

Polyesters with Small Structural Variations Improve the Mechanical Properties of Polylactide

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ABSTRACT: Improving the properties of biodegradable polymeric materials is needed to obtain materials competitive with current bulk plastics. Low-molecular weight polyesters with small differences in their backbone were synthesized using a straight-forward method and were subsequently blended with polylactide (PLA). The materials showed an improved ductility of up to 100% points and otherwise retained material properties. The changes in mechanical properties were shown to match the miscibility range of the materials and can be predicted by the solubility parameters of the materials up to a polyester content of roughly 10% w/w. The thermal stability of all the low-molecular weight polyesters was higher than that of PLA, and most 25% w/w blends showed a thermal degradation behavior similar to that of neat PLA. Low-molecular weight polyesters were demonstrated as being potential enhancers of the properties of PLA, while the materials degradability was maintained. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 127: 27–33, 2013

KEYWORDS: blends; structure–property relations; poly-esters; compatibility; biodegradable

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INTRODUCTION

The improvement of the properties of biodegradable polymeric materials is in focus both in the industry and in academic research to obtain materials competitive with current bulk plastics. The inherent benefits of polylactide (PLA), such as its degradability and production from renewable resources, are handicapped by certain drawbacks, especially its poor impact resistance and poor ductility, its slow crystallization rate, and its poor thermal stability.^{1–4} We have previously shown that methods to improve the PLA properties include copolymerization,^{5,6} surface modification,⁷ and the incorporation of plasticizers, nanoparticles, or fibers.⁸ One economic and straight-forward method is blending, where new material properties are obtained from the combination of the properties of the constituents. Other polyesters have been preferred materials for PLA blends due to their degradability and similarity in chemical structure. Unfortunately, the interactions between PLA and these polyesters have generally been found to be weak or nonexistent, rendering most blends immiscible. Immiscible blends of PLA include PLA blended with poly(ethylene succinate) (PES),⁹ poly(*p*-dioxanone),¹⁰ poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate),^{11,12} poly(butylene adipate-*co*-terephthalate),¹³ poly(butylene succinate) (PBS),¹⁴ poly(3-caprolactone),^{15,16} and copoly-

mers of PLA and PCL.¹⁶ However, PLA was found to be miscible with poly(3-hydroxybutyrate) (PHB),^{17,18} giving rise to materials with a fourfold increase in elongation at break but only a third of the initial modulus when 25% (w/w) PHB was blended with PLA.¹⁷ Improvement in one specific property is often obtained at the expense of a deterioration in one or more other properties. For PLA blends and plasticized materials, it has been shown that a significant improvement in the impact toughness is usually accompanied by a great loss of strength and stiffness.²

Nowadays, a number of monomers can be produced by fermentation processes, including dicarboxylic acids, amino acids, and diols, and these can hence be used to create green polymers.¹⁹ These monomers include succinic acid (SA), lactic acid, propan-1,2-diol, and propan-1,3-diol.¹⁹ Other monomers can be synthesized from renewable resources, such as ethylene glycol (EG).²⁰ Blends in which the main constituent is PLA and the minor component is a low-molecular weight green polyester such as poly(propylene adipate) (PPA), poly(1,2-propylene adipate) (1,2-PPA), poly(ethylene adipate) (PEA), and PES are of great interest, because these combine the retention of degradability with synthesis from renewable resources.

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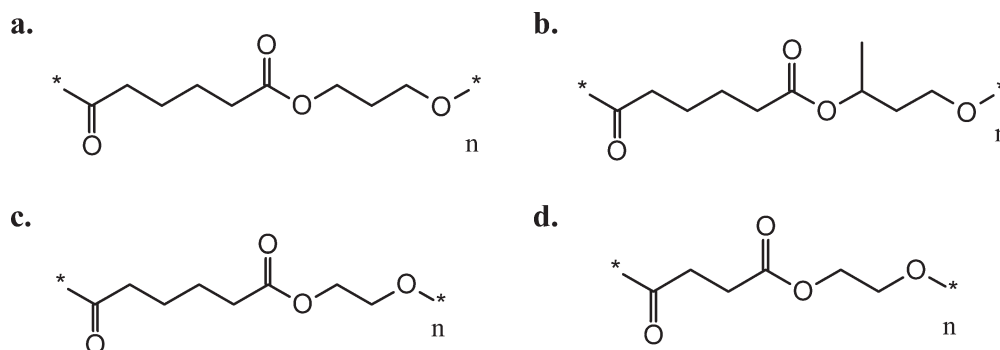


Figure 1. Chemical structures of (a) poly(propylene adipate) (PPA), (b) poly(1,2-propylene adipate) (1,2-PPA), (c) poly(ethylene adipate) (PEA), and (d) poly(ethylene succinate) (PES).

The aim of this work was to improve the ductility and thermal stability of PLA without any deterioration in other material properties. The approach adopted was to control the structure–property relationship of biodegradable polymer blends by creating miscible and immiscible systems of amorphous and semicrystalline degradable polyesters with only small alterations in their backbone with PLA as the major constituent. When combining a theoretically and experimental approach, by calculating the solubility parameters of the polymers and verifying the miscibility of the systems, the influence of seemingly small alterations in the polymer backbone on the mechanical and thermal properties can be determined. We synthesized low-molecular weight polyesters as a means to attain better miscibility^{21,22} and to create blends with a partial plasticizing effect, while trying to circumvent problems related to plasticizer migration.

EXPERIMENTAL

Materials

PLA was obtained from Nature Works Co., USA (5200D) and used as received. EG (SigmaAldrich, ReagentPlus, $\geq 99\%$), 1,3-propanediol (Aldrich, 98%), 1,2-propanediol (SigmaAldrich, ReagentPlus 99%), SA (SigmaAldrich, Reagent-Plus $\geq 99\%$), adipic acid (AA; Sigma, 99%), titanium (IV) isopropoxide (TIP) (Aldrich, purum $\geq 97\%$), chloroform (Fisher Scientific, HPLC grade), and methanol (Sigma-Aldrich) were used as received.

Stepwise Polymerization of Polyesters

Four low-molecular weight polyesters with small differences in their backbone were synthesized by stepwise polymerization; PPA, 1,2-PPA, PEA, and PES (Figure 1). PPA was synthesized by adding AA and 1,3-propanediol in a molar ratio of 1 : 1.08 to ensure hydroxyl functionalized end-groups. The polymerization was performed in two steps. First, direct esterification was started by immersing the reaction vessel in an 80°C thermostated oil bath. The temperature was raised to 190°C and held constant using an Ikatron ETC D3 temperature regulator (IKA Labortechnik, Germany). The reaction vessel was connected to a cooler and a small trap to collect the evaporated water. When approximately the theoretical amount of water was formed and no more water was produced, the catalyst, TIP, was added in a ratio of 1 : 1000 to the diacid. During this polycondensation, the pressure was slowly lowered to high vacuum (<0.20 mbar) followed by a gradual increase in temperature to 220°C, which

was maintained for a sufficient time to reach the desired molecular weight (Table I). The PPA was dissolved in chloroform and precipitated in ice-cold methanol followed by drying under vacuum. The other polyesters were synthesized with the same procedure and with the same monomer and catalyst ratios except for 1,2-PPA, which was synthesized at a lower temperature during the first step (175°C) due to the lower boiling point of 1,2-propanediol (188°C).

Solution Casting of Films

Solid polymer films were prepared by solution casting of 4% (w/w) solutions in chloroform of the homopolymers or polymer blends in presilanized Petri dishes and were kept under lids for at least 36 h. The lids were thereafter removed, and the films were dried in air followed by drying under vacuum until all the solvent has been removed and subsequently stored under vacuum until use. Blends containing 0, 5, 10, 15, 20, and 25% (w/w) of the polyester in a PLA matrix were prepared. The thickness of the films obtained was 180 ± 40 μm .

Characterization

Nuclear Magnetic Resonance. ¹H-NMR was used to confirm the chemical structures and to determine the compositions of the blends. Five milligrams of sample were dissolved in 1 mL of deuterated chloroform (CDCl₃) with nondeuterated chloroform as an internal standard ($\delta = 7.26$ ppm). The solution was then analyzed using a Bruker AC-400 nuclear magnetic resonance spectrometer operating at 400 MHz.

¹H-NMR (400.13 MHz, CDCl₃ δ): PEA: 4.22 (s, 4H, OCH₂CH₂O), 2.32 (s, 4H, COCH₂CH₂), 1.62 (s, 4H, CH₂CH₂CH₂CH₂); 1,2-PPA: 5.01 (m, 1H, OCH(CH₃)-CH₂), 4.04 and 3.92 (m, 2H, CH(CH₃)CH₂O), 2.20 (m, 4H, COCH₂CH₂), 1.53 (s, 4H, CH₂CH₂CH₂), 1.11 (s, 3H, CHCH₃); PPA: 4.07 (7, 4H, OCH₂CH₂), 2.26 (s, 4H, COCH₂CH₂), 1.89 (m, 2H, CH₂CH₂CH₂), and 1.58 (s, 4H, CH₂CH₂CH₂CH₂); PES: 2.64 (s, 4H, COCH₂CH₂CO), 4.28 (s, 4H, OCH₂CH₂O); PLA: 5.14 (q, 1H, COCH₂(-CH₃)O), and 1.56 (d, 3H, CHCH₃).

Size Exclusion Chromatography (SEC). The molecular weights and molecular weight distributions of PLA and the synthesized polyesters were determined using a Verotech PL-GPC 50 Plus system equipped with a PL-RI Detector and two Mixed-D (300 \times 7.5 mm) columns from Varian. The instrument was calibrated with polystyrene standards with a narrow molecular weight distribution in the range of 580–400,000 g/mol. The

Table I. Reaction Times for the Direct Esterification and the Polycondensation Steps During the Step-Wise Polymerizations of Poly(propylene adipate), Poly(1,2-propylene adipate) (1,2-PPA), Poly(ethylene adipate) (PEA), and Poly(ethylene succinate) (PES), the Number–Average Molecular Weights, Polydispersity Indices, the Polymers Densities and the Calculated Solubility Parameters

Polyesters	Reaction time step 1 (min)	Reaction time step 2 (min)	M_n (g/mol) ^a	PDI	Density (g/cm ³) ^b	δ_s (MPa ^{1/2})	T_g
PPA	130	30	5,800	1.91	1.2 ²³	20.4	−56.5 ± 0.1
1,2-PPA	240	1140	3,000	2.02	1.14 ^b	19.1	−40.5 ± 0.4
PEA	180	1200	4,600	1.71	1.12 ²⁴	18.9	−46.8 ± 0.8
PES	215	35	4,700	1.78	0.84 ²⁵	13.6	−13.4 ± 1.6
PLA	–	–	154,000	1.50	1.22 ²⁴	19.1	57.2 ± 0.5

^aMeasured for the precipitated polymers using size exclusion chromatography (SEC) calibrated with PS standards, ^bMeasured by weighing a known volume of the polymer, ^cCalculated using the Small equation for solubility parameter.

samples were injected with a PL-AS RT Autosampler for PL-GPC 50 Plus, and chloroform was used as the mobile phase (1 mL/min, 30°C). Corrections for flow rate fluctuations were made using toluene as an internal standard. Cirrus™ GPC Software was used to process the data.

Polarimeter. The *D*-content of the PLA was determined using a Perkin Elmer polarimeter 343 at ambient temperature. Measurements were performed with a sodium lamp at a wavelength of 589 nm. Duplicate samples of a series of PLA reference materials with known *D* and *L* contents were used to create a calibration curve from which the *D* content in the unknown sample was calculated.²³ All samples were precipitated three times and thoroughly dried under vacuum before testing.

Solubility Parameters. The miscibility of the materials was evaluated theoretically by calculating the solubility parameters for each material using the Small method²⁴:

$$\delta_s = \frac{\rho \sum_j F_j}{M} \quad (1)$$

where ρ is the density of the polymer, M is the molar mass of the repeating unit, and F is the sum of the group contributions to the cohesive energy density listed in the literature.²⁴

Tensile Testing. The mechanical properties of the neat PLA and of the blends of all compositions were evaluated by tensile testing performed on an Instron 5944 equipped with pneumatic grips operated by a Dell 466/ME computer, using a load cell with a maximum capacity of 50 N at a crosshead speed of 15 mm/min. The rectangular specimens (*width* = 5 mm, *length* = 8 mm) were preconditioned before testing for a minimum of 40 h at 23°C and 50% relative humidity according to ASTM D618-08. At least five samples for each composition were tested, and the average thickness of each sample was calculated from three independent measurements with a Mitutoyo micrometer.

Differential Scanning Calorimetry (DSC). The thermal properties of the neat PLA and of the blends were investigated using a DSC (Mettler Toledo DSC 820 module) under nitrogen atmosphere. Two to eight milligrams of the sample were placed in a 40- μ L aluminum cap without pin and sealed with a lid. Samples were heated and cooled under nitrogen gas flow of 60 mL/min using liquid nitrogen for cooling. The specimens were first held

isothermally for 5 min at −100°C, heated from −100 to 200°C at a rate of 10°C/min and then held isothermally for 5 min at 200°C. The samples were thereafter cooled to −100°C at a rate of 10°C/min and held there for 5 min. Finally, the samples were again heated from −100 to 200°C at a rate of 10°C/min. Duplicate samples of all materials were evaluated. The miscibility of the materials was investigated after melt quenching of the blends from 200 to −70°C followed by heating the samples to 200°C at 10°C/min. The melting point was noted as the maximum value of the peaks from the second heating scan, and the glass transition temperature was taken as the midpoint of the glass transition from the second heating scan. To calculate the enthalpy of heating, both the first and second heating (ΔH_f) were evaluated for the PLA fraction of the blend. PPA, PEA, and PES have previously been shown to be semicrystalline with $T_{g,PPA} = -69^\circ\text{C}$ and $T_{m,PPA} = 38^\circ\text{C}$ ²⁵; $T_{g,PEA} = -52.7^\circ\text{C}$ and $T_{m,PEA} = 45.4^\circ\text{C}$ ²⁵; $T_{g,PES} = -9.8^\circ\text{C}$ and $T_{m,PES} = 105.5^\circ\text{C}$.²⁶

Thermal Gravimetric Analysis (TGA). The thermal stability of the materials was evaluated using TGA conducted on a Mettler Toledo TGA/SDTA 851. About 3–50 mg of the sample was loaded in a ceramic cup. The samples were heated from 25 to 600°C at a rate of 10°C/min under nitrogen gas flow of 50 mL/min.

RESULTS AND DISCUSSION

Four biodegradable, low-molecular weight polyesters were successfully synthesized from combinations of five different monomers using a straight-forward two-step approach (Table I). The monomers were chosen based on potential future production from fermentation reactions or synthesis from renewable resources^{19,20} and to assess the effect of small chemical alterations in the polyester backbone on the properties of the blends. No purification of the monomers was necessary to reach the desired molecular weights and the notion of using as “green” chemistry as possible prevailed throughout the work. The reaction times for both steps were chosen to reach the desired molecular weight (around 4000 g/mol) while minimizing thermal degradation. The reactivity of the monomers varies depending on, for example, the use of a primary or secondary alcohols and the length of the methyl sequence in the monomers. The reaction

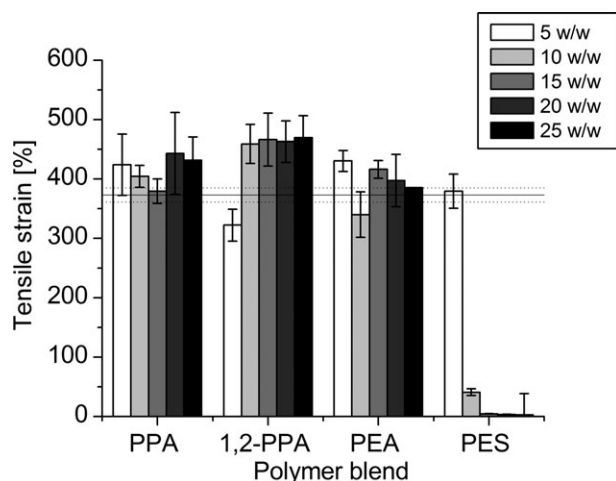


Figure 2. Tensile strain at break for the different blends. The solid horizontal line shows the mean value for the pure PLA film and the dashed lines the standard deviation.

times for the two steps are given in Table I. It should be mentioned that higher molecular weights were not reached for 1,2-PPA even after prolonged reaction times or at an elevated temperature. Instead, a visible darkening of the polymer occurred showing clear signs of decomposition.²⁷ The glass transition temperatures of the synthesized low-molecular weight polyesters match the values found previously.^{25,26}

The molecular weights of polymers determined by SEC have previously been shown to be overestimations,^{28,29} and more accurate values can be calculated using, for example, ¹H-NMR. However, these values are somewhat misleading in this case due to the incomplete hydroxyl end-group functionalization and the weak discrepancy between the carboxylic end-group and ester groups and they are therefore not given. ¹H-NMR was also used to determine the composition of the blends, and the results showed a good agreement between the theoretical and experimental results.

The miscibility of binary blends can be theoretically calculated using the Small equation, and the miscibility increases with decreasing difference between the solubility parameters. Accordingly, 1,2-PPA should be fully miscible with PLA, and PES should be at least partly miscible with PLA (Table I).

Mechanical Properties

The mechanical properties of the blend films were determined by tensile testing. Generally, all blends except PLA/PES showed mechanical properties better or at least similar to those of the reference PLA film (Figures 2 and 3). The most ductile materials were obtained with 1,2-PPA. Adding 10% or more 1,2-PPA increased the tensile strain by more than 100% points. This was not at the expense of a reduced tensile stress and strength as is often seen when plasticizers and/or other polymers are added to PLA (Figure 2).²

Particularly with 10% (w/w) added 1,2-PPA, the tensile stress increased slightly compared to that of neat PLA although the difference was within the standard deviation of the measurements. Above 10% (w/w) PLA/1,2-PPA, the tensile stress

decreased with increasing 1,2-PPA content. The addition of PEA increased the tensile strain of the material with a 5% (w/w) addition, but with higher PEA amounts [20–25% (w/w)], the tensile strain was of the same order as that of the neat PLA (Figure 3).

An increase in the elongation at break after blending PLA with PEA was also observed by Okamoto et al.³⁰ The addition of PPA did not affect the mechanical properties of PLA to any great extent, although both the tensile stress and tensile strain were somewhat higher with a PPA content of 20–25% (w/w). This is somewhat unexpected, because it is generally considered that the tensile strain increases with decreasing T_g of the blend. The T_g of PPA and 1,2-PPA was -56.5 and -40.5°C , respectively. The higher tensile strain of 1,2-PPA/PLA is probably due to their similar solubility parameters and the amorphous character of 1,2-PPA itself, which results in a more homogeneous and thereby more ductile material.

In contrast, blending PES into PLA led to a deterioration in the mechanical properties and especially the tensile stress decreased rapidly with increasing PES content. This is probably due to the poor miscibility between the two polyesters that results in phase separation. The large difference in solubility parameters (19.1 for PLA and 13.6 for PES) also predicts this outcome. Although the PLA/PES blends were very brittle, the modulus of the PLA/PES blends increasing with increased PES content, and these were the stiffest of all the materials tested (Figure 4).

The modulus of neat PLA was ~ 250 MPa whereas the modulus of the 25% (w/w) PLA/PES blend was ~ 600 MPa. The moduli of the other PLA/polyester blends were fairly similar to that of neat PLA regardless of polyester content. Lu et al.⁹ have reported an increase elongation at break and a decrease in modulus with increasing PES content in PLA/PES blends. However, they used a high-molecular weight PES ($M_w = 213,000$) and the increase in elongation at break was observed only with a PES content greater than 40%. The ductile behavior and reduced stiffness were probably due the properties of PES itself,

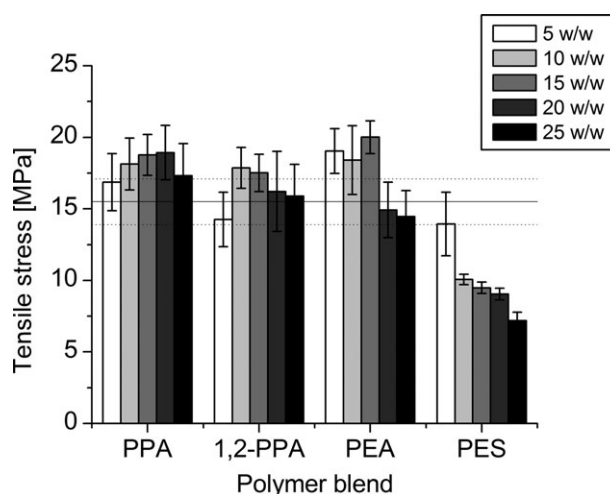


Figure 3. Tensile stress at break for the different blends. The solid horizontal line shows the mean value for the pure PLA film and the dashed lines the standard deviation.

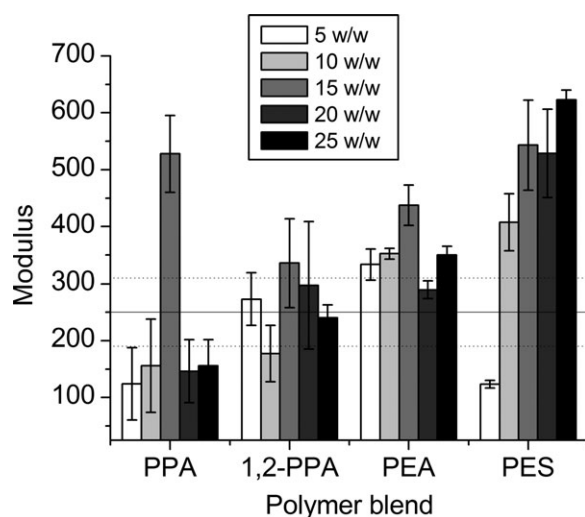


Figure 4. Modulus for the different blends. The solid horizontal line shows the mean value for the pure PLA film and the dashed lines the standard deviation.

which is also endorsed by their finding that PLA was immiscible with PES.

Blending 1,2-PPA into the PLA matrix gave the most ductile material, and the properties were maintained when the amount added was increased. This may be a result of the similarity in solubility parameters of PLA and 1,2-PPA and their resemblance in chemical structure (Table I and Figure 1, respectively). PPA improved the tensile strain of PLA to approximately the same extent as PEA, although the solubility parameter deviates more from that of PLA. This is explained by the T_g of PPA, which is the lowest of all the polyesters tested. The elongation at break of PLA/polyester blends has been reported to increase with decreasing T_g of the blend.³⁰ Thus, 1,2-PPA seems to be an effective agent for decreasing the brittleness of PLA without reducing the tensile stress.

Thermal Properties

The miscibility and the thermal properties of the PLA/polyester blends were evaluated by DSC. It is well known that the T_g of two materials changes if the materials are partially miscible and merge into one if the materials are fully miscible. A single T_g of a polymer blend does not, however, guarantee full miscibility, because the minor component in the blend is not always detected by the DSC instrument.^{31,32} Miscibility or partial miscibility in this study was therefore defined as a lowering of the T_g of the PLA phase. However, the T_g of PLA was very close to the T_m of both PPA and PEA, which made the determination of T_g very difficult. T_g values of the PLA blends were therefore evaluated after quenching the materials from the melt, a method which has been proven useful in studying PLA/polyester blends.^{9,10,17,22,25,27,31} As with the mechanical properties, all low-molecular weight polymers except PES were able to lower the T_g of the PLA phase (Table II).

The addition of 10% (w/w) PEA or 1,2-PPA lowered the T_g the most, from 49°C to 37°C and 40°C, respectively. Adding larger

amounts of PEA or 1,2-PPA did not, however, affect the T_g more. Up to 10% (w/w), the addition of PPA also decreased the T_g of the PLA phase but not to the same extent (44°C). The T_g of the PLA phase in the PLA/PES blends was not greatly affected by blending, in contrast to previously reported results for high-molecular weight PES and PLA blends.⁹ The T_g of the blends containing up to 10% (w/w) PES was slightly lowered, and this agrees well with previous reports that the molecular weight plays an important role for the miscibility.^{21,22} Hence, it appears that the low-molecular weight polyesters, with the exception of PES, are partially miscible with PLA. Furthermore, the PLA bulk phase becomes saturated with polyester at a composition of about 10% (w/w). About 10% (w/w) also seemed as an appropriate amount to improve the material properties (cf. Mechanical Properties), especially for 1,2-PPA.

DSC was also used to evaluate the melting temperature and degree of crystallinity in the blends. The melting temperatures of the PLA and low-molecular weight polyesters in the blends were virtually unchanged compared to that of the neat polymers. As previously observed, the homopolymer of PLA did not crystallize during the second heating scan. However, all PLA/polyester blends showed an increased crystallinity with increasing amount of polyester (Figure 5). The values for the enthalpy of heating (corresponding to the degree of crystallinity) were adjusted to compensate for the compositions. Apparently, the added low-molar mass polyester promotes the crystallization of PLA, acting as nucleation points for the PLA chains to crystallize.

This phenomenon has been explained by residual crystal fragments from the polyesters after melting acting as nucleation agents for the cold crystallization of PLA upon further heating. This would not however explain the much more pronounced crystallization of the blends with PEA and PPA due to their low melting temperatures or 1,2-PPA, because it is amorphous. In these cases, it is more probable that molten droplets of the low-molecular weight polyesters act as nucleation agents for PLA, as has been found with PBS/PLA blends.³³ Although it is amorphous, adding 1,2-PPA results in the same degree of crystallinity as the semicrystalline polyesters. The nucleating effect is substantially higher with the addition of 10% (w/w) than with 5% (w/w), but further addition of polyester has a limited effect on the degree of crystallinity. This coincides with the approximate maximum amount of low-molecular weight polyester miscible in the PLA matrix. If more than 10% (w/w) PEA, 1,2-PPA, and PPA is added, the crystallinity of PLA does not increase further. PES does not induce crystallization of PLA to any significant extent, and the reason could be its immiscibility. The thermal properties also illustrate that these polyester blends are interesting candidates for future biodegradable materials, and the blends are partially miscible up to ~ 10% addition of polyester.

Thermal Stability

The thermal stability of the neat polyesters and the blends containing 25% (w/w) low-molecular weight polyester was investigated using TGA. All the neat polyesters showed a single weight loss step at the maximum degradation temperature (T_{max} ; Table II), and less than 5% (w/w) residue remained at 600°C. The low-molecular weight polyesters all showed significantly higher T_{max} values than the neat PLA, which had a T_{max} in the range of 371–

Table II. Thermal Properties of the Neat Samples and Blends Determined Using DSC and TGA

Sample	Composition	T_g^a	T_g^b	$T_{5\%}^c$ (°C) ^c	T_{max} (°C) ^c
PLA	100/0	48.9 ± 0.2		308	341
PLA/PEA	95/5	50.5 ± 1.2	49.8		
	90/10	37.1 ± 3.0	42.7		
	85/15	38.6 ± 0.2	35.9		
	80/20	37.1 ± 0.1	29.4		
	75/25	35.6 ± 1.1	23.2	305	358
	0/100			333	371
PLA/1,2-PPA	95/5	49.5 ± 1.3	50.4		
	90/10	43.6 ± 0.0	43.9		
	85/15	41.2 ± 1.0	37.7		
	80/20	32.6 ± 0.9	31.6		
	75/25	39.8 ± 3.0	25.8	283	323/381
	0/100			354	388
PLA/PPA	95/5	46.6 ± 4.5	48.8		
	90/10	44.0 ± 0.2	40.8		
	85/15	47.3 ± 3.2	33.1		
	80/20	47.1 ± 3.5	25.8		
	75/25	45.8 ± 3.1	18.9	304	353/386
	0/100			343	398
PLA/PES	95/5	51.3 ± 5.9	52.8		
	90/10	50.3 ± 6.1	48.5		
	85/15	53.7	44.3		
	80/20	46.9 ± 0.5	40.2		
	75/25	49.0 ± 5.6	36.2	302	322/357/379
PES	0/100			311	381

$T_{5\%}$ and T_{max} correspond to the temperature at which 5% (w/w) weight loss had occurred and the maximum degradation temperature, respectively.

^aDetermined from the second heating scan of a quenched sample, ^bCalculated using the Fox equation, ^cDetermined using TGA.

398°C. The initial thermal stability was characterized as the temperature at which 5% (w/w) weight loss had occurred ($T_{5\%}$). PEA, PPA, and 1,2-PPA all showed higher $T_{5\%}$ values than PLA and PES.

The thermal degradation profile of the blend with 25% (w/w) PEA showed a single T_{max} value intermediate those of the neat components of the blends, whereas the 1,2-PPA, PPA, and PES blends all showed a clear maximum degradation temperature together with one or two additional inflection temperatures. The T_{max} values that appeared at the lower temperature were closer to that of neat PLA, and the latter one was closer to that of the low-molecular weight polyester. The $T_{5\%}$ values of all blends were similar to the value of neat PLA except for PLA/1,2-PPA, where the $T_{5\%}$ value was ~ 20 and 70°C lower than those of PLA and 1,2-PPA, respectively. In addition, a wide temperature range of thermal degradation was observed, indicating that this particular blend, although showing signs of miscibility up to 10% (w/w) 1,2-PPA in PLA, has interactions that result

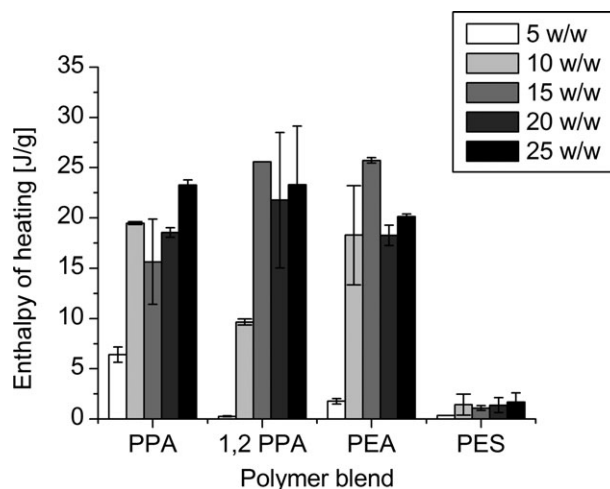


Figure 5. Enthalpy of heating for PLA in the blends at different compositions during the second heating scan obtained by DSC.

in unfavorable thermal stability. Hence, all the neat low-molecular weight polyesters were more thermally stable than PLA, and all the blends except 1,2-PPA/PLA showed a thermal degradation behavior similar to that of neat PLA.

CONCLUSIONS

Adding low-molecular weight polyesters to PLA improved the mechanical properties and thermal stability without any deterioration in other material properties. Blends of PLA and 5–25% (w/w) purposely designed low-molecular weight polyester showed greater ductility and otherwise retained material properties. The overall best blend was obtained by adding 10% (w/w) 1,2-PPA, which increased the tensile strain by 100% points compared to that of neat PLA. This was not however at the expense of a lowered tensile stress. Although the structures of the synthesized polyesters were very similar, the small differences in the polymer backbone had a large effect on the properties of the blends. The polyester with the shortest carbon chains PES gave the most brittle PLA blend with inferior mechanical properties compared to those of pure PLA. Adding two more carbon atom to the main chain, as in PEA, slightly increased the toughness compared to that of pure PLA, and blending PLA with 1,2-PPA gave the most ductile material. The change in mechanical properties correlated with the miscibility range of the materials determined by DSC and was predictable from the materials' solubility parameters up to a blending degree of roughly 10% (w/w). At 10% (w/w) of PEA, 1,2-PPA, or PPA, PLA also showed an ability to crystallize, in contrast to neat PLA. Hence, crystallinity was induced in PLA regardless of whether the low-molecular weight polyester was amorphous or semicrystalline. The thermal stability of all the neat low-molecular weight polyesters was greater than that of PLA, and most 25% (w/w) blends showed a thermal degradation behavior similar to that of neat PLA. The synthesized low-molecular weight polyesters were proven to be potential material property enhancers for PLA while maintaining a green material and inherent degradability.

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