consumption. This, however, generates large amount of waste, which causes serious environmental problems. Petroleum-based polymer wastes require long decomposition time, as the

material is highly resistant to environment influences. Various degradable polymers, especially aliphatic polyesters, offer effective solutions to this problematic issue. Among these, polylactic acid (PLA) has received vast attention, because of its renewability, biocompatibility, and ease of processing [1-3]. However, PLA has low impact

strength and thermal stability, which limits its use in certain applications. In contrast, aromatic polyesters, especially poly(ethylene terephthalate) (PET), exhibit excellent mechanical properties and processability, which are suitable for various commercial applications. PET has been employed in the property modification of aliphatic polyesters by copolymerization [4-6]. In addition, this also enhances the degradability of PET, making the material more environmental friendly [7-9].

It is challenging to synthesize high molecular weight (MW) copolymers of PET and PLA, especially by polycondensation, which results in insufficiently-low mechanical properties of the products. Several modification methods have been practiced to improve properties of polymers, such as blending and plasticization. Among these, blending is regarded as a useful and economical way to optimize the material's property for specific applications. This is achieved by formation of specific interactions between the blend's components [10-12]. A compatibilizer can be employed to enhance compatibility of polymer blends. In our previous work, copolymers of lactic acid and terephthalate were synthesized by employing various types of diols [13-15]. Processability and degradability of the copolymers and their blends were assessed [16, 17].

In this work, a medium-sized poly(ethylene terephthalate-co-lactic acid) (PET-co-PLA) copolymer is synthesized and blended with commercial PLLA(4042D) resin by solution and mechanical blending methods. Effect of the blend composition on miscibility and properties of the blend products is investigated by employing Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron microscopy (SEM),

Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and Dynamic Mechanical Analysis (DMA). Hydrolytic degradation behaviors of the blends are examined by UV-Visible spectroscopy, FTIR, ^1H NMR and weight loss measurements.

2. MATERIALS AND METHODS

2.1 Materials

PET-co-PLA copolymer ($\bar{M}_n = 3.90 \times 10^3 \text{ g/mol}$) was synthesized by polycondensation of LA, DMT, and EG monomers, with a molar ratio of 1:1:2, as described earlier [13, 15]. Commercial PLLA resin (4042D, $\bar{M}_n = 1.20 \times 10^5 \text{ g/mol}$) was obtained from NatureWork. Dichloromethane (CH_2Cl_2), trichloroacetic acid (CCl_3COOH), potassium dihydrogen phosphate (KH_2PO_4), and potassium bromide (KBr) were purchased from Carlo Erba. Bis(2-hydroxyethyl terephthalate) (BHET) was obtained from Sigma-Aldrich. Deuterated trichloromethane (CDCl_3) and trifluoroacetic acid (CF_3COOH) were supplied from Merck. All chemicals were used without further purifications.

2.2 Blending Processes

The copolymer was blended with commercial PLLA by mechanical and solution blending methods. A Brabender mixer (PLASTI-CORDER® LAB STATION+ W50EHT) was employed in a preparation of mechanical blends at 160°C . Solution-blended samples were prepared by using CH_2Cl_2 solvent for PLLA and $\text{CCl}_3\text{COOH}/\text{CH}_2\text{Cl}_2$ for the copolymer. Effect of the blend compositions on properties of the materials was examined by varying the PLLA/PET-co-PLA blend ratio (80/20, 65/35, 50/50, 35/65, 20/80 w/w). The samples are denoted as PL80C20, PL65C35, PL50C50, PL35C65, and PL20C80, respectively. Miscibility,

physical, mechanical, and thermal properties of the blends were characterized.

2.3 Hydrolytic Degradation Tests

Hydrolytic degradation test was performed in a 0.1M phosphate buffer solution (KH_2PO_4) pH 7.2, at accelerated conditions (powder sample, at 60°C)[17]. The sample (0.2 g) was placed in vials containing the buffer medium (10 ml). After interval times of incubation, the remaining solid was removed, and dried in a vacuum oven at 60°C for 1 week. The weight of the dried sample was recorded and its percentage weight loss was calculated. The sample chemical structure and composition was characterized by ^1H NMR and FTIR spectroscopy. The buffer medium was not renewed during the degradation tests, where its pH was measured as a function of time using a pH meter (Ecoscan pH5). The aromatic ester content comprising in the degraded species, which are soluble in the buffer medium, was analyzed by UV-Vis spectroscopy[17]. UV-Vis spectra were recorded on a Spectronic Genesys 10 UV Spectrophotometer. The buffer medium obtained at hydrolysis time intervals was transferred into a quartz cuvette. Absorption spectra were recorded from 200-400 nm. Solutions of alkali-degraded BHET in the phosphate buffer were used to construct a standard curve in the determination of soluble aromatic esters content.

2.4 Characterizations

^1H NMR spectra were recorded at 500 MHz on a Bruker ZHO48201 AV500D spectrometer. The sample was dissolved in a 7% v/v $\text{CF}_3\text{COOD}/\text{CDCl}_3$ mixed solvent. The spectra were recorded immediately to avoid end-group esterification [4, 18]. FTIR spectra were recorded on a Thermo Nicolet 6700 spectrometer, with a total of

16 scans at 2 cm^{-1} resolution. The sample was cast as a film on a KBr pellet from a 2% solution in $\text{CCl}_3\text{COOH}/\text{CH}_2\text{Cl}_2$. The peak fitting module integrated in the OMNIC program was employed in a quantitative analysis of the FTIR spectra. DSC measurements were performed in an atmosphere of N_2 on a Mettler Toledo DSC 822. Transition temperatures were derived from the second heating curves. Samples were scanned from 0 to 240°C at a heating rate of $10^\circ\text{C}/\text{min}$. TGA measurement was carried out under N_2 atmosphere on a Mettler Toledo TGA/SDTA851e from 20 - 1000°C at a $20^\circ\text{C}/\text{min}$ heating rate. Crystalline characteristics were characterized by XRD (JEOL JDX-3530) using $\text{Cu K}_{\alpha 1}$ radiation. The samples were scanned from 2θ of 5 - 50° at 0.02 step size. Morphology of the blends was analyzed using SEM microscope (HITASHI S3400N). The samples were prepared by cryogenically fracturing in liquid N_2 . Mechanical properties were characterized by DMA (Mettler Toledo DMA/SDTA861e) in a tension mode. The experiment was performed in the temperature range of 0 - 100°C , using a heating rate of $3^\circ\text{C}/\text{min}$ at 1 Hz frequency. Film samples were prepared by a compression molding machine (Lab Tech) at 165 - 170°C , with a pressure of 350 psi.

3. RESULTS AND DISCUSSION

3.1 Blends Miscibility

Miscibility of PLLA/PET-co-PLA blends prepared from mechanical and solution blending methods were examined. DSC thermograms of the blends as a function of the blend compositions are compared with their single-component constituents in Figure 1. All spectra (both cooling and 2nd heating scans) exhibit a single glass transition temperature (T_g) characteristic, indicating a miscible blend for all compositions.

Crystallization (T_c) and melting (T_m) temperature peaks due to the copolymer's aromatic domains are clearly observed at around 120 and 177°C in those of the solution-blended samples, which are rarely found in the mechanical-blended counterparts. This is due to a higher degree of miscibility of the mechanical blends, as a result from the applied mechanical shear force and transesterification reaction, which leads to a decrease in the polymer molecular weight [1]. Insufficient dissolution of the copolymer during the preparation of the solution blends partly plays a role in the existent of the aromatic crystalline characteristic [17].

T_g values of PLLA/PET-*co*-PLA blends as a function of the blend content are summarized in Figure 2. The observed T_g of PET-*co*-PLA (46.3°C) is lower than that

of neat PLLA (59.4°C), due to the copolymer's low MW. T_g of mechanical-blended samples varies with the blend contents, ranging from 40.6-47.1°C, which is slightly different from those of the solution blended samples. This is likely due to the slight differences in degree of miscibility and the presence of trace amount of residue solvent in the solution blends. T_g of the blends from both systems is lower than those calculated from the Fox theory [19], as shown in the equation below. The theory estimates a T_g value of miscible blends by weighted average, with an assumption that there is no specific intermolecular interaction. The deviation of the observed T_g from the theoretical values reflects that the blend components bind strongly to themselves, compared to the inter-association [10].

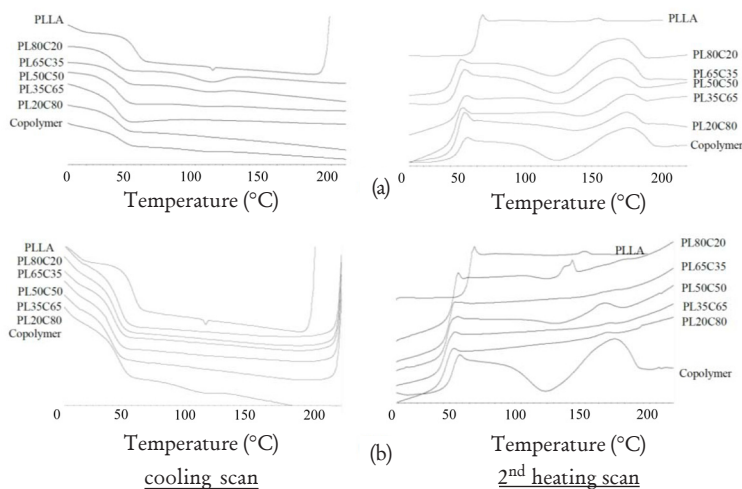


Figure 1. DSC thermograms of PLLA/PET-*co*-PLA blends prepared from (a) solution blending and (b) mechanical blending methods, as a function of the blend compositions.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \text{ The Fox theory}$$

where

T_g = theoretical glass transition temperature of the blend

T_{g1} and T_{g2} = glass transition temperatures of the blend components

W_1 and W_2 = weight fraction of the blend components

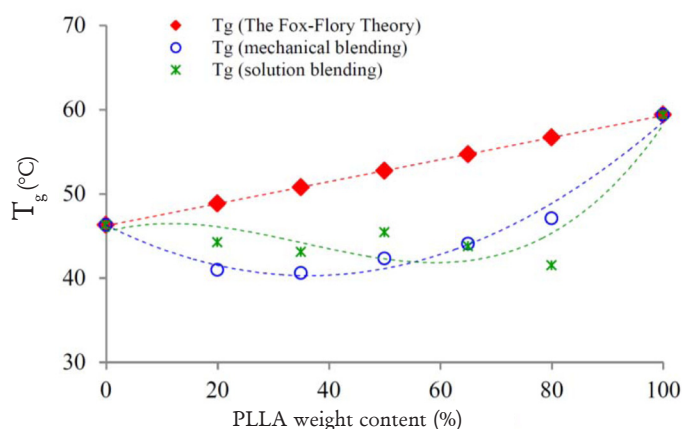


Figure 2. T_g of PLLA/PET-*co*-PLA blends as a function of the blend compositions.

Due to their higher degree of miscibility, detailed investigations are focused on the mechanical blended samples. FTIR spectra of PLLA/PET-*co*-PLA blends with different compositions, as shown in Figure 3, illustrate characteristic bands of the copolymer at 1720 cm^{-1} (aromatic C=O stretching), 1280 cm^{-1} (C-O-C aromatic asymmetric stretching), 1207, 1125, 1104 and 1019 cm^{-1} (ring C-H in-plane bending) and 730 cm^{-1} (ring C-H out-of-plane bending), and those of aliphatic PLLA at 1760 cm^{-1} (C=O stretching), 1455 cm^{-1} ($-\text{CH}_3$ asymmetric bending), 1383 and 1360 cm^{-1} (C-H bending of lactate group), and 1184, 1125 and 1094 cm^{-1} (C-O stretching)[20]. The intensities of the C-O-C stretching bands at 1280-1100 cm^{-1} and the aromatic ring mode at 730 cm^{-1} vary with the copolymer content. The latter mode is therefore employed in a normalization of the spectra for quantitative analyses.

The second derivative FTIR spectra (not shown) reveal additional bands in the C=O stretching region, *i.e.*, 1760 and 1740 cm^{-1} , which are characteristic modes of “free” and hydrogen bonded (HB) C=O of

PLLA and the copolymer’s lactates[11, 12]. The C=O band of aromatic units in the copolymer is observed at 1720 cm^{-1} . A vibrational mode located at 1645 cm^{-1} is due to -COOH end-groups. Curve resolving is applied to quantify these bands, in which that of PL35C65 is shown in Figure 3. Normalized band area of the corresponding modes as a function of the blend compositions are summarized in Table 1. The intensity ratio of the 1740/1760 modes is much higher than that of the neat PLLA and varies with the PLLA content in the blend, confirming a formation of hydrogen bonding interaction, probably from PLLA’s carbonyl and carboxylic acid/hydroxyl end groups of the copolymer [11, 12]. It is apparent that a closer match in the solubility parameters of the blend components is responsible for the miscibility enhancement [10]. The detected specific interaction, however, plays some roles in the blend’s miscibility. As the band area is normalized based on the characteristic mode of aromatic units, the results confirm that these carboxylic acid end-groups are mainly derived from the medium sized copolymer.

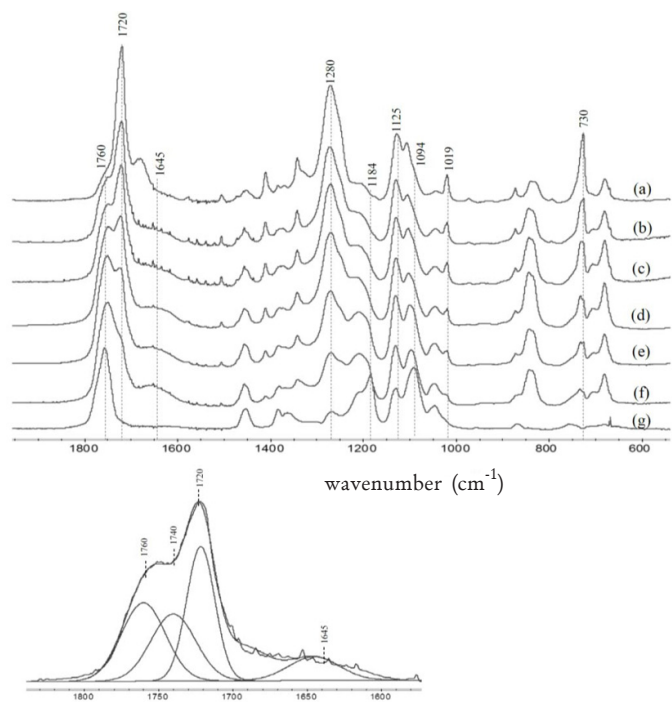


Figure 3. FTIR spectra of (a) PET-*co*-PLA, (g) PLLA, and PLLA/PET-*co*-PLA blends at various compositions: (b) 20/80, (c) 35/65, (d) 50/50, (e) 65/35, and (f) 80/20. The inset shows curve resolving of C=O stretching bands of a PL35C65 blend.

Table 1. Normalized band area of C=O modes and normalized crystallinity of PLLA/PET-*co*-PLA blends as a function of the blend compositions.

Sample	Normalized FTIR band area					Normalized crystallinity (%)	
	Aliphatic free C=O	Aliphatic HBC=O	HB/free C=O	Aromatic C=O	-COOH	PET- <i>co</i> -PLA	PLLA
	I_{1760}	I_{1740}	I_{1740}/I_{1760}	I_{1720}	I_{1645}		
PL20C80	0.26	0.18	0.68	0.47	0.10	37	0
PL35C65	0.34	0.15	0.43	0.46	0.10	45	0
PL50C50	0.45	0.11	0.24	0.39	0.11	33	0
PL65C35	0.63	0.02	0.03	0.29	0.11	33	0
PL80C20	0.71	0.01	0.02	0.17	0.14	0	2
PLLA	0.94	0.06	0.05	-	-	0	18

Phase morphology of PLLA/PET-*co*-PLA blends is analyzed. Figure 4 shows SEM images of the blend samples with different compositions after cryogenically fracturing.

Homogeneous crack patterns are clearly observed in all blends. This indicates miscible blends, which strongly agrees with those observed from DSC and FTIR experiments.

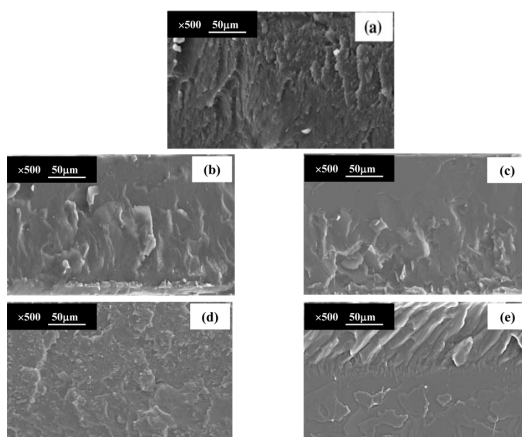


Figure 4. SEM images of (a) PET-*co*-PLA, (e) PLLA, and PLLA/PET-*co*-PLA blends: (b) 20/80, (c) 50/50, and (d) 80/20.

3.2 Thermal Decomposition

TGA thermograms and DTGA curves, as shown in Figure 5, indicate that PET-*co*-PLA copolymer has 3 main weight loss steps. The decompositions with midpoints at 320 and 390°C are due to aliphatic lactate (L) sequences and the copolymer's ethylene glycol (EG) units, respectively. A major weight loss step at 445°C is associated with the copolymer's aromatic (T) units. The thermogram of PLLA exhibits a single decomposition step centered at 380°C. For blend samples, L sequences of PLLA start to decompose at lower temperatures than that of the neat PLLA. The degree of

temperature shift increases with the decrease of PLLA content, as the PLLA domains are largely disrupted by the copolymer counterparts. This leads to retardation of PLLA crystallization and its lower thermal stability, *i.e.*, the lower the relative PLLA content, the higher the degree of disruption. A slight shift in the decomposition of the aromatic domains to lower temperature is also observed, *i.e.*, the inflection point shifts from 455 to 445°C with the decrease of copolymer content. This clearly indicates a mutual effect of crystallization retardation of the 2 components, as a result from miscible blend formation.

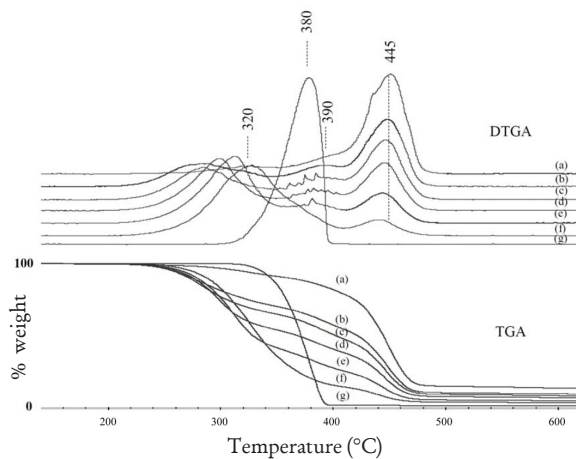


Figure 5. TGA and DTGA thermograms of (a) PET-*co*-PLA, (g) PLLA, and PLLA/PET-*co*-PLA blends: (b) 20/80, (c) 35/65, (d) 50/50, (e) 65/35, and (f) 80/20.

3.3 Dynamic Mechanical Properties

Dynamic mechanical properties of PLLA and PLLA/PET-*co*-PLA blends are examined. Figure 6(a) shows that commercial PLLA exhibits the highest storage modulus value. Upon blending with the copolymer, the modulus of the blends (in glassy state) decreases with the copolymer content. This is likely because the medium-sized copolymer acts as a plasticizer in PLLA matrix, leading to a softening of the material. This phenomenon is observed even though the copolymer contains stiff aromatic sequences, indicating that an effect of MW is more significant. A large decrease in the storage modulus is observed at 30-80°C, reflecting the glass transition process.

In a rubbery state, however, the blends with higher PET-*co*-PLA contents show higher storage modulus, reflecting that role of stiff aromatic sequences. Loss tangent ($\tan \delta$) value, a ratio of loss and storage moduli, as a function of temperature, is shown in Figure 6(b). The placement of its maximum value indicates a temperature where relaxation process takes place, especially the glass transition process. All samples exhibit a single T_g , where commercial PLLA has the highest value at around 65°C. T_g of the blends decreases as a function of the copolymer composition due to the plasticizer effect. This is in good agreement with those observed from DSC experiments.

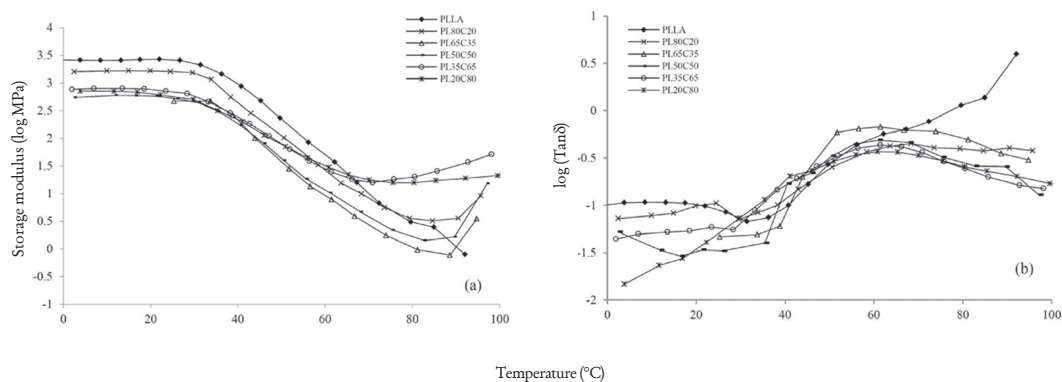


Figure 6. (a) Storage modulus and (b) $\tan \delta$ values, measured at 1 Hz, of PLLA/PET-*co*-PLA blends, as a function of the blend compositions and temperature.

3.4 Crystalline Characteristics

Figure 7 shows XRD traces of mechanical blended samples, where a variation in crystalline characteristics as a function of the blend contents is observed. The crystalline patterns are dominated by those of the copolymer, indicating that the crystalline domains of PLLA are largely interrupted by those of the copolymer. Normalized crystallinity of each blend components is

calculated based on their corresponding weight fractions, as summarized in Table 1. Crystallinity of the blends consisting of copolymer-rich compositions is similar, which is approximately 25% lower than that of the neat copolymer, whereas those of PLLA are not detectable. The PL80C20 blend shows almost no crystalline patterns of both blend constituents, reflecting a complete mutual disruption of their crystalline formation.

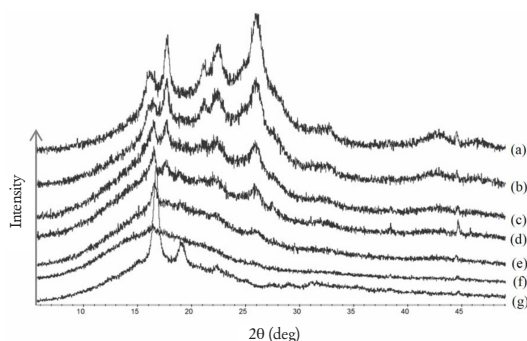


Figure 7. XRD traces of (a) PET-*co*-PLA, (g) PLLA, and PLLA/PET-*co*-PLA blends: (b) 20/80, (c) 35/65, (d) 50/50, (e) 65/35, and (f) 80/20.

3.5 Hydrolytic Degradation Behaviors

Degradation behaviors of the blends and their single component counterparts are examined by monitoring their percentage weight loss as a function of hydrolysis time. Figure 8(a) indicates that commercial PLLA possesses higher weight loss value than that of PET-*co*-PLA, as the copolymer contains

hydrophobic aromatic units in its structure. All blends show an increase in weight loss with an increase in the PLLA composition, where the highest weight loss of 30% is observed in PL80C20 at 24 weeks of hydrolysis. This is because aliphatic lactate sequences are major components that undergo hydrolytic degradation[7].

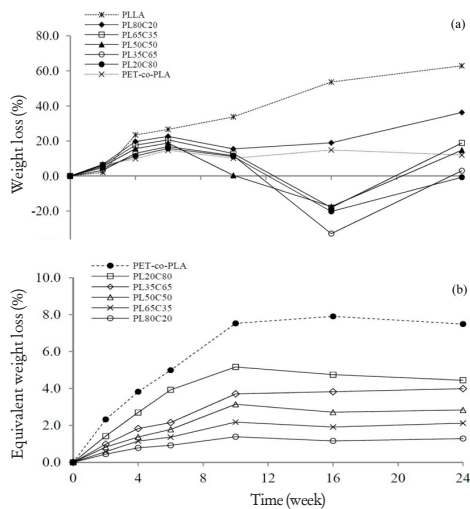


Figure 8. Percentage weight loss values (a) obtained from weight loss experiments and (b) equivalent weight loss calculated from content of degraded aromatic species of PLLA/PET-*co*-PLA blends at various blend compositions, as a function of hydrolytic degradation time. Appearance of a PL35C65 blend during hydrolytic degradation at (c) 4, (d) 16, and (e) 24 weeks.

The cumulative weight loss increases with the degradation time, where a sharp increase is observed during the first 4 weeks and levels off after this period. This indicates a saturation of degraded species soluble in the buffer solution, as the medium is not renewed during the hydrolysis. An anomalous decrease in the cumulative weight loss of the copolymer and all blended samples is observed at 16 weeks of hydrolysis, where some blends even exhibit negative weight loss values. This is in concert with an observation of flocculants formation, which is not observed during the first 16 weeks of measurements, as shown in Figure 8(c-e). The origin of this phenomenon is likely because the degraded species from the blends can partially dissolve in the buffer medium due to the interplay between ionic charges at the scission points and the hydrophobic nature of the copolymer fragments. The content of these species increase with hydrolysis time and reaches a saturation concentration. At this point, the degraded species flocculate by binding with or absorbing water molecules into their structures and precipitate onto the solid samples. The strong interaction in the bound structure prevents the evaporation of water molecules during the drying process (60°C for 1 week), resulting in a large increase in the weight of the remaining “dried” solid samples, which is reflected in the negative weight loss values. After 20 weeks of hydrolysis, however, further degradation of the soluble degraded species generates smaller-sized species, which exhibit a higher charge/hydrophobic ratio and hence a higher solubility in the buffer medium. This is evident from the disappearance of the flocculation and a reappearance of the increasing trend of the cumulative weight loss values, as shown in Figure 8(e).

To gain further insight into changes in chemical structures of the blends as a function

of hydrolysis time, UV-Vis spectroscopy is employed to examine the content of soluble species in the buffer solution. BHET is employed as a standard model for quantitative analysis of aromatic esters, as the compound shows similar absorption patterns to those of the soluble degraded products of the blends[17]. Figure 8(b) illustrates the content of degraded aromatic species in the buffer medium, calculated from UV-Vis spectra. The concentration is dependent on the copolymer composition, as this is a direct measurement of the aromatic esters degraded from the copolymer in the blends. All samples show an increase in the concentration of soluble aromatic ester fragments during the first 10 weeks, which reaches a saturation stage after this period. This agrees with those observed from the weight loss experiments, implying the maximum degradability of the solid sample. Subsequently, the soluble degraded fragments undergo further degradation by chain scission of their remaining aliphatic ester bonds. However, this does not alter the concentration of the aromatic units soluble in the buffer medium.

FTIR spectra of the remaining solid sample of PL35C65 blend obtained at different hydrolysis time are shown in Figure 9(a). The spectra are normalized based on the aromatic ring mode at 730 cm^{-1} . Band area of the normalized C=O bands is measured and compared across different samples, as illustrated in Figure 10(a). The relative intensity (band area) of the C=O band of PLLA (1760 cm^{-1}) decreases with time, reflecting an increase in the degree of hydrolytic degradation. An unusual increase in the band intensity, however, is observed at 16 weeks of measurement, which subsequently decreases to be a weak band after 24 weeks. The origin of this anomalous behavior is investigated by washing the degraded solid samples with a

0.1 M NaOH solution and excess amount of water. The corresponding results after washing are shown in Figures 9(b) and 10(b). The aliphatic C=O band at 1760 cm^{-1} almost disappears after 10 weeks of hydrolysis, which confirms that the maximum degree of hydrolysis has been reached. The resulting large content of degraded products in the buffer medium subsequently

leads to a precipitation onto the remaining solid sample, as discussed earlier. The precipitate can be eliminated by washing the solid sample with an alkali solution. In addition, carboxylate groups are largely generated as a result from the hydrolysis, reflected by an increase in intensity of a broad band centered at 1590 cm^{-1} , as a function of time.

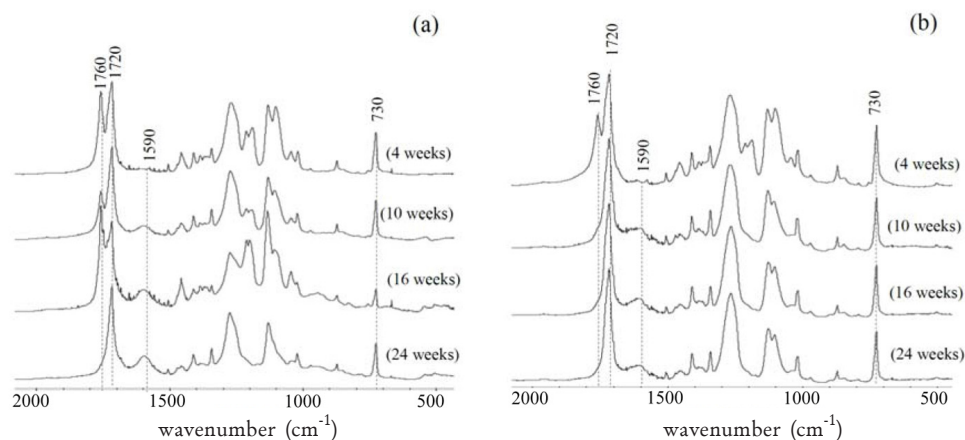


Figure 9. FTIR spectra of the remaining solid samples of PL35C65 blend, as a function of hydrolysis time: (a) original degraded sample and (b) the degraded sample after washing with NaOH solution.

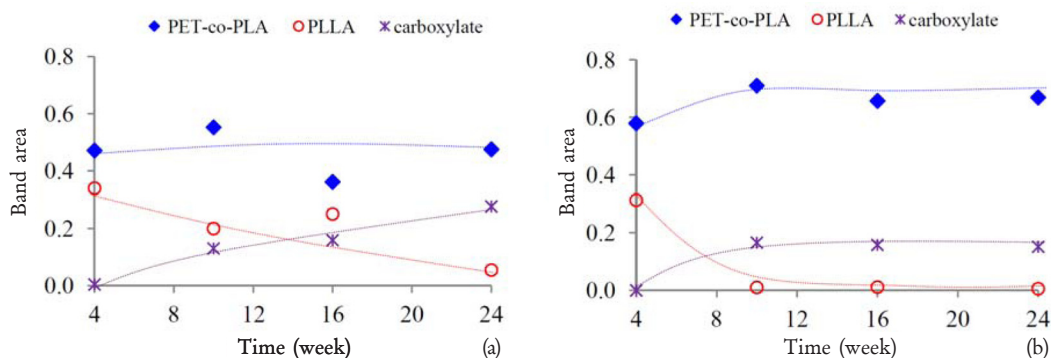


Figure 10. Normalized band area of ester's C=O and carboxylate modes of PL35C65 blend, as a function of hydrolysis time, (a) original degraded sample and (b) the degraded sample after cleaning with a NaOH solution.

^1H NMR spectra of solid sample of PL35C65 blend before and after 10 weeks of hydrolysis(not shown) exhibit signals due to aromatic at 8.1 ppm (H^1), lactate at 5.4 ppm (H^2), and $-\text{CH}_2\text{CH}_2$ at 4.5 and 4.7 ppm ($\text{H}^{5,6}$). The resonances of lactate in PLLA homopolymer are observed at 5.3 ppm (H^8) and 1.6-1.7 ppm ($\text{H}^{4,9}$). The signal of the copolymer chain end- CH_2 (H^3) is located at 4.2 ppm, and that of the PLLA chain end- CH_3 (H^7) is at 1.3 ppm [13, 15]. The intensities of H^3 and H^7 signals increase after hydrolysis, as these signals are associated with species generated by scission of the ester bonds.

Chemical compositions of PLLA/PET-co-PLA blends were also analyzed from ^1H NMR spectra, as summarized in Table 2. The aromatic/aliphatic molar ratios of all samples are lower than those obtained from FTIR and TGA, due to the low solubility of the samples which contain aromatic ester sequences[17]. On hydrolysis of the PL35C65 blend, the values increase with time from 0.42 to 0.71 at 0 and 24 weeks, indicating that lactate sequences are degraded at a faster rate than the aromatic counterparts. The results also show an unusual decrease in the ratio at 16 weeks, which agrees with those discussed earlier. After 20 weeks, the normal increasing trend of the ratio is observed.

Table 2. Aromatic/aliphatic ratio of PL35 C65 blend, determined from ^1H NMR spectra, as a function of hydrolytic time.

Hydrolytic time (week)	aromatic/aliphatic ratio
0	0.42
4	0.53
10	0.64
16	0.42
24	0.71

4. CONCLUSIONS

PET-co-PLA copolymer was synthesized and blended with commercial PLLA by mechanical and solution blending methods to optimize its mechanical properties. Miscible blends are obtained for all blend compositions. A decrease in storage modulus and T_g of the blends, despite the inclusion of the stiff aromatic copolymer, indicates a plasticizer effect of the copolymer in the blends. The blend's hydrolytic degradability is retained, as the copolymer has appreciable degradability. Anomalous degradation behavior of the samples in phosphate buffer solution was observed, due to the re-precipitation of degraded species onto the remaining solid sample. Given the improved physical properties and degradability of the copolymer and its blends, the materials show high potential for use in various applications, especially in packaging and agricultural fields, which require good mechanical properties and high degradation rates.

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