

Poly(Ester-Co-Ether) as a Potential “Green” Plasticizer for Poly(Lactic Acid)

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Abstract—Poly (ester-co-ether) as a potential “green” plasticizer for poly(lactic acid) (PLA) was synthesized from diethylene glycol adipate (DEAP) with neopentylglycol adipate (NPAP). The chemical structure of poly (diethylene glycol adipate -co-neopentylglycol adipate) (PDNA) was characterized by FTIR. PLA was plasticized by adding various PDNA contents. Tensile measurements results showed that with the addition of plasticizer, the tensile strength of the PLA/PDNA blends decreased and the elongation at break was greatly improved. Rheological properties of PLA/PDNA blends were investigated by a parallel plate rheometer (PPR).

Keywords-poly (lactic acid); plasticizer; rheology

I. INTRODUCTION

Poly (lactic acid) is an aliphatic thermoplastic polymer that can be produced from lactic acid obtained through fermentation of renewable resources like sugar beets, corn [1,2]. PLA can be used for producing packaging materials because it has a good biodegradability, biocompatibility [3-5], and mechanical properties [6-9]. If PLA could be used in packaging applications to replace polyolefin, it would be of great benefit to the environment. However PLA is very rigid and brittle at room temperature. Currently, many researchers had to find ways to improve the shortcomings of PLA. It could be blended with other polymers including poly(ethylene oxide) [10], starch [11] and poly(hydroxy butyrate) [12,13]. The results showed that the properties of PLA can be modified by blending with polymers to improve the ductility and flexibility of PLA-based materials.

Citrate esters [14], triacetate [15], poly(propylene glycol) [16], and poly(ethylene glycol) (PEG) [17,18] as low molecular weight plasticizers were found to be blended with PLA. The role of plasticizer reduces the modulus of elasticity in PLA and decreases the glass transition temperature (T_g) significantly to be soften. However, the plasticizers with low molecular weight have a tendency to migrate from internal to surface of the plasticized samples. Consequently, the application of plasticized PLA is restricted due to easy migration of plasticizers.

In this paper, we synthesized a new kind of polyester block copolymer containing ether bond called (diethylene glycol adipate -co- neopentylglycol adipate) (PDNA). The ether bonds in soft segments render good compatibility with many polymers and weak the interaction of biodegradable materials [19]. Poly(ester-co-ether) plasticizer combined with two kinds of structure unit has complementary advantages. The chemical structure of PDNA was characterized by FTIR. The

mechanical properties and the rheological behaviors were studied in order to assess PDNA plasticizing effect for PLA.

II. EXPERIMENTAL

A. Materials

Poly (lactic acid) supplied by Hisun chemical company was the type of (PLA Revode101). Adipic acid (AA) (99%), neopentyl glycol (NPG) (98%), diethylene glycol (DEG) (98%) and tetrabutyl titanate (TBT) (97%) were purchased from Tianjin Kewei chemical company.

B. Synthesis of Poly (Diethylene Glycol Adipate -Co-Neopentylglycol Adipate) (PDNA)

Synthesis route of PDNA can be described as follows: Poly(diethylene glycol adipate) (DEAP) was conducted by adipic acid (AA) with diethylene glycol (DEG) in 1.2 mol ratio and added 0.5 wt% catalysts of tetrabutyl titanate (TBT). The mixture was heated at 180 °C for 4 hours under nitrogen gas. Poly (neopentylglycol adipate) (NPAP) was polymerized by adipic acid with neopentyl glycol (NPG) in 1/1.2 mol ratio with excess (DPG) under nitrogen gas at 200 °C for 6 hours with the same catalysts. Poly (diethylene glycol adipate -co-neopentylglycol adipate) (PDNA) with a two-stage polymerization was synthesized by 65 wt% of DEAP and 35 wt% of NPAP with a pressure at 0.01MPa at 190 °C. At last, PDNA was purified with deionized water and then the solutions were removed on a rotator evaporator at 190 °C under a reduced pressure at 0.09 MPa.

C. Sample Preparation

Before extrusion, PLA and PDNA were dried under vacuum at 60 °C for 24 h. PLA/PDNA blends were prepared by melt mixing with the weight ratios of 100/0, 95/5, 85/15, and 75/25, which were correspondingly denoted as PLA, PDNA-5, PLA/PDNA-15, and PLA/PDNA-25.

D. Fourier Transform Infrared Spectroscopy (FT-IR)

Samples prepared for FTIR analysis was described as follow: 0.1g of sample was dissolved in THF (Tetrahydrofuran), and coated on a KBr plate and then evaporates in a vacuum oven for 10 hours to ensure that thin films were produced. FTIR analysis was performed on a Bruker Tensor 27 FTIR spectrometer. FTIR spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} .

E. Tensile Measurements

The tensile samples were prepared between two flat molds at 170 °C and compressed for 5 minutes to produce a thin sheet with 0.5 mm in thickness, and then using a compression

mold with water circulation to cool the samples to the room temperature. The samples were cut into standard dumb-bell shape. Tensile tests were performed on the specimens using an Instron-5582 at room temperature according to a British Standard BS2782-3:326 F:1997. The tension tests were done at a strain rate of 20 mm/min and the stress-strain curve was recorded using an extensometer with a gauge length of 25 mm.

F. Rheology of PLA/PDNA Blends

The rheological properties of PLA/PDNA blends were investigated at 170°C on a HAKKE-MARS III Rheometer. A parallel-plate geometry with a fixed gap of 1 mm and 20 mm in diameter was selected for all of the measurements. The blends with 1mm in thickness were prepared using a compression molder at 170 °C for 5 minutes, and then cut into 20 mm in diameter.

III. RESULTS AND DISCUSSION

The FTIR spectrum of PDNA were shown in Figure 1. All major peaks related to ether and ester groups are observed. The absorption band observed at 3450 cm⁻¹ corresponds to the OH stretching vibration of PDNA because of the existence of hydroxyl groups at the end of PDNA chains. The absorption bands at 2900 cm⁻¹ can be observed which is linked to the saturated CH stretching vibration. The carbonyl groups at 1720cm⁻¹ have a stretching vibration. Another strong spectral band at 1170 cm⁻¹ is stretching vibration of ether groups. The result of FTIR demonstrates the structure of PDNA containing ether and ester groups was successfully synthesized.

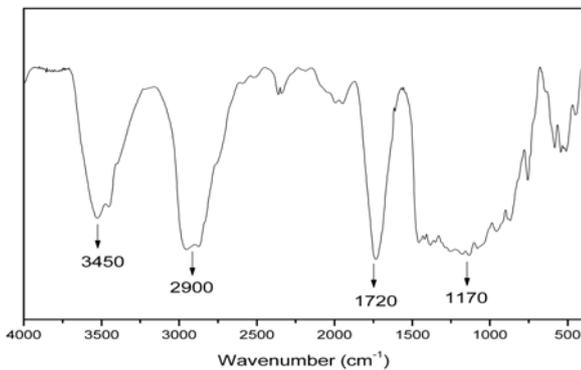


FIGURE I. FTIR SPECTRUM OF POLY(DIETHYLENE GLYCOL ADIPATE -CO- NEOPENTYLGLYCOL ADIPATE)

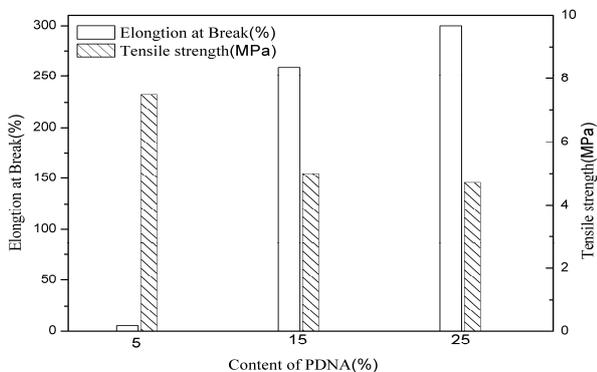


FIGURE II. TENSILE STRENGTH AND ELONGATION AT BREAK AS A FUNCTION OF PDNA CONTENT

The tensile strength and elongation at break obtained from the tensile tests were shown in Figure 2. PLA showed a brittle fracture behavior because of a low elongation at break (~3%) and a high tensile strength (~44 MPa), which was in agreement with the results previously reported [10]. With the addition of PDNA, the elongation of PLA/PDNA blends was significantly enhanced, whereas their tensile strength decreased. It illustrated that PDNA was an effective plasticizer because PDNA molecules diffused among PLA molecules and weakened the intermolecular aggregation. An addition of PDNA (15~25 wt%) to PLA is an effective approach to obtain flexible film.

Figure 3 showed steady shear rate versus viscosity of PLA and PLA/PDNA blends at 170°C. The viscosity of PLA/PDNA blends were lower than that of neat PLA. It was noted that the blends with low PDNA content (5 wt% of PDNA) exhibited shear-thinning behaviors at shear rates (< 5S⁻¹). At the high PDNA content (≥ 15wt%), PLA/PDNA blends exhibited Newtonian behaviors. In addition, the viscosity of PLA/PDNA blends decreased with an increase of PDNA content. It was apparent that plasticizer PDNA immersed into PLA molecular chains, by which it could decrease the friction and increase the mobility of PLA molecular chain.

In general, adding plasticizer could increase the spacing between the molecular chains, and shield polar groups in macromolecules, and reduce the interaction between molecular chains. The plasticizing coefficient can be described according to Eq.(1).

$$\eta = \eta_{[0]} e^{-K\phi} \quad (1)$$

where K is the plasticizing coefficient, ϕ is the percentage of plasticizer, $\eta_{[0]}$ is the zero viscosity of PLA, η is the zero viscosity of PLA/PDNA blends. The value K was calculated according to Eq.(1). TABLE 1 showed the plasticizing coefficient for PLA/PDNA blends. The plasticizing coefficient increased with PDNA content. PLA/PDNA-25 and PLA/PDNA-15 have similar plasticizing coefficient. They are high than that of PLA/PDNA-5. It demonstrates that the plasticizing effect approaches to maximum, when PDNA content is over 15wt%.

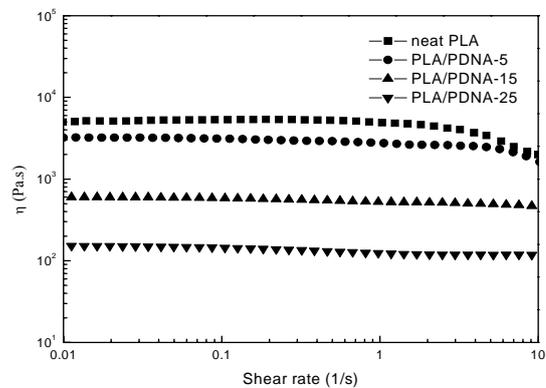


FIGURE III. STEADY SHEAR VISCOSITY OF PLA AND PLA/PDNA BLENDS AT 170 °C

TABLE I. PLASTICIZING COEFFICIENT OF PLA/ PDNA BLENDS

Sample ^o	Viscosity η (Pa·s) ^o	Plasticizing coefficient ϕ ^o
PLA ^o	3300 ^o	1 ^o
PLA/PDNA-5 ^o	3080 ^o	1.40 ^o
PLA/PDNA-15 ^o	550 ^o	11.95 ^o
PLA/PDNA-25 ^o	165 ^o	11.98 ^o

IV. SUMMARY

PDNA as a new plasticizer was successfully synthesized from DEAP and NPAP. PLA was plasticized by various amount of PDNA. With an increase of plasticizer, the tensile strength of PLA/PDNA blends decreased and the elongation at break was greatly improved. Viscosity of PLA/PDNA blends decreased with an increase of PDNA content. According to the plasticizing coefficient for PLA/PDNA, PDNA is an effective plasticizer and may therefore be a promising plasticizer for the applications of flexible PLA films.

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