Toughening Biosourced Poly(lactic acid) and Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) Blends by a Renewable Poly(epichlorohydrin-co-ethylene oxide) Elastomer

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ABSTRACT: A series of sustainable polymer blends from renewable poly(lactic acid) (PLA), poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3,4HB), and poly(epichlorohydrin-co-ethylene oxide) (ECO) elastomer were fabricated via a melt blending method to gain balanced physical performance. The interplay of the composition, mutual miscibility, and viscosity ratio of the pristine PLA, P3,4HB, and ECO elastomer resulted in diverse phase structures of the ternary blends. An excellent flexibility at an elongation of 270% was achieved for the PLA/P3,4HB/ECO (70/20/10) blend with a core–shell structure. The PLA/P3,4HB/ECO (70/10/20) blend with a phase-separated structure exhibited a high impact strength of 54 kJ/m², which is 25 times over that of the neat PLA. The relationship between the phase structure and physical performance of the blend was analyzed based on the compositions, surface tension, and physical characteristics of the neat components. Combining the compatibilization of the P3,4HB phase and ECO elastomer toughening played a crucial role in enhancing the mechanical properties of the blends.

1. INTRODUCTION
Sustainable polymers derived from biomass resources are gaining increasing attention because of the concern over energy crisis and environmental problems in recent years.1,2 Among the commercially available bioplastics, biodegradable and renewable aliphatic polyesters such as poly(lactic acid) and polyhydroxyalkanoates (PHAs) are considered as the most promising alternatives to petroleum-based polymers in many application areas. As a star renewable polyester, poly(lactic acid) (PLA) is enjoying very fast growth in the market owing to its attractive attributes such as high strength, good processability, and large-scale availability at a competitive price. The application of PLA has expanded from packaging to automotive and electric applications, which are currently mainly dominated by the petroleum-based plastics.3–5 Yet, the poor impact resistance and flexibility are major hurdles for the wide and diverse applications of PLA. Considerable efforts have been devoted to toughening PLA via different strategies including plasticization, copolymerization, blending, and compositing.6–12 Blending PLA with ductile polymers to obtain highly toughened PLA-based materials is a very facile method with the advantages of cost-effectiveness and easy large-scale production.13–15 P3,4HB is a new commercially available member of the PHA family synthesized by microorganisms from renewable resources. Compared to other commercial PHAs, the P3,4HB polymer has a lower degree of crystallinity and lower melting temperature but better flexibility owing to the introduction of 4-hydroxybutyrate (4HB) comonomer unit in the main chain. Consequently, P3,4HB has broad application prospects ranging from biomedical to consumer products such as packaging. The sustainable characteristics and complementary performance of the commercial P3,4HB and PLA have aroused a lot of interest in their binary blend to achieve fully renewable materials for wide applications.16–19 Unfortunately, because of limited miscibility between the PLA and P3,4HB components, it is indeed very difficult to obtain a desirable toughening effect for their simple binary blend.

Recently, a multiphase blend having more than two components was proved to be a very effective strategy for PLA modification. Compared to the simple binary blend, the multiphase blend has more complex and diverse morphologies, a more excellent balance of properties, and new functionalities. To achieve excellent toughness, Liu et al. formulated PLA, ethylene methyl acrylate glycidyl methacrylate (EMA-GMA), and a commercial ionomer.20 Recently, Zhang et al. reported a multiphase blend of sustainable PLA, poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV), and poly(butylene succinate) (PBS) exhibiting complicated morphologies and synergistic physical properties.21 Supertough PLA-based multiphase blends from PLA, EMA-GMA, and biorenewable polyether...
block amide were also reported by Zhang et al., which could be used as promising matrices for natural fibers to fabricate high-performance biocomposites. 22–24 Recently, Ali et al. reported a series of PLA-based multiphase blends with improved mechanical properties from PLA and other biobased polymers including PBS, poly(butylene adipate-co-terephthalate) (PBAT), etc. 25,26 Mohanty et al. developed a series of ternary blends including PLA/PBS/PBAT ternary blends and novel reactive multiphase blends from Nylon 6, polypropylene, and PLA. 27,28 Guo et al. adopted poly(methyl methacrylate) (PMMA) as a compatibilizer for a PLA/PBAT blend to achieve a highly toughened PLA-based blend. 29 These previous works inspired us that fabricating a multiphase blend from PLA and other components with complementary properties is a very cost-effective, practical, and promising method to obtain high-performance materials. However, to date, the petroleum-based polymers are the most used modifying agents for the PLA and PHA blends in the literature. It neither goes with the trend of bioeconomy nor is it favorable for solving environmental problems. In this context, developing renewable multiphase blends with high performances from the biobased polymers is highly pursued for achieving sustainable development goals.

Combining interfacial compatibilization and toughening modification is a key point for improving the properties of the multiphase PLA blends. 26–28 Using renewable elastomers having good compatibility with the biopolymer matrices as toughening agents will be a very promising and effective method to achieve high-performance renewable polyester-based multiphase blends. Poly(epichlorohydrin-co-ethylene oxide) copolymer (ECO), manufactured by the polymerization process of epichlorohydrin and ethylene oxide monomers, is an important commercial elastomer enjoying wide application areas such as automotive and electronic applications. The polyether backbone coupled with side bulky chlorine groups endows the ECO elastomer excellent performance including good low-temperature flexibility and high resistance to aging, weathering, and fuel. More importantly, the epichlorohydrin monomer can now be commercially produced from glycerin, which is a byproduct of the transformation of plant oils. 30,31 Through their own patented glycerin-to-epichlorohydrin processes, chemical companies such as Dow and Solvay have already supplied biobased epichlorohydrin products from the biosourced glycerin in the market. Based on this progress, biobased ECO rubber derived from the bioderived epichlorohydrin shows huge potential and bright prospects. For example, Toyota in collaboration with Zeon has made impressive progress in producing the biobased ECO rubber (Biohydridin) for the usage of fuel-oil-resistant applications of automobile gaskets, hose diaphragms, etc.

Considering the encouraging progress in the biosourced ECO and its excellent properties, the ECO elastomer is an ideal sustainable modifying agent for enhancing the mechanical property of brittle polymers. 32,33 We previously reported that the ECO elastomer could improve the crystallization behavior and toughness of PLA even with only a limited miscibility. 32 More interestingly, the ECO elastomer was also found to have very good miscibility with PHAs such as poly(3-hydroxybutyrate) (PHB) or PHBV. 34–36 Given the environmental advantages, good miscibility, and complementary properties of the PLA, P3,4HB, and ECO components, in this work, we focused on fabricating ternary blends from the renewable PLA, P3,4HB, and ECO elastomer to achieve fully renewable and toughening multiphase biobased polymer blends. The miscibility, phase morphology, crystallization behavior, and mechanical properties of the multiphase blends were thoroughly studied to figure out the relationship between the phase structure and physical property.

2. RESULTS AND DISCUSSION

2.1. Miscibility of the Blends. Dynamic mechanical analysis (DMA) was first applied to characterize the mutual miscibility of the three different components in present blends. Figure 1a shows the damping factor (tan δ) for neat PLA; neat P3,4HB; and binary blends from PLA, P3,4HB, and ECO. Neat PLA and P3,4HB exhibit a glass transition at 76 and 11.8 °C, respectively. Compared to that of the neat components, the transition of each component shifts slightly close to each other for the binary PLA/ECO blend, demonstrating a limited compatibility between PLA and ECO phases. This result is in agreement with our previous report. 27 It was reported that the PHB and PHBV having similar functional groups as P3,4HB were miscible with the ECO copolymer. 34–36 Consequently, it is reasonable to expect that P3,4HB will also show good compatibility with the ECO copolymer. As shown in Figure 1a, a little shift toward each other was observed for the P3,4HB/ECO (70/30) binary blends, suggesting that the P3,4HB and ECO phases have some compatibility. Several reports indicated that PLA and P3,4HB were immiscible in their binary blend. 17,18 However, as for the PLA/P3,4HB binary blends in the present work, we find that the glass transition temperatures
of the components move more clearly toward each other compared to that of the PLA/ECO and P$_{3,4}$HB/ECO binary blends. This result implies that the P$_{3,4}$HB and PLA phases have better compatibility than the PLA/ECO and P$_{3,4}$HB/ECO blends. To further figure out the miscibility between the components, Fourier transform infrared (FTIR) spectroscopy was performed on the neat polymer and their binary blends, and the results are presented in Figure S3 (Supporting Information). For the PLA/ECO blend, the bands ascribed to the C=O stretching modes of PLA slightly shifted to higher regions, indicating some intermolecular interaction between the PLA and ECO phases. In addition, the peaks became narrower, which may be due to the improved crystallization of PLA in the presence of ECO phases. It has been noted that the carbonyl stretching region for PLA/P$_{3,4}$HB is very complicated, which is because of the crystallization of the components and possible transesterification between the phases. However, an apparent shift of the peaks to high wavenumbers was observed for the bands, suggesting that the miscibility is attributed to interassociation between the phases. As for the P$_{3,4}$HB/ECO binary blend, an obvious interassociation shoulder was exhibited in the spectra, demonstrating good miscibility between the ECO and P$_{3,4}$HB phases. The interassociation may be attributed to interactions of the ester groups of P$_{3,4}$HB with the ether moieties and the chlorine group of the ECH unit in the ECO copolymer. The partial miscibility of P$_{3,4}$HB with the PLA and ECO phases suggests that the P$_{3,4}$HB component can be utilized as a potential compatibilizer for PLA and the ECO elastomer. Our speculation is verified in the results of the following ternary blends. Figure 1b shows the DMA traces of the ternary blends with various concentrations. The content of P$_{3,4}$HB showed an obvious influence on the miscibility among the components in the blends. For the blend with a higher content of P$_{3,4}$HB, such as PLA/P$_{3,4}$HB/ECO (45/45/10), the tan$\delta$ peaks of the components shift toward each other more apparently. This result demonstrates that the introduction of P$_{3,4}$HB improves the miscibility of PLA and ECO, which will be beneficial to improve the toughening effect of the ECO elastomer for the PLA matrix.

2.2. Phase Morphology of the Blend. Phase behavior plays a very important role in determining the mechanical property of polymer blends. Figures 2 and 3 present the scanning electron microscopy (SEM) images of the surface of all of the blends. In agreement with our previous report, a phase-separated structure is clearly observed for the PLA/ECO binary blend with the ECO dispersing in the PLA matrix due to the very limited miscibility of PLA and ECO. In contrast, for the P$_{3,4}$HB/ECO and PLA/P$_{3,4}$HB blends, the smaller size of dispersed phases and a very unclear interface indicate the good compatibility of the P$_{3,4}$HB phase with both the PLA and ECO phases. This result is also consistent with the DMA result. Figure 3 presents the SEM micrographs of cryomicrotomed surfaces of the PLA/P$_{3,4}$HB/ECO ternary blends. The morphologies of two minor phases in PLA/P$_{3,4}$HB/ECO (70/10/20) and PLA/P$_{3,4}$HB/ECO (70/15/15) blends are typical dispersed phase separation. The P$_{3,4}$HB and ECO phases tend to separately disperse as particles in the PLA matrix. With the content of P$_{3,4}$HB increasing, there is a trend to form a core−shell morphology. For example, although a kind of mainly phase-separated structure is observed in Figure 3b for the PLA/P$_{3,4}$HB/ECO (70/15/15) formulation, a small amount of composite-droplet structure can also be distinguished in the SEM image (shown in Figure S3, Supporting Information). Due to the composite-droplet structure, the core−shell particles are prone to become bigger and uneven distribution. Interestingly, the core−shell structure is more clearly observed in Figure 3c for the PLA/P$_{3,4}$HB/ECO (70/20/10) blend. One can clearly note the composite-droplet structure with some holes from detaching of the dispersed ECO particles. The PLA/P$_{3,4}$HB/ECO (45/45/10) blend presents a co-continuous phase structure of PLA and P$_{3,4}$HB phases with the selective location of the ECO phase in the P$_{3,4}$HB phases. Considering the better miscibility of P$_{3,4}$HB/ECO pairs than that of PLA/ECO pairs and the low binary blend with the ECO dispersing in the PLA matrix due to the very limited miscibility of PLA and ECO. In contrast, for the P$_{3,4}$HB/ECO and PLA/P$_{3,4}$HB blends, the smaller size of dispersed phases and a very unclear interface indicate the good compatibility of the P$_{3,4}$HB phase with both the PLA and ECO phases. This result is also consistent with the DMA result. Figure 3 presents the SEM micrographs of cryomicrotomed surfaces of the PLA/P$_{3,4}$HB/ECO ternary blends. The morphologies of two minor phases in PLA/P$_{3,4}$HB/ECO (70/10/20) and PLA/P$_{3,4}$HB/ECO (70/15/15) blends are typical dispersed phase separation. The P$_{3,4}$HB and ECO phases tend to separately disperse as particles in the PLA matrix. With the content of P$_{3,4}$HB increasing, there is a trend to form a core−shell morphology. For example, although a kind of mainly phase-separated structure is observed in Figure 3b for the PLA/P$_{3,4}$HB/ECO (70/15/15) formulation, a small amount of composite-droplet structure can also be distinguished in the SEM image (shown in Figure S3, Supporting Information). Due to the composite-droplet structure, the core−shell particles are prone to become bigger and uneven distribution. Interestingly, the core−shell structure is more clearly observed in Figure 3c for the PLA/P$_{3,4}$HB/ECO (70/20/10) blend. One can clearly note the composite-droplet structure with some holes from detaching of the dispersed ECO particles. The PLA/P$_{3,4}$HB/ECO (45/45/10) blend presents a co-continuous phase structure of PLA and P$_{3,4}$HB phases with the selective location of the ECO phase in the P$_{3,4}$HB phases. Considering the better miscibility of P$_{3,4}$HB/ECO pairs than that of PLA/ECO pairs and the low
viscosity of P3,4HB vs ECO and PLA, it is reasonable for the ECO phase selectively locating in the P3,4HB phases. These phase morphologies of the ternary blends are further confirmed in the complementary SEM and atomic force microscopy (AFM) images of cryofracture surfaces (shown in Figures S4 and S5, respectively). Especially in the SEM images with high magnification of cryofracture surfaces for the typical ternary blends (shown in Figure S4), one can clearly observe the composite-droplet structure for the PLA/P3,4HB/ECO (70/15/15) and PLA/P3,4HB/ECO (70/20/10) blends.

The morphology of ternary blends is usually very complex because of different interfacial tensions and viscosity ratios between the components.\(^3^8\) The spreading coefficient model is widely adopted to predict the phase morphology of the multiphase blends.\(^3^9\) Using the interfacial tensions between the components, it can calculate the values of the spreading coefficient according to the following equation proposed by Hobbs et al.\(^4^1\)

\[
\lambda_{CB} = \alpha_{BA} - \alpha_{CA} - \alpha_{BC}
\]

\(\lambda_{CB}\) is the spreading coefficient of C over B and \(\alpha_{CB}\) is the interfacial tension between C and B. In polymer A, B, and C multiphase blend, taking A as the matrix, if the value of \(\lambda_{CB}\) is positive, the component B tends to be encapsulated by C. When both \(\lambda_{CB}\) and \(\lambda_{BC}\) are negative, B and C will be predicted to form a phase-separated structure. To figure out the morphology of the PLA/P3,4HB/ECO ternary blend, the spreading coefficient model was applied to predict the morphology of the PLA/P3,4HB/ECO blend. The interfacial tension can be calculated according to the harmonic mean equation

\[
\alpha_{AB} = \frac{1}{\frac{1}{\gamma_A} + \frac{1}{\gamma_B}} - \frac{4r_{AB}^2 d_{AB}}{r_A^2 + r_B^2} - \frac{4r_{PA}^2 P_A}{r_A^2 + r_B^2} - \frac{4r_{PB}^2 B}{r_A^2 + r_B^2}
\]

based on the surface tension data listed in Tables S1 and S2 (Supporting Information). Based on these data, the interfacial value and spreading coefficient for each polymer pairs at processing temperature were calculated and are presented in Table 1. For the PLA/P3,4HB/ECO (70/10/20) and PLA/P3,4HB/ECO (70/15/15) blends, the theoretical calculation results are consistent with the actual morphologies shown in Figure 3. According to the calculations, the P3,4HB and ECO particles tend to form dispersed phases in the PLA matrix for the two PLA/P3,4HB/ECO (70/10/20) and PLA/P3,4HB/ECO (70/15/15) formulations. However, the calculated result is not in agreement with the core–shell structure of the PLA/P3,4HB/ECO (70/20/10) blend. In multiphase polymer blends, interfacial tension is not the only factor controlling the phase morphology. The melt viscosity and torque ratio of the components are also very important and non-negligible factors in determining the phase behavior.\(^4^2\) The theoretically predicted morphologies are simply based on the static interfacial tensions. Yet, in fact, the viscosity of each component will also have a significant influence on the morphology. Even when the two dispersed phases had equal compositions in ternary polymer blends, it was reported that the dispersed phase with a lower viscosity tended to form a shell encapsulating the other phase with a higher viscosity.\(^4^3\) Figure 4 shows rheological curves of the PLA, P3,4HB, and ECO components at the processing temperature. The ECO elastomer possesses a much higher viscosity than P3,4HB at the processing shearing rate. Consequently, considering the significantly lower viscosity of P3,4HB compared to that of ECO and the higher content of P3,4HB in the PLA/P3,4HB/ECO (70/20/10) formulation, it is reasonable that the P3,4HB phase with the lower viscosity tends to encapsulate the ECO phases, thus forming the core–shell structures. In addition, since it is a dynamic and nonequilibrium thermodynamic process, these core–shell-structured particles with polydisperse sizes are found to be unevenly distributed in the PLA matrix of the PLA/P3,4HB/ECO (70/20/10) formulation. The lower viscosity of P3,4HB may be due to the poor thermal stability during the melt-processing above 170 °C. Doh et al. had pointed out P3,4HB was thermally unstable and its molecular weight decreased rapidly with time at temperatures above 170 °C.\(^4^4\) During the processing at high temperature above 160 °C, random chain scission at ester groups will occur for the P3,4HB phase.\(^4^4\) Consequently, melt-processing below 160 °C is preferable for P3,4HB to avoid its thermal degradation. However, this processing temperature is unfortunately unsuitable for the present PLA/P3,4HB/ECO system. The poor thermal stability will also have a negative impact on the mechanical performance of P3,4HB and its blend.

### 2.3. Mechanical Properties
Figure 5a presents the tensile properties of the pristine PLA, P3,4HB, and binary blends. Neat PLA is a typically rigid and brittle plastic with a high tensile strength of up to 68 MPa and low elongation below 20%. Compared to PLA, neat P3,4HB is a relatively flexible polymer with a lower strength of 23 MPa and better elongation up to 30%. As reported in our previous report, the ECO elastomer was proved to be a good toughening agent for PLA.\(^3^5\) Addition of 30 wt % ECO improves the elongation of PLA to 100% yet greatly decreases the strength to 30 MPa. Blending 30 wt % ECO with P3,4HB significantly enhances the flexibility of the neat P3,4HB with the elongation increasing to 550% and the

![Complex viscosities of neat PLA, P3,4HB, and ECO.](image-url)

Table 1. Interfacial Tension and Spreading Coefficient Values for Polymer Pairs at 180 °C

| polymer pairs     | interfacial tension, \(\gamma_i\) (mN/m) | spreading coefficient, \(\lambda_i\) |
|-------------------|----------------------------------------|---------------------------------|
| PLA/P3,4HB        | 0.56                                   | \(\lambda_{AB} = 1\)            |
| PLA/ECO           | 5.99                                   | \(\lambda_{AC} = -2.12\)        |
| P3,4HB/ECO        | 7.55                                   | \(\lambda_{CB} = -12.98\)       |

\(^*\)Herein, taking A as the PLA matrix and B and C as the dispersed P3,4HB and ECO phases, respectively.

The P3,4HB component in the ternary blend will adversely affect the mechanical properties. The results also suggest that finding an effective way for enhancing the thermal stability of P3,4HB and PLA during the melt-processing is very important to further improve the tensile property of the present ternary blend.

Figure 6 shows the Charpy impact strength of the samples. Neat PLA shows an impact strength of only around 2 kJ/m² in a clearly brittle broken pattern. In contrast to the tensile property of the neat P3,4HB, the impact strength of P3,4HB is only at 1.4 kJ/m², which is even worse than that of the neat PLA. The poor thermal stability and low content of 4HB are considered as the main reasons for the poor toughness of the neat P3,4HB. The ECO elastomer was proved to be a very effective toughening agent for the brittle polymer like PLA. The impact strength of PLA/ECO (70/30) blends is extremely high up to 55 kJ/m². Although ECO has a certain degree of compatibility with P3,4HB, the impact property of the P3,4HB/ECO binary blend enjoys only a limited enhancement with an impact strength of 8 kJ/m². As for the ternary blends, the impact strength is remarkably improved compared to the pristine PLA. In the ternary blends, the ECO elastomer is considered as the main contribution to absorb the impact energy. The impact strength increases with increasing of the ECO contents in the ternary blends. The PLA/P3,4HB/ECO (70/10/20) blend shows a significant increase in impact strength to 54 kJ/m², which is 25 times over that of the neat PLA. Inconsistent with the tensile test results, the PLA/P3,4HB/ECO (70/20/10) formulation with a core–shell structure has only a very limited improvement in the impact strength. The unsatisfied toughening effect may be ascribed to the very poor impact strength of the neat P3,4HB during the high-speed impact test, which is inconsistent with the tensile property at a slowly constant tensile rate. High content of P3,4HB tends to result in a more adverse effect for the high-speed impact test. On the contrary, the ECO particle is more facile to transfer energy in dispersed-phase morphology than the core–shell phase morphology. In general, the content of the ECO in the ternary blends is the key factor in the impact behavior (Figure 7).

2.4. Impact Fracture Surface Morphology. The impact strength of the blend is strongly affected by the interfacial adhesion, size, and dispersion of the disperse phase.

Figure 5. Tensile stress–strain curves: (a) neat PLA, P3,4HB, and the binary blends; (b) ternary blends with various concentrations. 

Figure 6. Notched Charpy impact strength of neat components and binary blends: (A) neat PLA, (B) neat P3,4HB, (C) PLA/ECO 70/30, (D) P3,4HB/ECO 70/30, (E) PLA/P3,4HB 70/30, and (F) PLA/P3,4HB 30/70.
Favorable interfacial compatibility and a good distribution of the dispersed phases in the matrix play significant roles in toughening the blend. Aiming to figure out the native toughening mechanism in the blends, SEM was used to observe the morphology of the impact fracture surface of the samples. As shown in Figure 8, a typical brittle fracture behavior is observed for the pristine PLA: a very smooth surface without much deformation. The fracture surfaces of the PLA/ECO blend are rugged in agreement with its higher impact strength. Although the phase interfaces of rubber particles and PLA matrix can be distinguished due to their limited compatibility with PLA, the ECO elastomer still can effectively improve the toughness of PLA. As for the P$_3$$_4$HB/ECO blend, a relatively smooth surface is observed with no distinct phase separation, which is mainly because of the poor toughness of neat P$_3$$_4$HB. Although ECO has better compatibility with P$_3$$_4$HB than PLA, the toughening effect of the ECO elastomer for P$_3$$_4$HB may be greatly compromised by the thermal degradation of the P$_3$$_4$HB component due to its poor thermal stability. For the PLA/P$_3$$_4$HB binary blends, the surface exhibits moderate roughness with a little matrix deformation.

Compared to those of the binary blend, more and longer fibrils and threads are noticed in the ternary blends, which is clear evidence for the ductile fractures. Especially for the PLA/P$_3$$_4$HB/ECO (70/10/20) blend, a very rough surface can be observed in the impact fracture surface owing to the PLA matrix deformation, which will absorb a large amount of fracture energy during the impact test. In recent reports of PLA-based ternary blends, the relationship between the interfacial structure and physical property had stimulated intensive research interest as a guide for the fabrication of high-performance PLA. Most of the reports focused on the interfacial structure including interfacial layer thickness, interfacial dispersion, and interfacial adhesion. However, our results indicate that the native physical properties of the interfacially located components also have a non-negligible influence on the performance. For the ternary blends with a kind of soft and tough rubber at the interface of PLA and the third component, an excellent toughening effect will be achieved, for example, the recently reported PLA/EMA-GMA/Pebax and PLA/EMA-GMA/LLDPE ternary blends. However, for the ternary blends using a brittle polymer at the interface, the composition of the interfacially located polymer has a complicated influence on the toughening efficiency. For example, in a PLA ternary blend using brittle PMMA as the interfacial component, it was reported that low content of PMMA showed a positive toughening effect, while the toughening effect decreased for the high composition of PMMA. In the present work, although P$_3$$_4$HB locating at the interface improves the compatibility of PLA and ECO phases, the poor toughness of P$_3$$_4$HB still plays a negative role in the toughening effect, especially for the impact strength. As shown in the PLA/P$_3$$_4$HB/ECO (70/20/10) formulation with a core–shell structure, it has a limited toughening efficiency compared to the other two PLA/P$_3$$_4$HB/ECO ternary formulations with phase-separated structures. To gain a satisfied toughening effect, it is better to carefully select interfacial components with good flexibility and toughness beside the good compatibilization. As for the present PLA/P$_3$$_4$HB/ECO ternary system, the key point to achieve a better toughening effect is finding an efficient strategy to enhance the thermal stability of the P$_3$$_4$HB component at high processing temperature.

### 2.5. Thermal and Crystallization Behavior

In the present multiphase blend, PLA and P$_3$$_4$HB are typical semicrystalline polyesters. Their physical properties are greatly influenced by the crystallization behavior and crystal structure. Accordingly, differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) were employed to characterize the thermal behavior and crystalline structure of the multiphase system, respectively. Figure 9 presents the melting behavior of the neat PLA, P$_3$$_4$HB, ECO, and their binary and ternary blends after quenching. As shown in Figure 9a, no obvious shift is observed for the glass transition
temperature of PLA in the PLA/ECO (70/30) binary blend resulting from the limited miscibility between the two components. However, the cold crystallization peak of PLA is clearly observed to become sharper compared to that of the neat PLA. The $T_{cc}$ of PLA shifts from 125.2 °C for neat PLA to a low temperature of 104.1 °C in the PLA/ECO (70/30) blend, indicating that the ECO phase accelerates the cold crystallization of PLA. Based on the $\Delta H_c$ and $\Delta H_m$ data of PLA, the degree of crystallinity of PLA in the PLA/ECO (70/30) blend increases to 5.2% compared to the neat PLA with a value of 3.4%. The ECO phases played a role of nucleating agents for the PLA matrix, which is inconsistent with our previous report. Yet, for the P3,4HB/ECO (70/30) blend, the glass transition temperature of P3,4HB is found to move from −6.8 °C toward the low temperature of −9.7 °C of the binary blend. This phenomenon agreed well with the DMA result, which further proves that the P3,4HB and ECO phases show partial miscibility. In addition, one can note that the crystallization peak of P3,4HB shifts a little toward high temperature. These results suggest that the ECO phases have a dilution effect, which will confuse the cold crystallization of the P3,4HB phases owing to the partial miscibility. At the same time, the thermal degradation of P3,4HB also plays a negative role in its crystallization ability because of the poor thermal stability of P3,4HB. As for the binary PLA/P3,4HB blends, the glass transition of PLAs unfortunately overlapped with the cold crystallization of the P3,4HB phase, which makes it difficult to be analyzed. However, compared to that of the neat PLA, the cold crystallization peak of PLA in the PLA/P3,4HB (70/30) and (30/70) binary blends is clearly observed to shift toward the lower-temperature range, illustrating that P3,4HB promotes the cold crystallization of PLA. The enhanced crystallization of PLA will be helpful for keeping the strength of the blends with soft elastomers. At the same time, one can also note that the presence of the PLA phase restricts the cold crystallization of P3,4HB with the $T_{cc}$ of P3,4HB moving to a higher temperature region. These phenomena in crystallization of the binary PLA/P3,4HB blend also demonstrate the compatibility of the components of PLA and P3,4HB. Figure 9b shows the thermal behavior of the ternary system. Except for PLA/P3,4HB/ECO (45/45/10), all of the other ternary formulations mainly show the thermal behavior of the PLA matrix. In the ternary blends, the presence of P3,4HB and ECO phase enhanced the cold crystallization of the PLA matrix. Moreover, it is found that the $T_{cc}$ of PLA shifts to a lower-temperature region with the content of P3,4HB increasing due to the improved compatibility. Figure 10 shows the crystallization curves of the PLA binary and ternary blends at a cooling rate of 2 °C/min from the melt. As shown in Figure 10a, for the neat polymers and their binary blends, the ECO phase plays a different role in the crystallization of neat PLA and P3,4HB in the binary blends. For PLA, the ECO phases play as nucleating agents for the crystallization of PLA, resulting in the $T_c$ of PLA shifting to high temperature and an obvious crystallization peak. In contrast, the crystallization temperature ($T_c$) of P3,4HB moves slightly to low temperature in the P3,4HB/ECO binary blend because of the dilution effect of the ECO phase. As for the PLA/P3,4HB binary blends, P3,4HB improves the crystallization of PLA from the melt state. For the ternary blends shown in Figure 10b, the crystallization temperature ($T_c$) of PLA in the PLA/P3,4HB/ECO (70/10/20) and (70/15/15) formulations shifts to a high-temperature
region and becomes sharp because of the nucleating effect of phase-separated ECO and P3,4HB phases. However, for the PLA/P3,4HB/ECO (70/20/10) formulation with a core–shell structure, the nucleating effect is compromised due to the decrease in the number of dispersed-phase particles given the ECO phase being encapsulated by the P3,4HB phase. Moreover, the uneven distribution and heterogeneous particles with the core–shell structure also lead to the complicated crystallization behavior of PLA exhibiting complicated and multiple wide peaks.

Figure 11 shows the crystal structure of the samples characterized by WAXD. The neat PLA shows two sharp peaks at 2θ = 16.7 and 19.0. These peaks are corresponding to the (200/110) and (203) planes of the orthorhombic unit cell, respectively. The neat P3,4HB exhibits three diffraction peaks at 2θ = 13.4, 19.9, and 25.4, which are ascribed to the diffraction peaks (020), (021), and (031/131), respectively. The characteristic peaks of each component exist in all of the blends. The characteristic peaks of PLA are observed to become sharp owing to the nucleating effect of ECO and P3,4HB phases. However, no new peaks appear for all of the blends, indicating that the PLA and P3,4HB crystallized separately in the blends without changing the crystal structure.

3. CONCLUSIONS

In this work, we formulated a renewable multiphase blend system by blending PLA with the renewable P3,4HB and the ECO elastomer to achieve an excellent balanced mechanical property. The presence of P3,4HB improved the compatibility of the PLA matrix and ECO phase. A variety of structures including phase separation, core–shell, and co-continuous phase morphologies were tuned by optimizing the blend composition, mutual miscibility, and viscosity ratio of the components. A significant improvement in flexibility with an elongation at 270% was obtained for PLA/P3,4HB/ECO (70/20/10) with a core–shell structure. A supertough PLA/P3,4HB/ECO ternary blend was achieved by blending 10 wt % P3,4HB and 20 wt % ECO in PLA with an impact strength of 45 KJ/m². Combining compatibilization and elastomer toughening coupled with the influence of the native property of the interfacial component played a vital role in enhancing the properties of the blends. To further enhance the mechanical performance, improving the thermal stability of P3,4HB is very important for the present multiphase system.

4. EXPERIMENTAL SECTION

4.1. Materials. Poly(lactic acid) (Ingeo PLA, 3001D) with an L-content of 98.5%, a weight-average molecular weight (Mw) of 1.7 × 10⁶, and a density of 1.25 g/cm³ was purchased from Nature Works Inc. Poly(epichlorohydrin-co-ethylene oxide) (ECO, Epichlomer C, 49 mol% epichlorohydrin unit) was purchased from Osaka Soda Co., Ltd, Japan. Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3,4HB) with a Mw of 2.6 × 10⁶ and 4HB of approximately 8 mol% (characterized by GPC and ¹H NMR) was obtained from Tianjin Green Biomaterial Co., Ltd. (Tianjin, China).

4.2. Preparation of Blends. PLA, P3,4HB, and ECO were vacuum-dried at 60 °C for at least 24 h prior to processing. PLA/P3,4HB/ECO blends with different compositions were melt-processed in a Haake internal mixer (Rheomix 600, Germany) with a barrel volume of 69 cm³. The blends were mixed at 180 °C for at least 5 min at a screw speed of 60 rpm. To ensure the same thermal history, the neat PLA and P3,4HB were also subjected to the same mixing treatment.

4.3. Characterizations. Dynamic mechanical analysis (DMA) was performed on a TA Instrument (DMA Q800) in a single-cantilever mode with a frequency of 1 Hz and an amplitude of 15 μm. At least three samples (30 mm × 10 mm × 2 mm) were tested from −80 to 125 °C at a heating rate of 3 °C/min to ensure the reproducibility.

The Charpy impact strength of the samples was measured using a GOTECH pendulum impact tester according to the ISO178 standard. The notched impact samples were obtained by the Haake Minijet machine. According to the ISO 527-1 standard, the tensile property of the samples was tested using a universal tensile testing machine at a tensile rate of 10 mm/min. Five replicates were conducted to ensure the accuracy and reproducibility.

Differential scanning calorimetry (DSC) characterization was performed using a TA Q2000 thermal analysis system under a N₂ atmosphere. First, the samples were heated from 25 to 180 °C at a rate of 10 °C/min and cooled to −80 °C at 30 °C/min after holding the temperature for 3 min. The next scan was heated to 180 °C at 10 °C/min and cooled to −80 °C at 2 °C/min. Finally, the samples were heated to 180 °C at 10 °C/min after maintaining the temperature for 3 min. The glass transition temperature (Tg), cold crystallization temperature (Tc), crystallization temperature (Tc), and melting temperature (Tm) were obtained from the curves.

The morphology of the blends was observed by scanning electron microscope (SEM) on a Hitachi S4800 SEM under an...
accelerating voltage of 10 kV. The cryofractured samples were prepared after being cooled in liquid nitrogen for at least 30 min and then dried at 40 °C in a vacuum. Then, the samples were fastened using a conductive paint on a specimen holder and sputtered with gold before fractographic examinations. The impact fracture surfaces of the samples were also characterized by SEM.

Wide-angle X-ray diffraction (WAXD) measurements were carried out using a D8 Advance Diffractometer (Bruker, Germany). The angle range was set at 5°–40° at 2°/min. Thermogravimetric analyses (TGA) were carried out at a heating rate of 10 °C/min in a TA Instrument Q50 using a temperature range of 25–700 °C in nitrogen.

The rheological measurements were carried out on TA instrument HR-2. The frequency sweep for the samples was carried out under nitrogen at 180 °C using a 25 mm plate–plate geometry. The samples were prepared by melt-pressed method at 180 °C with 1 mm thick. The strain range was 5%, and the angular frequency range in the test was 0.01–600 rad/s.

Contact angles were measured by the POWEREACH Contact Angle Testing Machine. PLA, P₃,4HB, and ECO samples were dissolved in chloroform and then spin-coated on a cover glass (24 mm × 32 mm). All samples were dried at 40 °C in a vacuum oven for at least 12 h. The contact angles were measured in 50 μL of the wetting solvent at 25 °C, and the mean values of five reduplicates were reported. The ⁰H NMR spectra were recorded with a 400 MHz Bruker AVANCE III spectrometer with reference to the solvent residual signal (⁰H NMR, DMSO-d₆ 2.5 ppm) at room temperature.

The FTIR measurements were carried out using an attenuated total reflectance (ATR) model on an IR Tracer-100 spectrometer (Shimadzu) at room temperature. All of the samples at 1 mm thickness were directly measured in the wavenumber range of 4000–400 cm⁻¹ with 32 scans. For AFM, the MultiMode 8 AFM system from Bruker Nano Inc., CA, was used. Image processing and data analysis were performed using the Nanoscope Analysis software. Imaging in the tapping mode and peak force tapping (PFT) mode was done with RTESPA Si cantilevers with a spring constant of 40 N/m (Bruker AFM probes, CA) in air. Peak force quantitative nanomechanical property mapping (PF-QNM) AFM was carried out at a constant oscillation of the sample at 2 kHz using an amplitude of 150 nm. The specimens for AFM imaging were prepared by cryomicrotoming with a tungsten knife to create a perfect plane face using a Leica Microtome, Germany, equipped with a cryochamber.
Intermediate Phase.

Macromolecules

Compatibility.

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