

Research article

## Increased processing temperature assisted reactive toughening of poly(lactic acid)

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**Abstract.** Toughening efficiency of poly(ethylene-*n*-butylene-acrylate-*co*-glycidyl methacrylate) (EBA-GMA) in poly(lactic acid) (PLA) matrix has been found to significantly increase at elevated blending temperature. In the case of PLA/EBA-GMA blends having 10.0 or 12.5 wt% EBA-GMA contents, the accelerated PLA degradation at raised processing temperature resulted in reduced mechanical performance. At 15.0 wt% EBA-GMA ratio, however, increased elongation and by 250% improved notched Izod impact strength was achieved when the blending temperature was raised from 240 to 260 °C. This beneficial effect is attributed to the accelerated compatibilization reactions between the components in the presence of short-chain PLA molecules, which allow the rapid formation of a toughening enhancer interphase (TEI) during melt processing. As a result, the brittle-ductile transition can be reached at lower elastomer content than expected. Decreased melt flow index (MFI) values besides stabilized blend morphology indicated efficient PLA–EBA-GMA compatibilization at elevated processing temperature. Accordingly, enhanced nucleation ability of the PLA/EBA-GMA interphase and hindered chain crystallization of PLA were found by differential scanning calorimetry (DSC) analyses. In association with the intensified compatibilization reactions cross-linking of the terpolymer was also revealed using the thermally stimulated depolarization current (TSDC) technique.

**Keywords:** biopolymers, biocomposites, processing technologies, mechanical properties, thermal properties

### 1. Introduction

Nowadays, there is a shift in the focus toward developing and applying environmentally friendly polymers. Commonly used non-biodegradable plastics, accumulating in massive landfills, are dangerous for human health and cause depletion in soil fertility [1]. The aim is to produce materials that, when released into the environment, naturally degrade into non-toxic substances. Among the few commercially available biobased thermoplastic polymers, poly(lactic acid) (PLA) has undergone the most investigation [2]. PLA is a biodegradable aliphatic thermoplastic

polyester derived from renewable sources. It has many excellent mechanical properties (such as strength and stiffness), making it suitable for industrial applications [3].

In comparison with similar biopolymers, such as polyhydroxyalkanoates (PHAs), poly(ethylene glycol) (PEG), and poly(caprolactone) (PCL), PLA has better thermal processibility [4]. On the other hand, PLA's poor toughness significantly hinders its application in many fields [2]. Although the tensile strength and Young's modulus of PLA are comparable with those of polystyrene (PS) and poly(ethylene

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terephthalate) (PET), due to its brittleness, PLA has limitations in electric, electronic, and other industrial applications [4–6]. In order to widen the application possibilities of PLA, its toughness needs to be improved, which can be achieved by modifications. Various toughening strategies have been used to overcome this drawback [7], such as copolymerization [8], plasticization [9], the addition of organic/inorganic fillers [10], and melt blending [11, 12].

Melt blending with flexible polymers is one of the most industrially feasible and economic solutions for improving the impact resistance of an inherently rigid polymer [6]. The elastomer blended with the brittle polymer effectively dissipates the stress so that the material shows ductility and plastic deformation. The disadvantage of this toughening method is that the dispersed particles often have poor compatibility with the matrix and are prone to aggregate, resulting in insufficient dispersion. The interfacial tension can be reduced by improving the compatibility between the components, which allows for better mechanical properties [6, 13]. In contrast, the dispersion can be improved by changing the proportions of the compounds, their viscosity ratios, or the production parameters, for example, blending temperature or shear rate.

Since PLA has poor miscibility with the majority of polymer modifiers, to increase miscibility and interfacial adhesion, reactive blending has been demonstrated to be an effective and convenient way to achieve high-impact-resistant PLA materials [14]. The most frequently used modifiers are functionalized copolymers. Glycidyl methacrylate-containing elastomers may be suitable for this purpose, as their functional groups allow reactive compatibilization [15]. It is generally accepted that the carboxyl and/or hydroxyl group of PLA reacts with the epoxide group of the reactive elastomer [16, 17]. Nevertheless, it has to be noted that while the reactive interfacial compatibilization between PLA and the other (mostly petroleum-based) rubbery polymer generally largely improves the toughening efficiency, it sacrifices the biodegradability of PLA adversely [18].

Oyama [19] used poly(ethylene-glycidyl methacrylate) (EGMA) for reactive blending with PLA, while the effects of crystallinity and annealing treatment on the properties of the compound were investigated. Using differential scanning calorimeter (DSC) measurements, they found that the crystallinity of

PLA/EGMA (80/20) blends increased from 6 to 40% after annealing the blend at 90 °C for 2.5 hours. Also, the impact strength increased by approximately 50 times, in which a remarkable role was attributed to crystallinity.

The blending temperature also has a significant effect on the efficiency of the toughening mechanism. Increasing the temperature can promote compatibility and the possibility of elastomer cross-linking, while at lower processing temperatures, the number of PLA-elastomer compatibilization bonds tends to be much lower [20]. Yuryev *et al.* [3] applied poly(ethylene-*n*-butylene-acrylate-*co*-glycidyl methacrylate) (EBA-GMA) as a reactive compatibilizer for PLA. They used elevated temperatures (up to 270 °C), which are not typical for PLA, to show the effects on bonding and interfacial adhesion. To reduce the role of degradation, they used chain extenders (CEs) in blends that created bonds between PLA chains. They found that with the help of the CE, degradation was not as significant as before; moreover, the interfacial compatibilization has improved.

Liu *et al.* [21] investigated the effect of zinc ionomer of ethylene/methacrylic acid copolymer (EMAA-Zn) in PLA/EBA-GMA/EMAA-Zn blends manufactured at different blending temperatures ranging between 185 and 240 °C. In order to show the effect of the functional group of EBA-GMA, in one case, they replaced it with poly(ethylene-butylene-acrylate) (EBA). The impact strength and tensile strength significantly decreased in this case. Rheological studies showed that the addition of EMMA-Zn catalyst promoted the cross-linking reactions of the elastomer and helped the interfacial compatibilization as well. The greater the mixing temperature was, the more noticeable the toughening effect was.

In the present investigation, our aim was to show that EBA-GMA can be used as a reactive toughening agent for PLA and that the effectiveness of the reactive compatibilization can be noticeably improved by using optimized processing conditions. The elevated melt blending temperature (*i.e.*, higher than 200 °C, commonly used in the case of PLA) is expected to promote the reactive compatibilization, and elastomer cross-linking but accelerate the PLA degradation during processing at the same time [22]. Therefore, in this study, the effect of blending temperature and composition was optimized in terms of the mechanical properties of the PLA/EBA-GMA

blends, while corresponding changes in the crystalline structure, phase morphology, and rheology were explored.

## 2. Experimental

### 2.1. Materials

In this work, Ingeo™ Biopolymer 3100HP PLA (NatureWorks LLC Minnetonka, MN, USA), with a D-lactide content of 0.5%, glass transition temperature ( $T_g$ ) in the range of 55–60 °C, and melting temperature ( $T_m$ ) in the range of 170–190 °C, was used. The melt flow index of this PLA grade is in the range of 22–24 g/10 min (at 210 °C, with a 2.16 kg load). As an impact modifier, EBA-GMA was used. For that, Elvaloy PTW was provided by DuPont Co. (Wilmington, USA) with 28% acrylate monomer content.

#### Sample preparation

Compounding was performed using an LTE 26-44 (Labtech Scientific, Muang, Samutprakarn, Thailand) type twin-screw extruder. Before processing, the PLA materials were dried at 80 °C for 12 hours. Extrusions were performed by setting three different end zone temperatures; 220, 240, and 260 °C, respectively (Table 1). It has to be noted that since no CE was used in the blends, a significant drop in the processibility occurred at blending temperatures exceeding 260 °C due to a drastic decrease in melt viscosity and noticeable degradation of PLA. The screw speed was 60 rpm in all cases. After being pelletized and dried at 80 °C for 12 hours, all pellets were injection molded into a dumbbell shape at 200 °C, while the mold temperature was 40 °C. The holding pressure was 60 MPa, and the back pressure was 3 MPa.

### 2.2. Methods

#### Izod impact test

Izod impact tests were performed using a 5113.100/01 type (Zwick, Ulm, Germany) impact tester, with an

Izod impact hammer of 2.75 J at room temperature, according to ISO 180 standard. Ten notched (Type A) specimens were tested in each case.

#### Tensile test

Tensile tests were carried out by L3369 (Instron, Norwood MA, USA) universal mechanical tester according to ISO 527-2 standard. A crosshead speed of 1 mm/min was used to determine modulus; 20 mm/min was applied for tensile tests. For each investigation, 5 specimens were tested at room temperature.

#### Torque rheology

Torque measurements during melt mixing were performed in a Brabender Plasti-Corder Lab-Station type (Brabender GmbH & Co. KG, Duisburg, Germany) internal mixer equipped with a W 50 EHT 3Z kneading chamber. In one case, a given amount of pre-dried PLA pellets had been weighted according to the compositions and then added into the 50 cm<sup>3</sup> mixing chamber and mixed at 260 °C with rotors rotating at 50 rpm for 4 min. At this time point, the required amount of EBA-GMA pellets (PLA and EBA-GMA together added up to 60 g in each case) were added and mixed for an additional 2 min. In the other case, equally 51 g of pre-dried PLA pellets had added in the mixing chamber set to 220, 240, or 260 °C, respectively, and mixed at 50 rpm for 4 min. At this time point, equally 9 g of EBA-GMA pellets were added and mixed for an additional 2 min. The variation of torque moment during melt mixing was continuously recorded.

#### Melt flow index (MFI)

Melt flow rate measurements were conducted by LMI-5000 (Dynisco, Franklin MA, USA) tester. Before the investigation, PLA pellets were dried at 80 °C for 2 hours. The applied temperature was 190 °C, the applied mass was 2.16 kg, and the cutting time was 10 s.

#### Scanning electron microscopy (SEM)

The morphology of PLA/EBA GMA blends was observed by EVO MA10 (Zeiss, Oberkochen, Germany) scanning electron microscope. Samples were embedded in epoxy resin, then the rubber phase of the samples was selectively extracted with toluene (1 hour immersion at room temperature). The applied gold

**Table 1.** Zone temperatures during extrusion.

|                 | Zone temperatures during extrusion [°C] |           |           |             | Die |
|-----------------|-----------------------------------------|-----------|-----------|-------------|-----|
|                 | 1–3. zone                               | 4–6. zone | 7–9. zone | 10–11. zone |     |
| 220 °C end zone | 205                                     | 210       | 215       | 220         | 220 |
| 240 °C end zone | 225                                     | 230       | 235       | 240         | 240 |
| 260 °C end zone | 245                                     | 250       | 255       | 260         | 260 |

coating was 5 nm, and the accelerating voltage was 15.75 kV.

#### Differential scanning calorimetry (DSC)

Investigations of the crystalline phase were carried out by DSC131 EVO (Setaram, Lyon, France) DSC. Heat-cool-heat cycle was applied at heating and cooling rates of 10 °C/min under a nitrogen atmosphere, in the temperature range of 30–200 °C. 5–8 mg samples were taken from the same part of the injection-molded specimens each time. The crystallinity of PLA was calculated from the first heating scan with the help of Equation (1):

$$X_c [\%] = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1 - \alpha)} \quad (1)$$

where  $\Delta H_m$  [J/g] is the enthalpy of melting,  $\Delta H_{cc}$  [J/g] is the enthalpy of cold crystallization,  $\Delta H_f$  [J/g] is the enthalpy of 100% crystalline PLA, and  $\alpha$  [–] is the ratio of the EBA-GMA additive.

#### Thermally stimulated depolarization current (TSDC)

The glass transition temperature of EBA-GMA was determined by TSC II (Setaram, Lyon, France) equipment using the thermally stimulated depolarization current (TSDC) technique. This method allows the temperature-dependent characteristics of the polymers, namely their phase transitions and molecular mobility, to be studied with high sensitivity. Therefore, it is also suitable for examining small relaxations in multi-component systems [23, 24].

0.5 mm thick specimens were analyzed, obtained from the center of the neck area of the 4 mm thick injection molded dumbbell-shaped samples. The two 1.75 mm thick edge layers were removed using an LS Twin (Remet, Italy) polisher.

During all measurements, the sample was polarised at 0 °C ( $T_p$ ) with 300 V ( $U_p$ ) polarisation voltage for 5 minutes ( $t_p$ ). Then a cooling step followed with a 10 °C/min ( $r_c$ ) cooling rate to the -80 °C freezing temperature ( $T_0$ ) while the electric field was still present. The holding time at  $T_0$  was 1 minute ( $t_0$ ), and the polarisation was turned off in this step. In the next step, a 5 °C/min heating rate was used to reach the final temperature ( $T_f = 0$  °C), while the depolarisation current was recorded as a function of the temperature.

### 3. Results and discussion

#### 3.1. Effects of blending temperature and EBA-GMA content on the toughening of PLA

In general, higher loadings of 20–25 wt% of EBA-GMA type reactive terpolymer are necessitated to reach the brittle-ductile transition in polyesters [25–29]. Yuryev *et al.* [3] demonstrated a distinct temperature dependence in the toughness of PLA/EBA-GMA blends having over 20 wt% EBA-GMA content and containing CE as well. In this work, the experiments were designed with the aim to analyse the hypothesis that low-molecular-weight PLA chains, forming *in situ* during high-temperature processing, may enhance the rate of compatibilization reactions on the PLA/EBA-GMA interface and, consequently, the brittle-ductile transition may be reached at lowered terpolymer content. Therefore, two-component blends were prepared from PLA and EBA-GMA, and without using CE, with the blending ratio of the elastomer ranging from 10.0 to 15.0 wt% with 2.5 wt% ranging steps. The PLA/EBA-GMA blends were extrusion processed at 220, 240, and 260 °C, respectively, and then comprehensively analyzed.

Figure 1 illustrates the result of Izod impact tests performed on notched injection-molded specimens. The notched Izod impact strength of neat PLA was measured to be 3.4±0.2 kJ/m<sup>2</sup>. It can be seen that the elevated blending temperature was not effective at lower EBA GMA contents; however, at a 15.0 wt% EBA-GMA ratio significant increase in the impact strength can be observed for the blend prepared at

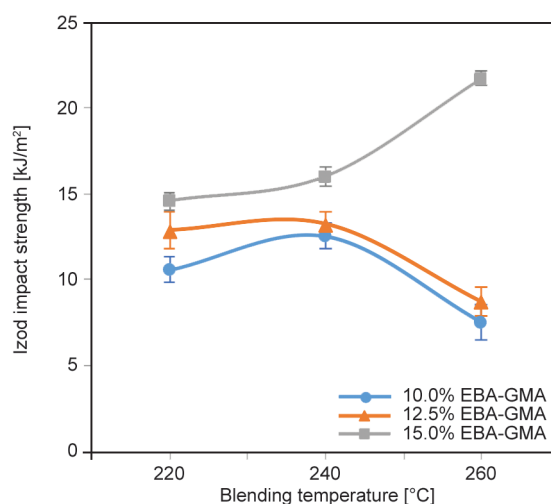


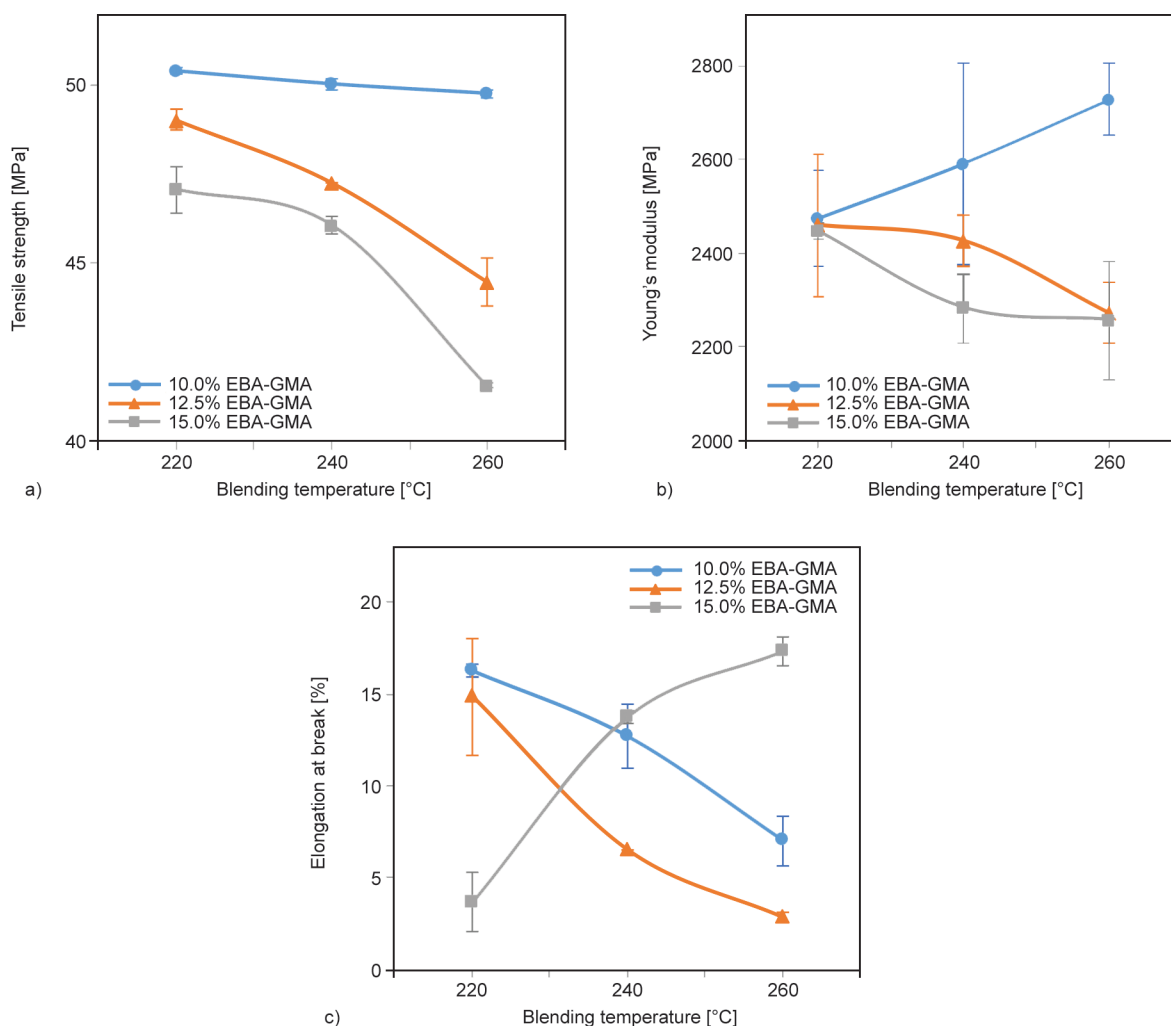
Figure 1. Notched Izod impact strength of the PLA/EBA-GMA blends.



260 °C. Despite the identical elastomer content of 15.0 wt%, at elevated blending temperature, 30% higher impact strength was achieved compared to the blends prepared at 240 °C or lower. It is claimed that the high processing temperature of 260 °C accelerates the degradation of PLA, but also the compatibilization reactions between PLA and the epoxy functionalized elastomer [3]. Since no CE was used in the blends that could compensate for the molecular weight decrease, the harmful effect of thermal degradation of PLA is clearly manifested by the noticeable (about 35–40%) decrease of the impact resistance of the blends with 10.0 and 12.5 wt% EBA-GMA contents. At 15.0 wt% of EBA-GMA, however, the degree of PLA/EBA-GMA interface bonding increases, so it can compensate for thermal degradation effects. Nevertheless, it is proposed that the compatibilization reactions are increasingly facilitated in the presence of the short-chain PLA molecules formed *in situ* during processing at 260 °C. As a result, the brittle-ductile transition is reached at lower (15.0 wt%) EBA-GMA content than expected based on previous research studies [19, 25]. This conclusion is analogous to our earlier findings, where the low-molecular-weight PET fractions, whether from waste [25] or formed *in situ* during melt processing [29], were successfully utilized to enhance the efficiency of the reactive impact modifier in PET/EBA-GMA blends. Tensile tests were performed to examine the quasi-static mechanical properties of the PLA/EBA GMA blends prepared at different processing temperatures. As a reference, tensile strength, Young's modulus, and elongation at break values for neat PLA were measured to be 61.9±1.3 MPa, 3262±70 MPa and 3.1±0.4%, respectively. Figure 2 shows the testing results obtained for the blends. The tensile strength of the blends containing 10.0 wt% EBA-GMA remained unchanged as extrusion temperature increased, while at higher EBA-GMA contents, a slightly decreasing trend can be observed (Figure 2a). Tensile modulus values changed similarly to the tensile strength; however, at 10.0 wt% EBA-GMA ratio, the stiffness of the blends even slightly increased with increasing blending temperature (Figure 2b). This may be attributed to the increasing crystalline ratio of PLA in the blends due to the easier arranging of shorter molecular chains, which are likely formed at increased processing temperatures. The observed decrease in strength and modulus at 12.5 and 15.0 wt% EBA-GMA as a function of

increasing blending temperature is likely associated with the reduction in PLA molecular weight that obviously occurs at elevated processing temperatures. (Unfortunately, the determination of the molecular weight of PLA in the blends is rather difficult due to the EBA-GMA yielding insoluble fractions.) But as the effect of thermal degradation is less pronounced at lower (10.0 wt%) EBA-GMA content, it suggests that the decrease in molecular weight is not detrimental even at 260 °C. It is assumed that viscosity may also be an important factor in the mechanical performance of the blends. Namely, under the same processing conditions, at a lower EBA-GMA ratio, droplets of smaller size are formed, and thus finer dispersion can be achieved. The mechanical performance of such a fine dispersion is less sensitive to the smaller defects of the matrix material. Nevertheless, it is claimed that the changes in the tensile strength and moduli are not significant in the examined temperature range.

Since elongation at break is more sensitive to morphology and interfacial bonding, this parameter showed noticeable changes both with composition and blending temperature (Figure 2c). The elongation of the blends with EBA-GMA ratios of 12.5 and 10.0 wt% showed decreasing tendency with increasing processing temperature, likely due to increasingly intense degradation of PLA and insufficient interfacial bonding. However, the blends containing 15.0 wt% EBA-GMA showed increasing elongation as a function of increasing blending temperature, indicating a significant degree of chemical bonding between the PLA matrix and the toughening phase. Toughness and elongation of the blends followed similar tendencies, and the blend with 15.0 wt% EBA-GMA and prepared at 260 °C showed the best performance in both respects. These results further reinforce the assumption that the presence of highly reactive short-chain fractions, formed during processing at high temperature, boosts the reactive toughening of PLA by forming a toughening enhancer interphase (TEI) [25]. In former research studies, catalysts were added with the aim of lowering the activation energy of reactive compatibilization on the PLA/EBA-GMA interface [21, 30]. Our results suggest that the low-molecular-weight PLA chains, being present in the blends that are produced at higher temperatures, due to their increased mobility and higher number of functional end groups, can also enhance the rate of compatibilization reactions on the



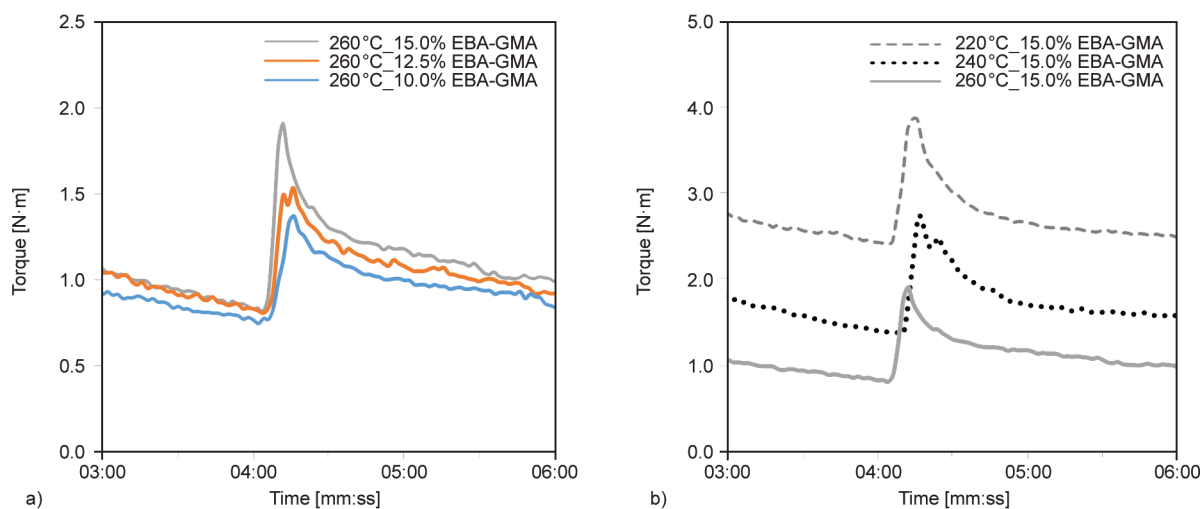
**Figure 2.** a) Tensile strength, b) tensile modulus, and c) elongation at break of the PLA/EBA-GMA blends.

PLA/EBA-GMA interface. Consequently, noticeable improvement in toughness can be achieved at a reduced terpolymer ratio by optimizing (increasing) the blending temperature.

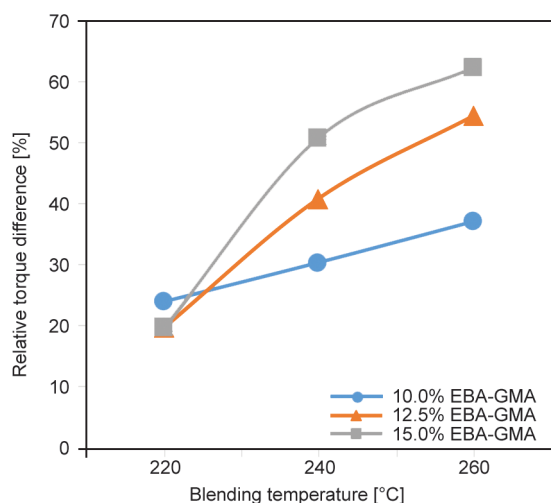
### 3.2. Rheology of the PLA/EBA-GMA blends

In order to detect the chemical reactions, including degradation and cross-linking, during melt-processing, torque values were recorded during melt-mixing of the blend components. The torque change was continuously recorded as a function of mixing time during melt-mixing of PLA either with an increasing amount of EBA-GMA (Figure 3a) or with identical 15.0 wt% EBA-GMA content but by applying increasing mixing temperature (Figure 3b). As can be seen in Figure 3a, both the peak of the torque response after EBA-GMA addition and the equilibrium torque value at 6 min increase when the EBA-GMA proportion is increased. These results indicate

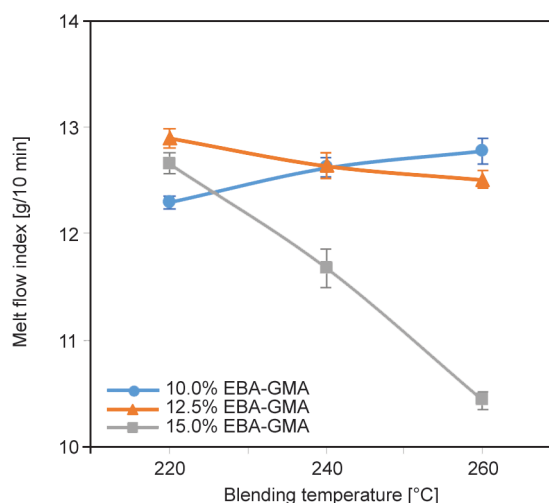
increasing viscosity of the PLA blends with increasing EBA-GMA content, likely due to the increasing occurrence of compatibilization reactions taking place between the components. As can be seen in Figure 3b, the viscosity-related equilibrium torque values, recorded either after complete melting of the PLA pellets or after blend formation with EBA-GMA, are highly dependent on the processing temperature. Based on the torque curves recorded during melt-mixing, the relative change in the equilibrium torque value, which occurred as a result of 15 wt% EBA-GMA addition, can be evaluated at each applied processing temperature. In Figure 4, the thus determined relative torque difference (as a percentage) is presented for each examined PLA/EBA-GMA blend. The relative torque difference was found to increase with EBA-GMA content and processing temperature as well. Accordingly, both factors are supposed to increase the occurrence of compatibilization reactions.



**Figure 3.** The torque responses as a function of mixing time during melt-mixing with a) increasing amount of EBA-GMA (at 260 °C); b) increasing mixing temperature (at 15.0 wt% EBA-GMA content).



**Figure 4.** Relative torque difference determined for the PLA/EBA-GMA blends.



**Figure 5.** Melt flow index of the PLA/EBA-GMA blends (190 °C, 2.16 kg).

### 3.3. MFI of the PLA/EBA-GMA blends

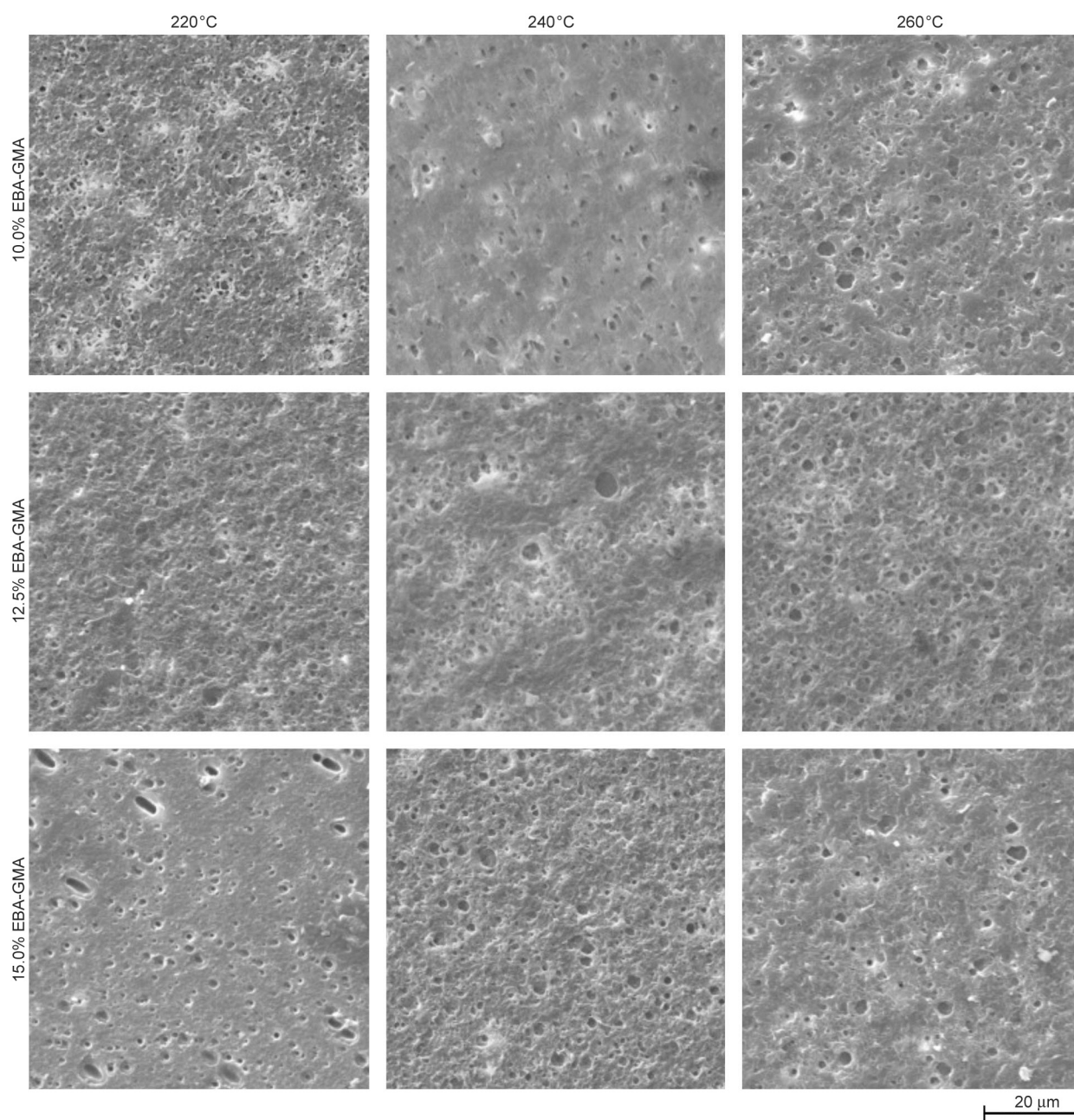
With the help of the melt flow index measurements, the rate of degradation during production and the reactions between the components can be indirectly deduced. Figure 5 shows the MFI values of the PLA blends differing in EBA-GMA contents and processing temperatures. The MFI values were determined at 190 °C in all cases, so it is proposed that the viscosity did not change noticeably during measurement, but it is mainly determined by the structure formed during extrusion processing. At 190 °C, closely identical MFI values of  $12.8 \pm 0.4$  g/10 min and  $12.7 \pm 0.5$  g/10 min were measured for the EBA-GMA additive and the additive-free PLA (after extrusion processing), respectively. It can be seen in Figure 5 that the MFI values measured for the PLA/EBA-GMA blends, after extrusion processing at 220 °C,

vary in the same MFI range of 12–13 g/10 min as those of the starting components, indicating a minimal rate of chemical reactions taking place between the components at this relative low processing temperature. The slight increase in the melt flow rate of the 10.0 wt% EBA-GMA-containing blends as a function of raising blending temperature is associated with accelerated PLA degradation and indicates an insufficient rate of PLA/EBA-GMA compatibilization. At higher EBA-GMA content of 12.5 wt%, however, a decreasing melt flowability can be observed with elevating blending temperatures suggesting increasingly effective compatibilization reactions between the components, which compensate for the decrease in melt viscosity due to thermal degradation. At an even higher EBA-GMA ratio of 15.0 wt%, the increased degree of reactive compatibilization

exceeds the level of thermal degradation effects and results in appreciable reductions in melt flow rates. The noticeably increased resistance to flow when the melt is processed at an elevated blending temperature of 260 °C supports the assumption that reactions between the components occur that seem more determinative with the increase of blending temperature. It can also be concluded that a sufficient amount of epoxy functionalized elastomer is needed to achieve considerable structural change in the system and thus reach the brittle-ductile transition zone.

### 3.4. Phase morphology of the EBA-GMA blends

The morphology of the blends was investigated by scanning electron microscopy (SEM). Figure 6 shows the SEM micrographs of PLA/EBA-GMA blends taken after the selective dissolution of the EBA-GMA phase. With the increasing amount of EBA-GMA, the size of the dispersed particles increases at each set temperature. When considering the effect of the processing temperature at a given EBA-GMA ratio, the particle size of the elastomer



**Figure 6.** SEM micrographs of PLA/EBA-GMA blends after selective extraction of the terpolymer.



droplets does not show any definite trend. Generally, the smaller droplet size results in greater interfacial boundary, favoring compatibilization. Superior impact resistance was observed for the blend with 15.0 wt% of EBA-GMA when prepared at 260 °C; which blend, however, does not show a distinct morphology. It was therefore concluded that the increased impact strength could not be explained only by morphological effects (*i.e.*, size and dispersion of the droplets), but it must depend on the nature of the interactive phases and their interfacial interaction.

### 3.5. Crystalline structure and crystallization of the PLA matrix

The thermal characteristics and crystalline structure of PLA in the blends were investigated by DSC measurements. The obtained DSC thermograms are presented in Figure 7, while corresponding thermal characteristics are shown in Table 2. It can be seen in Table 2 that the glass transition temperature ( $T_{g1}$ ) and melting temperature ( $T_{m1}$ ) do not show any definite trend with the change of blending temperature or composition; they range between 60.9–63.4 and 175.8–176.8 °C, respectively. Based on the crystallinity ( $X_{c1}$ ) of the PLA/EBA-GMA blends, as determined from the first heating scan, it was concluded that, in the examined range, the blending temperature does not significantly affect the crystallinity of the injection molded products; similarly to the findings of Liu *et al.* [20]. In contrast with the conclusions of Oyama, here, the difference in crystallinity phase structure does not have a clear relation with impact strength [19].

In order to examine the crystallization behavior of PLA in the blends, relative crystallinity ( $X_{c2}$ ) was determined from the second heating cycle (*i.e.*, crystals formed from the cooling cycle were examined). It can be seen in Figure 8 that the relative crystallinity

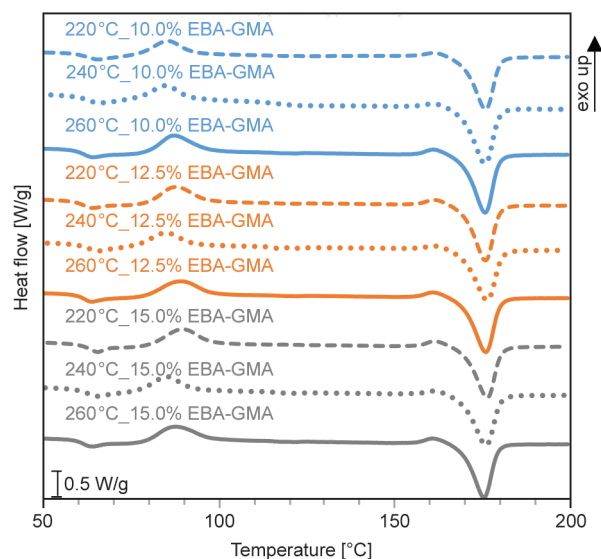


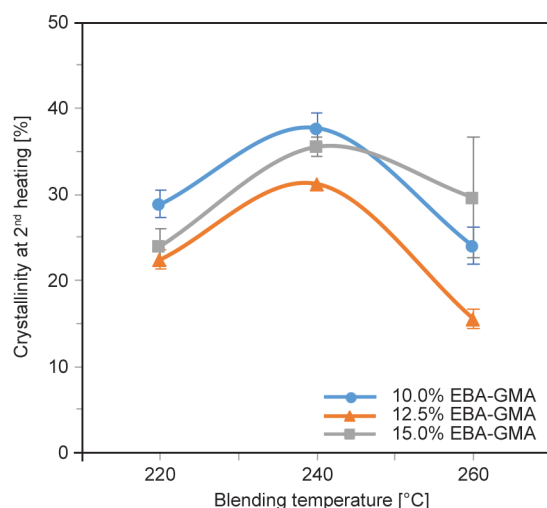
Figure 7. DSC curves of the PLA/EBA-GMA blends.

( $X_{c2}$ ) shows a maximum curve as a function of increasing blending temperature suggesting two opposing effects that affect the crystallization of PLA. The increase in the crystalline ratio when the processing temperature is increased from 220 to 240 °C is associated with the decreasing molecular weight of PLA due to accelerated degradation. Further increase in the blending temperature to 260 °C leads, however, to noticeably lower crystallinity. At this elevated temperature, crystallization of PLA chains is assumed to be restricted by the facilitated compatibilization reactions between the carboxyl or hydroxyl end groups of the PLA chains and the epoxy groups of EBA-GMA.

The trends observed in the cold crystallization temperatures ( $T_{cc1}$ ) (derived from the first heating cycle) and in the temperatures of crystallization ( $T_c$ ) during cooling also support this theory. It can be seen in Table 2 that at 15.0 wt% EBA-GMA content and an elevated processing temperature of 240 °C, the  $T_{cc1}$  of the blends shifts to a lower temperature while the

Table 2. Results of DSC analyses.

| Blending temperature [°C] | EBA-GMA content [wt%] | $T_{g1}$ [°C] | $T_{m1}$ [°C] | $T_{cc1}$ [°C] | $X_{c1}$ [%] | $T_c$ [°C] |
|---------------------------|-----------------------|---------------|---------------|----------------|--------------|------------|
| 220                       | 10.0                  | 61.0±0.8      | 175.8±0.1     | 87.1±2.2       | 34.4±1.1     | 93.9±0.3   |
|                           | 12.5                  | 62.1±1.3      | 176.1±0.3     | 87.5±0.7       | 28.2±3.1     | 93.0±0.1   |
|                           | 15.0                  | 61.8±1.0      | 176.8±0.5     | 88.8±0.9       | 25.2±0.8     | 93.3±0.2   |
| 240                       | 10.0                  | 61.3±0.6      | 175.8±0.2     | 85.9±1.3       | 36.2±3.0     | 94.4±0.5   |
|                           | 12.5                  | 61.2±0.5      | 176.5±0.6     | 86.5±0.7       | 27.1±1.2     | 93.3±0.4   |
|                           | 15.0                  | 63.4±0.2      | 175.8±0.3     | 85.2±0.3       | 35.4±3.4     | 95.0±0.1   |
| 260                       | 10.0                  | 61.7±0.2      | 175.8±0.2     | 87.3±0.9       | 28.3±0.8     | 93.3±0.2   |
|                           | 12.5                  | 62.3±0.9      | 176.3±0.4     | 87.7±2.2       | 25.9±2.2     | 93.3±0.7   |
|                           | 15.0                  | 60.9±0.8      | 176.1±0.9     | 87.2±0.6       | 26.6±1.2     | 93.2±0.2   |



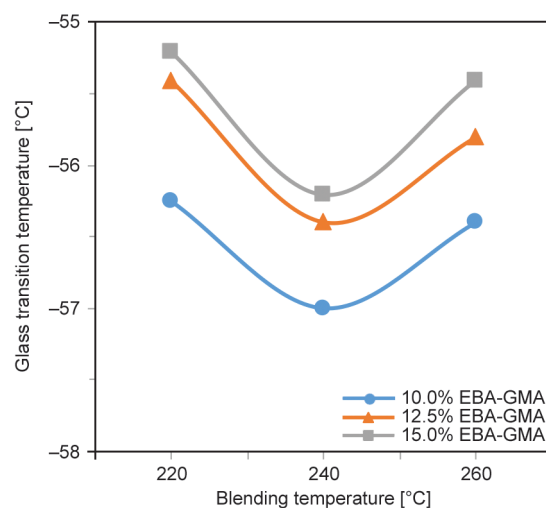
**Figure 8.** Relative crystallinity ( $X_{c2}$ ) of the PLA/EBA-GMA blends derived from DSC second heating curves.

$T_c$  shifts to a higher temperature, both indicating increased nucleation efficiency of the PLA/EBA-GMA interphase [3, 31]. At a higher processing temperature of 260 °C, however,  $T_{cc1}$  and  $T_c$  fall back to similar values as measured for the blends processed at 220 °C. It is proposed that even though the short polymer chains can form crystals more readily than long chains, due to the intensified PLA–EBA–GMA compatibilization reactions at 260 °C, the motion of these shorter PET chains becomes increasingly restricted, accompanied by increasing  $T_{cc1}$  and decreasing  $T_c$  values [3, 31].

The DSC results further reinforce the assumption that the outstanding impact strength of the 15.0 wt% EBA-GMA containing blend, when processed at 260 °C, is mainly related to the intensified PLA–EBA–GMA compatibilization reactions that allow excellent toughening efficiency.

### 3.6. Structure of the EBA-GMA phase

Compatibilization reactions are almost always associated with cross-linking of the terpolymer, and in the case of cross-linking, an increase in the glass transition temperature ( $T_g$ ) of the elastomer can be expected [25]. The thermally stimulated depolarization current (TSDC) method was used to determine the  $T_g$  of the EBA-GMA phase in the blends produced at different blending temperatures. The obtained results are shown in Figure 9. The  $T_g$  of the elastomer shows a minimum curve as a function of blending temperature, likely as a result of two effects. The changes in  $T_g$  are, on the one hand, related to the particle size of the dispersed phase; the finer



**Figure 9.** Glass transition temperature ( $T_g$ ) of the EBA-GMA phase in the PLA/EBA-GMA blends derived from TSDC curves.

dispersion results in depression of the  $T_g$  [32]. On the other hand, the  $T_g$  of the elastomer increases with the degree of cross-linking.

It can be seen in Figure 9 that at a given blending temperature, the  $T_g$  increases with increasing EBA-GMA ratio parallel as the particle size increases, as also observed by SEM imaging (Figure 6). When the blending temperature was increased from 240 to 260 °C, the  $T_g$  increased at all EBA-GMA ratios, suggesting the formation of cross-links in all cases. The results of the TSDC study confirmed our hypothesis that increasing the compounding temperature improves interfacial compatibility and parallels the cross-linking of the elastomer. Consequently, a significant increase in impact strength can be achieved, but only when the interparticle distance can be reduced below the critical value. The latter can be reached by increasing the EBA-GMA content or by improving the dispersion of the elastomer phase.

## 4. Conclusions

Toughening of PLA by EBA-GMA was found to be increasingly efficient when the blends were processed at elevated temperatures. The notched Izod impact resistance and elongation at break of the PLA/EBA-GMA blend significantly improve, even though the harmful effects of accelerated thermal and hydrolytic degradation of PLA at elevated processing temperature have not been compensated by CE addition. On the contrary, it is proposed that the short-chain PLA molecules formed *in situ* during high-temperature thermomechanical processing play a key role in

enhanced toughening efficiency. Namely, low-molecular-weight PLA chains have a higher number of functional end groups and increased mobility which allows the rapid formation of toughening enhancer interphase between the PLA and the reactive elastomer, which provides a significant improvement in the impact strength. According to this theory, a similar beneficial effect on the toughening efficiency can be expected when the processing-induced PLA degradation is accelerated in the presence of humidity, *e.g.*, by omitting the drying step of PLA pellets before melt processing.

At EBA-GMA contents lower than 15.0 wt%, the intense PLA degradation during high-temperature blending resulted in reduced mechanical performance, *i.e.*, decreased impact strength, tensile strength and modulus. At 15.0 wt% EBA-GMA, however, the elongation at break increased, and the notched Izod impact resistance improved by approx. 250% only by applying a high blending temperature of 260 °C instead of 240 °C or below. Decreased flowability (MFI) of the melt accompanied by stabilized dispersed droplet size (as observed during SEM examination) indicated intensified compatibilization reactions between the components. Facilitated interphase nucleation accompanied by restricted crystallization ability (as obtained from DSC analyses) and increased degree of elastomer cross-linking (as found by TSDC measurements) provided further evidence for efficient reactive compatibilization on the PLA/EBA-GMA interphase. As a result, raising the blending temperature allows the production of high-impact-resistant ( $a > 20 \text{ kJ/m}^2$ ) PLA blends at reduced (15.0 wt%) elastomer content, *i.e.*, at a lower cost. This recognition may contribute to the widening of the application fields of this biopolymer.

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