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EFFECT OF PROCESSING CONDITIONS ON TOUGHENING OF POLYLACTIDE IN THE PRESENCE OF HYDROLYTICALLY DEGRADABLE IMPACT MODIFIERS

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Abstract - Herein we report on the preparation of high impact polylactide (PLA)-based materials containing 10 wt% of rubbery poly(ε-caprolactone-*co*-D,L-lactide) (P[CL-*co*-LA]) random copolyesters as novel biodegradable impact modifiers. The efficiency of the as-synthesized impact modifiers for PLA is highlighted upon the processing conditions used to prepare these PLA-based materials. In agreement, a special emphasis was made to highlight the influence of mains processing parameters on the impact strength. These processing conditions represent a key-parameter to tune the toughness of PLA-based materials. Accordingly, the influence of the residence time in the microcompounder, the type of molding techniques (compression or injection molding) and the time of compression-molding were investigated on the toughness of resulting PLA-based materials in a close relationship with the morphological investigations, i.e. average size and related size-distribution of the dispersed microdomains within PLA (as shown by SEM). Under selected processing conditions, it came out that the dispersion of a P[CL-*co*-LA] copolyester within PLA resulted in a significant increase in impact strength and was correlated to the morphological modification of the PLA-based blends and a fine tuning of the dispersed rubbery microdomains in terms of shape, average size and related size-distribution.

Keywords: biodegradability, impact modifier, polylactide, morphology, copolyester.

Introduction

Polylactide (PLA) is the most extensively investigated and utilized biodegradable and renewable thermoplastic polyester, with potential to replace conventional petrochemical-based polymers [1]. Despite its attractive properties in terms of high stiffness and biodegradability, which contribute to the success of PLA as substitute to traditional petroleum-based plastics in many applications (e.g. packaging, electronics), PLA suffers from its brittleness [2-4]. Indeed, PLA is characterized by a low notched Izod impact strength (i.e. 2.7 kJ/m^2). Accordingly, some efforts are being made on the toughness of these PLA-based materials using impact modifiers preferably [5, 6]. Such impact modifiers within the PLA matrix more likely act as rubbery (micro)domains that are able to absorb the impact stress [7-9]. However, almost all the commercially available impact modifiers are made of ethylene-based copolymers and are therefore not suitable when biodegradability is concerned, together with some reduction of transparency for the resulting PLA-based materials.

In this present work, we will aim at investigating the use of partially miscible impact modifiers on the impact resistance of PLA-based materials. Miscibility extent of impact modifiers toward the main matrix represents a key-parameter, affecting the interface strength, and therefore the phase-morphology of immiscible rubbery microdomains in the polymeric matrix [10-18]. Accordingly, rubbery poly(ε-caprolactone)-based copolyesters namely poly(ε-caprolactone-*co*-D,L-lactide) (P[CL-*co*-LA]) with different LA-enriched segments that are miscible with the PLA matrix were already employed as biodegradable impact modifiers for the production of highly impact-resistant materials made of PLA [19]. From this study, it was highlighted that PLA-based materials containing P[CL-*co*-LA] copolyester with a LA comonomer content of 28 mol% reveals oblong structure (fibrilar morphology), which is originated from a a straight miscible-immiscible balance, together with a significant effect on the toughness of the materials. To our current efforts toward development on new biodegradable impact modifiers for PLA, the present work was focused on the effect of processing conditions on toughening of polylactide in the presence of the P[CL-*co*-LA] random copolyesters. The objective was to highlight optimum processing conditions in order to maximize the effective interfacial compatibilization and the resulting improvement on the material performances. Accordingly, the influence of the main processing parameters was investigated on the PLA toughness and a relationship between morphological structure (rubbery microdomains size and related size distribution) and impact performance could be established.

Experimental

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) was used as received ($\overline{M_n}$ =133,500±5,000 g/mol, Đ=1.94±0.06 as determined by size-exclusion chromatography, 1.4±0,2% D-isomer content as determined by the supplier).

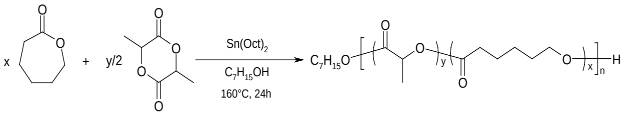
Synthesis of P[CL-co-LA]copolymers: Copolymerization was carried out in bulk by ring opening polymerization (ROP) of ε-caprolactone and D,L-lactide promoted by *n*-heptanol and tin(II) octoate for initial [alcohol]/[tin(II) octoate] and [comonomer]/[alcohol] molar ratios of 100 and 200, respectively. The reaction was carried out overnight 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. The copolymers were recovered by filtration and after drying under vacuum.

Melt-blending of PLA with random copolyesters: Prior to extrusion, PLA pellets were dried for at least 12h at 80°C in an oven. P[CL-*co*-LA] copolyesters at a content of 10 wt% were dispersed by melt-blending in a PLA matrix using a DSM twin-screw micro-compounder (15 cc) at 200°C and 60 rpm for 3 min. For impact testing, rectangular samples (35 x 12 x 3 mm^3) were prepared by injection molding at 200°C for 5 min or compression molding at 200°C using the following procedure: 9 min at ambient pressure, 3 degassing steps and 1 min at 200°C under 10 bars. The samples were then compressed at low temperature under 10 bars for 5 min.

Characterization techniques: Proton nuclear magnetic resonance (^1H NMR) spectra were recorded in $CDCl_3$ using a Bruker AMX-500 apparatus at a frequency of 500 MHz. Size-exclusion chromatography (SEC) was performed in THF 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 : 1mg/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=4J, mass=0.668kg and speed=0.46m/s). Room-temperature impact-fractured surfaces of specimens were sputter-coated with gold and then examined for morphological structure through scanning electron microscopy (SEM). Scanning electron microscopy was carried out using a Philips XL20 microscope (1 to 30 kV). Analysis software Scandium is used for the analysis of SEM images to estimate the average size and size distribution of the rubbery microdomains spread within the matrix.

Results and Discussion

In order to improve the impact strength of the materials by dissipation of the impact stress [21-23], it is required that impact modifiers have glass transition temperatures (T_g) at least 20°C lower than use temperature [24]. In this regard, a 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 simultaneous ring-opening polymerization (ROP) of the respective cyclic esters as promoted by *n*-heptanol and $Sn(Oct)_2$ (starting from [alcohol]/[$Sn(Oct)_2$] and [comonomer]/[alcohol] molar ratios of 100 and 200, respectively) through a coordination-insertion mechanism (**Sch. 1**) and selected as hydrolytically degradable impact modifier for PLA. It is worth noting that this copolyester could not alter the biodegradability or the transparency of the resulting PLA-based materials [19, 25].



Scheme 1 - Ring-opening polymerization of ε-caprolactone and D,L-lactide promoted by *n*-heptanol and tin(II) octoate.

As also highlighted in our previous works, an ultimate toughening effect for resulting PLA-based materials requires a contribution of the immiscible blend morphology of PLA/P[CL-*co*-LA] systems [26]. Concerning this investigation, the mean size and size distribution of these as-synthesized rubbery microdomains are responsible for the improvement in impact strength while tailoring the microdomain size represents an efficient way to toughen the PLA-based materials. Nevertheless, a control of the processing conditions is required to achieve the optimum particle size of the dispersed rubbery PCL-based copolymer within PLA. Accordingly and in a first consideration regarding the processing effect on the toughness of PLA-based blends, P[CL-*co*-LA] copolyester was added into a commercially available polylactide using a twin-screw microcompounder in order to reach a copolyester content of 10 wt%. First, influence of the processing time was investigated on the average size of rubbery microdomains dispersed within PLA, as determined by scanning electron microscopy (SEM) recorded on notched surfaces. In a first attempt, an increase in the residence time in the compounder (at 200°C and 60 rpm) was accompanied by a decrease in the rubbery microdomain size, attesting for a good quality of dispersion (not shown here). However, the residence time implements the size distribution of the dispersed microdomains formed in the materials recovered directly at the exit of the microcompounder. From these results, it can be assumed that homogeneous distribution and defined mean size are only observed after a residence time of 3 min (**Fig. 1**). Such observations are in perfect agreement with reproducibility in impact strength of the materials.

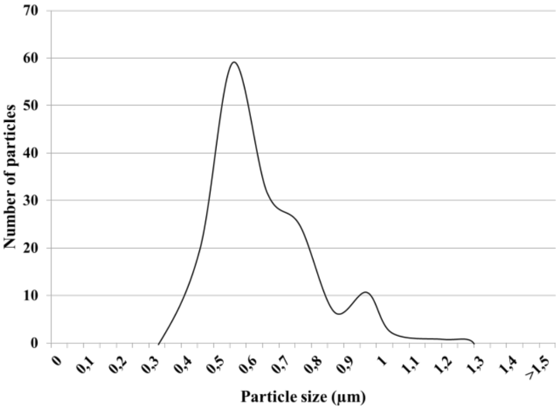


Figure 1 - Size distribution of dispersed rubbery microdomains in PLA-based materials containing 10 wt% of P[CL-*co*-LA] copolyester after melt-processing at 200°C and 60 rpm during 3 min in the microcompounder (at the exit of the die).

Moreover and as previously observed [26], the molding technique has also a significant effect on the microdomain size and the size-distribution of the dispersed rubbery modifier within PLA. It was highlighted that the mean size of the dispersed copolyesters within PLA is systematically and significantly higher for compression-molded samples than those produced via injection-molding (**Fig. 2**). Such particular morphologies with larger microdomain size results in an effective improvement in impact strength of PLA-based materials.

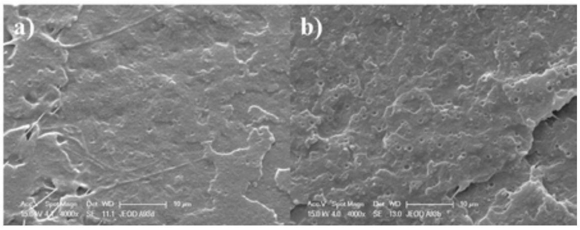


Figure 2 - SEM images of room-temperature notched surfaces of PLA-based materials containing 10 wt% of P[CL-*co*-LA] copolyester. Samples were produced at 200°C for 5 min by injection molding (a) and compression molding (b).

In addition, the materials as-recovered after (mini)extrusion was compression-molded and the residence time in the mold was investigated on the impact strength of resulting blends (**Fig. 3**). As shown in **Fig. 3**, the impact strength of PLA-based materials increases with the residence time in compression molding to reach an optimum value at about 10 min (in respect with error bars). This improvement in toughness more likely results from the shift to larger microdomain size with longer compression molding time (**Tab. 1**). This increase in the rubbery microdomain size is due to a phenomenon of coalescence that occurs at high temperature and pressure during the compression molding to achieve an optimum at around 10 min.

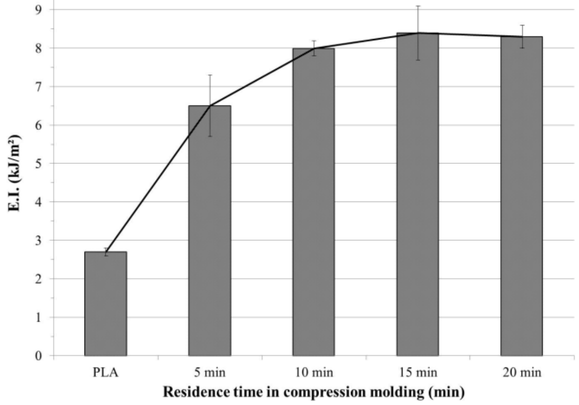


Figure 3 - Influence of the residence time in compression molding at 200°C on the impact strength of PLA-based materials containing 10 wt% of P[CL-*co*-LA] copolyester. Samples were produced by compounding 3 min at 200°C and 60 rpm.

As far as mechanical properties are concerned, coalescence must occur to reach optimum microdomain size able to absorb the impact stress and increase the impact strength of PLA-based materials. Accordingly, a detailed understanding of processing conditions and the resulting morphology has to be achieved to endowing PLA-based materials with new mechanical performances. In order to optimize the toughness and to reach a compromise between good dispersion (related to shear) and limited matrix (thermal) degradation for the PLA matrix (as measured by SEC), the following conditions has been selected : melt compounding for 3 min at 200°C and 60 rpm followed by compression molding for 10 min at 200°C.

Table 1 – Effect of processing conditions by compression molding at 200°C on the microdomain size of the dispersed phase of PLA-based samples containing 10 wt% of P[CL-*co*-LA] copolyester.

Entry	Residence time (min)	Microdomain size[a] (µm)
1	0	0.55
2	5	0.75
3	10	0.85

a) As determined by scanning electron microscopy (SEM).

Moreover, as far as transparency is concerned, incorporation of commercial impact modifiers within the PLA matrix is usually accompanied by some (partial) reduction of transparency [5, 24]. In contrast, the use of P[CL-*co*-LA] copolyesters as impact modifier for PLA allows maintaining high level of transparency of these resulting PLA-based materials (**Fig. 4**). Maintaining the overall transparency may be correlated to the very small size of rubbery domains finely dispersed within PLA matrix, along with the similar refractive indexes of both rubbery P[CL-*co*-LA] copolyester and PLA matrix. Maintaining the transparency for these PLA-based materials acceptable opens the door to many applications when both properties of transparency and toughness are required.

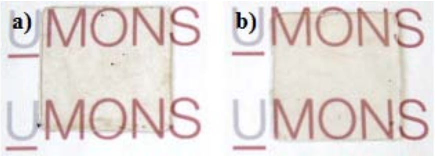


Figure 4 - Pictures of the materials PLA (a) and PLA containing 10 wt% of P[CL-*co*-LA] copolyester (72/28 mol% CL/LA) (b) (thickness : 0.5 mm).

Conclusions

The utilization of partially miscible impact modifiers was investigated in the design of impact PLA-based materials. Rubbery random aliphatic P[CL-*co*-LA] copolyesters were accordingly employed as impact modifiers to reach a copolyester content of 10 wt% within PLA. After a consideration of the influence of the main processing parameters on the microdomain size of the minor phase, the following procedure must be chosen to improve the toughness of the resulting PLA-based materials: compounding at 200°C and 60 rpm for 3 min followed by compression molding at 200°C for 10 min. The use of these processing parameters represents an efficient way to toughen the PLA-based materials by promoting optimum microdomain size and absorbing the impact stress. Dependence between toughness improvement and morphology of the resulting blends was established in terms of the domain shape, average size and related size-distribution of the dispersed rubbery microdomains within the PLA matrix. The overall results revealed that the dispersion of a P[CL-*co*-LA] copolymer provided a significant increase in impact strength for the resulting PLA-based blend upon these appropriate processing conditions. Accordingly, a fine tuning of the morphological issues (control in terms of domain shape, average size and size-distribution of the dispersed rubbery microdomains) should be required to endow PLA-based materials with new impact performances.

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