Polymerization and Properties of PLA(Polylactic Acid) High molecular weight

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1. INTRODUCTION

Poly(lactic acid) (PLA) is a highly versatile, biodegradable, aliphatic polyester derived from 100% renewable resources, such as corn and sugar beets. Because of the degradation mechanism, PLA is ideally suited for many applications in the environment where recovery of the product is not practical, such as agricultural mulch films and bags. Composting of post consumer PLA items is also a viable solution for many PLA products. However, the large growth seen for PLA in many applications dose not depend upon the biodegradability of the material. PLA resins can be tailor-made for different fabrication processes, including injection molding, sheet extrusion, blow molding, thermoforming, film forming, or fiber spinning. Lactic acid exists in two different optically active stereoisomeric forms; therefore, three different lactides can be formed: L(-)-lactide (s,s), D(+)-lactide (R,R) and the optically inactice meso-lactide (R,S).

PLA can be prepared by either condensation polymerization of the free acid or by catalytic, ring opening polymerization of lactide, which is the dilactone of lactic acid. PLA has certain good physical properties such as high strength, thermoplasticity and fabricability. However, PLA is still more expensive than conventional plastic, and the degradation rate is not completely satisfactory in some instances (e.g., municipal composting).

2. EXPERIMENYALS

2.1. Materials

L-Lactide(LLA) from PURAC was purified by recrystallization from dry toluene at 60℃ and then dried for 24h in vacuum at 30℃. Stannous 2-ethylhexanoate(stannous octoate, Sn-oct), toluene anhydrous 99.8% aqueous solution and Chloroform 99.9% aqueous solution

were purchased from Aldrich chemical.

2.2. Polymerization

A 250 mL two-necked flask was equipped with a thermocouple, a mechanical stirrer. PLA was polymerized by different time and content of L-lactide and Sn-Oct.

2.3. Measurements

Thermal properties of the synthesized polymers were measured using a differential scanning calorimeter(DSC, TA Instrument 2010, Dupont, U.S.A). The samples were heated at 10℃/min under nitrogen from 30℃ to 200℃, held at this temperature for 5min, and subsequently cooled down to 0℃ at a cooling rate of 20℃/min, and heated at 10℃/min from 0℃ to 250℃. A Thermogravimetric Analyzer(TGA, TA Instrument 2050, Dupont, U.S.A) was used to investigate the thermal stability of synthesized polymer. TGA experiment was performed at a scanning rate of 20℃/min from 30℃ to 600℃ under nitrogen atmosphere. Fourier-transform infrared spectroscopy(FT-IR) was used to analyze the chemical structure of synthesized polymers. The FT-IR spectrum from 4000cm^{-1} to 600 cm^{-1} of prepared samples in solid state was obtained by the KBr method.

Proten(^1H) nuclear magnetic resonance(NMR) spectra were recorded on a Bruker DPX-300 SY spectrometer at 300MHz for all the polymers. ^1H NMR chemical shifts in parts per million(ppm) are reported down-field from 0.00 ppm using tetramethylsilane(TMS) as an internal reference. For all the polymers, 30~40mg was dissolved in chloroform-*d* solvent. Using an Ubblohde viscometer, the molecular weight was determined in chloroform at 25℃ using the constsnts, $k=4.41\times10^{-4}$ and $a=0.72$ at 25℃, previously determined in the Mark-Houwink equation.

3. RESULTS AND DISCUSSION

In our experiment, we can find that the highest degree of polymerization is 10,000 times.(L-lactide : Sn-Oct). Fig. 1. is shown different molecular weight(Mw) according to the polymerization time. Fig. 2. and 3 are shown the DSC and TGA thermograms resulting during 30, 40, and 50 hours.

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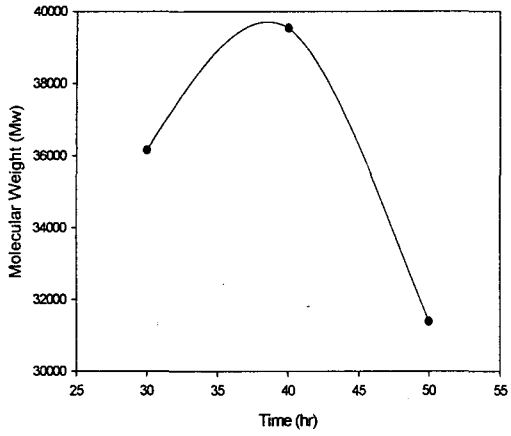

Fig. 1. Plot of molecular weight according time change.

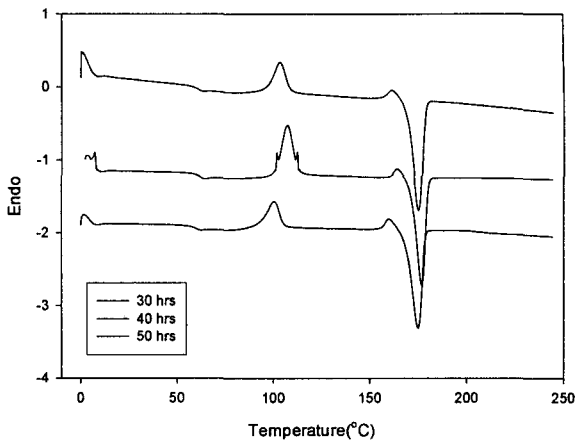

Fig. 2. DSC thermograms of PLLA according to the to different polymerization time change.

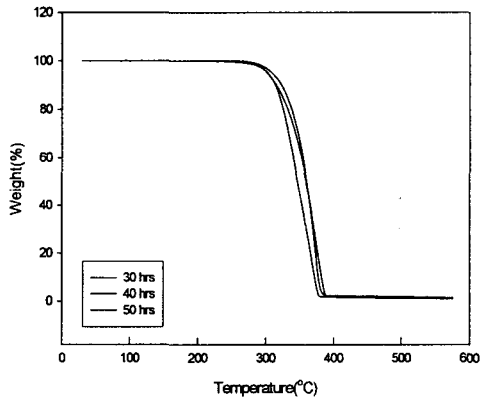

Fig. 3. TGA thermograms of PLLA according to the different polymerization time changing

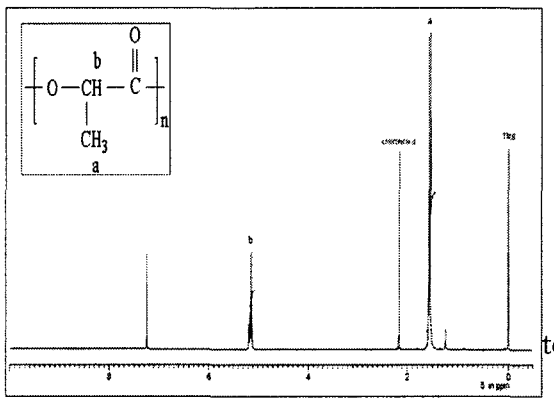

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Fig. 4. ^{1}H NMR spectrum of PLLA

4. REFERENCES

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