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Influence of monomer purity on molecular weight of racemic polylactic acid

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Abstract. Aiming at the low molecular weight of polylactic acid due to the presence of water molecules in the ring-opening polymerization of racemic lactide, this paper selected racemic lactide as the main raw material, stannous caprylate as the catalyst, and cetyl alcohol as the initiator, and studied the effects of recrystallization process conditions such as the number of recrystallization and drying time on the purity of monomer. The influence of initiator dosage on the properties of racemic polylactic acid was also studied. The purity, water content and free acid content of racemic lactide were determined by infrared spectrometer, differential scanning calorimeter, Gel Permeation Chromatography and tensile testing machine. The molecular weight and mechanical properties of racemic polylactic acid were characterized. The results show that the purity of racemic lactide after recrystallization can reach 99.3%, the water content is as low as 0.008% and the free acid content is less than 0.1%. When the amount of initiator is 0.13%, the molecular weight of the prepared racemic polylactic acid is 14.06 KDa and the tensile strength is 37 MPa.

Keywords: Recrystallization, molecular weight, racemic polylactic acid, tensile strength.

1. Introduction

As a biodegradable polymer, polylactic acid has good biocompatibility and bioabsorbability. Its degradation in vivo can be achieved through the hydrolysis and fracture of ester bonds on the molecular chain. Its degradation product lactic acid is a normal metabolic product of human body, so it has no toxic side effects on human body. It has been widely used in clinical and medical fields such as drug delivery, surgical sutures, bone fixation materials, anti-adhesion membranes and absorbable bone repair scaffolds. However, the low molecular weight and poor mechanical strength of clinically used polylactic acid limit its further application in the field of tissue repair [1-2].

At present, the commonly used polymerization methods mainly initiate ring-opening polymerization by adding monomer with hydroxyl end to initiate lactide. However, there is hydroxy-rich water in the actual reaction process, resulting in too many active sites for initiating polymerization, so that the number of monomers available at each active site decreases, the polymerization chain becomes shorter, and the relative molecular weight of the polymer decreases. Therefore, water in lactide monomer and polymerization system should be strictly controlled [3-6]. In this paper, high molecular weight racemic polylactic acid was prepared by melting polymerization of racemic lactide. The influence of monomer recrystallization process on the purity of monomer and the purity on the polymerization reaction were studied.

2. Experiment

2.1 Main raw material

Racemic lactide (D,L-LA) : Analytical pure, Shijiazhuang Jida Chemical Co., Ltd., Stannous octoate (Sn(Oct)2) : Analytically pure, cetyl alcohol: analytically pure, both supplied by Aladdin Chemical

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Reagent Co., Ltd., Ultra-dry dichloromethane: Analytically pure, Beijing Bailingwei Technology Co., Ltd., Anhydrous ethanol, etc.

2.2 Main instruments and equipment

Vacuum drying oven (Shanghai Senxin Experimental Instrument), Microcomputer control electronic universal testing machine (Shenzhen Wan Test Equipment Co., Ltd.), Gel permeation chromatography (GPC) instrument (WATERS, American, Waters2569), Differential scanning calorimeter (NETZSCH, Germany, DSC 214), etc.

2.3 Preparation of racemic polylactic acid

Firstly, D,L-LA was dissolved in ethyl acetate, completely dissolved by heating, left to room temperature.The same process was repeated 1~3 times, and vacuum drying at 60℃ to obtain refined D,L-LA. Then D,L-LA and cetyl alcohol were added into dry ampoules with magnetic stirrers in a certain proportion, and a certain amount of catalyst $Sn(Oct)_2$ was added. The ampoules were sealed under vacuum and placed in an oil bath at 140℃ for 12 h to obtain crude racemized polylactic acid. Finally, the crude polylactic acid was dissolved in methylene chloride, and anhydrous ethanol was slowly added, and the racemic polylactic acid was slowly precipitated. The racemized polylactic acid samples were obtained after vacuum drying at 60℃ for 24 h and stored for later use.

2.4 Characterization

The infrared spectrum of the polymer was measured by Fourier transform infrared spectrometer with a scanning range of 4000 ~ 500 cm^{-1}.

The average molecular weight of the polymer was determined by gel permeation chromatography (GPC). The mobile phase was tetrahydrofuran (THF), the flow rate was 1 mL/min, the test temperature was 35℃, and the standard sample was polystyrene (PS).

The purity of monomer was determined by differential scanning calorimeter (DSC 214).

An electronic universal testing machine was used to test the tensile strength of the sample, the test standard was GB/T1040-2006, and the spline tensile rate was 10 mm/min.

3. Results and discussion

3.1 Research on monomer recrystallization process

High purity monomer is the key factor for preparing high molecular weight polylactic acid. Impurities such as water, lactic acid and its oligomers in D,L-LA can be removed by recrystallization. This paper focused on the effects of recrystallization times and drying time on the purity, water content and free acid content of racemized lactide. Figure 1 shows the effects of drying time on the water content of racemized lactide.

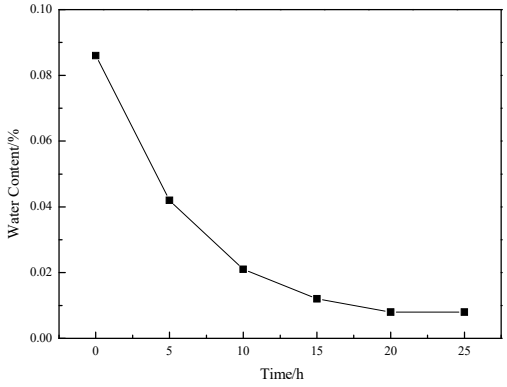

Figure 1. Effect of drying time on water content of racemic lactide

As shown in Figure 1, moisture in monomer can be effectively reduced with the increase of drying time. The water content of monomer without drying was 0.086%, and the water content of monomer gradually decreased with the increase of drying time. After drying for 20 h, the water content of monomer decreased to 0.008%, and when drying time increased for 25 h, the water content of monomer was 0.008%, with no change. Therefore, 20 h drying time is the best choice.

The effects of recrystallization times on the purity of lactide and the molecular weight of polylactic acid were discussed with other drying conditions unchanged. The results are shown in Table 1.

Table 1. Effect of recrystallization times on each index of D,L-LA

Nnmber	Crystallization times/times	Purity/%	Free acid content/%	$M_{w(PLA)}$
1	0	97.5	1.32	58723
2	1	98.7	0.56	98543
3	2	99.3	<0.10	140579
4	3	99.5	<0.10	148230

As shown in Table 1, with the increase of recrystallization times, the purity of D,L-LA can be effectively increased, the free acid content decreased, and the molecular weight of polylactic acid prepared from this monomer increased. When recrystallized twice, the purity of D,L-LA reached 99.3%, while when recrystallized three times, the purity of D,L-LA was 99.5%, and the molecular weight of polylactic acid prepared from this monomer was same as that prepared from recrystallization twice. The purity of monomer increased with the increase of recrystallization times, but the yield decreased. Therefore, it is most suitable for the purchased monomer to recrystallize twice.

3.2 Preparation and molecular structure analysis of racemic polylactic acid

D,L-LA was used as the main raw material, stannous caprylate catalyst and cetyl alcohol as initiator, racemic polylactic acid degradation material was prepared by melting polymerization, dissolved with methylene chloride, and anhydrous ethanol was gradually added to precipitate the polymer, remove impurities in the polymer, and obtain high purity polymer. Fourier transform infrared spectrometer was used to determine the molecular structure of the polymer, and the results were shown in Figure 2.

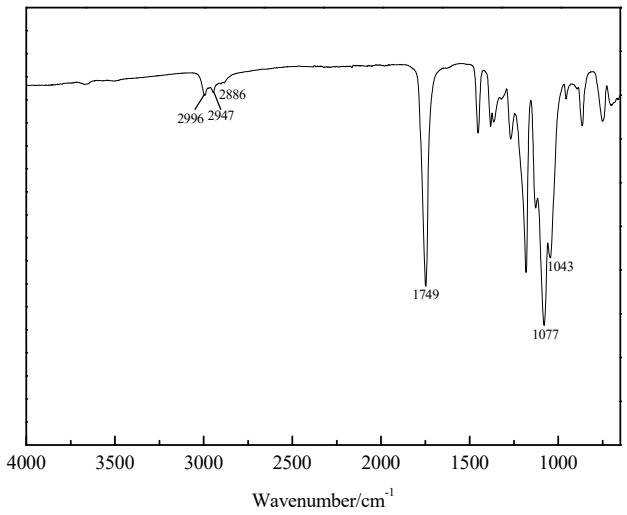

Figure 2. Infrared spectrum of the racemic polylactic acid

As shown in Figure 2, the stretching vibration peak of C=O in the racemic polylactic acid molecular chain is at 1749 cm^{-1}, the stretching vibration peak of C-O-C is at 1043 cm^{-1}, and the stretching vibration peak of C-H bonds of $-CH_3$ and $-CH_2-$ is at 2996~ 2886 cm^{-1}. The characteristic peak is not obvious at 3500, which is because the water content in the system is strictly controlled in this paper,

and the monohydroxyl hexetyl alcohol is selected as the initiator. The prepared polymer contains only hydroxyl groups at one end, and the characteristic peak corresponding to the hydroxyl groups is not obvious.

3.3 Influence of initiator dosage on performance of polylactic acid

The amount of initiator plays a decisive role in influencing the molecular weight of polylactic acid. Under the condition that other conditions remain unchanged, a series of polylactic acid polymers are prepared by changing only the amount of initiator. The influence of the amount of initiator on performance of polylactic acid is discussed.

Table 2. Influence of initiator dosage on performance of polylactic acid

Number	Initiator dosage/%	M_w/KDa	Dispersibility	Tensile strength/MPa
1	0.27	9.05	1.231	27.32
2	0.20	12.35	1.118	32.46
3	0.13	14.06	1.114	37.00
4	0.07	16.15	1.084	29.83

As shown in Table 2, with the decrease of initiator dosage, the molecular weight of the polymer gradually increased, and its tensile strength also increased to the maximum and then began to decline. As the amount of initiator decreases, the molecular weight of polylactic acid gradually increases. However, when the amount of initiator is 0.13%, the molecular weight of polylactic acid is 14.06KDa, and the tensile strength reaches a maximum of 37.00MPa. Continuing to reduce the amount of initiator, the molecular weight of polylactic acid increases, but the tensile strength decreases.Considering the tensile strength of racemic polylactic acid, 0.13% of initiator is the most suitable.

4. Conclusion

In this paper, racemic polylactic acid polymer was prepared by melting polymerization with racemic lactide as the main raw material, stnous caprylate catalyst and hexadecyl alcohol as the initiator. The influences of drying time and recrystallization times on the purity of lactide, as well as the effects of initiator dosage on the properties of racemic polylactic acid were studied, and the following conclusions were drawn: (1) The purity of race-lactide was effectively improved by recrystallization, and the content of water and free acid in the monomer was reduced. The optimal recrystallization process was 2 times of recrystallization, and the drying time was 20 h. (2) Using purified racemic lactide and 0.13% initiator, the molecular weight of racemic polylactic acid was 14.06 KDa and the tensile strength was 37 MPa.

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