Polyurethane Anionomers Based on Poly(butylene succinate), 4,4′-Methylenebis(phenyl isocyanate), and 2,2-Bis(hydroxymethyl)propionic acid

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Abstract: Polyurethanes may be able to replace biodegradable polyesters since the biodegradability and certain mechanical properties of polyurethanes can be adjusted by modifying their chemical structures. A prepolymer was prepared from poly(butylene succinate) diol (MW 1600) and 4,4′-methylenebis(phenyl isocyanate), and chain-extended with 2,2-bis(hydroxymethyl)propionic acid (DMPA). The resulting polyurethane (PU) was neutralized with a base to obtain polyurethane ionomers (PUIs). The thermal transitions of the PUIs were not much different from those of the PU. However, the mechanical strengths were greater than both the PU and a typical biodegradable aliphatic polyester. For those PUIs in which the degree of neutralization with NaOH was 50% and 100%, the hydrolytic degradation was very rapid in a 5% NaOH solution at 37 °C. Their weight loss was approximately 30 and 50% within 2 days, respectively, while the PU was degraded only about 15% under the identical conditions. Some polyesters (Mn 40000 and 80000) underwent a degradation of about 10-20%. Accordingly, this study suggests that the PUIs can be applicable to the fabrication of degradable plastic materials.

Keywords: Degradable polyurethane ionomer, Poly(butylene succinate), Mechanical strength, Hydrolytic degradation

1. Introduction

Most synthetic plastics have caused serious environmental problems mainly due to their low degradability in nature. In order to resolve this degradability problem, a lot of research effort has been focussed on biodegradable polymers [1,2]. Aliphatic polyesters, which can be prepared from dicarboxylic acids and diols, seem to be promising degradable synthetic polymers since they can be prepared by relatively easy processes with reasonable costs [3-6]. However, when polyesters are prepared with high molecular weights so as to enhance certain mechanical properties [7], their biodegradability usually becomes less satisfactory mainly due to the high crystallinity and low hydrophilicity.

Polyurethanes have been widely used industrially due to their versatile properties related to their chemical structures [8-11]. Fortunately, some polyurethanes are biodegradable and have already been used as biomaterials [12-14]. Recently, polyurethanes were synthesized from polyester diol, ethylene glycol, and aromatic or aliphatic diisocyanate, and the relationship between the chemical structure of the polyurethanes and biodegradation under composting conditions was reported [15]. Based on these results, polyurethanes prepared using polyester diols as the soft segment would appear to have the most potential to replace biodegradable polyesters since those

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polyurethanes have superior mechanical properties and are also biodegradable.

Recently, polyurethanes were synthesized from poly (butylene succinate) diol (PBS, MW 1000), poly (ethylene glycol) (PEG, MW 200), and 4,4′-methylenebis(cyclohexyl isocyanate) (H₂MDI). However, their hydrolytic degradation was not satisfactory due to the small hydrophilic PEG segment. Polyurethanes were also synthesized from PBS (MW 1470), PEG (MW 1000), H₂MDI, and a 1,4-butanediol (BD) chain extender [16,17]. The hydrolytic degradation rate of the polymers was significantly enhanced when compared to polyurethanes without any PEG content and also some other polyesters with comparable molecular weights.

Polyurethane ionomers usually exhibit excellent mechanical properties due to strong interchain interactions resulting from Coulombic forces and hydrogen bonds, and have been utilized in the form of water dispersions for coatings and adhesives. However, in spite of extensive research in this field [18], there have not been many systematic studies on the degradation of polyurethane ionomers.

In the current study, a polyurethane (PU) was synthesized by adding a 2,2-bis(hydroxyethyl)propionic acid (DMPA) chain extender to a prepolymer prepared from PBS (MW 1600) and 4,4′-methylenebis(phenyl isocyanate) (MDI). The PU was then neutralized with various bases to obtain polyurethane ionomers (PUIs). This paper describes some of the general properties of the PUIs including the hydrolytic degradation.

2. Experimental

2.1 Materials

The MDI, DMPA (98%) and titanium(IV) isopropoxide (99.999%) were purchased from Aldrich. The succinic acid and BD (99%) were purchased from Dongyang Chemical Co. and dried at 70 °C for 24 h before use. The potassium hydroxide, sodium hydroxide, and zinc acetate were purchased from Junsei Chemical Co. The dibutyltin dilaurate was purchased from Air Product.

2.2 Measurements

The chemical structures of the polymers were confirmed by the FT-IR and 1H NMR spectra obtained using a JASCO FT-infrared spectrophotometer and JEOL-JMN 400 (400 MHz) spectrometer, respectively. The thermal transitions of the polymers were observed with differential scanning calorimetry (DSC 2910, TA Instruments Co.). The average molecular weights of the polymers were measured with gel permeation chromatography (Waters 600) using a polystyrene solution in tetrahydrofuran as the calibration standard. The tensile test of the polymer films was performed using an United STM-10 at room temperature with a crosshead speed of 3 mm/min.

2.3 Synthesis

The synthetic route to the PU is shown in Scheme 1. Briefly, a mixture of BD and succinic acid in a 1.2:1 molar ratio was heated slowly to 180 °C. The reaction temperature was maintained at 180 °C for 2 h and then at 220 °C for 3-4 h under a nitrogen atmosphere. The mixture was further heated in the presence of titanium(IV) isopropoxide (0.02 wt%) at 220 °C for 2-3 h under a vacuum (100 mmHg) for a deglycol reaction. The titrations for the measurement of the hydroxy and acid numbers were conducted on the basis of ASTM D 1957-63 and ASTM D 1980-67, respectively. The number-average molecular weight of the PBS was calculated to be about 1600, based on the hydroxy and acid values.

The PBS was reacted with MDI at 60 °C for 2 h and the resulting prepolymer was chain-extended with DMPA under a nitrogen atmosphere. Dibutyltin dilaurate was added to complete the reaction (0.2 wt%). The molar feed ratio of PBS, MDI, and DMPA was 2:3:1. The mixture was allowed to react at 70-75 °C until the isocyanate peak in the FT-IR spectrum had disappeared. Based on the acid value of the polyurethanes determined, the PU was neutralized with appropriate amounts of various bases to obtain PUIs. The PUIs were then dried at 70 °C for 1 day in an oven and for a further 6 days in a vacuum.
oven (76 mmHg).

### 2.4 Water absorption

The polymer films (10 mm x 10 mm, 155-165 μm in thickness) were incubated in bottles containing a buffer of pH 7.0 at 37 °C for 24 h. The films were weighed after the water on the surface of the films had been removed. The percentage of water absorption was calculated by dividing the weight difference between the incubated film and the initial film by the initial weight, followed by multiplying by 100.

### 2.5 Hydrolytic degradation

Polymer films, with the same dimensions as above, were placed in small 25 mL bottles containing a 5% NaOH aqueous solution. The bottles were then incubated at 37 °C. After a certain period of time, the films were washed with distilled water and dried in a vacuum oven at 70 °C for 7 days. The percentage of weight loss was calculated by dividing the weight difference between the dried incubated film and the initial film by the initial weight, followed by multiplying by 100.

### 3. Results and Discussion

The FT-IR spectra of the PBS, MDI, and PU are presented in Figure 1. The peak for the NCO group of MDI at 2275 cm\(^{-1}\) disappeared completely in the spectrum of the PU. Instead, the peak for the -NH groups in the urethane bonds appeared at 3330 cm\(^{-1}\). The peaks for the ester carbonyls of the PBS and urethane carbonyls of the PU were overlapped and appeared at 1723 cm\(^{-1}\). This result indicates that the polymerization was almost completed. The proton resonance peaks for the PU were assigned as shown in Figure 2. The spectrum indicates that the PBS and DMPA were linked with MDI via urethane bonds to form the PU. The number- and weight-average molecular weights of the PU were estimated with GPC to be 20000 and 27000, respectively.

The glass transition (T\(_{g}\)), crystallization (T\(_{c}\)), and melting transition temperature (T\(_{m}\)) of the PBS, estimated from the second heating scan thermograms, were about -35 °C, 84 °C, and 110 °C, while the corresponding transition temperatures of the PU were -27 °C, 56 °C, and 99 °C, respectively, as shown in Figure 3.

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**Figure 1.** FT-IR spectra of PBS, MDI, and PU.

**Figure 2.** \(^1\)H-NMR spectrum of PU in CDCl\(_3\).

**Figure 3.** DSC thermograms of polymers. All the thermograms were obtained from the second heating scan and the scan rate was 10 °C/min.
Figure 4. Strain-stress behavior of polymer films.

Figure 5. Water absorption of polymer films incubated in distilled water at 37 °C for 2 days.

This result indicates that the thermal transitions of the PU resulted from the soft segments of the PBS were affected by the partially mixed hard segments [16].

The PU was completely neutralized with zinc acetate, potassium hydroxide, or sodium hydroxide, and the resulting PUIs were designated as PUI-Zn100, PUI-K100, and PUI-Na100, respectively. The T_g and T_m of the PUIs varied from those of the PU within a range of a few degrees, thereby suggesting that the incorporation of ionic groups into the PU would not appear to significantly affect the phase separation of the PBS and the hard segments. This result is understandable based on the fact that the PBS soft segments are highly crystalline and hence their thermal transition behavior is not seriously affected by the presence of other segments [19].

The degree of neutralization usually plays an important role in the mechanical properties of ionomers. A thin film of PBS could not be prepared due to its low molecular weight and high crystallinity. Thus, Esilon Green (EG), a polyester prepared from succinic acid and a mixture of BD and ethylene glycol (obtained from Saehan Co., Mn 40000, Mw 70000), was tested for comparison as shown in Figure 4. The modulus of the PU was greater than that of the EG, indicating that the mechanical strength of a polyester can be enhanced by the incorporation of urethane bonds, which provide interchain hydrogen bonds. The tensile modulus of PUI-Na50 was greater than that of PU, indicating that the strength of polyurethanes can be still further enhanced by the incorporation of ionic groups into the polymer chains, which produces stronger interchain hydrogen bonds and Coulombic forces [20-22]. According to Cooper et al. [23], the ionization of a polyurethane led to an increase of the extensibility and modulus at low level. At high levels of ionization, however, the polyurethane behaved like a plastic, exhibiting a high modulus and a low elongation at break. The mechanical properties of the PUIs showed a similar trend since the tensile modulus and elongation at break of the PUI-Na100 were slightly greater and lower, respectively, than those of PUI-Na50.

The water absorption behavior of the PU and PUIs was studied and the results are shown in Figure 5. The water absorption of PUI-Na50 was significantly enhanced compared with that of the PU, and slightly less than that of PUI-Na100. This result is understandable because the PUIs should absorb water more efficiently than the PU due to the hydrophilic ionic centers in their backbone. The water absorption of PUI-Zn100 was the lowest among the three PUIs, and that of PUI-Na100 was slightly higher than that of PUI-K100. It is known that the water absorption of ionomers containing divalent cations is usually less efficient than that of ionomers containing monovalent cations [24]. Therefore, this result confirms the fact that water absorption can be significantly affected by the nature of the counter cations even though the polymer main chain is unchanged. This result also indicates that Na^+ ions were the most effective in enhancing the water absorption of the PUIs among the metal cations employed.

Even though there are several possible approaches for assessing the biodegradability of polymers [15], the hydrolytic degradation of the polymers in alka
from PBS, MDI, and DMPA, with sodium hydroxide, potassium hydroxide, or zinc acetate. The T<sub>m</sub>s of the PU and PU1s were lower than that of the PBS because the PBS segments were responsible for the melting transition and at least partially mixed with the hard segments. The PU1Na50 and PU1Na100 showed significantly enhanced tensile strengths compared to a simple polyester and the PU, mainly due to enhanced interchain interactions. These PU1s underwent very rapid degradation in alkaline aqueous solutions due to hydrophilic ionic groups in the hard segments. This study suggests that since the incorporation of ionic groups into polyurethanes can greatly enhance their mechanical strength and degradation rate, PU1s can be used as degradable plastic materials.

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