

Properties of Crosslinked Polyurethanes Synthesized from 4,4'-Diphenylmethane Diisocyanate and Polyester Polyol

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ABSTRACT: Polyurethanes were synthesized using the high functional 4,4'-diphenylmethane diisocyanate (MDI), polyester polyol, and 1,4-butane diol. The synthesized polyurethanes were analyzed using differential scanning calorimeter (DSC), dynamic mechanical thermal analysis (DMTA), Fourier transform infrared (FTIR) spectrometer, and swelling measurement using *N,N'*-dimethylformamide. From the result of thermal analysis by DSC and DMTA, single T_g s were observed in the polyurethane samples at all the formulated compositions. From this result, it is suggested that the polyurethanes synthesized in this study have crosslinked structure rather than the phase-separated segmented structure because of the high functionality ($f = 2.9$) of the MDI. By annealing the polyurethane samples using DSC, the T_g s were increased by 4.7~16.0°C at the various annealing temperatures. From the results of FTIR and swelling measurement of polyurethanes, it is suggested that the increase of T_g of the polyurethanes by annealing is not due to increase of the hydrogen bond strength but mainly due to the increase of the crosslink density. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 624–630, 2000

Key words: polyurethane; crosslinking; glass transition temperature; hydrogen bond; swelling

INTRODUCTION

Polyurethanes are block copolymers based on polyol, diisocyanate, and often chain extender.^{1,2} Polyol of low glass transition temperature forms soft segment in polyurethanes, while diisocyanate and chain extender comprise hard segment. The hard block domain formed from hard segments gives the mechanical strength and higher temper-

ature performance to the polyurethane, whereas soft block domain formed from soft segments gives high extensibility and resiliency.^{1–6} Due to thermodynamically incompatibility between the hard domain and soft domain, polyurethanes have microphase-separated structure. In such a phase-separated structure, domain morphology by phase separation or phase mixing has a great influence on the properties of the polyurethanes.^{1–15} Therefore, it has been widely studied that qualitative and quantitative evaluation of degree of phase separation or degree of phase mixing^{3–6} and factors affecting the phase separation such as chemical structure,^{7,8} molecular

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weight,^{4,9} and functionality of component,^{10–12} and hydrogen bond between segments.^{13–15}

Crosslinking can influence the properties of polyurethanes also.^{10–13,16–18} Crosslinking by covalent bond between polymer chains can be introduced in several ways. By using the excess of diisocyanate (NCO/OH ratio > 1), allophanate or biuret bond formed from excess diisocyanate-urethane or excess diisocyanate-urea may cause chain branching and chemical crosslinking.^{13,18} When multifunctional components of polyol, diisocyanate, or chain extender are used, highly developed crosslinking can be obtained. Highly crosslinked polyurethane foams have been used as an insulator for liquefied natural gas storage tank.

Recently, Petrović et al.¹⁰ introduced the chemical crosslinking through the soft segment by using a mixture of diol and triol. They also introduced the chemical crosslinking through the hard segment by using a mixture of 2-functional and 3-functional chain extender.¹² They showed that the crosslink density of polyurethane was rather low since they used the low functional diisocyanate with functionality of 2.0. This *was maybe due* to the fact that each of the polyol and chain extender reacted with diisocyanate only.

In this study, chemical crosslinking has been directly introduced through the hard segment by using a high functional diisocyanate with the average functionality of 2.9. Therefore, highly crosslinked polyurethanes were obtained. Polyurethanes synthesized in this system did not dissolve in organic solvent since they were highly crosslinked. In our present study, we investigated the thermal properties such as the glass transition temperature (T_g) and the storage and loss modulus of the highly crosslinked polyurethane by differential scanning calorimeter (DSC) and dynamic mechanical thermal analysis (DMTA), respectively. Also, we examined the hydrogen-bond effect and the crosslink density of the polyurethanes by Fourier transform infrared (FTIR) spectrometer and swelling measurement using *N,N'*-dimethylformamide (DMF), respectively.

EXPERIMENTAL

Materials

The materials used in this study were obtained from commercial sources. Polymeric 4,4'-diphe-

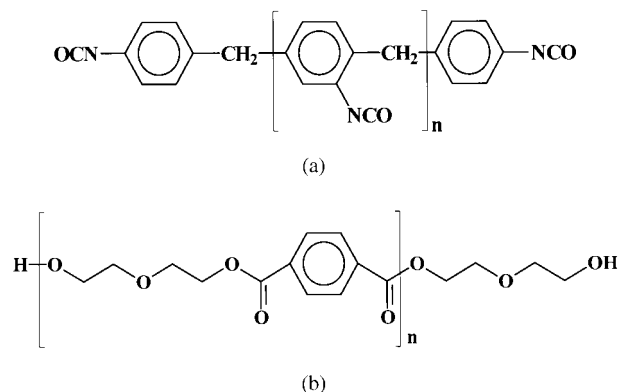


Figure 1 Chemical structure of the component: (a) polymeric 4,4'-diphenylmethane diisocyanate (MDI), $n \cong 1.0$; (b) phthalic anhydride based polyester polyol (POL), $n \cong 1.1$.

nylmethane diisocyanate (MDI) was supplied from BASF Co. Polyester polyol, synthesized from phthalic anhydride and diethylene glycol, was supplied from Stepan Co. 1,4-Butane diol was used as a chain extender. Triethylene diamine dissolved in dipropylene glycol, trade name of DABCO from Air Products, Inc., was used as a catalyst. Polyester polyol and 1,4-butane diol were dehydrated before use at 90°C for 24 h in a vacuum oven. MDI and triethylene diamine were used as received. The chemical structure and the characteristics of the materials are shown in Figure 1 and Table I, respectively.

Sample Preparation

MDI, polyol, and 1,4-butane diol were mixed for 1.5 min using a brushless type stirrer. Catalyst was added to the mixture after 1.5 min mixing, then additional mixing for 0.5 min was conducted. The stirrer speed was set at 3000 rpm throughout the mixing. Chemical composition and hard segment content of the polyurethanes are shown in Table II. The molar ratio of the polyol component was set at 1.0, and then molar ratio of the BD and MDI were varied. About 5 weight % of excess MDI (NCO/OH ratio = 1.05) was used for the completion of the reaction. Completion of the reaction was monitored by observing the disappearance of the characteristic isocyanate peak at 2275 cm⁻¹ of infrared spectra of the polyurethanes. From the sample code in Table II, the number denotes the hard segment percentage of the polyurethanes.

Measurements

Thermal properties of the polyurethane were measured by Perkin-Elmer DSC, Model DSC7.

Table I Characteristics of the Materials Used in this Study

Materials	Sample Code	Functionality	Equivalent Weight (g mol ⁻¹)
4,4'-Diphenylmethane diisocyanate ^a	MDI	2.9	133.5
Polyester polyol ^b	POL	2.0	175.0
1,4-Butane diol ^c	BD	2.0	45.1

^aSupplied from BASF Co.^bSupplied from Stepan Co.^cSupplied from Junsei Chemical Co.

Polyurethane samples of 5–10 mg were investigated in a nitrogen atmosphere from -70 to 200°C at a heating rate of 20 K min⁻¹. The samples were then reheated at the heating rate of 20 K min⁻¹ followed by 320 K min⁻¹ programmed cooling immediately between heats. To investigate the annealing effect on the thermal properties of the polyurethane, samples of 5–10 mg were annealed in the DSC at various temperatures in a nitrogen atmosphere for 5 min.

DMTA was done on the Advanced Rheometric Expansion System in torsion mode. Data were collected at a frequency of 1 Hz and at a shear strain of 0.5%. Samples were heated at a heating rate of 5 K min⁻¹ over the range from -120 to 200°C. Successive heating runs were conducted and the T_g data of polyurethane samples were found to increase slightly.

Table II Chemical Composition of the Polyurethanes (PU) Synthesized from Polyester Polyol (POL), 1,4-Butane diol (BD), and 4,4'-diphenylmethane diisocyanate (MDI)

Sample Code ^a	Molar Composition POL/BD/MDI	Hard Segment Weight Percent ^b
PU-43	1.0/0.0/0.7	43
PU-54	1.0/0.4/1.0	54
PU-61	1.0/0.8/1.0	61
PU-66	1.0/1.2/1.5	66
PU-70	1.0/1.6/1.8	70
PU-73	1.0/1.9/2.0	73
PU-79	1.0/2.9/2.7	79
PU-83	1.0/3.9/3.4	83
PU-100	0.0/1.0/0.7	100

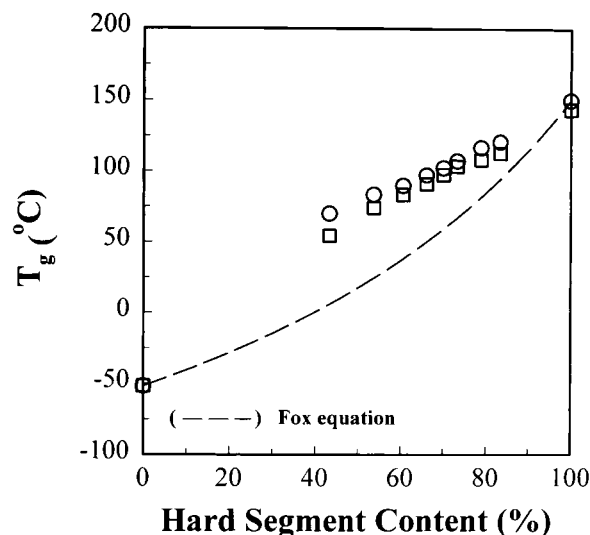
^aNumber in the sample code denotes the hard segment weight percent of the PU.^bCalculated as weight percentage of BD and MDI per total material weight.

Infrared spectra (600–4000 cm⁻¹) were obtained with a Perkin-Elmer FT-IR Series 2000. Scans of 32–128 at 2 cm⁻¹ resolution were signal averaged. By pressing the powdered polyurethane with KBr, samples were thin enough for spectroscopic analysis.

RESULTS AND DISCUSSION

DSC Analysis

Glass transition temperature (T_g) of the polyurethane samples with hard segment content is shown in Figure 2. From Figure 2, it is observed that the T_g s of polyurethane increase about 4.0–16.0°C at the second DSC heating scans. This may be due to the annealing effect, which occurs during the first DSC heating scans. Due to

**Figure 2** Glass transition temperature (T_g) of the polyurethanes with hard segment content: (□) the first DSC scan and (○) the second DSC scan.

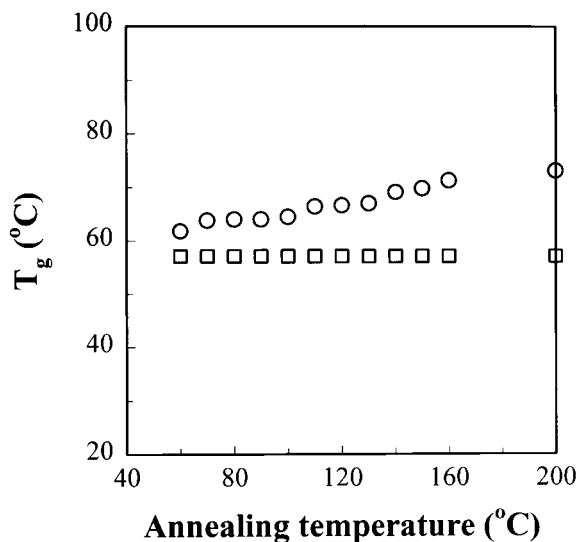


Figure 3 Effect of annealing temperature on the glass transition temperatures (T_g s) of the polyurethane (PU-43), (○) annealed, and (□) unannealed.

high functionality of the MDI used in this system, the polyurethane in this study may be crosslinked and has network structure rather than phase-separated segmented structure. From Figure 2, the values of T_g for polyurethanes determined by DSC show much higher values than the T_g calculated from Fox equation.¹⁹ Crosslinking is known to restrict mobility of the polymer chains and as a result the T_g increases.

To investigate the annealing effect on the thermal properties of the polyurethanes, samples were annealed in the DSC at various temperatures for 5 min and the T_g was measured. In Figure 3, the T_g s of the polyurethane (PU-43) after annealing are shown. From Figure 3, it is observed that the T_g s of polyurethanes after annealing increase by 4.7~16.0°C at various annealing temperatures. In the study of polyurethane elastomer by DSC measurement, Brunette and co-workers showed that chains with different chain length may coalescent to longer chains by annealing.³

Increase of T_g on annealing may be due to the increase of the physical crosslinking by hydrogen bonding or the increase of chemical crosslinking by covalent bonding in polyurethane chains or both of them. To investigate the effect of crosslinking on the annealed samples, hydrogen bonding and crosslink density have been studied by FTIR and swelling measurement, respectively, and will be discussed next sections.

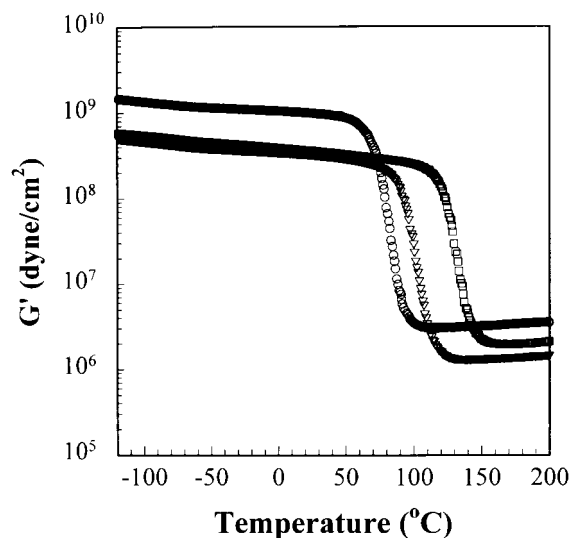


Figure 4 Storage modulus (G') of the polyurethanes: PU-43 (○), PU-66 (▽), and PU-83 (□).

DMTA

Figures 4 and 5 represents the storage modulus (G') and loss tangent peak ($\tan \delta$) of the polyurethanes (PU-43, PU-66, and PU-83) determined by DMTA. In Figure 4, a decrease of G' is observed at the temperatures around T_g s of the polyurethanes. In Figure 5, only a major α relaxation can be found in each polyurethane samples. The α relaxation in Figure 5 is associated with the T_g of the polyurethane. The values of T_g s determined by DSC and DMTA are found to be similar. From the DMTA results, it is shown that the polyure-

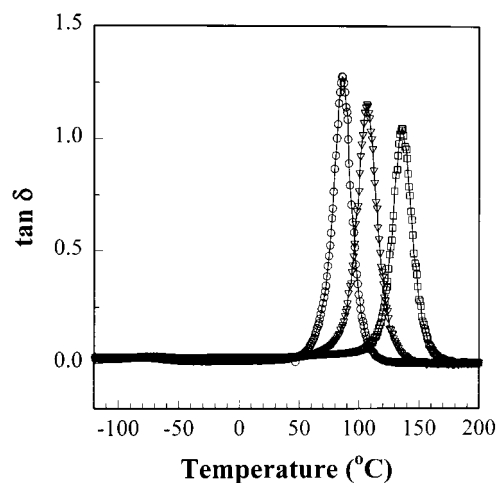


Figure 5 Loss tangent peak ($\tan \delta$) of the polyurethanes: PU-43 (○), PU-66 (▽), and PU-83 (□).

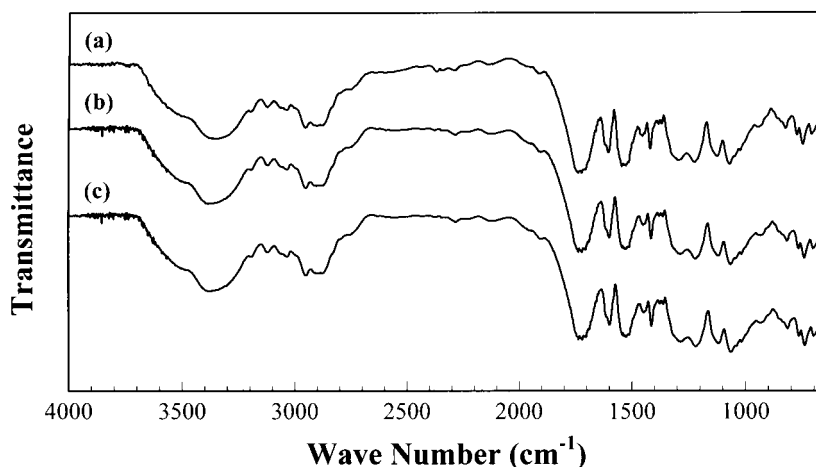


Figure 6 FTIR spectra of the polyurethane (PU-43): (a) unannealed, (b) annealed at 70°C for 5 min, and (c) annealed at 90°C for 5 min.

thane synthesized in this system has the network structure rather than phase-separated segmented structure.

FTIR Analysis

In Figure 6, infrared spectra of the annealed and unannealed polyurethanes (PU-43) are shown. The strong characteristic peak at about 2272–2275 cm^{-1} is generally associated with the NCO stretching. By observing the NCO peak, reaction rate can be monitored. From infrared spectra of the synthesized polyurethane samples, NCO peak at about 2272–2275 cm^{-1} is completely disappeared. Therefore, the reaction is assumed to be completed.

Polyurethane contains proton donor group (NH) and proton acceptor group (CO). Therefore, hydrogen bonding between hard segment–hard segment or hard segment–soft segment can exist. Hydrogen bonding have significant effect on the physical properties of polyurethane. Hydrogen-bonded NH peak in infrared spectra displays frequency shift, changes in intensity and band width.^{13–15} Hydrogen-bonded NH groups shift to lower frequencies (3300–3340 cm^{-1}), while non-hydrogen-bonded NH groups (3400–3460 cm^{-1}) do not show any frequency shift. Therefore, by measuring the frequency shift of NH groups, variation of strength of hydrogen bond can be measured.¹³

From Figure 6, infrared spectra of the polyurethanes do not show the significant change between the annealed and unannealed samples. Es-

pecially hydrogen bonded NH peak at about 3320 cm^{-1} do not show any frequency shift. From the FTIR results, it shows that average strength of hydrogen bond of the annealed samples does not change by annealing. From the FTIR results, it is suggested that the increase of the T_g s of polyurethanes by annealing is not related with the increase of hydrogen bond strength.

Swelling Measurement

By measuring the swollen volume of the crosslinked polymer, crosslink density can be determined by the following equation.²⁰

$$\frac{1}{M_c} - \frac{2}{M} = -\frac{\ln(1 - v_2) + v_2 + \chi_1 v_2^2}{\rho_2 V_1 (v_2^{1/3} - v_2/2)} \quad (1)$$

where M_c is the molecular weight between crosslinks; M , the molecular weight of linear polymer; v_2 , the volume fraction of the polymer in the swollen gel; χ_1 , the polymer–solvent interaction parameter; ρ_2 , the density of polymer in solution; and V_1 , the specific volume of solvent. The χ_1 is obtained from the solubility parameter by the following equation:

$$\chi_1 \approx 0.34 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (2)$$

where δ_1 is the solubility parameter of the solvent; and δ_2 , the solubility parameter of the polymer. DMF was used as a solvent. The δ_1 and V_1 of

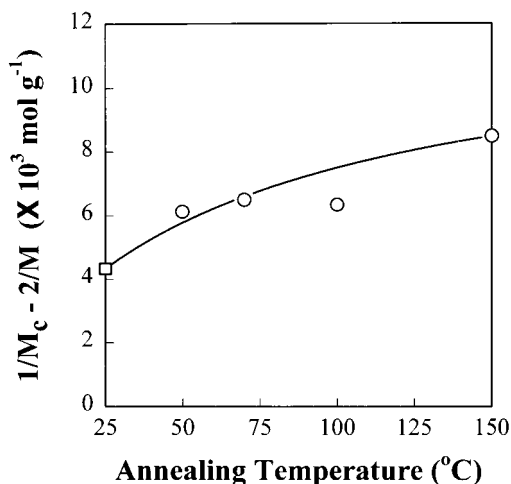


Figure 7 Effect of annealing temperature on the crosslink density of the polyurethane (PU-43): (□) without annealing and (○) annealed for 5 min.

the DMF is $24.9 \text{ J}^{1/2}/\text{cm}^{3/2}$ and $73.49 \text{ cm}^3/\text{mol}$, respectively.²⁰ The δ_2 of the polyurethane has been obtained by the group contribution method²¹ and found to be $25.54 \text{ J}^{1/2}/\text{cm}^{3/2}$. Therefore, χ_1 can be obtained from the eq. (2) and found to be 0.352.

Newer theory of rubber elasticity could be used in the interpretation of swelling.^{22–24} However, network parameter such as cycle rank, entanglement constraints, the average junction functionality, the number of chains, and the molecular weight of chains between two junctions could not be obtained due to the complexity of molecular structure of PU samples used in this study.

From Figure 7 and eq. (1), it is possible to calculate the M_c of PU-43. Since the M in eq. (1) is very large, the $1/M$ could be neglected. The M_c of PU-43 in eq. (1) is found to be between 118 and 231 g mol^{-1} . The M_c of polyurethane can be determined from the G' of rubbery plateau region²⁵ which is shown in Figure 4. The M_c of PU-43 from Figure 4 was found to be higher than the values obtained from the swelling data shown in Figure 7. For the preparation of PU samples, relatively small amount of moisture can react with the MDI generating CO_2 which inflate the PU samples. As a result, the synthesized PU samples may contain some bubbles and the M_c from the G' of Figure 4 could be overestimated.

It is known that M_c is decreased as the crosslinked density is increased. By assuming that M is constant, $1/M_c - 2/M$ in eq. (1) will be increased as the crosslink density increases. From Figure 7, it appears that the M_c is de-

creased after annealing at various temperatures, that is, the crosslink density is increased after annealing the polyurethane samples. Therefore, it is suggested that the increase of T_g of the polyurethanes by annealing is not due to the increase of the hydrogen bond strength but mainly due to the increase of the crosslink density.

CONCLUSIONS

Polyurethanes were synthesized using the high functional MDI, polyester polyol, and 1,4-butane diol. From the result of thermal analysis by DSC and DMTA, single T_g s were observed in the polyurethane samples at all the formulated compositions. From this result, it is concluded that the polyurethanes synthesized in this study have crosslinked structure rather than the phase-separated segmented structure because of the high functionality ($f = 2.9$) of the MDI.

By annealing the polyurethane samples using DSC, the T_g s were increased by $4.7\sim 16.0^\circ\text{C}$ at the various annealing temperatures. From the results of FTIR and swelling measurement of polyurethanes, it is concluded that the increase of T_g of the polyurethanes by annealing is not due to the increase of the hydrogen-bond strength but mainly due to the increase of the crosslink density.

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