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Synthesis and characterization of biodegradable polymer: Poly (ethene maleic acid ester-*co*-D,L-lactide acid)

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Abstract

A novel biodegradable polymer—poly (ethene maleic acid ester-*co*-D,L-lactide acid) was synthesized by copolymerizing lactide and prepolymer, which was prepared by the condensation of maleic anhydride and glycol, using *p*-toluene sulphonic acid as a catalyst, attempting to improve the hydrophilicity, increase flexibility and modulate the degradation rate. FTIR, ^{1}H NMR, MALLS and DSC were employed to characterize these polymers.

Keywords: Maleic anhydride; Glycol; Lactide; Copolymerization

Weak hydrophilicity, shortage of flexibility and uncontrollable degradation rate of poly (D,L-lactic acid) are major drawbacks that restrict its applications in drug controlled release [1–4]. Chemical modifications are often used to overcome these drawbacks and some good results were obtained [5–9]. In this study, a novel D,L-lactic acid-based biodegradable polymer was successfully synthesized by copolymerization modification. The copolymer, which comprises flexible glycol and ring-opened maleic anhydride, overcomes the weak hydrophilicity and increases the flexibility of polymer. At the same time, the double bond of the maleic anhydride could provide highly reactive group for the further linking reaction.

1. Experimental

The synthetic route of poly (ethene maleic acid ester-*co*-D,L-lactide acid) (PEMLA) is shown in Scheme 1.

The prepolymer (PEMA) was firstly prepared as follows: 9.8 g maleic anhydride and 6.51 g glycol were dissolved in 50 mL toluene, followed by addition of 0.05 g *p*-toluene sulphonic acid. The reaction was allowed to last for 24 h in vacuum at 100 °C. After reaction, ethylether was added to the prepolymer for dissolving the unreacted maleic anhydride. The prepolymer was characterized *via* FTIR and ^{1}H NMR. Its number–average molecular weight was titrated by KOH–ethanol solution (0.5 mol/L).

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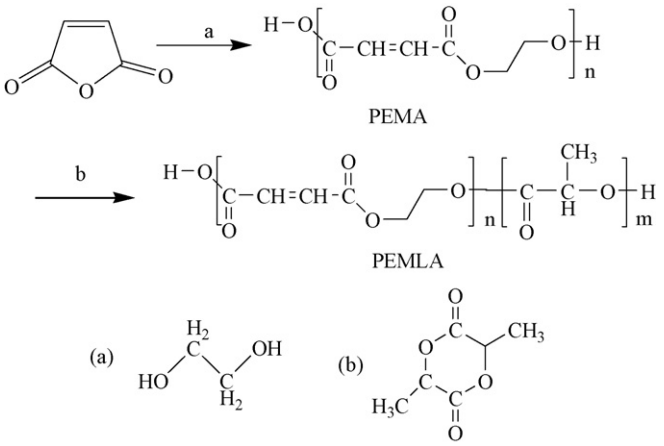

Scheme 1. Synthesis of the prepolymer and copolymer.

1.5 g prepolymer was mixed with 10 g lactide in a three-necked flask, then $Sn(Oct)_2$ (1/7000, 1/5000, 1/3000 of the prepolymer in mol) was added to the mixture, respectively. The reaction was allowed to last for 48 h at 160 °C in vacuum, and then 30 mL THF was added, the reaction mixture was precipitated with excessive distilled water to yield copolymer (PEMLA). The product was dried in vacuum. FTIR, ^{1}H NMR, MALLS and DSC were employed to characterize these copolymers.

FTIR were obtained on a Nicolet Magna 560 FTIR. Spectrophotometer and Nicolet data station with software at the resolution of 2 cm^{-1} in the region of 4000–400 cm^{-1}. ^{1}H NMR were measured on NMR instrument using $CDCl_3$ as solvent. The M_w and M_w/M_n were determined on a GPC-MALLS with RI detector at 25 °C. THF was used as solvent at a flow rate of 1.0 mL/min. Glass transition of the copolymer was measured by DSC under nitrogen at heating rate of 10 °C min^{-1}. The flexibility was charactered by the water absorption.

2. Results and discussion

The FTIR spectra are shown in Fig. 1. Comparing the FTIR spectra of prepolymer with that of glycol and maleic anhydride, two characteristic absorption bands at 1755.07 and 1647.76 cm^{-1} in Fig. 1c are attributed to the C–O stretching vibration of ester groups and the C=C stretching vibration, respectively. And the characteristic double-peak of anhydride groups in maleic anhydride disappeared in the prepolymer. These indicated that maleic anhydride has successfully reacted with glycol. Then the characteristic peak of CH (2994, 2944 cm^{-1}) and CH_3 (1455 cm^{-1}) of lactide in Fig. 1d indicated that the copolymer was obtained successfully.

The ^{1}H NMR spectrum was shown in Fig. 2. The peak at δ 6.0–7.0 ppm (Fig. 2A) was attributed to the proton of –CH=CH–, the peak at δ 3.8, 4.4 ppm (b and c) were due to the proton of $–CH_2–$ from glycol next to

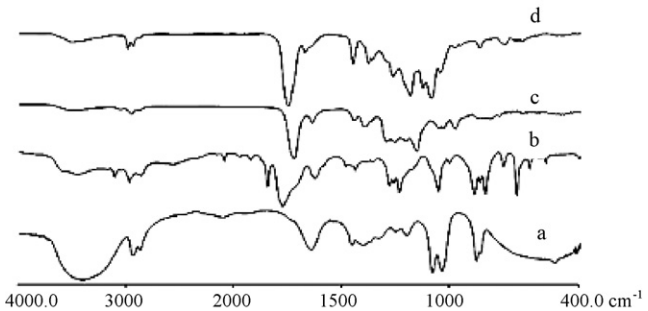

Fig. 1. FTIR spectra of glycol (a), maleic anhydride (b), prepolymer (c), and the PEMLA (d).