

Melt blending of polylactide and poly(methyl methacrylate): Thermal and mechanical properties and phase morphology characterization

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ABSTRACT: Blends of polylactide with poly(methyl methacrylate), PLA/PMMA, were prepared by a semi-industrial twin screw extruder and afterwards were injection molded. Blends were studied using different techniques as Fourier Transform Infrared Spectroscopy (FTIR), Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), and mechanical properties by means of tensile and impact tests, were also studied. This work helped better understanding of apparently contradictory results reported in the literature for PLA/PMMA blends prepared by melt compounding. DSC first heating scan and DMA results showed partially miscible blends, whereas the second DSC heating scan showed miscible blends. For miscible blends, T_g values were predicted using Gordon-Taylor equation. On the other hand, Small and Van Krevelen approaches were used to estimate the solubility parameters of neat PLA and neat PMMA, and Flory-Huggins interaction parameter was calculated from solubility parameters. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42677.

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INTRODUCTION

The consumption of plastics and their broad spectrum of applications in the current society support the need of continuous scientific research and development of new polymeric materials. Recently, biodegradable and/or renewable resource derived plastics have gained a lot of interest because of the increasing environmental consciousness and sustainability needs.^{1–4} Polylactide is a biodegradable and bioabsorbable aliphatic polyester which can be obtained from sugarcane, corn, etc. As PLA has good mechanical properties and processability, it is one of the most interesting bioplastics. However, PLA has some drawbacks when compared to other thermoplastics (e.g. PP, ABS, PET...) as poor impact strength, relatively high price, and low heat distortion temperatures.^{5–7} Besides, PLA degrades during thermal processing or under hydrolytic conditions, leading to a quick reduction of molecular weight which affects the final properties of the material.⁸ Many attempts have been made to modify poly(lactic acid) by blending.^{9–14} Blending of polymers is a relatively simple method to modify polymer properties. In a perspective of production scale-up, melt blending of PLA with other polymers could be a sustainable and effective approach to improve the thermo-mechanical behavior of PLA-based materials. Blends could exhibit advantageous physical and chemical properties which each indi-

vidual polymer does not possess. Properties of blends depend on the chemical composition and on the compatibility or miscibility of the components. Poly(methyl methacrylate) is a synthetic polymer with good chemical and physical properties. There is little scientific literature regarding PLA/PMMA blends and most of papers are for blends prepared by solution methods.^{15–19} However, two studies of PLA/PMMA blends prepared by melt processing can be found in the literature^{20,21} and reported results apparently seemed to be contradictory. Samuel *et al.*²⁰ observed that all PLA/PMMA blends prepared by melt compounding were miscible. PLA/PMMA blends prepared via melt processing were also studied by Le *et al.*²¹ They concluded that the obtained blends were immiscible and regions of co-continuous structures were identified using SEM images.

This work helps to better understand the contradictory results reported in the literature for PLA/PMMA blends prepared by melt compounding. In this work, melt blending of PLA with PMMA was carried out using a semi-industrial twin screw extruder and the characterization of different blends is presented and compared with the scarce results reported in the literature. Phase structure, morphology, thermal properties, and mechanical properties of obtained blends were studied. Flory-Huggins interaction parameter of PLA/PMMA blends was estimated using the

solubility parameters calculated by group contribution method according to Small and Van Krevelen. An attempt was made to relate miscibility, structure, and properties in the studied blends.

EXPERIMENTAL

Materials

PLA was purchased from NatureWorks LLC (Ingeo™ 3051D, $M_n = 106,000$ g/mol; PDI: 1,7; $\approx 4,6\%$ D-lactate) and PMMA was purchased from Evonic ROM GmbH (PLEXIGLAS® zk5BR, $M_n = 70,000$ g/mol; PDI: 2,3). Molecular weights and molecular weight distribution were determined by GPC.

Sample Preparation

PLA/PMMA blends with weight ratio of: 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100) were prepared by means of a Brabender DSE 20/40 corrotating twin screw extruder ($\varnothing = 20$ mm, L/D = 40). Manually premixed pellets were fed to the extruder using a gravimetric feeder at a constant 2 kg/h rate. Screws were configured with three separated high shear mixing stages based on kneading blocks. There was a vacuum aided venting zone after the third mixing stage and at the final stage of the screws a distributive mixing screw element. Prior to extrusion, all systems were dried for 4h at 80°C by a dehumidifying dryer. Neat PLA was extruded at 200°C (constant at the whole extruder length) and neat PMMA at 240°C (constant at the whole extruder length), the lowest recommended processing temperature for this grade. Due to the difference on the recommended processing temperatures of both polymers, all blends were extruded at 215°C (constant at the whole extruder length) and 180 rpm. Obtained blends were dried for 12h at 50°C and molded in a full electric DEMAG IntElect injection machine at 60 mm/s injection rate (600–700 bar injection pressure) to obtain $90 \times 90 \times 2$ mm³ platelets. Samples for FTIR, DSC, DMA, and impact tests were cut from the platelets. On the other hand, V type specimens (ASTM D638) for tensile tests were injected at 300 Bar injection pressure by means of a Haake MiniJet II injection machine. Neat PLA, all blends and neat PMMA were injection molded at 200°C, 215°C, and 240°C, respectively.

Characterization Techniques

The molecular weight and molecular weight distribution were determined by Gel Permeation Chromatography (GPC) with a PerkinElmer chromatograph equipped with a binary pump and a refractive-index detector. The mobile phase was THF and elution rate of 1 mL/min at 30°C was used. The separation was carried out with four Phenomenex columns, 10⁵ Å, 10³ Å, 100 Å, and 50 Å, with 5 μ m particle size. The columns were calibrated with polystyrene standards before the measurements according to standard procedures, Mark-Houwink constants taken from literature were used, $K_{PLA} = 0,0153$ mL/g, $\alpha_{PLA} = 0,759$, and $K_{PMMA} = 0,00944$ mL/g, $\alpha_{PMMA} = 0,719$.^{22,23} Fourier Transform Infrared transmission (FTIR) measurements were performed by a Nicolet Protégé 460 spectrometer from 400 to 4000 cm⁻¹. FTIR spectra were collected by performing 32 scans with a resolution of 4 cm⁻¹. Differential Scanning Calorimeter (DSC) was used to determine thermal properties of all systems. Samples of 6 to 8 mg were analysed. Two heating scans were performed from -10 to 250°C at a heating rate of 10°C/min using a TA Instruments Q100 model, previously calibrated by indium and sapphire standards following the indications of the supplier.²⁴ Dynamic Mechanical Analysis (DMA) was carried

out in a Rheometrics Solid Analyzer RSA II applying a 2% deformation at a 1Hz frequency by dual cantilever bending method. Specimens with $50 \times 5 \times 2$ mm³ dimensions cut from injection molded platelets were heated from 35 to 140°C at a rate of 2°C/min. Tensile tests were carried out according to ASTM D638 standard (1 mm/min) by means of a MTS Insight electromechanical tensile test machine equipped with a 2.5 kN load cell and a contact mechanical extensometer. Unnotched Charpy impact tests were carried out by means of an ATS faar IMPats-15 impact pendulum with a 2J hammer using a support span of 40 mm. Impact fractured surfaces coated with Au were analyzed by a Hitachi S-4800 Field Emission Scanning Electron Microscope (FE-SEM).

RESULTS AND DISCUSSION

FTIR spectroscopy is a powerful tool for investigating polymer blends. Differences in band positions and shapes in the spectra suggest interactions between two polymer components. Figure 1 shows FTIR spectra of neat polymers and PLA/PMMA blends. The differences between PLA and PMMA spectra were in the ranges 2000–1500 and 1050–750 cm⁻¹. The stretching mode of the carbonyl groups showed an absorption band at 1749 cm⁻¹ and 1724 cm⁻¹ for PLA and PMMA, respectively. A clear evolution of this band was noticeable in the spectra of the blends, increasing PMMA content in the blend the intensity of the band at 1724 cm⁻¹ was higher. PMMA showed a band at 987 cm⁻¹ due to C-C stretching influenced by CH₂ bending and a band at 841 cm⁻¹ related to CH₂ rocking band^{25,26} which were not present in PLA spectra. The band at 866 cm⁻¹ was related to skeletal stretching and CH₃ rocking of amorphous PLA²⁷ and it was not present in PMMA spectra. There were no obvious changes in PLA and PMMA band positions in blends, which suggested that interactions between the two components are weak or negligible.²⁸ Injection molded platelets are shown in Figure 2. Neat PMMA platelet was transparent due to the unique amorphous phase. Neat PLA platelet was almost transparent which indicated a very low crystallization degree. All blends were translucent suggesting the coexistence of more than one phase in all PLA/PMMA blends. The miscibility of PMMA and PLA was studied by Differential Scanning Calorimeter and Dynamic Mechanical Analysis. Glass transition temperature (T_g) of a polymer blend is one of the most important criteria to study the miscibility of its components. Miscibility between two polymers in the amorphous state is characterized by the presence of a single T_g intermediate between those of the two components. On the contrary, immiscibility of two polymers is demonstrated by retention of the T_g values of both individual components.^{15,29} Figures 3 and 4 show the first and second DSC heating scan thermograms for all systems, respectively. First and second scan thermograms were completely different. In Figure 3 two T_g were observed whereas in Figure 4 only one T_g was observed. In the first scans, the T_g of PLA remained almost constant at around 58–65°C until weight ratio reached 50/50, while the T_g of PMMA decreased from 107 to 65°C more rapidly. Hence, T_g variations of PMMA-rich and PLA-rich phases were very different. This peculiar behaviour seemed to indicate that interactions and the miscibility in PLA-rich phases and PMMA-rich phases were different and depend on blend

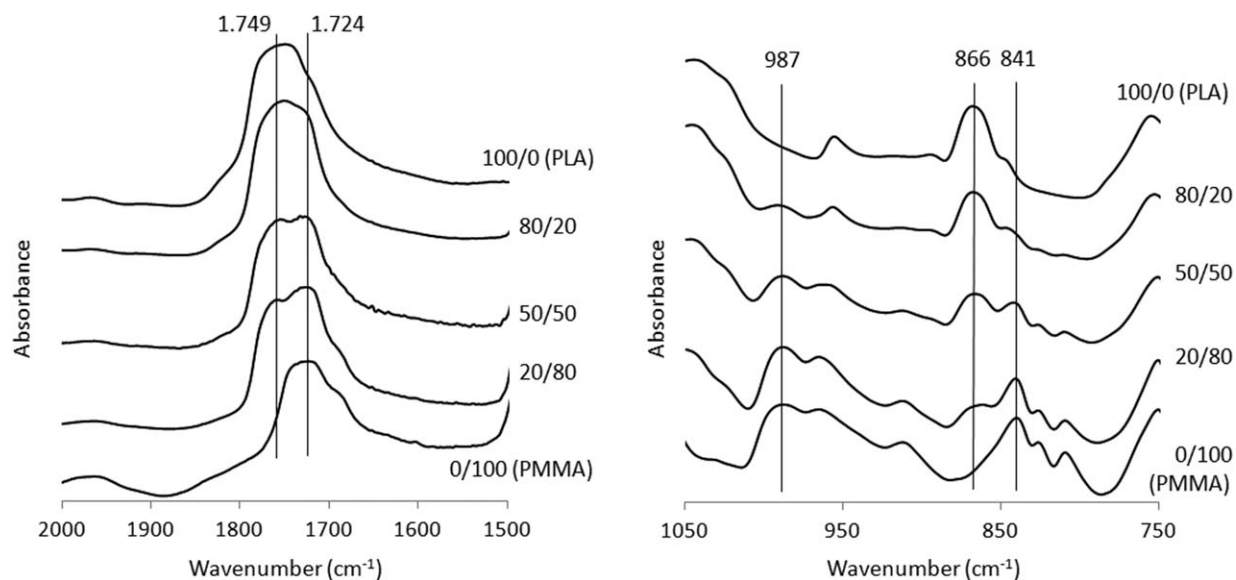


Figure 1. FTIR spectra of all systems.

composition. T_g variations observed in the first scans could indicate that PMMA-rich phases showed better miscibility than PLA-rich phases ones.

Figure 5 shows the evolution of $\tan\delta$ as a function of blend composition. A clear peak related to the blend major component T_g was observed and in some compositions a shoulder was noticed related to the blend minor component T_g . Partial miscibility of PLA and PMMA was demonstrated by a clear displacement of the glass transition temperatures of components in the blends. The peak and shoulder locations varied with the blend composition and the glass transition temperature of PLA increased as the proportion of PMMA in the blend was increased, indicating that after melt blending PLA and PMMA certain miscibility was achieved. From the analysis of the $\tan\delta$ peaks it was observed that neat PLA and 80/20 blend had relatively similar full widths at half maximum (FWHM), which has been related to the temperature range which is needed to gain mobility during glass transition.¹⁷ The FWHM of 50/50, 40/60, and 20/80 blends resembled to that of neat PMMA. The only

difference in terms of FWHM was observed in the 60/40 blend due to its shoulder peak. In the first DSC scan thermograms, neat PLA and some blends showed some degree of crystallinity (X_c) which was calculated using equation 1:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\omega_f \Delta H_o} \quad (1)$$

where ΔH_m , ΔH_c , and ω_f are the melting enthalpy, crystallization enthalpy, and weight fraction of PLA in the blend, respectively. Theoretical melting enthalpy value for a 100% crystalline PLA (ΔH_o) was estimated to be 93 J/g.³⁰ Thermal transition temperatures, crystallization enthalpies, melting enthalpies, and the degree of crystallinity of different samples are reported in Table I.

Neat PLA was almost amorphous and the addition of PMMA prevented the crystallization of PLA. Only when the content of PLA in blends was higher than 50% some crystallization took place during the heating scan (due to the low enthalpy, the melting peak of the 60/40 blend is hardly noticeable in Figure 3). Zhang *et al.* mentioned that crystallization kinetics of PLA

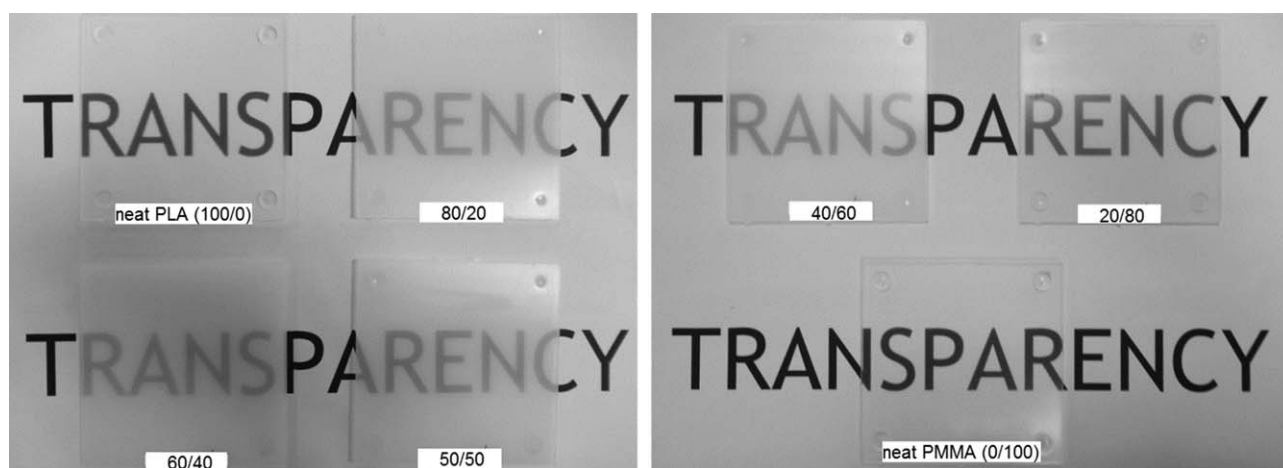


Figure 2. Injection molded platelets for all systems.

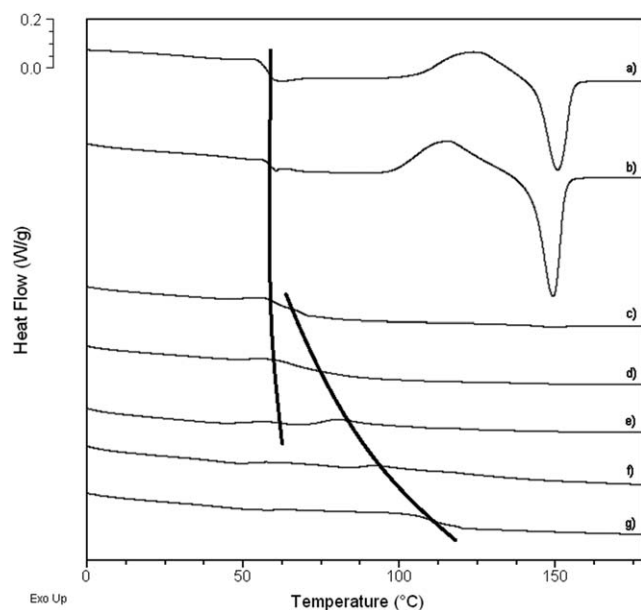


Figure 3. DSC first heating scan thermograms: a) 100/0 (neat PLA), b) 80/20, c) 60/40, d) 50/50, e) 40/60, f) 20/80 and g) 0/100 (neat PMMA).

was highly restricted by amorphous PMMA [15]. The DSC thermograms of the second heating scans were completely different. In the blends, PLA was amorphous and only one T_g was observed, located between the T_g of individual components. The T_g position changed with the composition of the blend indicating the miscibility between PLA and PMMA. The fact that no crystallization process was observed in the second DSC scan could be due to a better degree of miscibility between the components of the blend.¹⁵ Besides, PLA grade used in this work has low optical purity ($\approx 4.6\%$ D- enantiomer in L-) resulting in a low rate of crystallization kinetics of PLA. Nam *et al.*

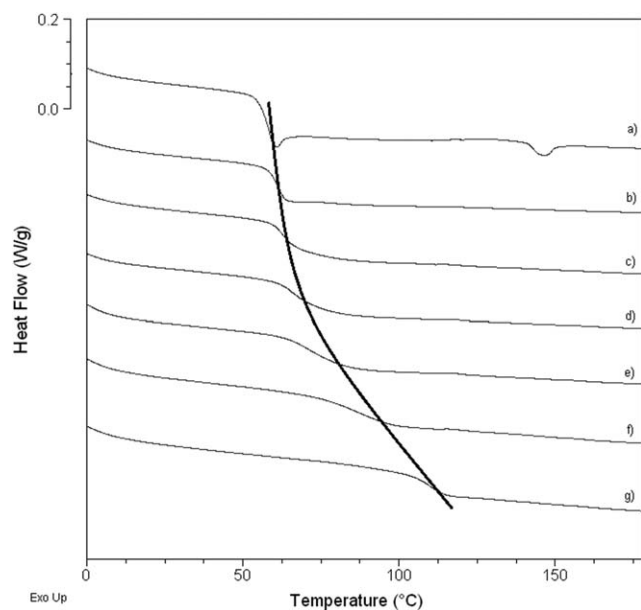


Figure 4. DSC second heating scan thermograms: a) 100/0 (neat PLA), b) 80/20, c) 60/40, d) 50/50, e) 40/60, f) 20/80 and g) 0/100 (neat PMMA).

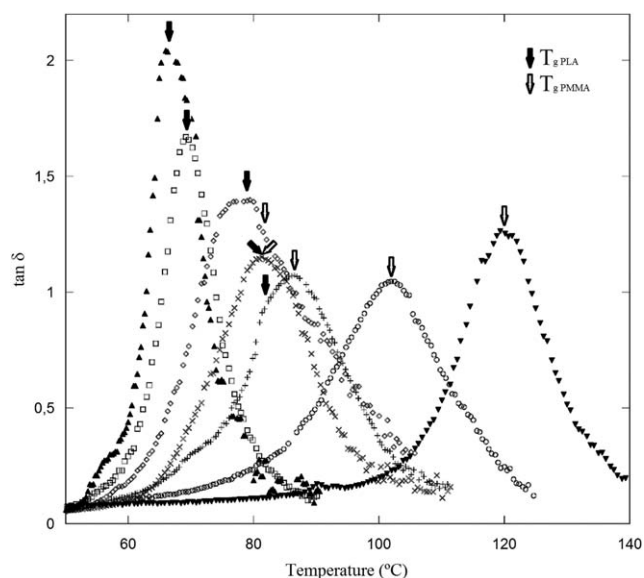


Figure 5. The influence of PMMA content in the evolution of blends $\tan \delta$: \blacktriangle 100/0 (neat PLA), \square 80/20, \diamond 60/40, \times 50/50, $+$ 40/60, \circ 20/80 and \blacktriangledown 0/100 (neat PMMA).

observed that crystallization rate of a PLA with D content of 0.8% was very slow.³¹

Eguiburu *et al.* obtained similar results for PLLA/PMMA blends prepared by solution/precipitation method. They reported a clear difference on the miscibility degree of polymers from the first to second DSC heating scans. In the first scan two T_g were noticeable slightly different from the T_g of the homopolymers in the pure state. Only one T_g was observed during the second heating scan and T_g value increased as the PMMA content increased in the blend.¹⁷

Only two works were found in the literature where PLA/PMMA blends were obtained by melt compounding.^{20,21} In contrast to the results reported in this work, Samuel *et al.*²⁰ observed that all PLA/PMMA blends processed at 210°C were miscible since they observed a unique α -relaxation transition and a unique glass transition at intermediate temperature between pure PLA and pure PMMA. They blended PLA ($M_n = 123,000$ g/mol) with two different PMMA grades with different average molecular weights $M_n = 52,000$ and $M_n = 37,000$ g/mol respectively. The molecular weight of PMMA used in our work was higher and even though the processing temperature was slightly higher (215°C) immiscible blends were obtained. DSC results confirmed that after heating the blends until the temperature of 250°C, miscible samples were obtained. The obtained results suggested that PLA/PMMA blends were miscible but the mixing process seemed to be controlled by the diffusion of PMMA chains. Increasing the temperature the diffusion of PMMA in the blends could be accelerated and this could be the reason for the miscibility after the first DSC scan.

Le *et al.*²¹ prepared PLA/PMMA blends using a single screw extruder at 200°C and 100 rpm. In agreement with the results reported in this work, they observed by SEM that the obtained blends were immiscible. Unfortunately Le *et al.* did not report the molecular weight of PMMA.

Table I. Transition Temperatures, Crystallization and Melting Enthalpies and the Degree of Crystallinity of Different Samples. Values in Brackets Correspond to DMA Data

PLA/PMMA	Scan	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	X_c (%)
100/0	First	58 (65)	124	151	14,4	17,5	3,3
	Second	58	-	146	-	1,0	1,1
80/20	First	58 (68)	116	149	18,7	20,6	2,5
	Second	62	-	-	-	-	0
60/40	First	61-69 (77-80)	-	150	-	0,8	1,5
	Second	63	-	-	-	-	0
50/50	First	65 (81)	-	-	-	-	0
	Second	65	-	-	-	-	0
40/60	First	64-86 (82-85)	-	-	-	-	0
	Second	71	-	-	-	-	0
20/80	First	76-97 (103)	-	-	-	-	0
	Second	87	-	-	-	-	0
0/100	First	107 (121)	-	-	-	-	0
	Second	110	-	-	-	-	0

For ideal systems that are miscible and amorphous over the whole composition range, the relationship between the T_g and the composition of the blend can be predicted by the Gordon-Taylor equation [eq. (2)].¹⁵

$$T_g = T_{g1} + \frac{k\omega_2(T_{g2} - T_{g1})}{(\omega_1 + k\omega_2)} \quad (2)$$

where ω_1 and ω_2 are the weight fractions, T_{g1} and T_{g2} are the glass transition temperatures of pure components, and k is the adjustment parameter. In this work, PLA and PMMA were components 1 and 2, respectively. k is an adjustable parameter which was related to the interaction strength between the components in the blend. The theoretical curve and experimental data (DSC second

heating scan) best fitted when k was 0,24. Experimental T_g values obtained were below to weight average (Figure 6). Although both polymers were miscible, this low value suggested that there was no strong interaction between PLA and PMMA macromolecules which agreed with FTIR results obtained. Similar results were found in the literature for the same blend system prepared by solution method.^{15,16}

In polymer-polymer mixtures, the entropy of mixing is very small, regarding the enthalpy of mixing, miscibility generally requires some favorable interactions such as hydrogen bonding, donor-acceptor interaction, charge transfer, and so forth, resulting in a negative exchange interaction contribution to the free energy of mixing. However, for the PLA/PMMA blends, no such strong specific interaction existed and only some kind of weak dipolar interaction could take place owing to the chemical structure of two polymers.¹⁵ Miscibility can also be studied by the differential solubility parameter ($\Delta\delta$) of blend components. The solubility parameter of a given material can be calculated either from the cohesive energy [eq. (3)] or from the molar attraction constant [eq. (4)]

$$\delta = \sqrt{\frac{E_{coh}}{V}} \quad (3)$$

$$\delta = \frac{F}{V} \quad (4)$$

where δ is the solubility parameter, E_{coh} the cohesive energy, F is the molar attraction constant, and V is the molar volume of the repeating unit.

The solubility parameters of PLA and PMMA were estimated (Table II) according to the group contribution approaches described by Small and Van Krevelen.³² The differential solubility parameter values calculated for PLA/PMMA were $\Delta\delta = 0,99$ (J/cm^3)^{1/2} and $\Delta\delta = 0,46$ (J/cm^3)^{1/2} for Small and Van Krevelen, respectively. Two polymers are thermodynamically miscible when the difference is $\Delta\delta < 5$. As $\Delta\delta$ values obtained are below,

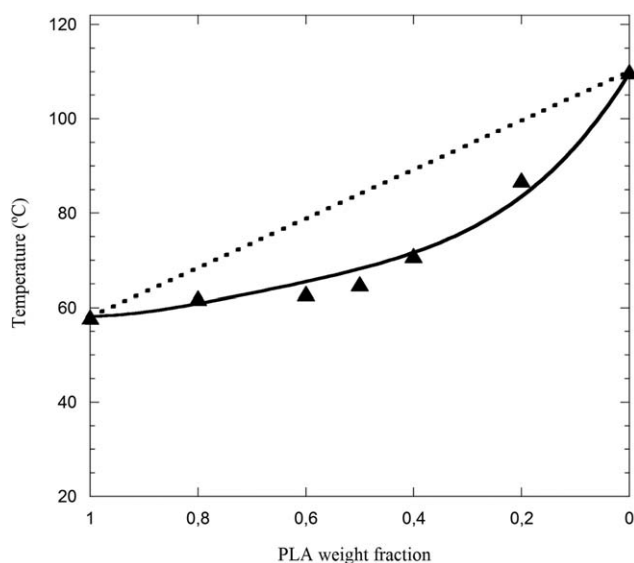


Figure 6. Glass transition temperature vs. weight fraction of PLA: experimental DSC T_g values (▲); Gordon-Taylor adjustment curve for $k = 0,24$ (line) and weight average T_g values (dots).

Table II. Estimation of the Solubility Parameters of PLA and PMMA According to the Group Contribution Approaches Described by Small and Van Krevelen

Component	M_o (g/mol)	Density (g/cm ³)	δ_{Small} (J/cm ³) ^{1/2}	δ_{VKrev} (J/cm ³) ^{1/2}
PLA	72	1,25	19,60	18,61
PMMA	100,1	1,17	18,61	19,08

PLA and PMMA are thermodynamically miscible. However, taking into account $\Delta\delta$ values obtained it could not explain why partially miscible PLA/PMMA blends were observed during the DSC first heating scan, while miscible blends were observed at the second heating scan. Even though the approach has several limitations the Flory-Huggins interaction parameter (χ_{12}) can be derived from the solubility parameter of the components using the equation (5) [eq. (5)]:

$$\chi_{12} = \frac{V_r}{RT} (\delta_1 - \delta_2)^2 + 0.34 \quad (5)$$

where the δ_1 and δ_2 are the solubility parameters of the components, V_r is a reference volume, which corresponds to the molar volume of PLA repeating unit, R is the universal gas constant, and T is the absolute temperature during blending process (473K). Using the solubility parameters estimated according to Small and Van Krevelen, Flory-Huggins interaction parameters calculated were 0,35 and 0,34; respectively. These similar values were below the critical value for miscible polymer blends, established at $\chi_{crit} = 0,5$,³² suggesting that from a thermodynamically point of view PLA/PMMA blends should be miscible. However, PLA and PMMA grades used have high molecular weights and at the processing temperatures selected especially PMMA has very high viscosity which could slow down the kinetics of mixing. Therefore, depending on polymer molecular weights and on the processing condition selected, partially or completely miscible PLA/PMMA blends might be obtained, which is in agreement with previously

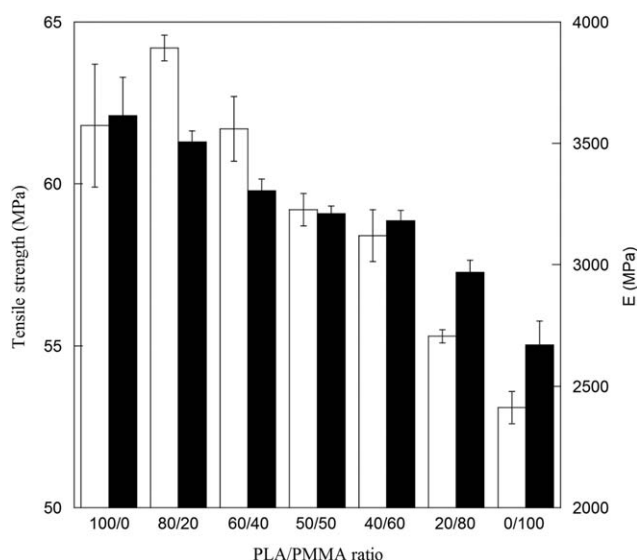


Figure 7. The influence of PMMA content in the tensile properties: tensile strength (white columns) and modulus (black columns).

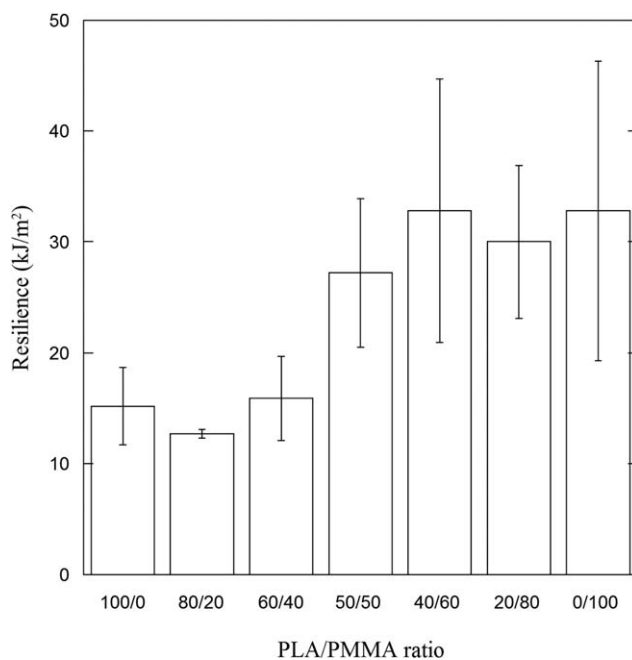


Figure 8. The influence of PMMA content in the impact resistance (resilience).

reported results.²⁰ Hence, the obtained experimental results suggested that the mixing process of PLA/PMMA blends seems to be diffusion controlled. Figures 7 and 8 show the influence of PMMA content in the mechanical properties of blends. Increasing the PMMA content in the blend resulted in a lower strength and modulus values. Regarding resilience, the blends based on a PLA-rich phase (80/20, 60/40) behaved like neat PLA, whereas in the blends based on a PMMA-rich phase (40/60, 20/80) behaved like neat PMMA (Figure 8). Thus, the blends exhibited similar impact resistance to the neat polymers. Impact performance is mainly influenced by the phase structure of the blends. Therefore, these results suggested a phase inversion at 50/50 composition. Figure 9a-g show SEM micrographs of fractured surfaces. Neat PLA (Figure 9a) showed smooth fracture surface indicating a brittle failure mechanism. On the contrary, neat PMMA (Figure 9g) showed a rougher fracture surface, indicating a more ductile behavior. All blends showed roughened fracture surfaces, due to the ductility gained by the addition of PMMA. In all blends, a sphere shaped dispersed phase (around 200–350 nm in diameter) were observed evenly distributed in the continuous phase. These dispersed spheres were supposed to be PMMA-rich phases in blends with high PLA contents and PLA-rich phases in blends based with high PMMA contents. In contrast to the morphology observed in this work, Li *et al.* observed a co-continuous morphology probably because they used polymers with different molecular weights and also different processing conditions.

Voids (resulted from removing of dispersed phase) and spheres with limited surface contact with the matrix were seen in the micrographs, indicating a poor interphase between the matrix and the dispersed spheres. Hence, limited interfacial adhesion can be expected. This is in agreement with the impact resistance of the blends, which showed similar resilience to the neat polymers, indicating that the dispersed phase was not able to enhance the

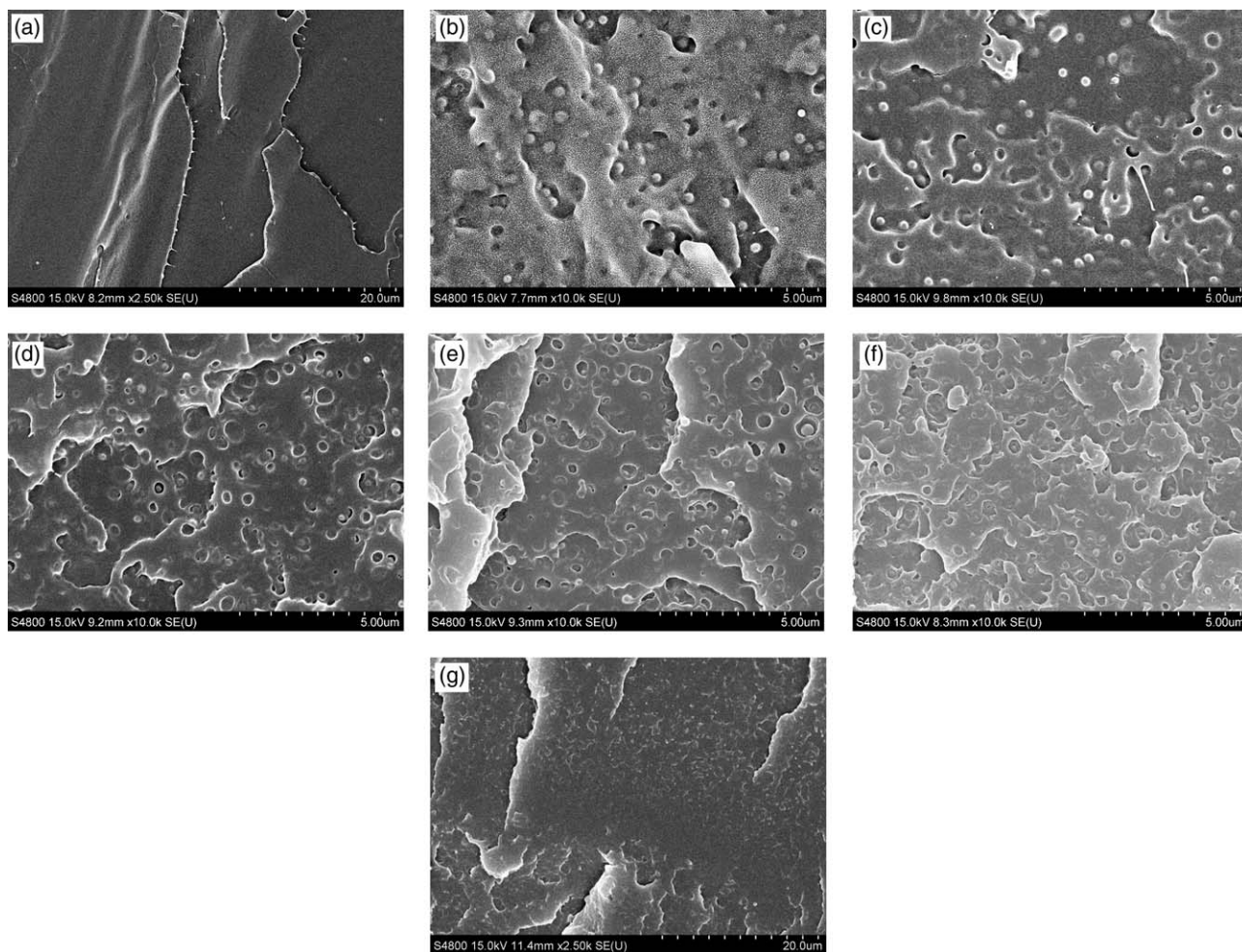


Figure 9. SEM micrographs of fractured surfaces: a) 100/0 (neat PLA), b) 80/20, c) 60/40, d) 50/50, e) 40/60, f) 20/80 and g) 0/100 (neat PMMA).

resilience of the matrix in the blends. On the other hand, needle-like and wave-like were observed in high PLA content blend micrographs (Figures 9a-9c). These effects are very common in SEM micrograph of amorphous PLA,^{33–35} which can be easily overheated by the electron beam at high resolutions due to its low T_g . The two thermoplastic grades used in this work seem not to be completely miscible by melt blending at the mixing conditions used, which was in agreement with the results obtained by DSC (first heating scans) and DMA.

CONCLUSIONS

The miscibility of PLA/PMMA blends prepared via melt processing seemed to be dependent to the mixing processing conditions (temperature and rpm) and polymers molecular weights. Injection molded platelets showed that PLA/PMMA blends were translucent suggesting the coexistence of more than one phase. In the first DSC run and DMA results two T_g were noticed but a clear displacement of T_g of neat components in the blends was observed, and the values of T_g increased as the presence of PMMA in the blend increased. This mutual influence on the mobility of molecules of each component indicated partial miscibility. SEM images showed the coexistence of two separated

phases in all blends, spheres below 400 nm in diameter were evenly dispersed in a continuous phase. Finally, the blends exhibited similar impact resistance to that of the neat polymer they were rich in. The impact resistance of blends when the presence of PMMA in the blend was 50 wt % or higher was similar to neat PMMA probably due to a phase inversion in the blend.

However, in the second DSC run blends showed only one glass transition temperature, located between the T_g of individual components, indicating miscibility of the same PLA/PMMA systems. Besides, no crystallization of PLA was detected in the second heating scan of the blends, probably due to a better blending degree of the components. Gordon-Taylor equation fitted well with the evolution of the T_g values of the blends when k was 0,24, which suggested that there was no strong interaction between PLA and PMMA which is in agreement with FTIR spectra observed. Flory-Huggins interaction parameters for PLA/PMMA were estimated using the solubility parameters. Interaction parameter values estimated were below the critical value for miscible polymer blends, which meant that from a thermodynamically point of view PLA/PMMA blends were miscible. However, the mixing process of PLA/PMMA blends

seemed to be diffusion controlled process. Therefore, depending on the mixing conditions as well as polymers molecular weights used, partially or completely miscible PLA/PMMA blends can be obtained.

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