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Stereocomplexation of Polylactide Enhanced by Poly(methyl methacrylate): Improved Processability and Thermomechanical Properties of Stereocomplexable Polylactide-Based Materials

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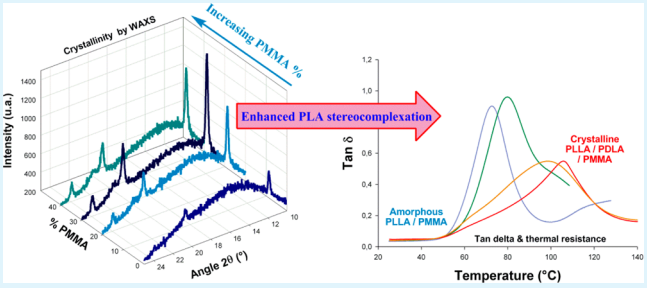
Supporting Information

ABSTRACT: Stereocomplexable polylactides (PLAs) with improved processability and thermomechanical properties have been prepared by one-step melt blending of high-molecular-weight poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(methyl methacrylate) (PMMA). Crystallization of PLA stereocomplexes occurred during cooling from the melt, and, surprisingly, PMMA enhanced the amount of stereocomplex formation, especially with the addition of 30−40 % PMMA. The prepared ternary blends were found to be miscible, and such miscibility is likely a key factor to the role of PMMA in enhancing stereocomplexation. In addition, the incorporation of PMMA during compounding substantially raised the melt viscosity at 230 °C. Therefore, to some extent, the use of PMMA could also overcome processing difficulties associated with low viscosities of stereocomplexable PLA-based materials. Semicrystalline miscible blends with good transparency were recovered after injection molding, and in a first approach, the thermomechanical properties could be tuned by the PMMA content. Superior storage modulus and thermal resistance to deformation were thereby found for semicrystalline ternary blends compared to binary PLLA/PMMA blends. The amount of PLA stereocomplexes could be significantly increased with an additional thermal treatment, without compromising transparency. This could result in a remarkable thermal resistance to deformation at much higher temperatures than with conventional PLA. Consequently, stereocomplex crystallization into miscible PLLA/PDLA/PMMA blends represents a relevant approach to developing transparent, heat-resistant, and partly biobased polymers using conventional injection-molding processes.



KEYWORDS: *poly(L-lactic acid), poly(D-lactic acid), stereocomplexation, poly(methyl methacrylate), polymer blends, miscibility*

INTRODUCTION

Poly(L-lactide) (PLLA) is one of the most promising biobased thermoplastic polyesters with high mechanical properties, a positive life cycle, and low-cost production from annually renewable raw materials.[1,2] Achieving technical and high-value applications is challenging for any biobased polymer, especially polylactide (PLA), because specific properties are required such as a thermal resistance to deformation and/or long-term durability. Actually, although its melting temperature is around 170 °C and its glass transition temperature ca. 60 °C, the thermal resistance to deformation of PLA is limited by a relatively low heat deflection temperature close to 50 °C. The crystallization rate of high-molecular-weight commercial PLA is generally low, which does not allow large-scale production of a semicrystalline thermoplastic polymer after processing such as injection molding.[3−8] Long-lasting durability is also a pending question because it has been demonstrated that PLA can undergo severe degradation during its service life,[8,9] linked with its ability to get readily degraded under industrial composting conditions or in an aqueous medium. In this regard, PLA crystallization from the melt state is one of the most

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challenging topics, and PLA stereocomplexes have progressively attracted a lot of attention in this field.

Since the 1990s and the pioneer works of Ikada et al., PLLA and its enantiomeric opposite, poly(D-lactide) (PDLA), have been known to form specific stereocomplexes upon mixing in solution or in bulk conditions. Stereocomplex formation can be easily identified by wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC). In particular, the stereocrystal melting point is in the range of 220−230 °C, i.e., values that are significantly higher than those of PLA homocrystallites (approximately 170 °C).[10−13] Their fast crystallization from the melt state,[14,15] their nucleating effect in neat PLA,[16] their superior thermomechanical properties,[13,17] and their lower thermal and hydrolytic degradation rates[18,19] are the most fascinating properties that clearly highlight the high potential of PLA stereocomplexes to develop semicrystalline PLA grades with enhanced properties for long-lasting applications. It was earlier reported that the ratio between PLLA and PDLA plays a key role in achieving full stereocomplexation between PLLA and PDLA, i.e., without any crystallization of the homopolymer. A 50:50 weight ratio between PLLA and PDLA generally promotes (nearly) complete stereocomplexation,[10−12] but the processing method, processing conditions, and homopolymer molecular weight have a profound influence on the relative amount of PLA stereocomplexes compared to PLA homocrystallites.[14,15,20,21] In particular, melt-processed, high-molecular-weight PLLA/PDLA blends are systematically characterized by the presence of both PLA stereocomplexes and PLA homocrystallites, which is more likely connected to some diffusion issues and/or poor blending. However, the most limiting factor to the future developments of stereocomplexable PLA grades is the low melt viscosities of these systems,[22] as a result of their intensive homopolymer degradation as well as the use of high temperatures needed to melt PLA stereocomplexes. In this regard, to take advantage of PLA stereocomplexes, any approach that could increase the processability of PLLA/PDLA blends without compromising stereocomplexation represents a great opportunity.

In this respect, several approaches have been investigated, namely, based on coupling reactions between low-molecular-weight PLLA and PDLA blocks. For instance, an advanced reactive process was developed to synthesize new poly(ester urethane)s, starting from oligo-PLLA, oligo-PDLA, and a diamine/diisocyanate system as a chain extender.[23] Sterecomplexation was evidenced, but a complex reactive process is requested involving the use of hazardous raw materials like diisocyanate. The syntheses of low-molecular-weight PLLA and PDLA from mono- or difunctionalized macroinitiators based on oligomers of poly(butylene succinate) (PBS)[24] or poly(ethylene oxide) (PEO)[25] were also reported with successful stereocomplexation, and a clear nucleating effect on neat PLA was observed.[24] However, to the best of our knowledge, melt-blending approaches between high-molecular-weight PLLA and PDLA with another immiscible or miscible third polymer are ill-documented, and only association with poly(3-hydroxybutyrate) is mentioned.[26,27] In the field of PLLA-based polymer blends, the use of poly(methyl methacrylate) (PMMA) represents an interesting approach, where high-molecular-weight PLLA and PMMA are reported to be miscible by melt-blending techniques. These processes appear to be a robust approach to tuning the thermomechanical and barrier properties of PLLA with the amount of PMMA incorporated.[28−31] As a consequence of the shear-induced miscibility, it could be possible to produce transparent miscible blends with enhanced thermal resistance without altering their mechanical properties, even for a PMMA content in the range of 20−50%.

Because high-molecular-weight PLLA and PMMA appear to be a miscible polymer pair after a melt-blending process, adding high-molecular-weight PDLA as a third partner during compounding is believed to promote crystallization of PLA by taking advantage of the fast stereocomplexation between the PLLA and PDLA fractions. In this work, ternary blends composed of high-molecular-weight PLLA, PDLA, and PMMA were developed by extrusion techniques. The effect of PMMA addition to PLA stereocomplexation was studied. However, crystallization and miscibility are known to be competitive processes and, here, the experiments were designed to investigate the extent of crystallization and miscibility in such ternary PLLA/PDLA/PMMA blends. Crystallization of PLA stereocomplexes into injection-molded specimens was accessed by WAXS and the effect of PMMA ascertained by DSC and dynamic mechanical analysis (DMA), especially for the extent of miscibility. Then, several melt-state parameters were addressed in order to reveal the influence of PMMA on the processability of stereocomplexable PLA. Finally, the thermomechanical properties of ternary blends were compared to those of binary amorphous PLLA/PMMA miscible blends. The influence of PMMA and of PLA stereocomplexes on the storage modulus, thermal resistance, and thermomechanical performances of the highly crystalline ternary blends obtained by thermal annealing was also highlighted in this work.

EXPERIMENTAL SECTION

Materials. Poly(L-lactide), hereafter called PLLA, was kindly supplied by NatureWorks LLC (grade 4032D, L isomer <2%, M_n = 123000 g·mol^{-1}, and M_w = 218000 g·mol^{-1}, obtained by size-exclusion chromatography (SEC) calibrated with PMMA standards in $CHCl_3$ at 25 °C). Poly(methyl methacrylate), hereafter called PMMA, was supplied by Evonik (grade 8N, M_n = 52000 g·mol^{-1}, and M_w = 97000 g·mol^{-1}, obtained by SEC calibrated with PMMA standards in $CHCl_3$ at 25 °C). From ^{1}H NMR analysis (500 MHz, $CDCl_3$, 25 °C), syndiotactic sequences rr (49%) and atactic sequences mr (42%) were found to be predominant in PMMA. Bis(2,4-di-*tert*-butylphenyl)-pentaerythritol diphosphite, Ultranox 626A, supplied by GE Speciality Chemicals, was selected as the thermal stabilizer and used at ca. 0.3% in all prepared blends. D-Lactide was kindly supplied by Purac (Purasorb D, purity 99.5%), and bis(2-ethylhexanoate)tin(II) (stannous octanoate, $Sn(Oct)_2$, Aldrich, purity 95%) and triphenylphosphine (Aldrich, purity 99%) were used for the synthesis of poly(D-lactide). Throughout this contribution, all percentages are given as weight percent.

Processing. Poly(D-lactide), hereafter called PDLA, was first synthesized by reactive extrusion (D isomer >99.9%, M_n = 35000 g·mol^{-1}, and M_w = 67000 g·mol^{-1}, obtained by SEC calibrated on PMMA standards in $CHCl_3$ at 25 °C), and detailed information about procedures and conditions can be found elsewhere.[32] Before melt processing, PLLA, PDLA, and PMMA were dried overnight at 60 °C under vacuum, and Ultranox 626A was dried overnight at 25 °C, to minimize the water content in each component and avoid any excessive degradation upon further processing. Typically, PLLA, PDLA, and PMMA were processed in a twin-screw DSM microcompounder at 230 °C and 60 rpm for 10 min under a dry nitrogen flow. A total mass of 14 g was selected, and the introduction of PLLA, PDLA, PMMA, and Ultranox 626A was performed at 30 rpm for 4 min. The force supplied by the motor drive of the DSM microcompounder was systematically recorded during compounding at a constant screw rotation speed. Five different PLLA/PDLA/PMMA formulations were studied (50% PLLA/50% PDLA, 40% PLLA/40% PDLA/20% PMMA, 35% PLLA/35% PDLA/30%

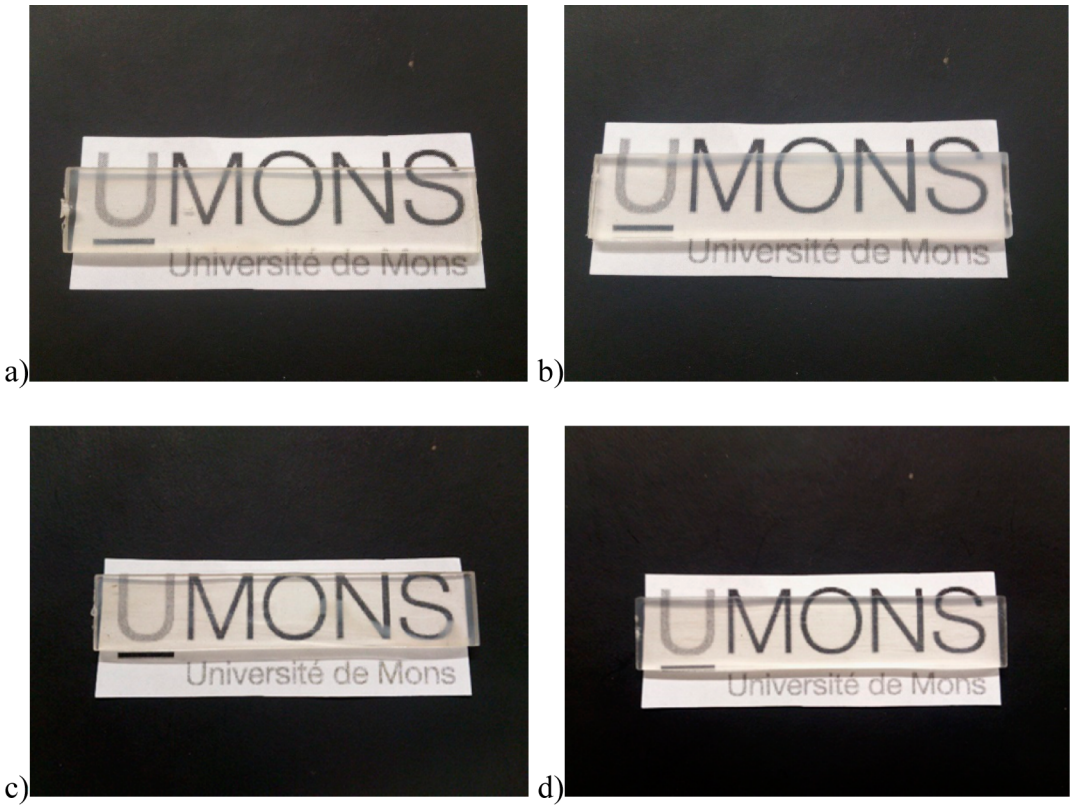

Figure 1. Optical observations of melt-processed 50% PLLA/50% PDLA (a), 40% PLLA/40% PDLA/20% PMMA (b), 35% PLLA/35% PDLA/30% PMMA (c), and 30% PLLA/30% PDLA/40% PMMA (d) blends (rectangular DMA samples as produced by injection molding; see the Experimental Section).

PMMA, 30% PLLA/30% PDLA/40% PMMA, and 25% PLLA/25% PDLA/50% PMMA). Binary PLLA/PMMA blends were also processed with the same equipment using a procedure reported elsewhere.[28]

Characterization. Melt-processed PLLA/PDLA/PMMA blends were injection-molded to obtain rectangular samples for DMA (specimens of 55 × 12 × 2 mm^3) using a DSM microinjection system with the following procedure: drying overnight at 60 °C under vacuum, preheating at 230 °C for 3 min, and injection molding at 230 °C with a mold temperature at 60 °C. Under our conditions, taking into account a retrieving time of approximately 15 s, a cooling rate from the melt state of approximately 680 °C·min^{-1} was applied to each injection-molded specimen. Cylindrical samples for rheology (diameter 25 mm; thickness 2 mm) were produced by compression molding with the following procedure: drying overnight at 60 °C under vacuum, preheating at 230 °C for 3 min, low-pressure cycling for 3 min at 1 bar, high-pressure cycling for 1 min at 9 bar, and cooling to 25 °C. Unless it is specifically mentioned in the text, non-annealed samples were used.

The transparencies of DMA rectangular specimens were investigated using a Varian Cary 5G UV−visible spectrophotometer. The blank reference was air, and transmittance spectra were recorded for wavelengths from 200 to 800 nm. DMA specimens were then examined by WAXS experiments after injection molding. WAXS analyses were performed on a Siemens D5000 diffractometer using Cu Kα radiation (wavelength 1.5406 Å) at room temperature. The samples were step-scanned from 10 to 25° in 2θ with steps of 0.02° with a fixed time sampling of 4 s (40 kV and 30 mA). DSC measurements were performed using a DSC Q200 calorimeter from TA Instruments under a nitrogen flow. The strands and injection-molded specimens were submitted to the following procedure: heating at 10 °C·min^{-1} to 230 °C (to erase the prior thermal history), cooling at 10 °C·min^{-1} to −40 °C, and heating at 10 °C·min^{-1} to 230 °C. This DSC cycle was repeated five times to highlight the stability of the observed thermal events. Glass transition temperatures (T_g) were determined at the inflection point. Polarized-light optical microscopy (PLOM) was also performed on a LEICA DMRXP polarized microscope, and crystallization experiments from the melt state were conducted. The strands were melted at 230 °C on a hot-stage LEICA FP82HT instrument equipped with a Mettler FP90 central processor. Samples were then allowed to cool at 10 °C·min^{-1} to 110 °C (the minimum controllable temperature at this cooling rate), and evolution of the crystalline structure was recorded every 5 °C step. Dynamic rheology experiments were carried out on an ARES rheometer from TA Instruments in a plate−plate configuration (diameter 25 mm and gap 1.5 mm) at 230 °C. Compression-molded specimens were dried at 60 °C overnight, and a strain-sweep experiment was performed at 1 rad·s^{-1} to determine the optimal strain (typically optimal strain = 25%). Then, a frequency-sweep experiment was performed from 100 to 0.1 rad·s^{-1} at the optimal strain previously chosen. Finally, a time-sweep experiment was performed at 1 rad·s^{-1} to quantify the extent of degradation. The strands were also submitted to MFI measurements, carried out on a Davenport melt-flow indexer with a mass of 2.16 kg at 230 °C. DMA was carried out on a DMA Q800 instrument from TA Instruments in a dual-cantilever bending mode with an amplitude of 20 μm and a frequency of 1 Hz. First, the storage modulus at 30 °C was twice measured, followed by measurement of the storage and loss moduli as a function of the temperature from 25 °C to 130−150 °C at a heating rate of 2 °C·min^{-1}.

RESULTS AND DISCUSSION

Transparency and Crystallinity of Injection-Molded Blends. PLLA/PDLA/PMMA ternary blends were melt-blended in a twin-screw extruder at 230 °C for 10 min. In these blends, the PLLA/PDLA ratio was maintained at a constant value of 0.5, the theoretical optimum ratio for full stereocomplexation,[10−12] while the PMMA content was

progressively increased from 0 to 50%. The different formulations were extruded and then injection-molded. The injection-molded specimens are shown in Figure 1. For all formulations, ternary blends show a good transparency, and compared to PLLA/PMMA binary blends, no major changes in the transparency can be noticed for injection-molded ternary blends[28] (S01 in the Supporting Information, SI). A quantitative evaluation of the transparency was further performed by UV−visible spectrophotometry, and Figure 2

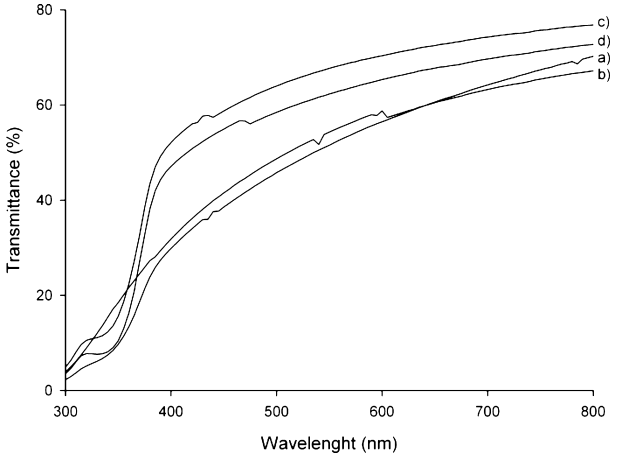

Figure 2. UV−visible spectra of melt-processed 50% PLLA/50% PDLA (a), 40% PLLA/40% PDLA/20% PMMA (b), 35% PLLA/35% PDLA/30% PMMA (c), and 30% PLLA/30% PDLA/40% PMMA (d) blends (evaluated on rectangular DMA samples as produced by injection molding; see the Experimental Section).

presents the UV−visible spectra related to injection-molded specimens. For all as-presented materials, the transmittance reached 75−65% at 800 nm and decreased to 50−35% for a wavelength of 400 nm. Murariu et al. evaluated the transparency of various PLLA grades to 80−65% within the same wavelength range on thin films made by compression molding (thickness 150−300 μm).[5] Therefore, a good transparency can be stated for the as-presented injection-molded specimens, taking into account their high thickness of 2 mm and classical defects related with injection-molding processes. Interestingly, higher transparencies were reached with 30 and 40% PMMA. However, the 50% PLLA/50% PDLA blend and the 40% PLLA/40% PDLA/20% PMMA blend displayed a slight decrease in the transparency, indicating a potential influence of the crystallinity degree within these blends. In this respect, the crystallinity of injection-molded specimens was evaluated using WAXS.

WAXS profiles were recorded on these injection-molded PLLA/PDLA/PMMA ternary blends to evidence the presence of crystallinity and the amount and type of crystallites (Figure 3). In all cases, a broad amorphous halo covering the entire 2θ range is observed, together with superposition of a few crystalline reflections. The stereocomplexable 50% PLLA/50% PDLA blend without PMMA only presents very small diffraction peaks, indicating a very small amount of stereocrystals. However, the introduction of PMMA has a major influence on the WAXS profiles. Three small diffraction peaks that progressively grow at approximately 12, 21, and 24° (2θ) can be attributed to the triclinic crystals of PLA stereocomplexes forming 3_1 helices.[13] No diffraction peaks at 14.8°, 16.6°, 19.0°, 22.4°, and 29.2° could be identified, indicating the

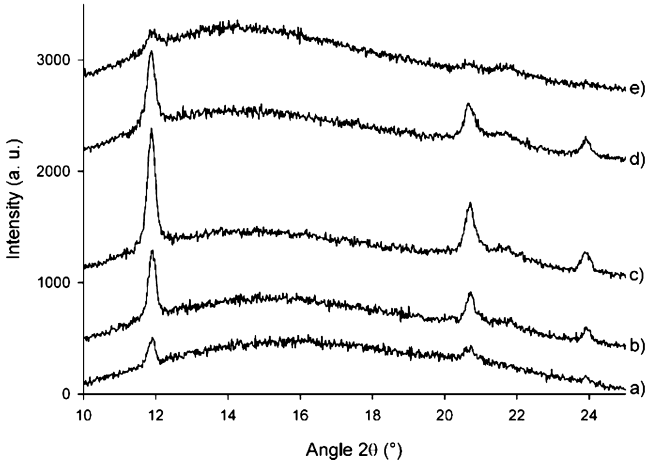

Figure 3. WAXS profiles for 50% PLLA/50% PDLA (a), 40% PLLA/40% PDLA/20% PMMA (b), 35% PLLA/35% PDLA/30% PMMA (c), 30% PLLA/30% PDLA/40% PMMA (d), and 25% PLLA/25% PDLA/50% PMMA (e) blends as analyzed after injection molding.

absence of PLA homocrystallization.[13] Therefore, it might be concluded that ternary blends containing 20%, 30%, and 40% PMMA are semicrystalline after injection molding and only PLA stereocrystals were able to form during high-speed cooling. Moreover, PMMA enhances the intensities of the diffraction peaks associated with PLA stereocomplexes, and a progressive increase in the crystallinity is observed with the amount of PMMA incorporated (Figure 3). The blends containing 30% and 40% PMMA indeed present the highest intensities, but a further increase to 50% PMMA is detrimental. In this regard, the introduction of PMMA in the range of 20−40% surprisingly enhances the amount of PLA stereocomplexes, and the use of PMMA appears to be crucial to obtaining PLA stereocomplex crystals after injection molding. In addition, no correlation between the transparency and crystallinity could be clearly established, indicating that the sizes of the PLA stereocrystals seem to be affected by the amount of PMMA. Crystallite sizes lower than approximately 0.4 μm were probably obtained because the samples shown in Figure 1 do not scatter light.

Miscibility and Crystallization from the Melt State. From these WAXS results, it can be stated that ternary blends contrast with binary PLLA/PMMA blends. Binary blends are known to be miscible after melt-extrusion processing, and the PLLA crystallization rate is consequently inhibited in these miscible blends.[28] As a consequence, the crystallinity of the binary blends is limited to very low values after injection molding (S02 in the SI). Here, crystallization of the PLA stereocomplexes surprisingly occurs in these ternary blends and allows us to discard any processing artefact by investigating (i) the miscibility extent by DSC and DMA and (ii) crystallization from the melt state at a controlled cooling rate.

The miscibility in these blends was first checked by DSC, and Figure 4 displays the second heating scan for each ternary blend. A glass transition is clearly observed in the range of 60−90 °C, and even if cold crystallization appears with the blend containing 20% PMMA, this glass transition seems to be the only one detectable. The glass transition temperature for stereocomplexable 50% PLLA/50% PDLA is recorded at 62 °C, and the introduction of PMMA tends to increase this single glass transition temperature (evaluated at the inflection point; see Figure 4). Between 0% and 40% PMMA, the glass

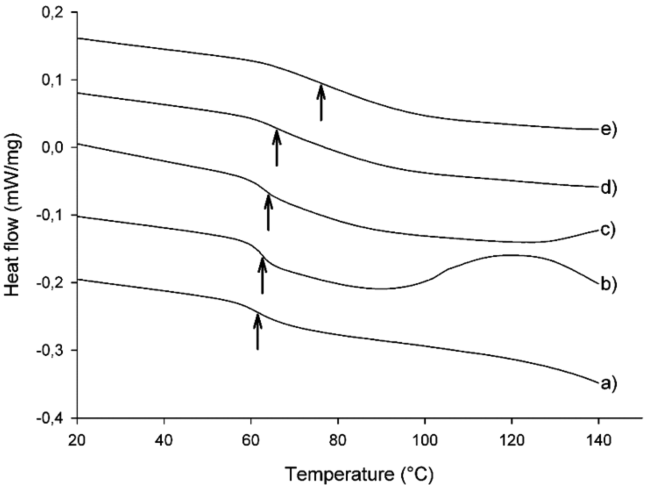

Figure 4. DSC second heating scan as a function of the temperature for 50% PLLA/50% PDLA (a), 40% PLLA/40% PDLA/20% PMMA (b), 35% PLLA/35% PDLA/30% PMMA (c), 30% PLLA/30% PDLA/40% PMMA (d), and 25% PLLA/25% PDLA/50% PMMA (e) blends.

transition temperature is slightly increased from 62 to 66 °C, but a higher increase in the glass transition temperature to 76 °C is observed when 50% PMMA is added to the blend. It is of importance to note that the glass transition temperature progressively broadens with increasing PMMA content, in accordance with the self-concentration model for miscible blends.[33] All of these calorimetric observations are consistent with the miscibility in PLLA/PDLA/PMMA ternary blends under the investigated conditions.

The storage modulus and tan δ were recorded as a function of the temperature for all injection-molded PLLA/PDLA/PMMA blends, and the effect of PMMA on tan δ profiles with temperature is presented in Figure 5. For all blends, the glassy plateau observed at low temperature is followed by a significant drop of the storage modulus, associated with a α-relaxation transition. Crystallization upon heating could be clearly identified for the 50% PLLA/50% PDLA and 40% PLLA/40% PDLA/20% PMMA blends, but these cold crystallizations differ from those observed by DSC in terms of onset and intensity. Different heating rates were employed between both DSC and DMA experiments, which could significantly affect the cold crystallization onset. However, the different cooling rates between the DSC samples (10 °C·min^{-1}) and injection-molded DMA samples (estimated at 680 °C·min^{-1}) could also induce different extents of crystallization, explaining the high intensity of cold crystallization during DMA experiments. Regarding the tan δ profiles, a unique peak associated with the α-relaxation transition may be detectable for all injection-molded ternary blends. Moreover, the α-relaxation temperature clearly increases with the PMMA content, as is observed by a progressive shift to higher temperature of the tan δ peak, a phenomenon also evidenced on the peak associated with the loss modulus (S03 in the SI). It could also be noticed that the tan δ peak progressively broadens with a reduction in the intensity, reflecting some severe modifications in the mobility of the amorphous phase ascribed to the presence of PMMA[28] and PLA stereocrystallites.[4,34] The monomodality, the shift to higher temperature, and the broadening of the α-relaxation transitions in ternary blends are in accordance with both the previous DSC experiments and the miscibility between PLA and PMMA chains.[28] In this regard, miscible ternary blends could be produced after injection at 230 °C and molding at 60 °C for a PMMA content from 0% to 50%. In other terms, semicrystalline ternary blends are produced with an amorphous phase containing PLLA, PDLA, and PMMA in a miscible state.

Figure 6 presents the cooling scans from the melt state for all ternary blends, and Table 1 gathers the observed crystallization temperatures and associated enthalpies. It is worth noting that the recorded crystallization enthalpies were normalized according to the amount of PLA within the blend. The stereocomplexable 50% PLLA/50% PDLA blend displays two crystallization peaks at 190.3 and at 131.9 °C, assigned to the crystallization of PLA stereocomplexes and homocrystallites, respectively.[14] The crystallization enthalpy related to PLA homocrystallites reaches 32 J·g_{PLA}^{-1}, and a high decrease in the crystallization enthalpy is observed with 20% PMMA (Table 1). Above 30% PMMA, no PLA homocrystallites could be formed during controlled cooling. These results are in accordance with an inhibited PLA homocrystallization in the presence of the miscible PMMA phase, previously observed in binary PLLA/PMMA blends.[28] Crystallization of PLA stereocomplexes was always observed at high temperatures in the range of 190−165 °C, depending on the PMMA content, and the normalized crystallization enthalpy of PLA stereocomplexes is interestingly enhanced with the introduction of PMMA (Table 1). Indeed,

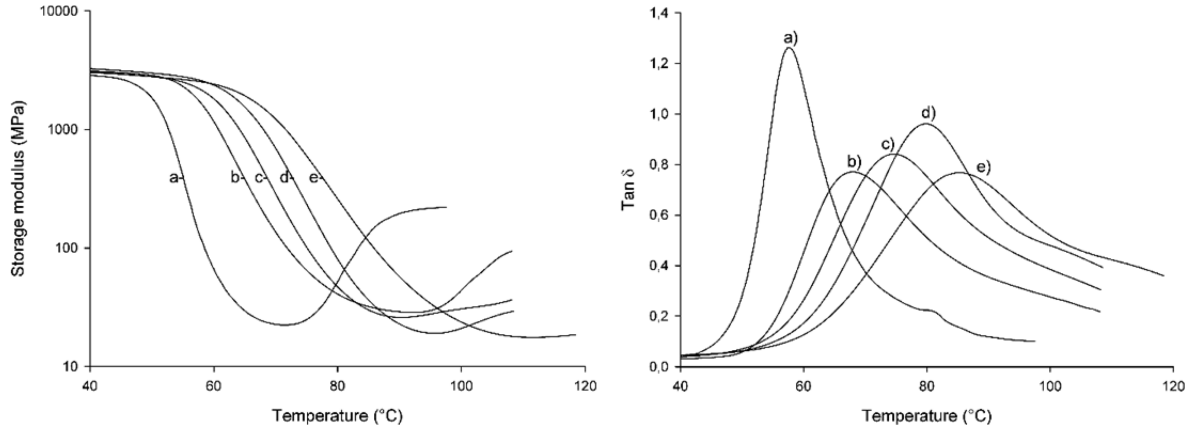

Figure 5. Storage modulus and tan δ as a function of the temperature for 50% PLLA/50% PDLA (a), 40% PLLA/40% PDLA/20% PMMA (b), 35% PLLA/35% PDLA/30% PMMA (c), 30% PLLA/30% PDLA/40% PMMA (d), and 25% PLLA/25% PDLA/50% PMMA (e) blends.

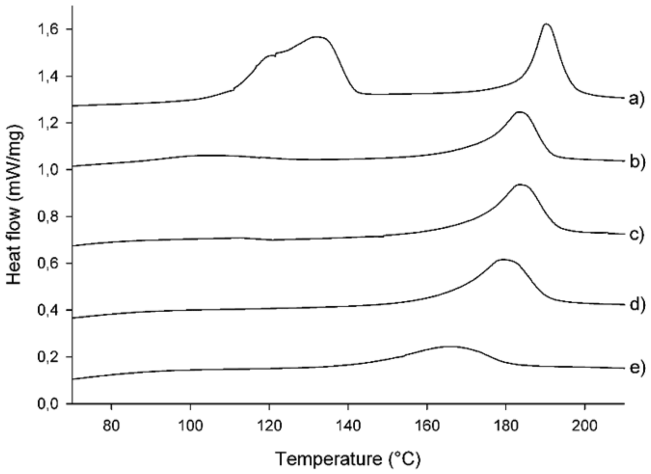

Figure 6. Controlled cooling from the melt at 10 °C·min^{-1} for 50% PLLA/50% PDLA (a), 40% PLLA/40% PDLA/20% PMMA (b), 35% PLLA/35% PDLA/30% PMMA (c), 30% PLLA/30% PDLA/40% PMMA (d), and 25% PLLA/25% PDLA/50% PMMA (e) blends.

the normalized crystallization enthalpy of PLA stereocomplexes passes from 17 J·g_{PLA}^{-1} without PMMA to 22 J·g_{PLA}^{-1} with 20% PMMA. Afterward, their normalized crystallization enthalpy continuously increases and a maximal enthalpy of 34 J·g_{PLA}^{-1} is reached with 40% PMMA. A further increase to 50% PMMA is detrimental to PLA stereocomplexation, more likely explained by a volume fraction of PMMA higher than that of PLA (PMMA density = 1.19 and PLA density = 1.25, according to suppliers). The effect of high temperatures reached during DSC heating, potentially inducing some thermal degradation reactions. They were explored, but the crystallization behavior remained unaffected, as attested to by the stability of thermal events after up to five multiple heat/cool/heat cycles (S04 in the SI). Therefore, the formation of PLA stereocomplexes under controlled cooling at 10 °C·min^{-1} was found to reflect, to some extent, crystallization of PLA stereocomplexes observed under cooling conditions from the injection-molding processes (approximately 680 °C·min^{-1}). These two cooling conditions highlight, upon the incorporation of PMMA into stereocomplexable PLA, a similar trend in terms of PLA stereocomplexes recovered per PLA unit and optimum PMMA content (30% vs 40%) Even if the PLA crystallization extent could not be strictly compared, crystallization of the PLA stereocrystals under the investigated cooling conditions is clearly enhanced by the presence of a miscible PMMA fraction up to 40%.

Enhanced crystallization into a miscible blend is a phenomenon classically encountered with the use of plasticizers and, for example, the crystallization rate from the melt state of PLLA could be easily increased upon blending with PEO.[35,39] With a glass transition temperature of approximately −60 °C, the miscible PEO fraction could efficiently act as a plasticizer for PLLA and increase the mobility of PLLA chains. However, PMMA cannot be considered as a plasticizer for PLLA because the glass transition temperature of PMMA lies at approximately 115 °C, ca. 55 °C higher than the PLLA one. Interestingly, PEO/PMMA blends represent a similar system with a crystallizable "low-T_g" PEO miscible with the amorphous "high-T_g" PMMA phase.[36−38] Under isothermal crystallization conditions, a reduction of the radial growth rate for PEO crystallites was established upon blending with PMMA,[38] a phenomenon also observed for crystallization of the PLA homocrystals within a binary PLLA/PMMA miscible blend.[29] However, an interesting and unexpected increase of the primary nucleus density of PEO was evidenced during nonisothermal crystallization from the melt state of miscible PEO/PMMA blends.[36,37] Some authors mentioned specifically that PMMA may influence the entire nucleation process, leading to an apparent increase in the nucleus density with the percentage of the amorphous high-T_g component. Several factors were stated to be responsible for this enhanced primary nucleation, i.e., the dilution effect of PMMA in the melt, reduction of the radius growth rate, which increases the volume for primary nucleation, and depression of the melting temperature due to strong interaction between PEO and PMMA. As far as ternary PLLA/PDLA/PMMA blends are concerned, a similar depression is observed on the melting and crystallization temperatures of PLLA stereocomplexes (Table 1) and an enhanced primary nucleation could fit with the discrepancies between the crystallinity and transparency of PLLA/PDLA/PMMA blends. Actually, strong interactions between the crystallizable PLLA/PDLA and amorphous PMMA fractions allow us to mention that a strong melt-memory effect could also have a high influence on crystallization of the PLA stereocomplexes, as previously reported in PLLA/PDLA blends.[21] In this respect, PLOM experiments were conducted to follow the evolution of the crystallinity during cooling from the melt state at 10 °C·min^{-1}. For the blend containing 40% PMMA, crystallization appears at approximately 194 °C and ended at approximately 164 °C, in good agreement with crystallization of the PLA stereocomplexes during some previous DSC studies (S05 in the SI). Interestingly, a homogenous dispersion of very small crystallites is observed with 40% PMMA. Without PMMA, bigger crystallites are unambiguously observed, but a clear conclusion about the nucleus density cannot be established yet. Meanwhile, further studies focused on the crystallization processes in ternary blends are being conducted to clarify the

Table 1. Crystallization Temperatures and Melting Temperatures with Enthalpies for PLA Stereocomplexes and PLA Homocrystallites Depending on the PMMA Content in PLLA/PDLA/PMMA Ternary Blends

PMMA content (%)	$T_{c\text{-PLA homocrystallites}}$ (°C)[a]	$\Delta H_{c\text{-PLA homocrystallites}}$ (J·g_{PLA}^{-1})[a,c]	$T_{c\text{-PLA stereocomplexes}}$ (°C)[a]	$\Delta H_{c\text{-PLA stereocomplexes}}$ (J·g_{PLA}^{-1})[a,c]	$T_{m\text{-PLA stereocomplexes}}$ (°C)[b]
0	131.9	32	190.3	17	220.1
20	103.0	4	183.5	22	218.4
30			183.3	29	217.8
40			179.4	34	216.8
50			165.7	26	215.1

[a]Measured by DSC, with a controlled cooling scan at 10 °C·min^{-1} from 235 °C. [b]Measured by DSC, with a second heating scan at 10 °C·min^{-1}. [c]Normalized enthalpy divided by the recorded enthalpy to the weight fraction of PLA.

role of PMMA in the crystallization process of PLA stereocomplexes, especially the nucleation process.

On the basis of these results, it can be concluded that PLA stereocomplexes can easily crystallize through a miscible PLLA/PDLA/PMMA blend during high-speed cooling in the injection-molding process. Processing effects are ruled out, and the introduction of PMMA plays a crucial role in crystallization of the PLA stereocomplexes. Without PMMA, no stereocrystals could be formed, and only 20% PMMA greatly enables recovery of the PLA stereocomplexes in significant yields during high-speed cooling. However, the highest quantities of PLA stereocomplexes are obtained with 30−40% PMMA, and semicrystalline miscible blends are efficiently recovered. In addition, a good transparency is maintained, more likely because of intensive effects on the nucleation of PLA stereocomplexes.

Melt-State Properties. In addition to the beneficial effect of PMMA on crystallization of the stereocomplexes, significant differences between ternary formulations were also noticed during extrusion compounding at 230 °C that lead us to investigate the effect of PMMA on the melt-state properties of stereocomplexable PLA. Ternary blends were subsequently submitted to dynamic rheology experiments, and Table 2 summarizes the melt force supplied by the motor drive of the DSM microcompounder (a good correlation with the torque), the plateau viscosity, the complex viscosity at high shear rate, and the melt-flow index (MFI) as a function of the PMMA content. All of these values were evaluated at 230 °C, and for the sake of comparison, the behavior of pure PLLA is also presented.

Table 2. Melt Force during Compounding, Complex Viscosity Parameters, and MFI as a Function of the PMMA Content in Ternary PLLA/PDLA/PMMA Blends

PMMA content (%)	melt force (N)[a]	η_0* (Pa·s)[b]	η* (Pa·s)[c]	MFI (g/10 min)[d]
0	300	40	30	n.m.
20	700	60	40	n.m.
30	1000	90	70	n.m.
40	1400	145	125	60
50	1750	245	185	50
100	6780	7350	1240	n.m.
pure PLLA	2200	580	440	21

[a]Evaluated during twin-screw extrusion at 230 °C for a compounding time of 10 min. [b]Plateau viscosity evaluated at 230 °C. [c]Evaluated at 230 °C and at 100 Hz. [d]Evaluated at 230 °C with a mass of 2.16 kg. n.m. = not measurable, i.e., a value too high or too low.

The stereocomplexable 50% PLLA/50% PDLA displays a surprisingly very low melt force upon compounding at 230 °C, in accordance with the very low viscosity at 100 Hz that was recorded close to 30 Pa·s by dynamic rheology (Table 2). The pure high-molecular-weight PLLA processed in the same conditions displays higher viscosities than the stereocomplexable 50% PLLA/50% PDLA. Therefore, melt blending with a homemade PDLA by reactive extrusion obviously induced an intensive and negative modification of the melt-state properties, as previously reported in the literature.[22] Degradation after twin-screw extrusion at 230 °C was qualitatively evaluated by SEC, and the molecular weights of PLA were considered (S06 in the SI). It is worth noting that determination of the molecular parameters of individual PLLA and PDLA is impossible for the stereocomplexable 50% PLLA/50% PDLA, and only a qualitative description is possible by comparing the melt-processed 50% PLLA/50% PDLA and the unprocessed one. Before melt blending, the apparent M_n and M_w are close to 57000 and 144000 g·mol^{-1}, respectively, but after processing, these values fall to 43000 and 96000 g·mol^{-1}. This attests for a significant degradation by chain-scission and transesterification reactions as well as the formation of some oligomers and monomers during compounding as a consequence of back-biting reactions.[5] In fact, the use of homemade PDLA with lower molecular weights than that of pure PLLA could lead to a possible plasticization, which was induced by some thermal degradation of the material (promoted by some trace of tin catalyst as well), and therefore modify the observed plateau viscosity.[39] As a direct consequence of the low viscosity, the MFI could not be evaluated and the stability of the injection-molding process is beyond our concern. Even if several DMA samples could be injected, these very low viscosity values are therefore not suitable for any industrial and stable injection-molding process.

Introduction of PMMA into stereocomplexable PLAs profoundly and positively modifies their melt-state properties. Melt force, plateau viscosity and complex viscosity at high shear rate progressively increase with the amount of PMMA (Table 2) and intermediate viscosities are observed between pure stereocomplexable PLA and pure PMMA. Moreover PMMA has a strong beneficial effect on the melt viscosity at 230°C and the degradation of the stereocomplexable PLA can be consequently overcome with 40 − 50% PMMA. It can be noticed that a clear negative deviation from the linearity of the viscosities is observed with increasing PMMA, which could be explained by the aforementioned degradation processes. Furthermore, for PMMA content lower than 30 wt %, the MFI values of the blends were still too high to be determined in a reliable manner, but at 40% and 50% PMMA, the MFI value reaches a value close to 60 and 50 g/10 min, respectively (Table 2). In other terms, the poor processability of stereocomplexable PLA associated to the intensive degradation and the low viscosity can be significantly improved with the introduction of PMMA. Based on the previous results about the crystallization of stereocomplexes in ternary blends, the use of 40% PMMA leads to a good compromise between the amount of stereocomplexes formed after injection-molding and the necessity to maintain a correct MFI for these processes.

Thermomechanical Properties. Injection-molded PLLA/PDLA/PMMA blends were subjected to DMA analyses, and the results were already shown in Figure 5. From evolution of the storage modulus and tan δ with the temperature of each blend, i.e., the storage modulus at 30 °C ($E_{30\ °C}$), the temperature at 1.8 GPa ($T_{1.8\ GPa}$), and α-relaxation temperature (T_α, evaluated at the tan δ peak) can be determined as a function of the PMMA content. The effect of PMMA has been reported for miscible PLLA/PMMA binary blends with a tunable thermal resistance, arising from the miscibility.[28] Such behavior is readily assessed on the basis of T_α and $T_{1.8\ GPa}$, which can be related to the thermal resistance to deformation. It is worth noting that $E_{30\ °C}$ remains almost constant with the PMMA content in binary PLLA/PMMA blends. In this regard, DMA analyses were carried out in order to highlight the influence of PMMA and PLA stereocomplexes on the thermal resistance and storage modulus of the semicrystalline ternary blends.

The $E_{30\ °C}$, $T_{1.8\ GPa}$, and T_α values as a function of the PMMA content for each ternary blends are gathered in Table 3. First, it

Table 3. α-Relaxation Temperature Measured at the tan δ Peak (T_α), Temperature for 1.8 GPa ($T_{1.8\ GPa}$), and Storage Modulus at 30 °C ($E'_{30\ °C}$) for PLLA/PDLA/PMMA Blends as a Function of the PMMA Content (Standard Deviations Are in Parentheses)

PMMA content (%)	T_α (°C)	$T_{1.8\ GPa}$ (°C)	$E'_{30\ °C}$ (MPa)
0	57.8	50.2	3040 (30)
20	67.9	57.4	3210 (60)
30	74.5	60.1	3230 (40)
40	80.0	63.7	3470 (30)
50	85.2	66.0	3220 (40)
100	115.8	76.4	2980 (30)

can be noticed that T_α gradually increases with the amount of PMMA, reflecting the miscibility between PLLA, PDLA, and PMMA. As far as $T_{1.8\ GPa}$ is concerned, $T_{1.8\ GPa}$ is determined at 50.2 °C for the pure stereocomplexable 50% PLLA/50% PDLA blend and up to 66.0 °C for the stereocomplexable 50% PLLA/50% PDLA blend containing 50% PMMA. In other terms, the thermal resistance to deformation progressively shifts to higher values with the amount of PMMA. The same trend for T_α can be also noticed in the case of ternary blends. For similar processing conditions, an efficient tuning of the thermal resistance is thereby provided upon the amount of PMMA in ternary blends, and in a first approach, PMMA globally controls the thermomechanical properties of these ternary blends.

The thermomechanical properties of ternary blends are here compared to those of the binary PLLA/PMMA blends to reveal any thermomechanical effects ascribed to crystallization of the stereocomplexes. It is worth noting that binary PLLA/PMMA blends are almost amorphous, as previously reported by some of us.[28,29,31] Figure 7 presents the evolution of $E_{30\ °C}$ and $T_{1.8\ GPa}$ with the amount of PMMA for semicrystalline PLLA/PDLA/PMMA blends and for PLLA/PMMA binary blends. Concerning PLLA/PMMA blends, the storage modulus at 30 °C, $E_{30\ °C}$, remains nearly constant in the range of 2.9−3.1 GPa whatever the amount of PMMA, but, interestingly, a different trend is observed for semicrystalline PLLA/PDLA/PMMA blends. The storage modulus at 30 °C significantly increases and the highest $E_{30\ °C}$ is reached for 40% PMMA with a storage modulus as high as 3.5 GPa. This represents a 25% increase compared to the value of amorphous blends. Previous WAXS and DSC analyses confirmed that the highest amount of PLA stereocomplexes is also obtained within this PMMA range, and a correlation clearly appears between the amount of PLA stereocomplexes and the storage modulus at 30 °C. The thermal resistance, $T_{1.8\ GPa}$, for ternary blends is also plotted as a function of the PMMA content in Figure 7 and compared to that for binary PLLA/PMMA blends. Both pure PLLA and pure stereocomplexable 50% PLLA/50% PDLA blends display a similar thermal resistance in the range of 50−51 °C. A slight degradation of the thermomechanical properties is noticed, more likely because of the use of high temperatures during melt compounding. As a consequence of the miscibility, $T_{1.8\ GPa}$ increases with the amount of PMMA, but the experimental $T_{1.8\ GPa}$ values for ternary blends are interestingly higher than the values recorded for the respective binary blends. Increases of 5 and 8 °C are measured for the blends containing 30% and 40% PMMA, respectively. Note that this trend is also observed on the α-relaxation temperature. From these data, it can be concluded that the presence of PLA stereocomplexes in ternary blends provides higher thermomechanical performances than the corresponding amorphous binary blends. Interestingly, a dual reinforcement effect coupled to higher thermal resistance is demonstrated for ternary blends, especially with PMMA contents in the range of 30−40%, because of the presence of PLA stereocomplexes. Subsequently, the real potential of PLA stereocomplexes in ternary blends for enhancing the thermal resistance has been demonstrated after an annealing step on a selected formulation.

The PLLA/PDLA/PMMA ternary blend containing 40 wt % PMMA was in this respect selected for all aforementioned reasons, and this blend was thermally annealed at 110 °C for 20 min. Figure 8 presents a visual inspection of the annealed sample and the subsequent DSC first heating scan. After injection molding and before annealing, the 30% PLLA/30% PDLA/40% PMMA blend is transparent, and interestingly enough the annealing step only triggers a limited change in the transparency. DSC analysis reveals a significant melting peak at 216 °C with an associated melting enthalpy of 50 $J \cdot g_{PLA}^{-1}$. A small melting peak at 172 °C is also observed, indicating that PLA homocrystallization can also occur during annealing but, with respect to PLA stereocomplexes, the quantity of PLA homocrystallites remains very limited. In other terms, a large

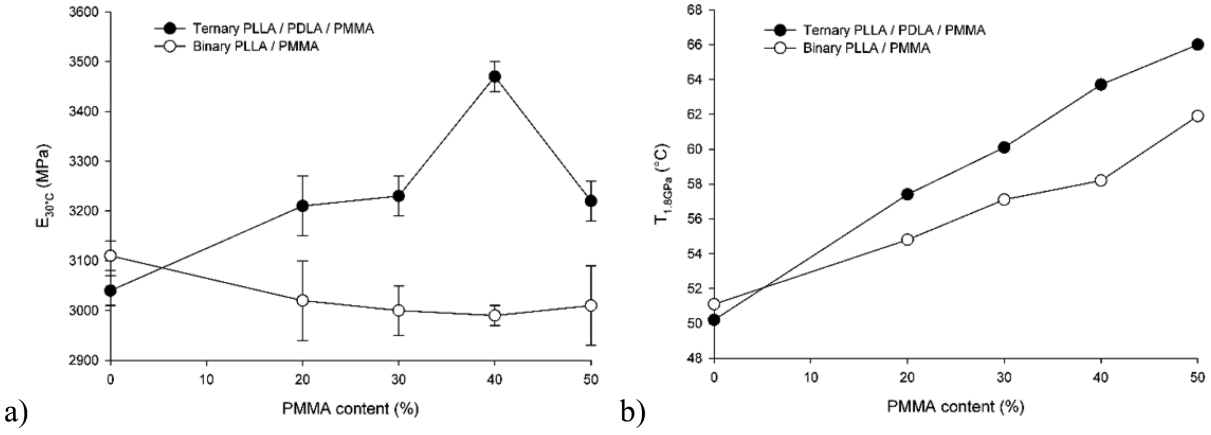

Figure 7. Evolutions of $E_{30\ °C}$ (a) and $T_{1.8\ GPa}$ (b) with the PMMA content for ternary PLLA/PDLA/PMMA blends compared to binary PLLA/PMMA blends.

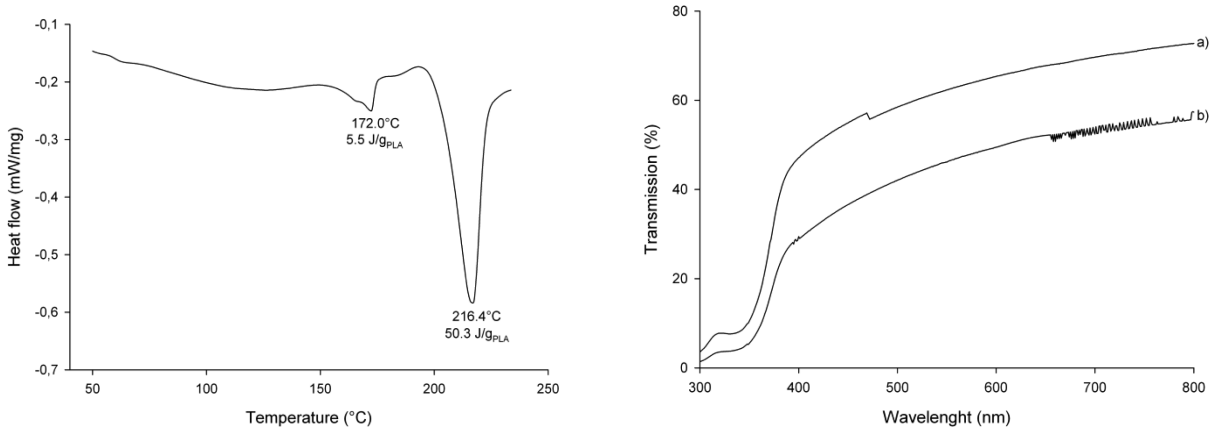

Figure 8. DSC first heating scan of 30% PLLA/30% PDLA/40% PMMA after annealing for 20 min and UV−visible spectra before (a) and after (b) annealing.

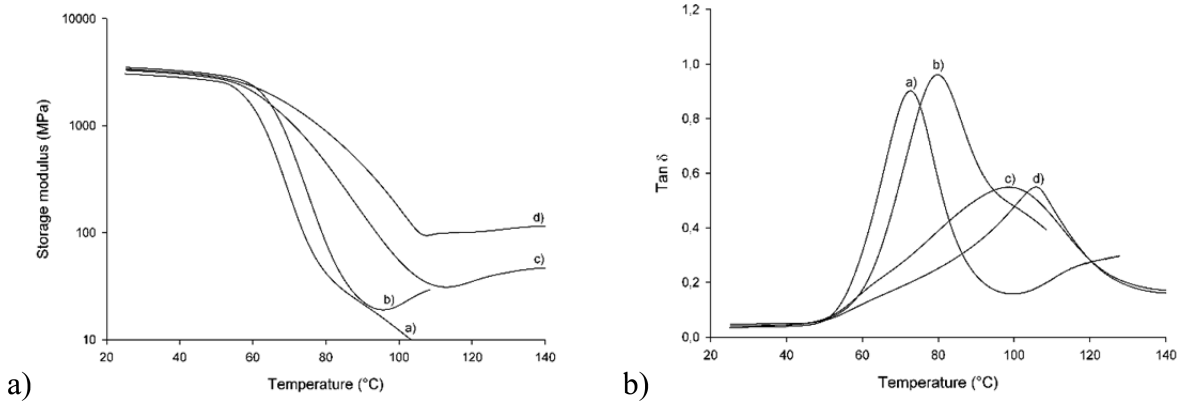

Figure 9. Storage modulus and tan δ as a function of the temperature for amorphous binary 60% PLLA/40% PMMA (a) and ternary semicrystalline 30% PLLA/30% PDLA/40% PMMA annealed for 0 min (b), 5 min (c), and 20 min (d).

amount of PLA stereocomplexes could crystallize during annealing. It is worth noting that the corresponding binary PLLA/PMMA blend is highly difficult to crystallize (S07 in the SI), and the quasi-absence of cold crystallization for the annealed ternary blend proved that the complete crystallization of stereocomplexes in less than 20 min. In addition, the transparency of the annealed blend is only slightly modified, as attested by the UV−visible spectra showing only a reduction by 15% of the transparency. Therefore, a higher amount of PLA stereocomplexes is successfully obtained after annealing, while maintaining a good transparency.

Figure 9 shows evolution of the storage modulus and tan δ with the temperature for PLLA/PMMA binary and PLLA/PDLA/PMMA ternary blends at various annealing times. Whereas the storage modulus at 30 °C remains nearly constant and the temperature at 1.8 GPa ($T_{1.8\ GPa}$) only increases from 63.7 to 68 °C within 20 min of annealing at 110 °C, massive crystallization of PLA stereocomplexes into a PLLA/PDLA/PMMA blend induces some major modifications of the thermomechanical properties. For temperatures higher than 80 °C, the storage modulus is progressively enhanced with the annealing time, and it can be noticed that a high storage modulus at 100 MPa can be reached for the rubbery plateau up to 140 °C. A drastic improvement of the resistance to deformation is subsequently observed for temperatures higher than 80 °C with respect to massive crystallization of PLA stereocomplexes. Regarding the tan δ peak, evolution is again highly spectacular after annealing with a tan δ peak observed at 106 °C for the annealed ternary formulation, close to the one observed for pure PMMA at 115.8 °C.[28] This impressive evolution demonstrates that massive crystallization of PLA stereocomplexes enables the recovery of a ternary PLLA/PDLA/PMMA blend with an exceptional heat resistance to deformation. The origin of this phenomenon remains obscure, but while crystallization of PLA stereocomplexes occurs, some thorough modifications would have appeared in the amorphous phase in terms of composition and organization, especially concerning the PMMA phase. Here, the most probable explanation is the recovery of an amorphous phase enriched in PMMA that could give rise to high thermal resistance.[40] This can be more likely supported by the high values obtained for the α-relaxation temperature of blends, in accordance with our experimental trend. In this regard, the amount of PLA stereocomplexes and the amount of PMMA in a miscible blend both control the thermomechanical properties of the resulting blends, even if the miscibility after annealing is not perfectly maintained because of a large broadening of the tan δ profile. It is of importance to briefly compare these previous results with those obtained by Li and Huneault about (homo)crystalline PLLA.[39] Actually, high thermal resistances were also achieved with the use of plasticizers, nucleating agents, and high molding temperature. Here, despite the high annealing times required, the use of PMMA provides not only an enhancement of PLA stereocomplexation and a high thermal

resistance but also an interesting transparency and a long-lasting potential of the resulting material, under intensive investigations for future use in durable applications. Indeed, this massive crystallization of PLA stereocomplexes from a miscible PLLA/PDLA/PMMA blend could represent a very elegant phenomenon that could contribute to the development of biobased materials with a very high heat resistance up to 140 °C for long-lasting applications such as in electronics.

CONCLUSIONS

Stereocomplexable PLAs with improved processability and thermomechanical properties were successfully developed using ternary miscible blends from high-molecular-weight PLLA, PDLA, and PMMA using a melt-extrusion technique. In contrast to binary PLLA/PMMA blends, ternary blends were semicrystalline after injection molding. PLA stereocomplexes were exclusively formed, and, surprisingly, the relative content in PMMA proved to enhance the amount of stereocomplexes, especially with 30−40% PMMA. The miscibility under the investigated conditions and composition range (PLLA:PDLA = 50:50 and 0% < PMMA < 50%) was maintained and processing artefacts were ruled out, confirming the key role of the miscible PMMA phase on stereocomplexation between PLLA and PDLA. Although further studies are under investigation to ascertain why PMMA induces stereocomplexation, it could be possible to produce semicrystalline miscible blends with a good transparency by melt-processing techniques.

Interestingly, PMMA also significantly modified the melt-state properties in ternary blends. The pure stereocomplexable PLA displays a very low viscosity at 230 °C, and no MFI could be determined for pure stereocomplexable PLAs like for ternary blends with PMMA contents lower that 30%. However, the incorporation of PMMA significantly increased the melt force during compounding at 230 °C and the corresponding viscosity, attesting to an improved processability of stereocomplexable PLAs with the incorporation of PMMA. While 40% PMMA promoted the highest amount of stereocomplexes, a MFI of 60 was noticed for this blend, reflecting a better stability in injection-molding processes. The ternary blend with 40% PMMA, consequently, represents the best compromise and could fulfill, to some extent, the requirements for industrial-scale injection-molding processes.

Ternary blends also presented significant improvements in the thermomechanical properties with a thermal resistance (evaluated either by the tan δ peak or by the temperature at 1.8 GPa) smoothly tuned by the amount of PMMA. Interestingly, a higher storage modulus at 30 °C and higher thermal resistance were recorded for the ternary blends compared to amorphous binary blends, especially with the incorporation of 30−40% PMMA, in accordance with the amount of PLA stereocomplexes formed during cooling. Higher amounts of PLA stereocomplexes were successfully recovered by an annealing treatment. No significant loss in transparency was noticed, and a dramatic shift of tan δ to a higher temperature than 100 °C was observed. In this respect, the thermomechanical properties of blends were simultaneously controlled by the amount of PLA stereocrystals, and a high thermal resistance to deformation could be reached up to 140 °C. Therefore, these ternary PLLA/PDLA/PMMA blends processed by conventional technologies represent a unique approach where biobased sterecomplexable PLAs can combine improved processing and transparency and outstanding thermal resistance.

ASSOCIATED CONTENT

Supporting Information

Visual inspections of binary PLLA/PMMA blends, DSC first heating scan and evaluation of the crystallinity for injection-molded binary PLLA/PMMA blends, loss modulus as a function of the temperature for ternary PLLA/PDLA/PMMA blends, multiple heat/cool/heat DSC cycles for ternary PLLA/PDLA/PMMA blends, crystallization from the melt of ternary PLLA/PDLA/PMMA blends as observed by PLOM experiments at a controlled cooling rate of 10 °C·min^{-1}, M_w, M_n, and SEC traces for the melt-processed 50% PLLA/50% PDLA compared to the unprocessed blend, isothermal crystallization at 110 °C of the binary 60% PLLA/40% PMMA blend. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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