

Study on the chain extension modification and properties of polyglycolic acid

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Abstract: To enhance the molecular weight and thermal stability of polyglycolic acid (PGA), low molecular weight PGA was modified through melt chain extension using epoxy chain extenders YMX-21 and YMX-48. Infrared spectroscopy analysis revealed the disappearance of characteristic epoxy peaks at 757 cm^{-1} and 910 cm^{-1} , confirming that the epoxy groups of the chain extenders underwent ring-opening reactions with the terminal hydroxyl/carboxyl groups of PGA, achieving chain extension. Thermogravimetric analysis and differential scanning calorimetry characterization indicated that despite thermal degradation during processing, the chain extenders significantly improved the thermal stability of PGA, and this stability increased with the addition level; both chain extenders enhanced the intrinsic viscosity, with YMX-48 demonstrating superior chain extension efficiency. When the addition level of the chain extender was $\leq 0.8\%$ (mass fraction), the intrinsic viscosity decreased due to thermal degradation; however, when the addition level exceeded 0.8% (mass fraction), both systems exhibited a stable viscosity increase effect.

Key words: polyglycolic acid; chain extension modification; epoxy chain extender; thermal stability; intrinsic viscosity

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PGA, as a kind of linear aliphatic polyester with complete biodegradability, is rich in ester groups in its molecular structure and can be thoroughly decomposed by microorganisms under natural environmental conditions. It is an ideal eco-friendly material for replacing disposable plastic products. PGA also exhibits excellent biocompatibility, good mechanical properties, and superior barrier properties. Its oxygen and water vapor transmission rates are significantly lower than those of commonly used materials such as polylactic acid, polypropylene, and polyethylene terephthalate, by several orders of magnitude. Therefore, it has significant application potential in agricultural mulching films and high-barrier food packaging fields.

However, the inherent degradability, narrow melting processing window, and brittle texture of PGA severely restrict its wide range of applications. High molecular weight PGA

can effectively enhance the thermal stability of materials, significantly improve mechanical properties, enhance processing performance, and provide more controllable degradation kinetics, thereby greatly expanding its application value in high-performance demanding scenarios, such as high-strength medical devices, engineering plastic substitutes, and durable degradable industrial components. Therefore, high molecular weight is a key path to enhance the comprehensive performance of PGA and achieve its high-performance applications.

Traditionally, high molecular weight PGA is primarily prepared through the ring-opening polymerization of glycolide monomers. However, this process faces challenges such as

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cumbersome workflow, difficulty in synthesizing glycolide monomers, and high cost. In contrast, China possesses abundant resources of glycolic acid monomers, which are more affordable, making the low-cost route using glycolic acid as the raw material more attractive. Therefore, exploring subsequent upgrading strategies based on low molecular weight PGA prepolymers has become a research hotspot. Among them, solid-state polycondensation and chain extension modification are the main technical paths to enhance its molecular weight. However, solid-state polycondensation generally suffers from the disadvantages of long reaction periods and high energy consumption, which are not conducive to efficient industrial production. In contrast, the chain extension modification process, with its advantages of high reaction efficiency and relatively simple operation, has become a more promising direction for preparing high molecular weight PGA.

This study focuses on the reactive modification of low molecular weight PGA using domestically produced epoxy chain extenders YMX-21 and YMX-48. The reactive extrusion process is achieved using a twin-screw extruder, and the emphasis is placed on investigating the influence of different types of chain extenders and their dosages on the key performance indicators of the modified PGA products, particularly the intrinsic viscosity (an indirect indicator of molecular weight) and thermal properties (such as thermal stability, crystallization and melting behavior). This provides theoretical basis and experimental support for optimizing the chain extension preparation process of high molecular weight PGA.

1 Experimental part

1.1 Experimental materials

Polyglycolic acid: Shanghai Pujing Chemical New Material Co., Ltd., with an average molecular weight of 50,000; Epoxy chain extender YMX-21: analytical grade, Suzhou Yumanxiang Plastification Co., Ltd.; Epoxy chain extender YMX-48: analytical grade, Suzhou Yumanxiang Plastification Co., Ltd.; Dimethyl sulfoxide: analytical grade, Chengdu Kelong Chemicals Co., Ltd.

1.2 Experimental equipment and instruments

Electrothermal blast drying oven, BPG-9070A, Shanghai Yiheng Scientific Instrument Co., Ltd.; torque rheometer,

RM200C, Harbin Hapu Electrical Technology Co., Ltd.; movable parallel twin-screw extrusion platform, SJSP-20×25, Harbin Hapu Electrical Technology Co., Ltd.; high-speed mixer, SHR-10, Jiangsu White Bear Co., Ltd.; Fourier transform infrared spectrometer: IS10, USA; differential scanning calorimeter (DSC): Q-20, USA (TA Instruments); thermogravimetric analyzer (TGA): Q-50, USA (TA Instruments); electronic balance counter, LQ-6, Rui'an Ant Weighing Equipment Co., Ltd.

1.3 Sample preparation

First, the PGA raw material was placed in a forced-air drying oven and dried at 60 °C for 20 hours to fully remove moisture. Subsequently, the dried PGA was mixed with a chain extender (YMX-21 or YMX-48) at a preset ratio (based on 100 parts of PGA, the addition amounts of chain extender were 0.4, 0.6, 0.8, 1.0, and 1.2 parts, respectively) in a low-speed mixer for 60 minutes to ensure uniform dispersion. Then, the premix was reacted and extruded through a parallel co-rotating twin-screw extruder, with the process parameters set as follows: screw speed of 8 r/min, and temperatures from the feeding section to the die in the order of 40 °C, 100 °C, 160 °C, 225 °C, 200 °C, 200 °C, and 195 °C. High-purity nitrogen was continuously introduced into the feed port to create an inert atmosphere and inhibit thermal oxidative degradation. Finally, the extrudate was air-cooled and solidified, crushed, and the resulting modified PGA was stored in a vacuum dryer in a sealed manner to avoid the influence of environmental moisture.

1.4 Analysis and Testing

(1) Infrared spectroscopy (FTIR)

Using a Fourier transform infrared spectrometer, the chemical structure of the sample was determined by the potassium bromide pellet method. The spectral acquisition conditions were set as follows: resolution of 4 cm⁻¹, 32 cumulative scans, and a wavenumber scanning range covering from 4,000 to 350 cm⁻¹, aiming to identify characteristic functional groups and changes in chemical bonds.

(2) Differential scanning calorimetry (DSC)

The melting behavior and crystallization characteristics of the blend were characterized using a differential scanning calorimeter (TA Instruments, DSC Q20, USA). Accurate samples (3~5 mg) were weighed and placed in a standard

aluminum crucible. The testing procedure was as follows: first, heat the sample from 30 °C to 250 °C at a rate of 10 °C/min to eliminate thermal history; then, cool it down to 30 °C at a rate of 10 °C/min, recording the cooling curve once; finally, heat it up again to 250 °C at a rate of 10 °C/min, obtaining the second heating curve.

(3) Thermogravimetric analysis (TGA)

The thermal stability changes of PGA samples were evaluated using a thermogravimetric analyzer (TA Instruments, TGA Q50, USA). Accurate samples (3~5 mg) were weighed and heated from room temperature (approximately 30 °C) to 500 °C at a constant rate of 10 °C/min under a nitrogen atmosphere (flow rate of 60 mL/min). The changes in sample mass with temperature were continuously monitored and recorded, and the thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained.

(4) Intrinsic viscosity measurement

Using dimethyl sulfoxide (DMSO) as the solvent, the intrinsic viscosity ($[\eta]$) of PGA was determined by the Ubbelohde viscometer method. The specific operational procedure is as follows: Add 20 mL of DMSO to a three-neck flask and heat it to 160 °C in an oil bath. Add 0.1 g of PGA sample and stir magnetically until it is completely dissolved. Transfer the fully dissolved PGA/DMSO solution at 160 °C to a preheated Ubbelohde viscometer maintained at the same temperature (Note: The Ubbelohde viscometer is vertically fixed inside a 1000 mL graduated cylinder filled with dimethyl silicone oil, and the graduated cylinder is placed in a 160 °C oil bath to maintain constant temperature). Conduct viscosity measurements at 160 °C, with each sample being tested in triplicate, and calculate the intrinsic viscosity by taking the average value.

2 Results and discussion

2.1 Infrared spectroscopy

As shown in Figure 1, it is a comparison of the infrared spectra of unmodified PGA, epoxy-based chain extenders (YMX-21/YMX-48), and chain-extended modified PGA materials. Spectrum analysis indicates that there are no significant differences in the overall spectra of PGA samples modified with different chain extenders. The characteristic absorption peaks of the chain extenders (at 757 cm⁻¹ and

910 cm⁻¹, attributed to the characteristic absorption peaks of epoxy groups) completely disappear in the spectra of modified PGA. This phenomenon confirms the occurrence of ring-opening reactions between epoxy groups and the ends of PGA molecular chains during the chain extension process, successfully achieving molecular chain extension of PGA. This is direct spectroscopic evidence of the occurrence of the chain extension reaction.

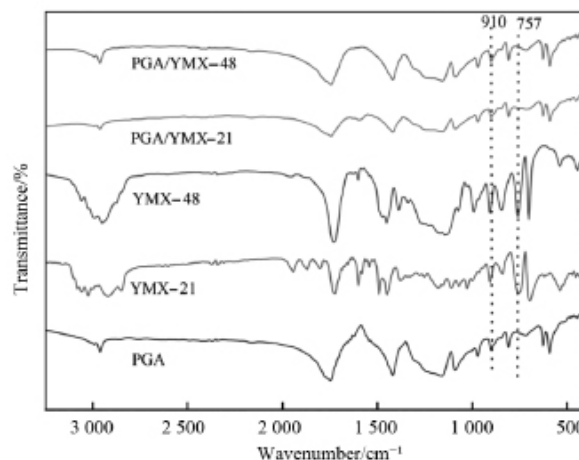


Figure 1 Infrared spectrum of PGA modified by chain extender

2.2 Differential scanning calorimetry analysis

Figure 2 illustrates the DSC cooling and secondary heating curves of modified PGA with varying amounts of YMX-21 added. Test data reveals that the crystallization temperature of unmodified PGA is 157.2 °C, and its melting point is 220.3 °C. Following chain extension modification, the melting points of all samples remain stably within the range of 219.2~220.5 °C, showing no significant change compared to the original PGA, indicating that the introduction of YMX-21 has minimal impact on the melting behavior of PGA. Notably, the crystallization temperature of the modified PGA exhibits an increase. When the amount of YMX-21 added reaches 1.2% (mass fraction), the crystallization temperature significantly rises to 159.7 °C. This phenomenon is attributed to the branched molecular chain structure induced by the chain extension reaction, where the branching points serve as heterogeneous nucleation sites, effectively facilitating the crystallization process and thereby elevating the crystallization temperature.

Figure 3 illustrates the DSC cooling and secondary heating curves of modified PGA with varying amounts of YMX-48

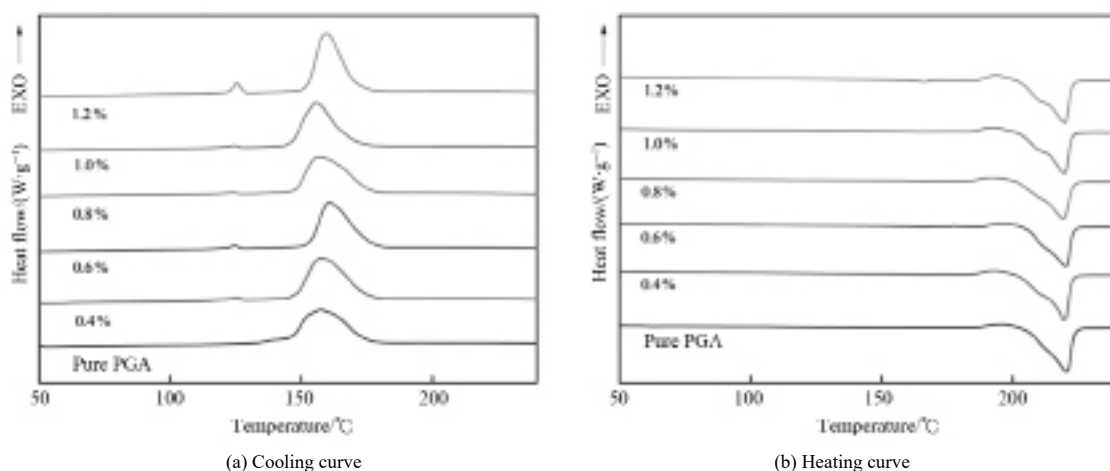


Figure 2 DSC curves of PGA modified with different amounts of YMX-21

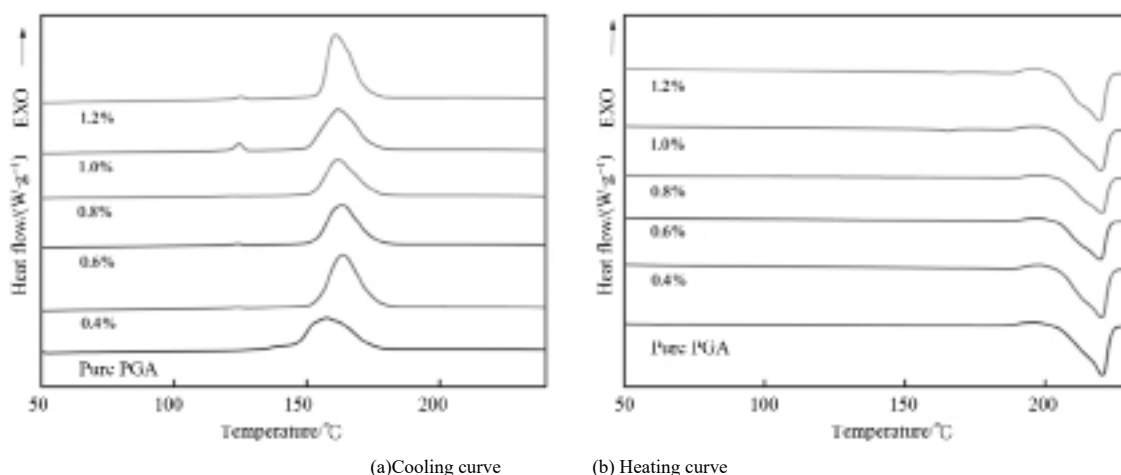


Figure 3 DSC curves of PGA modified with different amounts of YMX-48

added. Similar to the YMX-21 system, the melting points of all modified samples were maintained within the range of 219.5~220.8 °C (unmodified PGA: 220.3 °C), confirming that the introduction of YMX-48 also had a limited impact on the melting behavior of PGA. However, its crystallization behavior exhibited significant differentiation patterns: although the crystallization temperature of modified PGA was generally higher than that of the original sample (157.2 °C), it showed a systematic decreasing trend with increasing YMX-48 content (e.g., the crystallization temperature of the 1.2% (mass fraction) sample was 158.1 °C). This phenomenon is attributed to the dual effects of the branched structure. Firstly, the branching points serve as heterogeneous nucleation sites, initially elevating the crystallization temperature of PGA. However, as the amount of YMX-48 increases, excessive branching points induce a significant steric hindrance effect,

greatly limiting the flexibility of the molecular chains and resulting in a decrease in segmental mobility. When the branching density exceeds a critical value, the latter becomes dominant, hindering the diffusion ability of molecular chains towards the crystal nucleus surface, and the crystal growth rate sharply decreases. Even with nucleation sites present, it is difficult for the segments to achieve rapid and orderly lattice packing.

2.3 Thermogravimetric analysis

Figure 4 displays the thermogravimetric analysis (TGA) curves and their differential thermogravimetric (DTG) curves of polyglycolic acid (PGA) samples modified with different chain extenders. Table 1 details the corresponding initial thermal decomposition temperature and the fastest thermal decomposition temperature data. Unmodified PGA begins to exhibit significant mass loss at 229.99 °C, and its thermal

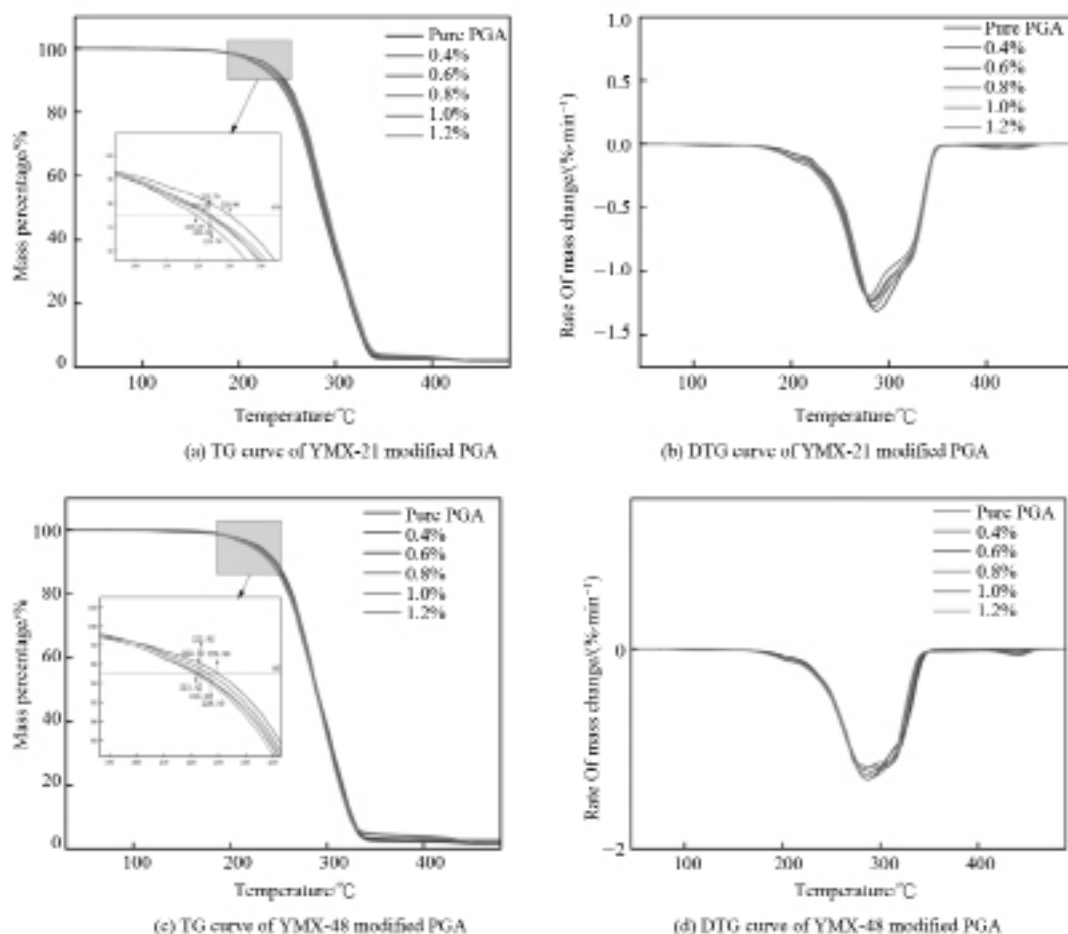


Figure 4 TGA curve and DTG curve of modified PGA

Table 1 Thermal decomposition temperature of modified PGA

Content	Initial thermal decomposition temperature / °C	Fastest thermal decomposition temperature / °C
Pure PGA	229.99	289.84
0.4% (mass fraction) YMX-21	219.20	278.22
0.6% (mass fraction) YMX-21	223.56	280.39
0.8% (mass fraction) YMX-21	223.76	282.57
1.0% (mass fraction) YMX-21	222.33	285.41
1.2% (mass fraction) YMX-21	223.70	282.58
0.4% (mass fraction) YMX-48	222.53	285.98
0.6% (mass fraction) YMX-48	226.10	284.63
0.8% (mass fraction) YMX-48	221.47	293.01
1.0% (mass fraction) YMX-48	222.92	285.52
1.2% (mass fraction) YMX-48	223.54	295.99

decomposition rate reaches a maximum at 289.84 °C. The initial thermal decomposition temperature of modified PGA is generally lower than that of the unmodified sample. When 0.4% (mass fraction) of chain extender YMX-21 is added, the initial decomposition temperature decreases the most, reaching 10.79 °C. As the amount of chain extender increases, the initial decomposition temperature slightly rises compared to samples with lower amounts, but it is still significantly lower

than that of unmodified PGA. In contrast, the fastest thermal decomposition temperature exhibits different patterns: although samples with low amounts of chain extender have lower temperatures than unmodified PGA, as the amount of chain extender increases, the modified PGA shows a phenomenon where its temperature is higher than the original material. Especially when 1.2% (mass fraction) of YMX-48 is added, its fastest thermal decomposition temperature significantly

increases to 295.99 °C, which is 6.15 °C higher than that of unmodified PGA.

The aforementioned phenomenon can be explained from the molecular structure level. Under the high-temperature and high-shear conditions of twin-screw extrusion processing, PGA's molecular chains are prone to breakage, resulting in low molecular weight segments with poor thermal stability. Although the chain extender effectively increases the molecular weight of some molecular chains by reacting with the end groups of PGA, the small molecular fragments generated during processing may not fully participate in the chain extension reaction. This residual low molecular weight component has poor thermal stability, which is a key factor leading to a generally earlier initial decomposition temperature of modified PGA. The fastest thermal decomposition temperature mainly characterizes the ease of breaking the chemical bonds in the polymer backbone. Under high chain extender addition conditions, the efficiency of the chain extension reaction increases, and more long-chain polymers are formed within the system. These long molecular chains have higher molecular weights, and their backbone breakage requires more energy absorption, which macroscopically manifests as a significant increase in the fastest thermal decomposition temperature. Therefore, chain extension modification can not only reduce the initial decomposition temperature but also enhance the thermal stability of the material's backbone by effectively increasing the molecular weight.

2.4 Intrinsic viscosity analysis

The intrinsic viscosity is an important parameter for measuring the viscous behavior of polymer solutions. It reflects the extension volume of the molecular chain in the solution and is directly related to the length of the polymer chain. It can be obtained as shown in equations (1) to (3):

$$[\eta] = \frac{\sqrt{2 \cdot (\eta_{sp} - L \eta_r)}}{C} \quad (1)$$

$$\eta_r = \frac{t}{t_0} \quad (2)$$

$$\eta_{sp} = \eta_r - 1 \quad (3)$$

Where t_0 represents the time taken for pure dimethyl sulfoxide (DMSO) solvent to flow through the Ubbelohde viscometer, t denotes the time taken for the DMSO solution of PGA to flow through, η_r stands for the relative viscosity of the polymer solution, η_{sp} signifies the specific viscosity of the

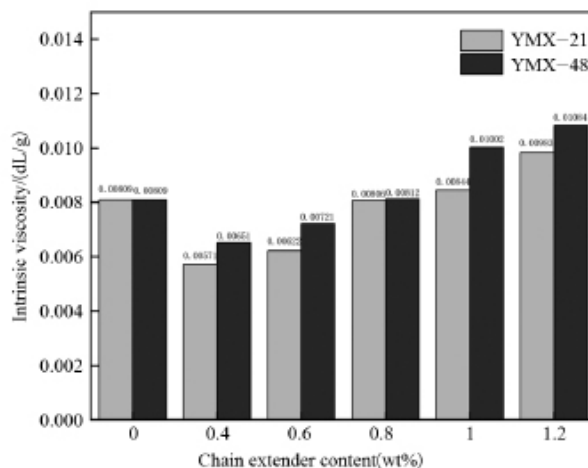


Figure 5 Effect of chain extender type and addition amount on the intrinsic viscosity of PGA

polymer solution, $[\eta]$ indicates the intrinsic viscosity of the polymer, and C is the concentration of the polymer solution. The results are presented in Figure 5.

As shown in Figure 5, with the increase in the addition amount of chain extender, the intrinsic viscosity of polyglycolic acid (PGA) generally shows an upward trend, indicating that both have the ability to increase viscosity and extend the chain. When the content of chain extender is $\leq 0.8\%$ (mass fraction), the intrinsic viscosity values of modified PGA are all lower than those of unmodified pure PGA. This phenomenon is mainly attributed to the poor thermal stability of PGA during processing, which leads to thermal degradation at high temperatures, resulting in a decrease in molecular weight, macroscopically manifested as a reduction in intrinsic viscosity. However, when the addition amount of chain extender is increased to above 0.8% (mass fraction), both chain extenders exhibit significant viscosity-increasing effects. Especially at addition ratios of 1.0% (mass fraction) and 1.2% (mass fraction), the reaction efficiency between the chain extender and PGA end groups is significantly improved, effectively extending the molecular chain, and the increase in intrinsic viscosity is most pronounced. The experimental data clearly indicates that the chain extender needs to reach a critical addition amount ($>0.8\%$ (mass fraction)) to overcome the negative impact of processing thermal degradation and achieve effective improvement in PGA molecular weight.

3 Conclusion

In this study, reactive modification of polyglycolic acid (PGA) was achieved through twin-screw extrusion technology, utilizing epoxy-based chain extenders YMX-21 and YMX-48. The thermal properties and molecular weight evolution of the chain-extended products were systematically characterized, and their reaction mechanisms were verified. The results indicated that the chain extenders bonded with the carboxyl groups at the ends of the PGA molecular chains through epoxy ring-opening

reactions, effectively increasing the molecular weight of the polymer. This chemical modification simultaneously enhanced the thermal stability of the main chain and significantly regulated the crystallization behavior of the material. When the addition level of YMX-48 was 1.2% (mass fraction), the modified system exhibited optimal comprehensive performance - the molecular weight reached a peak, and the thermal stability was most significantly improved.

