

Tensile Property of Modified Hydroxyl-Terminated Polybutadiene-Based Polyurethanes

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ABSTRACT: Modified hydroxyl-terminated polybutadiene (HTPB)-based polyurethanes (PUs) were prepared by three different processes: crosslinkage of the soft segment, complexation of the hard segment, and the interpenetrating network (IPN). Cross-linked PU films were prepared by the addition of a crosslinking agent of divinylbenzene (DVB) to the 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI) and 1,4-butanediol (1,4-BD)-based PUs. The ionic polymer was prepared by adding *N*-methyldiethanolamine (MDEA), which possesses tertiary amine used as chain extender, to the HTPB- H_{12} MDI-based PUs and then complexed by cupric chloride with MDEA. An IPN was formed by the introduction of 4-vinylpyridine (4-VP) to the benzoyl peroxide (BPO)-crosslinked HTPB- H_{12} MDI-1,4BD-based PUs. FTIR was utilized to identify the segregation between hard and soft segments and structure change, which affects the tensile properties. The change of the glass transition temperature was detected by DSC, which can be used to manifest the modified PUs. Thermal decomposition behaviors conducted by TGA were used to investigate the formation of an IPN. The hydrogen-bonding index (HBI), frequency difference, and shift as a measure of the phase segregation and the average strength of the interpolymer hydrogen bonds were utilized to study the intermolecular interaction and tensile property of the prepared PUs. The effect of the hard-segment content, DVB content, amount of cupric ion, and 4-VP content on the tensile property were investigated. The stress was largely increased by the modification of PUs, while the strain still remains an appreciable value compared with that of unmodified PUs. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1235–1245, 1997

INTRODUCTION

Polyurethane (PU) materials possess very attractive bulk mechanical properties due to the presence of phase-separated structures. Its applications are varied, such as for medical implants, membranes, adhesives, and coatings. Superior hydrolytic stabilities and high mechanical property performances of HTPB show surprising utility in many fields.^{1–3} HTPB-based PUs have been used for gas separation research because of their

low-temperature flexibility and high segregation between hard and soft segments.^{4,5} Pervaporation separation of an ethanol/water mixture⁶ was also studied with HTPB-based PUs due to the high swelling behavior of the HTPB soft segment with ethanol.

Many reports have dealt with the structure and mechanical properties of HTPB-based PUs.^{7–19} But the HTPB-based PUs generally exhibit inferior mechanical properties compared to the conventional PUs.²⁰ The purpose of this study was to prepare modified HTPB-based PUs for the improvement of mechanical properties. The modification was carried by the crosslinkage of the

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HTPB soft segment, complexation of the hard segment, and the interpenetrating network (IPN). From the reported literature, the crosslinkage of the PU polymer was generally obtained by the introduction of diol and triol mixtures to the PU prepolymer.^{21,22} Yoshikawa et al.²³ studied the crosslinking of polybutadiene (PB) membranes arising from chemical reactions with the crosslinking agent of bis(1-methyl-1-phenyl-ethyl)peroxide at the sites of unsaturation in the polymer chain. Sun and Ruckenstein prepared divinylbenzene (DVB)-crosslinked styrene/butadiene/styrene (SBS) and styrene/ethylene-butylene/styrene (SEBS) for alcohol permselective membranes, while PU ionomers were prepared by incorporating a chain extender containing tertiary amines and then reacting with alkyl halides²⁵ or glycolic acid.²⁶ Others are formed by the use of sulfonate containing a chain extender²⁷ or by the addition of LiClO₄ to the PUs.^{28,29}

This study attempted to prepare crosslinked HTPB-based PUs by using DVB to crosslink between hard and soft segments of butadiene. The PU complexes were obtained by adding cupric chloride to the HTPB-H₁₂MDI-MDEA-based PU solutions, while IPNs were prepared by adding 4-VP to the BPO-crosslinked HTPB-H₁₂MDI-1,4BD-based PUs. The effect of the hard-segment content, cupric chloride content, and 4-VP content on the tensile property was studied. Hydrogen-bonding index (HBI) values for indication of phase segregation were measured by FTIR. The measurements of DSC and FTIR were used to identify the degree of crosslinking and complexation and, hence, to correlate them with the tensile property. HBI values, the IR frequency difference, the frequency shiftment, and the glass transition temperature were used for the identification of phase homogeneity and for the effect on the tensile property.

EXPERIMENTAL

Materials

The chemicals used in this study were 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI Desmodur W of Mobay Co.), hydroxyl-terminated polybutadiene (HTPB, equivalent weight 1333 g, R-45M of ARCO Co.), 1,4-butanediol (1,4-BD), and *N*-methyldiethanolamine (MDEA) as chain extenders and dibutyltin dilaurate (DBTDL) was used as a catalyst. Dimethylformamide (DMF)

and toluene were used as solvents for the preparation of the PU solution. Benzoyl peroxide (BPO) was used as an initiator for the preparation of divinylbenzene (DVB)-crosslinked PUs and as a crosslinking agent to the PU solution of 4-VP/PU IPNs. The 4-VP monomer was purified by vacuum distillation.

Preparation of Polyurethane Membrane

The two-stage PUs were polymerized first by a —NCO-terminated prepolymer and then chain-extended with 1,4-BD (or MDEA) under 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 infrared absorption at 2280 cm⁻¹.

Uncrosslinked PU films were prepared by pouring the solution mixture onto a glass plate to a thickness of 600 μm. The solvent in the casting solution was evaporated by degassing at 65°C for 24 h. 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.

Crosslinked films were initially prepared by adding 0.5 wt % (based on solid PU content) of BPO to the HTPB-H₁₂MDI-1,4BD-based PU solution (15 wt % solid content) in the closed vessel at room temperature for 30 min. Then, 1.0, 2.0, 3.0, and 5.0 wt % of DVB (based on solid PU content) were added to the above PU solution at 65°C for 30 min, respectively, and then cooled to room temperature immediately. All the following film-preparation steps were the same as those of uncrosslinked films.

Complexed films were prepared by adding cupric chloride to the HTPB-H₁₂MDI-MDEA-based PU solutions. Cupric chloride with MDEA, of 1/3 or 1/4 mol ratio content, was added to the three different PU compositions, respectively. Cupric ion forms a complex with tertiary amine of MDEA by ion-dipole interaction.³⁰ The dried ionized films were peeled from the plate after it had been put into refrigerator and into the frozen state for several hours. All these films were then put in an oven under a vacuum at 70°C for 48 h for further degassing of the solvent residue. Finally, the samples were kept under a vacuum at room

temperature for at least 5 days prior to the property testing.

IPNs of HTPB-based PU and poly(4-VP) were synthesized by sequential polymerization. Initially, crosslinked films were prepared by adding 1.0 wt % (based on PU solid content) of BPO to the HTPB-H₁₂MDI-1,4BD-based PU solution and then reacted at 65°C for 6 h and cooled to room temperature immediately. Addition of BPO (0.5 wt %) and different weight contents of 4-VP and DVB (1.0 wt %) into the above BPO-crosslinked PU solution at room temperature were mixed homogeneously for about 20 min. All the following film-preparation steps were the same as those of uncrosslinked films.

Infrared Spectroscopy

Infrared spectra of PU films were obtained by a JASCO FTIR-310E spectrometer. Spectra were collected at a resolution of 2 cm⁻¹. The peak due to hydrogen-bonded C=O stretching is centered at 1700 cm⁻¹ and that due to free C=O stretching is centered at about 1717 cm⁻¹, while the peak of bonded —NH stretching is at 3320 cm⁻¹ and that of free —NH stretching is at 3442 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 or in the soft domains or at the interface.³¹ 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 the relative absorbancies of the hydrogen-bonded carbonyl peak ($A_{C=O, \text{bonded}}$) to that of free hydrogen-bonded carbonyl peak ($A_{C=O, \text{free}}$).³² The frequency difference is defined as $\Delta\nu = \nu_f - \nu_b$, where ν_f and ν_b are the frequencies of maximum absorption for the free and hydrogen-bonded —NH group, respectively. The frequency difference, $\Delta\nu$, in the stretching frequency is considered as a measure of the strength of the hydrogen bond between molecules.

Property Measurement

Testing of stress and strain at break were performed according to the ASTM D412 standard method at a crosshead speed of 50 cm/min, with

a clamp distance of 3 in. A DuPont 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. ΔT_g is the temperature difference between the glass transition temperature of the hard segment (T_{gh}) and the glass transition temperature of soft segment (T_{gs}). A Perkin-Elmer 240C, 2400EA, was used for the analysis of the pyridine content in 4-VP/PU IPNs. TGA thermograms were obtained by a DuPont 951 thermogravimetric analyzer with a heating rate of 20°C/min in the temperature range from 50 to 600°C under a continuous nitrogen flow of 30 mL/min for the investigation of IPN formation.

Crosslinking Reaction

The mechanism of DVB- or BPO-crosslinked PUs was as follows: BPO was decomposed first and an active site was produced by capturing the hydrogen atom nearing the double bonds of the HTPB soft segment. This active site then reacted with DVB and then with other HTPB chains with or without an active site.²⁴ BPO-crosslinked PUs are the same as the above description without the addition of DVB.^{5,23} Then, two crosslinking types between the HTPB soft segments of PUs was formed.

RESULTS AND DISCUSSION

Effect of Hard-segment Content on DVB Crosslinked PUs

HTPB-H₁₂MDI-based PUs were used in this study due to the linear structure and nonpolar property of H₁₂MDI, which does not have the effect of incompatibility (e.g., 4,4'-diphenylmethane diisocyanate with HTPB) or steric hindrance (e.g., isophorone diisocyanate with HTPB). Figures 1 and 2 show that the stress of PUs are all increased as the hard-segment content increases and, on the contrary, the strain decreases.³³ The hard domain acts as the physical crosslink due to the interchain hydrogen bonding between hard segments. The higher is the hard-segment content, the more crosslinks between the interchains produced. It was suspected that two effects may be introduced by the increase of hard-segment content. One effect was the enlargement of hard-segment aggregation and the other was the restriction of the movement of soft segments, which could be shown

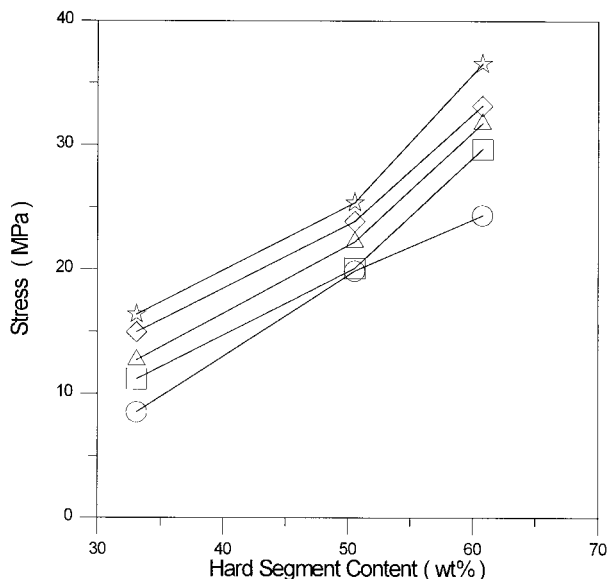


Figure 1 Effect of hard-segment content on the stress property of PUs with different DVB content (wt %): (○) 0; (□) 1.0; (△) 2.0; (◇) 3.0; (☆) 5.0.

by the HBI and T_{gs} values. As shown in Figure 3, the HBI values are increased with increase of the hard-segment content. The increase of HBI values indicated that the intermolecular attraction between the hard segments increased. Figure 4 shows that the T_{gs} increased as the hard-segment content increased. The increase of T_{gs} indicates the decrease of soft-segment mobility. This may

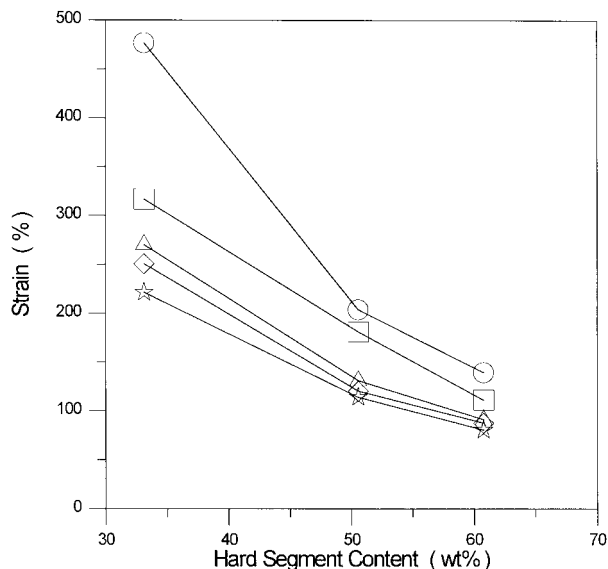


Figure 2 Effect of hard-segment content on the strain property of PUs with different DVB content (wt %): (○) 0; (□) 1.0; (△) 2.0; (◇) 3.0; (☆) 5.0.

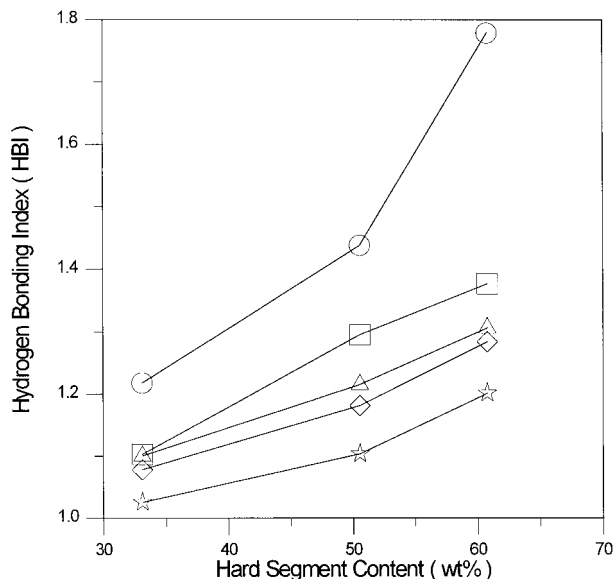


Figure 3 Relationship between hard-segment content and HBI value with different DVB content (wt %): (○) 0; (□) 1.0; (△) 2.0; (◇) 3.0; (☆) 5.0.

indicate that the introduction of DVB affects the morphology and tensile property.

Effect of DVB Content on Crosslinked PUs

Figures 5 and 6 show that the stress of PUs are all increased with increasing DVB content, while the strain decreases. The unsaturated double

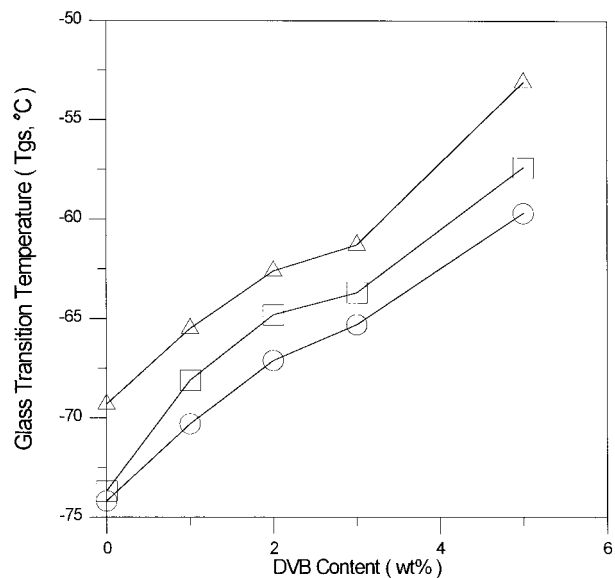


Figure 4 Effect of DVB content on the glass transition temperature of the soft segment of PUs with different composition: (○) 1/4/3; (□) 1/8/7; (△) 1/12/11.

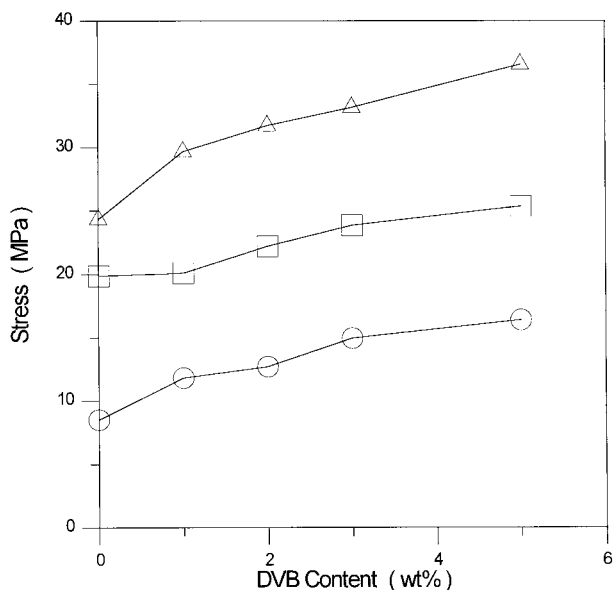


Figure 5 Effect of DVB content on the stress property of PUs with different composition: (O) 1/4/3; (□) 1/8/7; (Δ) 1/12/11.

bonds of the HTPB soft segment are crosslinked by DVB, which possesses a rigid benzene ring structure. These molecular chains of the cross-linked HTPB soft segment will be more extended and stretched tightly. The intermolecular attraction is then increased and, hence, the increasing stress and decreasing strain accompany with

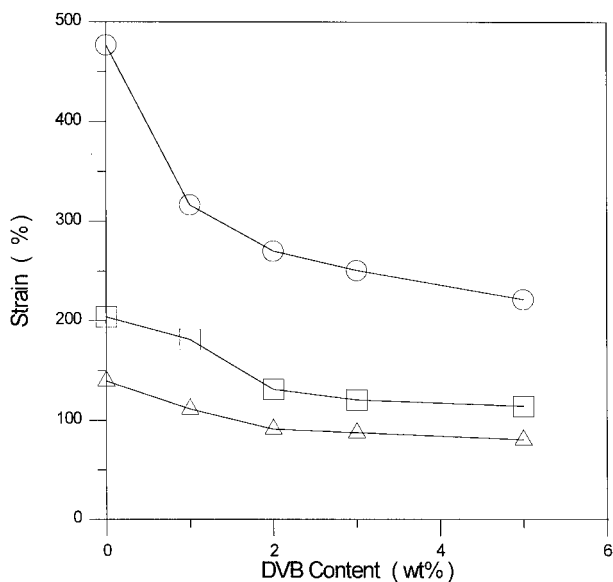


Figure 6 Effect of DVB content on the strain property of PUs with different composition: (O) 1/4/3; (□) 1/8/7; (Δ) 1/12/11.

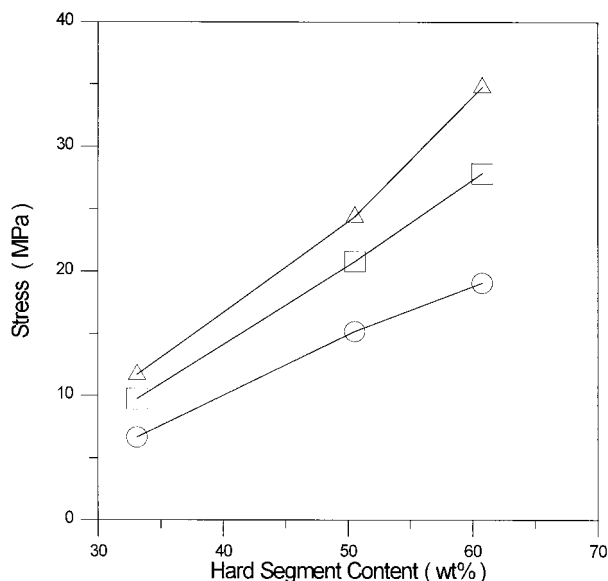


Figure 7 Effect of hard-segment content on the stress property of PUs with different content of cupric chloride (mol ratio): (O) 0; (□) 1/4; (Δ) 1/3.

the increase of DVB content. From the HBI measurement shown in Figure 3, we found that the HBI values decreased after DVB was introduced. The higher the DVB content possessed the lower is the HBI value. This indicates that the crosslinkage between soft segments hindered the hydrogen bonding between hard segments. The mobility of the soft segment decreased, which can also be evidenced by the increase of T_{gs} after DVB addition as shown in Figure 4. The degree of T_{gs} increases from 0, to 1.0, 2.0, and 3.0 wt % of DVB-crosslinked HTPB-based PUs is lower than that from 3.0 to 5.0 wt % of DVB-crosslinked PUs. There are two effects of DVB introduction on the T_{gs} : One is the increase of interchain spacing while the other is the increase of rigidity of the HTPB soft segment by the introduction of a benzene ring. The former effect decreases the T_{gs} , while the latter increases the T_{gs} of PUs. The competition of the above two effects shows that rigidity has the superior influence on the T_{gs} . Rigidity has special effect on the T_{gs} of crosslinked PUs with 5 wt % DVB content as shown in Figure 4.

Complexation of Hard Segment by Cupric Chloride

PU complexes were prepared by complexing cupric ion with the tertiary amine of MDEA. It was due to poor film formation; our studies were restricted to film containing cupric chloride lower than a 1/2 CuCl_2 to MDEA mol ratio. The film's

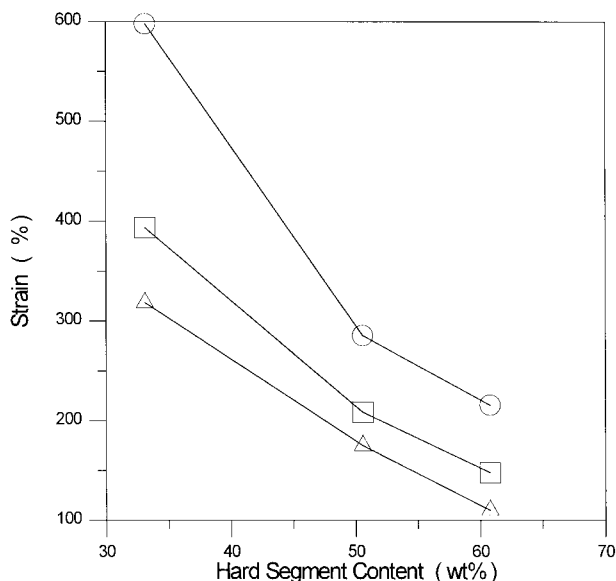


Figure 8 Effect of hard-segment content on the strain property of PUs with different content of cupric chloride (mol ratio): (O) 0; (□) 1/4; (Δ) 1/3.

tensile property of the ones containing lower than a 1/5 mol ratio of cupric ions was only slightly higher than that of the one without any cupric ion complexation. As shown in Figure 7, the stresses of PUs containing cupric ion were all higher than those of zero cupric ion content and increased as the cupric chloride content increased, while that of the strain property decreases as the addition of cupric chloride increased, as shown in Figure 8. It also shows that the stress of PUs increase with increasing hard-segment content, while the strain decreases. The cupric ion interacts with the tertiary amine of MDEA as well as with the carbonyl and secondary amine in urethane linkage³⁰; the cupric ion addition may enhance the binding between hard segments and subsequently acts as an increase of hard-segment content. As described in the above section, the stronger the intermolecular interaction possessed, the higher is the hard-segment content. This may explain why the tensile property of complexed PUs are varied by the addition of cupric chloride.

PUs with a higher hard-segment content have a larger variation of the stress property. The T_{gs} and T_{gh} values are all increased with the hard-segment content or the cupric chloride content as shown in Figures 9 and 10. The addition of cupric chloride restricts the chain mobility and increases the intermolecular attraction. This may contribute to the increase of the T_{gs} and T_{gh} of PUs containing cupric chloride.

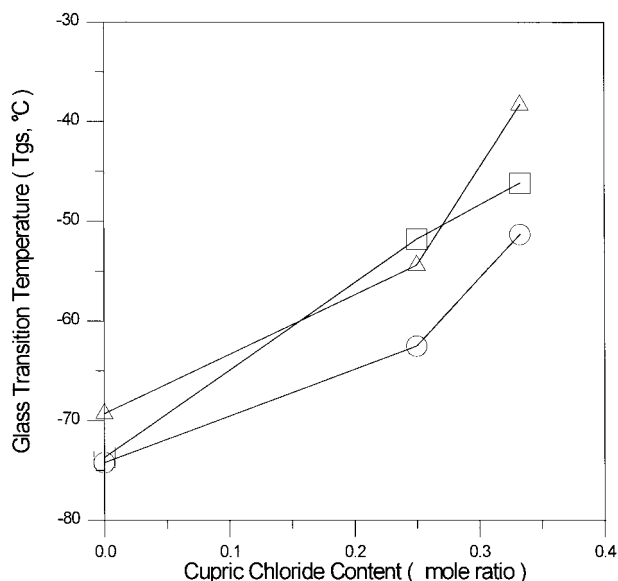


Figure 9 Effect of cupric chloride content (mol ratio) on the T_{gs} of PUs with different composition: (O) 1/4/3; (□) 1/8/7; (Δ) 1/12/11.

The change of the structure and tensile property of these PU complexes can be investigated by the variation of the HBI and ΔT_g values. The HBI and ΔT_g values of these complexed PUs are all lower than those of the ones without ion complexation as shown in Figures 11 and 12. The reduction of HBI values indicates that the hydrogen bonding between hard segments was disrupted by

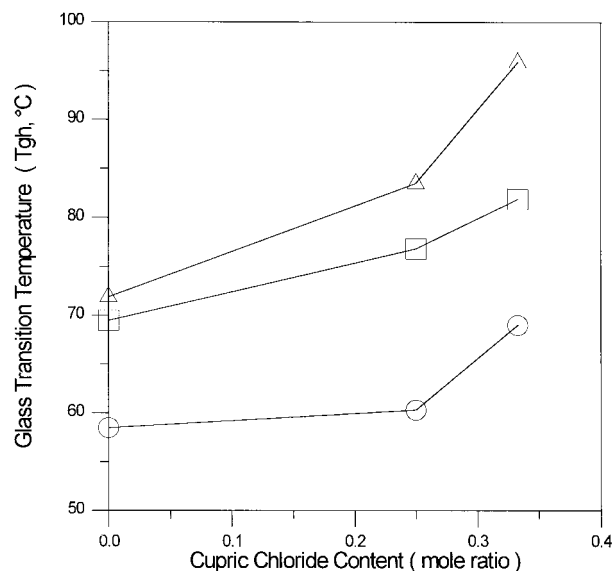


Figure 10 Effect of cupric chloride content (mol ratio) on the T_{gh} of PUs with different composition: (O) 1/4/3; (□) 1/8/7; (Δ) 1/12/11.

the cupric ion and replaced by the ion bonding. The increase of cupric chloride addition enlarges the disruption of hydrogen bonding and, hence, the HBI value decreases as the cupric chloride content increases, while the reduction of ΔT_g indicates increase of the microphase homogeneity and, hence, increase of the stress property. The morphology change of PUs with the addition of cupric chloride can also be evidenced by the infrared absorbance frequency shift of the hydrogen-bonded $-\text{NH}$ ($\nu_{\text{bonded},-\text{NH}}$) group and frequency difference ($\Delta\nu$) of the absorbance frequency between the free-bonded and hydrogen-bonded $-\text{NH}$ group. $\nu_{\text{bonded},-\text{NH}}$ changes from 3320 cm^{-1} for zero cupric chloride-containing PUs to about 3330 cm^{-1} for all cupric chloride-containing PUs. This also may indicate that the addition of cupric chloride changes the morphology of PUs and, hence, affects the tensile property.

Interpenetrating Network of PU and 4-VP

4-VP/PU IPNs were prepared by the addition of an electronegative group containing a monomer of 4-VP to the BPO-crosslinked PUs, which was studied in the previous report.⁵ The PU with an equivalent ratio of HTPB/ H_{12}MDI /1,4BD = 1/4/3 was used in this IPN study due to its larger increase of the tensile property by the addition of 4-VP. 4-VP can form hydrogen bonds with a proton-donating group through sharing the valence electrons of pyridine nitrogen

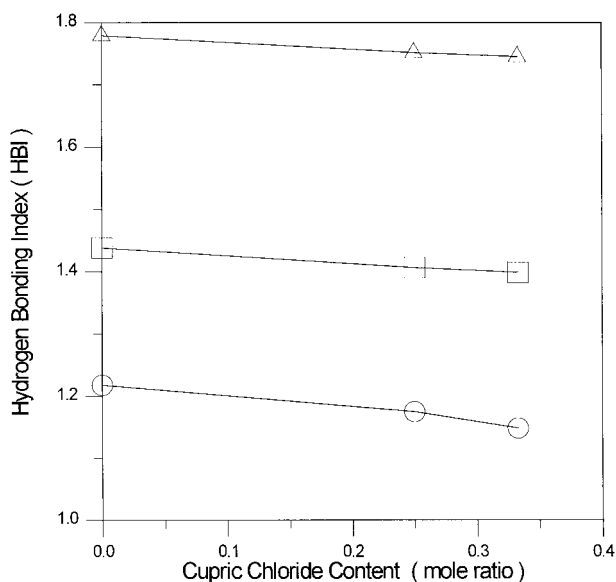


Figure 11 Effect of cupric chloride content (mol ratio) on the HBI values of PUs with different composition: (O) 1/4/3; (□) 1/8/7; (Δ) 1/12/11.

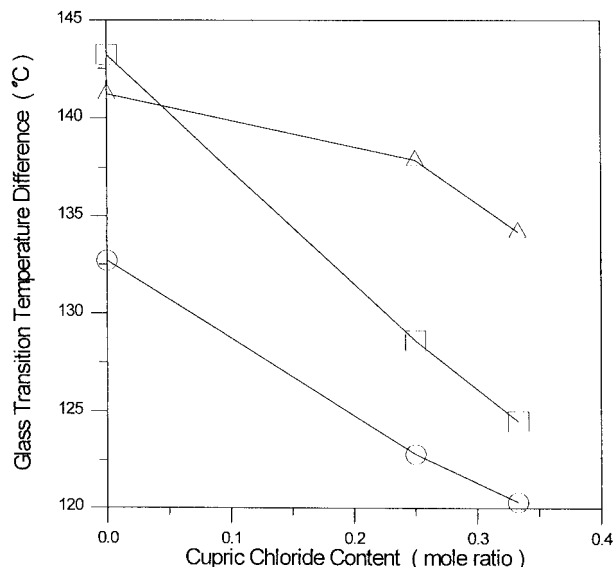


Figure 12 Effect of cupric chloride content (mol ratio) on the ΔT_g of PUs with different composition: (O) 1/4/3; (□) 1/8/7; (Δ) 1/12/11.

atoms. The presence of pyridine rings in the polymer leads to a competition with carbonyl groups for hydrogen bonding with $-\text{NH}$ groups. In other words, the associations between $-\text{NH}$ groups and pyridine prevails over those with a carbonyl association.³⁴ Therefore, two-component IPNs of PU and 4-VP were prepared for a high stress and strain property. The 4-VP contents were quantitatively detected by elemental analysis and qualitatively by FTIR. Figure 13 shows the characteristic infrared spectra of the pyridine groups at 1600 and 1643 cm^{-1} .

Figure 14 shows that the stress increases, while the strain increases to a maximum and then decreases, as the 4-VP content increases. The increase of 4-VP content induces the increase of intermolecular attraction on the tensile property. The frequency difference was utilized in this study to discuss the 4-VP content effect on the tensile property. The IR spectra indicates that the increase of interaction between the pyridine group and the $-\text{NH}$ group of these 4-VP/PU IPN films is evidenced by the increase of the frequency difference ($\Delta\nu$) which is the absorbance frequency difference between the free hydrogen-bonded $-\text{NH}$ and hydrogen-bonded $-\text{NH}$ groups. The frequency differences are increased as the 4-VP content increases as shown in Figure 15.

Coleman and co-workers³⁵ used the frequency difference ($\Delta\nu$) between hydroxyl groups and those of the hydrogen-bonded hydroxyl group as a measure of the average strength of the hydrogen

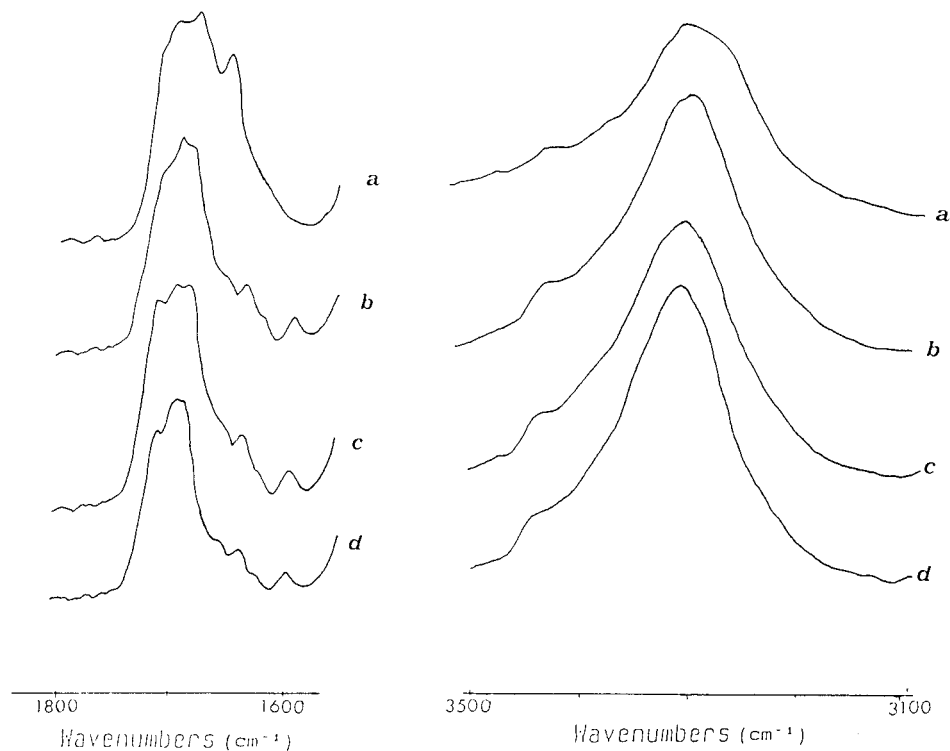


Figure 13 Infrared spectra of BPO-crosslinked PU and 4-VP/PU IPNs: (a) cross-linked PU; (b) IPN-8.44; (c) IPN-10.86; (d) IPN-17.42.

bonds between —NH groups and pyridine groups of 4-VP. The $\Delta\nu$, T_{gs} , and T_{gh} of these IPNs are increased as the 4-VP content increases as shown in Figure 15. The increase of $\Delta\nu$ indicates that the intermolecular average strength of these IPNs

are increased as the 4-VP content increased. The increase of T_{gs} and T_{gh} indicates that the chain mobility of the soft segment decreased and the interaction between the hard segments increased. On the other hand, the infrared study of the

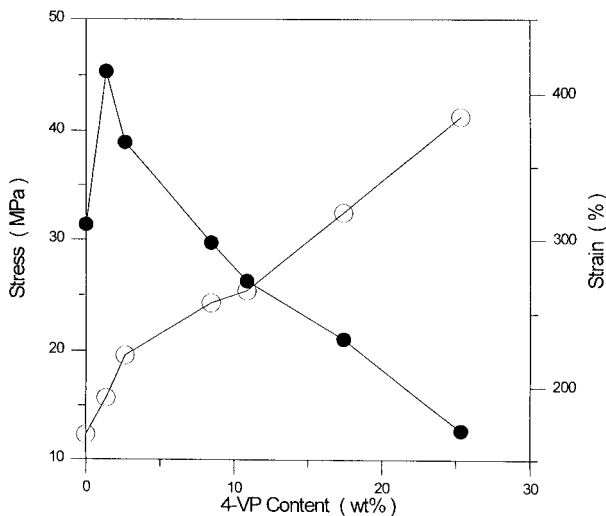


Figure 14 Effect of 4-VP content on the stress property of PUs: (○) stress; (●) strain.

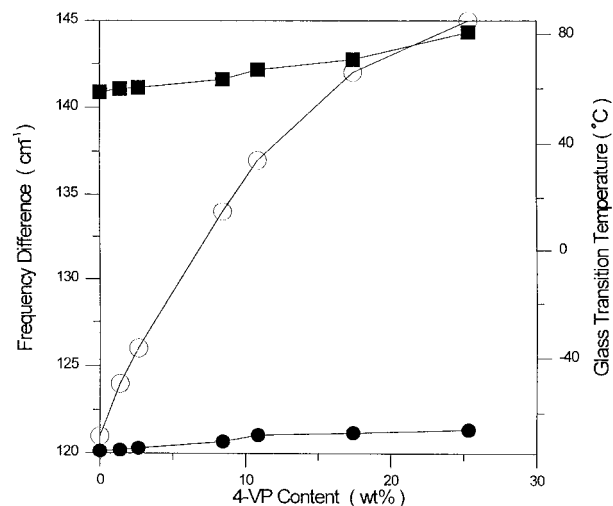


Figure 15 Effect of 4-VP content on the (○) frequency difference, (●) T_{gs} , and (■) T_{gh} of 4-VP/PU IPNs.

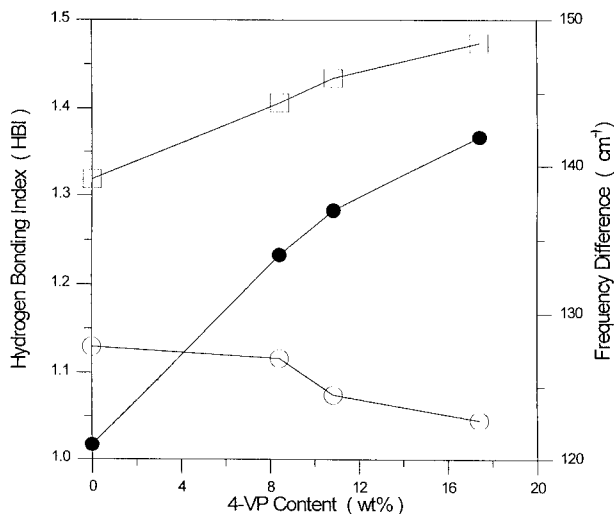


Figure 16 Effect of 4-VP content on the HBI values of 4-VP/PU IPNs: (○) $A_{\text{C=O,bonded}}/A_{\text{C=O,free}}$, (□) $A_{\text{NH,bonded}}/A_{\text{NH,free}}$, and (●) frequency difference ($\Delta\nu$) between hydrogen-bonded and freely bonded —NH groups.

bonded —NH group frequency of these 4-VP/PU IPN films shift to the lower frequency, which changes from 3321 to 3318, 3316, 3308, 3305, 3300, and 3297 cm^{-1} as the 4-VP content increases from 0 to 1.36, 2.63, 8.44, 10.86, 17.42, and 25.35 wt %. It indicates that the IPN association, the energy, and the force constant of the hard segment decreases, and the absorption frequency is therefore shifted to lower frequency.

Figure 16 shows that the HBI values of the $A_{\text{—NH,bonded}}/A_{\text{—NH,free}}$ of BPO-crosslinked PU and three 4-VP/PU IPN films change from 1.3184 to 1.4062, 1.4341, and 1.4735, as the 4-VP content increases from 0, 8.44 to 10.86 and 17.42 wt %, whereas the ratio of $A_{\text{C=O,bonded}}/A_{\text{C=O,free}}$ decreases from 1.1293 to 1.1162, 1.0746, and 1.0453. The reason may be that part of the —NH groups form hydrogen bonds with the pyridine nitrogen atoms which induces the increase of bonded —NH groups and free-bonded C=O groups. HBI values and the frequency difference and shift are used in this study to explain why there is higher stress in the 4-VP/PU IPNs than that in only-BPO-crosslinked PU films.

Characterization of 4-VP/PU IPN

Infrared Spectroscopy

The existence of 4-VP in the 4-VP/PU IPNs can be evidenced by the infrared spectra and the

strength of the hydrogen bonds³⁶ which are detected by FTIR. Figure 13 shows the characteristic spectra of the pyridine group at 1643 and 1600 cm^{-1} in the pyridine-containing PU polymer. Upon hydrogen bonding of —NH groups with pyridine groups, the frequency of the hydrogen-bonded —NH groups shift from 3331 cm^{-1} of BPO-crosslinked PU to 3297 cm^{-1} of 4-VP/PU IPNs with 25.35 wt % of 4-VP content. The frequency differences of 4-VP/PU IPNs ($\Delta\nu = 124\text{--}145 \text{ cm}^{-1}$) are all larger than those of BPO-crosslinked PU ($\Delta\nu = 121 \text{ cm}^{-1}$). The increase of $\Delta\nu$ indicates that strong intermolecular interactions induce the increase of the stress property between polymer chains due to the introduction of 4-VP into the PUs.

Differential Scanning Calorimeter

The change of glass transition temperatures give evidence for the existence of 4-VP in the 4-VP/PU IPNs. Figure 15 presents DSC data for a number of different 4-VP/PU IPNs and BPO-crosslinked PUs. It shows that the glass transition temperature of soft-segments (T_{gs}) and hard segments (T_{gh}) increased as the 4-VP content increased. Larger positive deviation in T_{gh} values than that in T_{gs} values observed indicates the stronger interactions between 4-VP and the hard segment of PU.

Thermogravimetric Analysis

In most cases, the thermograms of the IPN fall in between those of the two components.³⁷ TGA curves can be used to manifest the formation of 4-VP/PU IPNs, as reproduced in Figure 17. A three-step degradation was observed in all these polymers. It is stable up to 300°C and the polymer remains almost intact in the first step. The quantity of gaseous components, mainly water released in this step, is relatively small.

A rapid weight loss starts at approximately 300–500°C; the main quantity of gaseous components, e.g., water, carbon monoxide, and methane, are split off. Decomposition of step 2 corresponds to urethane-bond (i.e., hard segment) breaking and step 3 is the polyol decomposition.³⁸ BPO-crosslinked PUs have a lower second decomposition temperature, higher third decomposition temperature, and lower residue. However, the second decomposition temperature of 4-VP/PU IPNs increases as the 4-VP content increases, due to a higher thermal degradation temperature of 4-VP. With a lower oxygen atom content of the

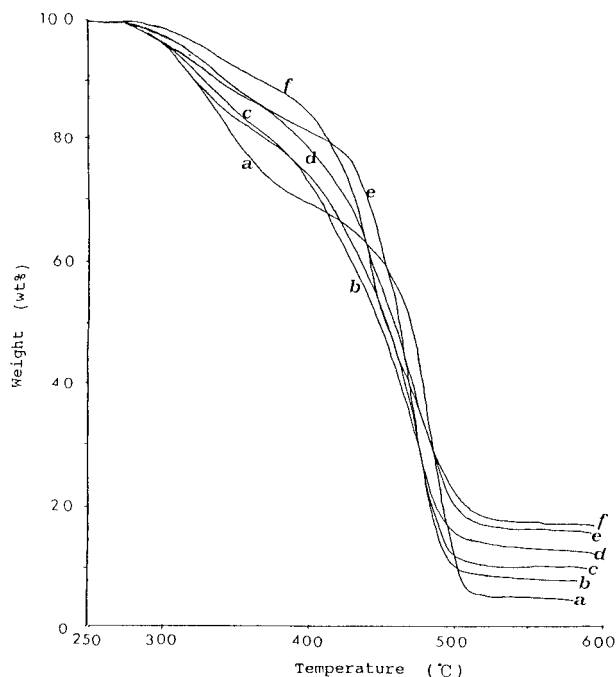


Figure 17 TGA thermogram of BPO-crosslinked PU and 4-VP/PU IPNs: (a) crosslinked PU; (b) IPN-2.63; (c) IPN-8.44; (d) IPN-10.86; (e) IPN-17.42; (f) IPN-25.35.

hard segment and higher carbon atom content in the molecular structure of 4-VP/PU IPNs, these polymers have a higher residue remaining after TGA analysis.

CONCLUSION

HTPB-based PUs crosslinked with DVB provided a higher stress property than that of uncrosslinked PUs. PUs with a higher hard-segment content have a higher stress and lower strain property. The stress at break of crosslinked PUs is greatly increased over that of uncrosslinked PUs. The degree of crosslinking can be determined by the change of the glass transition temperature, which indicates that the mobility of the soft segment decreased. HBI values decreased after DVB was introduced, meaning that crosslinkage between soft segments hindered the hydrogen bonding between the hard segments. The results of the FTIR and DSC measurements explain the crosslinking degree with different DVB content and, hence, the tensile property as well.

The stress property of HTPB- H_{12} MDI-MDEA-based PUs are all increased as the hard-segment content increased. The stress at break of

PUs with cupric chloride addition are all higher than those without cupric chloride. All the above results can be explained by the change of the glass transition temperature or difference, the frequency shift or difference, and the HBI values. Owing to the introduction of cupric chloride, the decrease in size and the disruption in packing of hard and soft segments will increase the stress property of PUs. By manipulating the amount of cupric chloride addition, 39.75 Mpa of stress and 110.4% of strain at break can be obtained by HTPB/ H_{12} MDI/MDEA = 1/12/11 two-stage polymerization of PU complexed with a 1/3 mol ratio of cupric chloride.

The stress at break of 4-VP/PU IPNs are all higher than that of BPO crosslinked PUs and increase as the 4-VP content increased, while these 4-VP/PU IPNs still remain an appreciable value of strain at break compared with BPO-crosslinked PUs. Stress of 41.3 Mpa and 170% of strain can be obtained by the 4-VP/PU IPNs with 25.35 wt % of 4-VP content. HBI values and the frequency shift and difference of free and hydrogen-bonded —NH groups were measured by FTIR and, hence, well explain the interpolymer hydrogen bonds with different 4-VP content. The change of the glass transition temperature and infrared spectra, which can be used to manifest the 4-VP content, was detected by DSC and FTIR, respectively. Thermal decomposition behaviors conducted by TGA were used to manifest the formation of IPNs.

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