JOURNAL OF Applied Polymer SCIENCE

Design of highly tough poly(L-lactide)-based ternary blends for automotive applications

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ABSTRACT: Technical renewable poly(L-lactide) (PLA)-based blends represent an elegant way to achieve attractive properties for engineering applications. Recently, the miscibility between PLA and poly(methyl methacrylate) (PMMA) gave rise to new formulations with enhanced thermo-mechanical properties but their high brittleness still remains a challenge to be overcome. This work here focuses on rubber-toughened PLA/PMMA formulations for injection-molding processes upon the addition of a commercially available ethylene-acrylate impact modifier (BS). The miscibility between PLA and PMMA is not altered by the presence of BS but the incorporation of BS (17% by weight) into a PLA/PMMA matrix could enhance both ductility and toughness of PLA/PMMA blends for PMMA content up to 50 wt %. An optimum range of particle sizes (d_n ~0.5 μm) of the dispersed domains for high impact toughness is identified. These bio-based ternary blends appear as promising alternatives to petro-sourced blends such as ABS-based blends in engineering injection-molding parts. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43402.

KEYWORDS: biopolymers and renewable polymers; blends; mechanical properties; morphology

Received 19 October 2015; accepted 4 January 2016
DOI: 10.1002/app.43402

INTRODUCTION

Renewable and biodegradable plastics are being more and more appealed due to the growing concerns on sustainability and end-of-life aspects.[1] Among them, polylactide (PLA) is definitely the most promising bioplastics for numerous applications.[2–4] Several key-points contribute to the success of PLA as a renewable alternative to traditional petroleum-based plastics, especially its excellent biocompatibility, bioresorbability, (bio) degradability as well as its attractive physical and mechanical properties such as high rigidity, strength, and easy processability.[5] Although PLA was initially designed as composting materials for packaging applications, owing to its (bio)degradability, industrial trend is now being pushed, in relationship to its renewability, towards high-added value applications, especially injection-molded items for engineering applications such as automotive or electronic industry. Although PLA can fulfill the environmental regulations of this sector, the development of technical PLA-based materials for automotive applications must encompass these following characteristics, not achieved yet, as sustainably, high durability, high toughness, high flexibility in the design, high resiliency, and high performance at affordable cost. Several strategies have thereby been carried out to overcome those drawbacks and to improve limited mechanical properties of PLA.

Recently, different ways of tailoring PLA properties for automotive applications have been developed such as the recent approach on plasticized PLA-based compositions as alternative to mineral-filled polypropylene.[3,4] Notta-Cuvier *et al.*[4] studied different compositions of binary, ternary and quaternary PLA-based blends with addition of impact modifier (a commercially available ethylene-acrylate: Biomax Strong®), plasticizer Tributyl Citrate (TBC), and/or nanoclay (Cloisite25A®). They showed that mechanical properties of blends (ductility and toughness) had been improved without affecting the PLA stiffness, yielding PLA-based blends, which could compete equally or outperform mineral-filled polypropylene. However, in the case of plasticized blends, this improvement can be counterbalanced by an undesirable stiffness drop, related to a phase-separation within

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blends, and an undesirable leaching of the plasticizer at longer time.[3,4,6–10]

As another way, blending PLA with (partially) miscible engineering thermoplastic polymers (petro-sourced or not) to tune up the properties of PLA-based materials has gained a tremendous interest in last few years. It represents a low-cost and efficient process to afford high performance PLA-based materials at acceptable cost.[11–20] Poly(methyl methacrylate) (PMMA) is often viewed as an excellent polymer partner with PLA, yielding blends of high miscibility, excellent thermal stability with higher heat deflection temperature (HDT), high mechanical properties, sustainability, and good ageing behavior.[12,21–23] Recently, Samuel *et al.* have reported on miscible PLA/PMMA blends with enhanced thermo-mechanical properties in terms of HDT.[12] The addition of even a moderate amount of PMMA can deeply modify the thermal properties of PLA, which are adjusted between those of pure PLA and pure PMMA, while maintaining the overall PLA transparency and storage modulus elevated. However, toughness of the blend still needs some improvement to make PLA-based compositions suitable for engineering applications.

To overcome toughness limitation and reduce brittleness, the use of impact modifier can be of high interest, as it allows to impart greater energy dissipation pathways throughout the materials, without affecting stiffness and thermal stability.[24] Many commercially available impact modifiers are specifically designed in order to toughen PLA[25–28] as dispersed rubbery microdomains (with an average size around 0.1–1.0 μm) within the PLA matrix able to absorb the energy upon an impact.[29] However, it is well-known that their toughening effects are of varying magnitudes, depending on their miscibility extent within the PLA matrix, their thermal stability under PLA processing temperatures, the interfacial adhesion between the dispersed rubbery phase and the continuous PLA matrix within the blend, etc. Impact modifiers providing an appropriate balance of these properties are therefore fundamental for these intended applications.

The present contribution aims at designing rubber-toughened PLA/PMMA-based formulations with enhanced HDT suitable for injection-molding processes via the addition of a commercially available impact modifier. Among them, Biomax® Strong 120 (BS) was selected as an efficient impact modifier commercially available from Dupont™, yielding, e.g., PLA-based materials with comparable yield stress and tensile modulus as well as better elongation at break than mineral-filled polypropylene (PP), together with improved impact strength (28.9 kJ/m^2 at 20 wt % of BS).[27] Hence, various PLA/PMMA formulations covering all over the composition range were melt-blended with a fixed BS content (17 wt %) and characterized by means of mechanical, thermo-mechanical and morphological analyses. The miscibility between each partner, the mechanical performances (toughness and ductility) and related morphologies are specifically addressed. Interfacial adhesion and coupling reactions in the melt-state are revealed in PLA-rich formulations and correlated with mechanical performances in terms of toughness and ductility. A mechanical mapping is finally set between the best PLA-based formulations and an ABS/PC blend, frequently used in automotive industry.[30–32]

Table I. Designation of As-Prepared PLA-Based Ternary Formulations

Sample Code	PLA content (wt %)	PMMA content (wt %)	BS content (wt %)
Neat PLA	100	0	0
PLA/BS	83	0	17
PLA80/PMMA20/BS	66.4	16.6	17
PLA70/PMMA30/BS	58	25	17
PLA50/PMMA50/BS	41.5	41.5	17
PLA30/PMMA70/BS	25	58	17
PLA20/PMMA80/BS	16.6	66.4	17
PMMA/BS	0	83	17
Neat PMMA	0	100	0

EXPERIMENTAL

Materials

A commercially available extrusion-grade poly(L-lactide) (NatureWorks 4032D, hereafter called PLA) was used as received ($\bar{M}_n$ = 133,500 ± 5,000 g/mol, Đ = 1.94 ± 0.06 as determined by size-exclusion chromatography in chloroform at 35 °C upon a relative polystyrene calibration, 1.4 ± 0.2% D-isomer content as determined by the supplier). Poly(methyl methacrylate) (Plexiglas® 8N, hereafter called PMMA) was supplied by Evonik ($\bar{M}_n$ = 50,000 g/mol± 2,000 g/mol, Đ =2.1± 0.1). Biomax® Strong 120, a commercially available ethylene-acrylate impact modifier bearing epoxy moieties specifically designed for PLA (hereafter called BS), was provided by Dupont™. Ultranox 626A (GE Specialty Chemicals) was used as a stabilizer at a content of 0.3 wt % in all PLA-based blends. For comparative purposes, a commercial ABS/PC blend (Novodur H801) designed for automotive interior and exterior parts, was supplied by Styrolution ($\bar{M}_n$ = 32,900 g/mol ± 3000 g/mol, Đ =3.4 ± 0.1).

Blend Preparation and Compounding

Prior to mixing, polymeric components were dried overnight at 60 °C in a vacuum oven to remove any residual water before processing. The additives were first premixed in a plastic container and then melt-blended in a Brabender internal mixer (model 50EHT) after 3 min premixing at 30 rpm followed by 7 min of mixing at 70 rpm. Standard samples of resulting PLA-based materials were then prepared by injection molding using DSM Mini Injection Molding apparatus upon the following procedure: 3 min at 210 °C and injection within a mold at 45 °C, except for PMMA content higher than 70 wt % (3 min at 220 °C and injection within a mold at 55 °C). Blends were processed as aforementioned at a constant concentration of impact modifier at 17 wt % and all formulations are gathered in Table I.

Characterizations

Differential scanning calorimetry (DSC) was performed using a DSC Q2000 from TA Instruments at both heating and cooling rates of 10 °C/min under nitrogen flow. The glass transition temperature (T_g), melting temperature (T_m), cold-crystallization temperature (T_{cc}), enthalpy of cold-crystallization (ΔH_{cc}), and melting enthalpy (ΔH_m) were evaluated from the resulting DSC thermograms at the second heating scan. Crystallinity index of PLA ($X_{c\text{-}PLA}$) was determined using the following relation (1)[33]:

$$X_{c-PLA}(\%)=\frac{\Delta H_m-\Delta H_{cc}}{X_{PLA}.\Delta H_m^0}\times 100 \quad (1)$$

With X_{PLA} the weight fraction of PLA in the sample and ΔH_m^0 (93 J/g) the melting enthalpy for 100% crystalline PLA.

Tensile tests were carried out on Tensile Universal testing Machine UTM (LR 100 K, Lloyds Instruments, UK) according to ASTM-D-638 norm, at a crosshead speed of 1 mm/min. Notched Izod Impact tests (5 tests per composition) were performed according to ASTM D256 norm using a Ray-Ran pendulum impact tester ($E = 3.99$ J, $m = 0.668$ kg, speed = 3.46 m/s). The related impact strength is expressed in terms of the difference between the potential energy of the hammer before and after the impact. Resiliency here is obtained by dividing the energy required to break the sample upon its width or cross-section area.

Dynamic mechanical thermal analysis (DMTA) was carried out using a DMTA Q800 from TA Instruments mounted in a dual cantilever mode at a constant frequency of 1 Hz, an amplitude of 20 µm and a heating rate of 2 °C/min. To determine the heat deflection temperature (HDT), a constant load of 0.45 MPa was applied at the center of a 3-point bending flexural bar sample (dimension of $55 \times 12 \times 2\text{mm}^3$), which was heated at the rate of 2 °C/min from room temperature to 130 °C. The temperature when the specimen reached a deflection of 250 µm was reported as the HDT value.

Impact-fractured surfaces of specimens were examined for morphological investigations through scanning electron microscopy (SEM) using a Hitachi SU8020 (100 V–30 kV) apparatus. Samples were cryofractured under liquid nitrogen and then coated using a gold sputtering technique to avoid any charging effect during the electron beam scanning. For the purpose of particle size of the dispersed BS microdomains within the blends, 100 − 300 diameters from two independent SEM images (5×5 µm^2) were analyzed using "Image J" software. The cross-sectional area (A_i) of each individual particle (i) was measured and converted into an equivalent diameter of a sphere by the equation $\left[di=(4A_i/\pi)^{0.5}\right]$. Number-average particle diameter (d_n) and volume average particle diameter (d_v) which are usually thought to give a correlation with notched impact strength, was determined from the following equations:

$$d_n=\frac{\sum n_i d_i}{\sum n_i} \quad (2)$$

$$d_v=\frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (3)$$

Where n_i is the number of particles having the apparent particle diameter d_i.

RESULTS AND DISCUSSION

The incorporation of PMMA into PLA by melt-blending techniques was previously investigated by our group and PLA/PMMA miscible blends display significant improvements in term of heat deflection temperature (HDT).[12] PLA/PMMA blends could be suitable for injection-molded parts in automotive or electronic industry. However, the low toughness and ductility still remain important challenges to be overcome with the use of impact modifiers. In this context, ternary PLA/PMMA/BS blends are developed and investigated by means of thermal, mechanical, thermo-mechanical, and morphological analyses. PLA/PMMA formulations all over the composition range were investigated to highlight the influence of PMMA on final properties. Rubber-toughening was ensured by BS at a fixed content of 17 wt % (based on the total weight) based on previous literature. Actually, BS allows reaching a right balance between rigidity and toughness of neat PLA.[27,34–36]

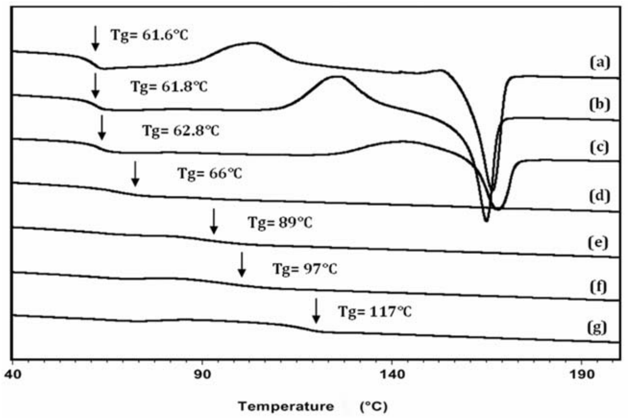

Figure 1. DSC thermograms recorded during the second heating scan for (a) PLA/BS, (b) PLA80/PMMA20/BS, (c) PLA70/PMMA30/BS, (d) PLA50/PMMA50/BS, (e) PLA30/PMMA70/BS, (f) PLA20/PMMA80/BS, (g) PMMA/BS blends (heating rate 10 °C/min).

Miscibility between components was first considered as an important requirement to achieve interesting mechanical properties for the final blends.[37] Miscibility extent of PLA/PMMA binary blends may depend on the processing techniques (solvent casting or extrusion technique).[12,38–40] Thermal treatments, process conditions and molecular parameters of each component must be controlled to ensure a good miscibility of PLA/PMMA blends and reach the full benefits in terms of thermo-mechanical improvements. Addition of impact modifier into a PLLA/PMMA blends to produce ternary PLLA/PMMA/BS blends can however lead to some change in the miscibility of PLA/PMMA blends. To investigate this point, glass transitions (and related glass transition temperatures, T_g) in PLA/PMMA/BS ternary blends were determined using DSC technique and corresponding mechanical relaxations (with the temperature at the tanδ peak, $T_{\tan\delta}$) were evaluated using DMTA. Figure 1 illustrates typical DSC thermograms of the PLA/PMMA/BS blends (arrows indicate the glass transition) and T_g values and crystallinity index of PLA are both reported in Table II. All curves exhibit a single glass transition, located at an intermediate temperature between those of pure PLA (61 °C) and pure PMMA (116 °C) and shifting towards higher values with the PMMA content. Similar trends were reported, for example by Zhang *et al.*[23] reporting the evolution of T_g for miscible P(D, L-LA)/PMMA blends obtained by solution/precipitation at

Table II. Glass Transition Temperature, Crystallinity Index, Relaxation Temperatures, and HDT for PLA/PMMA/BS Blends

Sample code	T_g (°C)	X_c (%)	$T_{\tan\delta 1}$ (°C)	$T_{\tan\delta 2}$ (°C)	HDT (°C)
Neat PLA	61	3	57	−42	54
PLA/BS	61.6	19	60	−42	53
PLA80/PMMA20/BS	61.8	9	64	−43	57
PLA70/PMMA30/BS	62.8	3	67	−43	58
PLA50/PMMA50/BS	66	–	76	−40	63
PLA30/PMMA70/BS	89	–	93	−40	70
PLA20/PMMA80/BS	97	–	100	−33	72
PMMA/BS	117	–	115	–	84
Neat PMMA	116	–	118	–	–
Neat BS	–	–	–	−35	–

different compositions. They confirm that the blends of both polymers exhibit a single T_g in a range between the T_g of the individual components. The location of the blend T_g appears to be more or less proportional to the composition of the blend, which is a clear indication for the miscibility of blends. In our work, such observations also confirm the miscibility between PLA and PMMA in ternary formulations. The glass transition temperature of the impact modifier in ternary blends (expected at around −35 °C) could not be detected by DSC. In addition, the crystallinity extent of PLA/PMMA/BS blends reduces gradually as the PMMA content increases (Figure 1 and Table II) and above 50 wt % in PMMA, the resulting blends become fully amorphous. It is worth noting that the addition of impact modifier BS to PLA results in a nucleation effect with the increase of crystallinity extent from 3% for neat PLA to 19% for PLA/BS.

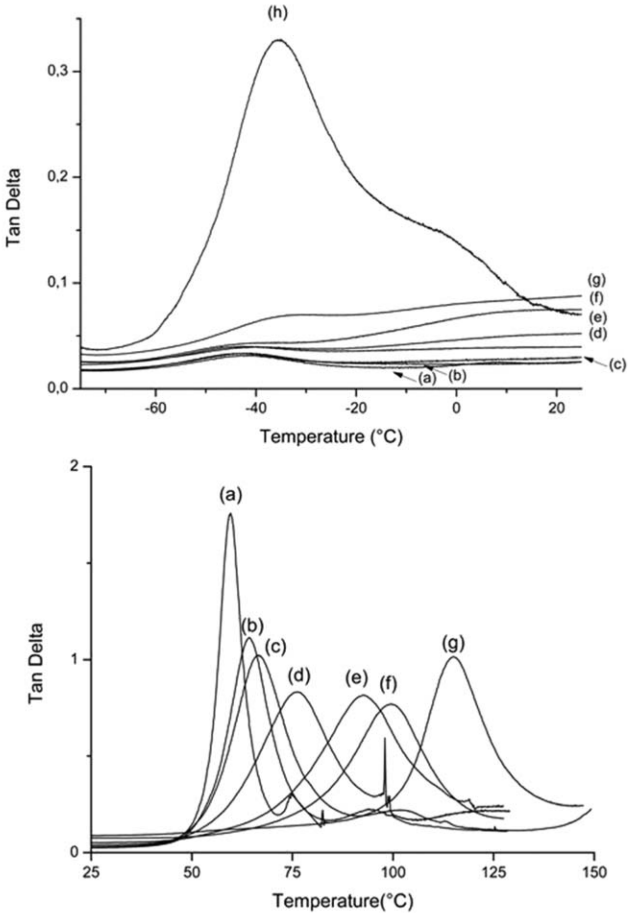

Figure 2. Tan δ curves of (a) PLA/BS, (b) PLA80/PMMA20/BS, (c) PLA70/PMMA30/BS, (d) PLA50/PMMA50/BS, (e) PLA30/PMMA70/BS, (f) PLA20/PMMA80/BS, (g) PMMA/BS, (h) neat BS.

Mechanical relaxations at high and low temperatures were also investigated and Figure 2 displays DMTA thermograms of PLA/PMMA/BS blends. Two distinct tanδ peaks were systematically observed for all ternary compositions. The high-temperature relaxation corresponds to the α-relaxation a miscible PLA/PMMA fraction, i.e., located at an intermediate temperature between those of the respective homopolymers in accordance with DSC results. The low-temperature relaxation appearing between −33 and −42 °C could be ascribed to α-relaxation of BS ($T_{\tan\delta} = -35$ °C for neat BS). The presence of these two distinct tanδ peaks therefore suggests that the PLA/PMMA matrix and the impact modifier are (partly) phase-separated. Table II presents the temperature at tanδ peaks for the high- and the low-temperature relaxation ($T_{\tan\delta 1}$ and $T_{\tan\delta 2}$, respectively) with the heat deflection temperature (HDT) determined from DMTA analyses for each PLA/PMMA/BS formulations. Related to their good miscibility and in accordance with the literature,[12] $T_{\tan\delta 1}$ of the matrix PLA/PMMA increases slightly with PMMA content until 30 wt % PMMA (reaching an improvement of 7 °C for $T_{\tan\delta}$ of 70/30). At PMMA content higher than 30 wt %, $T_{\tan\delta 1}$ increases significantly, e.g., by 16 °C between 30 wt % and 50 wt % of PMMA. In addition, HDT smoothly increases with the amount of PMMA into the ternary blend (an increase of 10 °C at 50% of PMMA) and the beneficial effect of PMMA on thermomechanical properties is also confirmed in ternary formulations. The incorporation of BS into a PLA/PMMA miscible blend has a limited influence on HDT. These ternary PLA/PMMA/BS formulations are therefore comparable to binary PLA/PMMA blends developed by Samuel *et al.*,[12] in terms of improved HDT, and a progressive increase of heat deflection temperature up to 61.9 °C with 50% PMMA is noticed.

Nominal strain-stress curves at a displacement rate of 1 mm min^{-1} for PLA homopolymer and all investigated PLA/PMMA/BS blends are shown in Figure 3. PLA is known for its high rigidity and tensile strength but a low elongation at break, even at low deformation rate.[17] The present results confirm this behavior for neat PLA with a very high rigidity of ≈3.2 GPa, a tensile strength of 68 MPa and a low elongation at break of 2.8%. The addition of BS strongly modifies the mechanical properties of PLA, as shown in Figure 3 and Table III. A high level of ductility is reached (elongation at break ≈148%) with the addition of BS at 17 wt % and a brittle-to-ductile transition is clearly highlighted. Nevertheless, the apparent rigidity and yield stress decrease of about 30% and 35% respectively with respect to neat PLA. The same phenomena were reported by Taib *et al.*[27] who have designed PLA blends with different amounts (0 − 50%) of a commercially ethylene acrylate

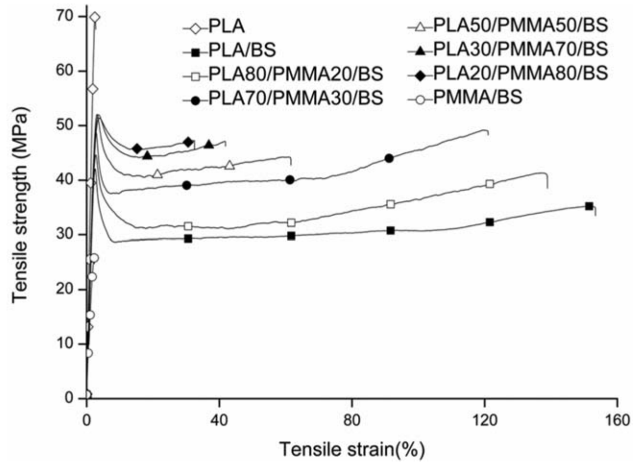

Figure 3. Tensile stress−strain curves of PLA and PLA/PMMA/BS blends.

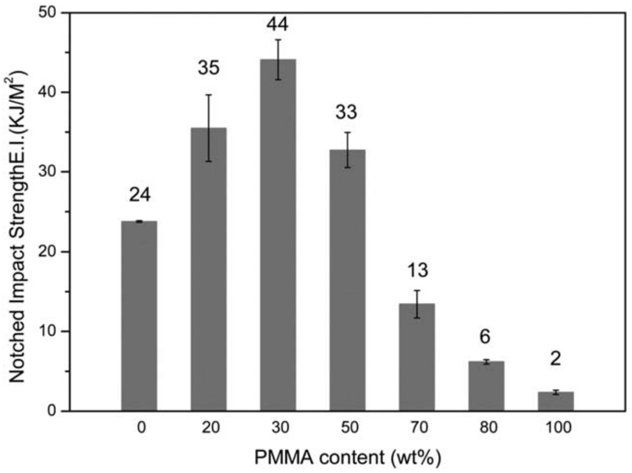

Figure 4. Effect of relative content of PMMA on the notched impact strength of PLA/PMMA/BS blends.

copolymer impact modifier (Biomax® Strong). They show that adding 20% of impact modifier can improve ductility of blends (128% of elongation at break) with a decrease of yield stress and apparent rigidity of about 34% and 36% respectively with respect to neat PLA. The ductile behavior of the ternary blends is not altered with the addition of PMMA up to 80-wt %. Both tensile modulus (*E*) and tensile strength (σ) increases while strain at break smoothly decreases. It can be noted that PMMA/BS binary blend shows a brittle behavior (2% of elongation at break) together with a low rigidity (1.6 GPa).

Aiming injection-molded parts for engineering applications in automotive or electronic industry, high impact toughness is also needed for these blends in addition to high tensile strength, rigidity and ductility. Figure 4 illustrates the effect of PMMA content on the notched impact strength of ternary PLA-based blends. Neat PLA presents low impact strength of around 3.4 kJ/m^2 and adding 17 wt % of impact modifier to neat PLA results in a significant improvement of toughness up to 24 ± 0.1 kJ/m^2 in accordance with literature.[27] A synergistic effect of BS and PMMA is surprisingly evidenced with an optimum impact toughness close to 44 ± 2.5 kJ/m^2 observed with the addition of 30 wt % PMMA to PLA/BS blends. The same impact strength (42.8 kJ/m^2) was also measured by Notta-Cuvier *et al.*[4] when performing PLA-plasticizer-impact modifier-nanoclay quaternary composition (80/10/10/1) designed for automotive applications. Nevertheless, mechanical tensile properties were much lower (1.74 GPa and 22.81 MPa, respectively for apparent rigidity and maximal nominal axial stress) compared to results obtained for ternary PLA70/PMMA30/BS17% blend). Further increase of PMMA content is also possible up to 50 wt % without sacrificing impact toughness. However, PMMA-rich formulations display a dramatic reduction of the materials toughness, more likely due to a lack of affinity between BS and matrix. Consequently, tensile mechanical and impact properties point out that BS has a strong positive effect on toughness and ductility for PLA-rich formulations (Figures 3 and 4). A main formulation could be selected for injection-molded parts, i.e., PLA70/PMMA30/BS with an optimum stiffness-toughness balance, high to moderate biobased content and improved HDT for high-performance applications. For information purpose, different blending procedures to form the ternary blends were initially tested. Interestingly, the direct blending of all components gives the best results in terms of impact strength and ductility. More precisely, two-stage blending processes such as mixing BS in a preformed PLA/PMMA blend result in lower mechanical performances (see Supporting Information Figure S1, Figure S2, Table S1, and Table S2).

Table III. Tensile Properties of Neat PLA and PLA/PMMA/BS Blends (Standard Deviations into Brackets)

Sample code	Tensile strength (MPa)	Elastic modulus (GPa)	Elongation at break (%)
Neat PLA	68 (2)	3.2 (0.1)	2.8 (0.2)
PLA/BS	44 (2)	2.3 (0.1)	148 (28)
PLA80/PMMA20/BS	46 (1)	2.4 (0.1)	133 (11)
PLA70/PMMA30/BS	49 (3)	2.5 (0.1)	116 (4)
PLA50/PMMA50/BS	52 (1)	2.6 (0.1)	66 (26)
PLA30/PMMA70/BS	53 (1)	2.5 (0.1)	44 (7)
PLA20/PMMA80/BS	52 (1)	2.4 (0.1)	33 (5)
PMMA/BS	23 (5)	1.7 (0.2)	2 (0.3)

The microstructure of rubber-toughened polymer is of prime importance on toughening mechanisms and the relationship between average size and distribution of rubbery microdomains, on one hand, and toughness, on the other hand, is often considered.[24,41] According to Perkins *et al.*,[24] an optimum range of particle sizes leading to the best toughness improvement exists for each polymeric matrix. However, the interfacial adhesion between rubber particles and the matrix also plays a key role and, in order to understand the evolution of toughness in PLA/PMMA/BS blends, microstructures were revealed by scanning electron microscopy (SEM). In particular, the influence of PMMA content on the average size of as-dispersed rubbery microdomains (BS) within PLA was first investigated. Figure 5 shows SEM micrographs of cryofractured surfaces of PLA/PMMA/BS ternary blends at different PMMA content. As

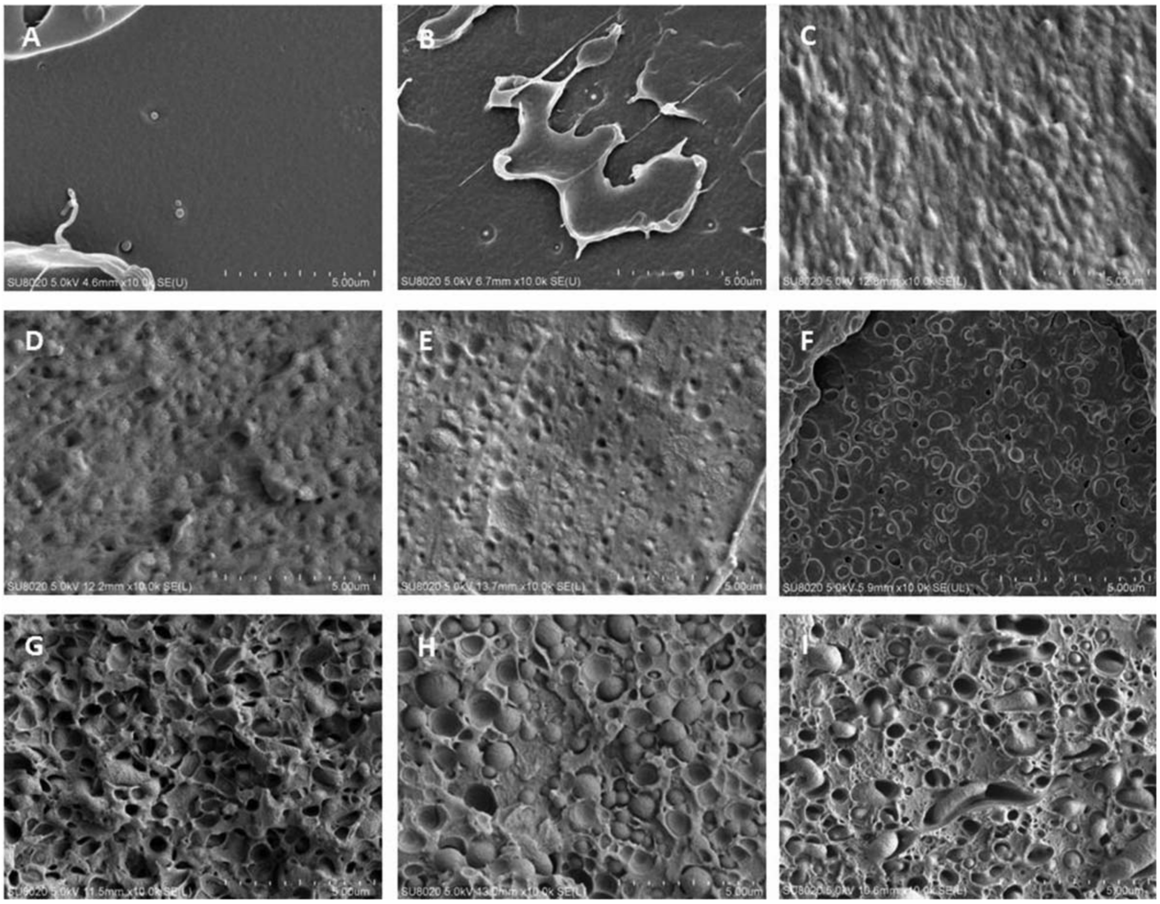

Figure 5. SEM micrographs of impact-fractured surfaces of (A) neat PLA, (B) PLA70/PMMA30, (C) PLA/BS, (D) PLA80/PMMA20/BS, (E) PLA70/PMMA30/BS, (F) PLA50/PMMA50/BS, (G) PLA30/PMMA70/BS, (H) PLA20/PMMA80/BS, (I) PMMA/BS.

shown in [Figure 5(A)], neat PLA specimen exhibits a smooth surface and a relatively brittle morphology after fracture and the SEM micrograph of PLA70/PMMA30, without BS also shows a homogenous morphology [Figure 5(B)], in accordance with the miscibility extent achieved within this brittle blend. In contrast, all PLA/PMMA/BS blends display phase-separated morphology, which is a necessary condition for toughening,[42,43] with dispersed BS droplets into PLA/PMMA matrices [Figure 5(C–I)] and these morphologies confirm the immiscibility of BS into the matrix as previously concluded by DSC and DMA. However, a strong influence of PMMA is clearly noticed on the morphology of cryofractured PLA/PMMA/BS blends. A large amount of plastically deformed material is observed for the PLA/BS binary blend. BS droplets with diameters lower than 500 nm are homogenously dispersed into PLA and a strong adhesion of BS to PLA matrix is noticed [Figure 5(C)]. This observation was in agreement with results reported by Afrifah *et al.*[28] who performed PLA/EAC impact modifier (Ethylene acrylate copolymer). They confirmed that for blends at 10 wt % or more impact modifier, the fracture mechanisms included impact modifier debonding, fibrillation, crack bridging, and matrix shear yielding resulting in a ductile behavior. Adding PMMA to PLA/BS binary blends preserves the plastic deformation and a good interfacial adhesion for blends containing up to 50 wt % of PMMA. At higher PMMA content, ternary blends also show phase-separated morphologies but larger BS microdomains of irregular shapes and large interfacial voids caused by mechanical debonding of BS from matrix are revealed. In this context, significant differences in terms of interfacial adhesion and BS microdomain size are clearly evidenced in PLA/PMMA/BS ternary blends and PLA-rich blends up to 50 wt % PMMA are specifically marked by a high interfacial adhesion. PLA-rich blends also seem to display smaller BS microdomains and a deeper analysis of BS droplet size was performed.

The number average diameter of as-dispersed rubbery microdomains within PLA (d_n), the volume average diameter (d_v) and the full size distribution curve were established. The spherical shape of particles rubber was first verified by longitudinal and transversal morphological views (see Supporting Information FigureS3). Figure 6 displays the evolution of BS droplet diameter with the amount of PMMA within PLA/BS blends. In the absence of PMMA, i.e. in PLA/BS blends, spherical BS droplets with diameter close to 400 nm (for d_v and d_n) is observed, in agreement with a study based on toughened PLA formulations (PLA/PBAT compounds) reported by Jiang *et al.* The blend comprised an immiscible two-phase system with the PBAT evenly dispersed in PLA with an average particle size at the level of 0.3–0.4 μm.[44] In our work, BS droplet

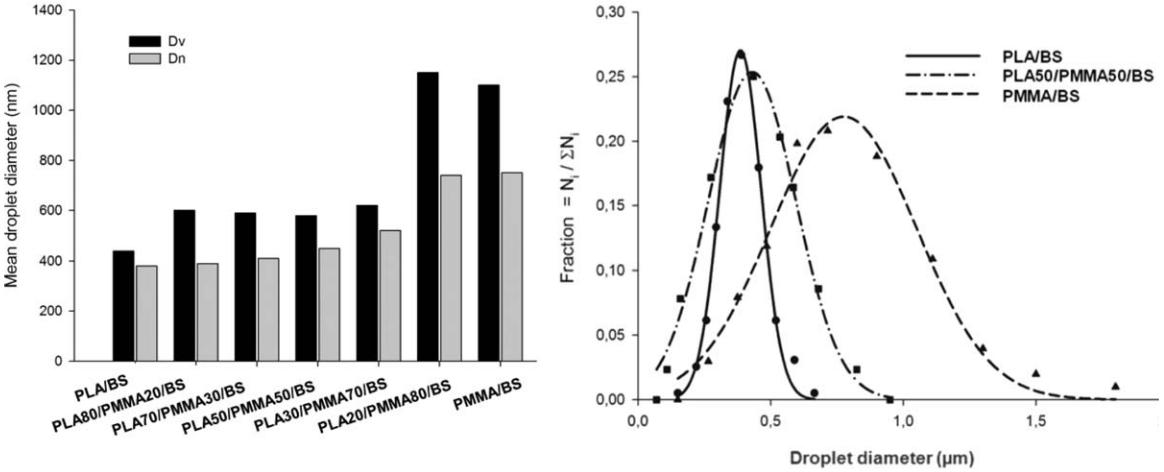

Figure 6. BS droplet diameter as a function of PMMA content (left) and associated size distributions of the rubbery BS microdomains (right) for various PLA/PMMA/BS formulations.

diameter slightly tends to increase upon the addition of miscible PMMA into PLA/BS blends up to 70 wt % PMMA, but the diameter of BS microdomains droplet size remains lower than 600 nm. On the contrary, PMMA-rich blends are marked by the presence of larger BS microdomains ranging from 0.5 µm to 1.5 µm. Figure 6 also displays the size distributions of BS microdomains for different PLA/PMMA/BS ternary blends. PLA-rich blends exhibit BS droplets with narrow size distribution reflecting a good dispersion of BS into PLA-rich blends. The size distribution of BS droplets significantly broadens with the addition of PMMA, and PMMA-rich blends are marked by a very broad distribution reflecting a poor dispersion of BS into PMMA-rich blends.

In this context, the interfacial energy between BS and the matrix plays a key role on the morphology developed during compounding. For less than 50% of PMMA, a high interfacial adhesion between BS and the matrix are observed [Figure 5(C−E)]. A clear relationship could be established between the dispersion of BS, its adhesion to the matrix and the final mechanical performances.[44,45] High toughness and ductility are observed for PLA-rich blends and mainly arise from a good dispersion of small BS droplets with a strong adhesion to PLA. The addition of PMMA up to 50 wt % remains possible without detrimental effect on BS droplet size and interfacial adhesion. However, significant differences are observed in terms of ductility and impact toughness for PLA-rich formulations with an optimum PMMA content close to 30 wt %. The size of rubbery domains also represents a key-parameter, affecting the final ductility and toughness.[35,46] It is generally accepted that an optimum in energy dissipation appears for particle diameter of 0.5 − 0.55 µm. This optimum particle size for our toughened PLA system seems reasonable. Recently, by correlating tensile toughness with dispersed particle diameter in PLLA/conjugated soybean oil binary blends, Gramlich *et al.*,[47] also reported the similar range of optimum particle diameter (i.e., 0.5 − 0.9 *µ*m) for toughening PLA. Beyond the optimum particle size (0.5 − 0.55 µm), the plastic deformation behavior of PLA-rich blends changes to a debonding fracture mechanism due to the phase-separated morphology generated with increased PMMA content (more than 50%). Increasing the PMMA amount can affect the morphology of blends and cause a poor adhesion of the matrix, resulting in restrained mechanical properties. Such trend is due to the poor affinity of impact modifier to the PMMA matrix. The low affinity of impact modifier with PMMA leads to the presence of BS microdomains with different sizes in these blends. This can be explained by the occurrence of crazing fracture as among the most important energy dissipation process involved in the impact fracture of toughened polymer systems.[24,48,49]

Another explanation could be more likely related to the *in situ* formation of "graft copolymers" as compatibilizers through coupling reactions between the functional end-groups (hydroxyl and carboxylic) of PLA chains and the complementary functional groups (epoxy functions) along the impact modifier (Figure 7). This hypothesis was also mentioned in different studies.[27,50]

As a result, improved interfacial adhesion and hence a fine dispersion are achieved in these blends. Quantitatively, reducing the relative amount of PLA in PLA/PMMA/BS blends affects the formation of the *in situ* generated copolymers and can subsequently alters both morphological and mechanical features of the blends, leading to a poor interfacial adhesion between all components. These results are in good agreement with the mechanical experiments and indicate that the impact modifier in the presence of PLA leads to the formation of

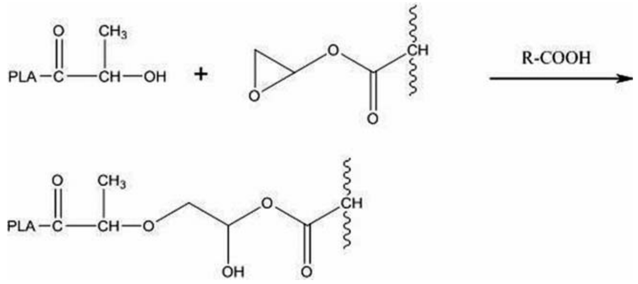

Figure 7. Probable coupling reaction between BS and PLA (COOH residues as catalysis could be derived from the hydrolysis and/or presence of acid end-groups of PLA chains).[27]

Table IV. Summary of All Mechanical Properties of PLA70/PMMA30/BS Compared to Those of ABS/PC

Compounds	ABS/PC	PLA70/ PMMA30/BS
Elastic Modulus (GPa)	2.3 (0.1)	2.5 (0.1)
Ultimate Strength (MPa)	52 (1)	49 (3)
Elongation at break (%)	19 (5)	116 (4)
Impact Strength (KJ/m2)	20 (1)	44 (2)

compatibilizers, resulting to a good interfacial adhesion between the different components of the blend.

Finally, the mechanical mapping between the most efficient bio-based compositions highlighted in this contribution, i.e.PLA70/PMMA30/BS, and a commercial ABS/PC blend used for automotive applications was performed. Due to its unique properties, polycarbonate (PC) and Acrylonitrile-Butadiene-Styrene (ABS) blend has encountered a great attention for the last decade. These blends are widely used in the automotive industry because they are affordable and combine the best properties of both constituents. In ABS/PC blend, mechanical and thermal properties are improved by the partner PC, while processability and impact resistance are improved by the ABS partner. Adding a small amount of ABS to PC helps processability, impact strength, and cost. On the other hand, adding a small amount of PC to ABS increases its thermal properties.[51–53] These blends are recommended for the manufacture of large automotive parts, e.g. dashboards and for automotive interior trims, seat and glove box components, which require the use of high strength materials.[54,55] Table IV presents a summary of results obtained from these mechanical experiments (elastic modulus, tensile strength, elongation at break and impact strength) for both ABS/PC and PLA70/PMMA30/BS. Based on these results, it can be concluded that PLA70/PMMA30/BS has better mechanical properties than ABS/PC blend. In fact, the PLA70/PMMA30/BS blend shows comparable yield stress and tensile modulus, but better elongation at break (+84%) and enhanced impact strength (+55%) compared to ABS/PC blend, which make this selected composition interesting for automotive application. The significant improvement in ductility (116% of deformation) can be very interesting for a dynamic tensile study, which will be the object of a forthcoming paper.

CONCLUSIONS

Thanks to its biodegradability, easy processability, affordable cost, and high stiffness, poly (lactic) acid (PLA) is regarded as the most promising bio-based alternatives to petropolymers. However, its use in automotive applications remains a challenge due to its low thermal stability and inherent brittleness. In the frame of this contribution, many efforts have been performed to enhance ductility of PLA through addition of ethylene-acrylate impact modifier and to improve the thermal stability in the presence of PMMA. New PLA/PMMA/BS ternary blends were successfully prepared using melt blending and injection molding processes. Miscibility extent was checked using DMTA, confirming the presence of two distinct tanδ peaks, the first one for the miscible PLA/PMMA matrix and the second one for the dispersed impact modifier. It was suggested that the miscible PLA/PMMA matrix and the impact modifier BS were phase-separated and formed immiscible blends. Thermal stability of the blends slightly increases depending on amount of PMMA in the blend. Regarding the mechanical properties, a significant gain in tensile elongation, and impact toughness are reached with a slight decrease in rigidity and tensile strength. The most promising composition is selected as the one that presents the better balance between ductility and stiffness and contains at least 50% of bio-sourced polymer in the blend. This way, PLA70/PMMA30/BS was selected, as it presented optimum results in terms of ductility and toughness. Using morphological analysis, size-distribution of rubber microdomains was studied for a better understanding of impact strength results, in particular. It revealed that impact toughness and fracture mechanisms of blends depend on rubber particle size with an optimum in the range of $0.5-0.55\mu$m, achieved at 30 wt % PMMA. PMMA contents higher than 50% led to poor mechanical properties and low interfacial adhesion between PLA/PMMA matrix and BS nodules due to the low affinity of impact modifier with PMMA. Finally, a comparative study between PLA70/PMMA30/BS and commercial ABS/PC was established and confirmed that the PLA-based ternary blend could represent a very promising bio-sourced alternative for automotive applications.

ACKNOWLEDGMENTS

LAMIH authors are grateful to CISIT, the Nord-Pas-de-Calais Region, the European Community, the Regional Delegation for Research and Technology, the Ministry of Higher Education and Research and the National Center for Scientific Research for their financial support. UMONS and Materia Nova authors are grateful to the “Region Wallonne” and European Community (FEDER, FSE) in the frame of “Pole d’Excellence Materia Nova” INTERREG IV—NANOLAC project and in the excellence program OPTI^{2}MAT for their financial support. Authors are grateful to Yoann Paint and Lisa Dangreau (Materia Nova, Belgium) for assistance in preparation of samples and realization of analyses. CIRMAP thanks the “Belgian Federal Government Office Policy of Science (SSTC)” for general support in the frame of the PAI-7/05. J. O. thanks F.R.I.A. for its financial support thesis grant. J.-M. Raquez is “Chercheur qualifié” by the F.R.S.-FNRS (Belgium).

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