JOURNAL OF Applied Polymer SCIENCE

Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

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Mechanical properties of biodegradable polylactide/poly(ether-block-amide)/thermoplastic starch blends: Effect of the crosslinking of starch

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ABSTRACT: Corn starch was crosslinked with epichlorohydrin (ECH) and then plasticized with glycerol. Subsequently, this thermoplasticized crosslinked starch (TPCLS) was melt-compounded with polylactide (PLA) and poly(ether-block-amide) (PEBA) to prepare biodegradable PLA/PEBA/TPCLS blend with high impact resistance. It was found that the crosslinking agent ECH had critical effect on the impact strength, tensile properties, and internal morphology of the ternary blend. The impact strength, tensile strength, and elongation at break increased with ECH content; thereafter, they decreased on further increasing the ECH content. At 0.5 wt % ECH content, impact strength, tensile strength, and elongation at break reached the maximum values and smaller salami structure particles were observed accordingly. These results were attributed to the competition of shear resistance of TPCLS and the chemical linkage between the crosslinked starch and PLA-g-MA. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42297.

KEYWORDS: biodegradable; crosslinking; mechanical properties; polylactide; starch

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INTRODUCTION

Shortage of fossil resource and environmental impact caused by nondegradable plastics motivated researchers to develop biodegradable polymers from renewable resources. Among commercially available bio-based thermoplastic polymers, polylactide (PLA) has attracted extensive investigation in the field of package material due to its low toxicity, good compostability, and comparable mechanical properties to those of conventional petroleum-based polymers.[1–3]

However, the application of PLA is often limited because of its brittleness and relatively high price.[4,5] Blending PLA with cheaper filler can reduce the cost of PLA composites. Starch is a promising organic filler for PLA due to its low price, abundant natural sources, and total biodegradability.[6] However, their compatibility is very poor due to the hydrophilic nature of starch,[7] and weak interfacial adhesion between starch and PLA.[8] As a result, direct incorporation of starch into PLA composites without chemical modification usually led to the deterioration in the mechanical properties of PLA/starch composites.[9,10] Therefore, modification strategies have been applied to improve the affinity between PLA and starch.[11–13] Besides, some modifications can also improve the properties of starch and then lead to the improvement of mechanical properties of PLA/starch derivative composite. Crosslinking is a frequently used method which can increase both mechanical properties and water resistance of starch.[14]

Currently, in most of the reports about PLA/starch composites, the improvement of tensile properties is more significant than that of impact resistance. For example, recently, in a series of interesting studies by Zhu's group,[15–18] it was shown that several kinds of plant oils were grafted onto starch granules during melt-compounding with PLA, and these oils acted as compatibilizer and plasticizer at the same time in the full bio-sourced PLA/starch/oil mixtures. The impact strength of the mixtures increased up to twice that of pure PLA while the highest elongation at break reached 140% compared to 5% for pure PLA.

According to the known reports, the impact resistance of PLA only can be minimally improved by adding starch individually. Thereby, the assistance of elastomer is necessary to increase impact resistance of PLA/starch composite to higher level. Meanwhile, elastomer can be partially substituted by starch. Until now, many kinds of nondegradable elastomers have been used to toughen PLA.[19–21] In order to prepare environmental benign PLA composite, biodegradable elastomer is more preferable. Partially bio-based polyether-block-amide copolymer (PEBA) is a biodegradable thermoplastic elastomer with outstanding flexibility, high strength, and good processability.[22–24]

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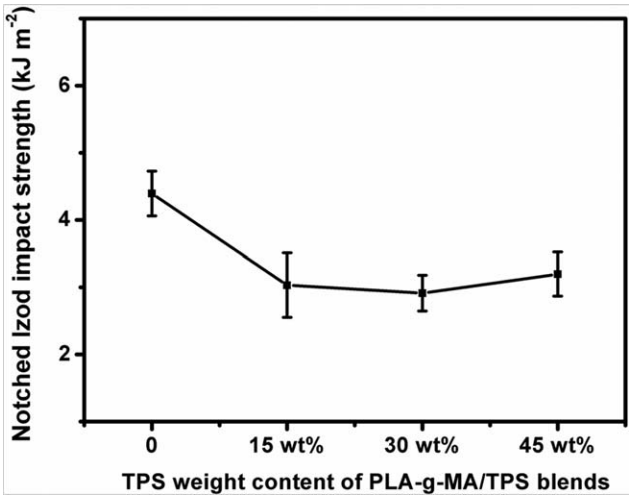

Figure 1. Notched Izod impact strength of PLA-g-MA/TPS blends as a function of TPS weight content at 20°C.

In this study, corn starch was crosslinked and plasticized before blending with PLA. PEBA elastomer was also used in order to prepare biodegradable PLA/PEBA/crosslinked starch composite with high impact resistance. The effects of crosslinking on impact strength, tensile properties, and morphology were investigated.

EXPERIMENTAL

Materials

The PLA (trade name 4032D) used in this study was obtained from Natureworks LLC (USA). The poly(ether block amide) (PEBA) was supplied by Arkema Company (France) with the trade name Pebax Rnew 25R53. PLA and PEBA pellets were dried at 80°C in a vacuum oven for 12 h to remove residual moisture. Normal corn starch was supplied by Beijing Chudama Food Co., Ltd. (Beijing, China). Epichlorohydrin (analytical reagent AR) was obtained from Xilong Chemical Co., Ltd. (Guangdong, China). Glycidyl methacrylate (GMA) (chemical pure grade) was obtained from Suzhou Anli Chemical Co., Ltd. China. *N*-vinyl pyrrolidone (NVP), dicumyl peroxide (DCP), 2, 5-dimethy-2, 5-di-(tert-butylperoxy) hexane (L101), glycerol, and maleic anhydride (MA) were all chemically pure grade and purchased from Beijing Chemical works, China.

Crosslinking of Starch

The crosslinking reaction of starch was carried out according to the procedure reported by Jyothi.[25] Native corn starch (100 g) was slurried with 200 mL distilled water to obtain a suspension of solid concentration 50% (w/v). The suspension was placed in a three-necked flask equipped with mechanical stirrer at 45°C. After the pH was adjusted to 10.5 by sodium hydroxide solution (2.5 M), epichlorohydrin (ECH) was added drop by drop. Two hours later, the crosslinking reaction was completed and the suspension was filtered and the residue was washed with plenty of water (2000 mL × 2). Finally, the crosslinked starch precipitate was dried in an oven at 70°C and the solid product was comminuted into powder. The degree of crosslinking was modulated by adding different weight contents of ECH based on the starch dry weight (0.25, 0.50, and 1.00 wt %).

Plasticization of Crosslinked Starch

Crosslinked starch (or native starch) and glycerol were premixed at the weight ratio of 60/40. The mixture was kept for 12 h at room temperature and then melt-blended in Haake Torque Rheometer at 150°C with a screw speed of 80 rpm for 10 min, the plasticization product: thermoplastic crosslinked starch (TPCLS) or thermoplastic starch (TPS) was then cut into small pieces.

Blend Preparation

PEBA copolymer (50 g), GMA monomer (1.42 g), NVP monomer (1.67 g), and initiator DCP (0.15 g) were melt blended to prepare PEBA-g-GMA. Subsequently, reactive blending of 35 g PLA and 15 g PEBA-g-GMA was carried out to prepare PLA/PEBA-g-GMA blend (70/30, wt/wt). Maleation of PLA was performed at the feed ratio: PLA (50 g), MA (1 g), initiator L101 (0.13 g).[26] Then, 35 g PLA-g-MA was blended with 15 g TPCLS to prepare PLA-g-MA/TPCLS blend (70/30, wt/wt).

The above PLA/PEBA-g-GMA blend (70/30, wt/wt) and PLA-g-MA/TPCLS blend (70/30, wt/wt) were melt-compounded to prepare PLA/PEBA-g-GMA/TPCLS blend. The weight ratio of PLA/PEBA-g-GMA to PLA-g-MA/TPCLS was 40:60, 45:55, or 50:50. The composition of the resultant PLA/PEBA-g-GMA/TPCLS blends was 70/12/18 (wt/wt/wt), 70/13.5/16.5 (wt/wt/wt), or 70/15/15 (wt/wt/wt). Additionally, PLA-g-MA/TPS blends (85:15 and 55:45, wt/wt) were also prepared. All the melt processes were performed on Haake Torque Rheometer at 180°C with rotation speed of 80 rpm for 5 min.

PLA/PEBA-g-GMA blend, PLA-g-MA/TPS blend, and PLA/PEBA-g-GMA/TPCLS blend were compression molded at 200°C with a holding pressure of 10 MPa for 5 min into 3.2-mm-thick sheets. After that, the mold was removed to another unheated compressor and cooled at room temperature at 10 MPa for 10 min. The sheets were cut into specimens for impact test with the dimension 63.5 × 12.7 × 3.2 mm. The sheets for tensile test were also compression molded by such methods and then were cut into dumbbell-shape specimens with a dimension of 50 mm (length-overall) × 4 mm (width of narrow section) × 1 mm (thickness).

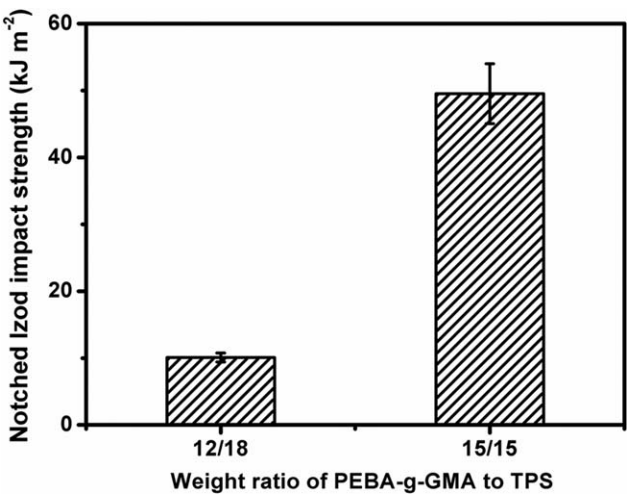

Figure 2. Notched Izod impact strength of PLA/PEBA-g-GMA/TPS blends with the weight ratio of PEBA-g-GMA to TPS at 20°C.

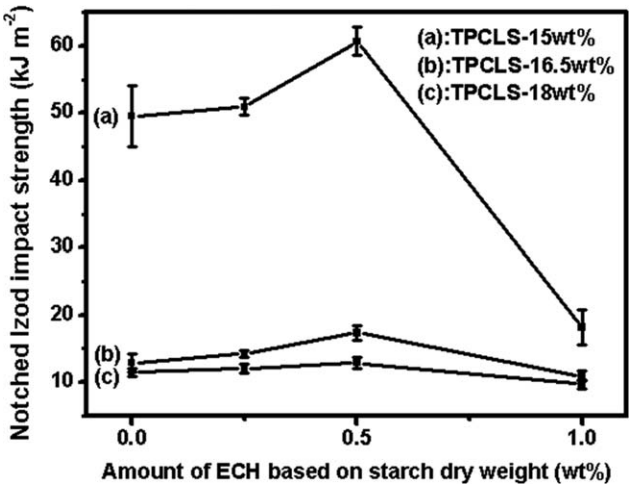

Figure 3. Notched Izod impact strength of PLA/PEBA-g-GMA/TPCLS blends (a: 70/15/15, wt/wt/wt; b: 70/13.5/16.5, wt/wt/wt; c: 70/12/18, wt/wt/wt) as a function of amount of ECH at 20°C.

Impact Test

Notched Izod impact test was carried out according to ASTM D-256 using a XJU-2.75 impact tester (Chengde Test Machine Company, China) at 20°C. The specimens were V-notched (45°) and conditioned at 20°C for 24 h prior to testing. Six specimens were tested for each composition and the average value was reported.

Tensile Test

The tensile properties were measured at 20°C according to GB/T 1040.1–2006 (this Chinese standard was equivalent to ISO 527-1:1993) with Instron 1121 material tester at a cross-head speed of 10 mm/min. Five specimens were used for each composition to obtain a reliable mean value and standard deviation.

Microstructure Characterization

Microstructure of PLA/PEBA-g-GMA/TPCLS blend was observed by JEOL JEM-1011 transmission electron microscope (TEM) with an accelerating voltage of 100 kV and field-emission-gun environmental scanning electron microscope (FEG ESEM) (XL30, FEI COMPANY) with an accelerating voltage of 10 kV. The PLA/PEBA-g-GMA blend and PLA/PEBA-g-GMA/TPCLS blend were microtomed into ultrathin sections of 50 nm thickness at −150°C and then stained with osmium tetraoxide vapor before TEM observation. The PLA/PEBA-g-GMA/TPCLS sample surfaces for SEM test were smoothed at −150°C by a microtome equipped with a glass knife and then extraction of TPCLS was performed in 6 mol/L hydrochloric acid at 25°C for 5 h. The etched surfaces were then coated with a thin layer of gold before SEM observation.

Dynamic Mechanical Analysis

TPCLS and TPS were injection molded into small cylinders (diameter: 10 mm; thickness: 3 mm) by using DSM Xplore twin screw micro-compounder and micro-injection machine (Royal DSM Co., Netherlands). The dynamic mechanical analysis (DMA) of TPCLS and TPS samples were performed with DMA/SDTA861^e from Mettler Toledo in the shear mode. The storage modulus (E′), loss modulus (E″), and dynamic loss factor (tan δ) were measured from −10 to 80°C at a heating rate of 3°C/min. The frequency was fixed at 1 Hz.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the variation of the notched Izod impact strength of the PLA-g-MA/TPS blends with TPS content. It is found that the impact strength decreased after the incorporation of TPS phase. This result indicates that the notched Izod impact resistance of PLA cannot be improved by adding TPS individually.

In this case, biodegradable elastomer PEBA was selected to toughen PLA together with TPS. Chemical reaction between epoxy group of GMA and end carboxyl group of PLA could enhance the interfacial adhesion between the toughener and PLA matrix.[27] Therefore, GMA-grafted PEBA, i.e., PEBA-g-GMA, was prepared and used in this study. The notched Izod impact strength of the PLA/PEBA-g-GMA blend (70/30, wt/wt) was 68.6 ± 3.6 kJ m^{-2}.

Table I. Tensile Properties of PLA and PLA/PEBA-g-GMA/TPCLS Blend (20°C).

Sample	Tensile strength (MPa)	Elongation at break (%)
Pure PLA	60.8 ± 1.4	4.4 ± 0.4
PLA/PEBA-g-GMA/TPS(70/15/15) (ECH: 0 wt %)	22.0 ± 0.4	37.7 ± 1.8
PLA/PEBA-g-GMA/TPCLS (70/15/15) (ECH: 0.25 wt %)	22.7 ± 0.3	48.9 ± 2.7
PLA/PEBA-g-GMA/TPCLS (70/15/15) (ECH: 0.50 wt %)	23.7 ± 0.9	67.5 ± 2.9
PLA/PEBA-g-GMA/TPCLS (70/15/15) (ECH: 1.00 wt %)	21.0 ± 1.0	17.2 ± 2.7
PLA/PEBA-g-GMA/TPS(70/13.5/16.5) (ECH: 0 wt %)	19.2 ± 0.6	18.6 ± 1.2
PLA/PEBA-g-GMA/TPCLS (70/13.5/16.5) (ECH: 0.25 wt %)	20.7 ± 0.9	19.2 ± 3.9
PLA/PEBA-g-GMA/TPCLS (70/13.5/16.5) (ECH: 0.50 wt %)	21.2 ± 0.2	25.2 ± 4.7
PLA/PEBA-g-GMA/TPCLS (70/13.5/16.5) (ECH: 1.00 wt %)	18.7 ± 0.5	13.7 ± 1.8
PLA/PEBA-g-GMA/TPS (70/12/18) (ECH: 0 wt %)	18.2 ± 0.4	8.5 ± 2.2
PLA/PEBA-g-GMA/TPCLS (70/12/18) (ECH: 0.25 wt %)	18.3 ± 1.1	9.7 ± 1.8
PLA/PEBA-g-GMA/TPCLS (70/12/18) (ECH: 0.50 wt %)	18.5 ± 0.2	11.9 ± 1.2
PLA/PEBA-g-GMA/TPCLS (70/12/18) (ECH: 1.00 wt %)	17.6 ± 1.3	7.6 ± 2.0

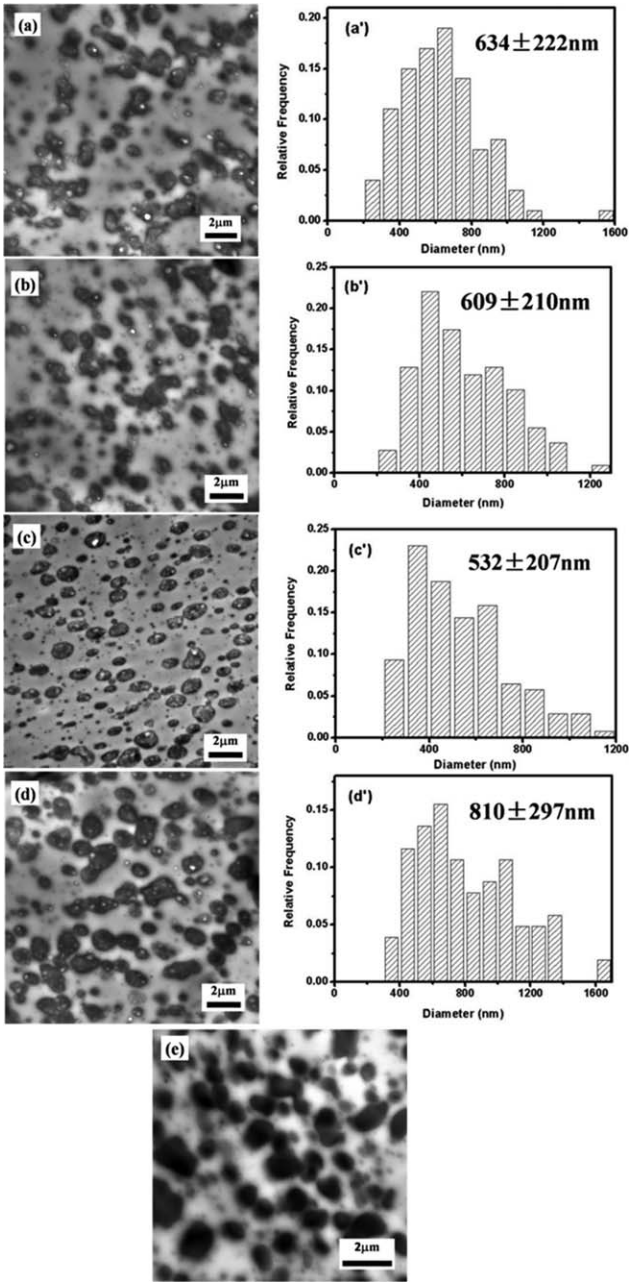

Figure 4. TEM photographs of PLA/PEBA-g-GMA/TPCLS blends (70/15/15, wt/wt/wt) (a–d) and particle size distribution (a′–d′). The degree of crosslinking of starch was modulated by the addition amount of ECH during the crosslinking reaction (a) 0; (b) ECH: 0.25 wt %; (c) ECH: 0.50 wt %; (d) ECH: 1.00 wt %. TEM photograph of PLA/PEBA-g-GMA blend (70/30, wt/wt) was shown in Figure 4(e).

Figure 2 shows the impact test results of PLA/PEBA-g-GMA/TPS blends. The total content of PEBA-g-GMA and TPS was fixed at 30 wt %, when the weight ratio of PEBA-g-GMA to TPS increased from 12/18 to 15/15, the notched Izod impact strength increased from 10.1 ± 0.7 to 49.5 ± 4.5 kJ m^{-2}. Namely, the blend underwent ductile fracture as incorporating 15 wt % of PEBA-g-GMA elastomer.

Despite the outstanding performance of PEBA-g-GMA in toughening PLA, the cost of PEBA is much higher than that of PLA or starch. From the economic view, it is worthy to increase the notched Izod impact strength of the trinary blends without increasing the amount of PEBA-g-GMA. Crosslinking reaction was considered as an effective method to improve the mechanical properties of starch.[28] Based on such consideration, native corn starch was crosslinked by epichlorohydrin (ECH) and then the plasticized crosslinked starch, i.e., thermoplastic crosslinked starch (TPCLS) was blended with PLA-g-MA. Figure 3 shows the notched Izod impact strength of PLA/PEBA-g-GMA/TPCLS blends as a function of amount of ECH based on starch dry weight at 20°C. It can be seen that the impact strength depended on the amount of ECH significantly. When the amount of TPCLS was 15 wt % (Figure 3, line a), the impact strength of the blends increased from 49.5 ± 4.5 kJ m^{-2} up to 60.7 ± 2.1 kJ m^{-2} with increasing the amount of ECH from 0 to 0.5 wt %, thereafter it reduced markedly to 18.2 ± 2.6 kJ m^{-2} with further increasing the amount of ECH to 1 wt %. A similar profile can be observed when the amount of TPCLS was 16.5 or 18 wt % (Figure 3, line b and line c). The difference is that all blends underwent brittle fracture for 16.5 or 18 wt % TPCLS content, whereas only one blend underwent brittle fracture for 15 wt % TPCLS content.

The tensile properties were listed in Table I. Pure PLA was a quite stiff material with high tensile strength (~60 MPa) but fairly brittle with low elongation at break (~4%). Since relatively soft PEBA-g-GMA elastomer and TPS (or TPCLS) were blended with PLA, elongation at break of the ternary mixture was improved, whereas tensile strength decreased markedly. For each batch of PLA/PEBA-g-GMA/TPCLS blends with fixed composition (70/15/15, 70/13.5/16.5, or 70/12/18), the amount of ECH was the only factor that dominated the tensile properties. As a result, both tensile strength and elongation at break changed in a manner similar to the variation of impact strength: increased first and then declined with increasing the ECH amount. The maximum value still appeared at ECH (0.50 wt %). When the amount of TPS (or TPCLS) was 15 wt %, elongation at break increased significantly and the maximum value could reach up to $67.5 \pm 2.9\%$ with increasing the amount of ECH from 0 to 0.5 wt %. However, further increasing the amount of TPS (or TPCLS) to 16.5 or 18 wt %, the ductility of PLA was improved relatively modestly.

Morphology

The internal structures of PLA/PEBA-g-GMA/TPCLS blends and PLA/PEBA-g-GMA blend were clearly revealed from the TEM photographs as shown in Figure 4. The size of the dispersed particles in PLA/PEBA-g-GMA/TPCLS blends was quantitatively analyzed; the mean size and standard deviation of these samples were given in Figure 4(a′–d′). Since only GMA group can be stained by the osmium tetraoxide, the black shell of the "Salami" structure particles [Figure 4(a–d)] and the black solid spheres [Figure 4(e)] should be PEBA-g-GMA phase. Comparing the micrographs of ternary blends [Figure 4(a–d)] with binary blend [Figure 4(e)], it can be concluded that the lighter color subinclusions inside the black salami particles should be TPCLS (or TPS) phase. For the PLA/PEBA-g-GMA/TPCLS (70/15/15, wt/wt/wt) blends, it is obvious that the amount of ECH (i.e., the degree of crosslinking) has critical

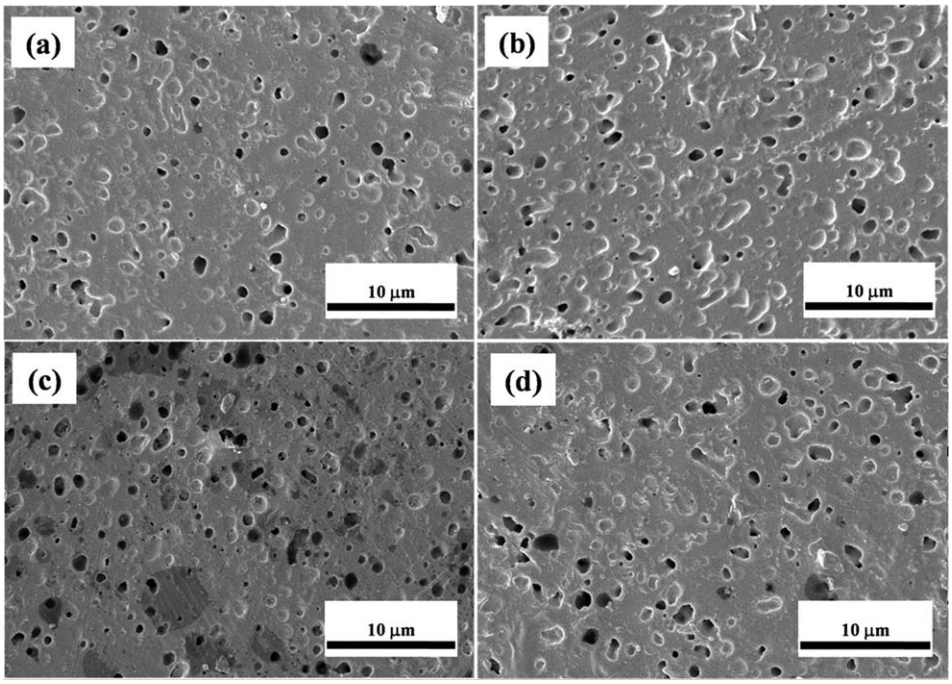

Figure 5. SEM photographs of PLA/PEBA-g-GMA/TPCLS blends (70/15/15, wt/wt/wt), the degree of crosslinking of starch was modulated by the addition amount of ECH during the crosslinking reaction (a) 0; (b) ECH: 0.25 wt %; (c) ECH: 0.50 wt %; (d) ECH: 1.00 wt %.

effect on the salami particle morphology [Figure 4(a–d)]. When the amount of ECH is 0.50 wt % [Figure 4(c)], the particle size is smaller than those of the other three blends [Figure 4(a,b,d)]. Compared to relative large particles, smaller particles could initiate crazing and induce shear yielding of the matrix more efficiently.[29–31] As a result, the fracture toughness of polymer blends containing smaller dispersed particles could be improved more significantly. Therefore, the impact strength, tensile strength, and elongation at break reached the maximum value when the amount of ECH was 0.50 wt % (as shown in Figure 3 and Table I).

The morphological difference of the dispersed particles in the PLA/PEBA-g-GMA/TPCLS blends can also be observed in the SEM photographs (Figure 5). The voids on the surfaces are attributed to the TPCLS (or TPS) phase since only TPCLS (or TPS) can decompose in the 6 mol/L hydrochloric acid while PLA or PEBA-g-GMA cannot during the process of extraction. Similarly, the particle size is smaller when the amount of ECH is 0.50 wt % [Figure 5(c)].

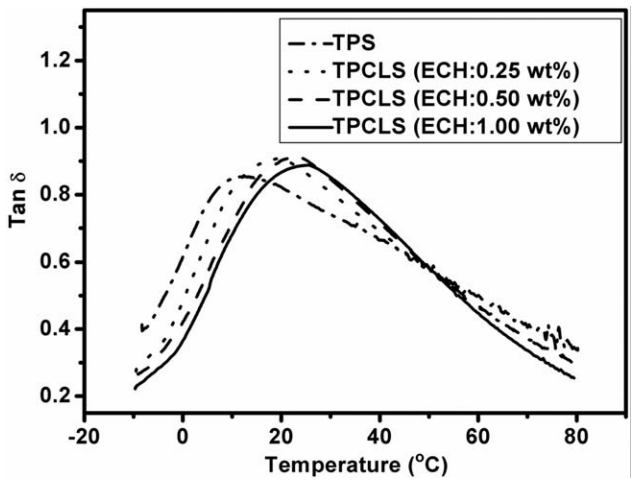

Figure 6. Dynamic mechanical analysis of TPS and TPCLS: damping parameter.

Effects of Crosslinking

The effect of amount of ECH (i.e., degree of crosslinking) on the properties of TPCLS was studied by dynamic mechanical analysis (DMA). The plots of tan δ against temperature show prominent peaks between 0 and 30°C, corresponding to the glass transition of thermoplastic starch (TPS) and thermoplastic crosslinked starch (TPCLS) (Figure 6). The maximum value for each peak is used to define *Tg* (temperature at glass transition). With increasing the amount of ECH from 0, 0.25, 0.50, to 1.00 wt %, *Tg* increases from 11.9, 20.1, 23.4, to 25.7°C respectively. Namely, *Tg* shifts to higher temperatures as the degree of crosslinking increasing.[32]

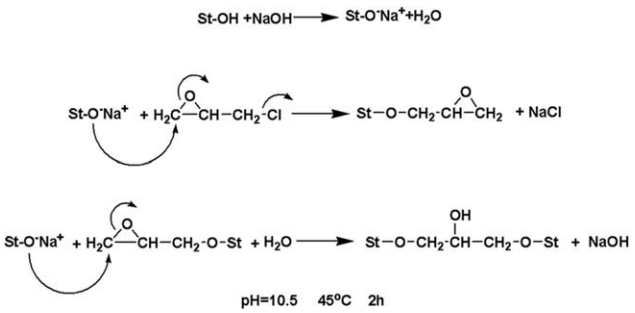

Figure 7. Crosslinking reaction of starch with epichlorohydrin.

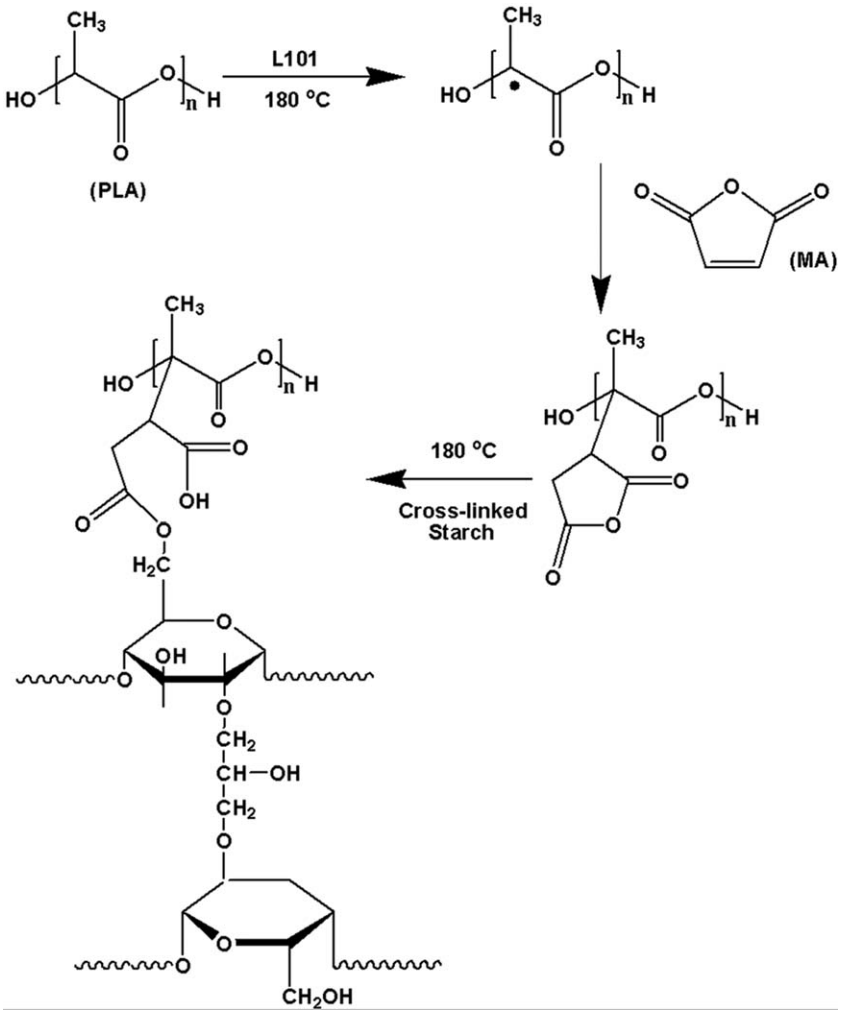

Figure 8. Possible reaction mechanism between crosslinked starch and PLA-g-MA.

The observed increment of *Tg* confirms the formation of network among the starch molecular chain and this network became denser for higher amount of ECH, i.e., the degree of crosslinking increased with the amount of ECH.

From the TEM photographs [Figure 4(a–d)], we have known that TPCLS (or TPS) phase was wrapped by PEBA-g-GMA phase in the PLA/PEBA-g-GMA/TPCLS blends. The soft TPCLS or TPS might act like elastomer when the ternary blends were subjected to impact test (or tensile test) and could absorb impact energy (or tensile stress) along with PEBA elastomer. However, plasticized natural starch (i.e., TPS) was not as tough as the artificial polymerized PEBA elastomer which had covalently linked soft block–hard block structure.[33] Therefore, TPS would be destroyed more easily than PEBA during impact test (or tensile test).

However, after the crosslinking reaction, starch macromolecule chains were linked by the glycerol diether bridges (Figure 7).[34] As a result, the mobility of starch macromolecule chain was restricted and the macromolecule structure of starch was more stable. The thermoplastic crosslinked starch (TPCLS) could be regarded as gel of crosslinked starch with plasticizer glycerol. Higher degree of crosslinking led to more shear-resistant gel.[35,36] The enhanced shear stability made TPCLS more fracture resistant. As a result, TPCLS could absorb more impact energy (or tensile stress) than TPS before being destroyed. Thus, it can be concluded that increasing the degree of crosslinking (i.e., increment of shear resistance of TPCLS) was beneficial for the improvement of impact strength and tensile properties of the PLA/PEBA-g-GMA/TPCLS blend.

On the other hand, maleic anhydride (MA) could strengthen the interface adhesion between starch and PLA.[37,38] Due to the steric hindrance effect of starch and PLA macromolecules, only the residual hydroxyl group on the crosslinked starch chain could react with the anhydride group of PLA-g-MA. As a result, crosslinked starch was chemically bonded to PLA-g-MA through newly formed ester group. The possible reaction process is shown in Figure 8 based on the mechanism proposed by Zhang and Sun.[39]

As increasing the amount of ECH, the residual hydroxyl group decreased followed by the number of the ester bond decreased. Namely, the interfacial adhesion between crosslinked starch and PLA-g-MA weakened as the amount of ECH increased. This

would lead to the deterioration of impact strength and tensile properties of the ternary blends.

In summary, the increment of amount of ECH (i.e., increasing the degree of crosslinking) on one hand improved the shear resistance of TPCLS and on the other hand weakened the chemical linkage between crosslinked starch and PLA-g-MA. The maximum values of impact strength and tensile properties (Figure 3 and Table I) were the competing result of these effects. This competition also affected the particle morphology as confirmed by the TEM and SEM characterizations (Figures 4 and 5). Smaller dispersed particles were observed in the sample with the maximum values of impact strength and tensile properties.

CONCLUSIONS

Native corn starch was crosslinked with epichlorohydrin and the DMA results show that the degree of crosslinking can be modulated by the amount of ECH. The shear resistance of TPCLS increased as the amount of crosslinking agent ECH and this was beneficial for the improvement of impact strength and tensile properties of PLA/PEBA-g-GMA/TPCLS blends. Meanwhile, the chemical linkage between crosslinked starch and PLA-g-MA weakened as the amount of ECH increased and that would lead to the deterioration of impact strength and tensile properties of the ternary blends. The competition of these two effects led to the appearance of peak values of impact strength and tensile properties. The TEM and SEM photographs indicated that the amount of ECH also affected the morphology of TPCLS particles significantly. Smaller dispersed particles were observed in the sample with the maximum values of impact strength and tensile properties.

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