

Stereocomplexed Poly(lactide) Composites toward Engineering Plastics with Superior Toughness, Heat Resistance and Anti-hydrolysis

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Stereocomplexed Poly(lactide) Composites toward Engineering Plastics with Superior Toughness, Heat Resistance and Anti-hydrolysis

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Electronic Supplementary Information

Abstract Poly(lactide), PLA, suffers from brittleness and low heat deflection temperature (HDT), which limits its application as an engineering plastic. In this work, poly(L-lactide)/poly(D-lactide)/ethylene-vinyl acetate-glycidyl methacrylate random copolymer (PLLA/PDLA/EVM-GMA = 1/1/*x*) composites were prepared by melt blending, and the *in situ* formed EVM-*g*-PLA copolymers improved the compatibility between PLA and EVM-GMA. Subsequently, the blends were subjected to a two-step annealing process during compression molding, *i.e.* first annealing at 120 °C to rapidly form a certain amount of stereocomplex (sc) crystallites as nucleation sites, and then annealing at 200 °C to guide the formation of new sc crystallites. Both differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD) measurements confirmed the formation of highly stereocomplexed PLA products. Mechanical results showed that the PLLA/PDLA blend with 20 wt% of EVM-GMA had a notched impact strength up to 65 kJ/m² and an elongation at break of 48%, while maintaining a tensile strength of 40 MPa. Meanwhile, dynamic mechanical analysis (DMA) and heat deflection tests showed that the PLA composite had an HDT up to 142 °C which is 90 °C higher than that of normal PLA products. Scanning electron microscopy (SEM) confirmed the fine dispersion of EVM-GMA particles, which facilitated to understand the toughening mechanism. Furthermore, the highly stereocomplexed PLA composites simultaneously exhibited excellent chemical and hydrolysis resistance. Therefore, these fascinating properties may extend the application range of sc-PLA material as an engineering bioplastic.

Keywords PLA composites; Stereocomplexation; Annealing; Heat resistance; Toughness

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INTRODUCTION

In recent years, poly(lactide) (PLA) has received tremendous attention due to its biodegradability and sustainable advantages in respect to petroleum-based materials.^[1–4] PLA is considered as a promising candidate for environmentally friendly materials because of the wide resource, satisfied mechanical strength, and easy processability.^[2,5,6] However, the commercial application of PLA is still quite limited due to the inherent brittleness and insufficient heat resistance. The notched impact strength (NIs) of PLA is only around 3 kJ/m² and the heat deflection temperature (HDT) of amorphous PLA is lower than its *T_g* of 60 °C. Therefore, great efforts are devoted to enhancing its toughness and heat resistance in order to extend the applications as engineering plastic in recent decades.

Reactive blending with elastomers is a simple and widely

used method for improving the toughness of PLA by forming compatibilizers at the interface.^[7–14] For example, the notched impact toughness of PLLA was improved from 1.2 kJ/m² to 61.2 kJ/m² by reactive blending with EVM-GMA elastomer in our previous work.^[15] The EVM-*g*-PLLA copolymers formed *in situ* by the reaction between terminal carboxyl/hydroxyl groups of PLLA and epoxy groups of EVM-GMA can improve the compatibility, thereby achieving effective toughening. However, these similar methods tend to sacrifice heat resistance of blends while improving toughness due to the low modulus of elastomers. Improving the crystallinity of PLA matrix by annealing can effectively enhance the heat resistance of the corresponding blend. For instance, HDT of the PLLA/EVM-GMA blend was improved from 50.3 °C to 94.2 °C after annealing treatment.^[15] However, due to the relatively low melting temperature (~175 °C) of PLA homocrystallites (hc), HDT of the annealed PLA-based materials is difficult to exceed 120 °C, which makes it still unavailable for some engineering fields requiring higher heat resistance.

Stereocomplex (sc) crystallites formed by stereoselective interaction between poly(L-lactide) (PLLA) and its enantiomer poly(D-lactide) (PDLA) have attracted much attentions.^[9,16–23]

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Since sc crystallites possess not only stronger interchain interactions but also denser chain packing relative to the hc crystallites, the stereocomplex type PLA (sc-PLA) materials exhibit many exceptional physical properties including higher mechanical strength, superior heat resistance due to the particularly high T_m , substantially improved chemical resistance, and hydrolysis resistance. These interesting properties enable it to be applied as engineering bioplastic. However, sc crystallization is significantly impeded and hc coexist with sc in a PLLA/PDLA (50/50) melt blend when the molecular weight (M_w) exceeds 6000 g/mol.^[24] Therefore, many studies have focused on improving the sc crystallinity of high-molecular-weight (HMW) PLLA/PDLA blends from melt.^[9,25–30] Zhang *et al.*^[29] found that the sc crystallization from HMW PLLA/PDLA melt was significantly accelerated with intense shear flow, so that almost exclusive sc crystallites and consequently high Vicat softening temperature (VST) of ~ 200 °C were obtained. Besides, they prepared the PLA products with high sc crystallinity and heat resistance by subjecting the PLLA/PDLA blends to simple injection molding and subsequent annealing. They demonstrated that a certain amount of sc crystallites pre-formed at the mold temperature of 120 °C could serve as nucleation sites (*i.e.*, template effect) to guide the growth of new sc crystallites during the annealing at 210 °C.^[30] However, the above materials were still brittle. In order to simultaneously improve the toughness and heat resistance, Oyama *et al.*^[9] introduced the poly(ethylene-methylacrylate-glycidyl methacrylate) (E-MA-GMA) elastomer into PLLA/PDLA blends by reactive blending at 200 °C, and then annealing at 220 °C for 30 min. As a result, the PLA-based material with a sc crystallinity of 50% was prepared and the high heat resistance and toughness were obtained. It was also proposed that the *in situ* formed sc crystallites during the blending could be used as nucleation sites for further growth of the sc crystallites during the annealing. However, the high melt viscosity of the blends induced by the *in situ* formed sc crystallites may make it difficult to be processed.

In this work, PLLA/PDLA/EVM-GMA blends are prepared by reactive blending at 230 °C (almost no sc formed *in situ* at 230 °C), and the compatibility between PLA and EVM-GMA is improved by the *in situ* formed EVM-g-PLA copolymers. Subsequently, the blends are subjected to the two-step annealing process during the compression molding to guide the formation of high content of sc, which would be beneficial to

the simultaneous realization of excellent toughness, heat resistance, chemical resistance, and hydrolysis resistance for PLA composites. The objective is to expand PLA applications as an engineering bioplastic.

EXPERIMENTAL

Materials

Poly(L-lactide) (PLLA, L130) was kindly supplied by Total Corbion PLA B.V., with $M_n = 125$ kDa and PDI = 1.6. Poly(D-lactide) (PDLA) with $M_n = 86$ kDa and PDI = 1.8 was prepared *via* ring-opening polymerization of D-lactide. Optical purity of PLLA and PDLA is approx. 99%. Both rubber grade ethylene-vinyl acetate (EVM) and ethylene-vinyl acetate-glycidyl methacrylate random copolymer (EVM-GMA) (containing 3.1 wt% glycidyl methacrylate) were kindly provided by Arlanxco Deutschland GmbH. All materials were dried at 60 °C in a vacuum oven for 12 h before use.

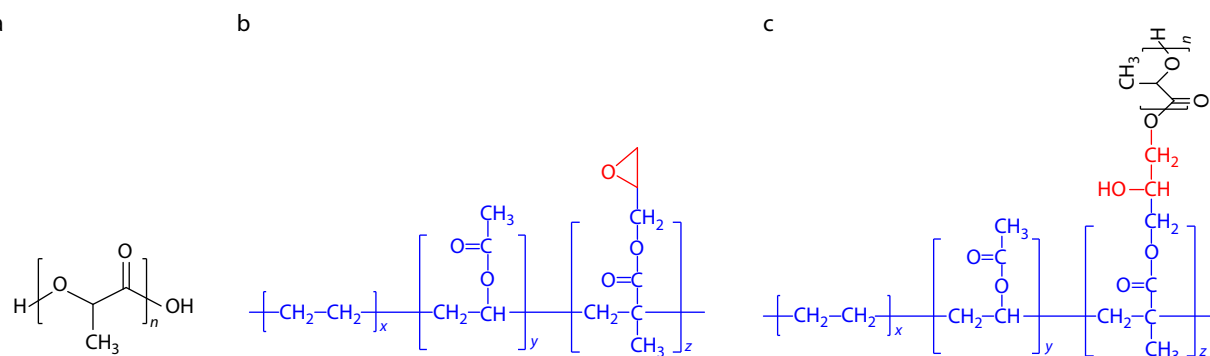
Sample Preparation

PLLA/PDLA blends (PLLA/PDLA = 1/1, W/W) with different amounts of EVM-GMA were prepared using a Haake rheometer at 230 °C and 60 r/min for 4 min. For comparison, PLLA/PDLA (50/50, W/W) and PLLA/PDLA/EVM (40/40/20, W/W/W) blends were also prepared *via* the same procedure. Scheme 1 demonstrates the reaction between the terminal carboxyl/hydroxyl groups of PLA chain (a) and the epoxy groups of EVM-GMA (b) to form EVM-g-PLA copolymer (c). The prepared samples were compressed into sheets at 230 °C for 1 min, followed by the two-step annealing treatments, *i.e.*, 120 °C for 10 min (first step) and then 160–220 °C for 10–30 min (second step). The pressure was fixed at 10 MPa in all procedures. For convenience, the prepared PLLA/PDLA (50/50, W/W) and PLLA/PDLA/EVM (40/40/20, W/W/W) blends were denoted as L/D and L/D/E20. PLLA/PDLA composites with different contents (x) of EVM-GMA were denoted as L/D/EGx.

Characterizations

Differential scanning calorimetry (DSC)

DSC characterizations were performed on a DSC 8000 analyzer (PerkinElmer, USA) under the nitrogen flow. The crystallinity of the homocrystal (hc) PLA (X_{c-hc}) and the stereocomplex PLA (X_{c-sc}) in the compression-molded samples was calculated by the first DSC heating scan at a heating rate of 10 °C/min according to the following equations:



Scheme 1 Chemical structure of (a) PLA, (b) EVM-GMA, and (c) EVM-g-PLA copolymer.

$$X_{c-hc} = \frac{\Delta H_{m-hc} - \Delta H_{cc}}{p \cdot 93 \text{ J/g}} \times 100\% \quad (1)$$

$$X_{c-sc} = \frac{\Delta H_{m-sc}}{p \cdot 142 \text{ J/g}} \times 100\% \quad (2)$$

where ΔH_{m-hc} and ΔH_{cc} are the melting enthalpy and the cold crystallization enthalpy of homocrystalites PLA, respectively, and ΔH_{m-sc} is the melting enthalpy of stereocomplex crystallites. p is the PLA percentage (wt%, including PLLA and PDLA) in the samples, and 93 J/g and 142 J/g are the melting enthalpy of 100% crystalline homocrystalites and stereocomplex crystallites, respectively.^[31]

Wide angle X-ray diffraction (WAXD)

WAXD measurements were performed using an X-ray diffractometer (Bruker AXS D8, Germany) equipped with a Ni-filtered Cu K α radiation source with a wavelength of 1.542 Å. The measurements were operated at 40 kV and 40 mA with scan angles from 5° to 35° and a scan rate of 3 (°)/min.

Mechanical properties

Tensile performance of the samples was tested using a tensile tester (Instron 5967, USA) at 50 mm/min according to GB/T 1040-92 standard and notched impact strength was measured using a pendulum impact tester (HIT-2492, China) according to the GB/T 1843-2008 standard. The mechanical measurements were performed at room temperature (23 °C) and at least five independent specimens were tested to obtain the average values for each formula.

Scanning electron microscopy (SEM)

The phase morphologies of cryo-fractured section of the samples were observed by SEM (S-4800, HITACHI, Japan). The elastomer phase was removed with xylene to study the dispersion of the elastomer particles. To determine the particle size and its distribution parameter, at least 300 particles in the SEM images of each sample were measured by using an ImageJ software. The weight-average particle diameter (d_w) and its distribution parameter (σ) were estimated by the following equations:^[32]

$$d_w = \frac{\sum_{i=1}^N n_i d_i^2}{\sum_{i=1}^N n_i d_i} \quad (3)$$

$$\ln \sigma = \sqrt{\frac{\sum_{i=1}^N n_i (\ln d_i - \ln d_w)^2}{\sum_{i=1}^N n_i}} \quad (4)$$

where n_i and d_i stand for the particle number and diameter, respectively. The matrix ligament thickness (τ) is calculated by the following equation:^[33]

$$\tau = d_w \left[\left(\frac{\pi}{6\phi} \right)^{\frac{1}{3}} \exp(1.5 \ln^2 \sigma) - \exp(0.5 \ln^2 \sigma) \right] \quad (5)$$

where ϕ represents the volume fraction of the elastomer.

The impact-fractured surfaces obtained from the notched impact testing were also observed by SEM to study the toughening mechanism.

Dynamic mechanical analysis (DMA)

The thermal dynamic mechanical properties of the samples were measured by a DMA-Q800 (TA Instruments). The specimens (15 mm $\times$ 4 mm $\times$ 1 mm) were heated in a tensile-film mode from 30 °C to 230 °C at 3 °C/min. The amplitude and

frequency were set as 15 μ m and 1 Hz, respectively.

Heat resistance behavior

The thermal deflection temperature (HDT) of the samples was measured by a thermal deflection temperature tester (HDT/V-3216) according to the GB/T 1634.2-2004 standard. The specimens (80 mm $\times$ 10 mm $\times$ 4 mm) were heated at 120 °C/h with a bending stress of 0.45 MPa until it reached the standard deflection of 0.34 mm. The span length was 64 mm. Each sample was measured 5 times and the average values were then obtained.

Chemical resistance and hydrolysis resistance

In order to investigate the chemical resistance of the PLA composites, some representative composites were immersed in chloroform for 24 h, and the digital photos were taken to observe the dissolution behaviors. For the measurement of hydrolysis resistance, the PLA samples were placed in an environmental aging box (H/GDWJS-100L) with a constant temperature of 70 °C and humidity of 80%, and the samples were taken out every 24 h for further mechanical and viscosity-average molecular weight (M_v) tests to evaluate the hydrolysis resistance. The Ubbelohde viscosity $[\eta]$ of the samples was measured by using a Ubbelohde viscometer at 25 °C, and a chloroform/hexafluoroisopropanol (9/1, V/V) mixture was used as the solvent. M_v was calculated as the following equation:^[34]

$$[\eta] = 0.0153 \times M_v^{0.759} \quad (6)$$

RESULTS AND DISCUSSION

Influence of Annealing Process on the Stereocomplex Crystallization of PLA

In order to enhance the sc crystallization behavior for PLA based composites, a two-step annealing treatment was applied. Step one: annealing at 120 °C, which would facilitate to form a certain amount of both hc and sc crystallites in a relatively short time because the lower temperature of 120 °C is favorable for nucleation; Step two: annealing at a higher temperature ranging from 160 °C to 220 °C, which would effectively avoid the formation of hc crystallites. Meanwhile, the sc crystallites formed during the first annealing would serve as nucleation sites to accelerate the growth of new sc crystallites during the second annealing.^[9,16,30] It is believed that the two-step annealing process will not only promote the growth of sc crystallites, but also shorten the annealing time. In order to optimize the annealing conditions, DSC was utilized to study the crystallization behaviors of the L/D/EG20 composite under different annealing conditions. Fig. 1(a) shows the hc and sc crystallinity of the PLA samples annealed at 120 °C for 10 min (step one) and then at 160–220 °C for 10 min (step two). The sample annealed only by step one shows both hc melting double peaks (175 °C, 180 °C) and sc melting double peaks (224 °C, 240 °C). In addition, the higher hc crystallinity (30.5%) than sc crystallinity (18.2%) indicates that the hc crystallization process dominated in the annealing process. Similarly, the melting peaks of hc and sc are also observed on other PLA composites treated via a two-step annealing method, but the crystallinity of both has changed. In general, with increasing the annealing temperature from 160 °C to 220 °C in the second step, the hc crystallinity of the samples decreases gradually while the

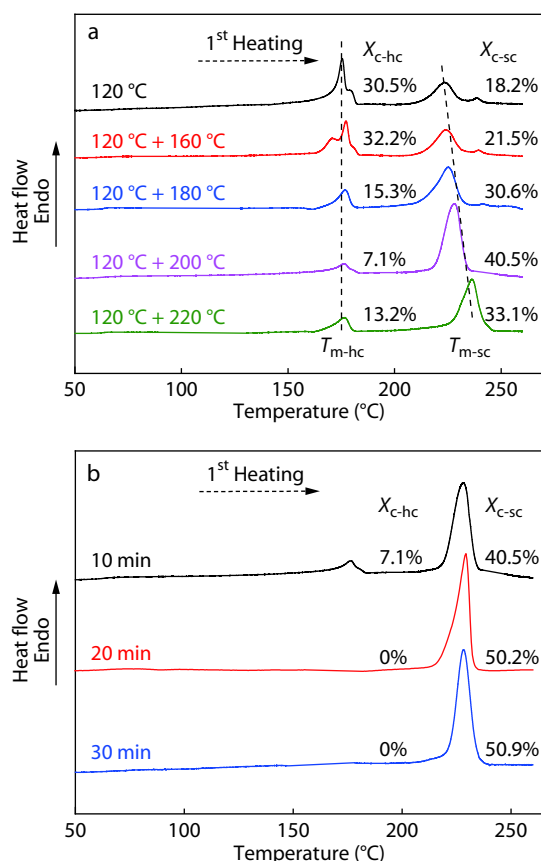


Fig. 1 DSC first heating curves of (a) the two-step annealed samples with different second step annealing temperature (160, 180, 200, and 220 °C) with a sample only annealed by the first step at 120 °C present as a reference, and (b) the two-step annealed samples with different second step annealing time (10, 20, and 30 min at 200 °C).

sc crystallinity increases. This could be explained by the following: in the case where a certain amount of sc crystallites (*i.e.* nucleation sites) were pre-formed by the first-step annealing, higher temperatures are beneficial to the movement of PLLA and PDLA chains, making it easier for the two to be closely aligned to form more sc crystallites.^[16,30,35] However, when the annealing temperature goes up to 220 °C, the crystallinity of hc increases and the crystallinity of sc declines instead. This is because some sc crystallites start to the melt at 220 °C, thereby reducing the number of nucleation sites for the growth of new sc crystallites. Therefore, 200 °C is the optimal second-step annealing temperature in this work.

Subsequently, the effects of annealing time at step two on the crystallization behavior of the L/D/EG20 composites were investigated and the results are shown in Fig. 1(b). When the annealing time increases from 10 min to 20 min, the sc crystallinity increases from 40.5% to 50.2%, while the hc crystallinity reduces from 7.1% to 0%. Thus, a L/D/EG20 composite with complete sc crystallization was obtained. When the annealing time is further increased to 30 min, the sc crystallinity almost no longer increases. In summary, the optimal condition for the second annealing step is 200 °C for 20 min.

In order to achieve high sc crystallinity for L/D, L/D/E20, and

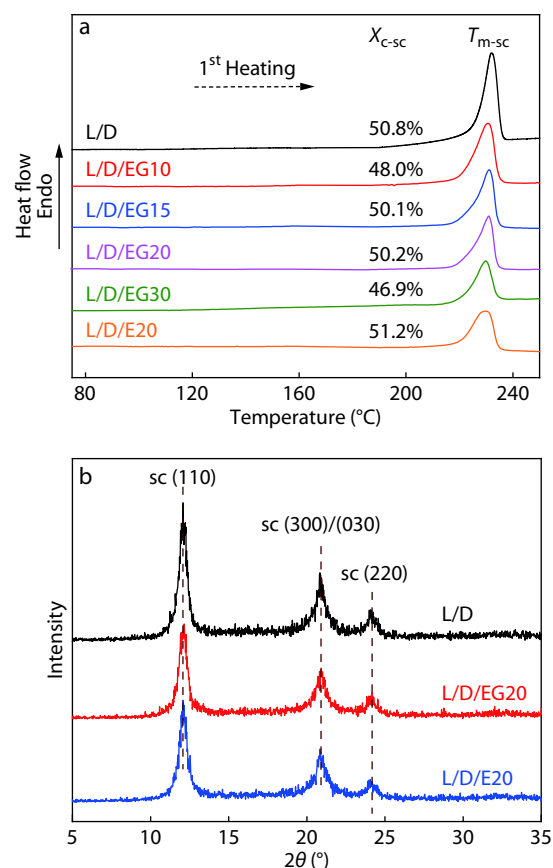


Fig. 2 (a) DSC first heating curves of L/D, L/D/EGx, and L/D/E20 composites; (b) WAXD patterns of L/D, L/D/EG20, and L/D/E20 composites.

L/D/EGx composites with other EVM-GMA contents, the annealing processes were also performed under the above optimal annealing conditions. Fig. 2(a) shows the DSC melting curves of the samples after annealing. Obviously, the melting curves of each sample show unique melting peaks of sc crystallites at ~230 °C, and all the sc crystallinity falls in the range of 46.9%–51.2%, which indicates that the two-step annealing method enables each sample to achieve high sc crystallinity.

To further confirm the high sc crystallinity of the annealed samples, WAXD characterization was performed for the annealed L/D, L/D/E20, and L/D/EG20 composites, as shown in Fig. 2(b). The diffraction peaks at $2\theta = 11.8^\circ$, 20.8° , and 23.8° are assigned to the (110), (300)/(030), and (220) crystal planes of the sc crystallites, respectively.^[36–38] In addition, the sc crystallinities of these three samples are all higher than 50%, and no diffraction peak of hc crystallites is observed in the diffraction patterns, which are consistent with the DSC characterization.

Mechanical Properties

The effect of EVM-GMA content on the mechanical properties of L/D/EGx composites is shown in Fig. 3 (all composites discussed in this section and the next two sections possess high sc crystallinity by two-step annealing). L/D has a high tensile strength of 67.8 MPa, but its elongation at break and notched

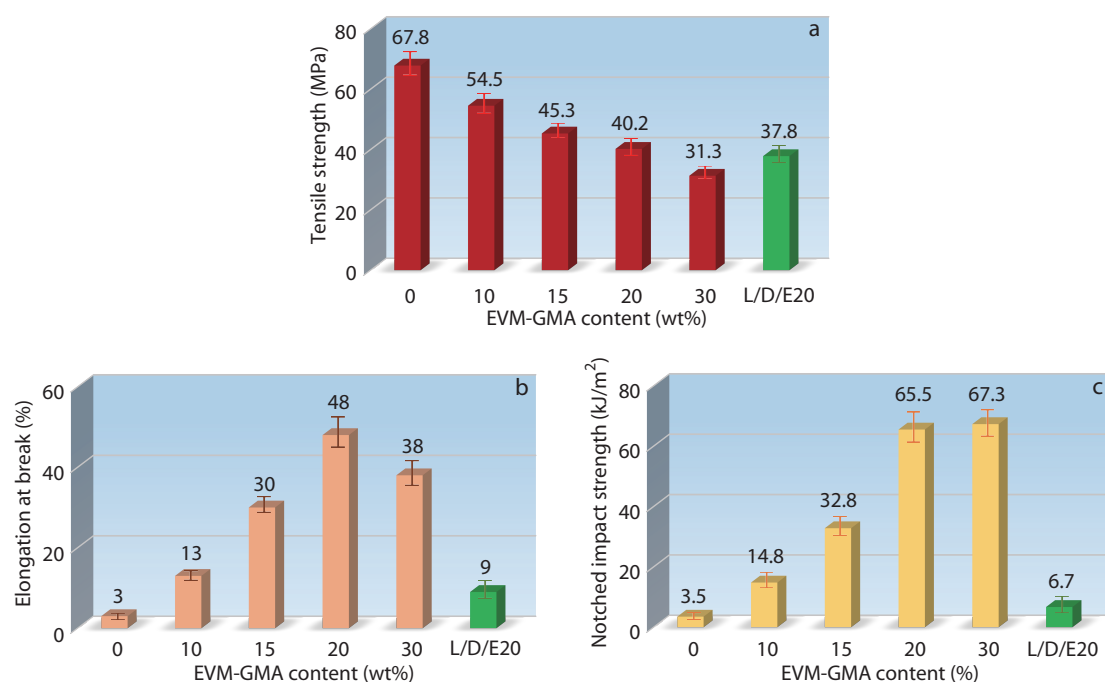


Fig. 3 (a) Tensile strength, (b) elongation at break, and (c) notched impact strength of L/D, L/D/EGx, and L/D/E20 composites.

impact strength are only 3% and 3.5 kJ/m², respectively. With the increase of EVM-GMA content, the tensile strength of L/D/EGx composites decreases gradually, but the elongation at break and notched impact strength show a clear increasing trend. When the EVM-GMA content is 20 wt%, the elongation at break and notched impact strength of the composite reach 48% and 65.5 kJ/m², which are 15 and 18 times higher than those of L/D sample, respectively, while maintaining a relatively high tensile strength (40.2 MPa). As a comparison, the elongation at break and notched impact strength of the L/D/E20 composite with the same elastomer content are only 9% and 6.7 kJ/m², respectively. This could be explained as that the epoxy groups of EVM-GMA would *in situ* react with the terminal carboxyl and hydroxyl groups of PLA chain to form EVM-g-PLA copolymer (Scheme 1) during the melt blending, while *in situ* compatibilization reaction would not occur between EVM and PLA, as confirmed in nuclear magnetic resonance (NMR) results (see the electronic supplementary information, ESI) and our previous work as well.^[15,39] Therefore, the compatibility between the PLA matrix and the EVM-GMA elastomer was improved, resulting in significantly toughened PLLA/PDLA blend.

Morphological Evolution

Fig. 4 shows the cross-section morphologies of L/D/E20 and L/D/EGx composites with various EVM-GMA contents (the elastomer phase has been removed with xylene), and their corresponding elastomer weight-average particle diameters (d_w), distribution parameter (σ), and matrix ligament thickness (τ) are listed in Table 1. It can be seen that the EVM-GMA content in the L/D/EGx composites has small effect on elastomer particle size, since d_w values just slightly increase when increasing the EVM-GMA content. In addition, the small d_w and narrow σ with respect to L/D/Ex composites are ascribed to the improved compatibility between PLA matrix and EVM-GMA elastomer due

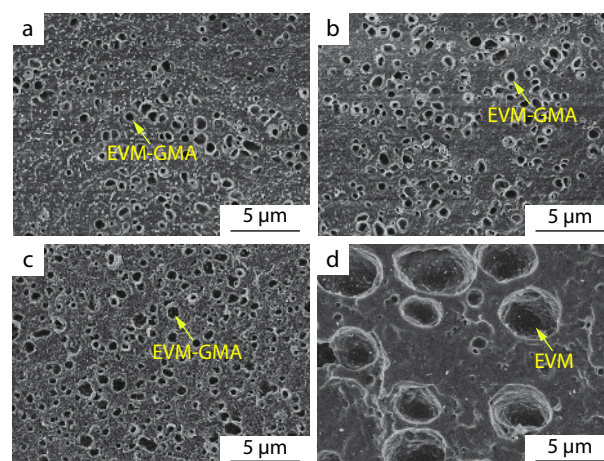


Fig. 4 SEM images of cryo-fractured surfaces of (a) L/D/EG10, (b) L/D/EG15, (c) L/D/EG20, and (d) L/D/E20 composites.

Table 1 Weight-average particle diameter (d_w), diameter distribution parameter (σ), and matrix ligament thickness (τ) of elastomer particles in the corresponding composites.

Sample	d_w (μm)	σ	τ (μm)
L/D/EG10	0.79	1.36	0.61
L/D/EG15	0.81	1.31	0.40
L/D/EG20	0.85	1.33	0.33
L/D/E20	3.58	1.82	3.48

to the *in situ* compatibilization reaction as discussed above. Obviously, in the case of L/D/E20 composite, the EVM elastomer particle size and its distribution parameter are significantly larger, which is responsible for the poor compatibility between EVM elastomer and PLA matrix.

Impact Toughening Mechanism

According to the classic toughening mechanism, an effective toughening approach for plastics by elastomers should meet two conditions: (1) sufficient interfacial adhesion between the elastomer particles and the plastic matrix to enable the elastomer to induce the plastic deformation of plastic matrix; (2) the stress field around the elastomer particles can overlap each other.^[40–42] Increasing the elastomer amount, namely reducing the matrix ligament thickness between the elastomer particles, is a simple approach to achieve the overlaps between the stress fields. SEM is helpful to understand the toughening mechanism and the impact section morphologies of L/D, L/D/EG10, L/D/EG20, and L/D/E20 composites are exhibited in Fig. 5. The impact section of L/D sample is smooth and no visible plastic deformation can be observed, indicating a brittleness behavior. In L/D/EG10 and L/D/EG20 composites, due to the good compatibility and strong interfacial adhesion between EVM-GMA elastomer and PLA matrix, the triaxial stress generated in the impact process will steadily transmit from PLA matrix to EVM-GMA elastomer. Then the surrounding PLA matrix is subjected to shear yielding, resulting in a rougher impact section and plastic deformation of the PLA matrix. In comparison with L/D/EG10, since L/D/EG20 composite has higher amount EVM-GMA elastomer, a more obvious matrix plastic deformation and thicker elongated fibrils (marked by yellow arrows in Fig. 5) could be observed on the impact fracture surface. It is believed to be ascribed to the higher range of stress field overlaps around the EVM-GMA elastomer particles, which will effectively dissipate the impact energy and significantly improve the notched impact strength.^[43,44] However, due to the weak interfacial adhesion between EVM elastomer and PLA matrix in the L/D/E20 composite, it is difficult to transfer the triaxial stress from the PLA matrix to EVM elastomer, resulting in a relatively smooth impact section and insufficient improvement of notched impact toughness. In short, the elastomer-induced plastic deformation and fibrillation are the main toughening mechanisms of L/D/EG20 composite.

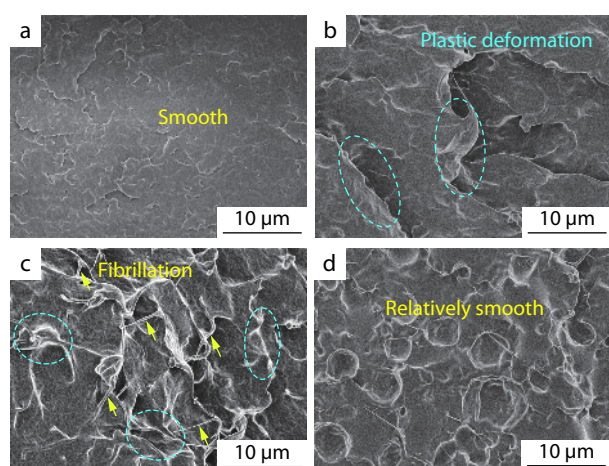


Fig. 5 SEM images of impact-fractured surfaces of (a) L/D, (b) L/D/EG10, (c) L/D/EG20, and (d) L/D/E20 composites.

Heat Resistance Behavior

Storage modulus (E') and heat deflection temperature (HDT) are used to evaluate the heat resistance of the composite and the results are shown in Fig. 6. It can be seen that E' of all three composites significantly decreases when the temperature reaches the T_g of PLA. When the temperature further increases to 152 °C, E' of the L/EG20 composite drops suddenly, which is attributed to the softening of the hc crystal near the melting point of hc. The small amount of sc crystallites present in the L-L/D/EG20 composite is not sufficient to form a dense sc crystal network, so it does not contribute much to the heat resistance of the composite (E' begins to decrease sharply when the temperature reaches 156 °C). However, in the case of H-L/D/EG20 composite, E' does not decrease suddenly until the temperature exceeds 200 °C, which is attributed to the formation of a dense sc crystal network and high melting point of sc crystallites (~230 °C).^[45] Furthermore, H-L/D/EG20 composite can still maintain relatively high E' value of 60 MPa at 200 °C. HDT (Fig. 6b) of L/EG20, L-L/D/EG20, and H-L/D/EG20 composites is 94.2, 97.6, and 142.3 °C, respectively, which are in accordance with the DMA results. In short, the high content of sc crystallites in H-L/D/EG20 composite contributes to the excellent heat resistance.

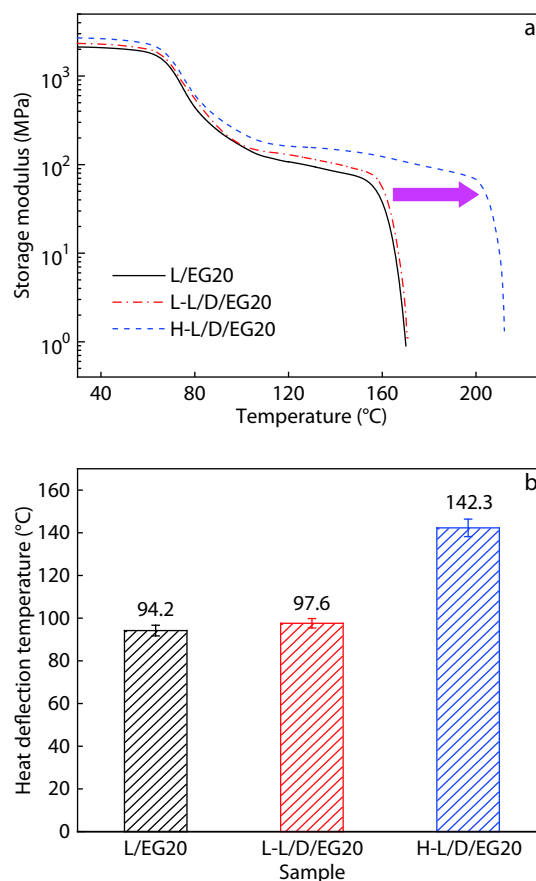


Fig. 6 (a) Variations of storage modulus with increasing temperature and (b) heat deflection temperature of PLLA/EVM-GMA (80/20) composite with high hc crystallinity of ~50% (denoted as L/EG20), low sc crystallinity (L-L/D/EG20, without the second annealing), and high sc crystallinity (H-L/D/EG20) composites.

Chemical Resistance and Hydrolysis Resistance

As well known, PLA has poor chemical resistance because both amorphous PLA and hc crystallized PLA are easily soluble in solvent such as chloroform, making it difficult to be used in some special fields, *e.g.* oil-water separation, which needs PLA to contact with solvents for a long time. Compared with hc crystallized and amorphous PLA, sc crystallized PLA is less soluble in solvent due to the tighter arrangement and stronger interaction between molecular chains.^[9,17] Therefore, enhancing the sc crystallites content for PLA-based composites is the key to improving their chemical resistance behavior. In this work, the chemical resistance of PLA composites was evaluated by dissolution experiments using chloroform as the solvent. Fig. 7 shows the digital photos of L/EG20, L-L/D/EG20, and H-L/D/EG20 composites before and after soaking in chloroform for 24 h. Obviously, the L/EG20 composite has completely dissolved in chloroform which is also a good solvent for EVM-GMA. However, the L-L/D/EG20 composite is only partially dissolved after 24 h of soaking and the film sample is obviously distorted due to the existence of a small amount of sc crystallites. Interestingly, in the case of H-L/D/EG20, chloroform seems difficult to penetrate into the material due to the formation of a high dense sc crystal network. The material could almost maintain its original shape after soaking for 24 h, indicating an excellent chemical resistance behavior.

The presence of a large number of ester bonds in PLA molecular chain results in the poor hydrolysis resistance, especially under the extreme condition, so PLA is difficult to be applied under high temperature and high humidity environment for a long time. As discussed above, sc crystallized PLA chains have a tighter arrangement and stronger interactions between molecular chains compared with hc crystallized or amorphous PLA, slowing water molecules to penetrate into the sc crystallites. So, enhancing the sc crystallite content for PLA-based composites is conducive to improving the hydro-

lysis resistance.^[16] In this work, the H-L/D/EG20 composite was firstly placed in an environment with a temperature of 70 °C and a humidity of 80% for a certain period of time, and then the mechanical properties and viscosity-average molecular weight (M_η) were measured to evaluate the hydrolysis resistance behavior. L/EG20 composite was used for comparison and the results are shown in Fig. 8. The mechanical properties of the L/EG20 composite deteriorate significantly after 24 h of aging, as tensile strength, elongation at break, and notched impact strength decline from 38.4 MPa, 62%, and 64.2 kJ/m² to 21.5 MPa, 26%, and 28.6 kJ/m², respectively; after 72 h, and the mechanical properties could not be even measured anymore due to the severe degradation. In contrast, the mechanical properties of H-L/D/EG20 composite slowly decrease after 48 h of aging, and the degradation degree in 72 h is comparable with that of L/EG20 sample aging for 24 h. Meanwhile, it can also be observed that the M_η results are consistent with the mechanical tests. For instance, M_η of the L/EG20 composite decreases from 15.0×10^4 g/mol to 8.1×10^4 g/mol after 24 h of aging, while it only declines from 14.4×10^4 g/mol to 13.2×10^4 g/mol for the H-L/D/EG20 composites. These results illustrate that the high content of sc crystallites in the H-L/D/EG20 composite can guarantee an improvement in hydrolysis resistance.

On the basis of the above discussion, it is clear that L/D/EG20 composite with super toughness, high strength, and excellent heat resistance properties can be prepared *via* a facile melt blending, and then two-step annealing process. Fig. 9 highlights the comparison of the L/D/EG20 with some widely applied petroleum-based engineering plastics (*e.g.*, poly(ethylene terephthalate) (PET),^[46] polycarbonate (PC),^[47] and poly(butylene terephthalate) (PBT)^[48]) in terms of some comprehensive performance, where L/D/EG20 shows quite high toughness and superior heat resistance.

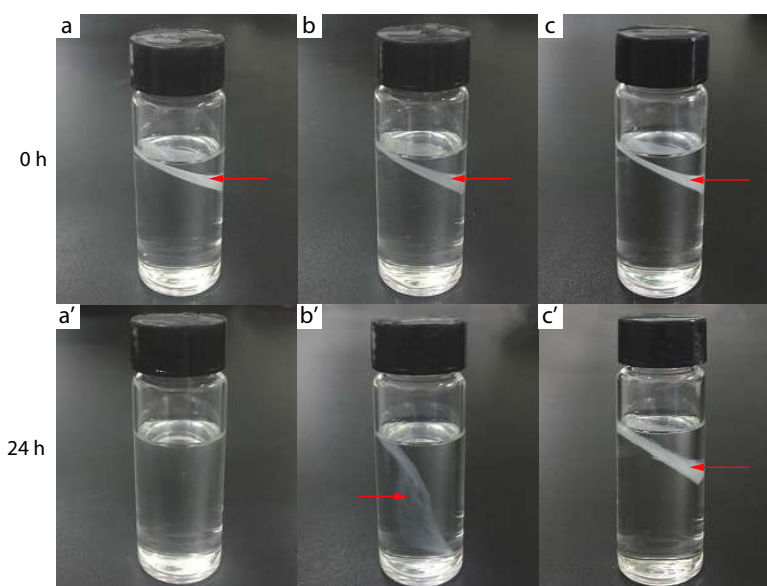


Fig. 7 Digital photos of (a, a') L/EG20, (b, b') L-L/D/EG20, and (c, c') H-L/D/EG20 composites after immersing in chloroform for (a–c) 0 and (a'–c') 24 h.

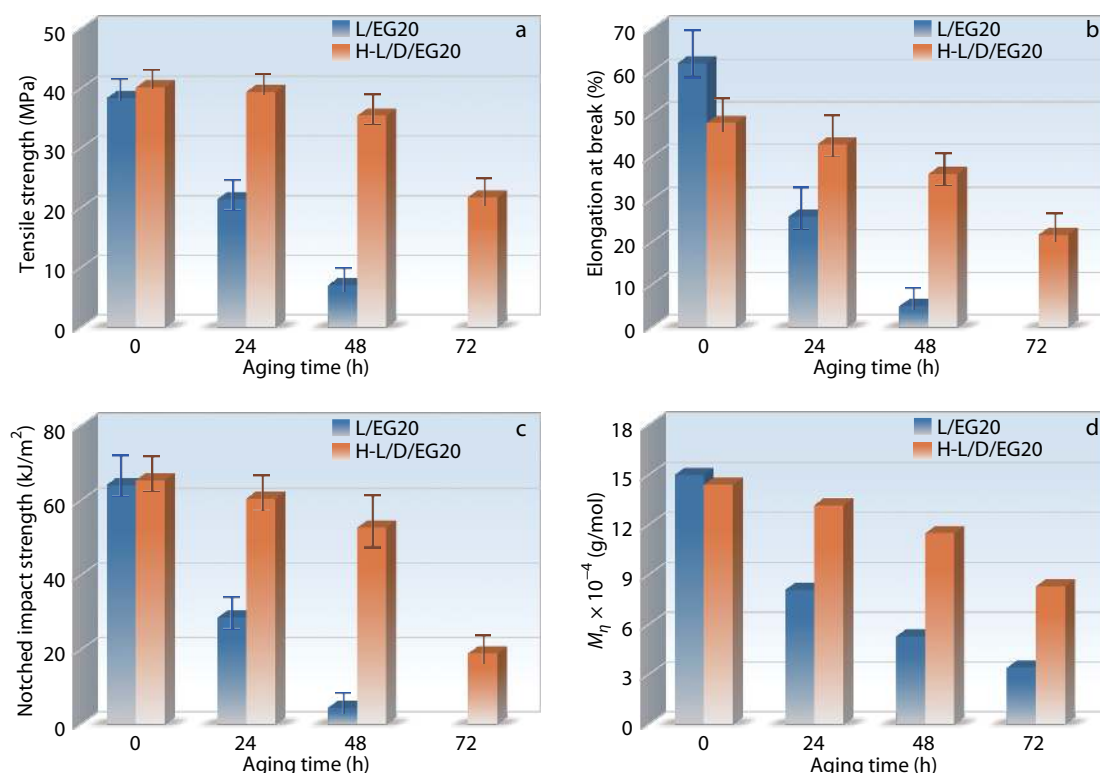


Fig. 8 (a) Tensile strength, (b) elongation at break, (c) notched impact strength, and (d) viscosity-average molecular weight of L/EG20 and H-L/D/EG20 composites after aging for 0, 24, 48, and 72 h, respectively.

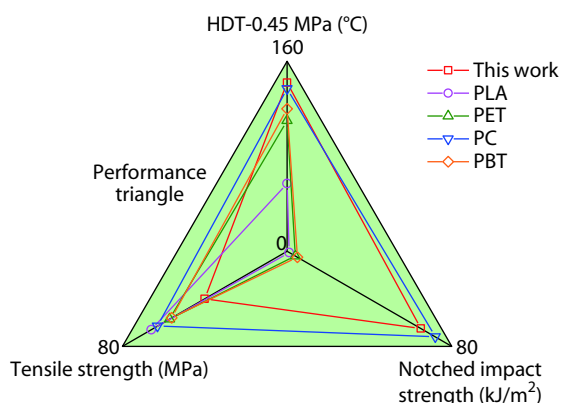


Fig. 9 Physical and mechanical properties comparison of neat PLA, PET, PC, PBT, and L/D/EG20 in this work.

CONCLUSIONS

In this study, the PLLA/PDLA composites with various contents of EVM-GMA elastomer were prepared by melt blending, and then subjected to the two-step annealing process during the compression molding. The compatibility between the PLA matrix and the EVM-GMA elastomer was significantly improved due to the *in situ* reaction between epoxy groups of EVM-GMA and terminal carboxyl/hydroxyl groups of PLA chain during the melt blending. The sc crystallites pre-formed in the first annealing step could serve as nucleation sites and facilitate the close alignment of PLLA and PDLA chains, consequently forming more sc crystallites under the optimal second annealing condi-

tion at 200 °C for 20 min. The good compatibility between PLA and EVM-GMA and the good dispersion of EVM-GMA elastomer were the main contributors to PLLA/PDLA blend toughening, which could be explained by the elastomer-induced plastic deformation and fibrillation mechanisms. Moreover, the highly stereocomplex crystallized PLA composites exhibit excellent heat resistance, chemical resistance, and hydrolysis resistance simultaneously. These fascinating properties enable the sc-PLA material as an engineering bioplastic for applications in some rigorous conditions.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2443-5>.

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