



STRUCTURE-TENSILE PROPERTIES OF POLYURETHANES

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Abstract—A series of hydroxyl terminated polybutadiene-(HTPB) based polyurethanes (PUs) were synthesized by solution polymerization with different types of diisocyanates, hard segment contents, NCO/OH ratio and polymerization methods. Spectroscopic and stress-strain studies were carried out to elucidate the structure-property relationships existing in these polymers. It was found that the binding of the hard segment and the flexibility of soft segments had subtle effects on the properties of stress-strain at break. The segregation between hard and soft segments was manifested by incompatibility between hard and soft segments, steric hindrance of urethane groups and the extent of interchain hydrogen bonding. The hydrogen bonding index (HBI) measured by FTIR was employed to show the extent of interchain hydrogen bonding, which affects the segregation and hence the stress-strain property of the prepared films. Films with higher hard segment content and NCO/OH ratio, 4,4'-diphenylmethane diisocyanate (MDI) and the one-stage polymerization method exhibit higher stress at break and lower strain at break. The measurement of FTIR was used to identify the degree of phase segregation and to correlate the stress-strain properties of PUs with different compositions. © 1997 Elsevier Science Ltd

INTRODUCTION

There have been considerable research put forth to develop an understanding of the property-structure relationships in segmented polyurethanes [1–3]. These materials derive many of their useful properties from the incompatibility of the hard and soft segments and subsequent phase segregation into separate domains. HTPB-based PUs provide no possibility of hydrogen bonding between the hard and soft segment, in contrast to the more familiar polyester or polyether macroglycol-based PUs. Since the hydrogen-bonding interactions are limited to the hard segment components, studies of HTPB-based PUs could focus on the role of hydrogen bonding in determining the extent of phase segregation and hence the related polyurethane stress-strain properties.

Many reports have dealt with the structure and mechanical properties of HTPB-based PUs toward chemical composition [4], morphology [5], molecular weight [6], hard segment content [7–8], types of component [9], thermal history [10], strain rate [11], triol crosslinking agent content [12] and phase segregation [13–15].

Due to the many factors affecting the mechanical properties of PUs [16–17], it is therefore of interest to examine the structure-property relations in a series of segmented HTPB-based PUs in which the polar and hydrogen-bonding interactions between hard and soft segment units are eliminated. The purpose of this study is to synthesize the HTPB-based PUs and investigate the segregation of the prepared PUs. The PU elastomers consist of HTPB, various diisocyanates, different hard segment contents, NCO/OH ratio, polymerization method. The degree of segre-

gation between hard and soft segments was studied in terms of incompatibility, steric hindrance and extent of hydrogen bonding. The hydrogen-bonding index (HBI) measured by FTIR was utilized to manifest the segregation and stress-strain property of the prepared PUs.

EXPERIMENTAL

Materials

The chemicals used in this study were 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI Desmodur W of Mobay Co.), isophorone diisocyanate (IPDI), hydroxyl-terminated polybutadiene (HTPB, equivalent weight 1333 g, R-45M of ARCO Co.), 1,4-butanediol (1,4-BD) as a chain extender, and dibutyltin dilaurate (DBTDL) is used as catalyst. Dimethyl formamide (DMF) and toluene are used as solvent for the preparation of PU solution.

Preparation of polyurethane membrane

The two-stage PUs were polymerized first by a —NCO-terminated prepolymer and then chain extended with 1,4-BD to give a 25 wt% solid content after the theoretical —NCO content was reached. It was diluted to a 15–20 wt% solid content after the chain extended reaction proceeded for 30 min. The reaction was terminated as the —NCO groups were completely consumed, as confirmed by the disappearance of the IR absorption at 2280 cm⁻¹.

PUs films were prepared by pouring the solution mixture onto a glass plate. The solvent in the casting solution was evaporated by degassing at 50°C for 24 hr. The dried PU films were peeled from the plate after it had been immersed in deionized water for several hours. The PU films were dried in a desiccator and stored at a relative humidity of 50% and 25°C for 5 days before testing.

IR spectroscopy

IR spectra of dry films were obtained by a Jasco FTIR-300E spectrometer. Spectra were collected at a resolution of 2 cm^{-1} . The absorption peak due to hydrogen-bonded C=O stretching is centred at 1700 cm^{-1} and that due to free C=O stretching is centred at $\sim 1720\text{ cm}^{-1}$. Hydrogen-bonded carbonyl bands will correspond to those groups that are in the interior of hard segments, while the free bands may correspond to those groups in the hard segment domains, in the soft domains or at the interface [18]. In these butadiene-containing polyurethanes, hydrogen bonding occurs only between urethane segments since the carbonyl in the urethane linkage and the urethane alkoxy oxygen are the only proton acceptors. The extent of the carbonyl absorption group participating in hydrogen bonding is expressed by the hydrogen-bonding index (HBI), which is as the relative absorbances of the hydrogen-bonded carbonyl peak to that of free hydrogen-bonded carbonyl peak [19–21] and detected by FTIR.

Property measurement

A test of stress-strain at break was performed according to the ASTM D412 standard method at a crosshead speed of 50 cm/min , with a clamp distance of 3 in. A Du Pont 9000 instrument was used for DSC measurement, using liquid nitrogen for cooling and with a heating rate of 10°C/min in the temperature range between -120 and 150°C . The solubility parameter (δ) was estimated by the calculation of Fedors' molar attraction constant data and also checked by the intrinsic viscosity method [22–23].

RESULTS AND DISCUSSION

Types of diisocyanates

The compositions of HTPB-based PUs used in this section are given as equivalent ratios of HTPB/diisocyanate/1,4-BD = $1/3/2$, $1/4/3$, $1/8/7$, $1/12/11$ of MDI, H_{12} MDI and IPDI diisocyanate, respectively. The structure of MDI and H_{12} MDI is linear, while that of the IPDI possess steric structure. The polarity of MDI is high, H_{12} MDI and IPDI are non-polar with respect to the HTPB soft segment. The purpose of this section is to study the effect of chemical structure and polarity on the property of stress-strain at break.

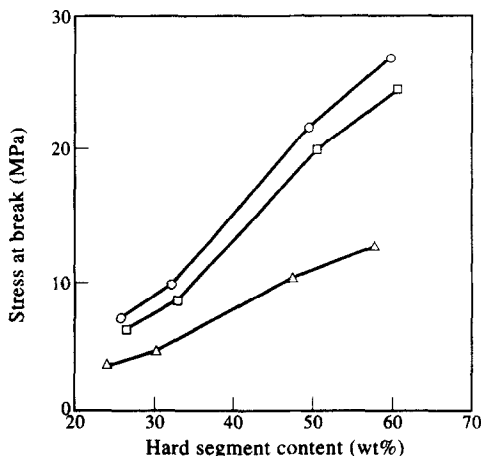


Fig. 1. Effect of hard segment content on the property of stress at break. (○) MDI series, (□) H_{12} MDI series and (△) IPDI series.

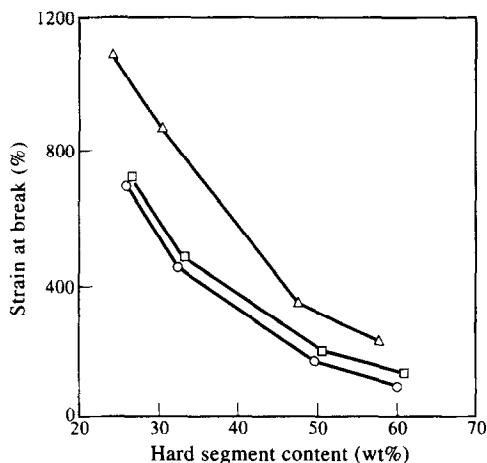


Fig. 2. Effect of hard segment content on the property of strain at break. (○) MDI series, (□) H_{12} MDI series and (△) IPDI series.

Figures 1 and 2 show that the properties of stress-strain at break of MDI-based PUs are almost the same as that of H_{12} MDI-based PUs and different from that of IPDI-based PUs at the same stoichiometry. In general, MDI-based PUs possess higher stress and lower strain property behaviour due to the fact that there are two symmetric, ordered aromatic rings in the main chain of MDI, which possess higher intermolecular interactions between hard and hard segments. However, the above explanation fails to account for almost the same stress-strain properties of MDI and H_{12} MDI-based PUs. On the other hand, we can obtain that the solubility parameter difference of $\delta_{\text{MDI}} - \delta_{\text{HTPB}}$ is larger than that of $\delta_{\text{H}_{12}\text{MDI}} - \delta_{\text{HTPB}}$, as shown in Table 1. The larger solubility difference (i.e. more incompatibility) causes higher segregation. The competition of the above two effects shows that intermolecular interaction is only slightly higher than incompatibility on the segregation and stress-strain property.

The properties of stress-strain at break of IPDI-based PUs are largely different from those of H_{12} MDI-based PUs. The solubility parameter difference of $\delta_{\text{IPDI}} - \delta_{\text{HTPB}}$ is almost the same as that of $\delta_{\text{H}_{12}\text{MDI}} - \delta_{\text{HTPB}}$, as shown in Table 1. It may be that the intermolecular interaction of IPDI-based PUs is lower than that of H_{12} MDI-based PUs due to the steric effect of IPDI structure.

From the view point of intermolecular hydrogen bonding, the HBI values of these H_{12} MDI and IPDI-based PUs are almost the same, but are lower than that of MDI-based PUs, as shown in Fig. 8. HTPB soft segments with H_{12} MDI or IPDI are more compatible than that with MDI, which is more polar than the former two diisocyanates. More polarity of MDI induces increased intermolecular interaction and hence greater HBI values. The greater HBI values indicate increased participation of the carbonyl group in hydrogen bonding of hard segment [24]. This may explain why the properties of stress at break of MDI-based PUs are higher than those of H_{12} MDI and IPDI-based PUs.

Table 1. Solubility parameter^a of raw materials

Materials	HTPB	IPDI	H ₁₂ MDI	MDI	1,4-BD
Solubility parameter (δ , cal ^{1/2} /cm ^{3/2})	8.67	8.66	8.98	13.95	11.00

^aObtained by an estimation method.

Effect of hard segment content

Figures 1 and 2 show that, regardless of any type of diisocyanate, the stress at break increases as the increase of hard segment content, while the strain at break decreases. The increase of hard segment content increases the intermolecular attraction between hard and hard segment due to the hydrogen bonding between —NH and —C=O of hard segment and hence, the increase of stress and the decrease of strain property. From the view point of the hydrogen-bonding index (HBI), which is the indication of the degree of hydrogen bonding of the carbonyl group, increases with the increasing hard segment content, regardless of any type of diisocyanate as shown in Fig. 3. The increase of HBI values as the increase of hard segment content will increase the phase mixing, which increases the stress property and decreases the strain property.

Effect of NCO/OH ratio

PU films with different NCO/OH ratios were prepared by casting the solution, which is a viscous fluid and polymerized 30 min after the addition of 1,4-BD to the —NCO terminated prepolymer. The NCO/OH ratio is defined as the equivalent ratio between the materials containing NCO groups and those containing OH groups. PU composition with steric structure of IPDI used in this section is due to the increase of NCO/OH ratio, which showed an appreciable effect on the stress-strain property compared with that of H₁₂MDI and MDI-based PUs. As the NCO/OH ratio is larger than one, the three-dimensional allophanate or biuret crosslinks [25] or polar urea structure will be formed and the number of urethane groups are increased. The introduction of chemical allophanate crosslinks has a

detrimental effect on the hard domains. The increase of chemical crosslinking leads to a change in morphology [26] and affects the mechanical properties [27].

The increase of these polar groups (urea or urethane) can be verified by the increase of HBI value as the NCO/OH value increases, as shown in Fig. 4. The existence of three-dimensional allophanate or biuret structure restricts the mobility of the molecular chain. The increase of intermolecular attraction of hard to hard segments by the increase of NCO/OH ratio tends to increase the stress property and decrease the strain property, as shown in Fig. 5.

Effect of mixed diisocyanate

The PU compositions used in this section are HTPB/MDI/1,4-BD = 1/3/2, 1/4/3, 1/8/7 and 1/12/11. While PUs compositions of mixed diisocyanate are HTPB/MDI/IPDI/1,4-BD = 1/2/1/2, 1/3/1/3, 1/6/2/7 and 1/8/4/11. Figure 6 shows that the change of stress at break of PUs with mixed MDI and IPDI were observed to be much lower than the membranes with single MDI at the same stoichiometry. While the strain at break has the contrary result in stress properties, as shown in Fig. 7. This phenomenon can be explained as the synergistic effect of high polarity of MDI and the asymmetric structure of IPDI contribute to the increase of segregation and hence the large change of the stress-strain property of PUs with mixed diisocyanate.

Effect of one- or two-stage polymerization method

H₁₂MDI-based PUs are used in this section due to their non-polar and symmetric structure. Focus on the effect of polymerization method can then be obtained. Figure 8 shows that the properties of stress

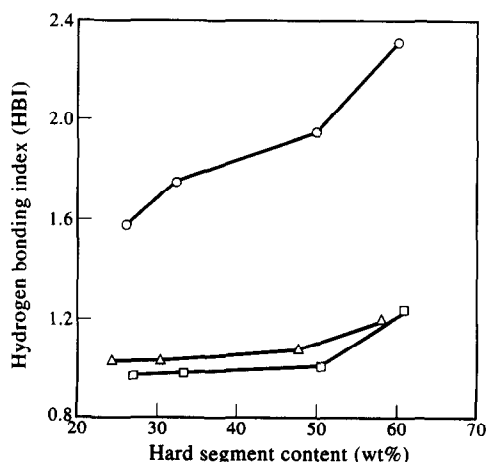


Fig. 3. Relationship between hydrogen-bonding index (HBI) and hard segment content. (○) MDI series, (□) H₁₂MDI series and (△) IPDI series.

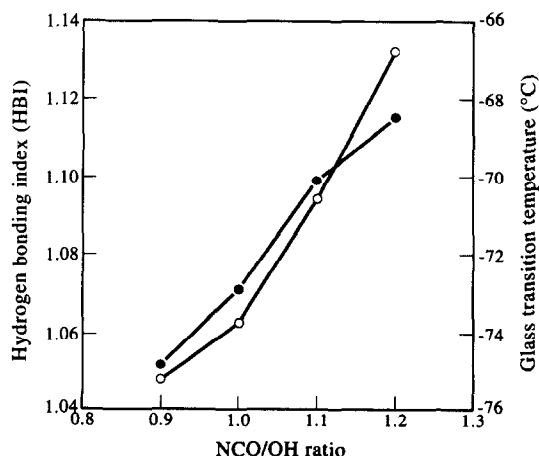


Fig. 4. Relationship between hydrogen-bonding index (HBI) (○), glass transition temperature (●) and NCO/OH ratio of HTPB/IPDI/1,4-BD = 1/5/4 based PUs.

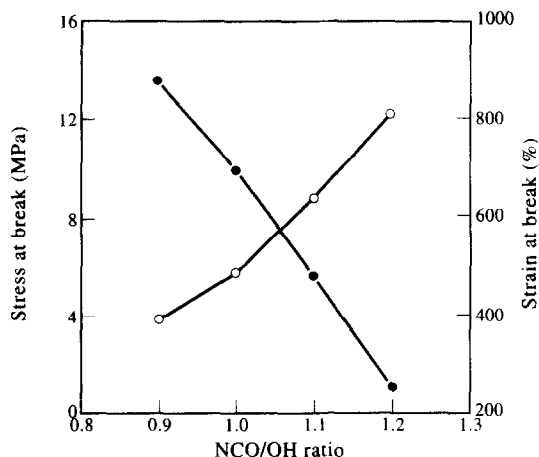


Fig. 5. Effect of NCO/OH ratio on the property of stress (○) and strain (●) at break of IPDI-based PUs.

at break of two-stage polymerized PUs are all lower than those of the corresponding one-stage ones. The properties of strain at break possess the contrary trend with respect to the properties of stress at break as shown in Fig. 9. It was shown that one-stage polymerized PUs contained hard segments of greater average length [28]. This can be shown by the hydrogen-bonding index (HBI) and glass transition temperature of PU polymers. Higher HBI values indicate stronger interaction between hard segments. It is clear that the HBI values of one-stage polymerized PUs were always higher than those of two-stage ones, as shown in Fig. 10. Comparing the glass transition temperatures of both soft and hard segment (T_{gs} and T_{gh}). We also found that one-stage polymerized PUs had lower values of T_{gs} and higher T_{gh} than that of two-stage polymerized PUs, as shown in Fig. 11. The above informations indicate that the one-stage polymerized PUs had more hard segments forming aggregates and less dispersing in the soft segment region. On the contrary, the two-stage

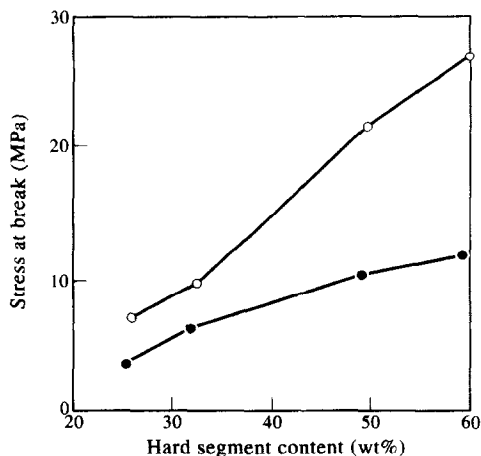


Fig. 6. Effect of diisocyanate on the property of stress at break. (○) MDI series and (●) mixed diisocyanate of MDI and IPDI series.

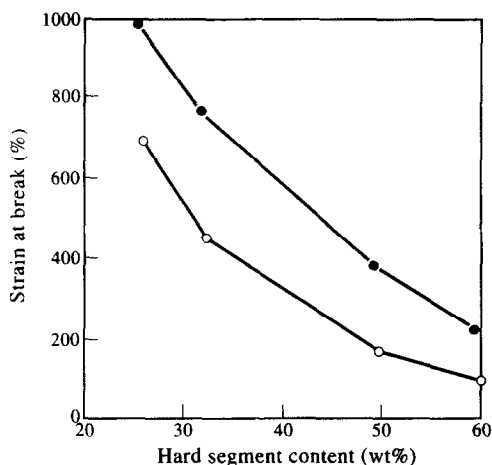


Fig. 7. Effect of diisocyanate on the property of strain at break. (○) MDI series and (●) mixed diisocyanate of MDI and IPDI series.

polymerized PUs contained more hard segments dispersing in the soft segment region, which causes more segregation between intermolecules. It may be the reason why one-stage PUs have higher stress and lower strain compared with the two-stage counterparts.

CONCLUSION

There is no greater extent of hydrogen bonding between hard and soft segments of these HTPB-based PUs. The driving force for segregation is between the polar hard segment and the non-polar HTPB soft segment. In this study, we use HBI values for illustrating the degree of segregation of non-polar HTPB-based PUs. The higher value of HBI was observed for higher NCO/OH values, hard segment content and one-stage PUs. The degree of segregation and strain at break are increased as the HBI value decreased. PUs with mixed diisocyanates of MDI and

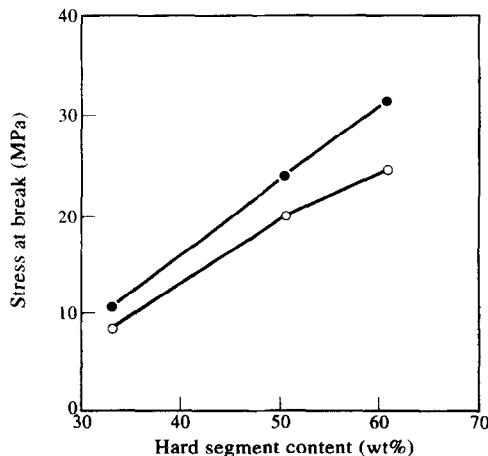


Fig. 8. Effect of polymerization method on the property of stress at break of H₁₂MDI-based PUs. (○) Two-stages and (●) one-stage.

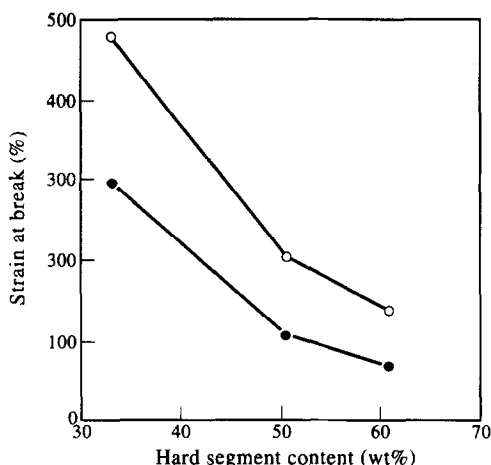


Fig. 9. Effect of polymerization method on the property of strain at break of H_{12} MDI-based PUs. (○) Two-stages and (●) one-stage.

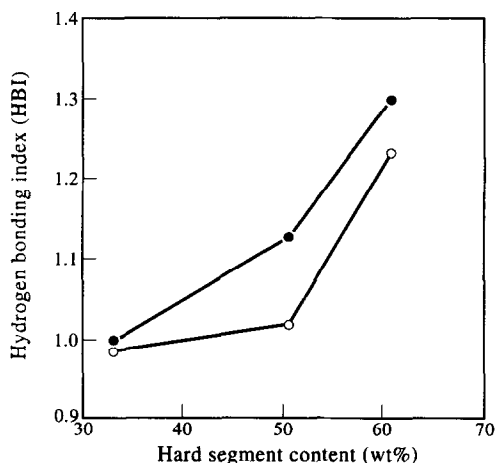


Fig. 10. Relationship between hydrogen-bonding index (HBI) and hard segment content of H_{12} MDI-based PUs with different polymerization method. (○) Two-stages and (●) one-stage.

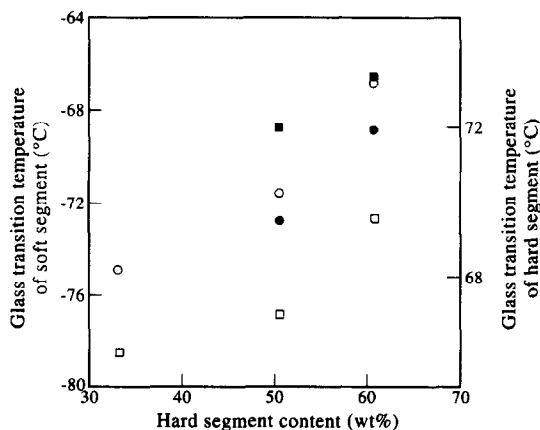


Fig. 11. Relationship between T_{gs} , T_{gh} and hard segment content of H_{12} MDI-based PUs with different polymerization method. T_{gs} : (○) two-stages, (□) one-stage; T_{gh} : (●) two-stages, (■) one-stage.

IPDI exhibit lower stress at break than that with the single diisocyanate of MDI-based PUs. PUs with MDI possess nearly the same tensile property as those with H_{12} MDI. Stress at break increases with the increase of NCO/OH values and hard segment content. PUs from the one-stage polymerization method have higher stress at break than those from two-stage polymerization method.

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