

Miscibility and Properties of Low Molecular Mass Poly(L-lactide) and Poly(methyl methacrylate) Blends



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Modification of biobased PLLA properties by mixing with conventional PMMA via melt mixing in Brabender mixer was performed. Despite negative results of theoretical miscibility calculations by the group contribution approach of Coleman, Graf and Painter, homogeneous blend morphologies were prepared as recorded with scanning electron microscopy (SEM). All PLLA/PMMA blends displayed a single glass transition temperature. With increasing fraction of PMMA in blends, the increase in T_g from 58 °C to 93 °C was recorded by differential scanning calorimetry (DSC). Added PMMA improved mechanical properties, while the flexibility of PLLA/PMMA blends gradually decreased as revealed by DMA measurements.

Keywords:

blends, morphology, manufacturing, mechanical properties, thermal properties

Introduction

Poly(lactide) (PLA) is the most important aliphatic polyester used for various applications in medicine and pharmacy for quite some time, in particular, due to its extraordinary characteristics of biocompatibility, nontoxicity, and processability. Additionally, the biodegradable nature and the renewable origins spur interest for PLA and enhance its application in various areas, such as packaging, cutlery, composting bags, agricultural foils, coatings, textile, etc.^{1,2} At the same time, demands for substituting conventional plastics produced from fossil sources are becoming louder. Consumption of fossil sources is usually marked as the main foundation of these demands. Although, it is not fully true because production of plastics consumes up to 10 % of the liquid fossil fuels^{3,4}, this approach should be complimented as any other attempt to introduce eco-friendly materials or green chemistry. Among all aliphatic polyesters, PLA was first produced cost-effectively from renewable sources at large scale⁵. That, along with its other good characteristics, speaks in favor of this material as a good replacement for some conventional plastics^{6,7}.

Poly(L-lactic acid) (PLLA), a biobased thermoplastic polyester, has good prospects to be used widely due to its favorable mechanical properties, positive life cycle assessment, low production costs,

and degradability in conditions of industrial composting. However, in order to be used for new advanced applications, specific properties such as high and long-term thermal stability, high impact strength, electrical conductivity, self-extinguishing, controlled degradation, etc., are required. Generally, polymer properties can be improved by copolymerization with other monomers or by blending with other polymers, whereat the latter presents a simpler way of tuning the desired physical and chemical properties. Synthesis of PLA copolymers with various monomers has been performed in order to modify the properties of materials^{8–13}. Preparation of PLA blends or composites with diverse conventional polymers opens up the possibility of combining biobased materials with fossil-based materials. Therefore, research aiming at preparation of (nano) composites or direct chemical modifications of the polyester chain have been reported^{14–18}. In case of blending PLA with synthetic thermoplastic polymers, melt blending proved as the simplest and least demanding method. Thus, poly(methyl methacrylate), PMMA, due to its good mechanical properties, high transparency, UV resistance and stability seems an interesting material for the modification of PLA. Therefore, PLA/PMMA blends have been investigated recently. Meanwhile, it has been established that the properties of prepared blends depend on the preparation methods (melt blending vs. solvent casting), process conditions (temperature, subsequent annealing), and characteristics of polymers involved [poly(L-lactide) (PLLA) vs. poly(D-lac-

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tide) (PDLA), tacticity of PMMA], etc.^{19–24}, which reveals the complexity of such an apparently simple system.

The work of Eguiburu *et al.*¹⁸ is among the pioneering ones; they studied the miscibility of PLLA or PDLA with poly(methyl methacrylate) (PMMA) or poly(methyl acrylate) in a systematic way. Based on the differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), they concluded that the preparation method had not influenced the characteristics of blends. A significant difference was noticed depending on the type of used lactide, amorphous PDLA or semicrystalline PLLA, respectively. In case of PDLA/PMMA blends, a single glass transition temperature was noted, which appeared between T_g s of neat homopolymers positioned depending on the blend composition. In the case of blending semicrystalline PLLA with PMMA, phase separation was registered, which resulted in the appearance of two T_g peaks and a melting endotherm characteristic for PLLA. In addition, it was found that the crystallization of PLLA acted as the promoter of phase separation. However, after heating to 200 °C in the second heating run, the system became miscible, displaying a single glass transition temperature. To the contrary, a similar study performed by Zhang *et al.*²⁰ on blends of PDLA or PLLA with PMMA, displayed the correlation between the preparation method and the behavior of blends. The PDLA/PMMA system displayed good miscibility and a single T_g when prepared using the solution/precipitation method, while in the case of casting from chloroform solution two separated and just partially miscible phases were obtained. The PLLA/PMMA blends prepared by solution/precipitation showed phase separation, whereat it was established that crystalline phase of PLLA enhanced the phase separation and formation of separated microdomains. However, by increasing the content of PMMA in the blends, the degree of crystallinity of PLLA decreased because the kinetics of crystallization of PLLA in blends was restricted in the presence of amorphous PMMA. Furthermore, there was no difference between PDLA/PMMA and PLLA/PMMA blends once the thermal history of the blend PLLA/PMMA was erased.

Samuel *et al.*²¹ have studied PLLA/blends prepared by solvent-casting method or twin-screw extrusion. Miscible PLLA/PMMA blends were prepared with the latter over a whole composition range, which was confirmed by a single glass transition and a single α -relaxation transition determined by DSC and DMA, respectively. This was in contrast to two separated glass transitions in non-miscible blends prepared by solution casting. However, based on a smaller or larger shift in glass

transition temperature of each phase after heating, one can conclude on a weak diffusion between PLLA and PMMA phases in blends.

It should be noted that PLA and PMMA polymers studied by various working groups differed greatly in molar masses^{18–22}, sometimes even within the same research report²⁰. Li *et al.*²² introduced the existence of immiscible/miscible phase transition, or UCST (upper critical solution temperature) type phase diagram, upon heating. PLLA (M_w 152000 g mol⁻¹) was blended with PMMA of three different molar masses (M_w : 53500, 100000 and 350000 g mol⁻¹), whereat all PLLA/PMMA blends prepared from solution displayed two glass transition temperatures and melting endotherm of PLLA phase. The phase morphology changed drastically after heating up to a high temperature, transforming from clearly separated phases into a homogeneous morphology. Samples quenched from 250 °C displayed a single T_g , while samples quenched from 185 °C displayed two clearly separated T_g s. Those findings were explained with the existence of a clarifying point between 185 °C and 250 °C, whereat the authors assumed the clarifying point to be in the range 225 – 250 °C depending on the content of PMMA, or even up to 350 °C in the case of PMMA of molar mass above 350000 g mol⁻¹.

An additional parameter that indicates the complexity of such a system, which might be considered, is tacticity of PMMA²³. It was established that atactic and syndiotactic PMMA (aPMMA and sPMMA) mixed with PLLA by casting from chloroform solution displayed similar behavior, UCST type, and a clarifying point in the range 210 – 255 °C depending on the composition. However, in the case of isotactic PMMA (iPMMA) and PLLA, their blend remained phase separated up to 300 °C, without the clarifying point. The difference between sPMMA and iPMMA was explained by the difference in solubility parameters (aPMMA and sPMMA: 19.43 and 19.53 (MPa)^{1/2}, which is close to PLLA (20.66 (MPa)^{1/2}) relative to iPMMA (18.98 (MPa)^{1/2}). These findings on the PLLA/PMMA blends indicate that their miscibility depends on the preparation method and structural characteristics of polymers. In the case of PLLA/PMMA blends prepared by extrusion melting, miscible PLLA/PMMA blends are expected, but co-continuous morphologies are formed, as well. It seems that it is possible to control morphology of blends from immiscible to miscible by thermal processing, tuning of processing parameters and molecular structure of PLLA and PMMA. The control of mixing the PLLA/PMMA blends presents an elegant way to fine tuning the final thermomechanical properties, or e.g., gas barrier properties, which points to a wide range of possible technical and other applications where specific characteristics are required.

This work is one more attempt to better understand the contradictory results on PLA/PMMA blends reported in the literature. The aim was to examine miscibility of polymers of similar molar masses: commercial PLLA and PMMA of adjusted molar mass, synthesized in our laboratory by conventional free radical polymerization. Generally, slow solution casting produces systems, which are closer to equilibrium due to increased mobility of polymer molecules; however, this may be impractical from the industrial point of view. Therefore, in this work, the blends were prepared by melt mixing, which is a method widely applied in industry. For the theoretical calculation of interaction parameter in PLLA/PMMA polymer blend, we applied the group contribution approach of Coleman–Graf–Painter²⁴. Based on the interaction parameter, the Gibbs energy of mixing in relation to PLLA and PMMA molar mass was determined. Molar masses of homopolymers before and after processing as well as their blends were determined by size exclusion chromatography (SEC). Blends prepared in Brabender mixer were used for the preparation of test tubes for evaluating surface properties of the prepared materials, while the morphology of prepared materials was studied by wide-angle X-ray scattering (WAX) and scanning electron microscopy (SEM). The thermal and dynamic-mechanical properties of materials were examined as well.

Experimental part

Materials

Poly(L-lactide) (PLLA) (pellets, Ingeo Biopolymer 3251D, NatureWorks LLC, USA) and PMMA synthesized in our laboratory were used for the preparation of polymer blends. For PMMA synthesis, methyl methacrylate monomer (polymerization grade, Sigma Aldrich), *tert*-butyl peroxy-2-ethylhexanoate (Trigonox 21[®], Akzo Chemie) as an initiator, and toluene (p. a., Carlo Erba Reagenti) as a solvent were used.

PMMA synthesis

Monomer (250 g) and toluene (275 g) were added into a batch reactor of 500 mL volume, equipped with a heating jacket that used oil as a heat exchange fluid. *Tert*-butyl peroxy-2-ethylhexanoate initiator, in quantity of 1 mass% with respect to the mass of the monomer, was added as a 10 mass% solution in toluene (25 mL), 5 mL at a time for 5 times each 15 minutes. Polymerization was conducted at 90 °C in nitrogen atmosphere for three hours. After the reaction completion, the resulting polymer solution was poured into Teflon molds and placed for drying in a vacuum oven at 60 °C up to constant mass. The PMMA was then crushed into

small shreds in order to enable simple feeding into the Brabender mixer chamber.

Polymer blend preparation

The melt blending was performed in a Brabender mixer at 190 °C. Polymer pellets were added into the chamber of the mixer, which was heated to 190 °C, and had blades rotating at 10 rpm. The plunger was then lowered to enclose the chamber, and the rotation was increased to 60 rpm. After 5 min, the blades were stopped and the blends were removed from the chamber using a spatula, and cut into pieces using scissors. The blends were allowed to cool to room temperature on a bench top. The obtained blends were then pressed in a laboratory compression molder for 5 min at 200 °C, and films for testing were obtained.

Characterization methods

Number, weight, and z-average molar masses (M_n , M_w and M_z , respectively) of polymer samples were determined by the size exclusion chromatography method (SEC) on a Polymer Laboratories GPC 20 instrument at room temperature. The narrow-distribution PMMA standards were used for calibration. Chloroform, at flow rate of 1.0 cm³ min⁻¹, was used as a solvent/eluent. Dispersity (\mathcal{D}) was calculated as M_w/M_n . The ¹H NMR spectra were recorded by NMR Bruker Avance instrument at 600 MHz with deuterated chloroform (CDCl₃) as solvent. Contact angle measurements for 2-μL water droplets on the surface of prepared polymer probes were measured at room temperature with an OCAH 200 Data Physics Contact Angle System. Scanning electron microscopy (SEM) recording was carried out using a Vega 3 Tescan microscope, with a detector of secondary electrons. All samples were previously sputter coated with Au or Pd in argon plasma to enhance their conductivity. XRD patterns of blends were obtained on a powder X-ray diffractometer Shimadzu X6000 with CuK α radiation, having a step size of 0.02 degrees and a scan speed of 2° min⁻¹. Differential scanning calorimetry (DSC) analysis was performed using a DSC823e Mettler Toledo instrument. Masses of examined samples were 9–12 mg. Three scans: heat-cool-heat, were performed whereat heating and cooling rates were 10 °C min⁻¹. Heating data of the second scan were discussed. Dynamic mechanical analysis (DMA) was performed using a DMA 983 TA Instruments apparatus. The test specimens were *ca.* 50 mm long, 10–13 mm wide, and *ca.* 2 mm thick. A constant frequency of jaw motion of 1 Hz, an amplitude of 0.2 mm, and a temperature interval from 0 °C to 130 °C at a heating rate of 5 °C min⁻¹ were applied. Thermogravimetric analysis was performed to de-

termine the thermal stability of polymers using a TA TGA Q500 instrument at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Results and discussion

Theoretical calculations of miscibility

In order to start with a theoretical insight into miscibility of PLA and PMMA constituents, we calculated the interaction parameter using the group contribution approach of Coleman, Graf and Painter²⁴. The interaction parameter for the mixing of (1) PLLA and (2) PMMA polymer segments was calculated according to the equation given by Ten Brinke and Karasz²⁵:

$$\Lambda_{12} = (\delta_1 - \delta_2)^2 \quad (1)$$

where, δ denotes the so-called non-hydrogen-bonding solubility parameter for a given structure unit of certain homopolymer that is calculated from the group interaction parameters. The corresponding formula is:

$$\delta_K = \frac{\sum_{i=1}^g v_{i,K} F_i^*}{\sum_{i=1}^g v_{i,K} V_i^*} \quad (2)$$

where, $v_{i,K}$ is the number of groups i in the polymer structure unit K , F_i^* is the attraction constant, and V_i^* is the molar volume.

The ideal behavior and genuine miscibility is characterized by the zero value of interaction parameter; values between zero and 0.5 J cm⁻³ imply compatibility, while values > 0.5 J cm⁻³ point to immiscibility due to the expressed repulsive molecular interaction between blend constituents. The calculated interaction parameter for poly(methyl methacrylate) and PLLA amounts to $\Lambda_{\text{PMMA/PLLA}} = 4.66 \text{ J cm}^{-3}$. It is much higher than the ideal zero value but still much lower than for, e.g., blends of structurally similar poly(methacrylate acid) and PLLA, where it amounts to 18.7 J cm⁻³. These calculations reveal a very high sensitivity of interaction parameter to the structural differences.

Further, the Gibbs energy of mixing PLA with PMMA was calculated from the calculated interaction parameter according to equation:

$$\Delta G_M = RT \left(\frac{\varphi_1}{v_1} \ln \varphi_1 + \frac{\varphi_2}{v_2} \ln \varphi_2 \right) + \Lambda_{12} \varphi_1 \varphi_2 \quad (3)$$

where φ_1 is the volume fraction, and v_1 is the molar volume of component 1. Here, volume fractions of polymers, φ_K , in the blend were calculated from:

$$v_K = \sum_{i=1}^g v_{i,K} V_i^* \quad (4)$$

$$\phi_K = \frac{x_K v_K}{\sum x_L v_L} \quad (5)$$

The calculations were performed for different molar masses of PLLA and PMMA, and the results are presented in Fig. 1. As expected, the Gibbs energy of mixing increases with the molar mass of polymers. However, the increase is much smaller for the molar masses above 25000 g mol⁻¹. Both homopolymers used in this work had close values of molar masses (M_w), which were far above the limit value (see Table 1).

Influence of blend preparation on the molar mass of polymers

Molar mass of a polymer has the greatest effect on its mechanical properties. A polymer with low M_w and low T_g (below ambient temperature) is a viscous liquid, while a polymer with high T_g is brittle. Polymers with higher M_w show more rubbery behavior and higher elongation before break. Mostly, polymers with M_w above 10⁵ g mol⁻¹ are more entangled and their elongation before break increases greatly. Polar polymers achieve maximum tensile strength and elongation at break at lower values of M_w in comparison to non-polar polymers²⁶. Here, PMMA with similar molar mass averages ($M_n = 30700 \text{ g mol}^{-1}$; $M_w = 73800 \text{ g mol}^{-1}$; $M_z = 152000 \text{ g mol}^{-1}$) to PLLA ($M_n = 33400 \text{ g mol}^{-1}$; $M_w = 76200 \text{ g mol}^{-1}$; $M_z = 156000 \text{ g mol}^{-1}$) was synthesized by radical polymerization (Table 1). Relatively low molar masses were chosen, because the indicative results from the study of Li *et al.*²² showed lower clarity point and slightly lower interaction param-

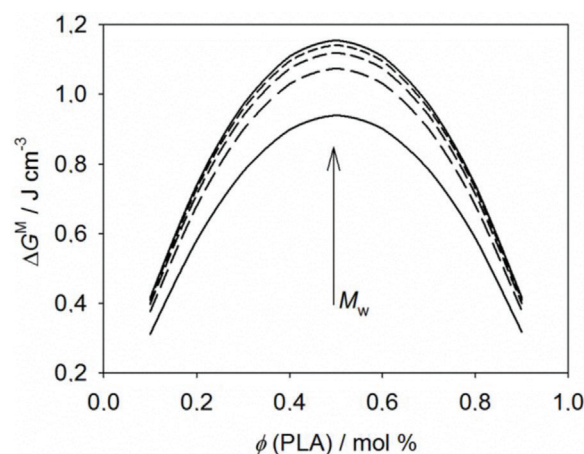


Fig. 1 – Gibbs energy of mixing for PLLA/PMMA blends with the increase in polymer molecular masses: 10000, 25000, 50000, 100000, and 250000 g mol⁻¹

Table 1 – Number (M_n), weight (M_w), and z-molar mass averages (M_z), dispersity (\mathcal{D}) of non-processed and processed poly(L-lactic acid) – PLLA, poly(methyl methacrylate) – PMMA, and their blends

		$M_n /$ g mol ⁻¹	$M_w /$ g mol ⁻¹	$M_z /$ g mol ⁻¹	\mathcal{D}
Non-processed	PMMA100	30700	73800	152000	2.40
	PLLA100	33400	76200	156000	2.28
Processed	PLLA100	22100	54800	109200	2.48
	PLLA80/PMMA20	24700	54600	108900	2.21
	PLLA60/PMMA40	28800	63500	132000	2.21
	PLLA50/PMMA50	27800	64000	133300	2.30
	PLLA40/PMMA60	29800	65100	134800	2.18
	PLLA20/PMMA80	30500	68700	144700	2.25
	PMMA100	30300	71500	138900	2.36
Processed and separated by dissolving PMMA	PLLA80	23400	52600	107300	2.25
	PLLA60	27600	59600	118000	2.16
	PLLA50	28200	68400	134700	2.16
	PLLA40	29600	65100	127800	2.20
	PLLA20	28100	64000	133800	2.28

ter (χ_{12}) in quasi-miscible state of PLLA/PMMA blend with PMMA-k53 ($M_w = 53500$ g mol⁻¹) compared to PMMA-k100 ($M_w = 100000$ g mol⁻¹). In order to investigate possible degradation during melt mixing of PLLA and PMMA, SEC analysis was performed (Table 1, Fig. 2). Processed pure PMMA had 1 % lower M_n , 3 % lower M_w , and 9 % lower M_z compared to non-processed PMMA, which indicated very small or negligible degradation effect of melt mixing. In the case of PLLA, the degradation was more pronounced and resulted in lowering molecular masses by around 30 % (processed PLLA had M_n lower by 34 %, M_w lower by 28 %, and M_z lower by 30 % than non-processed PLLA). PLLA is known to degrade rapidly when melted at high temperatures, losing from 20 to 80 % of its initial M_n on melt processing¹⁴. The reduction in molar mass averages in blends is inversely proportional to PMMA content (see data in Table 1). To determine if PMMA had some kind of protecting effect when added in blends with PLLA, the PLLA part of the blend was separated from PMMA by dissolving PMMA in toluene and filtering the solution through filter paper. A transparent filtrate was obtained, while undissolved PLLA residue was washed several times with toluene, dried in a vacuum oven, and analyzed by NMR and SEC. NMR analysis was done to confirm that there was no residual PMMA in the separated PLLA polymer to influence SEC results. As shown in Fig. 3, the signal belonging to $-\text{OCH}_3$ group from PMMA had more than 200 times (PLLA50/PMMA50), and more than 500

times (PLLA20/PMMA80) smaller area than $-\text{CH}_3$ signal from PLLA (which has the same number of protons), confirming that there was almost no residual PMMA left after separation.

Here, it was found that PMMA reduces the degradation of PLA, which is elsewhere achieved by, *e.g.*, adding inorganic fillers¹⁸. The results confirm a kind of protecting effect of PMMA that is especially expressed in blends with the PMMA content above 40 mass%. For those compositions, M_w was around 17 to 25 % higher than M_w of pure PLA processed in the absence of PMMA.

Characterization of PLLA/PMMA blends

The prepared PLLA/PMMA blends were characterized by measuring contact angle and performing morphology characterization with SEM. Crystalline structure of pure PLLA and its blends with PMMA was assessed by WAXD measurements. In addition, thermal and mechanical properties of homopolymers and prepared blends were studied by DSC, TGA and DMA analysis, respectively.

Contact angle

The contact angle measurements were undertaken in order to quantify the surface wettability of PLLA and PMMA homopolymers and their blends. Contact angle values measured on prepared films are given in Table 2. Measurements of contact angle revealed similar polarity, *i.e.*, hydrophobic character

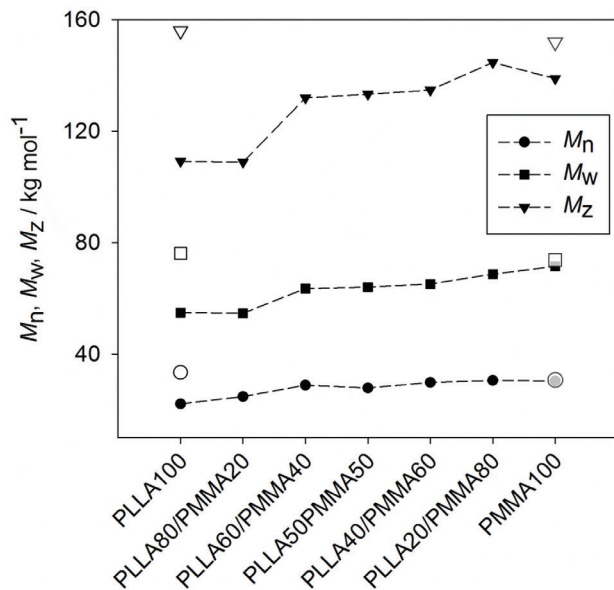


Fig. 2 – Number (M_n), weight (M_w), and z-molar mass averages (M_z) of non-processed (\square , \circ , \triangle), and processed PLLA, PMMA, and their blends

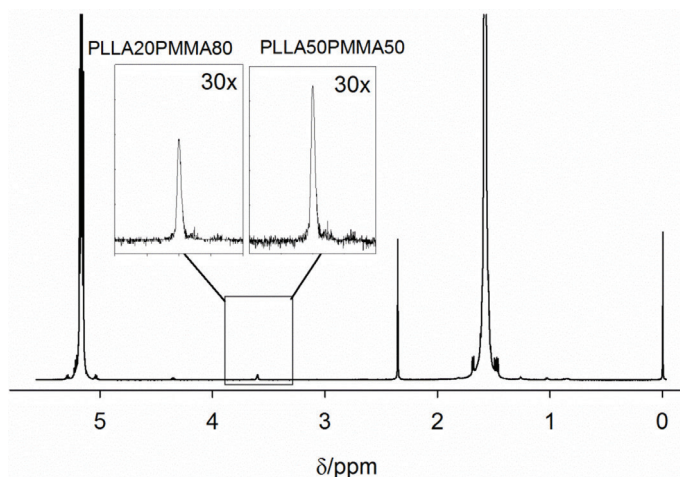


Fig. 3 – NMR spectra of separated PLLA20 and PLLA50 from PLLA20/PMMA80 and PLLA50/PMMA50 by dissolving and separating PMMA

Table 2 – Values of contact angle of water droplets on the examined surfaces of poly(L-lactic acid) – PLLA, poly(methyl methacrylate) – PMMA, and their blends

Sample	Contact angle/°	SD*/°
PLLA100	79.21	2.34
PLLA80/PMMA20	83.83	3.49
PLLA60/PMMA40	83.85	2.20
PLLA50/PMMA50	82.08	4.33
PLLA40/PMMA60	78.07	2.97
PLLA20/PMMA80	82.92	2.22

SD* – standard deviation

of PLLA (79.2°) and PMMA (81.7°). Accordingly, their blends displayed similar values, yet surprisingly, slightly higher relative to the pure components. The PLLA40/PMMA60 sample was an exception that displayed the lowest value among all samples. Small deviations of contact angle are probably the consequence of slightly different roughness of prepared testing probes.

Scanning electron microscopy

The compatibility of PLLA/PMMA blends was investigated by SEM. Fig. 4 shows the typical SEM micrographs taken from neat PLLA, PMMA, and PLLA/PMMA blends. The blend exhibited homogeneous morphology of fractured surface, which indicated that there were no separated phases and that a good compatibility was achieved. The behavior of PLLA80/PMMA20 sample resembled very much that of neat PLLA. The fracture surface changed, displaying more brittle fracture with increasing fraction of PMMA, whereat the smoothest surface was, surprisingly, noticed in PLLA20/PMMA80 sample. Such a surface indicates the brittle failure mechanism, *i.e.*, the absence of large-scale plastic deformation in the case of such a high content of PMMA in blend²⁷. There are SEM micrographs of PLA/PMMA blends presented in the literature corroborating the homogeneous morphology²² as well as opposite findings pointing to phase separation¹⁹, which shows a complex nature of those blends, and influence of different structural characteristics and processing conditions.

WAXD characterization

The crystalline structure of PLLA and PLLA/PMMA blends was examined using wide-angle X-ray diffraction (WAXD) analysis, and results are shown in Fig. 5. The PLLA sample showed two main diffraction peaks at $2\theta = 16.7^\circ$ and 19.3° , corresponding to (110) / (200) and (203) planes of PLLA, respectively, which belong to the α crystal form of PLLA²⁸. However, in PLLA/PMMA blends (and PMMA homopolymer), no peaks for homocrystal and stereocomplex crystal were observed, proving the amorphous state of the probes after the preparation process.

Differential scanning calorimetry

Thermal properties of neat PLLA and PMMA, and PLLA/PMMA blends were studied by DSC. A three-scan procedure in the range -30 to 200 °C started with the first heating scan, followed by the cooling scan, and ended with the second heating scan. The values of interest were collected from the second heating scan in order to minimize the thermal history effect. Typical non-isothermal DSC

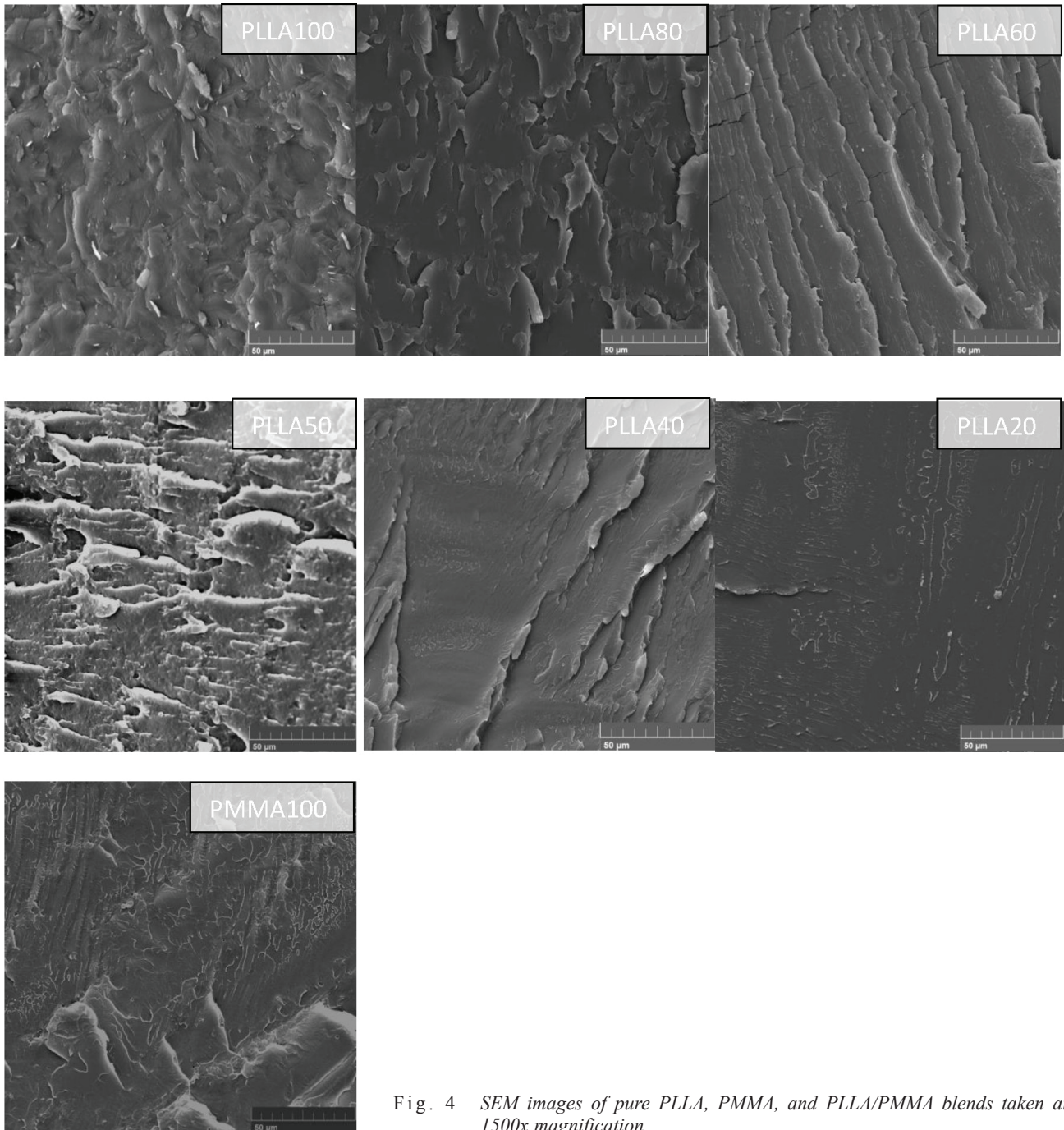


Fig. 4 – SEM images of pure PLLA, PMMA, and PLLA/PMMA blends taken at 1500x magnification

thermograms for all samples are shown in Figs. 6 and 7. In an attempt to obtain more correct values of enthalpy change, the integration of a broad segment of the scan, i.e., from the beginning of cold crystallization exotherm to the end of melting endotherm ($\Delta H_m - |\Delta H_{cc}|$), was made in the second heating scan. These and other thermal properties related values (glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting temperature of crystal domains (T_m) of homopolymers and their blends are summarized in Table 3. During the second heating scan, all examined sam-

ples displayed a single glass transition temperature, which would imply miscibility of PLLA and PMMA, as previously stated in the literature²². PMMA displayed the highest glass transition temperature, as expected. PLLA displayed T_g at 57.4 °C. PLLA/PMMA blends displayed an increase in T_g with respect to PLLA, but a significant one only for the PMMA content of 50 mass% or higher. Unlike Yoon *et al.*²⁹, who obtained two glass transitions in the first heating scan that became single T_g in the second heating scan, or unlike Li and Woo^{23g}, who achieved blending on molecular level only af-

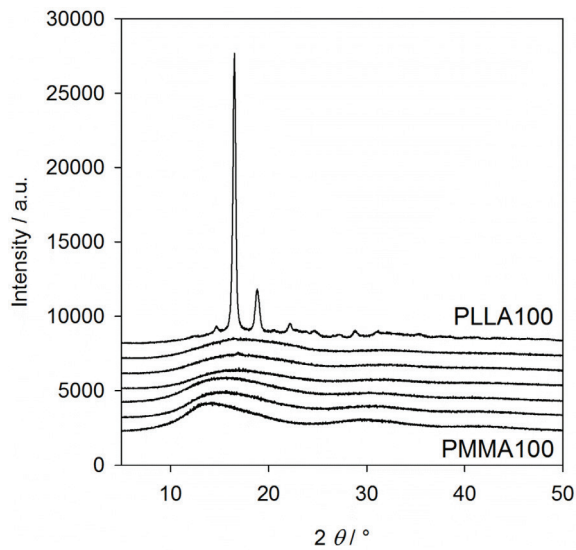


Fig. 5 – WAXD spectra of PLLA, PMMA, and PLLA/PMMA blends

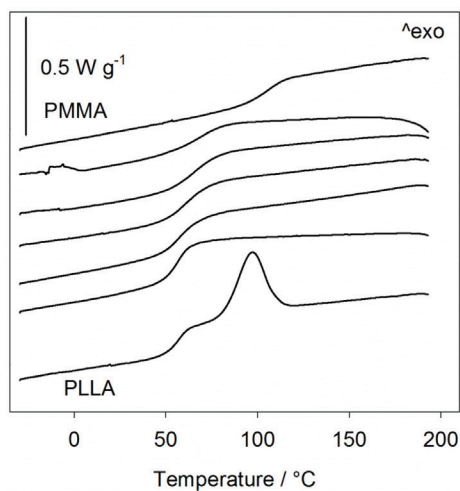


Fig. 6 – DSC cooling scan of PLLA, PMMA, and PLLA/PMMA blends recorded at $10\text{ }^{\circ}\text{C min}^{-1}$

ter quenching preceded by heating to $250\text{ }^{\circ}\text{C}$, we obtained single glass transition in both heating scans, whereas T_g values shifted upwards relative to the values in the first heating run. This might indicate that the melt blending temperature of $190\text{ }^{\circ}\text{C}$ surmounted the upper critical solution temperature (UCST) enabling good melt mixing of polymers^{21,23,30}. Since molar masses of our homopolymers were several times lower compared to some in literature^{23,30}, seemingly, the temperature of $190\text{ }^{\circ}\text{C}$ was sufficient to achieve complete melt mixing. In addition, despite lower molecular masses of our homopolymers in comparison to those in the literature, they displayed the same or close values of glass transition temperatures. The dependence of T_g on blend composition (in terms of mass fractions of polymer components, w_i) was analyzed by fitting the T_g s with some models developed for miscible systems. Fox equation, $1/T_g^{\text{blend}} = w_1/T_{g1} + w_2/T_{g2}$, did not show a good match (Fig. 8). An attempt to apply Gordon-Taylor equation with the assumption of $k = 0.5$ in order to achieve good matching of measured and calculated values was not successful for our system, as opposed to findings of Zhang *et al.*²⁰ However, when Gordon-Taylor equation was applied, $T_{g,\text{blend}} = (w_1 T_{g1} + w_2 T_{g2}) / (w_1 + k w_2)$, an empirical fitting parameter k of 0.168 for PLLA/PMMA blends was obtained, as shown in Fig. 6. It is lower than $k = 0.24$ obtained for $M_n(\text{PLA}) = 106000\text{ g mol}^{-1}$ and $M_n(\text{PMMA}) = 70000\text{ g mol}^{-1}$ blends or $k = 0.2$ obtained for blends with PMMA of molar masses of 53000 and 350000 g mol^{-1} and $k = 0.25$ for $M_w(\text{PMMA}) = 100000\text{ g mol}^{-1}$, respectively²³. Since in the last example $M_w(\text{PLA}) = 152000\text{ g mol}^{-1}$ was used, it showed that a higher value of fitting parameter k , *i.e.*, better miscibility was achieved in the case of close values of molecular masses. Although the low k value and negative deviation of T_g s relative to the values calculated for

Table 3 – Thermal properties of neat poly(L-lactic acid) – PLLA, poly(methyl methacrylate) – PMMA, and their blends prepared by melt mixing

Sample	2 nd heating run							
	$T_g / ^{\circ}\text{C}$	Fox	G-T	G-T ^[20] , $k = 0.5$	$T_{cc} / ^{\circ}\text{C}$	$T_m / ^{\circ}\text{C}$	$\Delta H_m - \Delta H_{cc} / \text{J g}^{-1}$	$X_{c(\text{PLA})} / \%$
PLA	57.4	57.4	57.4	57.4	98.0	163.0	-20.2	23.1
PLLA80/PMMA20	58.4	65.2	60.8	62.3	132.2	167.9	-0.3	0.5
PLLA60/PMMA40	61.7	73.4	65.5	68.5	–	168.2	-1.7	3.0
PLLA50/PMMA50	64.5	77.6	68.7	72.1	–	–	–	–
PLLA40/PMMA60	69.3	81.9	72.8	76.2	–	–	–	–
PLLA20/PMMA80	74.0	90.9	85.0	86.4	–	–	–	–
PMMA	110.4	110.4	110.4	110.4	–	–	–	–

ideal blends imply that strong interactions between PLLA and PMMA are lacking, the blends displayed single glass transition temperatures between the T_g s of neat polymers, which indicates their miscibility or, at least, compatibility. Here, two homopolymers of close values of molecular masses: PLLA (76200 g mol⁻¹ of non-processed or 54800 g mol⁻¹ of processed) and PMMA (73800 g mol⁻¹ or 71500 g mol⁻¹) displayed significant compatibility.

Along with some other semi-crystalline polymers, PLLA is known for its slow crystallization. Crystallization of the same pure PLLA sample during cooling scan was discussed previously where various composites prepared by melt mixing were studied³¹. In the studied PLLA sample, the crystallization developed during cooling (Fig. 7) shifted to a lower temperature, which was much smaller in extent in comparison with the first heating scan. In the second heating scan, the cold crystallization also shifted to a lower temperature like in the cooling scan (Fig. 8)³². Cold crystallization during second heating scan occurs consequently if no crystallization or one smaller in extent occurs during cooling^{33–35}. The results collected during the second heating scan show clearly that added PMMA hinders the crystallization process in PLLA (Fig. 8). PMMA, as a well-known amorphous material, does not display crystallization or melting. Regarding two characteristic transitions, pure PLLA sample displayed the cold crystallization peak in the range of 89 – 105 °C centered at about 98 °C, followed by melting in the range of 163 – 175 °C. A characteristic small exothermic peak preceded the melting peak. In an attempt to obtain more correct values of the enthalpy change despite unclear transition of the crystallization in the melting process, the whole scan, i.e., from the beginning of cold crystallization exotherm to the end of melting endotherm, was integrated. The calculated difference introduced in Eq. 6, and using enthalpy of fully crystalline PLLA ($\Delta H_m^\circ = 93.6 \text{ J g}^{-1}$)³¹, where α is the mass fraction of PLLA, enables calculation of the degree of crystallinity ($X_c = 23.1 \%$). As may be seen from Fig. 7, the as-blended PLLA80/PMMA20 also underwent cold crystallization during the second heating scan. In the sample PLLA80/PMMA20, an exothermic peak at about 132 °C and a melting peak at close to 168 °C were registered. Therefore, the onset and peak of cold crystallization had shifted upwards for more than 20 °C and 34 °C, respectively, relative to PLLA. The lower T_{cc} in pure PLLA is to be attributed to the partial crystallinity of the sample before the second heating scan, where crystals acted as cold crystallization nuclei^{33,35}. The slight endothermic peak persisted, but there was no evidence of cold crystallization under these conditions in PLLA60/PMMA40. In addition, blends with higher

PMMA content displayed neither melting nor cold crystallization during the second heating run. When Eq. 6 was used for calculation of the degree of crystallinity for the blends PLLA80/PMMA20 and PLLA60/PMMA40, X_c values of 0.5 % and 3 %, respectively, were obtained. The obtained results are consistent with findings of Zhang *et al.*³⁶ who have shown for the PLA and ethylene/methyl acrylate/glycidyl methacrylate terpolymer (EGA) blends that, the addition of EGA up to 20 % caused an increase in melting temperature, as well as an increase in the enthalpy of cold crystallization, i.e., added EGA induced a larger non-isothermal crystallization in PLA. However, the small difference between melting and cold crystallization enthalpies in the PLLA80/PMMA20 blend indicated that the cold crystallization of blend did not progress³⁷. Further increase in PMMA content did not contribute to the cold crystallization of PLLA, but oppositely.

$$X_c (\%) = \left[\frac{(\Delta H_m - |\Delta H_{cc}|)}{\Delta H_m^\circ (\alpha - 1)} \right] \cdot 100 \quad (6)$$

Thermogravimetric analysis

Thermal stability and degradation of PLLA, PMMA, and their blends prepared by melt mixing was examined by TGA, and results are displayed in Fig. 9. All samples were heated to 500 °C under a nitrogen flow, whereat the decrease in mass percentage was monitored. The one-step mass loss process was observed in PLLA, while the two-step process was recorded in pure PMMA. Thermal decomposition of PLLA took place in a single, smooth step that began at about 310 °C, and reached zero mass at 390 °C. PMMA displayed decomposition in the temperature ranges of 225 °C to 330 °C and 330 °C to 430 °C (Table 4). Two-step degradation is well documented for PMMA in literature^{38,39}. The process was explained to initiate with vinylidene end-groups, which resulted from the bimolecular radical termination by disproportionation during polymerization. The second degradation step resulted from random chain scission. Interestingly, in the work of Peterson and Vyazovkin³⁸, the occurrence of the first degradation step was registered in the temperature range of 180 – 350 °C, which was significantly lower in comparison to our results, although the molar mass of PMMA sample was significantly higher there ($M_w = 996000 \text{ g mol}^{-1}$). In addition, at lower heating rates, they observed an additional step that preceded the two previously mentioned. This was explained by Kashiwagi *et al.*⁴⁰ as the degradation of irregular head-to-head linkages formed as a result of termination by combination of growing polymer chains. On the other hand, Peterson *et al.*³⁸ concluded that the processes

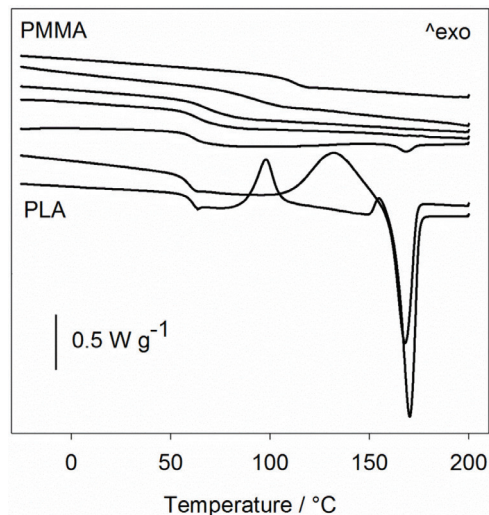


Fig. 7 – DSC second heating scan of PLLA, PMMA, and PLLA/PMMA blends recorded at $10\text{ }^{\circ}\text{C min}^{-1}$

of degradation initiated at the irregular head-to-head linkages and vinylidene end-groups were strongly overlapped. Here, added PMMA decreased the low-temperature thermal stability of PLLA and caused the appearance of small peaks around $200\text{ }^{\circ}\text{C}$ that preceded the major degradation steps in blends. The major degradation proceeded in three peaks characteristic for PMMA component (second and fourth) and PLLA component (third peak). Finally, the PLLA peak and second PMMA peak overlapped, and the total degradation of blends shifted to a slightly higher temperature.

The decomposition temperatures T_{95} , T_{90} , T_{50} , and T_5 are summarized in Table 4. The T_{95} , T_{90} , T_{50} , and T_5 are corresponding to the temperature at which the remaining mass of the materials is 95, 90, 50, and 5 %, respectively. Initially, pure PLLA was

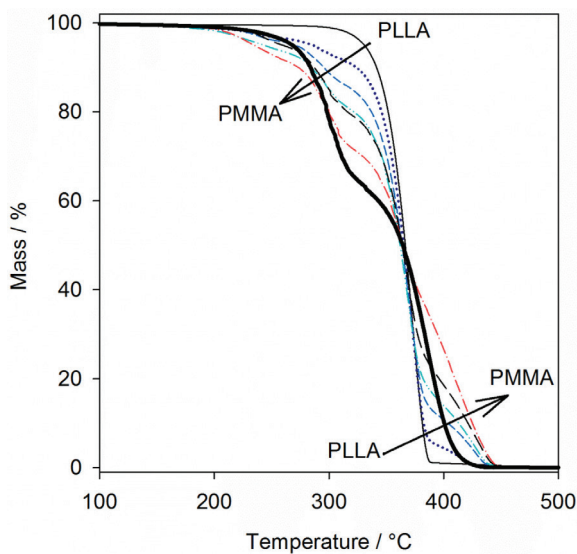


Fig. 9 – TG curves of pure PLLA, PMMA, and PLLA/PMMA blends, investigated under a stream of nitrogen at $10\text{ }^{\circ}\text{C min}^{-1}$

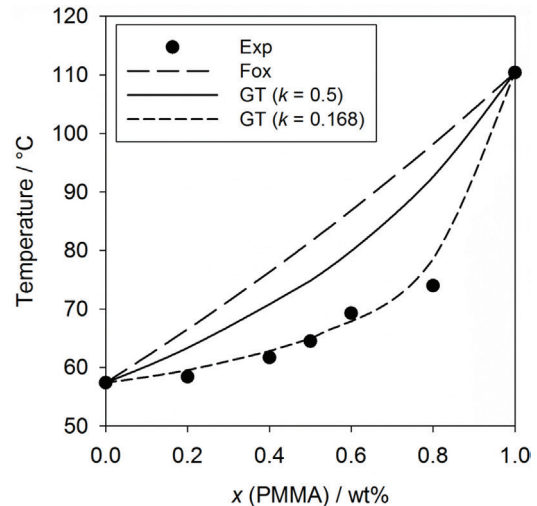


Fig. 8 – Glass transition temperatures of polymer blends with fitted Fox and Gordon-Taylor (GT) models

thermally the most stable, while blends displayed lower stability. The least stable among all samples was PLLA20/PMMA80 that displayed both the lowest T_{95} and T_{90} . Finding that added PMMA reduces the low-temperature thermal stability of PLLA is reasonable, since PMMA showed smaller stability relative to PLLA. However, it is interesting that prepared blends displayed even lower stability than neat PMMA. At the same time, added PMMA reduced the degradation of PLLA during melt-blending, *i.e.*, increased the resilience of PLLA against shear force and increased temperature during blend processing, as it was proved by SEC measurements (smaller decrease of molar masses). As opposed to the large difference regarding onset of degradation process, all samples displayed very similar T_{50} values, $\Delta T \sim 4\text{ }^{\circ}\text{C}$.

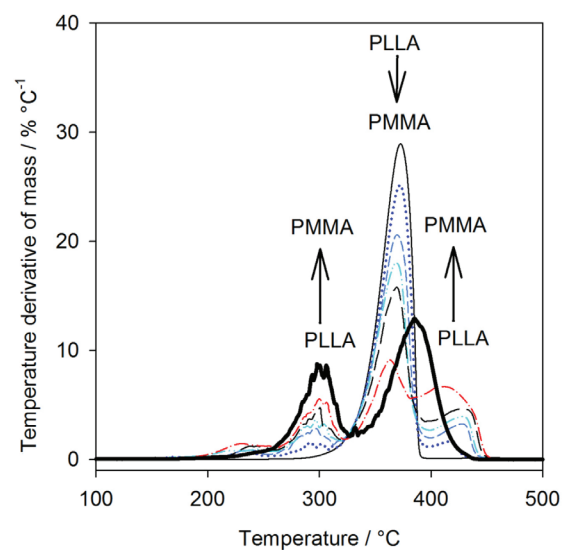


Fig. 10 – DTG curves of pure PLLA, PMMA, and PLLA/PMMA blends, investigated under a stream of nitrogen at $10\text{ }^{\circ}\text{C min}^{-1}$

Table 4 – Thermal degradation data of poly(L-lactic acid) – PLLA, poly(methyl methacrylate) – PMMA, and their blends

Sample	PLLA100	PLLA80/ PMMA20	PLLA60/ PMMA40	PLLA50/ PMMA50	PLLA40/ PMMA60	PLLA20/ PMMA80	PMMA100
$T_{95}/^{\circ}\text{C}$	330	286	271	243	259	235	288
$T_{90}/^{\circ}\text{C}$	341	324	296	285	287	274	283
$T_{50}/^{\circ}\text{C}$	366	365	364	363	364	365	364
$T_g/^{\circ}\text{C}$	384	395	423	427	432	437	408

Mechanical properties

DMA results for neat PLLA, PMMA, and their blends are shown in Figs. 11 and 12. The α transition temperatures, T_{α} , defined as the temperature of the main peak in the thermogram of loss factor ($\tan \delta$), are given in Table 5. In PLLA homopolymer, it was not possible to determine the T_{α} value due to the plateaued shape of the curve, but the T_{α} values of blends shifted downwards relative to PMMA. The intensity of $\tan \delta$ of blends increased, which can be taken as additional proof of their compatibility. With the increasing content of PMMA in blends, the glass transition temperature increase was recorded expectedly. The PLLA80/PMMA20 sample displayed a high T_{α} value close to that of the PLLA40/PMMA60 sample with a three times higher PMMA content. The explanation for it is that, although T_{α} of PLLA80/PMMA20 moved to the value of about 63 °C initially, with a further temperature increase, a recovery of mechanical properties took place and a maximum at 88.8 °C was recorded. The result from the loss factor (T_{α}) was consistent with the result of DSC measurement, where the cold crystallization was noted in the same

Table 5 – T_g values from DMA measurements; loss factor (T_{α} , $\tan \delta$), and loss modulus (T_g , E'') of poly(L-lactic acid) – PLLA, poly(methyl methacrylate) – PMMA, and their blends

Sample	T_{α} ($\tan \delta$)	T_g (E'')
PLLA100	n. d.	67.9
PLLA80/PMMA20	88.8	59.1
PLLA60/PMMA40	74.7	56.8
PLLA50/PMMA50	80.7	61.0
PLLA40/PMMA60	86.8	63.9
PLLA20/PMMA80	92.8	72.9
PMMA100	121.2	105.3

sample. Furthermore, the $\tan \delta$ peak height of the PLLA/PMMA blends gradually increased with increasing PMMA content, which is attributed to the gradually decreased flexibility of PLLA/PMMA blends.

In contrast, the $\tan \delta$ peak decrease with increasing PMMA content was observed in literature¹⁹. In addition, they recorded higher $\tan \delta$ values, especially for pure PLLA and PMMA that had three and two times higher M_n , respectively.

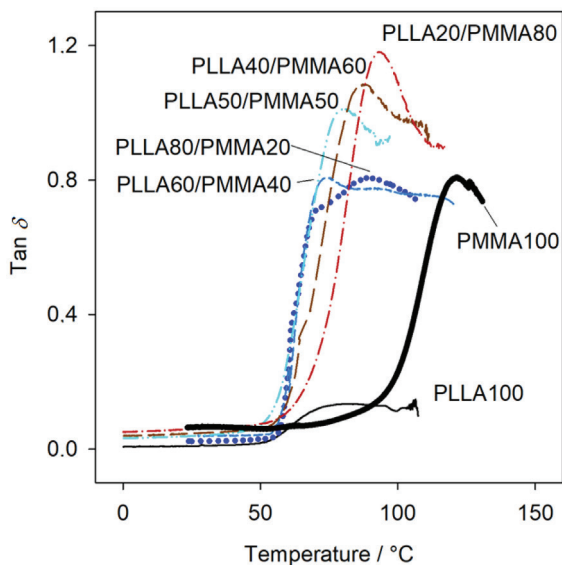
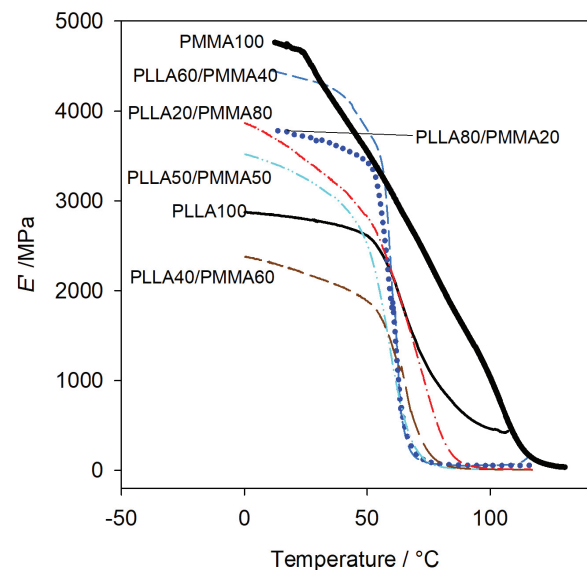
Fig. 11 – $\tan \delta$ of pure PLLA, PMMA, and PLLA/PMMA blends as a function of temperature

Fig. 12 – Dynamic storage modulus of pure PLLA, PMMA, and PLLA/PMMA blends as a function of temperature

PMMA showed a steady decrease in E' as approaching glass transition, Fig. 12. PLLA did not show a complete reduction in storage modulus due to cold crystallization, which is consistent with literature findings³⁰. One can see that added PMMA caused an increase in storage modulus. This indicates the increase in rigidity of blends due to present PMMA. Oppositely, the study of Anakabe *et al.*¹⁹ showed that increasing content of PMMA in blends caused a decrease in modulus. However, it is interesting that blends prepared in this work displayed comparable values of modulus despite much lower M_n values relative to theirs. Here, sample PLLA40/PMMA60 displayed the lowest E' of all samples, while the analogous sample showed the highest impact resistance (resilience)¹⁹. These findings suggest, once more, that the mixing process of PLA/PMMA blends seems to be diffusion-controlled, and is highly dependent on polymer molar masses and processing conditions.

Conclusions

Blends of biobased PLLA with PMMA in a wide range of composition (0 – 100 mass%) were prepared. The PMMA homopolymer sample of structural characteristics (M_n , M_w and dispersity, \mathcal{D}) very close to the commercial PLLA, was synthesized in our laboratory in order to exclude the influence of their divergence on the results. The initial theoretical calculations implied immiscibility of PLLA and PMMA ($\Delta_{\text{PLLA/PMMA}} = 4.66 \text{ J cm}^{-3}$, $\gg 0.5$). However, SEM images displayed homogeneous fracture surfaces without visibly separated domains of two homopolymers. In addition, single glass transition temperatures were recorded as additional evidence of homopolymers miscibility or at least high compatibility. Added PMMA positively influenced properties of PLLA in two ways; i) it obstructed the degradation of PLLA during melt processing as determined on the basis of molar mass monitoring, and ii) it shifted T_g s upwards, noticeably at higher PMMA content. At the same time, added PMMA reduced the low-temperature thermal stability of PLLA, while 50 mass% loss was observed at the same temperature in all samples. Mechanical properties of prepared blends assessed by the loss factor ($\tan \delta$) were improved significantly with respect to pure PLLA. All blends displayed upward T_g value shift with increasing PMMA content. Crystalline phase that was identified also in DSC measurement for the PLLA80/PMMA20 sample, contributed additionally to the improvement of mechanical properties, which correlated with its relatively higher T_g value. The height of $\tan \delta$ peak of the PLLA/PMMA blends gradually increased with

increasing PMMA content due to the decreased flexibility of PLLA/PMMA blends.

The results show that it is possible to improve properties of PLLA by blending it with PMMA. The designed material prepared by blending in Brabender mixer displayed better mechanical properties as well as higher glass transition temperature (T_g , T_g), and also proved more stable during processing.

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