Biobased Poly(ethylene terephthalate)/Poly(lactic acid) Blends Tailored with Epoxide Compatibilizers

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ABSTRACT: To increase the biobased content of poly(ethylene terephthalate) (PET), up to 30 wt % poly(lactic acid) (PLA) was blended with PET using twin-screw compounding and injection molding processes. Multifunctional epoxide compatibilizers including a chain extender and an impact toughening agent were used as blend modifiers to improve the poor mechanical properties of PET/PLA blends. The mechanical and thermodynamic performances were investigated along with the morphological features through scanning electron microscopy, atomic force microscopy, and interfacial tension determination. From rheological and differential scanning calorimetry results, it was observed that the molecular weight of both PET and PLA increased with compatibilizers because of epoxide reactions. The toughening agent, poly(ethylene-n-butylene-acrylate-co-glycidyl methacrylate) (EBA–GMA), provided a 292% increase in impact strength over the blend but reduced modulus by 25%. In contrast, 0.7 phr addition of the chain extender, poly(styrene-acrylic–co-glycidyl methacrylate) (SA–GMA), yielded comparable performance to that of neat PET without sacrificing the tensile and flexural properties. When both compatibilizers were present in the blend, the mechanical properties remained relatively unaltered or decreased with increasing EBA–GMA content. The differences in mechanical performance observed were considered in relation to the strengthening mechanism of the two differing compatibilizers and their effects on the miscibility of the blend.

INTRODUCTION

Biobased products are of high importance when considering climate change mitigation, greenhouse gas emission, and sequestration. This is because carbon absorbed by plants is used to produce biobased products, which is then released at the end of the product life cycle (so-called “green carbon”) without increasing atmospheric CO₂ concentration. In contrast, fossil-based products use fossil (“black”) carbon, which was previously stored underground and releases additional CO₂ into the atmosphere.¹

Under this consensus, biobased polymers have been a research hotspot in recent years. Poly(ethylene terephthalate) (PET) is one of the most commercially used thermoplastics and is found in products such as drink bottles, food packaging, automotive parts, household goods, and electronics.² PET is a clear thermoplastic with good barrier, stiffness, strength, and chemical resistance.³ The complete worldwide use of PET has expanded from 11.8 million metric tons in 1997 to 54 million tons in 2010. However, by 2013 only 0.6 million tons was bio-PET, which contains 20% biobased carbon derived from biobased ethylene glycol.⁵ Even though 100% bio-PET has been produced under the “Plant PET Technology Collaborative” launched by The Coca-Cola Company, it will still take time before its production surpasses the production of conventional PET and its adoption goes beyond the packaging sector.

Poly(lactic acid) (PLA) is 100% biobased and the best-established biobased thermoplastic polymer. In addition, PLA is available at comparable prices to those of fossil-derived thermoplastics.⁶ To achieve good mechanical performance and high biocarbon content, a large number of studies have been reported by blending different polymers (e.g., natural rubber) with PLA⁷⁻⁹ Similarly, blending PET with PLA would be an easier way to significantly increase the biobased component ratio and to have a competitive cost at the current technological level. As there is only a small price difference between PET and PLA ($1.97 and $2.11 US per kg, respectively, in July 2017)¹⁰ and with the demand for...
biopolymers growing and PLA being the most-prevalent biobased thermoplastic in the market, the price point of this resin will soon be on par with PET as the production costs reduce for the bulk synthesis of PLA. Previous studies with PET have included up to 40 wt % PLA in melt compounding, with most research focused on less than 20 wt %. However, these polymer blends show inferior mechanical performances because of the high loading of PLA in PET, making it unattractive to the industry due to reductions of 80% in impact strength, 50% in tensile strength, and 60% in elongation at both 20 and 40 wt % of PLA in a PET matrix.11−14 The main two reasons for these reductions are as follows: (a) the processing temperature of PET (∼260−300 °C), which is well above the melting temperature of PLA (∼160 °C), triggering the PLA decomposition15−17 and chain scission13 during blend compounding and (b) the immiscibility of the two polymers, which has been reported even for blends containing only small amounts of PLA (5 wt %).12,13 Yuryev et al. found that PLA was supertoughened using poly(ethylene-n-butylene-acrylate-co-glycidyl methacrylate) (EBA−GMA) (Figure 1a) through reactive compatibilization in the presence of an epoxy-based chain extender (Figure 1b) at temperatures greater than 250 °C.18 The authors noted that the epoxy groups in EBA−GMA react with hydroxyl and carboxylic groups of PLA and form a micelle structure as a nucleation center. Additionally, styrene-acrylic−GMA (SA−GMA) aided in reducing the thermal degradation effects of PLA by means of a similar epoxide reaction. The same theory was applied in a propylene carbonate (PC)/PLA blend, and the impact strength was increased more than 10 times compared with that of blends

![Figure 1. Chemical structures of (a) EBA−GMA and (b) SA−GMA, and (c) their reactions with PET and PLA.21−24](image1)

![Figure 2. SEM images of the (a, b) neat PET, (c, d) T90, (e, f) T80, (g, h) T70, and (i, j) neat PLA at different magnifications.](image2)
without these epoxides. However, a PET/PLA blend is quite a different case because PC has very limited reactivity with epoxides, while PET and PLA (polymers) show higher reactivity and compete to react with both EBA–GMA and SA–GMA, which leads to uncertainty in the performance and the effect the compatibilizers have on the PET/PLA blend system.

In this study, up to 30 wt % PLA, considered a relatively large amount as it is higher than that of other reports except for some specimens with very poor performance, was added into a PET matrix to obtain a product with greater biobased carbon content than that of PET alone. Both EBA–GMA and SA–GMA were employed to improve the properties of PET/PLA blends at minimal levels to maintain as much biobased content in the final formulations. Considering the same functional groups (epoxy groups) with a possibility to generate PET–EBA–GMA–PLA and PET–SA–GMA–PLA (Figure 1c), both were treated as compatibilizers. Comparison of their effects was also illustrated from morphological observations as well as mechanical and thermodynamic measurements.

### RESULTS AND DISCUSSION

#### Morphological Observations

Blending of two different polymers tends to result in compatibility issues, and poor miscibility between continuous and dispersed phases results in inferior mechanical properties. Therefore, morphologies of PET/PLA blends were compared using scanning electron microscopy (SEM). The images of PET/PLA blends without a compatibilizer are shown in Figure 2. Because of the ultrahigh processing temperature for PLA, T90 displays small PLA droplets with an average diameter of 1.5 μm and the size increases to 2.3 μm for T80. In these formulations, the interface does not show a distinct boundary, which relates to their sufficiently close values of Hansen solubility parameters.
were occupied by the new generated micelles from EBA. The cross-sectional surfaces become rougher. These rough areas are distinguished. With an increasing EBA amount, the PLA phase is etched by the electron beam. It indicates that PLA molecules were all associated with PET−GMA. After computation of the interfacial tension between the PET and PLA, the lowest sum found for EBA−GMA, implying that the two polymers have a greater surface energy than that of EBA−GMA. After computation of the interfacial tension between the constituent polymers, PET and PLA have the smallest value (21.5 and 22.6 for PLA and PET, respectively). In addition, the effects of transesterification between PET and PLA chains cannot be ignored. The decomposed PLA during processing exposed extra carboxyl and hydroxyl end groups, which can react with the acyl oxygen of PET to generate PET−PLA chains (Figure S1). Thus, the PET−PLA chains improve their compatibility. When PLA increased to 30%, the cross section shows a large average particle size of 3.6 µm with a wide size distribution as the coalescence opportunities of PLA droplets increase.

Figures 3–5 show the morphologies of PET/PLA blends compatibilized with EBA−GMA, SA−GMA, and both, respectively. The effects of different compatibilizers were easily distinguished. With an increasing EBA−GMA amount, the cross-sectional surfaces become rougher. These rough areas were occupied by the new generated micelles from EBA−GMA, where the long ethylene chains aggregated in the micelle center and the epoxy groups outside connected to PET and/or PLA. In contrast to the EBA−GMA system, the newly generated PET−SA−GMA−PLA in PET/PLA/SA−GMA blends increased the compatibility between PET and PLA. As a result, the increasing addition of SA−GMA largely decreased the droplet sizes of incompatible PLA. It is worth noting that the PET/PLA phases transfer to co-continuous phases when the SA−GMA amount is greater than 0.7 phr, while the PLA phase is etched by the electron beam. It indicates that PLA molecules were all associated with PET−SA−GMA−PLA chains and further connected to the PET phase. Thus, the PET and PLA regions were continuously distributed along PET−SA−GMA−PLA chains and formed co-continuous phases. In addition, this morphology indicates that both components can enhance the mechanical properties of the system.

Therefore, the SA−GMA amount was fixed at 0.7 phr and the introduction of different amounts of EBA−GMA in PET/PLA blends was tested. However, the co-continuous phases were disturbed by the EBA−GMA micelles because of the reactions competition of epoxy groups in both compatibilizers with hydroxyl/carboxylic groups in the polyesters.

To further evaluate the miscibility of PET/PLA blends, contact angles were measured and subsequent surface tensions and interfacial tensions were calculated, as seen in Table 1. It was observed that the contact angle for PET was the smallest when subjected to both water and diiodomethane. Next, PLA was found to have a contact angle in the low 60° range for both polar and nonpolar liquids showing slightly less affinity than that of PET, while EBA−GMA had a hydrophobic characteristic to it with regards to the water droplet contact angle and an organophilic nature when diiodomethane was present on its surface. These differing liquid affinities resulted in the calculated surface tensions for the individual polymers that were extrapolated to the processing temperature. The polar components are similar for both PET and PLA, while EBA−GMA demonstrates almost no polar portion. For the dispersive components, PET and EBA−GMA are comparable with values of 18 mN m⁻¹ while the PLA is approximately half this value. For the polymers’ overall surface tensions, they had a descending magnitude starting from PET to PLA with the lowest sum found for EBA−GMA, implying that the two polyesters have a greater surface energy than that of EBA−GMA. After computation of the interfacial tension between the constituent polymers, PET and PLA have the smallest value of 2.1

### Table 1. PET, PLA, and EBA−GMA Contact Angles, Extrapolated Surface Tensions, Including Polar and Dispersive Components, and Geometric Mean Interfacial Tensions

| material      | contact angle (°) | surface tension (mN m⁻¹) @ 270 °C | interfacial tension (mN m⁻¹) @ 270 °C |
|---------------|------------------|----------------------------------|--------------------------------------|
|               | water            | diiodomethane                    | γ | γ⁻ | γᵣ | PET/PLA | 2.1 |
| PET           | 55.4 (±0.3)      | 43.7 (±1.2)                      | 36.2 | 18.5 | 17.7 | PET/PLA | 2.1 |
| PLA           | 61.6 (±4.4)      | 63.0 (±0.9)                      | 27.3 | 8.2 | 19.2 | PET/EBA−GMA | 15.3 |
| EBA−GMA       | 101.8 (±0.6)     | 51.9 (±0.8)                      | 18.3 | 18.2 | 0.1 | PLA/EBA−GMA | 18.7 |

Figure 5. SEM images of (a, b) T66.5-E3.5-J0.7, (c, d) T63-E7-J0.7, (e, f) T59.5-E10.5-J0.7, and (g, h) T56-E14-J0.7 at different magnifications.
referring to preferential miscibility between them over EBA—GMA. This infers that the PLA chains will tend to form droplets within the PET matrix phase. On the contrary, EBA—GMA will remain immiscible in the blends when present, though PET is expected to act as an intermediate between EBA—GMA and PLA because of the slightly lower interfacial tension compared to that of PLA/EBA—GMA. However, both polyesters will still vie for epoxide reactivity during extrusion that may alter the final morphology of the blend systems by providing more attraction between the different constituents.

To provide morphological data of samples prior to a mechanical test, atomic force microscopy (AFM) was conducted with four of the blends, as depicted in Figure 6.

From the initial image of the T70 blend, there are areas of elongated and varying sized PLA regions within the PET matrix, emphasizing nonuniformity of the minor phase and a lack of miscibility (Figure 6a). Upon the introduction of SA—GMA at 0.7 phr, the PLA regimes are more strandlike and show signs of co-continuous features along with a reduction in the size of the dispersed droplets (Figure 6b), as seen with SEM. As for the blend containing EBA—GMA at 10.5 wt % (Figure 6c), there remain globular PLA zones throughout the PET matrix, with EBA—GMA dispersed randomly throughout the blend. For the combination of the two compatibilizers (Figure 6d), the observed architecture resembles that of the SA—GMA sample with PLA close to co-continuity. EBA—GMA in this blend is then situated at the boundaries of PET and PLA as the reacted epoxide groups help with miscibility of the base polymers causing EBA—GMA to preferentially situate at interfacial sections, though these are still scattered haphazardly throughout the blend.

**Mechanical Properties.** The tensile properties and impact performances of several PET/PLA blends are shown in Figures 7 and 8, where all specimens were obtained at the processing temperature of 270 °C, except neat PLA at 190 °C. The remainder of the mechanical results for all samples along with the flexural properties are reported in Table S1 in the Supporting Information. Following the mixing rule, both the tensile and flexural strength/modulus slowly increased with the addition of PLA, while the notched impact strength and elongation at break dramatically decreased, indicating a brittle performance of PET/PLA blends without a compatibilizer. The impact strength of PET/PLA blends was improved using EBA—GMA, but the elongation at break was still low even when compatibilized with 14% EBA—GMA. Interestingly, the addition of a small amount of SA—GMA was able to recover the impact strength and elongation at break even at 0.3 phr and reach the highest values of 30.1 J m⁻¹ impact strength and 125.4% elongation at break at 0.7 phr, which is similar to the performance of neat PET without sacrificing the tensile and flexural properties. Furthermore, the blend properties of PET/PLA/SA—GMA do not show notable improvement with the...
assistance of EBA—GMA, indicating that SA—GMA is more effective in PET/PLA blends.

Regarding the thermomechanical performance of the blends, there is an incremental decrease in the heat deflection temperature (HDT) as PLA is added, as illustrated in Table 2, which is due to the glass transition temperature of PLA.

Table 2. Heat Deflection Temperature (HDT) of PET/PLA Blends

| Blend      | HDT (°C) |
|-----------|----------|
| PET       | 70.0 ±0.35 |
| T90       | 68.8 ±0.28 |
| T80       | 67.5 ±0.43 |
| T70       | 62.3 ±0.72 |
| PLA       | 52.8 ±0.29 |
| T70-J0.3  | 66.5 ±0.49 |
| T70-J0.5  | 64.9 ±0.71 |
| T70-J0.7  | 68.3 ±0.36 |
| T70-J1.0  | 65.8 ±0.46 |
| T66.5-E3.5| 67.3 ±1.02 |
| T63-E7    | 66.9 ±0.81 |
| T59.5-E10.5| 65.4 ±0.71 |
| T56-E14   | 60.1 ±0.49 |
| T66.5-E3.5-J0.7| 67.6 ±0.35 |
| T63-E7-J0.7| 66.5 ±0.39 |
| T59.5-E10.5-J0.7| 65.0 ±0.58 |
| T56-E14-J0.7| 63.0 ±0.47 |

However, this loss in stiffness at elevated temperatures is reduced as SA—GMA is incorporated up to 0.7 phr. Similarly, EBA—GMA showed an enhancement in the HDT over the 70:30 PET/PLA blend at low loadings, though this gradually reduced as the higher content of the compatibilizer was present in the system because of the rubbery phase present. The same trend was prevalent in the combined blends with both SA—GMA and EBA—GMA.

**Thermal Properties.** Differential scanning calorimetry (DSC) characterization was carried out to further illustrate the effects of compatibilizers on PET/PLA blends. As shown in Table 3, two separate glass transition temperatures for PET and PLA were detected for all blend formulations and these shifted to higher temperatures by the addition of compatibilizers for both polymers. This indicates that the generated PET—SA—GMA—PLA and PET—EBA—GMA—PLA by epoxide reactions induced a molecular weight increase and these highly cross-linked molecules further enhanced the entanglement of PET and PLA chains. Compared with those of neat PET and PLA, $T_g$ differences of the two polymers become closer, which shows partial miscibility with the help of compatibilizers. It is noteworthy that the $T_g$ positions are closer when using SA—GMA, while they get larger with EBA—GMA, when taking T70 as a reference: the addition of 0.7 phr of SA—GMA resulted in $T_g$ increases from 61.6 to 63.7 °C and from 50.6 to 54.8 °C for PET and PLA, respectively, suggesting that the $T_g$ gap was shortened from 11.0 to 8.9 °C while the corresponding $T_g$ gap was enlarged to 16.9 °C with 14% EBA—GMA (T56-E14). In addition, SA—GMA shows larger effects on $T_g$ shifts of PLA while EBA—GMA exhibit larger effects on those of PET: up to 4.7% (PET) and 8.9% (PLA) increase using SA—GMA; up to 15.6% (PET) and 7.8% (PLA) under the addition of EBA—GMA. These findings reveal that the compatibility of PET/PLA/S—GMA is higher than that of the EBA—GMA system by cross-linking more decomposed PLA while EBA—GMA has a relatively high affinity to react with PET. This result is in accordance with other reports that SA—GMA displays partial miscibility with PLA and an array of other polyesters while EBA—GMA and PLA are immiscible forming separate phases with weak adhesion.

As shown in Table 3, the addition of different compatibilizers leads to crystallinity changes. The crystallinities of both PET and PLA are higher in the EBA—GMA system than those in the SA—GMA system. This can be explained by the micelle structure of PET—EBA—GMA—PET acting as a nucleation center to accelerate crystallization, while the highly branched structure of PLA—SA—GMA—PET cannot be readily incorporated into the crystal lattice. Interestingly, the crystallinity of PET primarily increased with the addition of the SA—GMA content and the crystallinity of PLA decreased, whereas the
opposite tendency was presented in the EBA−GMA system. It might be caused by the following reasons: for the SA−GMA scenario, PET will crystallize first during cooling and will have more crystallinity from the increased molecular weight with the help of SA−GMA. This will segregate the PLA component, reducing the crystallization capability of PLA, which in turn lowers the PLA crystallinity. For the alternative case with EBA−GMA, the rubbery component impedes the crystallinity of PET during cooling because of viscous characteristics that prevent PET to flow easily together reducing the PET crystallinity. At the same time, PLA having a low viscosity at the crystallization temperature of PET will be able to form larger PLA regions that allow for increased crystallization.

**Rheological Characterization.** The angular-frequency-dependent complex viscosity modulus for PET/PLA blends are shown in Figures 9a and 10a. It was detected that the complex viscosities of all PET/PLA blends with EBA−GMA and/or SA−GMA more than doubled, which further demonstrated that epoxide reactions caused a molecular weight increase. Specifically, shear-thinning behaviors were shown at all frequencies, and shear-thinning of the blends with EBA−GMA exhibited this effect more significantly. It can be explained by the following hypothesis. Although the epoxy group density of SA−GMA is greater than that of EBA−GMA, the total amount of epoxy groups in PET/PLA/EBA−GMA is close or even higher than that in PET/PLA/SA−GMA. Therefore, there are more polyester arms grafted on EBA−GMA chains, indicating a comb architecture and greater degree of shear thinning.

Figures 9b,c and 10b,c show evolutions of the storage and loss modulus at different angular frequencies. Significant increases of $G'$ can be observed with increasing concentrations of SA−GMA and/or EBA−GMA. Gel-like behavior ($\tan \delta < 1$, Figures 9d and 10d) was seen only in blends with EBA−GMA. In the case of T59.5-E10.5, T56-E14, and T56-E14-J0.7, the dependence of $G'$ on frequency was weak and $G''$ was totally independent of the frequency at a low-frequency range, revealing nonterminal low-frequency behaviors. It can be explained by a large agglomeration of ethylene chains as well as fixed PET and PLA chains in the samples, resulting in effectively restrained polymer chains. These results illustrated different strengthening mechanisms. The long ethylene-chain-based EBA−GMA was able to form a micelle structure with hydrophobic ethylene chain inside and fixed PET/PLA chains by epoxide reactions outside. This structure acts as an elastomeric reinforced center that can absorb and dissipate impact energy to avoid craze and crack propagation. However, the micelles show relatively poor adhesion with the
PLA phase. On the other hand, SA−GMA with a high density of glycidyl methacrylate units cross-linked both PET and PLA into the same molecule, which connected both PET and PLA phases and increased their compatibility. Combined with their mechanical properties, the lower value of elongation at break for EBA−GMA-reinforced samples was likely caused by the low adhesion among micelle and PET/PLA phases.

**CONCLUSIONS**

Up to 30 wt % biobased PLA was successfully introduced into a PET matrix, and two different compatibilizers, EBA−GMA and SA−GMA, were used for improving the mechanical properties of the blends. Both compatibilizers increased the impact strength as compared to that of neat PET. Unlike the effects of EBA−GMA that resulted in a decrease of modulus and elongation at break, blends with 0.7 phr of SA−GMA showed a high impact strength of 30.1 J m⁻¹, compared with the base 70:30 wt % PET/PLA blend, without sacrificing the tensile and flexural properties. The use of both compatibilizers together did not show substantial improvements, which can be explained by their different strengthening mechanisms. SA−GMA cross-linked PET and the decomposed PLA by elevated temperature processing and increased their compatibility, resulting in co-continuous phases in the blend, while the micelle in the EBA−GMA system showed relatively poor adhesion to the PLA phases.

Overall, 0.7 phr of SA−GMA, acting simultaneously as a chain extender and a compatibilizer, was sufficient in overcoming all of the challenges related to PET/PLA blends including PLA degradation at high processing temperatures, the lack of miscibility between PET and PLA, and minimal use of a compatibilizer to retain biobased carbon content. It also provided a satisfactory mechanical performance on par with or superior to neat PET. These findings were observed from AFM and SEM morphologies, along with the interfacial tension calculations, crystallinity and glass transition observations, and viscosity from rheological analysis. Considering the cost–performance balance, blending PET/PLA with SA−GMA is an attractive approach to replace a portion of the PET and to increase the biobased carbon content simultaneously.

**EXPERIMENTAL SECTION**

**Materials.** Two injection-grade polymers were used in this study: PET (Laser+, B90A) was produced and supplied by DAK Americas and PLA (Ingeo 3251D) was purchased from Nature Works LLC. Additionally, poly(ethylene-n-butylene-
Table 4. Sample Names and Characteristics of DifferentCompatibilizers

| sample names  | PET (wt %) | PLA (wt %) | EBA−GMA (wt %) | SA−GMA (phr) |
|---------------|------------|------------|----------------|--------------|
| neat PET      | 100        |            |                |              |
| T90           | 90         | 10         |                |              |
| T80           | 80         | 20         |                |              |
| T70           | 70         | 30         |                |              |
| neat PLA      |             |            | 100            |              |
| T66.5-E3.5    | 66.5       | 30         | 3.5            | 0.3          |
| T63-E7        | 63         | 30         | 7              | 0.5          |
| T59.5-E10.5   | 59.5       | 30         | 10.5           | 0.7          |
| T56-E14       | 56         | 30         | 14             | 0.7          |
| T70-J0.3      | 70         | 30         |                | 1.0          |
| T70-J0.5      | 70         | 30         |                | 0.7          |
| T70-J0.7      | 70         | 30         |                | 0.7          |
| T70-J1.0      | 70         | 30         |                | 0.7          |
| T66.5-E3.5-J0.7 | 66.5   | 30         | 3.5            | 0.7          |
| T63-E7-J0.7   | 63         | 30         | 7              | 0.7          |
| T59.5-E10.5-J0.7 | 59.5  | 30         | 10.5           | 0.7          |
| T56-E14-J0.7  | 56         | 30         | 14             | 0.7          |

Acrylate−co-glycidyl methacrylate) (EBA−GMA) was supplied by DuPont company under the trade name Elvaloy PTW. This terpolymer chain consists of 66.75 wt % ethylene, 28 wt % butyl acrylate, and 5.25 wt % glycidyl methacrylate. Another compatibilizer, poly(styrene−acrylic−co-glycidyl methacrylate) (SA−GMA) known as Joncryl ADR-4368C (flakes), was supplied by BASF. It has an average molecular weight of 6800 g mol$^{-1}$ with an epoxy equivalent weight of 285 g mol$^{-1}$, indicating 49.8 wt % glycidyl methacrylate ($M_w = 142.15$ g mol$^{-1}$) according to the equation34

$$\text{epoxy equivalent weight} = \frac{\text{molecular weight of Joncryl}}{\text{number of epoxy groups}}$$

(1)

The chemical structures of EBA−GMA and SA−GMA have significant similarities, but these terpolymers have a large variation in reactivity on the account of the 10-fold difference in epoxy groups due to the amount of glycidyl methacrylate.

**Processing.** PET and PLA pellets were dried for 16 h at 80 °C to remove the moisture. EBA−GMA and SA−GMA were kept under room-temperature conditions (23 °C, 50% relative humidity), with the chain extender ground into a powder before utilization. The processing materials based on different formulations were blend-compounded and subsequently injection-molded using a lab-scale co-rotating twin-screw extruder and an injection molding machine (DSM Xplore, Netherlands). The processing conditions were as follows: a mixing temperature of 270 °C (except for neat PLA processed at 190 °C), a screw speed of 100 rpm, a residence time of 2 min, a mold temperature of 30 °C, and an injection pressure of 6 bars with a holding pressure of 8 bars and holding time of 10 s. Tensile, flexural, and impact specimens were prepared for further analysis. Abbreviations of the sample names are listed in Table 4.

**Characterizations.** A SEM (Phenom Pro X, Phenom-World, Netherlands) was used for morphological observations. The observation areas were directly collected from the cracked cross section parts after notched impact test and followed by Au coating for 10 s.

An Instron Universal Testing Machine (model 3382) was used to perform tensile (ASTM standard D638) and flexural tests (ASTM standard D790). Crosshead speeds of 14 mm min$^{-1}$ for the flexural test and 50 mm min$^{-1}$ for the tensile test were used. A Testing Machine Inc. Instrument equipped with a 5 lbs per ft Izod impact pendulum was used for notched Izod impact strength measurements (ASTM standard D256).

A differential scanning calorimetry (DSC) analysis was performed in a TA Instruments Q200 setup under N$_2$ flow (flow rate: 50 mL min$^{-1}$). The heating and cooling rates were 10 and 5 °C min$^{-1}$, respectively. Cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), cold crystallization enthalpy ($ΔH_{cc}$), and melting enthalpy ($ΔH_m$) of specimens were determined in the first heating scan. The glass transition temperature ($T_g$) values were obtained from the second heating scan. The degree of crystallinity ($χ_c$) of PET and PLA were calculated according to the following equation35,36

$$χ_c = \frac{ΔH_m - ΔH_{cc}}{ΔH_m^0} \times 100\%$$

(2)

where $ΔH_m^0$ is the melting enthalpy of the completely crystalline PET or PLA and $χ_c$ is the weight fraction of PET or PLA in the individual specimens. Here, the values of $ΔH_m^0$ of PET and PLA were 140 and 93.7 J g$^{-1}$, respectively.37,38

The heat deflection temperature was determined using a dynamic mechanical analysis equipment Q800 from TA Instruments, using a three-point bending test with a 0.455 MPa load and a heating rate of 2 °C min$^{-1}$, according to ASTM D648.

A strain-controlled rheometer (Anton Paar, MCR 302) was used to study the rheological properties. Tests were conducted using parallel-plate geometry (diameter = 25 mm) with a gap of 1 mm between the plates. A dynamic frequency sweep test was conducted using a fixed shear strain of 1% with a frequency range of 0.01–100 Hz (from low to high frequency). The rheological measurements were all performed at 255 °C under N$_2$ atmosphere.

Contact angle analysis was performed with a ramé-hart standard goniometer 260-U1 (ramé-hart Instrument Co.) on neat samples of PET, PLA, and EBA−GMA, while SA−GMA, being a powder, could not be characterized following this method. Both deionized water (polar) and diiodomethane (nonpolar) were used as the standard liquids for sessile drop analysis with DROPimage software (version 2.8.0S) using the
cycle method. The Owens–Wendt–Rabel–Kaelble model was used for surface tension calculations followed by extrapolation to processing temperatures, which were taken for interfacial tension determination with the geometric mean equation, as discussed in a previous publication.29

Atomic force microscopy (AFM) was conducted using a Multimode 8 (Bruker Nano Inc.) with a Nanoscope V controller and Nanoscope Software (version 8.15) for capturing images. An RTESPAS25 Si cantilever was used as the probe, and scans were carried out in a tapping PeakForce quantitative nanomechanical property mapping mode. Samples were ultramicrotomed prior to imaging with a Leica Ultracut (Leica) to provide a smooth surface plane for imaging. The images were then analyzed with Nanoscope Analysis Software.

ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01353.

Reactions of PLA decomposition and transesterification between PET and PLA at a processing temperature of 270 °C (Figure S1); mechanical properties and heat deflection temperature (HDT) of all PET/PLA blends (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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