

Mechanical Toughening of Telechelic Copolymer to Poly(lactic acid) Blends: Perspectives of Microstructural Comparison and Molecular Simulation

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Electronic Supplementary Information

Abstract Poly(lactic acid) (PLA) is a renewable polyester material with excellent properties, such as processability, biocompatibility, and biodegradability, and is widely used in packaging and medical applications. However, neat PLA has the performance limitations of high brittleness and poor toughness, strongly restricting its practical use. In this study, three poly(ethylene glycol) (PEG)-based telechelic polymers were synthesized with different microstructures: linear epoxidized poly(ethylene glycol) (linear EPEG), 4-arm star-shaped epoxidized poly(ethylene glycol) (4A-EPEG), and 4-arm star-shaped poly(lactic acid-glycolic acid)-epoxidized poly(ethylene glycol) (4A-PLGA-EPEG). These telechelic polymers that take the reactive epoxy groups on the terminals of the chains endowed the reactive compounding with the PLA matrix to achieve the mechanical enhancement of the blends. At a low loading level (3 wt%), the introduction of 4A-PLGA-EPEG significantly improved the toughness of the PLA-based blends with a substantial increase in elongation at break of 107.43% compared to only 3.84% for the neat PLA material. In contrast to linear EPEG and 4A-EPEG, the 4A-PLGA-EPEG copolymer served as a mechanical toughening agent because of its enhanced compatibility and the formation of topological entanglements with the polymeric matrix in the blends. The calculation of the efficiency factor (η) quantified the improvement in the microstructure stability and stress transfer efficiency of blends derived from the chain entanglements of the added copolymer, and molecular simulations further confirmed the formation of a micro-topological structure by reactive compounding in PLA-based blends.

Keywords Poly(lactic acid); Telechelic copolymer; Blends; Molecular simulation

Citation: Hong, J. C.; Tao, Y. W.; Yu, Z. C.; Zhu, G.; Lin, N. Mechanical toughening of telechelic copolymer to poly(lactic acid) blends: perspectives of microstructural comparison and molecular simulation. *Chinese J. Polym. Sci.* <https://doi.org/10.1007/s10118-026-3808-1>

INTRODUCTION

As a widely used material, poly(lactic acid) (PLA) is regarded as a promising alternative to petroleum-based polymers owing to its remarkable combination of high mechanical strength, biodegradability, and biocompatibility. It has been extensively utilized in food packaging and biomedical applications. In addition to its conventional use in medical sutures and bone plates, PLA can also serve as a drug carrier for delivering therapeutic agents, such as curcumin.^[1–4] PLA with high molecular weight is generally synthesized by ring-open polymerization derived from lactide using a suitable catalyst.^[5] As a polyester, PLA can be degraded *via* hydrolysis or enzymatic degradation to carbon dioxide and water, and is therefore regarded as a biodegradable and implantable material, as approved by the environmen-

tal and FDA regulations.^[6] However, the inherent drawbacks of high brittleness and inferior toughness, generally only 3%–7% elongation at break, strongly restrict the practical applications of PLA, which requires mechanical toughening modification for PLA with various approaches.^[7,8] The addition of polymer-based toughening agents is a promising strategy to enhance the toughness of PLA materials, with reported studies of unsaturated poly(ether-ester), polyurethane, natural rubber, and polycaprolactone.^[9–13] Commonly, these polymeric toughening agents should be added at loading levels of more than 10 wt%–30 wt% with or without the other compatibilizers. For instance, the incorporation of 20 wt% polyurethane in melted PLA was reported to increase the elongation at break to more than 150% for the blends.^[14] In the case of epoxidized natural rubber as a toughening agent,^[15] the loading level was reported to be 20 wt% for PLA-based blends with an increase in elongation at break of 212.5%. To overcome the brittleness and poor thermal stability of PLA, a quaternary melt-blended system comprising bio-based polycarbonate (PC), compatibilizer (BPM), poly(*D*-lactic acid) (PDLA), and PLA was developed. This strategy successfully yielded a blend with an enhanced heat resistance and

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Special Topic: Non-Food Biomass Materials

Received June 21, 2026; Accepted July 7, 2026; Published online September 29, 2026

good toughness. The optimized blend achieved a heat deflection temperature of 106.5 °C and elongation at break of 113.6%.^[8]

Owing to the good flexibility of polyether chains, poly(ethylene glycol) (PEG) is an extensively studied polymeric toughening agent for PLA blends, with preservation of biocompatibility and biodegradability at a controlled molecular weight.^[16] The early studies have reported that high loading levels of pure PEG enhanced the toughness of PLA/PEG blends.^[17] However, the different polarities of the PEG and PLA components induced serious incompatibility and even phase separation of the blends, especially with the addition of excessive PEG as a toughening agent.^[18,19] Furthermore, in these cases, the toughness was improved by the introduction of high loading levels of PEG at the expense of the strength and modulus of the resultant blends.^[20] Another strategy of combining PEG and PLA as toughened blends is ternary blending, that is, introducing a third component or phase such as polymers or nanoparticles. Some studies have reported the preparation of ternary blends from PLA matrices with simultaneous enhancement of the mechanical strength and elongation at break, including PLA/PEG/lignin, PLA/PEG/starch and PLA/PEG/polyurethane blends.^[21–23] Regarding the nanoparticles and PEG toughening strategy, a synergistic toughening effect of silica nanoparticles and PEG by surface grafting was reported for the resultant PLA-based blends.^[24] Similar results were observed in blends of PLA/PEG/nanodiamond and PLA/PEG/nano glass flakes,^[25,26] exhibiting mechanical enhancement of elongation at break and tensile strength. Although the ternary blending approach can contribute to an effective improvement in the mechanical toughening effect, it should be noted that additional ingredients may induce a change in some original properties of PLA, involving biodegradability and biocompatibility in various systems.

Therefore, the concept of polymeric toughening agents at relatively low loading levels to enhance the mechanical performance of PLA and preserve its intrinsic biodegradation is always attractive in both academic and industrial demands. Reactive compounding is a technique involving the incorporation of chemically modified compounds into a polymeric matrix to initiate covalent linkage during the processing stage, with the purpose of enhancing the mechanical properties of blends. Several studies have reported a crosslinked toughening strategy based on the reaction between the epoxidized agent and PLA matrix to simultaneously enhance the toughness and impact strength of epoxidized soybean oil, ethylene-methyl acrylate-glycidyl methacrylate (EMA-GMA), and epoxy-functionalized methyl methacrylate-co-glycidyl methacrylate (PMMA-GMA) epoxidized copolymers.^[27–29] Inspired by these studies, we designed reactive compounding of epoxidized PEG as a telechelic toughening agent for PLA blends. Linear epoxidized PEG (linear EPEG) and 4-arm star-shaped epoxidized PEG (4A-EPEG) were synthesized, and their toughening effects to PLA material were studied. To further improve the compatibility between epoxidized PEG and PLA, poly(lactic acid-glycolic acid) (PLGA) segments were introduced into the 4A-EPEG chains, producing a 4-arm star-shaped poly(lactic acid-glycolic acid)-epoxidized

poly(ethylene glycol) (4A-PLGA-EPEG). The prepared 4A-PLGA-EPEG effectively improved the toughness of the PLA material at a low loading level (3 wt%), which was attributed to the good interfacial compatibility and topological structure under reactive compounding. This study offers a scientific case for the molecular structural design of polymeric toughening agents for PLA-based blends, with a comprehensive understanding of the mechanical enhancement of polymeric blends at the molecular level.

EXPERIMENTAL

Materials

PLA as a polymeric matrix ($M_n=2.3\times10^5$ g/mol) was supplied by Jinan Daigang. PEG ($M_n=4000$ g/mol), 4-dimethylaminopyridine (99%), glycolide (99%), pentaerythritol (98%), *L*-lactide, and stannous octoate (95%) were purchased from Macklin. Epichlorohydrin (AR, analytical reagent), triethylbenzylammonium chloride (TEBAC, AR), succinic anhydride (99%), and *N,N*-dicyclohexylcarbodiimide (DCC, 99%) were supplied by Shanghai Aladdin. Dichloromethane (AR), sodium hydroxide (AR), anhydrous sodium sulfate (AR), methyl *tert*-butyl ether (AR), triethylamine (AR), hydrochloric acid (37%), methanol (AR), diethyl ether (99.5%), sodium bicarbonate (AR), sulfuric acid (98%), and acetone (AR) were acquired from Sinopharm Chemical Reagent Co., Ltd. Prior to use, the dichloromethane, diethyl ether, and acetone were dehydrated using molecular sieves.

Synthesis of Linear Epoxidized Poly(ethylene glycol) (Linear EPEG)

PEG (2.7 g) and TEBAC (1.0 g) were dissolved and mixed in an aqueous NaOH solution (24 g, 49.5 wt%). Under vigorous stirring, epichlorohydrin (23 mL) was slowly added to the mixed solution under continuous stirring at 50 °C for 1 h. After the reaction, the product was purified by successive washing with dichloromethane and dried over anhydrous sodium sulfate. After rotary evaporation, the product was recrystallized from cold methyl *tert*-butyl ether to precipitate the purified linear EPEG. The mass yield of this reaction was approximately 60%.

Synthesis of 4-Arm Star-shaped Epoxidized Poly(ethylene glycol) (4A-EPEG)

The protocol of synthesizing 4A-EPEG was concerned with three stages.

(1) Carboxylation of pentaerythritol (PTOL). Succinic anhydride (0.75 g) was dissolved in anhydrous dichloromethane (150 mL) with the introduction of 4-dimethylpyridine (DMAP, 0.915 g) and triethylamine (0.75 g) to start the reaction at room temperature for 1 h. Then, the desired amount of pentaerythritol (0.204 g) was added, and the reaction was continued at 40 °C for 48 h. After the reaction, the dichloromethane was removed by atmospheric distillation at 50 °C. The product was extracted with diluted hydrochloric acid and distilled water three times and finally vacuum-dried at room temperature for 48 h to obtain the powder product of carboxylated pentaerythritol (CPTOL).

(2) Dehydration esterification. CPTOL and PEG were dissolved in anhydrous dichloromethane (200 mL). With the addition of DCC (6 mmol) and DMAP (3 mmol), the reaction was performed at room temperature for 48 h under nitrogen protection. After the reaction, the residual DCC was converted in-

to a milky-white powdery precipitate 1,3-dicyclohexylurea (DCU) by adding 2–3 drops of water, followed by filtration to remove the precipitates. Subsequently, dichloromethane was removed by atmospheric distillation at 50 °C, and the products were further dissolved in hot water at 80 °C. After setting, the products appeared in the lower layer and were vacuum-dried at room temperature for 48 h to obtain a 4-arm star-shaped poly(ethylene glycol).

(3) Telechelic epoxidation. The terminal epoxidation of the obtained 4-arm star-shaped poly(ethylene glycol) followed the same protocol as that used for preparing linear EPEG with epichlorohydrin to obtain 4A-EPEG. The mass yields of the above three reactions were 87%, 74%, and 55%, respectively.

Synthesis of 4-Arm Star-shaped Poly(lactic acid-glycolic acid)-epoxidized Poly(ethylene glycol) (4A-PLGA-EPEG)

4A-PLGA-EPEG was prepared using a two-stage protocol.

(1) 4-arm star-shaped poly(lactic acid-glycolic acid) (4A-PLGA). 4A-PLGA was synthesized *via* classic melt polymerization.^[30] The monomers of *L*-lactide (5.0 g) and glycolide (1.3 g) were mixed with pentaerythritol as the initiator (0.13 g) in a three-necked flask. The Sn(Oct)₂ catalyst dissolved in dichloromethane was added to the mixture to initiate the reaction at 160 °C for 8 h under the protection of nitrogen. After the reaction, the product was dissolved in dichloromethane, precipitated, and purified twice using anhydrous methanol. Finally, solid product 4A-PLGA was obtained by vacuum drying for 48 h. The yield in this step was approximately 90%.

(2) Reaction of 4A-PLGA and linear EPEG. The reaction between the previously synthesized 4A-PLGA and linear EPEG was performed under catalysis by diluted sulfuric acid at 65 °C for 1.5 h. Ammonium bicarbonate (3 wt% of the total amount) was added to quench the reaction. The mixture was then cooled to room temperature with the removal of precipitates, recrystallized with the addition of methyl *tert*-butyl ether, and finally, the product of 4A-PLGA-EPEG was obtained by filtration and drying. The complete routes of the chemical reactions by synthesizing three telechelic copolymers of linear EPEG, 4A-EPEG, and 4A-PLGA-EPEG, as well as the reaction mechanism of epoxidized polymers with the PLA matrix, are shown in Fig. 1. The final yield was about 63%.

Preparation of Poly(lactic acid)-based Blends

The PLA-based blends were prepared *via* reactive casting evaporation. Typically, solid PLA was dissolved in dichloromethane (30–50 mL) to form a viscous solution. Three synthesized polymers as toughening agents were added to the dissolved PLA solution at ratios of 1 wt%, 3 wt%, and 5 wt%. Subsequently, several drops of HCl solution (1 mol/L) were added to the mixture as a catalyst to initiate the reaction for 8 h at 60 °C under condensation reflux, as shown in Fig. 1(d), with the acid-catalyzed mechanism of PLA and epoxidized polymers.^[31] After the reaction, the mixture was cooled at room temperature with continuous stirring, poured into a polytetrafluoroethylene (PTFE) mold, and evaporated at room temperature for 24 h. Subsequently, the films were dried in a vacuum drying oven at 40 °C for 8 h.^[32] Moreover, the thicknesses of all films ranged from 150 µm to 180 µm. The prepared films were denoted as F-0 (neat PLA), F/(lin)E-1/3/5 (blends filled with linear EPEG), F/(4a)E-1/3/5

(blends filled with 4A-EPEG), and F/(4a)LE-1/3/5 (blends filled with 4A-PLGA-EPEG).

Characterizations

(1) Fourier transform infrared spectroscopy (FTIR). The chemical structures of the three synthesized polymers (linear EPEG, 4A-EPEG, and 4A-PLGA-EPEG) were analyzed using a Fourier transform infrared spectrometer (Nicolet FTIR iS50, Thermo Fisher Scientific, USA). Typically, the powder sample was compressed with dried KBr pellets in the scanning wavenumber range of 4000–400 cm⁻¹ and 16 scans were performed.

(2) ¹H-nuclear magnetic resonance (¹H-NMR). The three synthesized polymers were further investigated using a nuclear magnetic resonance spectrometer (Bruker 300 MHz, Germany) with deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal standard.

(3) Gel permeation chromatography (GPC). The molecular weights and distributions of the three synthesized polymers were measured by GPC, which was performed on an Agilent 1100 system with tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min and column temperature of 35 °C. A calibration curve was established using monodisperse polystyrene standard samples to determine their molecular weights and distribution parameters.

(4) Transmission electron microscopy (TEM). The morphologies of the three synthesized polymers were observed using a transmission electron microscope (JEM-1400Plus, Japan), which were dissolved in dichloromethane to prepare 0.02 wt% solutions. The sample solutions were pipetted and dropped onto a copper grid with a carbon support film, and left to stand for 10 min to allow the samples to deposit on the grid. The excess liquid was then blotted off at the edge of the filter paper. The samples were negatively stained with 1 wt% uranyl acetate for 10 min, excess staining solution was removed, and the samples were dried at room temperature for 24 h before observation.

(5) Tensile testing. The tensile properties of the PLA-based blends were measured using a WDW-5D electronic universal testing machine (Chuanbai, Jinan, China). Before the measurement, all film samples were treated as standard dumbbell specimens, and tensile tests were conducted at a constant rate of 20 mm/min with a 500 N load cell. Each sample was measured five times, with the average values of mechanical data including Young's modulus, tensile strength, and elongation at break for the prepared blends.

(6) Dynamic mechanical analysis (DMA). Thermodynamic analysis of the blends was performed using a NETZSCH DMA 242C dynamic mechanical analyzer under a nitrogen atmosphere. The samples were treated with dimensions of 20 mm × 4 mm as tensile specimens. The conditions of the measurements were set as: the tensile mode with a frequency of 1 Hz, heating rate of 3 °C/min, and temperature range of 20–140 °C.

(7) Differential scanning calorimetry (DSC). The thermal properties of the blends were determined using differential scanning calorimetry (TA-DAC2500). Under a nitrogen atmosphere, the sample was heated from room temperature to 200 °C at a heating rate of 10 °C/min and held at this temperature for 5 min to eliminate the thermal history. The sample was then cooled to room temperature, reheated to 250 °C at the same rate, and the second heating curve was recorded.

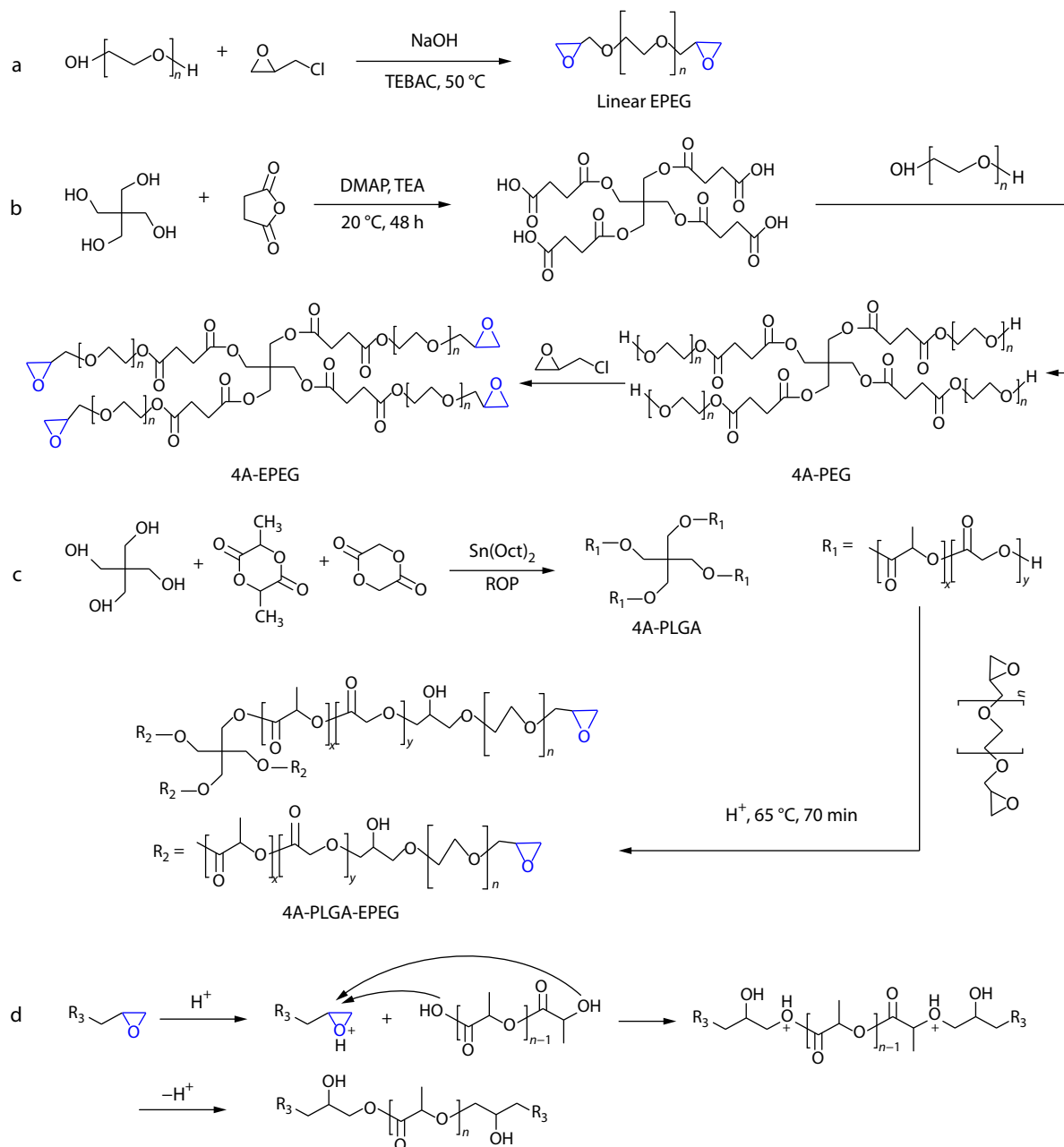


Fig. 1 Synthesis routes of (a) linear EPEG, (b) 4A-EPEG, (c) 4A-PLGA-EPEG in this study and (d) reaction mechanism of epoxidized polymers with PLA matrix.

The crystallinity (X_c) of the PLA-based blends was calculated using the following equation:

$$X_c (\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \omega} \times 100 \quad (1)$$

where ΔH_m and ΔH_{cc} are the melting enthalpy and cold crystallization enthalpy of the blends, respectively, and ΔH_f represents the theoretical enthalpy of the completely crystallized PLA as 93.7 J/g. ω denotes the mass fraction of the PLA matrix.

(8) Polarized optical microscopy (POM). Polarized optical microscopy (Leica DM2700P) was employed to observe the samples and evaluate their crystallization behavior and plasticizer distribution.

(9) Scanning electron microscopy (SEM). The microstructures of the blends were observed using field-emission scanning electron microscopy (JSM 7500F, JEOL, Japan). The blended films were quenched, fractured in liquid nitrogen, and sputter-coated with gold for cross-sectional observation.

RESULTS AND DISCUSSION

Structures and Morphologies of Three Synthesized Copolymers

Three telechelic polymers viz. linear EPEG, 4A-EPEG, and 4A-PLGA-EPEG taking the terminal epoxy groups were synthesized as toughening agents for PLA-based blends. The chemical struc-

tures of these polymers are shown in Figs. 2(A)–2(C). In the $^1\text{H-NMR}$ spectrum of linear EPEG, the peaks at 2.55 and 2.74 ppm were attributed to the characteristics of hydrogen from methylene groups on the epoxy group (H^a), and the peak at 3.11 ppm was ascribed to the characteristic of hydrogen from the methine group on epoxy groups (H^b). The featured peaks located at 3.44 and 3.74 ppm were attributed to the hydrogen from methylene groups connected to epoxy groups (H^c), while the main peak at 3.64 ppm resulted from methylene group on the main chain of PEG segments (H^d). Compared to that of linear EPEG, two additional peaks located at 2.63 and 4.21 ppm on the $^1\text{H-NMR}$ spectrum of 4A-EPEG, attributed to the chemical structures of pentaerythritol (H^e) and succinic acid (H^f). Seven characteristic peaks of $\text{H}^{(a-g)}$ were observed in the $^1\text{H-NMR}$ spectrum of the synthesized 4A-PLGA-EPEG, confirming the chemical structure of this 4-arm telechelic copolymer. In the spectrum, the peaks at 4.12 and 5.17 ppm were attributed to the methylene hydrogen of pentaerythritol (H^e) and methine hydrogen in the lactide structure of blocked segments PLGA (H^b). The peaks at 1.25–1.53 and 4.52 ppm were ascribed to the characteristic resonance of hydrogen in lactide (H^c) and methylene hydrogen in glycolide (H^d). The peak at 3.60 ppm resulted from methylene hydrogen on the main chain of the blocked PEG segments (H^g), as well as the characteristic chemical shift of 3.66 ppm (H^f) for the connected methylene hydrogen. The multiplet located at 3.05 ppm was attributed to the methylene hydrogen on the epoxy groups (H^a) of 4A-PLGA-EPEG.

The chemical structures of several intermediate products in the synthesis of the three copolymers were further investigated by FTIR, including linear EPEG, 4A-EPEG, 4A-PLGA-EPEG, and their precursor substances, as shown in Figs. 2(D)–2(F). The infrared characteristic bands of the epoxy groups appeared at 762, 842, and 1241 cm^{-1} for linear EPEG, indicating

that we have successfully achieved terminal epoxidation modification of PEG chains. After the reaction between pentaerythritol and succinic anhydride, the stretching vibration band of the carbonyl groups ($-\text{CO}-$) (1735 cm^{-1}) and ether band ($\text{C}-\text{O}-\text{C}$) (1300–1050 cm^{-1}) appeared. Moreover, after the introduction of the PEG segments and epoxy groups, characteristic bands were observed. In the spectrum of the synthesized 4A-PLGA, the characteristic band of the ester groups (1756 cm^{-1}) was detected, demonstrating the successful synthesis of PLGA polyesters. Following the introduction of linear EPEG segments, the characteristic band of epoxy groups (835 cm^{-1}) appeared,^[23] along with the enhancement of the C–H stretching vibration band (2800–2900 cm^{-1}) in methylene ($-\text{CH}_2-$) and the enhancement of the hydroxyl group ($-\text{OH}$) stretching vibration band (3400–3500 cm^{-1}). These FTIR results confirm the chemical synthesis and structure of 4A-PLGA-EPEG.

To verify the possible reaction between the epoxidized polymers and the PLA matrix, we compared the FTIR spectra of the synthesized 4A-PLGA-EPEG, the blends of F/(4a)LE, and PLA films, as shown in Fig. S1 (in the electronic supplementary information, ESI). The characteristic band appearing in the spectrum of 4A-PLGA-EPEG at 835 cm^{-1} ascribed to epoxy groups, was not observed in the spectrum of F/(4a)LE, indicating that 4A-PLGA-EPEG underwent reactive compounding with the PLA matrix. Compared with the infrared spectrum of pure PLA material, the featured band located at 3300–3500 cm^{-1} belonged to hydroxyl groups was observed in the spectrum of F/(4a)LE because of the generation of additional hydroxyl groups during the chemical reaction between the epoxy and PLA matrix in the reactive compounding.

The morphological observation of linear EPEG, 4A-EPEG, and 4A-PLGA-EPEG from the TEM images in Figs. 3(a)–3(c) ex-

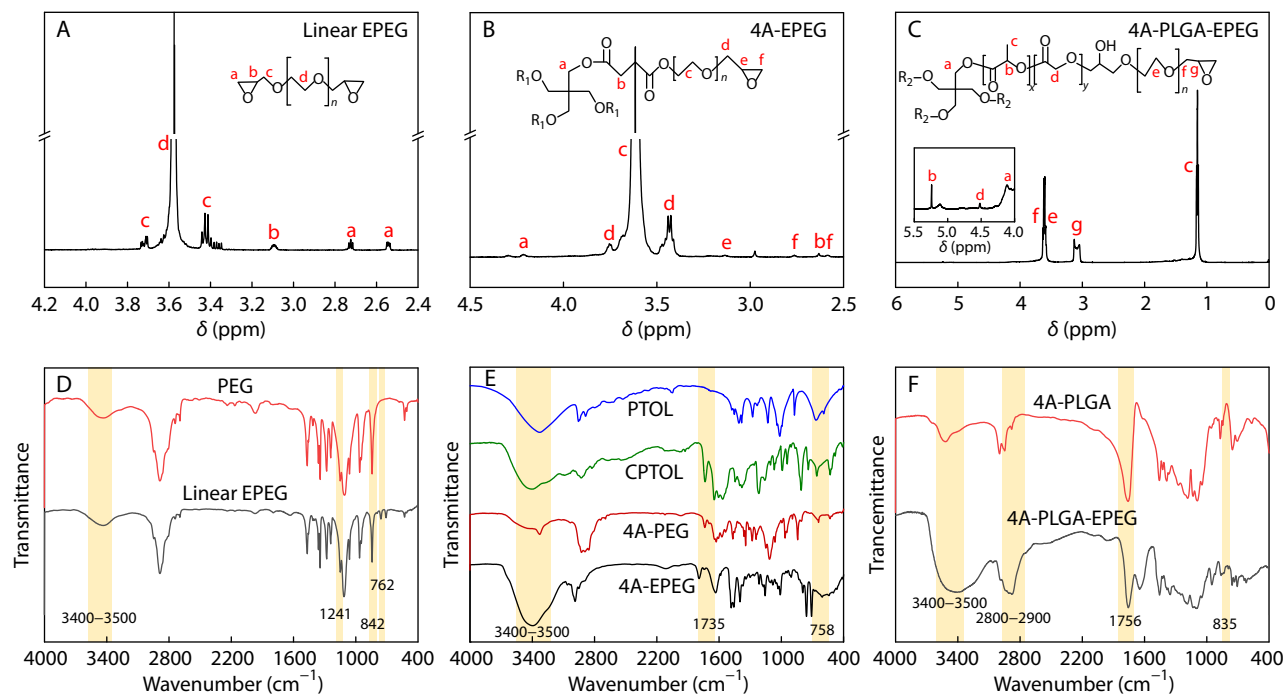


Fig. 2 $^1\text{H-NMR}$ spectra of synthesized (A) linear EPEG, (B) 4A-EPEG and (C) 4A-PLGA-EPEG, and (D–F) FTIR spectra of three synthesized polymers and their precursors in reactions.

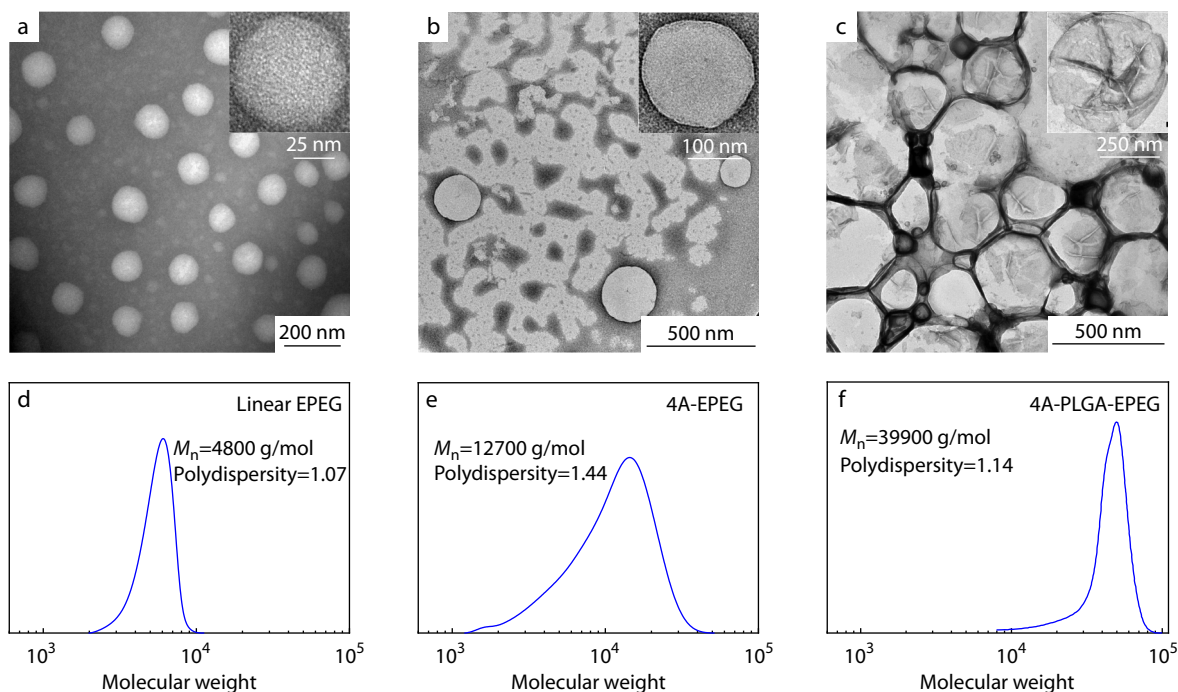


Fig. 3 (a–c) TEM images and (d–f) molecular weight distributions of the prepared copolymers for linear (a, d) EPEG, (b, e) 4A-EPEG and (c, f) 4A-PLGA-EPEG.

hibited spherical shapes for the three synthesized polymers in dichloromethane. During sample preparation, these polymers spontaneously contracted into spherical shapes to maintain a low surface free energy and formed spherical morphologies after solvent evaporation. Furthermore, the diameters of these particles gradually increased from approximately 50 nm for linear EPEG to approximately 150 nm for 4A-EPEG and further 300–500 nm for 4A-PLGA-EPEG, which was attributed to the increase in their molecular weights and additional polymer segments. According to the GPC results, the molecular weights of the three synthesized polymers were 4800, 12700, and 39900 g/mol for linear EPEG, 4A-EPEG, and 4A-PLGA-EPEG (Figs. 3d–3f). The molecular weight of the polymerized PLGA segments in the product of 4A-PLGA-EPEG can be calculated as approximately 6000 g/mol, resulting from the molecular weight of 4000 g/mol for the introduced PEG as the starting material.

Thermomechanical Properties and Microstructures of Blends

The films were cut into specimens with the dimensions shown in Fig. S2 (in ESI). The mechanical properties of the blends were evaluated through tensile testing, with the presence of stress-strain curves shown in Figs. 4(a)–4(c), and the detailed data are listed in Table S1 (in ESI). Typically, the toughness of PLA-based blends is enhanced by the addition of the three synthesized polymers at different degrees of improvement. Specifically, the critical parameters of the mechanical properties of the blends were obtained from the stress-strain curves, viz. the tensile strength, elongation at break, and Young's modulus (Figs. 4d–4f). The elongation at break of the neat PLA film was measured to be only 3.84% and it exhibited a typical brittle fracture. As a toughening agent to the PLA matrix, the three synthesized polymers exhibited varied mechanical enhancements for the

blends. In the case of the F/(lin)E blends, the optimal loading level of linear EPEG was 1 wt% for an improved elongation at break of 24.73%. Compared with linear EPEG, 4A-EPEG exhibited a better improvement in the mechanical enhancement of the F/(4a)E blends, with a higher value of elongation at break at a loading level of 3 wt%. Given their identical chemical compositions, the multi-arm architecture of 4A-EPEG, compared with linear EPEG, likely offers a higher probability of forming crosslinks with the terminal groups of the PLA chains. This resulted in a more pronounced plasticizing effect and enhanced chain mobility within the PLA matrix. These influences facilitated greater deformation during the tensile stretching tests for the two blend series. A plateau region emerges before yielding in the stress-strain curves, as shown in Figs. 4(a) and 4(b). This phenomenon originates from the internal voids and microcracks within the material, whereas the plateau is jointly induced by void expansion and interfacial debonding. Regarding the blends of F/(4a)LE, the introduction of the multi-arm copolymer 4A-PLGA-EPEG contributed to the best toughening effect, with a significant increase in elongation at break of 107.43% at a loading level of 3 wt%. Similar to the microstructure of 4A-EPEG, the multiarm architecture of 4A-PLGA-EPEG formed more chemical cross-links with the PLA matrix. Furthermore, the presence of PLGA blocking segments enhanced the compatibility between 4A-PLGA-EPEG and the PLA matrix, promoting its dispersion and minimizing possible structural defects. The effective mechanical enhancement of 4A-PLGA-EPEG endowed the F/(4a)LE blends with remarkable toughness at low loading levels (1 wt%–3 wt%) while preserving the inherent mechanical strength and modulus of the PLA material. It should be noted that the excessive addition of the three polymers (at a loading level of 5 wt%) reduced the toughening efficiency, likely due to incompatibility and phase separation. Fig. S3 (in ESI) shows the

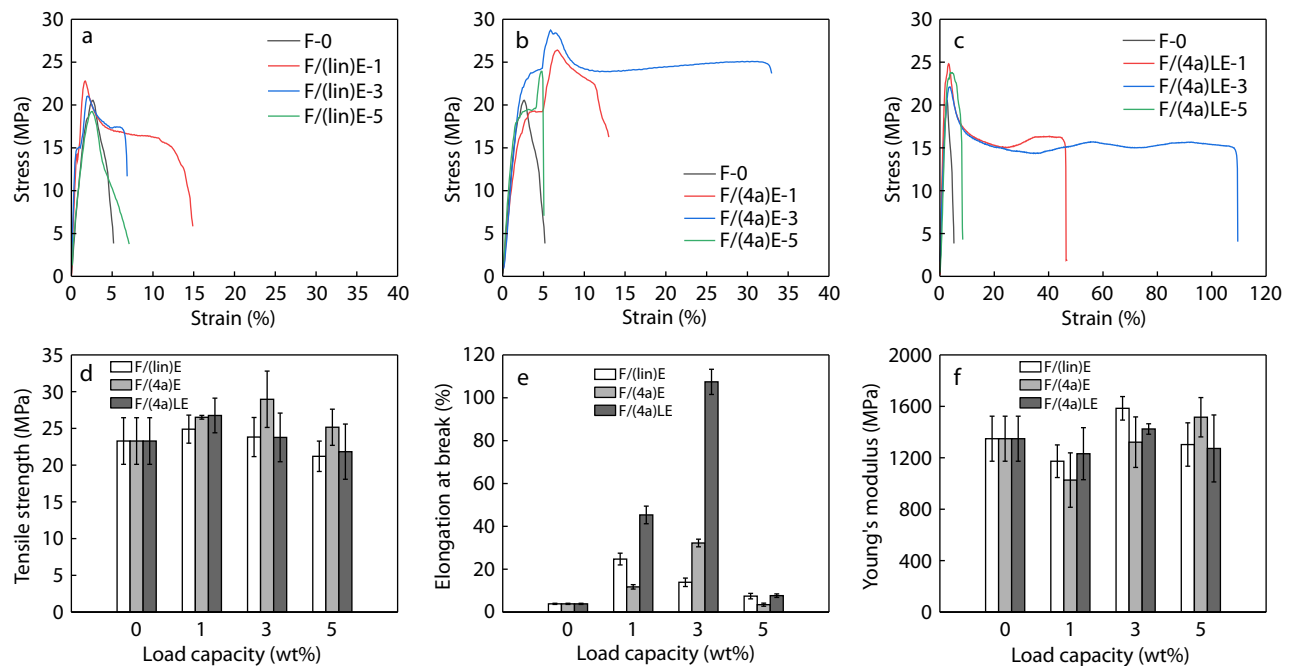


Fig. 4 (a–c) Stress-strain curves and (d) tensile strength, (e) elongation at break, (f) Young's modulus of the blends EPEG/PLA, 4A-EPEG/PLA, 4A-PLGA-EPEG/PLA as well as the neat PLA.

fracture morphology of the specimens after tensile testing, exhibiting typical ductile fracture characteristics, such as stress whitening and necking.

To investigate the microstructures of the prepared blends, POM images were obtained, as shown in Figs. 5(a)–5(c). The bright spots observed in these images correspond to the microcrystals of the PLA chains formed in different blends. Owing to the different polarities, the incorporation of the PEG component may induce a disordered arrangement of PLA chains and hinder the migration of PLA segments toward the crystal nuclei in the blends. Therefore, the observation of spherulitic structures partially reflects the compatibility of the three blends. It is apparent that more spherulitic crystals were observed in the F/(4a)LE-3 (Fig. 5c) than in the others, indicating a possible increase in the crystalline regions of the growth sites from the introduced PLGA chains under this compatible system.

Scanning electron microscopy (SEM) observations revealed the cross-sectional morphologies of the blends. Compared with the smooth morphology of the neat PLA material (Fig. S4 in ESI), the addition of linear EPEG and 4A-EPEG resulted in rough morphologies with many scattered holes (Figs. 5d and 5e), indicating the insufficient compatibility of the microstructures of the two blends resulting from the introduction of hydrophilic EPEG components in the PLA matrix. The SEM image of F/(4a)LE-3 (Fig. 5f) shows an intact morphology devoid of cracks or holes. This observation is attributed to the PLGA segments in 4A-PLGA-EPEG, which effectively improved the compatibility with the PLA matrix, together with the chemical bonding between the reactive EPEG segments and PLA chains, contributing to the continuous interface and microstructure of this blend.

To further investigate the dispersion state of the three toughening agents within the blends, two-dimensional (2D)

micro-FTIR was performed, as shown in Figs. 5(g)–5(i). For each blended film, a defined area was selected and subdivided into five grids of sub-regions. Micro-FTIR spectra were collected from each subregion, and the spatial distribution uniformity of the toughening agents was evaluated based on the absorption intensity in the hydroxyl (—OH) stretching region across the grid.^[33] The reason for choosing hydroxyl absorption as the characteristic signal to evaluate the dispersibility of the three toughening agents in the blends was related to the appearance of hydroxyl in the three blends (ascribed to the reaction between the epoxy and PLA matrix), but its absence in the neat PLA material (as shown in Fig. 2 and Fig. S1 in ESI). The notable variation in hydroxyl absorption intensity among different sub-regions was visually observed as distinct color contrast in the 2D micro-FTIR images of the F/(lin)E-1 and F/(4a)E-3 blends. However, F/(4a)LE-3 exhibited consistent hydroxyl absorption intensity across all sub-regions, corresponding to a uniform color distribution in the 2D micro-FTIR image. These observations further supported the inference that the incorporation of 4A-PLGA-EPEG enhanced the compatibility with the PLA matrix, leading to a homogeneous dispersion of this toughening agent within the blend.

The thermomechanical properties of the blends were investigated by DMA and DSC. As presented in Fig. 6(a), all modified blends possessed a higher initial storage modulus (E') at room temperature than neat PLA (F-0), among which F/(lin)E-1 exhibited the maximum initial E' value. After the linear EPEG segments were incorporated into the PLA matrix, the epoxy groups reacted with the PLA chains to form covalent crosslinking networks. The restrained network counteracted the softening effect of the flexible EPEG chains and increased the overall rigidity of the blend. 4A-EPEG contains abundant potential crosslinking sites, generating stronger chain entanglement and intermolecular interactions be-

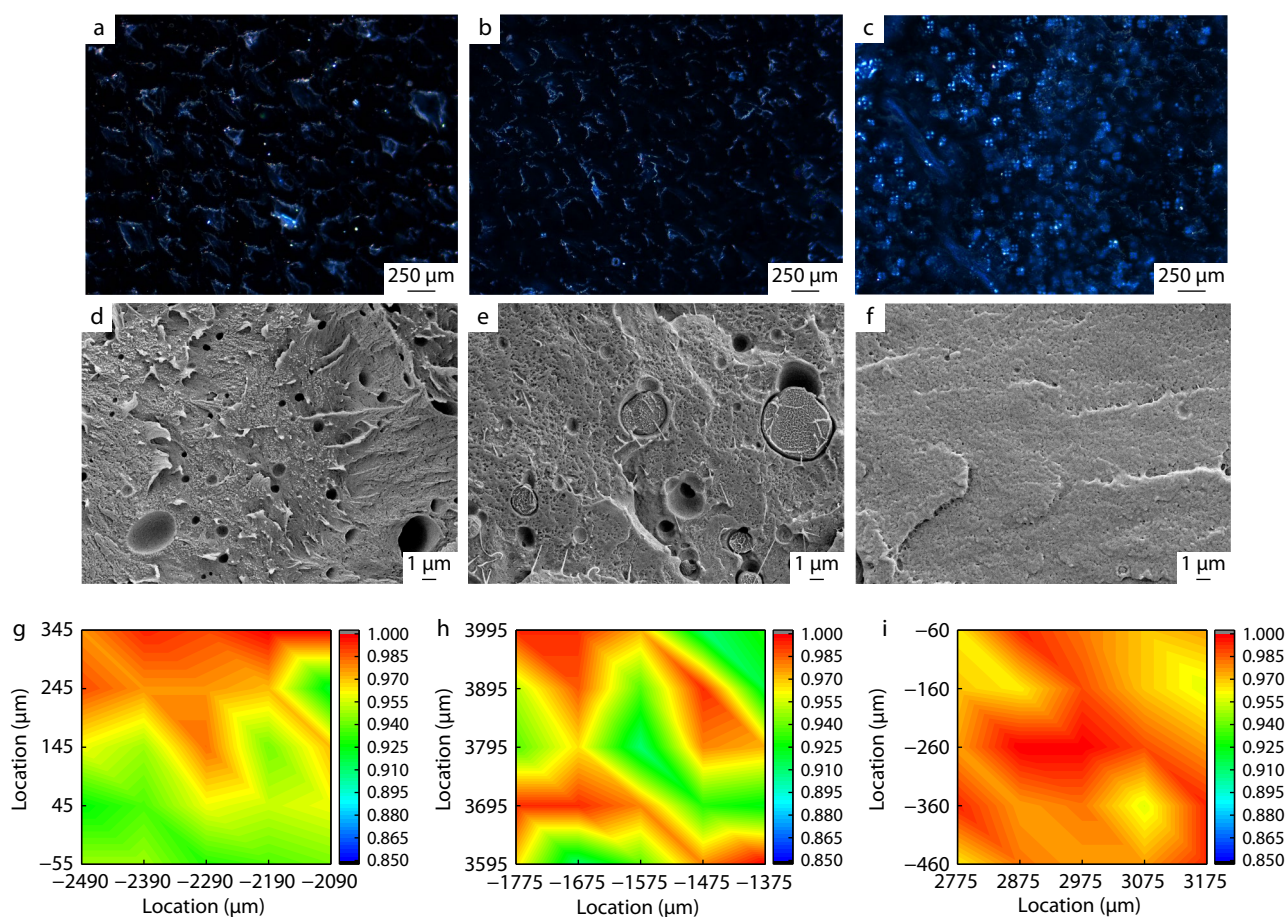


Fig. 5 (a–c) POM, (d–f) SEM and (g–i) 2D micro-FTIR images of (a, d, g) F/(lin)E-1, (b, e, h) F/(4a)E-3 and (c, f, i) F/(4a)LE-3 blends.

tween the branched chains. Nevertheless, the prominent plasticizing effect induced by the massive branched chains led to a lower E' of F/(4a)E-3 than that of F/(lin)E-1. Benefiting from the rigid PLGA segments in the toughener, F/(4a)LE-3 achieved a slight increase in E' relative to F/(4a)E-3. The loss modulus (E'') curves (Fig. 6b) reflect intramolecular friction and energy dissipation of the polymer systems. The peak value of F/(lin)E-1 is lower than that of F/(4a)E-3. The multi-branched topology of 4A-EPEG greatly amplified intramolecular friction and facilitated more energy dissipation during deformation; hence, F/(4a)E-3 had a much higher E'' than F/(lin)E-1. For F/(4a)LE-3, well-compatible PLGA promoted compact and ordered chain entanglement, reducing intramolecular friction and resulting in a decreased E'' in contrast to F/(4a)E-3. Neat PLA exhibited the lowest E'' because of its homogeneous composition without interfacial friction between the two phases. The loss factor ($\tan\delta$) curves in Fig. 6(c) correspond to the glass transition temperature (T_g). Relative to neat PLA, the $\tan\delta$ values of F/(lin)E-1 and F/(4a)E-3 shifted toward higher temperatures. Covalent crosslinking in F/(lin)E-1 and dense branched-chain entanglement in F/(4a)E-3 restricted the mobility of PLA chains and increased the activation energy for segmental motion, leading to an elevated T_g . Slight plasticization from 4A-PLGA-EPEG caused a marginal reduction in T_g of F/(4a)LE-3 compared with that of F/(4a)E-3.

The DSC thermal curves (Fig. 6d) show the heat flow

changes of the blends at different temperatures, and the parameters obtained from the thermal properties of the blends are listed in Table S2 (in ESI). The cold crystallization temperature (T_{cc}) corresponds to the exothermic peak in the secondary heating curve of polymeric materials. With the introduction of the three reactive polymers, the T_{cc} values for the blends significantly decreased by 10–40 °C in comparison with the pure PLA material, attributed to the introduction of flexible PEG segments in these blends. In fact, PEG is a soft polyether with a T_{cc} of 40.5 °C, which is much lower than that of PLA. With the incorporation of the PEG component, the energy barrier for crystal formation was reduced, accompanied by weakening of the intermolecular forces in the blends. Therefore, this effect facilitated the rearrangement of molecular chains during cold crystallization at lower temperatures, leading to a decrease in T_{cc} for the three blends. The dilution effect of the low-molecular-weight toughening agents of linear EPEG, 4A-EPEG, and 4A-PLGA-EPEG induced a slight decrease (1–5 °C) in the melting temperatures (T_m) of the three blends. As a semi-crystalline polymer, the crystallinity is an important parameter that affects the mechanical performance of PLA-based blends. According to the DSC enthalpy (ΔH_m) calculations, the crystallinity (X_c) increased from 12.21% for the neat PLA material (F-0) to 24.1% for F/(4a)LE-3, consistent with the previous observation of POM and mechanical enhancement in this compatible blend.

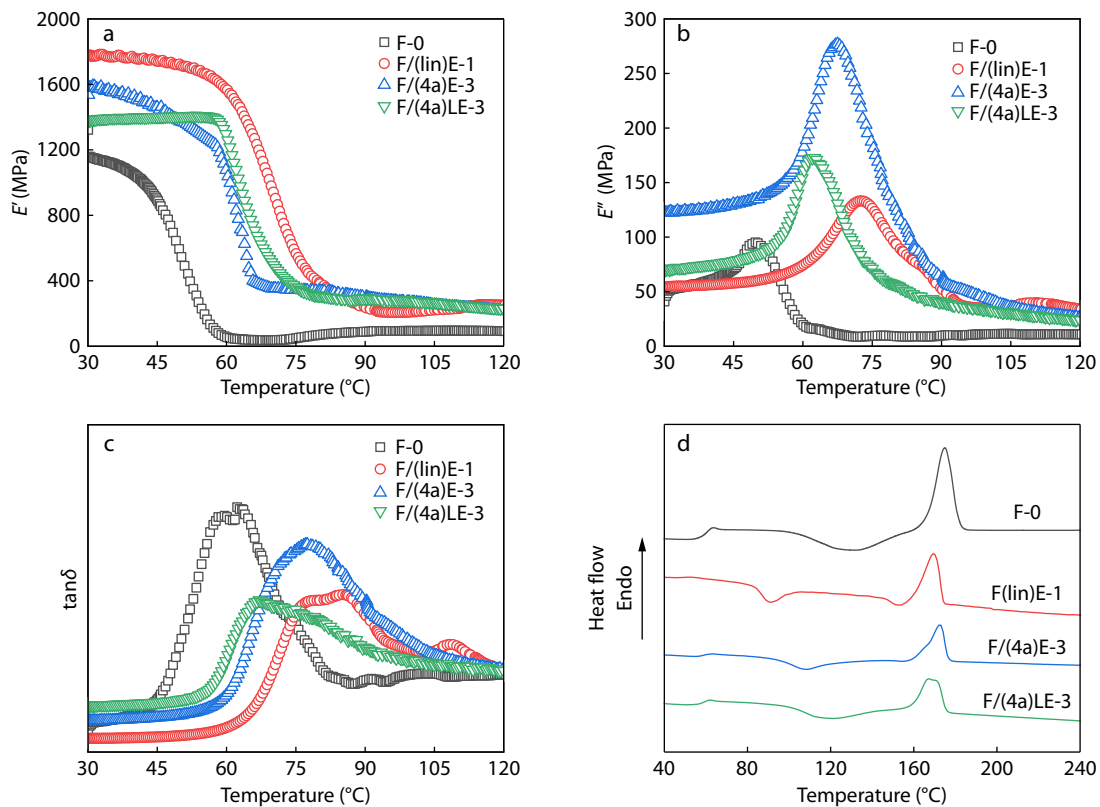


Fig. 6 DMA curves of (a) storage modulus, (b) loss modulus, (c) $\tan\delta$ and (d) DSC curves of blends.

Molecular Simulation and Model Explanation on Microstructures of Blends

Based on the molecular weights of the PLA matrix relative to the three synthesized polymers as toughening agents, we created coarse-grained models of polymers with 100-bead and 5-bead chains, representing PLA molecules and toughening agents, respectively. As shown in Fig. 7, PLA was modeled by a matrix of 1000 chains with 100-bead length, and the toughening agents were modeled by 1000 10-bead chains, generated by the algorithm developed in the previous study.^[34] The beads in the PLA were labeled as P1, the terminal beads in the toughening agents were labeled as L1, and the central bead was labeled as L2. These two models were combined and sent for equilibration, with the force field parameters set against a previous study on coarse-grained PLA models.^[35] Note that both the PLA and toughening agent beads shared the same set of parameters without further detailing, because we aimed to employ the model to reflect the difference between topological structures formed in systems with 2-arm (linear EPEG) and 4-arm (4A-EPEG/4A-PLGA-EPEG) crosslinkers. The linear EPEG was modeled by creating bonds between the L1 and P1 beads so that each crosslinker connected two P1 beads. The 4A-EPEG and 4A-PLGA-EPEG with 4-arm branched microstructures were modeled by first creating L2-L2 bonds to form X-shaped molecules and then creating L1-P1 bonds, so that each X crosslinker connected the four P1 beads. In the two crosslinking schemes, each crosslinker was regarded as activated if all the two or four arms were bonded to P1. To investigate the difference between the two schemes, we prepared linear models with 0 to 1000 activated crosslinkers at intervals of 100, and 4-arm models with 50 to

500 activated crosslinkers at intervals of 50. Consequently, 21 models were prepared, equilibrated, and tested in triaxial tensile tests at a maximum strain of 200%. Equilibration and simulated triaxial tests were performed using LAMMPS.^[36] Codes for model generation and molecular dynamics simulations are available in ESI.

Fig. 8(a) shows 2-arm and 4-arm particle models, and triaxial test is performed on both models. The stress-strain curves in Figs. 8(b) and 8(c) exhibit a similar peak at a triaxial strain of 0.04 for all models, corresponding to the breakdown of cohesive interactions in the PLA polymers. At this initial peak, the strength arose primarily from the interchain van der Waals forces, as the polymer chains were not fully stretched. Compared to area under the stress-strain curves relative to pure PLA model (Fig. 8d), these loops served as critical local features that maintained structural integrity, and their relationship with the crosslink density was quantified, as shown in Fig. 8(e). Because pure PLA consists of linear, non-looped chains, the stress eventually drops to zero at a strain of 2, as illustrated in Fig. 8(f). In contrast, the crosslinked models contained chain loops that can interpenetrate, forming topological linkages that enhance the mechanical performance, particularly the maximum strain. Under high strain, the crosslinked systems developed net-like structures (Figs. 8g and 8h).

PLA polymers are composed of long linear molecular chains that do not branch. The introduction of linear or four-arm molecules capable of bonding with PLA monomers can form a crosslinked network, thereby enhancing the elongation capacity of the polymer system. Coarse-grained molecu-

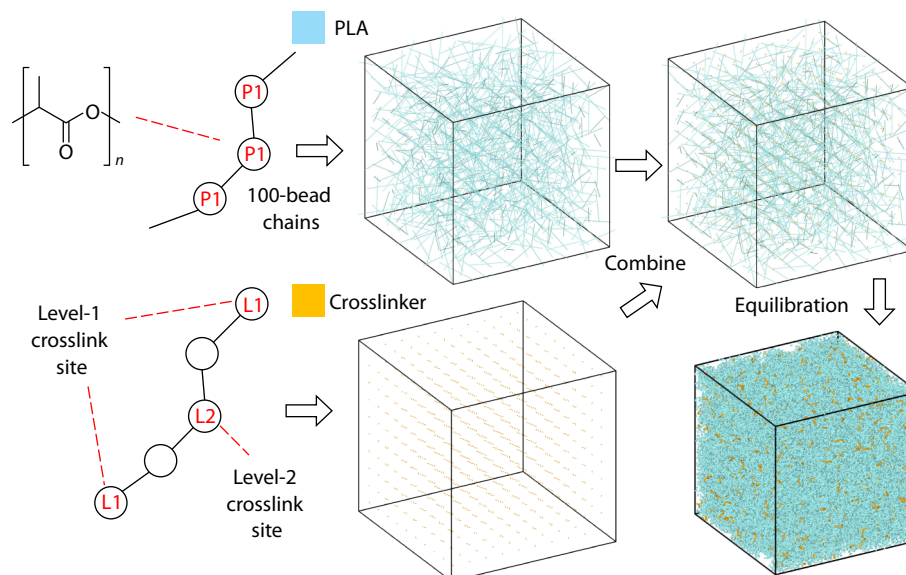


Fig. 7 Illustrated description of coarse-grained models for the synthesized polymers in PLA-based blends in this study.

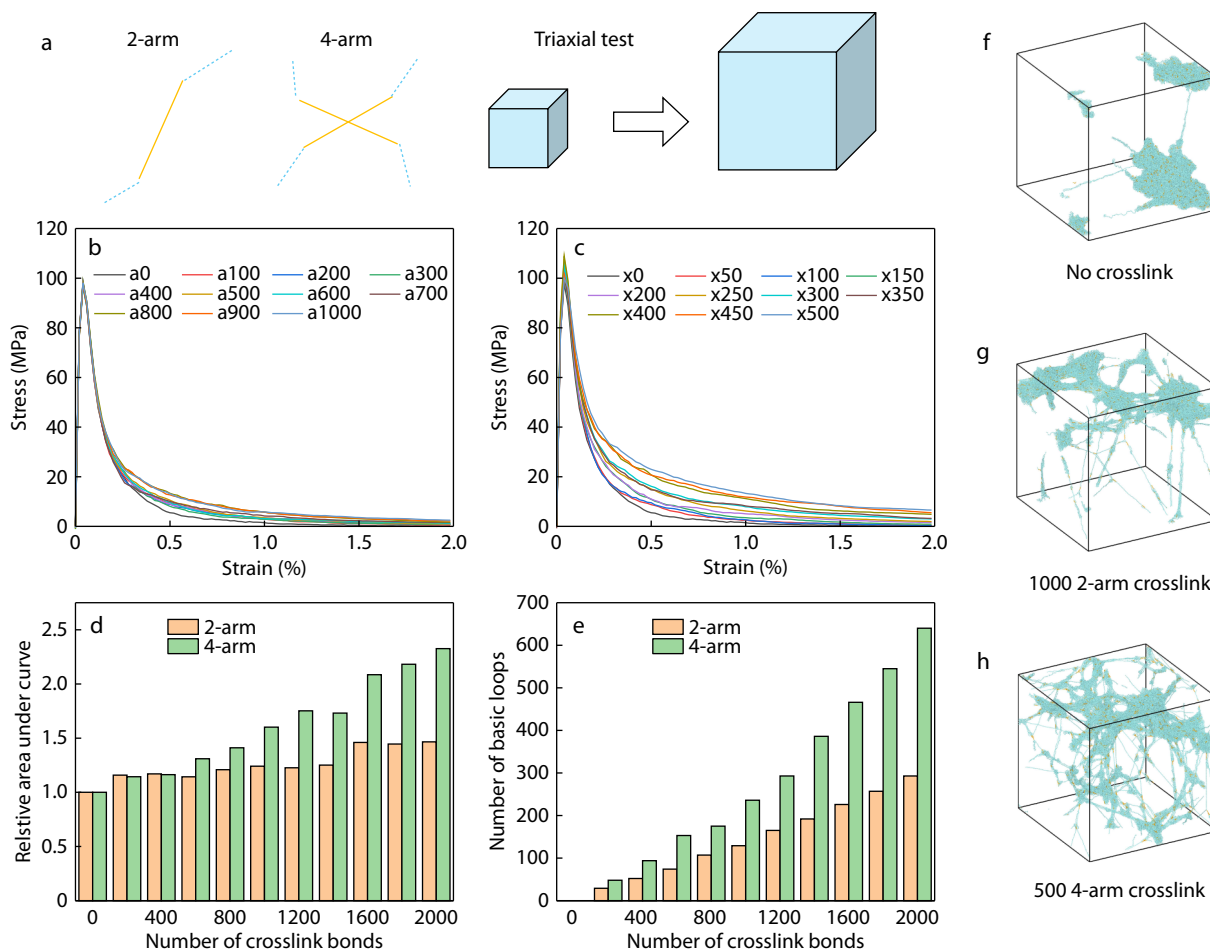


Fig. 8 (a) Schematic diagrams of crosslinking scheme and triaxial tests; Stress-strain curves for (b) 2-arm and (c) 4-arm models with increasing number of crosslinking bonds; (d) Area under the stress-strain curves relative to pure PLA model; (e) Number of basic loops versus crosslinking bonds in 2- and 4-arm cases; Configurations of polymer models at triaxial tensile strain of 2, for (f) non-crosslinked, (g) 2-arm and (h) 4-arm cases.

lar dynamics simulations revealed that the two crosslinked systems exhibited similar behaviors during the early stages of

deformation, with differences emerging only at larger strains. This reflected the distinct mechanisms of action of the two

types of crosslinking molecules. With 2-arm crosslinker (linear EPEG), each crosslinking event created a connection between a pair of PLA particles, which was essentially equivalent to increasing the chain length of the PLA. A closed loop was formed only when the 2-arm crosslinking events occurred on the same pair of PLA molecular chains. In contrast, for the 4-arm molecules (4A-EPEG and 4A-PLGA-EPEG), chain lengthening occurred only when all four crosslinked PLA chains were distinct. However, if the four crosslinking points were not fully distributed across the four separate chains, the 4-arm molecule could form closed loops. Adjacent closed loops can further establish topological connections, thereby significantly improving the toughness of the polymer system.

The rule of mixtures (ROM) was employed to analyze the enhancement mechanism of the blends.^[37] The star-shaped polymer of 4A-PLGA-EPEG featured a structure with multiple chains different from the linear EPEG, which contributed to the formation of multiple connection sites with the PLA matrix and constructed a network-like bridge-like structure. The formed microstructure could effectively transfer stress and enhance the structural stability of the blends. In the 4A-PLGA-EPEG enhanced PLA-based blend, the geometric constraint and multi-interface load transfer effects can be applied to explain the toughening behavior of F/(4a)LE-3. An increase in the number of arms leads to a higher entanglement density of the molecular chains, and multiple arms can simultaneously form stress transfer paths with the matrix, which can effectively transfer the impacted stress. First, the mass fraction (ω_f) of the reinforcing phase was converted to volume fraction (V_f) using Eq. (2), where ρ_f is the density of the reinforcing

phase and ρ_m is the density of the PLA matrix (1.25 g/cm³).

$$V_f = \frac{\omega_f / \rho_f}{\omega_f / \rho_f + (1 - \omega_f) / \rho_m} \quad (2)$$

By referring to the densities of PLA and PEG, the density (ρ_f) of 4A-PLGA-EPEG is defined as 1.2 g/cm³. Consequently, we obtained that the volume fraction of 4A-PLGA-EPEG (V_f) in F/(4a)LE-3 was 0.031.

Assuming that the Young's modulus of 4A-PLGA-EPEG (E_f) was 2000 MPa, the E_c for F/(4a)LE-3 was 1423.81 MPa, and the E_m for the PLA was 1348.19 MPa (according to Fig. 4f). Finally, the efficiency factor (η) reflecting the interfacial transfer capability of 4A-PLGA-EPEG in F/(4a)LE-3 was calculated as 1.04 according to Eq. (3).

$$E_c = \eta E_m (1 - V_f) + E_f V_f \quad (3)$$

Because $\eta > 1$, this star-shaped copolymer 4A-PLGA-EPEG can significantly improve the stress transfer efficiency through multi-arm entanglement with a polymeric matrix.

This is visually modeled, as shown in Fig. 9. The core distinction of the three toughening agents lies in their interfacial compatibility and topological crosslinking efficiency, rather than merely their morphological differences. Linear EPEG forms binary covalent bridges between PLA chains, resulting in discontinuous crosslink networks and poor interfacial affinity owing to the pure polyether segments. The 4-arm topology of 4A-EPEG multiplies reactive crosslinking sites, yet the inherent polarity incompatibility between PEG and PLA still generates weak phase boundaries prone to debonding under tension. In contrast, 4A-PLGA-EPEG incorporates PLGA

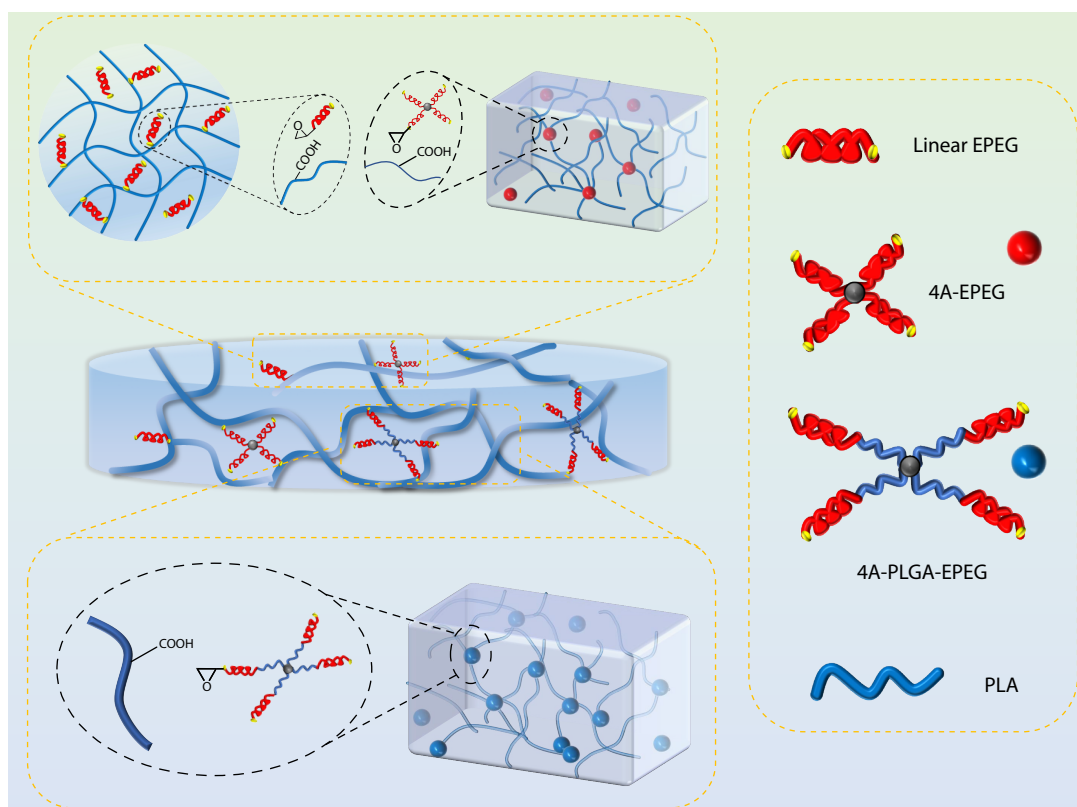


Fig. 9 Schematic models of PLA-based blends enhanced by three synthesized polymers.

segments chemically matched with the PLA matrix, which homogenized the blend phase and eliminated interfacial defects at the molecular scale. Its four epoxy-terminated arms simultaneously bonded with multiple PLA macromolecules to build interconnected topological entanglement networks. Under tensile loading, the well-adhered interface prevents premature interfacial detachment, while the multi-arm crosslinked network disperses the applied stress across numerous molecular chains and consumes deformation energy *via* chain slippage and entanglement disentanglement. This dual mechanism of interfacial compatibilization and topological stress transfer fundamentally accounts for the outstanding low-loading toughening performance of 4A-PLGA-EPEG modified PLA blends, which was further quantitatively verified by the efficiency factor η and molecular simulation results.

CONCLUSIONS

This study develops a reactive toughening strategy for PLA *via* three epoxy-terminated telechelic copolymers with linear and 4-arm star architectures, overcoming the drawback of the high loading levels required for traditional PEG modifiers. The terminal epoxy groups on all copolymers formed covalent crosslinks with the PLA chains during blending, alleviating the PEG-PLA interfacial incompatibility. Among all the modifiers, 4A-PLGA-EPEG achieved optimal toughening at only 3 wt% loading. Its 4-arm topology supplies abundant crosslink sites to build topological entanglements, and incorporated PLGA segments are highly compatible with PLA to eliminate phase separation defects, enabling uniform dispersion of the toughening phase. The synergistic interfacial bonding and chain entanglement drastically boosted the PLA ductility without an obvious loss of stiffness and strength. The DSC results demonstrate that 4A-PLGA-EPEG acts as a heterogeneous nucleation site to increase the PLA crystallinity. Coarse-grained molecular simulations revealed that four-arm crosslinkers construct interconnected loop networks for continuous stress transmission, and the efficiency factor $\eta > 1$ quantitatively verified its superior interfacial load transfer capacity compared with linear analogs. Overall, this work clarifies the multiscale correlation between the modifier molecular structure, blend microstructure, and mechanical properties. The low-content star-shaped telechelic copolymer design offers a facile route to fabricate high-toughness biodegradable PLA blends, and the combined experimental-simulation framework provides a general method to unravel the reactive toughening mechanisms in polyester blends.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3808-1>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGMENTS

This work was financially supported by the Wuhan Key Research and Development Program (No. 2024020702030117).

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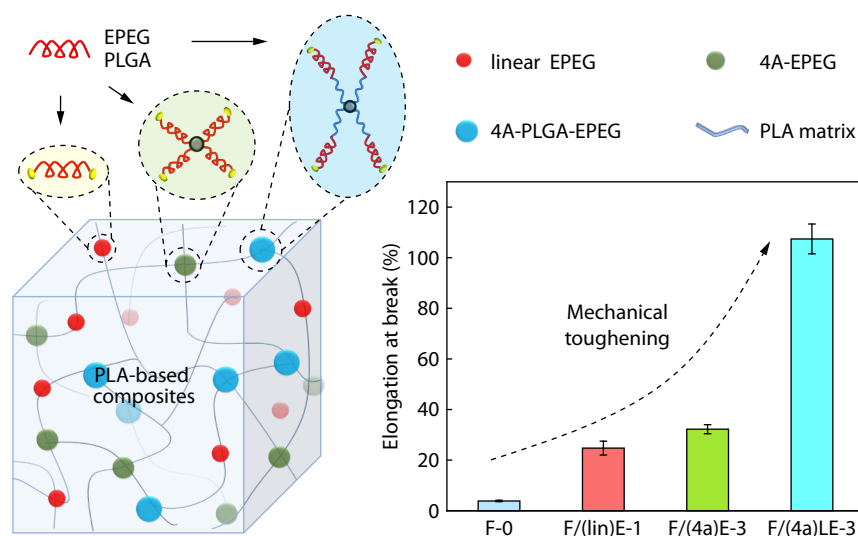
Graphical Abstract

Mechanical Toughening of Telechelic Copolymer to Poly(lactic acid) Blends: Perspectives of Microstructural Comparison and Molecular Simulation

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Three telechelic polymers with terminal epoxy groups were synthesized as toughening agents for poly(lactic acid) composites with high elongation at break. Molecular simulation analysis confirmed the establishment of topological connections and interfacial transfer capabilities for the mechanical toughening effect of the composites.



Chinese J. Polym. Sci. 2026

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