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Ultra-tough polylactide-based materials synergistically designed in the presence of rubbery ε-caprolactone-based copolyester and silica nanoparticles

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Ultra-tough polylactide-based materials are synergistically obtained through melt-blends of polylactide (PLA), rubber-like poly(ε-caprolactone-*co*-D,L-lactide) copolyester and silica nanoparticles using extrusion techniques. Co-addition of rubber-like copolyester and silica nanoparticles into PLA matrix results in a peculiar alteration for the phase-morphology of the rubbery phase within PLA matrix. Surprisingly, regularly obtained spherical nodules convert into almost continuous features after adding nanoparticles in the PLA-based melt-blend. Toughness of PLA-based materials is considerably enhanced on, at least, 15 times in comparison to unfilled PLA.

1. Introduction

The morphological features of polymer blends such as the average size of the dispersed phase and interfacial adhesion play an important role to determining the final mechanical performances [1]. To achieve a control over the morphology and therefore the performances for the resulting melt-blends, compatibilization routes are required, namely via the use of organic compatibilizers such as block or graft copolymers. These copolymers can be either added directly or in situ generated within polymeric blends during flow-created processes in order to specifically localize them at the interface of polymer blends [2–6]. In the case of in situ generated copolymers, Macosko et al. reported that compatibilization extent depends on the interfacial area created during processing flows [7]. Because the interfacial reactions are reactively-guided towards the formation of covalently/permanently formed domains, the extent of interfacial area (related with the Rayleigh's instability) scarcely addressed in the existing literature, is difficult to control during processing flow. This limits its contribution to the morphology of polymer blends [7,8]. However, it appears that, if well-controlled, the interfacial area could greatly increase on three orders of magnitude in the early stage of mixing, i.e. less than 2 min, affording an elegant way to tailor the morphology of polymer blends [8–10], and therefore to tune up the material performances on-purpose. Meanwhile, other compatibilization methods have been reported upon the addition of nanoparticles into immiscible polymer blends [11–13]. Nanoparticles act specifically by localizing at the interface of both polymeric partners, strengthening the interfacial adhesion between both partners and therefore the performance materials [14–16]. Unlike polymer-based compatibilizers, nanoparticles are non-reactive, unspecific to the nature of immiscible polymer blends, and readily incorporated on blending [17,18]. Tailoring the phase-morphology of polymer blends in the presence of nanoparticles represents a universal platform to control the material performances.

This prompted us to investigate polymer blends made of polylactide (PLA) and impact rubber-like modifiers designed in the presence of nanoparticles in order to elaborate ultra-tough PLA-based blends. Due to its renewability, biodegradability and high stiffness, PLA is the most extensively investigated biobased polymer as one of the best substitutes for petroleum-based polymers to both short-time and durable applications such as in packaging, automotive and electronic industries [19–21]. However, the applications of PLA remain restricted due to its brittle nature [22]. Among the strategies to enhancing its impact strength without compromising its inherently high stiffness, the addition of impact modifiers is widely used, yielding the dispersion of round-like rubbery (micro)nodules in the polyester matrix [23,24]. Grijpma et al. first reported that toughening of PLA-based materials could be readily achieved by blending hydrolytically degradable rubbery materials made of trimethylene carbonate-based triblock

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copolymers or diblock copolymers within amorphous PLA [25]. However, only very limited improvement in impact toughness can be achieved in most cases, except after enhancing the crystallinity degree of PLA matrix in PLA/impact modifier blends through annealing process [26] or stereocomplexation [27]. Recently, some of us have demonstrated that the use of partially miscible impact modifiers made of hydrolytically degradable poly(ε-caprolactone-*co*-D,L-lactide) (P[CL-*co*-LA]) copolyesters can substantially enhance the toughness of PLA materials [28], without compromising the overall biodegradability or the transparency of the resulting PLA-based materials [29,30]. Depending on the affinity between the P[CL-*co*-LA] copolyesters and the PLA matrix, an optimum in terms of toughness improvement was obtained for a molar content in LA of 28 mol%. Interestingly, in addition to the presence of round-like rubbery (micro)nodules currently observed in PLA/impact modifier blends, the presence of some oblong (nano)structures was noticed for the rubbery phase at this optimal composition. These preliminary results more likely indicated that the toughness improvement could be implemented by the presence of these peculiar morphologies within blends. To favor and to further increase the extent of these oblong (nano)structures for the rubbery phase and therefore to greatly enhance the toughness of PLA-based materials, the present communication hence aims at investigating the phase-morphology and related toughness of PLA/poly(ε-caprolactone-*co*-D,L-lactide) (P[CL-*co*-LA]) used as impact modifiers as controlled by addition of silica nanoparticles here selected as representative and universal nanofiller model. These PLA-based materials were readily obtained through a two-step process based on extrusion technology.

2. Experimental section

2.1. Materials

ε-Caprolactone (99%, Acros) was dried for 48 h over calcium hydride and distilled under reduced pressure. D,L-lactide (>99, 5%, Purac) was conserved in a glove box. *n*-Heptanol (98%, Aldrich) was dried over molecular sieve (4 Å) and tin(II) octoate ($Sn(Oct)_2$) (95%, Aldrich) was used as received without any purification, and diluted in dry toluene (0.01 M). A commercially available extrusion-grade PLA (NatureWorks 4032D) designed especially for realization of biaxially oriented films was used as received ($\bar{M}_N$ = 133,500 ± 5000 g/mol, D = 1.94 ± 0.06 as determined by size-exclusion chromatography, 1.4 ± 0.2% D-isomer content as determined by the supplier). CAB-O-SIL TS530 (silica nanoparticles) is a high surface area fumed silica (225,000 m^2/kg) which has been surface modified with hexamethyldisilazane and was supplied by Cabot.

2.2. Characterization techniques

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded in $CDCl_3$ using a Bruker AMX-300 apparatus at a frequency of 300 MHz. Size-exclusion chromatography (SEC) was performed in THF (containing 2 wt% NEt_3) at 35 °C using a Agilent liquid chromatograph equipped with a Agilent G322A degasser, an isocratic HPLC pump G1310A (flow rate: 1 mL/min), a Agilent autosampler G1329A (loop volume: 100 μL, solution concentration: 1 mg/mL), a Agilent-DRI refractive index detector G1362A and three columns: a guard column PLgel 10 μm and two columns PLgel mixed-B 5 μm. Molecular weight and molecular weight distribution were calculated by reference to a relative calibration curve made of polystyrene standards. Differential scanning calorimetry (DSC) was performed using a DSC Q2000 from TA Instruments at heating and cooling rates of 10 °C/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 J, mass = 0.668 kg and speed = 0.46 m/s). Tensile tests were performed according to ASTM D638 using a Zwick universal tensile testing machine (speed = 1 mm/min and preload = 5 N). Room-temperature impact-fractured surfaces of specimens were examined for morphological structure through transmission electron microscopy (TEM). For recording TEM images, the samples were ultra-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.

2.3. Synthesis of poly(ε-caprolactone-co-D,L-lactide) copolyester

The copolymerization was carried out in bulk by ring opening polymerization (ROP) of ε-caprolactone and D,L-lactide promoted by *n*-heptanol and tin(II) octoate for an initial molar [alcohol]/[tin(II) octoate] ratio of 100. The reaction was carried out for 24 h in an oil bath at 160 °C, and stopped by quenching it in an ice bath. The crude product was dissolved in a minimum volume of $CHCl_3$, followed by precipitation into a 10-fold excess of heptane. They were recovered after filtration and drying under vacuum until reaching a constant weight. The number-average molecular weight of resulting copolyesters was of 35,400 g/mol (equivalent polystyrene), together with a dispersity index of 2.0 (as determined by GPC analyses). The molar LA content was of 28 mol% (as determined by ^{1}H NMR analyses) and characterized by a low glass transition temperature of around −36 °C (as determined by DSC analyses).

2.4. Sample preparation and compounding

For safety reasons, a two-step process was carried out. PLA/silica nanoparticles masterbatches were prepared by solvent-casting using chloroform and dried for at least 12 h at 80 °C under reduced pressure (10^{-1} mbar) in order to remove residual organic solvent and water. The resulting masterbatch was subsequently melt-blended in the presence of 10 wt% poly(ε-caprolactone-co-D,L-lactide) copolyester (previously dried for at least 12 h at room temperature and under reduced pressure of 10^{-1} mbar) using a DSM twin-screw micro-compounder (15 cc) at 200 °C and 60 rpm for 3 min. For a sake of comparison, the simple blend exclusively made of PLA and poly(ε-caprolactone-co-D,L-lactide) copolyester was prepared using a DSM twin-screw micro-compounder (15 cc) at 200 °C and 60 rpm for 3 min, starting directly from PLA pellets (previously dried for at least 12 h at 80 °C and under reduced pressure of 10^{-1} mbar) and 10 wt% poly(ε-caprolactone-co-D,L-lactide) copolyester (previously dried for at least 12 h at room temperature and under reduced pressure of 10^{-1} mbar). For tensile and impact characterizations, the PLA-based materials were prepared by compression molding at 200 °C for 10 min.

3. Results and discussion

As partially miscible impact modifier, hydrolytically degradable P[CL-*co*-LA] statistical copolyester with a molar LA content of 28 mol% and characterized by a low glass transition temperature of around −36 °C was readily obtained by random ring-opening copolymerization (ROP) of the respective cyclic esters as catalyzed by tin octoate and using heptanol as initiator (Scheme 1) [28].

In a subsequent step, 10 wt% of the resulting P[CL-*co*-LA] random copolyester was melt-blended into PLA by melt-extrusion at 200 °C in a twin-screw microcompounder. The resulting blend was recovered and compression molded at 200 °C. Transmission