

Effect of Chain Extenders on Polyurethanes Containing Both Poly(butylene succinate) and Poly(ethylene glycol) as Soft Segments

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Polyurethanes have been widely used industrially due to their versatile properties.^{1,2} Some of them are biodegradable and have been used as biomaterials.³ Biodegradable polyurethanes may be able to replace nondegradable polymers such as polyethylene and polypropylene in fabrication of packaging films in near future as long as their mechanical properties are comparable to those of the common film-forming materials.

Polyurethanes containing poly(ethylene glycol) (PEG) are interesting since the hydrophilic PEG segments can enhance the degradation. Furthermore, PEG itself has been frequently used as comonomers in preparing biodegradable polymers due to its good biocompatibility and biodegradability.^{4,5} Recently, polyurethanes were synthesized from poly(butylene succinate) (PBS), PEG, and 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI) without using any chain extender in order to obtain moderate molecular weights.⁶ PBS, a crystalline polymer, was employed in order to raise the melting temperature (T_m) of the resulting polyurethanes, which may facilitate their fabrication process. But, the molecular weights of the polyurethanes were not high enough to show desirable mechanical properties even though their hydrolytic degradations were efficient.

Polyurethanes were also synthesized from PBS, PEG, and H₁₂MDI by using 1,4-butanediol (BD) as chain extender.⁷ Their number-average molecular weights and melting temperatures were found to be in the range of 30,000-38,000 and 99-101 °C, respectively. The tensile strengths (2.0-2.4 kg/mm²) of the polymers were slightly greater than the reported value of PBS (1.6 kg/mm²) with a comparable molecular weight (M_n 20,000).⁸ Their elongations at break (230-330%) were significantly greater than that of the PBS (42%), but still not satisfactory for fabrication of packaging films.

In the present study, H₁₂MDI-based polyurethanes were prepared by using PBS/PEG (2/1, mol/mol) as soft segments. Three different combinations of chain extenders such as BD (PU-1), BD/ED (1/1) (PU-2), and ethylenediamine (ED) (PU-3) were employed to synthesize the polyurethanes. This paper discusses briefly some thermal and mechanical

properties of the resulting polymers.

Experimental Section

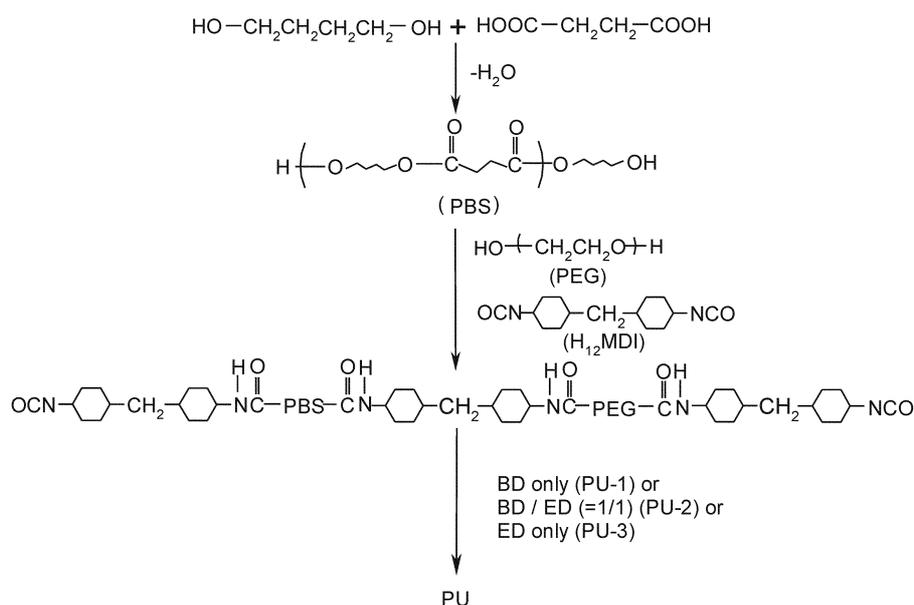
Synthesis. The synthetic route to the polyurethanes is illustrated in Scheme 1. PBS was prepared by employing the reported procedure.^{6,7} The M_n of PBS was calculated to be about 1,620, based on the hydroxy (67.4) and acid values (1.65). PBS (30 g, 18.5 mmol) was dried at 70 °C for 24 h, and melted together with PEG₁₀₀₀ (M_n = 1000, 9.26 g, 9.26 mmol) at 120-130 °C in a reaction flask, followed by the addition of H₁₂MDI (9.70 g, 37.0 mmol) for 2 h under a nitrogen atmosphere. After the formation of NCO-terminated prepolymer was confirmed, BD (0.83 g, 9.26 mmol) and DMF (120 g) were added. The resulting solution was reacted in the presence of dibutyltin dilaurate (0.02%) at the same temperature until the isocyanate group disappeared based on the FT-IR spectrum (~2270 cm⁻¹). The resulting mixture was cast in a mold and heated at 70 °C and 50 torr for 24 h to complete the polymerization and at the same time to remove DMF. The resulting polymer was precipitated into methanol in order to remove any remaining starting materials and impurities. The purified polyurethane is designated as PU-1. PU-2 and PU-3 were prepared by following the same procedure, but using BD/ED (1/1) and ED, respectively, instead of BD as chain extenders.

Measurements. The thermal transitions of polymers were observed with differential scanning calorimetry (DSC, DuPont 2000). The number- and weight-average molecular weights (M_n/M_w) of the polymers were measured with gel permeation chromatography (GPC, Maxima 820) in chloroform using polystyrene standards. The tensile strength, elongation at break and modulus were measured with a universal test machine (Lloyd Co.) at a strain rate of 50 mm/min. The wide angle X-ray diffraction was studied using a X-ray diffractometer (Rigaku, Co., Cu target) at 40 kV and 30 mA.

Result and Discussion

The M_n of PU-2 is slightly greater than those of PU-1 and PU-3, but the M_w of the polymers are pretty close to each other, as shown in Table 1. The DSC thermograms obtained

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Scheme 1. Schematic representation of a synthetic route to PU-1, PU-2, and PU-3.

from the second heating scans are illustrated in Figure 1. The glass transition temperatures (T_g s) of the polymers are very close to each other. The T_m s of PU-1, PU-2, and PU-3 at maximum heat capacity were measured to be 104, 101, and 105 °C, respectively, while that of PBS was 113 °C. This result suggests that the melting transitions arise from the PBS segments in the polyurethanes.^{6,7} On the other hand, the PEG segments of these polymers did not show any melting transition in the same temperature range even though the T_m of the PEG₁₀₀₀ itself is 39 °C. Polyurethanes were prepared using PEG₁₀₀₀ or PEG₂₀₀₀, H₁₂MDI and BD. Polyurethanes prepared from PEG₁₀₀₀ did not exhibit any melting transition while those prepared from PEG₂₀₀₀ showed a T_m at about 38 °C (data not shown). This result indicates that the absence of melting transition of PEG soft segments in the present polyurethanes is due to the low molecular weight of the PEG employed. Any T_m of the hard segments was not observed in the temperature range up to 250 °C. The absence of melting transition of hard segments in our present polyurethanes results from the inefficient packing of the segments because H₁₂MDI exists in three different isomers of *cis-trans*, *trans-trans* and *cis-cis* conformations.⁹

The T_m and ΔH_m values of PU-2 are lower than those of PU-1 and PU-3. In the case of PU-2, the isocyanate-

terminated prepolymers react with BD and ED in the chain extension reaction step, resulting in the formation of urethane and urea groups in their hard segments, respectively. PU-1 contains urethane groups in the hard segments, but

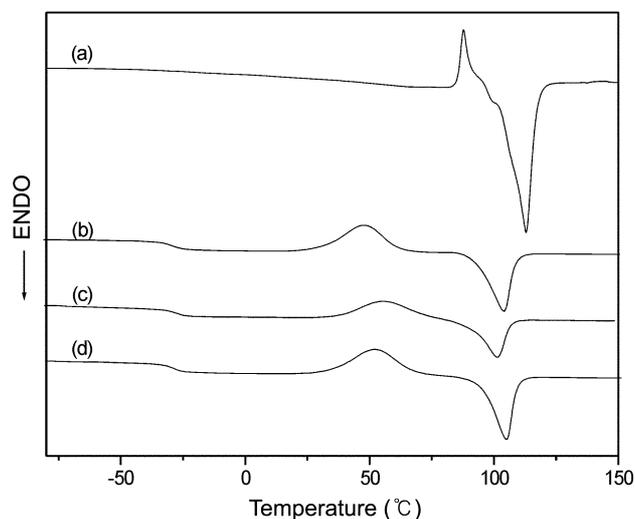


Figure 1. DSC thermograms obtained on the second heating scans: (a) PBS, (b) PU-1, (c) PU-2, and (d) PU-3 (scan rate, 10 °C/min).

Table 1. Average molecular weight (M_n/M_w), glass transition temperature (T_g), melting transition temperature (T_m), melting transition enthalpy (ΔH_m), tensile strength, elongation at break, and modulus of synthesized polyurethanes. The T_m , T_g and ΔH_m were measured from the second heating scanned DSC thermograms

PU	M_n	M_w	T_g (°C)	T_m (°C)	ΔH_m (cal/g)	Tensile strength (kgf/mm ²)	Elongation at break (%)	Modulus (kgf/mm ²)	Hard segment (wt%)
PBS	1,620	—	—	113	22.1	—	—	—	—
PU-1	16,000	42,000	-32	104	10.5	1.7	410	12.0	21.3
PU-2	20,000	47,000	-31	101	7.0	1.9	1100	13.0	21.1
PU-3	15,000	41,000	-32	105	10.3	2.0	140	14.0	21.0

PU-2 contains equal amounts of urethane and urea groups. On the other hand, PU-3 contains only urea groups in the hard segments. Urea groups have two nitrogen atoms suitable to form hydrogen bonds, whereas urethane groups have only one nitrogen in this case. The two different groups in PU-2 cannot be closely packed together in the same hard domains due to the mismatching of their chemical structures as well as the isomeric nature of H_{12} MDI. Thus, as compared to PU-1 and PU-3, the hard segments of PU-2 may be mixed to more extent with PBS and PEG soft segments, as shown in Figure 2. This probably lowers the degree of crystallization of PBS segments in PU-2, resulting in the lower T_m and smaller ΔH_m values.

The wide angle X-ray diffraction experiment revealed that two peaks appeared simultaneously at 2θ values of approximately 19 and 22° for all of the three different polyurethanes as well as for PBS as described in the previous papers.^{6,7} However, the diffraction peaks for the polyurethanes appear

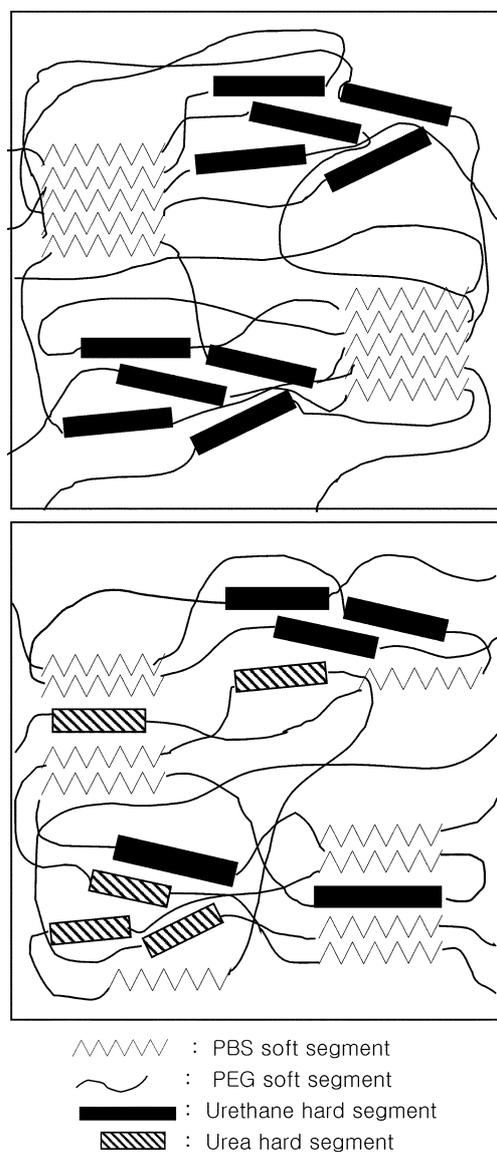


Figure 2. Schematic representation of polymer morphology: (a) PU-1 and (b) PU-2.

less sharply than those for PBS and cannot be easily distinguished from one another. This experimental finding confirmed that the crystallinity of the polymers resulted from the PBS segments and their crystal structures were not much affected by the PEG and hard segments even though their T_m and ΔH_m values are slightly different. The changes in the T_m and ΔH_m values simply reflect variations in the degree of crystallization of PBS segments in the films.

The initial purpose of present research was to observe any change in physical properties of the polyurethanes when both ED and BD were used as chain extenders. Thin films (thickness, 0.8-1.0 mm) of the polyurethanes were easily prepared by following the hot press method, while those of PBS could not be prepared since PBS was too brittle due to its low molecular weight. The tensile strengths of PU-2 and PU-3 were slightly greater than that of PU-1. The urea groups in the hard segments of PU-2 and PU-3 increase the intermolecular interactions due to the additional hydrogen bonding. The modulus behavior of the polymers can also be explained in terms of the hydrogen bonding interaction.

The sequence of elongation at break of the polymer films was observed to be PU-2 > PU-1 > PU-3. In fact, it is well-known that in the case of polyurethane elastomers, the soft segments usually contribute to the high extension and elastic recovery while the hard segments contribute to the high modulus.^{10,11} The soft segments in this system are the same for the three different polymers. The molecular weights of the three different polymers are not much different from each other, either. First of all, the elongation of PU-1 film at break was much greater than those of PU-3 film. It is known that the elastic property of polyurethanes can be enhanced at the expense of tensile strength and modulus when diol is used instead of diamine as chain extender.^{12,13} As explained above, PU-1 contains urethane groups in its hard segments, but PU-3 contains urea groups instead. The urea groups in PU-3 increase the degree of intermolecular hydrogen bonding and, consequently, its rigidity and brittleness.

Interestingly, the elongation of PU-2 film at break was much greater than those of PU-1 and PU-3 films. The elongation behavior of PU-2 film can be explained by a similar reason as that for the melting transition behavior. As proposed in Figure 2, PU-2 has more free PBS and urethane/urea hard segments escaped from the corresponding PBS and hard domains, respectively, due to more phase mixing between the soft and hard segments. The more phase mixing is due to the mismatching between the urethane- and urea-based hard segments. The urethane and urea groups in the hard segment domains can form hydrogen bonding even though they cannot be crystallized due to the different isomeric structures of H_{12} MDI. The free segments of polymer chains are usually significantly entangled in the amorphous state. On stretching, however, the free segments become aligned on a common axis. This means that the elongation is largely affected by the free segments of amorphous state in elastomers. In other words, the more the free segment content of polyurethane, the greater is the elongation of its film. Because of the mismatching between the urethane- and

urea-based hard segments, PU-2 has more free segments than PU-1 and PU-3, leading to the significant elongation of its film.

Conclusion

Polyurethanes containing PBS and PEG as soft segments were synthesized by using chain extenders of BD (PU-1), BD/ED (1/1) (PU-2), and ED (PU-3). The T_m and ΔH_m values of PU-2 were smaller than those of PU-1 and PU-3. The tensile strength and modulus of the polyurethane films were increased when ED was used as chain extender. On the other hand, the elongation at break of PU-2 film was much greater than that of either PU-1 or PU-3 film. The enhanced elongation of PU-2 film is probably due to more free segments which result from the mismatching between the urethane- and urea-based hard segments. This strategy of using a mixture of diol and diamine as chain extenders may be applicable to other polyurethane systems especially when the elastic property of polyurethanes containing crystalline soft segments needs to be enhanced significantly.

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