

A NEW PARADIGM FOR THE TOUGHENING OF POLYLACTIDE-BASED MATERIALS

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Abstract - In this work, we report immiscible polymer blends made of polylactide (PLA) toughened with impact rubber-like modifiers in order to elaborate ultratough PLA-based blends mediated with nanoparticles. Accordingly, a commercially available impact modifier specifically designed for PLA was selected as a model. In this study, 10 wt% of Biomax Strong 100 (BS) and silica nanoparticles (SiO_2) were melt-blended within PLA using microcompounder in order to investigate the microstructure and related mechanical performances for the resulting blends upon the processing methods and nanoparticles content. A synergistic toughening effect of impact modifier and silica nanoparticles is highlighted, together with a clear alteration of the blend morphology. This led to the exclusive conversion of rubbery spherical cavities into elongated structures in the presence of SiO_2 . Related with the microstructure of rubbery microdomains, the use of PLA/BS-based systems containing 10% weight silica nanoparticles resulted in toughness improvement, actually reaching a eleven-fold increase in impact strength. The improvement in mechanical properties could be attributed to the morphological modification of the PLA-based blends mediated by the presence of the dispersed nanoparticles, and the concomitant fine tuning of the dispersed rubbery microdomains in terms of shape, average size and related size-distribution.

Keywords: impact modifier, morphology, polylactide, nanoparticles, ultratoughness.

Introduction

Due to its renewability and biodegradability, polylactide (PLA) is the most extensively investigated biopolymer as a biosourced substitute to conventional petroleum-based polymers in different types of applications such as in automotive and electronic industries [1, 2]. However, the applications of PLA are currently limited by its brittle nature [3, 4]. Among the strategies developed to overcome this limitation and to greatly enhance impact strength of PLA, the addition of impact modifiers is widely used [5, 6] and dispersed in the polyester matrix as rubbery nodules [7-9]. When the toughness efficiency is considered, it is recognized that there is an optimum size of these rubbery nodules at which the impact strength of the blend is maximized [10, 11]. Accordingly, the rubber phase morphology (domain size and related size-distribution) and polymeric matrix-rubbery domain interfacial properties must be properly controlled [12-15]. Recently, compatibilization methods have been reported via the use of nanoparticles into immiscible polymer blends [16, 17]. This represents a universal platform to tailoring the phase morphology of polymer blends, and therefore to control the material performances.

In this work, we investigated polymer blends made of PLA and impact rubber-like modifiers designed in the presence of nanoparticles in order to elaborate ultra-tough PLA-based blends. The role of nanoparticles is to specifically localize at the interface of both polymeric partners, to strengthen the interfacial adhesion between both partners and therefore the performance materials [18, 19]. Hence, an appropriate

control about the nature of nanoparticles and their processing on blending provides a straight strategy to tailoring the phase morphology of polymer blends, and therefore to controlling the material performances. We have recently demonstrated that the use of as-synthesized impact modifiers made of hydrolytically degradable poly(ϵ -caprolactone-co-D,L-lactide) (P[CL-co-LA]) copolyesters can enhance the toughness of PLA materials and reveal peculiar morphologies for the resulting blends (from round-like to oblong structures for rubbery phase) [20]. The most interesting feature was that the highest enhancement in impact strength achieved in the case of oblong structures within PLA matrix, indicating the importance for controlling the affinity and the interfacial compatibilization between the blend components. Hence, the present work aims at extending our approach to design ultratough PLA-based materials through an appropriate incorporation of nanoparticles into PLA-based materials toughened with Biomax Strong 100, which is a commercially available impact modifier specifically designed for the polyester matrix. In this study, we will report some efforts to control the phase structure of PLA-based materials containing 10 wt% of Biomax Strong 100 (BS) and silica nanoparticles (SiO_2) by adjusting the interfacial interaction within the resulting blend upon the processing methods and nanoparticles content. The relationship between morphological features and the synergistic toughening effect of rubbery-like system and nanoparticles are investigated.

Experimental

Materials: A commercially available extrusion-grade PLA (NatureWorks 4032D) was used as received ($\overline{M}_n=133,500\pm 5,000$ g/mol, $\overline{D}=1.94\pm 0.06$ as determined by size-exclusion chromatography, $1.4\pm 0.2\%$ D-isomer content as determined by the supplier). Biomax Strong 100 (BS), a commercially available impact modifier specifically designed for PLA was provided by Dupont. CAB-O-SIL TS530 (Silica nanoparticles, SiO_2) is a high surface area fumed silica ($225 \text{ m}^2/\text{g}$) which has been surface modified with hexamethyldisilazane and was supplied by Cabot. Cloisite 20A (CL20A), a dimethyl-dihydrogenated tallow-ammonium treated MMT (modifier concentration: 95 meq/100 g), Cloisite 25A (CL25A), a dimethyl-dihydrogenated tallow-(2-ethylhexyl)-ammonium treated MMT (modifier concentration: 95 meq/100 g) and Cloisite 30B (CL30B), a methyl-tallow-bis(hydroxyethyl)-ammonium treated MMT (modifier concentration: 90 meq/100 g) were supplied by Southern Clays Products INC.

Melt-blending of PLA-based materials: Prior to extrusion, PLA pellets were dried for at least 12h at 80°C in an oven. Both binary and ternary systems based on PLA were prepared in a DSM twin-screw micro-compounder (15 cc) at 200°C and 60 rpm for 3 min. Two processing methods were employed to prepare ternary PLA/BS/nanoparticles composites upon how these nanoparticles were dispersed, i.e., either directly into the blend (so-called one-step process) or first into one both partners before blending (so-called two-step process) into PLA/BS-based systems. In the one-step process, both impact modifier (BS) and nanoparticles were directly compound with PLA, while in the two-step process, nanoparticles were mixed first in one of both partners by dissolving the compounds in a minimal of chloroform followed by a slow evaporation of solvent under stirring and then blended following the same procedure as the one-step process. Standard samples of resulting PLA-based materials were then prepared by compression molding at 200°C for 10 min.

Characterization techniques: Differential scanning calorimetry (DSC) was performed using a DSC Q2000 from TA Instruments at heating and cooling rates of $10^\circ\text{C}/\text{min}$ under nitrogen flow (2nd scan). Notched Izod impact tests were performed according to ASTM D256 using a Ray-Ran 2500 pendulum impact tester ($E=4\text{J}$, mass=0.668kg and speed=0.46m/s). Tensile tests were performed according to ASTM D638 using a Zwick universal tensile testing machine (speed=1m/s and preload = 5N). Room-temperature impact-fractured surfaces of specimens were examined for morphological structure through transmission electron microscopy (TEM). For recording TEM images, the samples were cryomicrotomed at -100°C by a Leica UCT microtome. Transmission electron microscopy was carried out using a Philips CM20 microscope operated at 200 kV. Analysis software ImageJ is used

for the analysis of TEM images to estimate the particles size and their distribution within the matrix.

Results and Discussion

In this work, 10 wt% of Biomax Strong 100 (BS), a commercially available impact modifier specifically designed for PLA, was used and melt-blended at 200°C within PLA using a twin-screw microcompounder (15 cc). The resulting blend was recovered and compression molded at 200°C . Toughness of the PLA-based materials was determined by notched Izod impact testing using a pendulum impact tester, while tensile properties were determined at a tensile rate of 1 mm/min (**Fig. 1**). Unfilled PLA itself behaves as a stiff and glassy materials characterized by a high Young's Modulus of ca. 1860 MPa, a tensile strength of ca. 58 MPa, an elongation at break of ca. 4% and an impact strength of $2.7 \text{ kJ}/\text{m}^2$. When loaded at 10 wt% BS as impact modifier, a significant improvement in toughness are highlighted (impact strength passing from 2.7 for PLA matrix to $11.3 \text{ kJ}/\text{m}^2$), together with an increase in elongation at break (at ca. 24 % in elongation) and a decrease of the Young's modulus (at ca. 1780 MPa in modulus). When nanoparticles were loaded into the binary blend, the tensile properties of resulting ternary PLA-based nanocomposites are not altered and the Young's modulus is even preserved. For instance, Young's modulus passes from ca. 1780 to ca. 1700 MPa for PLA/BS blend and PLA-based ternary nanocomposites containing 5 wt% silica nanoparticles, respectively. The most striking feature concerns the significant increase, up to seven-fold, in the impact strength recorded in the case of PLA-based ternary nanocomposites (**Fig. 1**). For instance, in the presence of only 5 wt% of Silica nanoparticles, a very significant increase in the impact strength was recorded, i.e., $18.5 \text{ kJ}/\text{m}^2$ vs. $2.7 \text{ kJ}/\text{m}^2$ for the unfilled PLA. An eleven-fold increase in impact strength was even recorded at 10 wt% silica nanoparticles ($30.2 \text{ kJ}/\text{m}^2$), together with Young's modulus at ca. 1720 MPa.

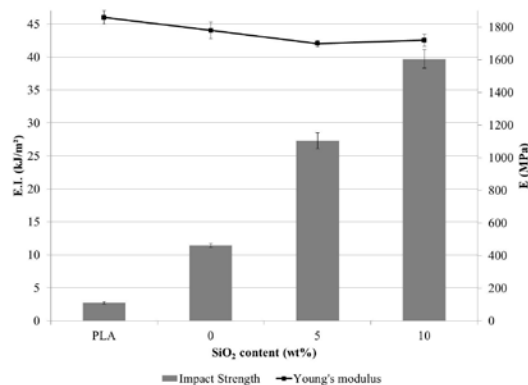


Figure 1 - Influence of the Silica nanoparticles content on the notched Izod impact strength and Young's modulus of PLA-based materials containing 10 wt% of BS impact modifier.

Importantly, the ultra-toughness behavior is highly dependent on how silica nanoparticles are incorporated into PLA-based melt-blends (Fig. 2). When impact modifier and nanoparticles were used together, both simultaneous increase of the toughness and stiffness in ternary composites were only achieved by using an appropriate processing method, i.e. by adding first silica nanoparticles into PLA, followed by a consecutive melt-blending with BS (two-stage melt-process). Changing the mode of silica dispersion in the melt-blend allows tuning the toughness. For instance, the direct dispersion of 5 wt% silica nanoparticles into the blend of PLA and BS (90/10, wt/wt) or the other two-stage melt-process, i.e., first melt-mixing of Silica into BS, followed by processing within PLA resulted in a drastic decrease in toughness. The close relationship between mechanical performance and microstructure of these PLA-based blends may explain why processing methods appear to be suitable techniques to reach acceptable toughness. Accordingly, an appropriate processing method in two-step, in which silica nanoparticles were first added into PLA partner, is required to greatly enhance the mechanical performances by adjusting the morphological features and promoting optimum mechanical performances.

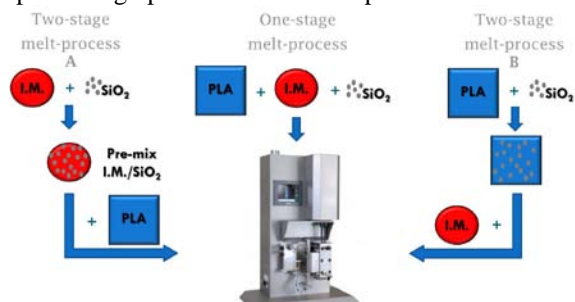


Figure 2 – Investigated processing method of PLA-based materials containing an impact modifier (I.M.) and silica nanoparticles (SiO_2). Samples produced via direct dispersion of Silica into both PLA and I.M. partners (middle), via pre-mixing of I.M. and SiO_2 followed by blending within PLA (left) and via pre-mixing of PLA and SiO_2 followed by blending within I.M. (right).

As attested by differential scanning calorimetry (DSC), silica nanoparticles loading has no real effect on the thermal properties of the PLA/BS blends (Tab. 1). The melting (T_m) and glass transition temperatures (T_g) of PLA matrix remain unchanged at 169 and 61°C, respectively. Regarding the crystallinity degree for PLA-based blends, a slight increase is recorded by adding a rubber-like impact modifier into PLA (from 3% to 13%). However, the crystallinity degree for ternary PLA-based composites is not modified by the incorporation of silica nanoparticles. This indicates that the enhancement in toughness is directly related to the formation of peculiar morphologies for the rubbery phase in the presence of silica nanoparticles, without any modification of crystallinity degree for PLA/BS blends in the presence of silica nanoparticles.

Table 1. Thermal properties of unfilled PLA, PLA/BS blends (10 wt%) and the corresponding ternary blends.

Entry	SiO_2 content (wt%)	T_g^a (°C)	T_c^a (°C)	ΔH_c^a (J/g)	T_m^a (°C)	ΔH_m^a (J/g)	χ^b (%)
1	PLA	62	113	29	170	32	3
2	PLA/BS	62	114	28	169	32	11
3	+ 5 wt%	62	107	18	168	27	11
4	+ 10 wt%	62	103	8	168	27	13

- As determined by DSC (under N_2 flow, heating rate of 10°C/min, second scan).
- As determined on the first scan and calculated taking into account the contribution of both impact modifier and silica nanoparticles with $\chi = (\Delta H_m - \Delta H_c) / \Delta H_m^0$ and $\Delta H_m^0 = 93.6 \text{ J/g}$.

Transmission electron microscopy (TEM) analyses of PLA/BS blend shows the presence of round-like nodules regularly dispersed within the PLA matrix that are ascribed to the dispersed rubbery phase. When silica nanoparticles were dispersed by a two-stage melt-process (by adding first Silica into PLA partner), morphological features (domain shape, average size and related size distribution) are clearly affected, mediated by the presence of nanoparticles. TEM analyses show that silica nanoparticles are mostly located at the interface PLA/BS, promoting the formation of peculiar morphologies. According to our previous work, the improvement in PLA toughness was namely explained by blend-morphology of the dispersed phase in PLA matrix, where silica nanoparticles were previously highlighted as an interesting strategy to tailoring the phase morphology of resulting PLA/impact modifiers blends. Recently, we have already demonstrated that the co-addition of a P[CL-co-LA] copolyester (72/28 mol% CL/LA, 10 wt%) and silica nanoparticles in PLA through a two-step process increased significantly the material toughness by promoting spherical nodules commonly observed in immiscible blends into nanosized ribbon-like structures [21]. Surprisingly, such positive effect of silica nanoparticles can be achieved when commercially available impact modifiers like Biomax Strong was used to toughen PLA-based materials instead of P[CL-co-LA] copolyester. It is moreover highlighted that the impact properties can be directly correlated to morphological alterations of the PLA-based blends, not only upon the average size and related size-distribution, but also upon the shape of the dispersed rubbery microdomains. Accordingly, a fine tuning of the morphological issues (control in terms of domain shape, average size and size-distribution of the dispersed rubbery microdomains) is governed by the presence of nanoparticles and endows PLA-based materials with new impact performances.

Another interesting feature about the co-addition of BS and Silica into PLA is to check whether such positive effect of nanoparticles can be achieved with other nanoparticles within PLA-based materials. Remarkably, the addition of organomodified layered aluminosilicate (clays) has also shown a significant

improvement in the impact strength and leads to the formation of ultra-tough materials (**Tab. 2**). For instance, a value of 37.6 ± 2.1 kJ/m² has been achieved with only 1 wt% of CL25A; this value is in the same range of the toughness obtained with 10 wt% of silica nanoparticles. From these results, it becomes evident that silica and other nanoparticles should be combined with conventional impact modifiers in order to develop synergistic systems with high efficiency and acceptable impact strength.

Table 2. Notched Izod impact strength of unfilled PLA, PLA/BS blends (10 wt%) and the corresponding ternary blends containing 1 wt% of clays.

Entry	Type of Clay	E.I. ^a (kJ/m ²)
1	PLA	$2,7 \pm 0,1$
2	PLA/BS	$11,3 \pm 0,8$
3	+ 1 wt% CL20A	$32,6 \pm 1,0$
4	+ 1 wt% CL25A	$37,6 \pm 2,1$
5	+ 1 wt% CL30B	$21,9 \pm 1,2$

a) As determined by Notched Izod impact tests.

Conclusions

In this paper, we report the toughness and phase morphology of PLA/impact modifier/nanoparticles ternary nanocomposites. In this respect, 10 wt% of BS and silica nanoparticles were melt-blended within PLA using microcompounder in order to investigate the microstructure and related mechanical performances of the resulting blend upon the processing methods (one-step or two-step) and nanoparticles content. From this investigation, only a two-step process with an addition of Silica into PLA first, followed by this into BS leads to high impact performances. In this way, the co-addition of a commercially available impact modifier (BS) and Silica within PLA significantly increase the material toughness as attested by the recorded eleven-fold increase in impact strength, while maintaining high level of rigidity. This synergistic toughening effect of BS and Silica are observed together with a clear alteration of the blend morphology, promoting new peculiar morphologies in the presence of silica nanoparticles. Directly related to the microstructure of rubbery microdomains and the morphological modification of the PLA-based blends mediated by the presence of nanoparticles (fine tuning of the dispersed rubbery microdomains in terms of shape, average size and related size-distribution), an unprecedented toughness enhancement was achieved. Moreover, the material performances show similar behavior when an as-synthesized hydrolytically degradable P[CL-co-LA] statistical copolyester are employed instead of BS; highlighting the use of nanoparticles as a simple and universal strategy to endowing PLA-based materials with new mechanical properties. In this regards, the use of other nanoparticles like nanoclays can be also beneficial for applications requiring high performance polymeric materials for environmentally friendly polymers like PLA.

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