

Effect of Epoxy Chain Extender on the Properties of Polylactic Acid

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Abstract

Modification of polylactic acid (PLA) by chain extension is a method used to improve its melt strength and heat resistance. In this study, the chemical structure, viscosity average molecular weight, thermal properties, melt viscosity, mechanical properties and Vicat softening temperature of PLA before and after the modification were measured by Fourier-transform infrared spectroscopy (FTIR), a viscometer (Mv), differential scanning calorimetry (DSC), a melt index instrument (MI), a rotary rheometer, a universal material testing machine, and a Vicat softening temperature tester, respectively, to characterize the effect of chemically modifying PLA with KL-E4370. The experimental results showed that the epoxy group contained in KL-E4370 reacted with the carboxyl group of PLA. In addition, the modified PLA showed increased molecular weight, enhanced melt strength, decreased melt fluidity, a significantly decreased melt index, significantly increased complex viscosity and modulus, enhanced impact and tensile strengths, and an increased Vicat softening temperature. When the content of KL-E4370 was 0.1%, the viscosity average molar mass increased from 2.88×10^3 g/mol (that of neat PLA) to 4.02×10^3 g/mol, the crystallinity increased from 17.0% (that of neat PLA) to 32.5%, the melt index decreased from 6.0 g/10 min (that of neat PLA) to 2.2 g/10 min, the Vicat softening temperature increased from 67.9 °C (that of neat PLA) to 160.1 °C, and the heat resistance of PLA was improved significantly.

Keywords: Polylactic Acid, Chain Extension, Modification, Viscosity Average Molecular Weight, Melt Index, Vicat Softening Temperature

Introduction

Although plastic has many important applications, improper disposal of plastic has created significant environmental pollution, which is referred to as “white pollution”. Therefore, biodegradable plastics have received increasing attention in recent years as a more environmentally friendly alternative to traditionally used types of plastic.

Polylactic acid (PLA) is a polymer that is chemically synthesized using lactic acid produced by corn starch fermentation. It is a typical biodegradable plastic [1-3] that can reduce the use of fossil oil [4]. PLA is currently frequently used in disposable packaging [5-6]. Because PLA is associated with drawbacks such as low melt viscosity and the tendency to be degraded by heat during processing, it is difficult to perform extrusion and tape casting processes using PLA. Therefore, the applications of PLA are limited in comparison with some other types of plastic [7-8].

A chain extender can be used to modify PLA by reacting with its terminal carboxyl and hydroxyl groups, thus increasing the length

of the molecular chain of PLA, as well as its relative molecular weight. These changes can improve the processing performance of PLA, thus expanding its range of applications [9].

Several recent studies have demonstrated the feasibility of extending PLA. Woo et al. extended the lactic acid homo polymer using hexamethylenediisocyanate to obtain a PLA derivative with an average molecular weight of 76,000 g/mol. Tuominen et al. used bis-oxazoline and HDI as chain extenders to extend the chain of lactic acid oligomers and obtained a product with a high molecular weight. Penco, et al. used bis(chloroformates) containing acyl chloride as a chain extender to extend the chain of a lactic acid-glycolic acid co-polymer and obtained a PLA multi-block polymer with a high molecular weight [10-13]. Bikiaris et al. used a synthetic diglycidyl ester compound containing an imide ring as a chain extender to extend the chain of polyesters [14]. Dean K M et al. used lauroyl peroxide as a source of alkyl radicals to react with the hydrogen atoms on the PLA backbone in a chain extension reaction [15]. They also characterized the efficacy of chain extension by measuring the dynamic rheological changes of the melt.

Li H et al. added an epoxy chain extender in a blend of polylactic acid/thermoplastic starch copolymer (PLA/TPS) and characterized the efficacy of modification by measuring the dynamic changes in blend

viscosity through oscillating shear rheology [16]. Najafi, et al. added an epoxy chain extender named Joncryl ADR 4368 into a PLA nanocomposite compound material and used a rheometer to determine the dynamic rheological properties of PLA [17]. They demonstrated that Joncryl 4368 had an adequate chain extension effect on PLA. Rathi et al. blended Joncryl 4368 and 2-(2-ethoxyethoxy ethyl) acrylate with PLA, and measured its molecular structure using a nuclear magnetic resonance spectrometer [18]. The results showed that the epoxy groups in the chain extender preferentially reacted with the carboxylic acid groups in PLA to improve the reaction between the PLA chain and the chain extender.

Baimark et al. added Joncryl 4368 to a PLLA/PDLA (50%/50%) melt blend, which significantly reduced its melt index (MI), but increased the melt strength of the chain extension product [19].

Plista et al. used a block copolymer of poly(1,4-butanediol adipate) and poly(1,4-butanediol adipate) as a chain extender for PLA. They characterized the reaction between epoxy groups and terminal carboxyl groups using a nuclear magnetic resonance spectrometer [20]. The results showed that the tensile strength of PLA was decreased slightly by the addition of the chain extender, but its elastic modulus was increased.

Epoxy chain extenders can react with carboxyl and hydroxyl groups, have a wide range of sources, and are relatively low-cost materials [21]. The chain extender KL-E4370 is an epoxy functionalized chain extender (Chinese Patent No. ZL 201210486946.4) synthesized using styrene monomers (50 to 75 parts) and acrylic acid ester monomers (25 to 50 parts) in conjunction with an initiator (2 to 12 parts). The structure of KL-E4370 contains a moderate number of epoxy functional groups. Its molecular weight is 6,500–7,000, whereas its epoxy equivalent is 270–300 g/mol.

In this paper, PLA and KL-E4370 were blended in a molten state to achieve chemical modification of PLA. The effect of chain extender KL-E4370 on PLA was characterized in detail using a combination of different approaches. The chemical structure, viscosity average molecular weight, thermal properties, melt viscosity, mechanical properties and Vicat softening temperature of PLA before and after the modification were measured by Fourier-transform infrared spectroscopy (FTIR), a viscometer (Mv), differential scanning calorimetry (DSC), a melt index instrument (MI), a rotary rheometer, a universal material testing machine, and a Vicat softening temperature tester, respectively.

Materials and methods

Materials

PLA (4032D, density 1.25 g/cm³, melt index 6.0 g/10 min) was purchased from NatureWorks Inc. Chain extender KL-E4370 (relative molecular weight 6,500–7,000, epoxy equivalent 270–300 g/mol) was purchased from Shanxi Chemical Additives Co., Ltd., China.

Sample preparation

The PLA was placed in a vacuum oven (DZF-6053, Shanghai Yiheng Scientific Instrument Co., Ltd.) and dried for 12 h at 60 °C. The dried PLA was blended with the chain extender in a molten state using an XSS-300 torque rheometer (E85-582, Shanghai Kechuang Rubber and Plastic Machinery Co., Ltd.). The experimental temperature was 190 °C. The rotor speed was 60 rpm. The blending process was

continued for 8 min. Mixtures were produced containing 0%, 0.1%, 0.3%, 0.5%, 0.7% and 1% chain extender KL-E4370 (hereafter referred to as PLA, PLA/KL-E4370 (0.1%), PLA/KL-E4370 (0.3%), PLA/KL-E4370 (0.5%), PLA/KL-E4370 (0.7%) and PLA/KL-E4370 (1%), respectively).

The PLA/KL-E4370 blend was pressed on a press vulcanizer (LP-S-50, LAB TECH Inc., Sweden) to obtain a plate. The specific parameters used for hot pressing are shown in Table 1.

Table 1: Hot pressing parameters

Processing temperature (°C)	Preheat time (min)	Exhaust time (s)	Pressing time (min)	Cooling time (min)	Plate thickness (mm)
190	6	3	4	12	4

Structural characterization and performance testing

Fourier Transform Infrared Spectroscopy (FTIR)

The samples were mixed with KBr powder and pressed into thin plates, which were measured in an infrared spectrometer (NicoletZ10, Thermo Scientific, USA). The plates were scanned within the range of 400–4,000 cm⁻¹.

Viscosity Average Molecular Weight (Mv)

PLA samples (0.1 g) were dissolved in a chloroform solution and placed into an Ubbelohde viscometer, which was subsequently incubated for 15 min in a water bath set at a constant temperature of 25 ± 0.1 °C (NWC- 4, Shanghai S.R.D Scientific Instruments Co., Ltd.) [22]. The samples were then measured to record the time required for the solution to pass through the capillary. The viscosity average molecular weight (Mv) of PLA was calculated by the Mark-Houwink formula (1):

$$[\eta] = KMv^a \dots \dots (1)$$

Where K and a are empirical constants related to the solvent, polymer and temperature (K = 1.13 × 10⁻⁴ and a = 0.78) [23].

Differential Scanning Calorimetry (DSC)

A portion (5–10 mg) of the sample was weighed and placed into a crucible. The measurement was carried out in a nitrogen atmosphere. First, the differential scanning calorimeter (Q100, TA, USA) was quickly heated to 200 °C and held for 5 min to eliminate the heat history of the instrument. It was quickly cooled down to 40 °C. In the second heating process, the temperature was increased to 200 °C at a rate of 20 °C/min. Calculation of the crystallinity of PLA was performed according to formula 2.

$$X_c(\%) = \left(\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times (1 - W_t\%)} \right) \times 100\% \dots \dots (2)$$

Where X_c is the relative crystallinity of PLA, ΔH_m is the melting enthalpy of PLA, and ΔH_{cc} is the enthalpy of PLA cold crystallization. The ΔH_m⁰ of PLA is 93.6 J/g. W_t% is the mass percentage of the added chain extender.

Melt Mass Flow Rate (MFR)

The rheological properties of the sample were measured using a melt mass flow rate meter (XNR-400, Jinjian Inspection Instrument Co., Ltd.). The diameter of the die was 1 mm, and the aspect ratio of the capillary was 10. The measurement was performed according to ISO 1133:1997 at a temperature of 190 °C and with a load of 2.16 kg.

Testing of Rheological Properties

The sample was placed on a rotary rheometer (MABS, Thermo Fisher) between parallel circular plates with a diameter of 20 mm. The test interval was 1 mm. The PLA melt was subjected to shear scanning at a temperature of 190 °C. The angular frequency scanning range (ω) was 0.1–100 rad/s. The plots of the composite viscosity and modulus of different PLA samples versus the angular frequency were recorded.

Mechanical properties

The pressed PLA plates were cut into 15×2 cm bars on a cutter (XXZ, Chengde Jinjian Inspection Instruments Co., Ltd.) and milled into dumbbell-shaped tensile samples. A computer controlled electronic universal material testing machine (CMT4304, Shenzhen Xinsansi Measurement Technology Co., Ltd.) was used to test the samples (ISO 527-1: 1993, IDT). Each group contained six samples, and the results were averaged.

The pressed PLA plates were cut into standard 8×1 cm bars on the cutter for the impact test. A modular and digital impact testing machine was used to test the samples (ISO 179-1: 2000, IDT). Each group contained six samples, and the results were averaged.

Vicat Softening Temperature (VST)

The samples were cut into $10 \times 10 \times 4$ mm specimens and tested (ISO 527-1: 1993, IDT). Each group contained two samples, and the results were averaged.

Results and discussion

FTIR analysis

Fig.1 shows an infrared spectrogram of neat PLA, chain extender KL-E4370 and PLA/KL-E4370 (0.1%).

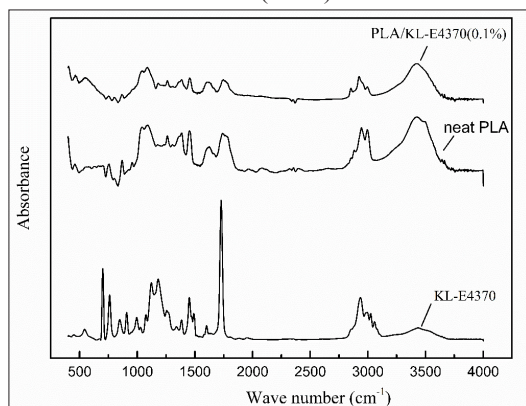


Figure 1: Infrared spectrogram of neat PLA, chain extender KL-E4370 and PLA/KL-E4370 (0.1%).

As shown in Fig.1, the characteristic peaks in the PLA infrared spectrogram mainly included the absorption peaks for the asymmetric and symmetric flexural vibrations of methyl C-H at $1,495 \text{ cm}^{-1}$ and $1,386 \text{ cm}^{-1}$, as well as the peaks for the stretching vibration corresponding to the O-H in -COOH from $3,100 \text{ cm}^{-1}$ to $3,478 \text{ cm}^{-1}$. In the infrared spectrogram of KL-E4370, the characteristic peaks mainly included the stretching vibration peaks corresponding to the C-O-C in the ester groups at $1,074 \text{ cm}^{-1}$, $1,112 \text{ cm}^{-1}$ and $1,178 \text{ cm}^{-1}$, as well as the characteristic peaks of the epoxy functional groups at 904 cm^{-1} and 846 cm^{-1} . These peaks corresponded to the structure of glycidyl methacrylate. The peak at $1,726 \text{ cm}^{-1}$ was the stretching vibration peak of the carbonyl group. The peaks at

758 cm^{-1} and 701 cm^{-1} corresponded to the out-of-plane flexural vibration of the C-H bond in the benzene ring. The peaks at $1,601 \text{ cm}^{-1}$, $1,493 \text{ cm}^{-1}$ and 452 cm^{-1} corresponded to the benzene skeletal vibration. These peaks corresponded with the structural unit of styrene in the chain extender. In the infrared spectrogram of PLA/KL-E4370 (0.1%), the absorption peaks for the asymmetric and symmetric flexural vibrations of methyl C-H at $1,495 \text{ cm}^{-1}$ and $1,386 \text{ cm}^{-1}$ were the characteristic peaks of PLA. There was a stretching vibration corresponding to the C-O-C in the ester groups at $1,074 \text{ cm}^{-1}$, $1,112 \text{ cm}^{-1}$ and $1,178 \text{ cm}^{-1}$. The peaks at 758 cm^{-1} and 701 cm^{-1} corresponded to the out-of-plane flexural vibration of the C-H bond in the benzene ring. The peaks at $1,601 \text{ cm}^{-1}$, $1,493 \text{ cm}^{-1}$ and 452 cm^{-1} corresponded to the benzene skeletal vibration. These were the characteristic peaks of KL-E4370. However, the peaks for the stretching vibration corresponding to the O-H in -COOH from $3,100 \text{ cm}^{-1}$ to $3,478 \text{ cm}^{-1}$, as well as those of the epoxy functional groups at 904 cm^{-1} and 846 cm^{-1} , were very weak in intensity because of the reaction between the terminal carboxyl groups of PLA and the epoxy groups of KL-E4370.

Based on the above analysis, the chain extension reaction between PLA and KL-E4370 is illustrated in Fig.2.

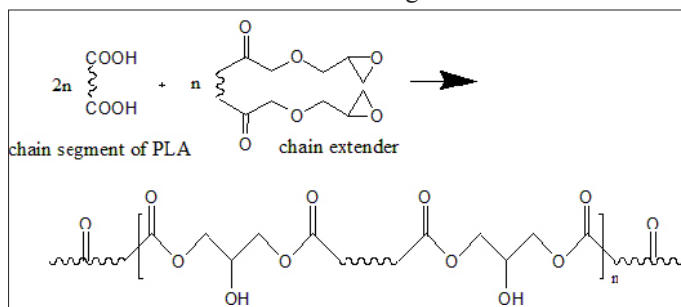


Figure 2: Illustration of the chain extension reaction between PLA and KL-E4370

As shown in Fig.2, the terminal carboxyl groups of PLA and the epoxy groups of KL-E4370 underwent a ring-opening and polymerization reaction when blended in a molten state, thus resulting in chain extension.

Viscosity average molecular weight analysis

Fig.3 is a plot showing the relationship between the added amount of chain extender KL-E4370 and the viscosity average molecular weight of PLA.

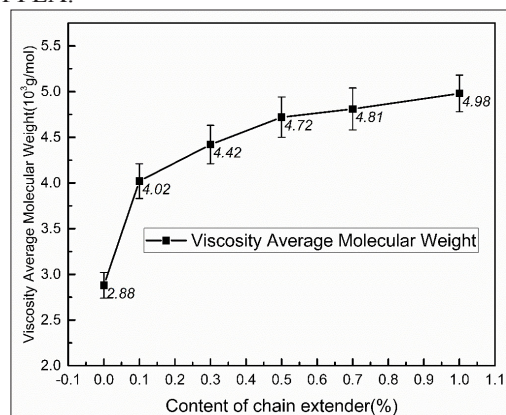


Figure 3: The viscosity average molecular weight of PLA with different amounts of chain extender KL-E4370.

As shown in Fig.3, the viscosity average molecular weight of neat PLA was 2.88×10^3 g/mol, whereas the viscosity average molecular weights of PLA/KL-E4370 (0.1%), PLA/KL-E4370 (0.3%), PLA/KL-E4370 (0.5%), PLA/KL-E4370 (0.7%) and PLA/KL-E4370 (1%) were 4.02×10^3 g/mol, 4.42×10^3 g/mol, 4.72×10^3 g/mol, 4.81×10^3 g/mol and 4.98×10^3 g/mol, respectively. The viscosity average molecular weight of PLA increased as the amount of chain extender was increased. The magnitude of increase in the viscosity average molecular weight was more apparent when a relatively small amount of the chain extender was added, and the viscosity average molecular weight plateaued when greater amounts of the chain extender were added. The reason for the increase in the viscosity average molecular weight of PLA was the reaction between the terminal hydroxyl or carboxyl groups of PLA and the epoxy groups of KL-E4370, which resulted in chain extension and an increase in relative molecular weight, which in turn increased the viscosity average molecular weight of PLA. When the amount of chain extender was relatively small, more activity points were available to initiate a faster chain extension reaction. As the reaction progressed, the number of activity points decreased, which reduced the capacity for the PLA chain extension reaction to occur, and thus the molecular weight of PLA plateaued.

DSC analysis

Fig.4 shows the DSC curves of PLA extended using different amounts of KL-E4370. Table 2 shows the results of DSC analysis of PLA extended using different amounts of KL-E4370.

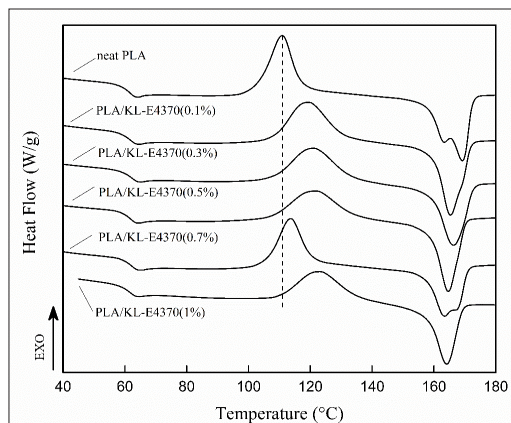


Figure 4: DSC curves of PLA extended using different amounts of KL-E4370.

Table 2. DSC results of PLA extended using different amounts of KL-E4370.

KL-E4370 (%)	T_g (°C)	T_m (°C)	T_{cc} (°C)	X_c (%)
0	61.85	157.20	102.83	17.0
0.1	61.43	158.52	108.13	32.5
0.3	62.44	159.67	108.81	18.0
0.5	62.34	157.44	107.71	24.7
0.7	62.62	154.08	105.34	6.5
1	62.89	157.82	119.68	13.2

The DSC curves corresponding to different PLA samples show that the cold crystallization peaks always appeared during the second heating process (Fig.4). This timing was due to the fact that the molecular backbone of the semi-crystalline polymer PLA is a hard

segment associated with a slower crystallization rate [24]. Therefore, a cold crystallization peak was seen during the second heating. The crystal discontinuity in the crystallization of PLA led to discontinuity in the growth rate of the PLA crystals, thus triggering the formation of double melting peaks in the molten state and reflecting the degree of crystal refinement of PLA during the crystallization process [25-30]. The temperature of cold crystallization tended to increase as the amount of chain extender KL-E4370 was increased.

As shown in Table 2, the crystallinity of neat PLA was 17.0%, whereas the crystallinity of PLA/KL-E4370 (0.1%), PLA/KL-E4370 (0.3%), PLA/KL-E4370 (0.5%), PLA/KL-E4370 (0.7%) and PLA/KL-E4370 (1%) was 32.5%, 18.0%, 24.7%, 6.5% and 13.2%, respectively. The crystallinity of PLA/KL-E4370 increased first and then decreased. When the amount of the chain extender was 0.1%, its crystallinity was highest and was 1.9 times that of neat PLA. When the amount of KL-E4370 was relatively low, the addition of the chain extender increased the length of the molecular chain and the ability of the PLA chain to enter the lattice, thus increasing the crystallinity of the sample. As the amount of added KL-E4370 gradually increased, the number of chain terminals in a unit mass of PLA was greatly reduced. During the process of crystal nucleation growth, it was difficult for the chain terminals to fold and enter the crystals to form nuclei, thus hindering the growth of the crystals. As a result, both the crystallization rate and crystallinity percentage were decreased [31-32].

MFR analysis

Table 3 shows the melt indices of neat PLA and PLA extended using different amounts of KL-E4370.

KL-E4370 (%)	0	0.1	0.3	0.5	0.7	1
MFR ($g \cdot (10 \text{ min})^{-1}$)	6	2.24	1.38	0.50	0.14	0.11

As shown in Table 3, the MFR of PLA decreased as the amount of chain extender increased. The MFR of neat PLA was $6 g \cdot (10 \text{ min})^{-1}$, while the MFR of PLA/KL-E4370 (0.1%), PLA/KL-E4370 (0.3%), PLA/KL-E4370 (0.5%), PLA/KL-E4370 (0.7%) and PLA/KL-E4370 (1%) were $2.24 g \cdot (10 \text{ min})^{-1}$, $1.38 g \cdot (10 \text{ min})^{-1}$, $0.50 g \cdot (10 \text{ min})^{-1}$, $0.14 g \cdot (10 \text{ min})^{-1}$ and $0.11 g \cdot (10 \text{ min})^{-1}$, respectively. The MFR decreased as the amount of chain extender increased because KL-E4370 contained multiple epoxy groups that opened their rings and underwent polymerization to form a micro-crosslinked structure during processing. When the molecular chains of PLA changed from short chains to long chains, their molecular weight and degree of branching increased; the molecular chains began to entangle with each other vigorously, and the movement of the molecular chains became difficult, thus reducing the MFR of PLA [33].

Rotational Rheology Test

Effect of chain extension on the complex viscosity of PLA

Fig.5 shows the changes in PLA complex viscosity (η) versus angular frequency after PLA was extended using different amounts of KL-E4370.

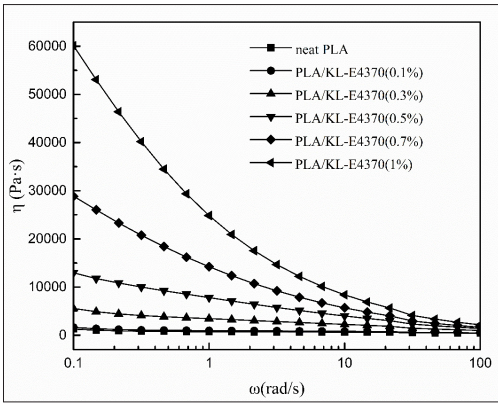


Figure 5: Changes in PLA complex viscosity (η) versus angular frequency after PLA was extended using different amounts of KL-E4370.

As shown in Fig.5, the extended PLA showed shear thinning typical of a pseudoplastic fluid.

In the low frequency region, the complex viscosity (η) increased as the amount of KL-E4370 increased. Because KL-E4370 initiated the chain extension reaction of PLA, the relative molecular weight of PLA increased, and intermolecular interaction was enhanced. The samples underwent physical entanglement during dynamic scanning and required a long relaxation time, thus increasing the value of η . At the same time, η decreased as the frequency was increased, because the chain extension process increased the molecular weight of PLA, so that molecular chains with fixed orientations could not relax easily, thus reducing flow resistance and decreasing viscosity.

In the high frequency region, the stretching and unwrapping of molecular chains gradually reached a steady state, so that the η of the samples barely changed as the angular frequency was increased.

Effect of chain extension on PLA modulus

Fig.6 shows the change in the storage modulus (G') of PLA versus shear frequency after chain extension. Fig.7 shows the change in the loss modulus (G'') versus shear frequency.

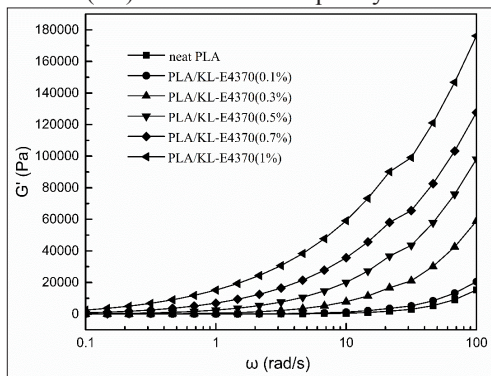


Figure 6: Change in the storage modulus (G') of PLA versus shear frequency after the chain extension.

As shown in Fig.6, the storage modulus (G') of PLA increased as the amount of KL-E4370 increased. An increased G' value indicates improved melt elasticity and enhanced melt strength. In comparison with neat PLA, the increase in the G' value of the extended PLA was faster at a higher frequency after the content of chain extender

was increased above 0.3%, because the increase in branch chain content became more apparent when the chain extender content was greater, while the storage modulus increased faster, thus significantly improving the melt strength of PLA.

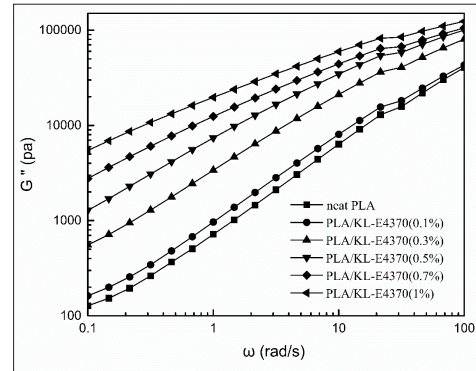


Figure 7: Plots showing the loss modulus of PLA/KL-E4370.

As shown in Fig.7, the G'' of PLA increased after the addition of chain extender KL-E4370, indicating that the melt viscosity of PLA increased because of the PLA chain extension reaction initiated by KL-E4370. The value of G'' increased gradually as the amount of KL-E4370 increased. The slope of the G'' curve was highest for neat PLA, followed by that of the samples containing 0.1%, 0.3%, 0.5%, 0.7% and 1% KL-E4370, respectively. The slope obtained after the chain extension was higher than that before the chain extension, indicating that it was difficult for the molecular chain structure of PLA to relax after the chain extension, so the chains tended to get intertwined, thus forming a more stable structure.

Mechanical properties

Influence of the amount of chain extender on tensile strength

Fig.8 shows the change in the tensile strength of PLA as the amount of KL-E4370 added to it was changed.

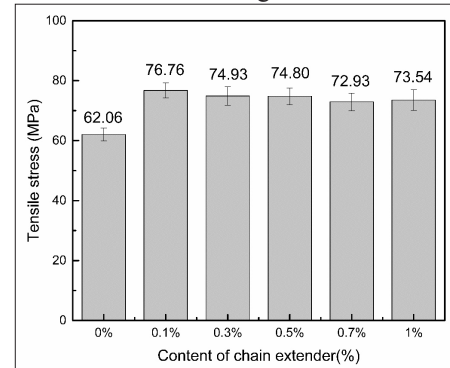


Figure 8: Change in the tensile strength of PLA versus the amount of KL-E4370 added as a chain extender

As shown in Fig.8, the tensile strength of neat PLA was 62 MPa, whereas the tensile strength of PLA/KL-E4370 (0.1%), PLA/KL-E4370 (0.3%), PLA/KL-E4370 (0.5%), PLA/KL-E4370 (0.7%) and PLA/KL-E4370 (1%) was 76.7 MPa, 74.9 MPa, 74.8 MPa, 72.9 MPa and 73.5 MPa, respectively. It can be seen that the addition of chain extender KL-E4370 greatly improved the tensile strength of PLA. When the amount of KL-E4370 was 0.1%, the tensile strength of PLA was highest (1.24 times that of neat PLA). When the amount of KL-E4370 was less than 0.1%, KL-E4370 reacted with PLA to increase the molecular weight of PLA. At the same time, the

regularity of the molecular alignment was increased, accompanied by increased crystallinity and intermolecular interaction, thus increasing the tensile strength of PLA. However, when the amount of KL-E4370 was greater than 0.3%, the tensile strength of PLA decreased slightly as the amount of KL-E4370 was increased, because the degree of branching in the molecular chains of PLA increased after KL-E4370 had reacted completely with PLA, while the distance between molecules also increased, which in turn decreased the crystallinity and intermolecular force of PLA, thus decreasing its tensile strength.

Influence of the amount of chain extender KL-E4370 on the impact strength of PLA

Fig.9 shows the influence of the amount of KL-E4370 used as a chain extender on the impact strength of PLA.

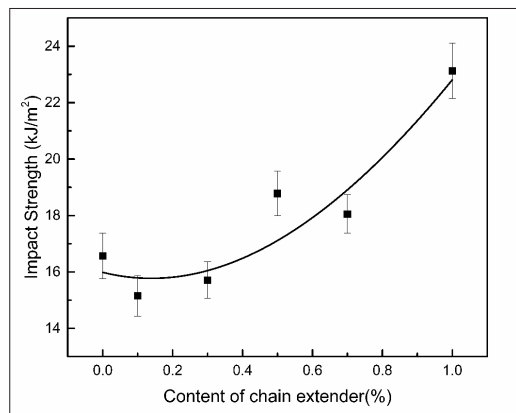


Figure 9: Influence of the amount of KL-E4370 used as a chain extender on the impact strength of PLA.

As shown in Fig.9, the impact strength of neat PLA was 16.58 KJ/m², whereas the impact strength of PLA/KL-E4370 (0.1%), PLA/KL-E4370 (0.3%), PLA/KL-E4370 (0.5%), PLA/KL-E4370 (0.7%) and PLA/KL-E4370 (1%) was 15.15 KJ/m², 15.71 KJ/m², 18.78 KJ/m², 18.05 KJ/m² and 23.12 KJ/m², respectively. As the amount of KL-E4370 increased, the impact strength of PLA decreased first and then increased. When the amount of KL-E4370 was 0.1% and 0.3%, the impact strength of PLA was slightly lower than that of neat PLA, because the crystallinity of PLA significantly increased after it underwent chain extension and its molecules became more tightly packed, thus reducing its porosity. When the material was under impact, there was not much room for its molecular chains to move, and the impact strength decreased. The impact strength of PLA was significantly higher than that of pure PLA when the amount of KL-E4370 was greater than 0.5%, and the impact strength of PLA gradually increased as the amount of KL-E4370 was increased beyond this point, indicating that the reaction between the chain extender and PLA was more complete, and the molecular weight of the molecular chains of PLA also increased. The degree of branching was increased, and the PLA chains changed from short chains to long chains, thus increasing the entanglement between different molecular chains of PLA. Therefore, when PLA was hit by an external force, the molecular chains absorbed energy through deformation, thus significantly increasing the impact strength of PLA after chain extension.

Vicat softening temperature

Table 4 shows the Vicat softening temperature of PLA with different amounts of KL-E4370 used as a chain extender.

Table 4: The Vicat softening temperatures of PLA/KL-E4370 blends containing different amounts of KL-E4370

KL-E4370 (%)	Vicat softening temperature (°C)
0.0	67.9
0.1	160.1
0.3	159.0
0.5	158.2
0.7	158.0
1	156.1

As shown in Table 4, the Vicat softening temperature of neat PLA was 67.9 °C, whereas the Vicat softening temperatures of PLA/KL-E4370 (0.1%), PLA/KL-E4370 (0.3%), PLA/KL-E4370 (0.5%), PLA/E4370 (0.7%) and PLA/KL-E4370 (1%) were 160.1 °C, 159.0 °C, 158.2 °C, 158.0 °C and 156.1 °C, respectively. As the Vicat softening temperature increases, the dimensional stability of the material when heated improves, and the resistance of the material against thermal deformation is enhanced. These results indicate that the Vicat softening temperature of PLA was greatly increased after it underwent chain extension and modification. When the amount of KL-E4370 was 0.1%, the Vicat softening temperature reached its maximum value, because the molecular chains of PLA changed from short chains to long chains after KL-E4370 reacted with PLA, while the relative molecular weight of the chains increased, which in turn led to increased crystallinity and hindrance against movement among molecular chains. As a result, the migration energy of the molecular chains was decreased, and the Vicat softening temperature was significantly increased. Afterwards, when the amount of KL-E4370 further increased, the reaction between KL-E4370 and PLA became more complete, and the degree of branching in the molecular chains of PLA increased, which in turn led to increased distance among molecules and decreased crystallinity, thus decreasing the Vicat softening temperature.

Conclusion

1. From FTIR and viscosity average molecular weight measurements, it can be seen that the epoxy groups of KL-E4370 underwent a chain extension reaction with the carboxyl groups of PLA, thus increasing the relative molecular weight of PLA.
2. When the amount of KL-E4370 was 0.1%, the crystallinity of PLA increased from 17.0% to 32.5%, and the Vicat softening temperature increased from 67.9 °C to 160.1 °C, thus improving the heat resistance performance of PLA.
3. Rotational rheological tests showed that PLA exhibited the typical characteristics of a pseudoplastic fluid after chain extension, with shear thinning in the range of the shear rate. In addition, the complex viscosity, storage modulus and loss modulus of PLA after chain extension increased as the amount of the chain extender was increased. The melt viscosity of PLA increased after chain extension, whereas its melt index decreased as the amount of the chain extender was increased. The melt index of PLA decreased from 6 g/10 min (that of neat PLA) to 0.11 g/10 min when 1% KL-E4370 was added.
4. The impact strength of PLA increased as the amount of the chain extender was increased (from 16.57 KJ/m² for neat PLA to 23.12 KJ/m² for PLA with 1% KL-E4370). With the addition of KL-E4370, the tensile strength of PLA increased from 62.0 MPa (that of neat PLA) to 76.7 MPa (PLA with 0.1% chain KL-E4370).

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