

The effect of the addition of poly(styrene-co-glycidyl methacrylate) copolymer on the properties of polylactide/poly(methyl methacrylate) blend

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ABSTRACT: The effect of the addition of poly(styrene-co-glycidyl methacrylate) P(S-co-GMA) copolymer on the properties of melt blended polylactide/poly(methyl methacrylate) (PLA/PMMA) 80/20 (wt %) composition was studied. In the literature high ductility levels were achieved by melt blending PLA with different additives. However, the gained ductility was counter balanced with drastic drops in strength and modulus values. The novelty of this work was the preparation of PLA-based blends with polylactide content higher than 75 wt % which showed an impact resistance value improvement of about 60% compared with the neat PLA and maintained similar tensile strength and modulus values as well as glass transition temperature to neat PLA. The addition of only 3 pph of copolymer to PLA/PMMA blend improved the impact resistance almost 100%. The chemical reaction between PLA/PMMA blend and P(S-co-GMA) copolymer were analyzed by FTIR, rotational rheometry, and GPC/SEC. Phase structure and morphology were studied by Differential Scanning Calorimetry and Scanning Electronic Microscopy. Tensile and impact properties as well as thermal stability were also studied. Results showed that as the amount of copolymer in the blend was increased then higher was average molecular weight and polydispersity index. After the addition of P(S-co-GMA) copolymer to the PLA/PMMA blend the impact resistance, elongation at break and thermal stability were improved while tensile strength and elastic modulus remained almost unaltered.

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INTRODUCTION

Development of biodegradable polymers from renewable resources has received considerable research interests in the recent years because of increasing environmental consciousness and sustainability needs.^{1–4} Poly(lactic acid) (PLA) is a linear aliphatic biodegradable polyester derived from biomass which has become a potential candidate for various large-scale industrial applications in the areas of packaging, biomedical, and pharmaceutical.^{5–7} Recently different ways of tailoring PLA properties for automotive applications have been developed as alternative to mineral filled polypropylene.⁸ Bouzouita *et al.* designed rubber-toughened PLA/PMMA formulations processes for automotive applications.⁹ PLA has good mechanical properties and processability, which make it one of the most interesting bioplastics. However, the glass transition temperature at around 60 °C makes it brittle at room temperature. Besides, it has low heat distortion temperature and higher price than petrochemical commodities.^{10–12} Melt blending

is a relatively simple method to modify polymer properties being one of the most studied approaches to overcome the limiting properties of different thermoplastics, including PLA.^{13–19}

In a previous work²⁰ different PLA/PMMA compositions were prepared by melt blending and all blends showed the coexistence of two phases. A clear displacement of T_g of the neat components in the blends was observed by DMA, indicating partial miscibility. The glass transition temperature of PLA-rich phase increased as the proportion of PMMA in the blend was increased. Although the thermomechanical properties of prepared PLA/PMMA blends were better than those of neat PLA, blends exhibited similar impact resistance to neat polymers. In SEM micrographs of PLA/PMMA blends dispersed phase around 200–350 nm in diameter was observed evenly distributed in the continuous phase. However, the dispersed phase was not able to enhance the impact resistance of the matrix because of the observed limited interfacial adhesion. Therefore, to make PLA/PMMA blends suitable for

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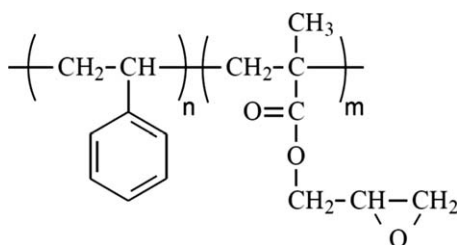


Figure 1. The chemical structure of poly(styrene-*co*-glycidyl methacrylate).

engineering applications, toughness, and impact resistance should be improved. In this sense, reactive processing with epoxy groups has been reported to improve the compatibility of PLA containing systems.^{21,22} The reaction of the epoxy groups with PLA's carboxyl and hydroxyl end-groups can lead to branching and consequently enhances melt strength and some mechanical properties.^{23,24} On the other hand, styrenic-glycidyl acrylate copolymers has been previously studied to cause chain extension of PLA in order to melt strengthen the neat polymer with the objective to enlarge its processing window²⁵ or enhance the extrusion and injection foamability of PLA.^{23,26} Besides, glycidyl methacrylate-based copolymers have been studied as reactive compatibilizer to improve interfacial adhesion between immiscible blends like PLA/PCL²⁷ PLA/ABS,²⁸ PLA/SEBS,²⁹ PLA/PBSA,³⁰ or to improve the dispersion of nanoclays in a PLA matrix.³¹ Core-shell structured GMA functionalized MMA-BA or MB-g-GMA copolymers have also been used to toughen PLA.^{32,33} In this work, the effect of the addition of poly(styrene-*co*-glycidyl methacrylate) copolymer on the rheology, phase morphology, thermal stability, mechanical properties, and impact resistance of melt compounded PLA/PMMA 80/20 (wt %) blend has been studied. As observed in a previous work²⁰ this blend composition showed the highest thermal stability, tensile strength, and elastic modulus among all compositions studied. However, this composition showed low impact resistance because of the poor interfacial adhesion between the PLA-rich matrix and the dispersed PMMA-rich phase.

EXPERIMENTAL

Materials

PLA was purchased from NatureWorks LLC (Ingeo™ 3051D, $M_n = 106,000$ g/mol; PDI: 1.7; $\approx 4.6\%$ D-lactate) and PMMA from Evonic ROM GmbH (PLEXIGLAS® zk5BR, $M_n = 70,000$ g/mol; PDI: 2.3). Molecular weights were measured by GPC/SEC. Poly(styrene-*co*-glycidyl methacrylate) copolymer (CAS: 25167-42-4; $M_n = 29,000$ g/mol; PDI: 1.9) was kindly supplied by Macro-M (Kuo Group). NMR ¹³C analysis indicated that copolymer composition consisted of 80% styrene and 20% methacrylate, and glycidyl substitution was present at 50% of the

methacrylate groups. Figure 1 shows the molecular structure of the copolymer.

Sample Preparation

All blends were prepared by means of a Brabender DSE 20/40 corrotating twin screw extruder ($\varnothing = 20$ mm, $L/D = 40$). Manually premixed pellets were fed to the extruder by using a gravimetric feeder. Screws were configured with three separated high shear mixing stages (based on kneading blocks), a vacuum aided vent opening after the third mixing stage and distributive mixing screw elements at the final stage (Figure 2).

PLA and PMMA were dried for 4 h at 80 °C by a dehumidifying dryer before extrusion. All samples were extruded at 180 rpm and processing temperature was set at 215 °C. In addition to PLA/PMMA 80/20 (wt %) system, blends containing 1, 2, 3, and 5 g of P(S-*co*-GMA) copolymer per hundred grams of PLA/PMMA blend were prepared, subsequently designated as 1, 2, 3, and 5 pph. Produced pellets were dried for 12 h at 50 °C and then injection moulded in a Haake MiniJet II (8 s of injection plus 25 s holding time at 300 bar) to obtain V type specimens (ASTM D638) for tensile and impact tests. Mould temperature was set at 25–30 °C.

Characterization Techniques

The average molar masses and the polydispersity index were measured by GPC/SEC using a Waters Gel Permeation Chromatography apparatus equipped with a Waters 410 differential refractive index detector. The analyses were carried out at 30 °C and 1 mL/min in chloroform on two PLgel columns (Polymer Laboratories, 10 μ m particle size, 10⁵ Å and 10³ Å). The calibration was performed with PS standards from 2500 to 1.8x10⁶ g/mol. Samples from injection moulded platelets weighing 6–8 mg were analyzed by means of Differential Scanning Calorimeter (DSC) to determine thermal properties. Two heating scans were performed from 0 °C to 220 °C at a heating rate of 10 °C/min using a TA Instruments Q100 model, previously calibrated by indium and sapphire standards. Micrographs were taken by means of a Hitachi S-4800 Scanning Electron Microscope (SEM) after coating the samples with Au. Analyzed fracture surfaces were obtained from impact fractured injection moulded platelets. Rotational rheometry analysis was carried out using a HAAKE MARS III device, equipped by parallel plates. Hot pressed samples of PLA/PMMA 80/20 wt % were die-cut to obtain specimens ($\varnothing = 20$ mm, 400–500 mg) and 1, 2, 3, and 5 pph of P(S-*co*-GMA) copolymer was added to monitor the reaction. The temperature of 215 °C was set, the same as for extrusion process. The radius of the plates (r) and the gap between the plates (h) were 10 and 0.5 mm, respectively.

The apparent viscosity was calculated from the shear stress and shear strain values by the following equations:



Figure 2. The screw configuration used for melt compounding.

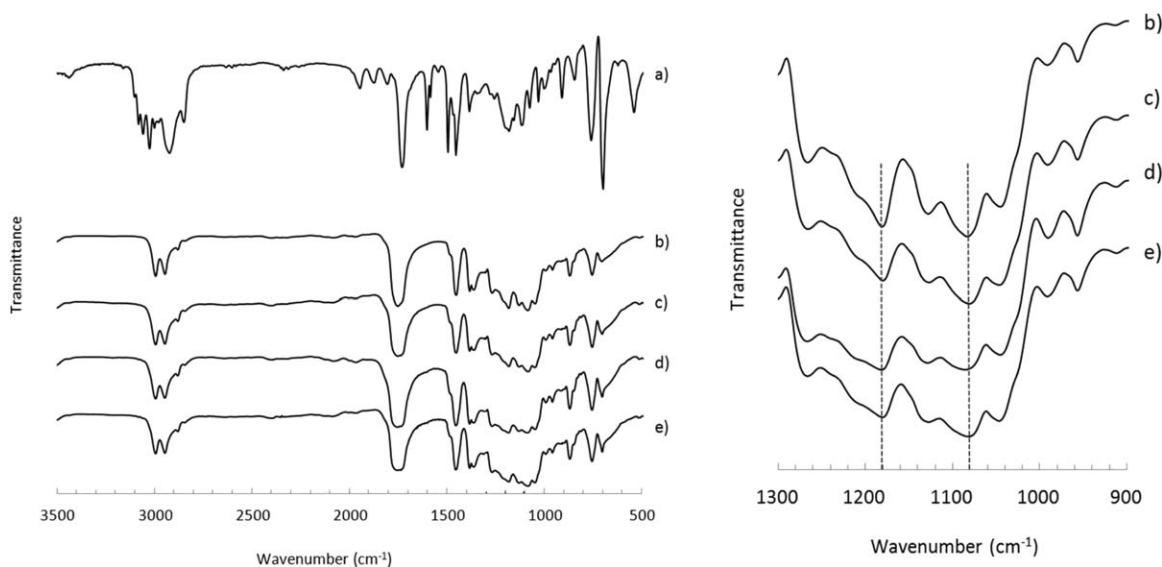


Figure 3. FTIR spectra of (a) P(S-co-GMA) copolymer, and PLA/PMMA (80/20) blend with different copolymer contents: (b) without copolymer, (c) 1 pph, (d) 2 pph and (e) 3 pph.

$$\eta_{ap} = \frac{\sigma}{\gamma_{ap}} \quad (1)$$

$$\sigma = \frac{2}{\pi r^3} M_d \quad (2)$$

$$\gamma_{ap} = \frac{r}{h} \times \frac{2\pi n}{60} \quad (3)$$

where r and h are the radius of the plates and the gap between the plates, respectively; M_d is the torque (Nm); and n is the rotating speed (min^{-1}).

Infrared transmission measurements were performed by a Nicolet Protégé 460 spectrometer from 4000 to 400 cm^{-1} . FTIR spectra were collected by performing 32 scans with a resolution of 4 cm^{-1} . Tensile tests were carried out according to ASTM D638 standard (1 mm/min rate) by means of a MTS Insight electromechanical tensile test machine, equipped with a 2,5 kN load cell and contact mechanical extensometer. Unnotched Charpy impact tests were carried out by means of an ATS faar IMPats-15 impact pendulum with a 2J hammer with a support span of 40 mm. Even though sample geometry used for impact test did not follow any standards, for comparison purposes injection moulded V type specimens were cut to have the length of 63.5 mm and the constant section of 3.18 x 3.29 mm^2 . Thermogravimetric measurements were carried out using samples of about 10 mg on a TA Q50 thermobalance. Mass loss was recorded at 10 $^{\circ}\text{C}/\text{min}$ during a heating scan from 30 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ in N_2 atmosphere.

RESULTS AND DISCUSSION

FT-IR Analysis

Figure 3 shows FTIR spectra of the P(S-co-GMA) copolymer and PLA/PMMA (80/20) blends with different copolymer contents.

Styrenic groups in the P(S-co-GMA) copolymer showed absorption bands of aromatic C-H stretches at 3059 and 3025 cm^{-1} , aromatic ring breathing modes at 1600, 1493, and 1452 cm^{-1} ,

and out of plane C-H bending of monosubstituted aromatic ring at 757 and 698 cm^{-1} . On the other hand, the copolymer spectrum showed bands at 1728 and 1180–1113 cm^{-1} corresponded to C=O and C–O stretching of the methacrylate groups, respectively. The bands at 908, 1255, and 849 cm^{-1} were related to glycidyl characteristic group.^{33–35}

The bands at 1083 and 1181 cm^{-1} were assigned to the C–O stretching of the $-\text{CH}(\text{CH}_3)-\text{OH}$ end group of PLA.³³ These bands showed slightly lower intensity when the copolymer was added to the blend, regardless the amount of copolymer (Figure 3). This loss in intensity suggested that some of the end groups of PLA seemed to react, leading to ester and ether linkages (Figure 4). In addition a slight sharpening of the band at 700 cm^{-1} because of the presence of styrenic groups of the copolymer, no other important changes were noticeable in the spectra of PLA/PMMA blend modified with copolymer. Epoxy groups of copolymer could react with carboxyl and hydroxyl end-groups of the PLA chains^{21,23} creating new ester groups. However, as unmodified PLA/PMMA blend contained ester linkages of PLA, the presence of those new ester groups was not easily detectable by FTIR. In the literature it was reported that the reactivity of the epoxy ring was greater with carboxyl groups [Figure 4(a)] than with hydroxyl groups [Figure 4(b)] of polyesters.^{36–40} These possible primary reactions would lead to chain extension, but grafting/cross-linking could happen by subsequent secondary reactions between the epoxy rings and the new side hydroxyl groups, inducing a branched or even cross-linked architecture, especially at high copolymer concentrations. Similar reaction mechanism was recently proposed by Ojijo *et al.* for PLA/PBSA blends in presence of styrene-acrylic oligomer with epoxy functionalities.³⁰

The Effect of the Addition of P(S-co-GMA) on the Melt Rheology

During the extrusion process of PLA/PMMA blends with copolymer a rise in melt viscosity was noticed indicating reactive

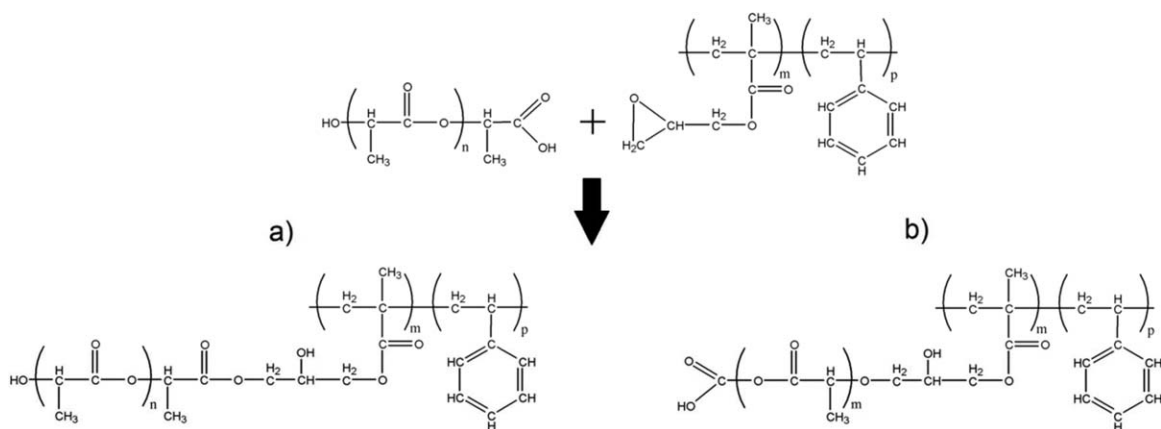


Figure 4. Possible primary reactions between PLA and the P(S-co-GMA) copolymer.

extrusion. The higher was the amount of added copolymer, the higher was the torque needed to process the blend by the twin screw extruder. When processing PLA/PMMA blend with 3 pph of copolymer the needed torque was at the limit of the extrusion machine capacity. Hence, blends containing more than 3 pph of copolymer cannot be processed by extrusion.

The effect of the addition of copolymer on the melt viscosity of PLA/PMMA blend was analyzed by rotational rheometry. Although it was not possible to process by extrusion, a blend containing 5 pph of copolymer was also studied by rotational rheometry.

Concerning the neat copolymer, a slight increase in viscosity, from 220 to 330 Pa s, was measured during the analysis, probably because of the self-reaction. The blend without copolymer showed a decrease in viscosity during the test, suggesting thermo-oxidative degradation. On the contrary, as the presence of the P(S-co-GMA) copolymer was increased, the viscosity of the blend showed an exponential rise. The reaction times observed by rotational rheometry were not equivalent of those needed when processing by twin screw extrusion, however, rheometric characterization evidenced that the viscosity of

PLA/PMMA blends increased in presence of the copolymer (Figure 5). Such increase in viscosity during reactive processing of polyesters has been attributed to chain extension/branching.⁴¹ The blend containing 5 pph of copolymer showed a huge increase in viscosity, beyond the double of that showed by the compound containing 3 pph, being this viscosity value excessive for extrusion process.

Rheological results suggested that the molecular architecture of the blends was changed when the P(S-co-GMA) copolymer was added, leading to a more viscous melt probably because of chain extension and a partially branched architecture which restricted the polymer flow.

The Effect of the Addition of P(S-co-GMA) on the Molecular Weight Distribution

The effect of the addition of P(S-co-GMA) copolymer on the molecular weight distribution of the blends is shown in Figure 6.

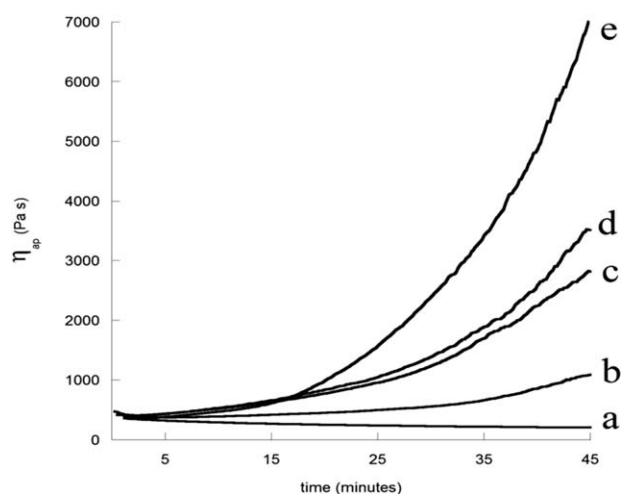


Figure 5. Viscosity plotted against reaction time measured by rotational rheometer of PLA/PMMA blends with different copolymer contents: (a) without copolymer, (b) 1 pph, (c) 2 pph, (d) 3 pph, and (e) 5 pph.

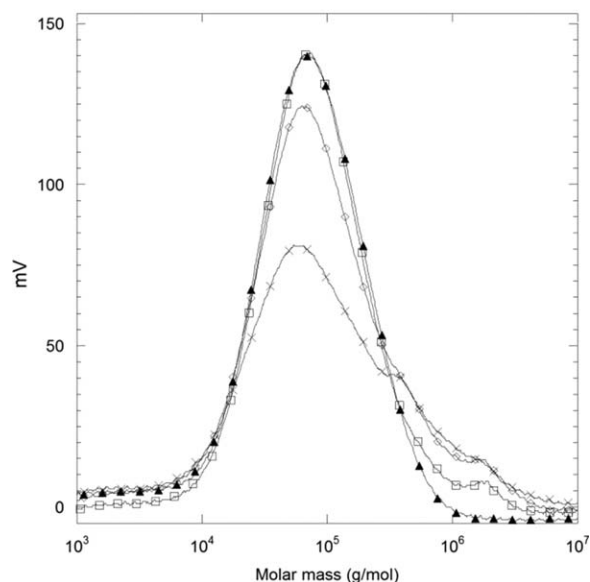


Figure 6. Molecular weight distribution of PLA/PMMA (80/20) blend with different copolymer contents: ▲ without copolymer, □ 1 pph, ⋈ 2 pph and × 3 pph.

Table I. Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w), and Polydispersity Index (PDI) for PLA/PMMA Blends with Different P(S-*co*-GMA) Copolymer Contents

Blend	M_n (g/mol)	M_w (g/mol)	PDI
Without copolymer	51,100	109,500	2.1
1 pph	51,000	113,500	2.2
2 pph	49,150	123,700	2.5
3 pph	47,600	137,200	2.9

The PLA/PMMA blend without copolymer showed a monomodal distribution. On the contrary, after the addition of the copolymer a bimodal distribution was detected, where the second peak corresponded to an important group of molecules with higher hydrodynamic volume. The evolution of the peaks indicated that the greater was the amount of copolymer added, the bigger was the population corresponding to higher molecular weights and smaller the population corresponding to lower molecular weights. The main peak, which corresponded to lower molecular weights, was attributed to the initial unreacted molecules and the second peak to the extended/branched population of polymers.⁴² The weight average molecular weight and the polydispersity index increased as the presence of the reactive copolymer in the blend was increased (Table I), which was in agreement with the results obtained by rheometry.

The Effect of the Addition of P(S-*co*-GMA) on Thermal Properties

Figure 7 shows the first and second heating DSC scans for the P(S-*co*-GMA) copolymer. Two overlapped glass transitions were detected during the first heating scan. The first, related to the methacrylate segments, at 63 °C and the second, related to the styrene segments, at 89 °C. Besides, some reaction enthalpy was detected above 150 °C, probably because of the reaction of the epoxy rings. On the other hand, only one T_g was detected at 81 °C during the second heating scan. The reaction which took place during first heating scan seemed to create a different macromolecular structure. Results suggested that the miscibility between methacrylate and styrene segments was improved because only one T_g was detected during the second heating scan.

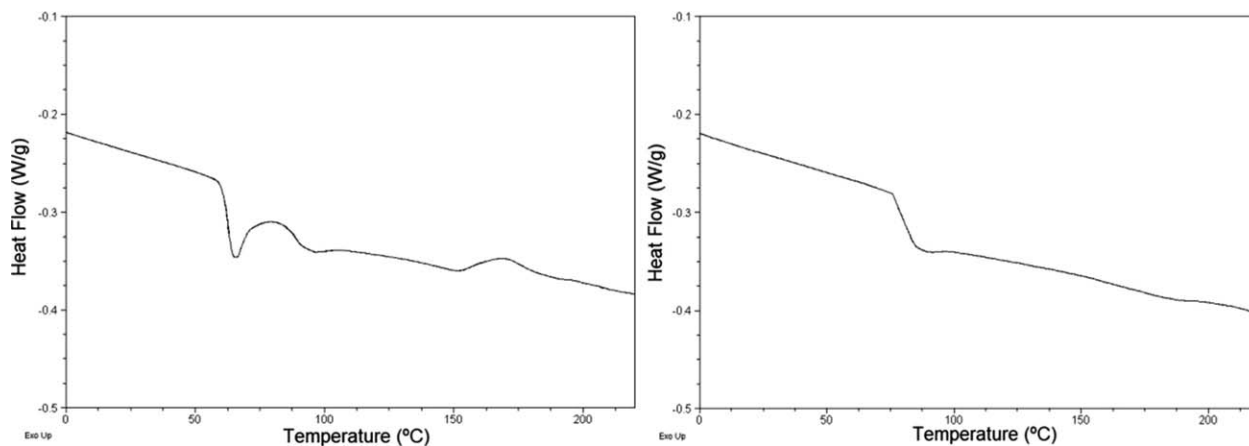


Figure 7. DSC. First (left) and second (right) heating scans of P(S-*co*-GMA) copolymer.

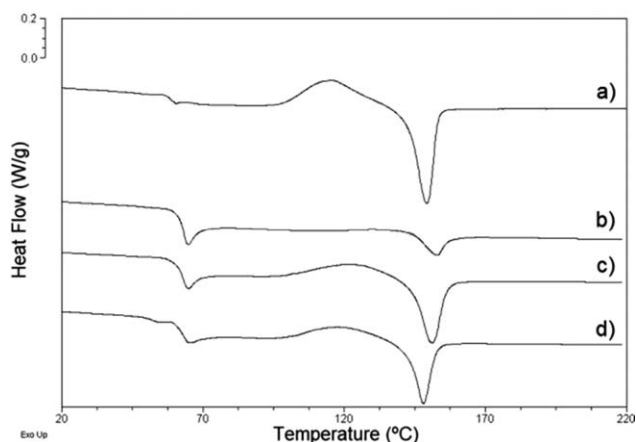


Figure 8. DSC first heating scans of PLA/PMMA blend with different copolymer contents: (a) without copolymer, (b) 1 pph, (c) 2 pph, and (d) 3 pph.

Unmodified PLA/PMMA blend showed one T_g at 58 °C in the first heating run (Figure 8). After the addition of the copolymer the glass transition temperatures of the blends raised to 63 °C, regardless the amount of added copolymer. The glass transition temperature of a particular polymer increases together with the molecular weight until a maximum value. The higher molecular weight of the reacted blends, as observed by GPC, caused a reduction of chain-end concentration and therefore decreased the free volume. Bouzouita *et al.* studied different rubber-toughened PLA/PMMA formulations for injection-moulding processes upon the addition of a commercially available ethylene-acrylate impact modifier (BS).⁹ In all blends 17 wt % of ethylene-acrylate impact modifier was added and the ratio of PLA/PMMA was varied. By DSC technique they determined the glass transition temperatures of studied ternary blends (PLA/PMMA/BS) heating samples at 10 °C/min. They obtained a T_g value similar or higher to 63 °C only when the PLA content in the blend was 58 wt % or lower, which means that the PLA content of the studied blends was considerably lower than the PLA content in our work. On the other hand, all the blends showed very low crystallinity (3.5–7.3%), and the blends containing copolymer showed slower crystallization kinetics during cold crystallization than the blend without

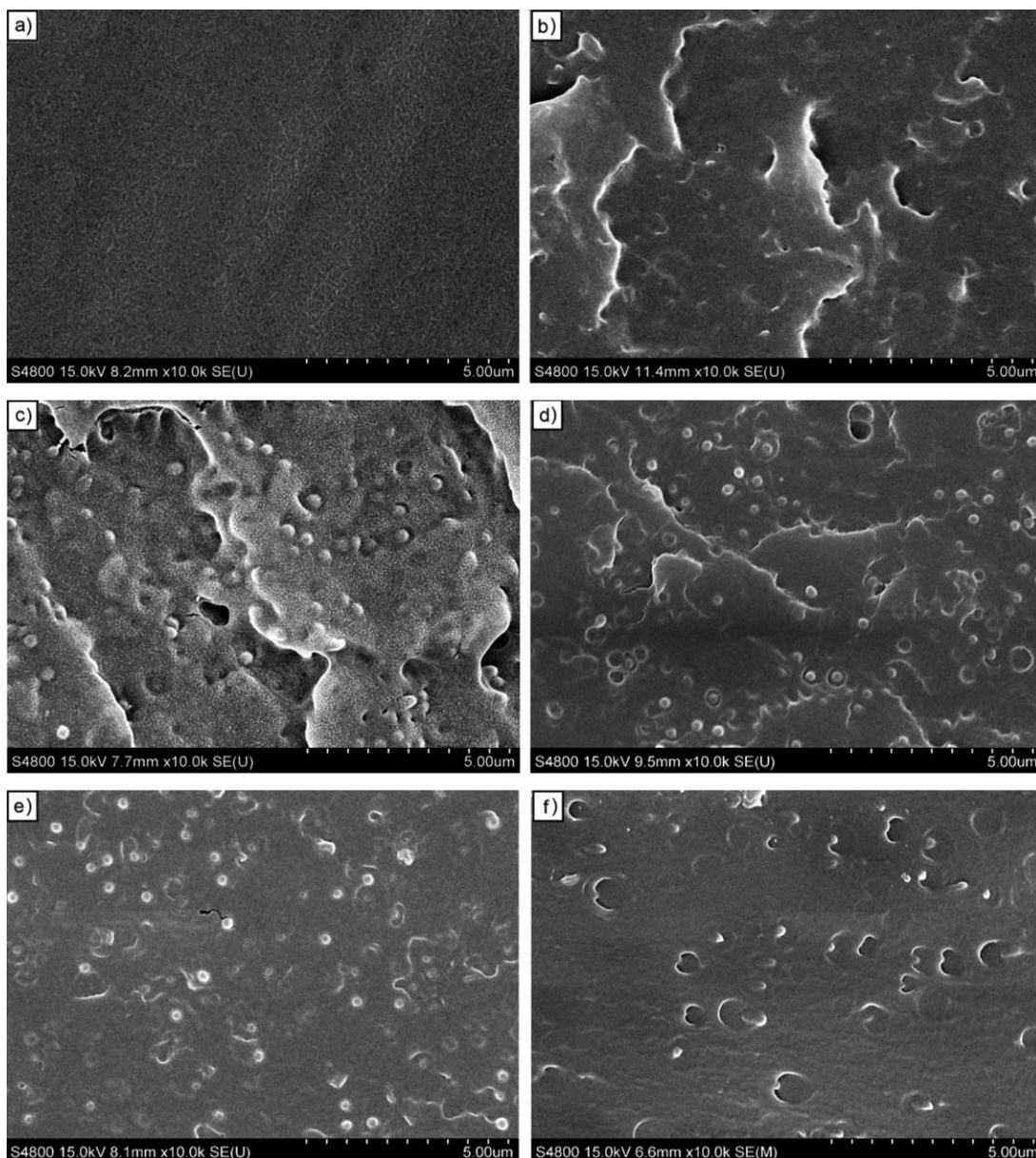


Figure 9. SEM micrographs of: (a) neat PLA, (b) neat PMMA, (c) PLA/PMMA (80/20) blend, (d) blend + 1 pph copolymer, (e) blend + 2 pph copolymer, and (f) blend + 3 pph copolymer.

copolymer. The slight decrease in the melting point of the PLA crystals shown by the blend with 3 pph copolymer compared with the unmodified PLA/PMMA blend could be a result of the imperfect crystal formation. The restricted chain mobility in the branched structure could lead to difficulties in the thickening of the lamella, hence, thinner and imperfect crystals with lower melting point could be formed.³⁰ The reaction happened because of the presence of copolymer seemed to reduce the chain mobility of PLA, leading to a higher glass transition and slower crystallization kinetics.

The Effect of the Addition of P(S-co-GMA) on the Phase Morphology

SEM micrographs of impact-fractured surfaces of the neat PLA and neat PMMA and the blends are shown in Figure 9. Neat

PLA [Figure 9(a)] showed a smooth fracture surface indicating a brittle failure mechanism, while neat PMMA [Figure 9(b)] showed a rougher fracture surface, indicating a more ductile behavior. The SEM micrograph of the unmodified PLA/PMMA blend showed the coexistence of two separated phases [Figure 9(c)]. The dispersed phase, which was supposed to be a PMMA-rich phase, was evenly distributed in the continuous phase, which was supposed to be a PLA-rich phase. The dispersed phase showed a limited surface contact with the continuous phase in the SEM micrographs, suggesting a poor interfacial adhesion between them.¹⁸ Blends with P(S-co-GMA) copolymer [Figure 9(d-f)] also showed a dispersed PMMA-rich phase of around 300–350 nm in diameter in the continuous matrix, confirming that phase separation was also observed after the addition of the copolymer. However, micrograph of PLA/PMMA with 3 pph

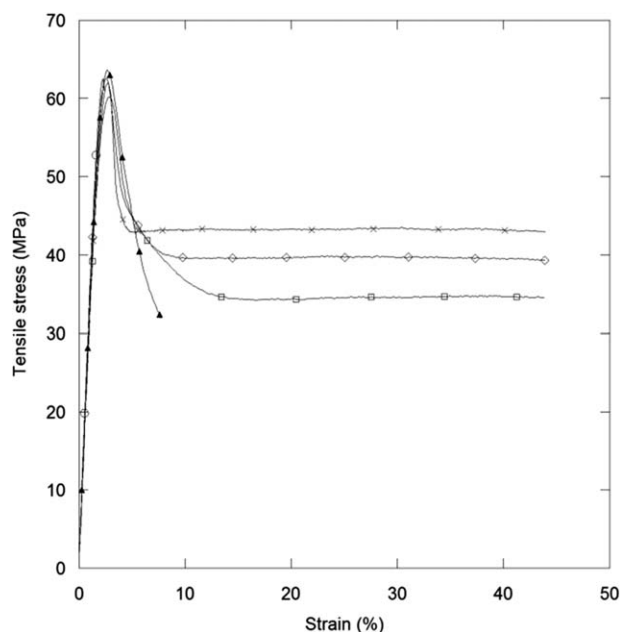


Figure 10. Tensile stress vs. strain curves of PLA/PMMA blend: ○ neat PLA, ▲ 80/20, □ 80/20 + 1pph, ▨ 80/20 + 2pph, × 80/20 + 3pph.

copolymer [Figure 9(f)] showed a more strained morphology, which indicated a better interfacial adhesion between the dispersed phase and the continuous matrix. Besides, a lower volume fraction of the dispersed PMMA-rich phase could be observed in this blend indicating that the addition of 3 pph of the copolymer improved the miscibility between both phases.

The Effect of the Addition of P(S-co-GMA) on Mechanical Properties

Figure 10 shows tensile stress vs. strain curves of neat PLA and PLA/PMMA blends with different copolymer content. PLA showed a brittle behavior since samples broke before yield. Unmodified PLA/PMMA blend showed a slightly higher deformation at break

than neat PLA and the failure happened after yield point. After the addition of P(S-co-GMA) copolymer the strain at break of this blend was hugely improved. Very low quantities, even 1 pph, were enough to improve the strain at break above >44%, which corresponded to the maximum measurable elongation of the mechanical extensometer that was used. All blends modified with copolymer showed a more ductile breakage, with a significant necking effect. After the addition of 3 pph of copolymer the modulus decreased 6.5%, while tensile strength remained constant and deformation at break increased more than 1300% with respect to neat PLA. The achieved values, 62 MPa and 3.4 GPa for tensile strength and modulus, respectively, were higher than the values reported in the literature for PLA-based blends.^{8,9}

Notta-Cuvier *et al.*⁸ studied different PLA based formulations with the aim of their potential use in automotive applications. They observed an increment of ductility of PLA after the addition of tributyl citrate plasticizer when samples were tested at low testing rates of 1 and 2 mm/min. However, the material remained brittle when 5 and 10 mm/min testing rates were used. The high levels of ductility obtained were counterbalanced by drastic drops in apparent rigidity and the maximum nominal axial stress values with respect to neat PLA, 42% and 46%, respectively. The obtained tensile strength and modulus values were around 31 MPa and 1.7 GPa, respectively. They also studied mechanical properties of ternary blends based on PLA, tributyl citrate plasticizer and a commercial impact modifier but the obtained results were not satisfactory. Finally they studied quaternary blends based on PLA, tributyl citrate, impact modifier, and organomodified layered silicate. They obtained interesting levels of ductility but the apparent rigidity and the maximum nominal axial stress values decreased about 41% and 60%, respectively, with respect to neat PLA. The tensile strength and modulus values obtained were around 23 MPa and 1.7 GPa, respectively.

Bouzouita *et al.*⁹ studied ternary blends based on PLA, PMMA, and a commercial ethylene-acrylate impact modifier bearing epoxy moieties specifically designed for PLA. After the addition of

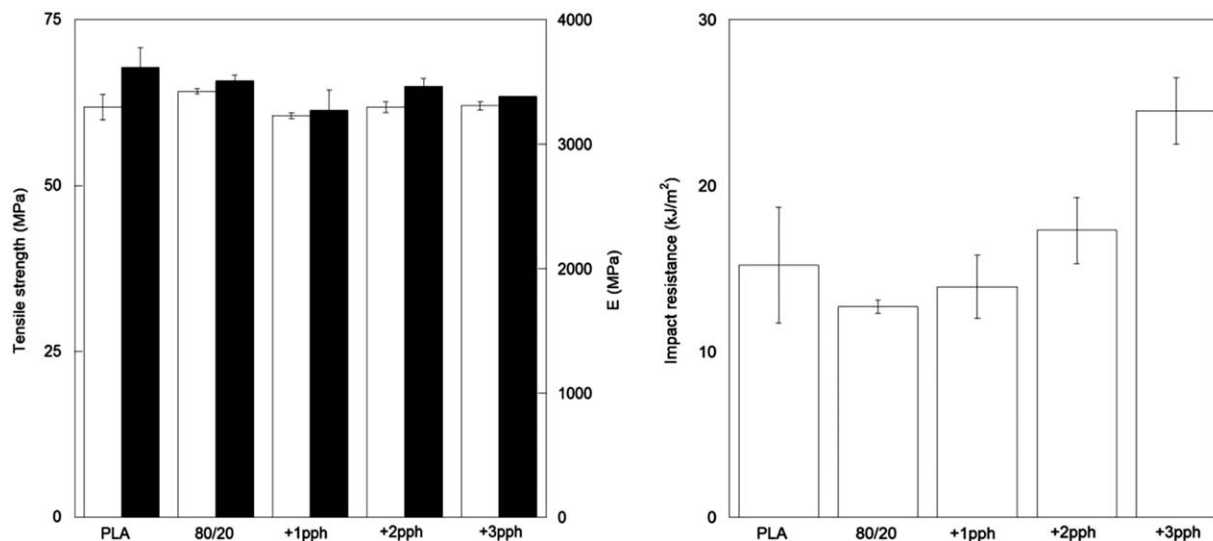


Figure 11. Tensile strength (white columns) and moduli (black columns) (left) and impact resistance (right) of neat PLA and PLA/PMMA (80/20) blend with different P(S-co-GMA) copolymer contents.

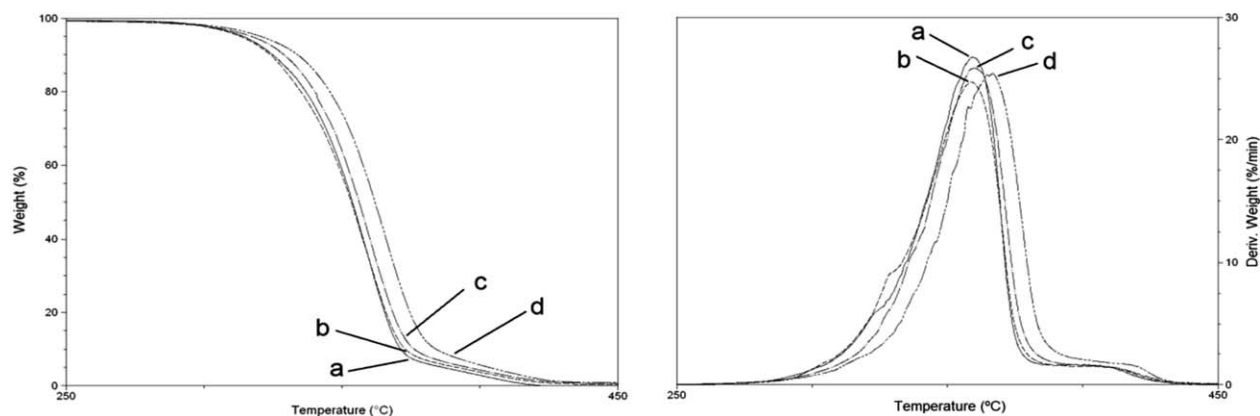


Figure 12. Thermogravimetric analysis. Weight loss and derivative weight loss of PLA/PMMA (80/20) with different copolymer contents: (a) without copolymer, (b) 1 pph copolymer, (c) 2 pph copolymer, and (d) 3 pph copolymer.

17 wt % of impact modifier to PLA/PMMA blends, a brittle to ductile transition was highlighted. However, the apparent rigidity and yield stress decreased about 30% and 35%, respectively, with respect to neat PLA. The tensile strength and modulus values obtained for 58 wt % PLA, 25 wt % PMMA, and 17 wt % of impact modifier were 49 MPa and 2.5 GPa, respectively. Therefore, the PLA-based material prepared in our work, with polylactide content higher than 75 wt %, in addition to improve about 60% the impact resistance respect to neat PLA, also showed considerably higher tensile and modulus values than the values reported in the literature for similar PLA-based systems.

On the other hand, the addition of the copolymer improved the behavior of the blends above yield point. The stress drop at yield point was decreased as the amount of copolymer in the system was increased. The blend with 3 pph of copolymer maintained 69% of its tensile strength above yield point (dropped from 62 to 43 MPa), while pure 80/20 blend failed at 50% after yield point (dropped from 64 to 32 MPa). This was important as the strain at yield remained constant around 2.7% when copolymer was added. Addition of copolymer slightly decreased tensile strength and modulus, even though the loss was not significant as the values were still similar to neat PLA.

Although unmodified PLA/PMMA blend showed a rougher breakage surface than neat PLA ones, it showed slightly lower impact resistance (Figure 11) because of the poor interfacial adhesion between the matrix and the dispersed phase.²⁰ After adding the P(S-*co*-GMA) copolymer to the blends, the impact resistance was improved. The blend modified with 1 pph copolymer showed a slightly higher impact resistance than unmodified PLA/PMMA blend, and the impact strength increased together with the copoly-

mer content in the blend. The addition of 3 pph copolymer increased the impact resistance of PLA/PMMA blend from 12.7 to 24.5 kJ/m², which was an improvement of 93%. This improvement seemed to be related with the improved interfacial adhesion between PLA-rich and PMMA-rich phases achieved when 3 pph of copolymer was added, as observed in the SEM micrograph [Figure 9(f)]. Jazskiewicz *et al.*²⁴ studied the effect of similar epoxidized styrene-acrylic copolymers (i.e., CESA and Joncryl) on the impact resistance of PLA 3051D from NatureWorks LLC. They concluded that the addition of Joncryl led to no detectable improvement and more than 5% of CESA was needed to achieve detectable results. These results suggest that the addition of P(S-*co*-GMA) copolymer, although led to branching/chain extension of PLA, the obtained branching/chain extension was not enough to improve considerably the impact resistance. Therefore, the main reason for impact resistance improvement in PLA/PMMA blends modified with poly(styrene-*co*-glycidyl methacrylate) copolymer seemed to be because of the interfacial adhesion improvement between the two phases present in blends, as observed in SEM micrographs.

On the other hand, Notta-Cuvier *et al.*⁸ increased the impact strength from 2.7 kJ/m² for unfilled PLA to 42.8 kJ/m² for a quaternary blend based on PLA, an impact modifier, tributyl citrate plasticizer, and organomodified clay. However, for long-term applications such as automotive parts, low molecular weight plasticizers have the undesirable tendency to migrate, thus material properties could change.

Bouzouita *et al.*⁹ increased the impact strength of neat PLA from 3.4 to 24 kJ/m² after adding 17 wt % of impact modifier. Furthermore, they observed an optimum impact resistance of 44 kJ/m² when PLA was modified with both PMMA and impact modifier for the composition of 58 wt % PLA, 25 wt %, and 17 wt %. However, as mentioned previously, the impact strength improvement was linked to a significant drop in tensile strength and modulus values.

The Effect of the Addition of P(S-*co*-GMA) on Thermal Stability

TGA results showed that thermal stability of the PLA/PMMA blends was improved when copolymer was added (Figure 12).

Table II. Thermal Degradation of PLA/PMMA (80/20) Blend with Different P(S-*co*-GMA) Copolymer Contents

Blend	T_{onset} (°C)	T_{offset} (°C)	T_p (°C)
Without copolymer	314	387	359
1 pph	314	391	359
2 pph	319	398	360
3 pph	321	403	367

Thermal degradation onset and offset temperatures were shifted to higher temperatures as the amount of added copolymer was increased (Table II). Compared with neat PLA, unmodified PLA/PMMA blend showed lower T_{onset} but higher T_{offset} because of the higher thermal stability of PMMA. With the addition of P(S-co-GMA) copolymer the PLA/PMMA blend showed similar T_{onset} to PLA along with improved T_{offset} and temperature at maximum degradation rate (T_p). This enhancement might be related to the fact that PLA degraded and lost molecular weight during melt processing at 215 °C, but the loss in molecular weight was counterbalanced by chain extension reactions when the blend was in presence of the copolymer. This is in agreement with what was proposed by Ojijo *et al.*³⁰ who studied PLA/PBSA blends modified by a similar reactive styrene-acrylic oligomer (Joncryl[®] ADR 4368 CS).²⁸ However, they observed that T_{onset} values did not vary within the range of the tested oligomer concentrations, i.e., 0.3–1 wt %. On the contrary, as it can be observed in Figure 12, the concentration of P(S-co-GMA) (1, 2, and 3 pph) had a clear influence on the thermal stability of the obtained blends, obtaining higher stability at higher copolymer concentrations. A possible explanation of the different performance of analyzed systems can be the different reactive group concentration in those systems.

CONCLUSIONS

Reactive extrusion of PLA/PMMA blends with poly(styrene-co-glycidyl methacrylate) was shown to be a good approach to overcome the intrinsic brittleness of PLA maintaining tensile strength and modulus values similar to neat PLA. PLA/PMMA blend, with polylactide content higher than 75 wt %, with improved mechanical and thermal properties were obtained by this approach. All blends showed a dispersed PMMA-rich phase in a continuous PLA-rich phase. The addition of poly(styrene-co-glycidyl methacrylate) copolymer improved the interfacial adhesion between both phases improving the elongation capability and impact resistance of blends. After the addition of 3 pph of copolymer to the blend the deformation at break increased more than 1300% and the impact resistance increased around 60% compared with neat PLA, and keeping the modulus and tensile strength values almost constant. This overall improvement of PLA's mechanical properties has not been achieved by other reported approaches like plasticization or addition of impact modifiers. Besides, the thermal stability of the blend was also improved since the onset temperature increased from 314 °C for neat PLA to 321 °C for the PLA/PMMA blend with 3 pph of copolymer. Regarding processability, viscosity was considerably increased by the addition of the copolymer; therefore, the amount of added reactive copolymer is a key factor in order to achieve melt-processable modified PLA/PMMA blends.

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REFERENCES

1. European Commission, **2013**, Available at ec.europa.org.
2. E. Plastics Europe Association of Plastics Manufacturers, E. PRO, **2007**, Available at www.plasticseurope.org.
3. Shen, L.; Worrell, E.; Patel, M. *Biofuels Bioprod. Biorefining* **2010**, *4*, 25.
4. Gómez, E. F.; Michel, F. C. Jr. *Polym. Degrad. Stabil.* **2013**, *98*, 2583.
5. Södergård, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123.
6. Lunt, J. *Polym. Degrad. Stabil.* **1998**, *59*, 145.
7. Van de Velde, K.; Kiekens, P. *Polym. Test.* **2002**, *21*, 433.
8. Notta-Cuvier, D.; Odent, J.; Delille, R.; Murariu, M.; Lauro, F.; Raquez, J. M.; Bennani, B.; Dubois, P. *Polym. Test.* **2014**, *36*, 1.
9. Bouzouita, A.; Samuel, C.; Notta-Cuvier, D.; Odent, J.; Lauro, F.; Dubois, P.; Raquez, J. M. *J. Appl. Polym. Sci.* **2016**, *133*, 19. DOI: 10.1002/app.43402.
10. Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2004**, *4*, 835.
11. Kale, G.; Auras, R.; Singh, S. P.; Narayan, R. *Polym. Test.* **2007**, *26*, 1049.
12. Auras, R. A.; Lim, L.-T.; Selke, S. E.; Tsuji, H. In *Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications*; Wiley: New York, **2011**; Vol. 10.
13. Zembouai, I.; Bruzaud, S.; Kaci, M.; Lopez-Cuesta, J.-M. *J. Polym. Environ.* **2013**, *22*, 131.
14. Zhang, C.; Huang, Y.; Luo, C.; Jiang, L.; Dan, Y. *J. Polym. Res.* **2013**, *20*, 1.
15. Pluta, M.; Piorkowska, E. *Polym. Test.* **2015**, *41*, 209.
16. Lai, S. M.; Lan, Y. C. *J. Polym. Res.* **2013**, *20*, 1.
17. Spinella, S.; Cai, J.; Samuel, C.; Zhu, J.; McCallum, S. A.; Habibi, Y.; Raquez, J.-M.; Dubois, P.; Gross, R. A. *Biomacromolecules* **2015**, *16*, 1818.
18. Patrício, T.; Bártolo, P. *Procedia Eng.* **2013**, *59*, 292.
19. Nofar, M.; Maani, A.; Sojoudi, H.; Heuzey, M. C.; Carreau, P. J. *J. Rheol.* **2015**, *59*, 317.
20. Anakabe, J.; Zaldua Huici, A. M.; Eceiza, A.; Arbeláiz, A. *J. Appl. Polym. Sci.* **2015**, *132*, 42677.
21. Sun, S.; Zhang, M.; Zhang, H.; Zhang, X. *J. Appl. Polym. Sci.* **2011**, *122*, 2992.
22. Al-Itry, R.; Maazouz, A. 3rd International Conference on Biodegradable and Biobased Polymers (BIOPOL), Strassbourg, **2011**.
23. Mihai, M.; Huneault, M. A.; Favis, B. D. *Polym. Eng. Sci.* **2010**, *50*, 629.
24. Jaszkiwicz, A.; Bledzki, A. K.; van der Meer, R.; Franciszcak, P.; Meljon, A. *Polym. Bull.* **2014**, *71*, 1675.
25. Corre, Y. M.; Duchet, J.; Reignier, J.; Maazouz, A. *Rheol. Acta* **2011**, *50*, 613.
26. Pilla, S.; Kim, S. G.; Auer, G. K.; Gong, S.; Park, C. B. *Polym. Eng. Sci.* **2009**, *49*, 1653.

27. Wei Kit Chee, N. A. I. *Adv. Mater. Sci. Eng.* **2013**, *2013*,
28. Jo, M. Y.; Ryu, Y. J.; Ko, J. H.; Yoon, J. S. *J. Appl. Polym. Sci.* **2012**, *125*, E231.
29. Hashima, K.; Nishitsuji, S.; Inoue, T. *Polymer* **2010**, *51*, 3934.
30. Ojijo, V.; Ray, S. S. *Polymer* **2015**, *80*, 1.
31. Najafi, N.; Heuzey, M. C.; Carreau, P. J. *Compos. Sci. Technol.* **2012**, *72*, 608.
32. Li, W.; Wu, D.; Sun, S.; Wu, G.; Zhang, H.; Deng, Y.; Zhang, H.; Dong, L. *Polym. Bull.* **2014**, *71*, 2881.
33. Hao, Y.; Liang, H.; Bian, J.; Sun, S.; Zhang, H.; Dong, L. *Polym. Int.* **2014**, *63*, 660.
34. Thanh, N. C.; Ruksakulpiwat, C.; Ruksakulpiwat, Y. *J. Mater. Sci. Chem. Eng.* **2015**, *3*, 102.
35. Wang, Y.; Fu, C.; Luo, Y.; Ruan, C.; Zhang, Y.; Fu, Y. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2010**, *25*, 774.
36. Japon, S.; Boogh, L.; Leterrier, Y.; Månson, J. A. E. *Polymer* **2000**, *41*, 5809.
37. Lamnawar, K.; Baudouin, A.; Maazouz, A. *Eur. Polym. J.* **2010**, *46*, 1604.
38. Nguyen, Q. T.; Japon, S.; Luciani, A.; Leterrier, Y.; Månson, J. A. E. *Polym. Eng. Sci.* **2001**, *41*, 1299.
39. Bikiaris, D. N.; Karayannidis, G. P. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 1337.
40. Inata, H.; Matsumura, S. *J. Appl. Polym. Sci.* **1985**, *30*, 3325.
41. Aharoni, S. M.; Forbes, C. E.; Hammond, W. B.; Hindenlang, D. M.; Mares, F.; O'Brien, K.; Sedgwick, R. D. *J. Polym. Sci. Part Polym. Chem.* **1986**, *24*, 1281.
42. Cailloux, J.; Santana, O. O.; Franco-Urquiza, E.; Bou, J. J.; Carrasco, F.; Gámez-Pérez, J.; Maspocho, M. L. *Express Polym. Lett.* **2013**, *7*, 304.