Poly(Lactic Acid) Based Flexible Films

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Abstract—Poly(lactic acid) (PLA) is a biodegradable polymer which has good mechanical properties, however, its brittleness limits its usage especially in packaging materials. Therefore, in this work, PLA based polyurethane films were prepared by synthesizing with different types of isocyanates; methylene diisocyanate (MDI) and hexamethylene diisocyanates (HDI). For this purpose, PLA based polyurethane must have good strength and flexibility. Therefore, polycaprolactone which has better flexibility were prepared with PLA. An effective way to endow polylactic acid with toughness is through chain-extension reaction of the polylactic acid pre-polymer with polycaprolactone used as chain extender. Polyurethane prepared from MDI showed brittle behaviour, while, polyurethane prepared from HDI showed flexibility at same concentrations.

Keywords—Biodegradable polymer, flexible, poly(lactic acid), polyurethane.

I. INTRODUCTION

POLY(LACTIC ACID) (PLA) is an aliphatic polyester derived from renewable resources such as corn starch. It has excellent biodegradability, biocompatibility, and high strength. For this reason, PLA has potential for use in various applications such as for biomedical and packaging materials. Instead of all this interesting mechanical properties, PLA is brittle in nature and also has poor thermal stability, which limit its usefulness for packing and appliance applications [1]. Therefore, significant efforts are being put in improving the flexibility of PLA. Few approaches have been used such as blending PLA with flexible polymers as it is possible approach due to its simplicity and low cost. However, this method did not exhibit significant improvements in the property of PLA-based polymer blends possibly due to the high immiscibility between the two different polymers [2]-[8]. Therefore, fillers were added to improve on the miscibility of the polymer blends and also enhanced the properties [9]. Ramie fibre was used to reinforce the PLA/PCL blends and furthermore the fibre should be treated with coupling agent to improve on the compatibility and strengthen the interface of the fibre and polymers.

Considering on the properties of polymers, miscibility and processing methods, PLA based polyurethane was suggested where the PCL is attached to the PLA by urethane bond which also strengthens the polymers. PCL is also a biodegradable polymer and hence it will not reduce the biodegradability of the polymers. The aim of the research was to synthesize thermoplastic elastomer based on PLA and PCL. The effect of different isocyanates (MDI and HDI) used as linker on thermal and mechanical will be discussed. To the best of our knowledge, the synthesized PLA based polyurethane showed high elongation at break and modulus which was never reported. This high performance of polymer can be used in various applications.

II. EXPERIMENTAL SECTION

A. Materials

Commercially-available reagents were used without further purification unless otherwise stated. L-lactide, stannous octoate, and polycaprolactone-diol (PCL-diol, M_n = 2000 g/mol) were supplied by Sigma-Aldrich Co., Ltd.; 1,4-butanediol, dibutyltindilaurate, methylene diisocyanate (MDI) and hexamethylene diisocyanate (HDI) were purchased from TCI-Korea Co. Ltd.; the L-lactide was recrystallized from ethyl acetate before use. Organic solvents (e.g., toluene and ether) were used as anhydrous solvents.

B. Experiments

1. Synthesis of PLA-diol

PLA-diol was prepared by a condensation polymerization [10]. L-lactic acid (5.0×10^{-2} mol) and 1,4-butanediol (4.5×10^{-3} mol) were placed into a 250-mL, three-necked flask under a nitrogen atmosphere. Thirty-two milliliters of toluene were placed into the flask, and the mixture was stirred for 10min. Then, stannous octoate (2.5×10^{-4} mol) was added, and this mixture was stirred for 5min. Then, the temperature of the reactants was increased steadily up to 160°C, and the reactants were refluxed for 6h. The resulting reaction product was purified by dissolution in chloroform, after which it was precipitated in excess methanol. The product was dried in a vacuum oven, and a white solid was produced (3.8g): ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.05-5.25 (m, 2H), 4.27-4.38 (m, 0.4H), 4.14-4.18 (m, 0.8H), 1.68-1.71 (m, 0.4H), 1.52-1.59 (m, 6H), 1.43-1.52 (m, 1.2H):ATR-FTIR (cm^{-1}) 3340 (brs, -OH): M_n = 1,400 g/mol, PDI = 1.70.

2. Synthesis of PLA-HDI Pre-Polymer (PLAHDI)

The pre-polymer was synthesized as follows: PLA-diol (1g, 7.14×10^{-4} mol), stannous octoate (2.9mg, 7.14×10^{-4} mol), and toluene (14mL) were combined under a nitrogen atmosphere. Then, HDI (0.12g, 7.14×10^{-4} mol) was added and stirred for 2h at 70°C. The HDI was added in the mole ratio of 1:1 with PLA-diol. The resulting product was precipitated in excess methanol. The product was dried in a vacuum oven, producing

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a white solid: ATR-FTIR (cm^{-1}) 3400 (s, -HN-C=O-), 2276 (s, -N=C=O-).

3. Synthesis of PLA-MDI Pre-Polymer (PLAMDI)

The reaction was same as PLAHDI and instead of HDI, MDI is used.

4. Synthesis of PLA-based Polyurethanes (PLAPUs)

A chain-extension reaction was applied to produce high M_w PLAPU polymers. PCL-diol was used as a soft segment for preparing high M_w PLAPU polymers and incorporated to the pre-polymer mixtures (PLAHDI and PLAMDI). The PCL concentrations were based on balancing the isocyanate:diol content of the PCL at a 1:1 mole ratio. The reaction vessel was kept at 70°C for 4h under a nitrogen atmosphere. The polymer solution was collected and placed into diethyl ether, and the polymer was precipitated. The precipitated product was filtered, rinsed with methanol, and dried in a vacuum oven at 40°C overnight. The molecular weights of the PLAPU polymers are shown in Table I. ATR-FTIR (cm^{-1}) 3665(s,-HN-C=O-), 3392 (s, -HN-C=O-).

5. Characterizations

^{1}H NMR spectra were obtained with a Bruker 400 MHz spectrometer. Sample concentrations in 5-mm tubes were 10% by weight in CDCl$_3$ with TMS as the internal reference.IR spectra were recorded on a Bruker Alpha spectrometer with ALPHA's platinum attenuated total reflectance (ATR). Total of 256 scans at nominal resolution 2cm^{-1} between 4000 cm^{-1} and 400cm^{-1}. Tensile properties were measured using universal testing machine (INSTRON 5583) at 25°C and with a crosshead speed of 10 mm/min according to ASTM D412 specifications. The tensile test was used to determine the elongation at break, modulus and tensile strength.

III. RESULTS AND DISCUSSION

The chemical structure of PLLA-diol (PLLA-OH) was characterized by ^{1}H NMR spectra (Fig. 1). The signals occurring at 1.68 (δH^d) and 4.11 (δH^c) ppm could be reasonably assigned to the inner and outer methylene protons of –OCH$_2$CH$_2$CH$_2$CH$_2$O- , respectively. The peaks of methyl proton and methine proton at the terminus of PLLA-OH molecular chain were observed at 1.48 ($\delta H^{b'}$) and 4.36 ($\delta H^{a'}$) ppm, while the signals of those protons in the repeating units of PLLA-OH were found at 1.58 (δH^b) ppm and 5.18 (δH^a) ppm, respectively.

PLA-PCL polyurethanes (PLAPUs) were produced through chain extension of PLLA-OH with HDI using PCL-OH as chain extender. The chemical structure of PLAPU was also determined by ^{1}H NMR spectra (Fig. 2). It was found that all the related peaks of PLLA and PCL existed in the spectrum. The peak at 3.7 (δH^g) was attributed to the methyl protons of HDI. Moreover the peaks at 5.18 (δH^a) ppm and 4.06 (δH^c) ppm belonged to PLLA and PCL, respectively. From the spectra, it indicated the successful reaction of PLA-PCL polyurethane.

TABLE I
MOLECULAR WEIGHTS OF PLAPU(HDI) AND PLAPU(MDI)

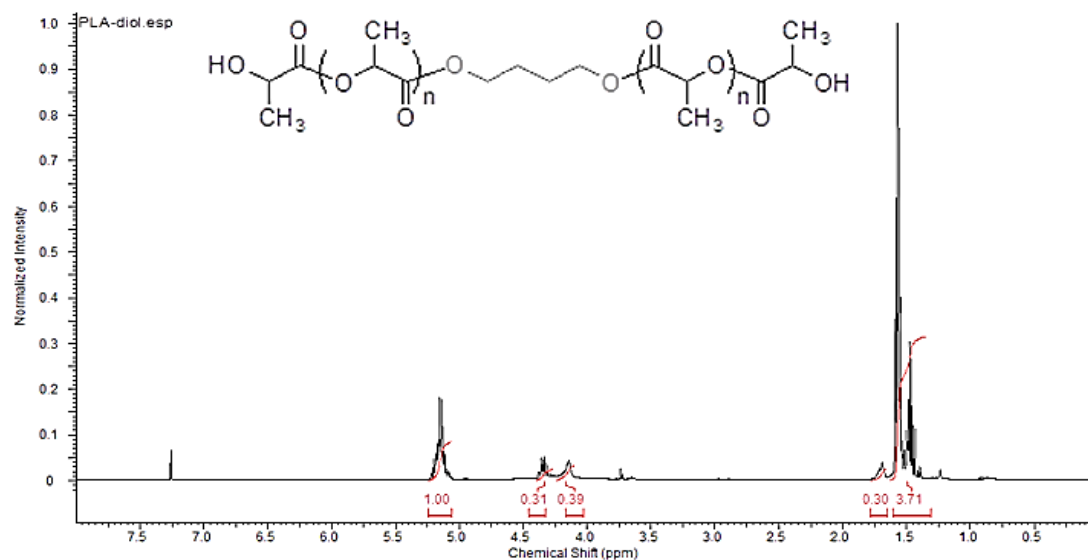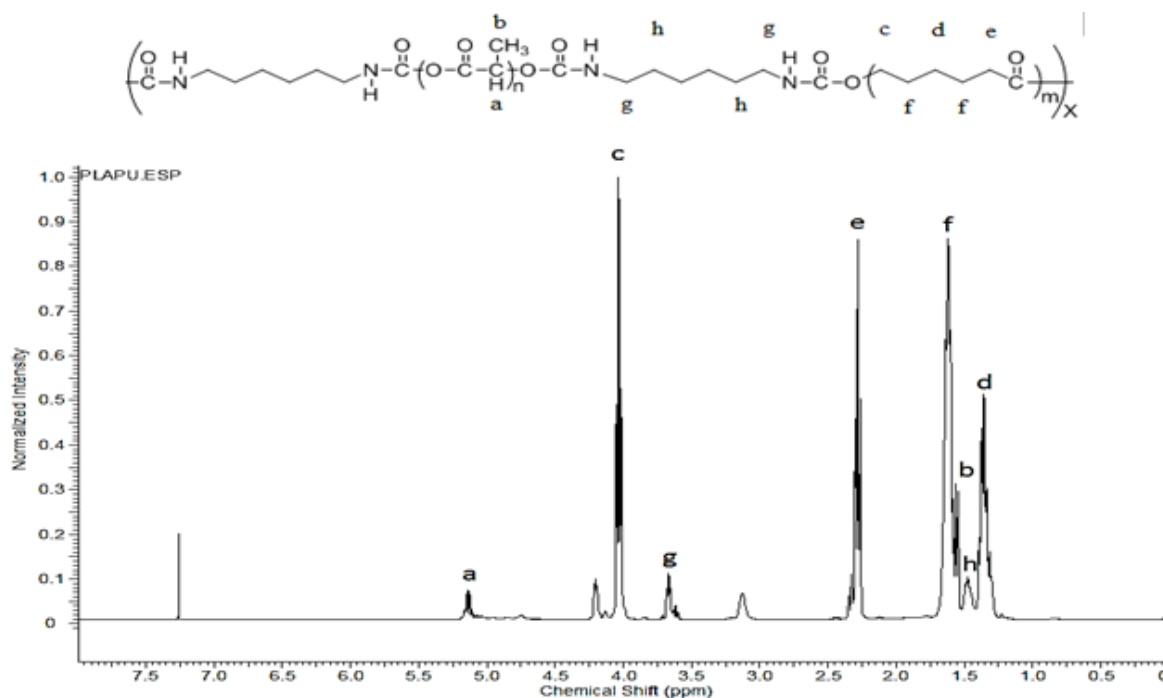| Sample	M_w (g/mol)	M_n(g/mol)	PDI
PLAPU(HDI)	124,700	63,900	1.95
PLAPU(MDI)	47,564	27,201	1.75

Fig. 1 ^{1}H NMR spectra of PLLA-OH

Fig. 2 ¹H NMR spectra of PLAPU (HDI)

ATR spectra of PLLA-OH and PLAPU are shown in Figs. 3 and 4. It can be seen the characteristic peak of the hydroxyl group of PLLA-OH at 3520cm^{-1} (Fig. 3). After the reaction with HDI and PCL-OH, the OH stretching band of PLLA-OH disappears (Fig. 4). While new bands at 3340cm^{-1}(NH stretching) and at 1600cm^{-1} (NH bending) are observed. In the C=O stretching region, the 1750cm^{-1} band for the PLA (PLLA-OH) carbonyl shifts to 1726 cm^{-1} (PLAPU). These new peaks revealed the existence of polyurethane in the polymeric chains [11].
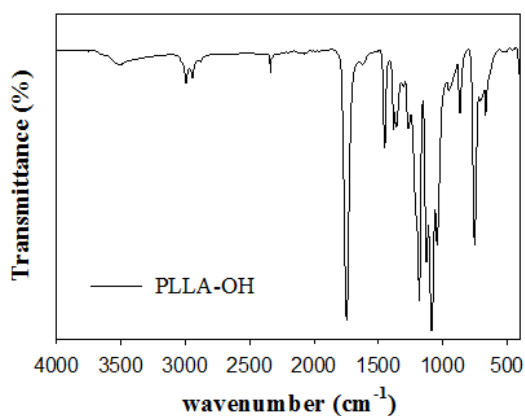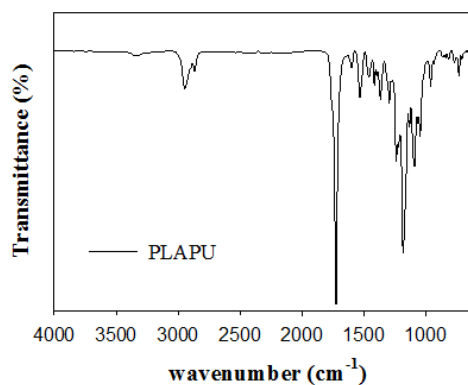

Fig. 4 FTIR spectra of PLAPU(HDI)
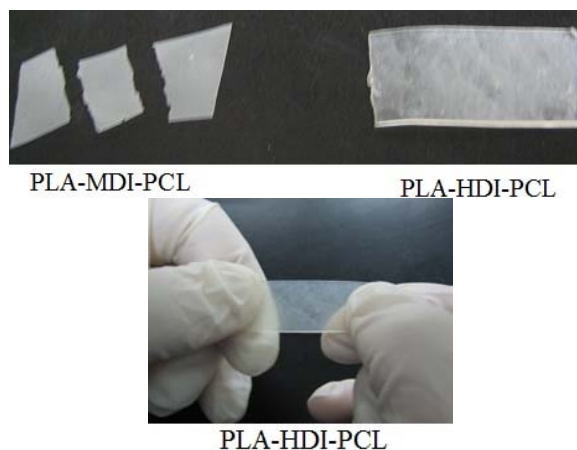

Fig. 3 FTIR spectra of PLLA-OH

Fig. 5 Flexibility of PLAPU(MDI) and PLAPU(HDI)

PLAPU prepared from MDI did not show any flexibility and exhibited brittleness (Fig. 5). Whereas, PLAPU (HDI) showed flexibility and the mechanical property is presented in Table II. This result showed that flexible polyurethane was prepared using HDI and the selection of linker is crucial in the sample preparations.

TABLE II
MECHANICAL PROPERTIES OF PLAPU (HDI)

Sample	Tensile Strength (MPa)	Strain at break (%)	Modulus (MPa)
PLAPU(HDI)	24.6	1053	51.8

IV. CONCLUSIONS

PLA-PLA polyurethanes (PLAPUs) were prepared by using PLA, HDI/MDI and PCL as soft segment, hard segment and chain extender, respectively. The properties of polymers prepared by different isocyanates differed largely in properties. The syntheses of the polymers were successful and the chemical structure and functional groups of polyurethanes were confirmed by ^{1}H NMR and ATR.

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