Properties of Isocyanate-Reactive Waterborne Polyurethane Adhesives: Effect of Cure Reaction with Various Polyol and Chain Extender Content

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ABSTRACT: Three series of isocyanate-reactive waterborne polyurethane adhesives were prepared with various contents of chain extender (4.25/8.25/12.50 mol %) and polyol (20.75/16.75/12.50 mol %). Each series had a fixed amount of excess (residual) NCO group (0.50–2.00 mol %). FTIR and ^{1}H-NMR spectroscopy identified the formation of urea crosslink structure mainly above 80°C of various cure temperatures (20–120°C) with excess diisocyanate. The molecular weight, tensile strength, Young's modulus, and adhesive strength depend on excess NCO content and cure temperature and also varied with polyol and chain extender content. The optimum cure temperature was 100°C for all the samples. The tensile strength, Young's modulus, and adhesive strength increased with increasing cure temperature above 60°C up to the optimum temperature) (100°C) and then almost leveled off. Among all the samples, the maximum values of tensile strength, Young's modulus, and adhesive strength were found with 63.22 wt % polyol, 0.93 wt % chain extender, and 1.50 mol % excess (residual) NCO content at 100°C optimum cure temperature. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3767–3773, 2009

Key words: polyurethanes; adhesive; adhesion

INTRODUCTION

The moisture-cured polyurethane–ureas are being widely used in sealant productions, high-performance coating sectors, and adhesive industries.[1,2] The urea network in polyurethane dramatically improved the thermal and mechanical properties. During the urea network formation, soft and hard microphase mixes and provides a delicate balance between the phase mixing and phase separation. Therefore, by controlling the chemical structures, compositions, and conditions, it is possible to obtain high-strength polyurethane with an extremely wide range of mechanical and thermal properties.[1,2]

From last decade, the waterborne polyurethane (WBPU) is being used as an adhesive material commercially. The main advantage of WBPU adhesive is environmentally friendly system. However, poor adhesive strength of WBPU adhesive comparing to conventional solvent-borne polyurethane restricted its wide applications. Moreover, the WBPU adhesive materials are inferior with respect to their hydrolytic stability, mechanical strength (tensile strength), and thermal stability. To overcome these limitations, there have been many fruitful techniques, such as surface modification, blending, and crosslinking, which were used by several research groups.[3–8] Recently, the inclusion of CNT/clay in WBPU adhesives significantly improved the thermal, mechanical, and adhesive properties.[9–12]

One of the most preferred methods to prepare a WBPU dispersion is the prepolymer mixing process. There are three steps in this process: (1) formation of isocyanate-terminated prepolymer, (2) neutralization and emulsification of the NCO-terminated prepolymer for particle formation, and (3) chain extension for higher molecular weight and urea-linkage formation.[4,7] Generally, the WBPU dispersions are prepared by maintaining the stoichiometric ratios of polyol/hydrophilic agent/chain extender (50%) and diisocyanate (50%) following the aforementioned three steps.[5–7] However, it is hard to find any report using excess diisocyanate in WBPU dispersions and the effect of cure temperature on properties of these WBPU films.

In this report, we prepared isocyanate-reactive WBPU adhesives with excess diisocyanate (4,4-dicyclohexylmethane diisocyanate H_{12}MDI, 0.50–2.00 mol % excess). Three series of isocyanate-reactive

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TABLE I
Sample Designation and Composition of WBPU dispersions (mol)

Sample designation	Composition					Excess H_{12}MDI (mol %)
	H_{12}MDI	EDA	PTMG	DMPA	TEA	
A0	2.00	0.17	0.83	1.00	1.00	0
A2	2.02	0.17	0.83	1.00	1.00	0.50
A4	2.04	0.17	0.83	1.00	1.00	1.00
A6	2.06	0.17	0.83	1.00	1.00	1.50
A8	2.08	0.17	0.83	1.00	1.00	2.00
B0	2.00	0.33	0.67	1.00	1.00	0
B2	2.02	0.33	0.67	1.00	1.00	0.50
B4	2.04	0.33	0.67	1.00	1.00	1.00
B6	2.06	0.33	0.67	1.00	1.00	1.50
B8	2.08	0.33	0.67	1.00	1.00	2.00
C0	2.00	0.50	0.50	1.00	1.00	0
C2	2.02	0.50	0.50	1.00	1.00	0.50
C4	2.04	0.50	0.50	1.00	1.00	1.00
C6	2.06	0.50	0.50	1.00	1.00	1.50
C8	2.08	0.50	0.50	1.00	1.00	2.00

WBPU adhesives were prepared with various ratios of polyol, poly(tetramethylene oxide glycol) (PTMG), and chain extender, ethylene diamine (EDA). The cure reaction was monitored by FTIR and ^{1}H-NMR spectroscopy. The molecular weight, tensile strength, Young's modulus, and adhesive strength were measured with respect to excess (residual) NCO content (0–2 mol %). These properties were also compared with various cure temperatures (20–120°C).

EXPERIMENTAL

Materials

Poly(tetramethylene oxide glycol) ($M_n = 2000$, Sigma Aldrich) was vacuum dried at 90°C and a pressure of 1–2 mmHg for 3 h before use. 2,2-Dimethylol propionic acid (DMPA, Sigma Aldrich), triethylamine (TEA, Junsei Chemical, Tokyo, Japan), *N*-methyl-2-pyrrolidone (NMP, Junsei Chemical), 4,4-dicyclohexylmethane diisocyanate (H_{12}MDI, Sigma Aldrich), and ethylene diamine (Sigma Aldrich) were used after dehydration with 4-Å molecular sieves for a week. Dibutyltin dilaurate (DBTDL, Sigma Aldrich), dimethyltin diacetate (DMTDA, Sigma Aldrich), and thickener (L75N, Bayer, Leverkusen, Germany) were used without further purification.

Preparation of WBPU dispersions

The composition of WBPU dispersion is summarized in Table I. The WBPU dispersions were prepared by prepolymer mixing process.[7] PTMG was degassed under vacuum at 90°C for 30 min in a four-necked separating flask equipped with a thermometer, stir bar, condenser with drying tube, dry nitrogen inlet, and heat jacket. DMPA/NMP (1/1 w/w) was added to the flask, and the mixture was allowed to cool to 45°C under moderate stirring (175–200 rpm). One drop of DBTDL was added to the reaction mixture. Then, H_{12}MDI was added to the flask, and the mixture was heated to 85°C under same stirring rate (175–200 rpm). The reaction was continued for 3 h. The change in the NCO value during the reaction was determined by the standard dibutylamine back-titration method (ASTM D 1638). Methyl ethyl ketone (MEK, 20 wt %) was added to the NCO-terminated prepolymer mixture to adjust the viscosity of the solution. TEA was added to the reaction mixture to neutralize the carboxyl group of the NCO-terminated prepolymer. After 30 min of neutralization, distilled water (60 wt %) was added to the reaction mixture with vigorous stirring (1300–1500 rpm). The resulting dispersion was chain-extended by dropwise addition of EDA (with water) at 20°C for 1 h. FTIR spectroscopy confirmed the remaining NCO group in WBPU dispersion at 2270 cm^{-1}. Isocyanate-reactive WBPU dispersions (40 wt % solid content) were obtained after evaporation of MEK.

Preparation of WBPU films

WBPU films were prepared by drying the aqueous dispersion (10 g) on Teflon disks (7 cm in diameter) under specific cure temperatures (20–120°C) and then peeled off from the Teflon disk. These films (typically about 0.5-mm thick) were then dried further in vacuum for 1 day and stored in a desiccator at room temperature.

Preparation of WBPU adhesives

WBPU adhesive materials were prepared by mixing the WBPU dispersion with a thickener and DMTDA catalyst. We used DMTDA catalyst to facilate the reaction between the NCO groups and water. An appropriate amount of WBPU dispersion (100 g) was mixed with thickener (0.5 wt %) and DMTDA (one drop) to obtain a homogeneous viscous material at room temperature. The viscous material was coated onto a nylon fabric, and another nylon fabric was placed on the coated surface and then cured at specific temperatures (20/40/60/80/100/120°C) at a fixed optimum pressure (15 kg/cm^2) for 10 min.

Characterization

A Fourier transform infrared spectrometer (Impact 400D, Nicolet, Madison, WI) was used to identify the WBPU structure. For each sample, 32 scans at a 4 cm^{-1} resolution were collected in the transmittance mode. During preparation of WBPU dispersion, the dispersion was coated on the thallium-bromide/thallium-iodide crystal surface as a thin liquid film and dried for analysis. The cured films were analyzed in KBr disc.

^{1}H-NMR spectra of WBPU films were recorded on a Fourier transform Bruker 300 MHz spectrometer model AC-300. Thirty milligrams of WBPU film was dissolved in 4 mL of deuterated chloroform. Tetramethylsilane was used as an internal reference.

A gel permeation chromatograph (Model 500, Analytical Scientific Instruments, USA) with a refractive index (RI) detector (RI2000, Schambeck, Germany) and two columns of Jordi gel DVB (divinyl benzene) mixed bed (Jordi FLP, USA) at 30°C were used to measure the molecular weight distribution relative to polystyrene standards. The calibration curve was obtained using eight standards in the molecular weight range 3420–2.57 × 10^6. The carrier solvent was tetrahydrofuran at a flow rate of 1 mL/min.

The tensile properties of WBPU films were measured at room temperature with a United Data Systems Tension Meter (SSTM-1 United Data Systems, Instrom, Japan) according to ASTM D 638 specifications. A crosshead speed of 50 mm/min was used throughout these investigations to determine the ultimate tensile strength and modulus, and the elongation at break (%) for all samples. The quoted values are the averages of five measurements. The adhesive strength was measured with a United Data Systems Tension Meter according to ASTM D 1876-01 (T-peel test). A peel rate of 0.1 m/min was used. The adhesive test was conducted at room temperature. The quoted values are the average of five measurements.

RESULTS AND DISCUSSION

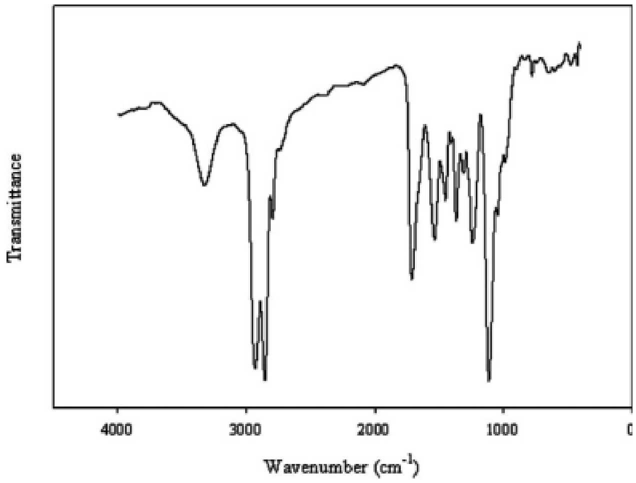
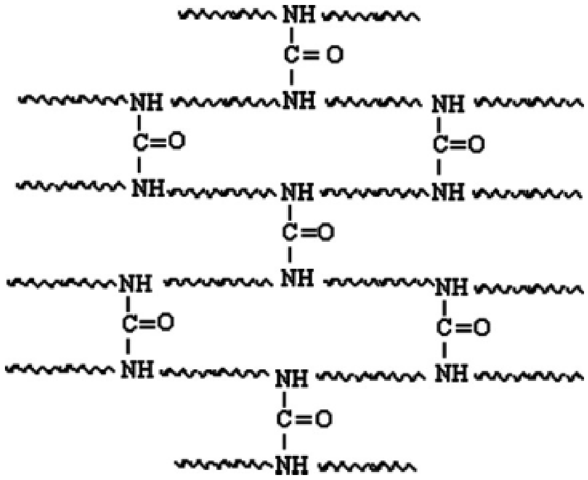


Figure 1 Typical FTIR spectrum of B6 sample cured at 100°C.

The reaction of NCO group with water in WBPU dispersion at various cure temperatures was monitored by FTIR spectra. Figure 1 shows the typical infrared spectrum of B6 sample cured at 100°C temperature. The spectrum is mainly characterized by the bands at 3150–3600 cm^{-1} (NH stretching vibrations), 2800–3000 cm^{-1} (CH stretching vibrations: antisymmetric and symmetric stretching modes of methylene groups), 2795 cm^{-1} (O—CH$_2$ stretching), 1600–1760 cm^{-1} (amide I: C=O stretching vibrations), 1540 cm^{-1} (amide II, $\Delta_{\text{N—H}}+\nu_{\text{C—N}}+\nu_{\text{C—C}}$),[13,14] 1376–1388 cm^{-1} (νC—N), 1226–1292 cm^{-1} (amide III, $\nu_{\text{C—N}}$), 1105 cm^{-1} (C—O—C stretching vibration, ether group), and 766 cm^{-1} (amide IV). The band at 1445 cm^{-1} is attributed to CH$_2$ scissoring and CH$_3$ deformation. Absorbance in between 1002 and 1012 cm^{-1} is attributed to the stretching and rocking vibrations of the C—C and CH$_2$ groups, respectively. Amide I vibration consists of several components reflecting C=O groups in different environments and is sensitive on the specificity and magnitude of hydrogen bonding. Amide I mode is a highly complex vibration and involves the contribution of the C=O stretching, the C—N stretching, and the C—C—N deformation vibrations.[2,13,14] Amide II mode is a mixed contribution of the N—H in-plane bending, the C—N stretching, and the C—C stretching vibrations and is sensitive to both chain conformation and intermolecular hydrogen bonding. Amide III mode involves the stretching vibration of the C—N group. Amide III is highly mixed and complicated by coupling with NH deformation modes and is observed between 1226 and 1292 cm^{-1}.[2,13,14] Amide IV, V, and VI bands are produced by highly mixed modes containing a significant contribution from the NH out-of-plane deformation mode. They are expected to be in the 800–400 cm^{-1} region. A very weak single band is observed at 838 cm^{-1}, which might be originating either from the coupled vibration of the C—O stretching or CH$_2$ rocking modes. The strong infrared band assigned to the asymmetric stretching vibration of the C—N group is



Scheme 1 Urea network formation in WBPU film by cure reaction of NCO group.

expected at 1040 cm^{-1}.[2,13] This band overlaps with the very strong band at 1105 cm^{-1}, the C—O—C stretching vibration of ether groups in WBPU films.[2,13,14] Now let us see the structure changes that occur during the cure reaction. Scheme 1 shows the network formation (branching) by cure reaction, whereas Figure 2 shows the decay of NCO group vibration with increasing cure temperature for B6 sample. The peak at 2170 cm^{-1} disappears with increasing cure temperature suggests that the moderate high temperature (above 80°C) is required to promote the cure reaction (polyurethane branching). The polyurethane branching can be formed by urea/allophanate/biuret groups in polyurethane. To identify the urea/allophanate/biuret groups in polyurethane, we applied ^{1}H-NMR spectroscopy. In Figure 3, the typical ^{1}H-NMR spectra of B6 sample cured at 20 and 100°C are shown. The identical peaks for urethane and urea groups are found in both spectra confirmed the successful synthesis of polyurethane. The peak at 6.91 ppm is assigned to the —NH group of the urethane unit, whereas the peak at 6.81 ppm is assigned to the —NH group of the urea unit. The large increase of intensity of this peak at 6.81 ppm confirmed the formation of urea groups cured at 100°C (see Fig. 3). This is very hard to find any new peak in spectrum confirmed that mainly urea groups (almost no allophanate/biuret group) are formed by cure reaction at 100°C.[15] Our previous study also confirmed that very little amount of allophanate/biuret groups are formed by the cure reaction between free NCO group and urethane/urea group at 100°C.[15] Here, we used residual NCO group which might be make more difficult for reaction with urethane/urea group to form allophanate/biuret group. As a result, the allophanate/biuret groups are almost not (or very slightly) formed during the cure reaction, and the peak for allophanate/biuret group is not identified by ^{1}H-NMR spectra. More detailed studies should be consider to explain the less (or almost absent) amount of allophanate/biuret groups in cure reaction at 100°C.

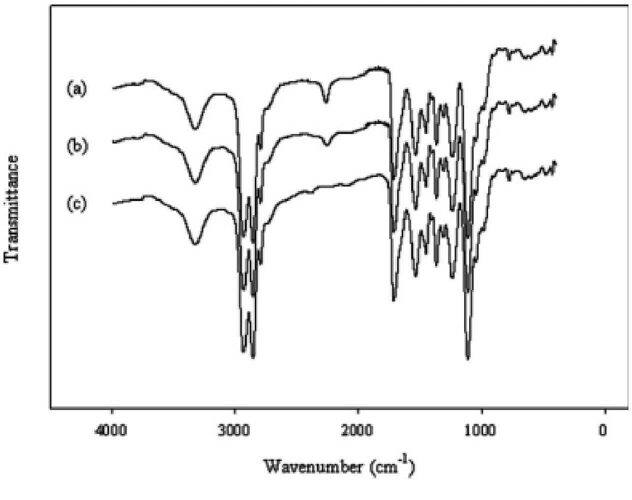


Figure 2 FTIR spectra of B6 sample at various cure temperatures (°C) (a) 60, (b) 80, and (c) 100 with optimum time (10 min).

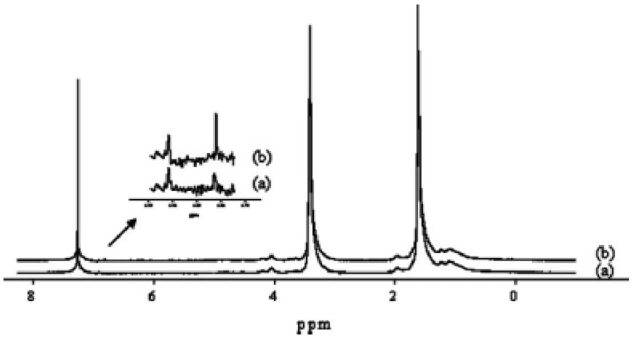


Figure 3 Typical ^{1}H-NMR spectra in CDCl3 of B6 sample cured at (a) 20 and (b) 100°C.

The molecular weight is considered as one of the most important parameters of polymer. It was shown earlier that the mechanical and adhesive properties are significantly affected by molecular weight of the polyurethane.[13,14,16] The maximum tensile strength and adhesive strength were found with higher molecular weight of polyurethane. Generally, the molecular weight of WBPU builds up in chain extension step by reaction of residual NCO group with EDA. Moreover, the molecular weight is maximum after complete reaction of residual NCO group. Therefore, it is very important to measure the molecular weight with various excess NCO content with different cure temperatures. The effect of NCO contents and cure temperatures (20 and 100°C) on molecular weight of WBPU film was characterized by GPC. The molecular weight of B series at two different cure temperatures (20 and 100°C) is shown in

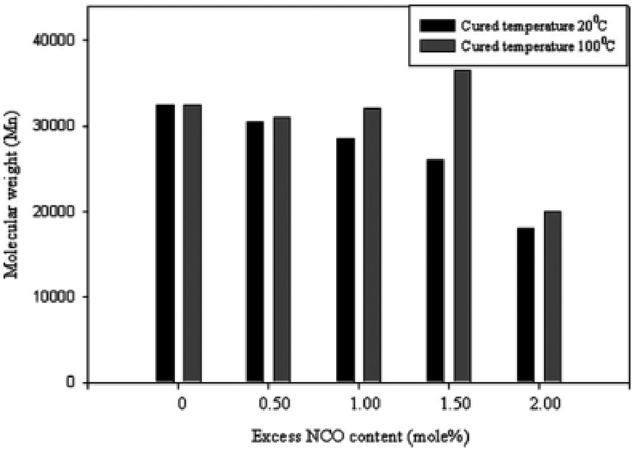


Figure 4 Molecular weight of WBPU films cured at two different temperatures (20 and 100°C) with various excess (residual) NCO content of B series.

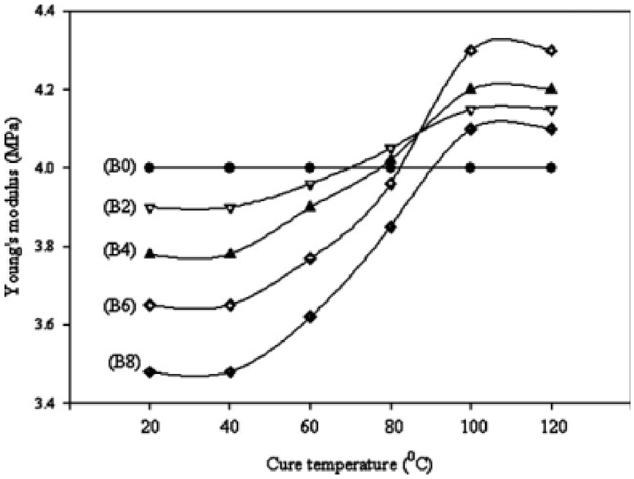


Figure 6 Young's modulus of WBPU films of B series at various cure temperatures with excess (residual) NCO content (mol %) (B0) 0%, (B2) 0.50%, (B4) 1.00%, (B6) 1.50%, and (B8) 2.00%.

Figure 4. It was found that the molecular weight dependent on both NCO content and cure temperatures in all three series. At 20°C, the molecular weight decreased with increasing NCO content. However, the molecular weight shifted to higher value at 100°C. The molecular weight decreased at 20°C with increasing NCO content might be due to the insufficient chain growing during chain extension of dispersion as well as unsuitable reaction condition between the water and NCO group in curing stage (absence of branching). At 100°C (optimum), the molecular weight built up due to urea branching by complete reaction of NCO groups. The maximum molecular weight was found with 1.50 mol % excess $H_{12}MDI$ content only for A6 and B6 in A series and B series, respectively. The molecular weight was higher for B6 than A6 at 100°C cured temperature. Although NCO group reacted fully in A6 and B6 at 100°C, the B6 sample might contain optimum polyol and chain extender and showed the higher molecular weight.[13] The molecular weight was different for C series. Although the molecular weight was slightly increased cured at 100°C than those for 20°C, the molecular weight gradually decreased with increasing NCO content. This might be due to the less polyol content.[13]

The effect of NCO content and cure temperatures on tensile strength, Young's modulus, and elongation at break (%) of WBPU films was measured (Figs. 5–7). The tensile strength and Young's modulus of the film decreased with increasing NCO content cured at 20–60°C, whereas the elongation at break (%) increased following the same conditions. With increasing cure temperature above 60°C, both

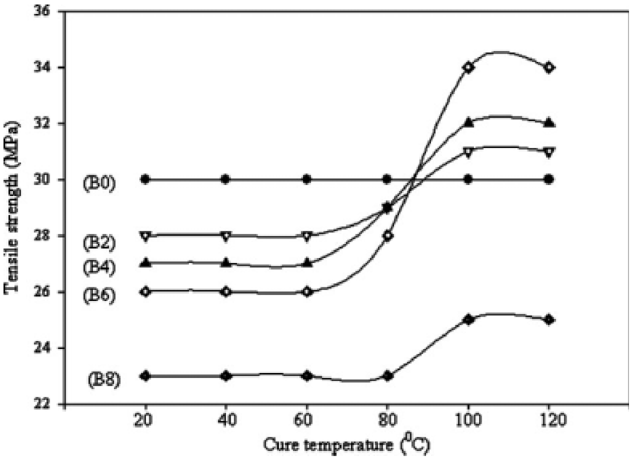


Figure 5 Tensile strength of WBPU films of B series at various cure temperatures with excess (residual) NCO content (mol %) (B0) 0%, (B2) 0.50%, (B4) 1.00%, (B6) 1.50%, and (B8) 2.00%.

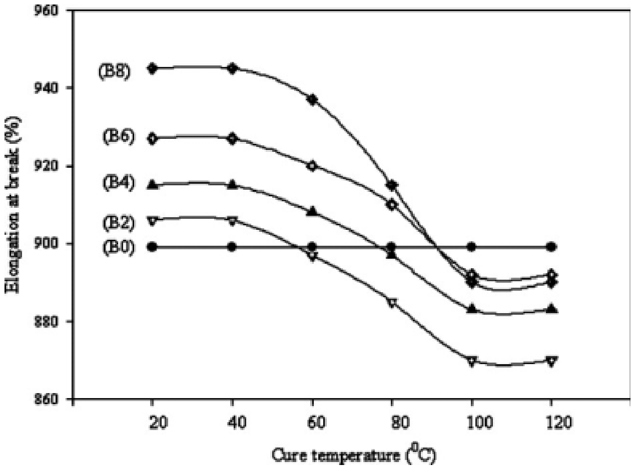


Figure 7 Elongation at break (%) of WBPU films of B series at various cure temperatures with excess (residual) NCO content (mol %) (B0) 0%, (B2) 0.50%, (B4) 1.00%, (B6) 1.50%, and (B8) 2.00%.

tensile strength and Young's modulus started to increase up to the optimum value and then almost leveled off (A2, A4, A6/B2, B4, B6/C2, C4, C6). However, with large excess NCO content (A8/B8/C8), the tensile strength and Young's modulus increased slightly even cured at high temperatures (80/100/120°C). This might be due to the insufficient molecular weight of WBPU films because of the less chain growing in chain extension step.[13] The tensile strength and Young's modulus decreased with increasing NCO content cured at 20–60°C because of the increasing unreacted NCO group, which followed less molecular weight of WBPU film. The tensile strength and Young's modulus increased with increasing cure temperature above 60°C because of the higher molecular weight as well as additional urea networks (branching) of the film. If we compare the tensile strength and Young's modulus of three series prepared by same conditions (same cure temperatures and NCO content), the corresponding maximum values (A6/B6/C6) are found at 100°C cured temperature of each series. However, the increasing rate of tensile strength and Young's modulus with increasing cure temperature at a fixed NCO content is not same for those three series. The tensile strength and Young's modulus increased faster for B series than A and C series with same NCO content and cure temperature. Moreover, at optimum cure temperature) (100°C), the tensile strength and Young's modulus of B6 sample are higher than those for A6 and C6 samples. The tensile strength and Young's modulus depend on many factors, such as DMPA content, molecular weight, side reaction, and branching.[4,6,8,13,17] The B6 sample has higher molecular weight than A6 and C6 samples and makes the film more rigid and shows higher tensile strength and Young's modulus. Moreover, it contain optimum polyol and chain extender to maintain the elastomeric character of the film.[13,17] The tensile strength and Young's modulus values of B6 increased 45 and 17%, respectively, cured at 100°C comparing to those for 20°C. However, with similar excess diisocyante and cured temperature, the tensile strength increased 17 and 15% for A6 and C6, respectively. Most importantly, the tensile strength was higher for B6 than B0, whereas the tensile strength was lower for A6 and C6 than A0 and C0, respectively.

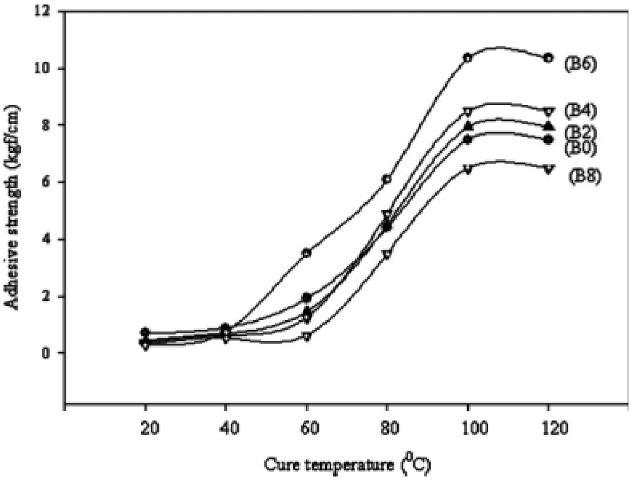


Figure 8 Adhesive strength of B series at various cure temperatures with excess (residual) NCO content (mol %) (B0) 0%, (B2) 0.50%, (B4) 1.00%, (B6) 1.50%, and (B8) 2.00%.

Figure 8 shows the effect of excess NCO content and cure temperatures on adhesive strength of reactive isocyanate WBPU adhesives of B series. The locus of failure was assessed by visual inspection of the failed joint surfaces. It was found that the failure was cohesive in the adhesive layer instead of the nylon fabric-adhesive interfacial for all the samples. The adhesive strength increased with increasing temperature above 60°C and the maximum value was found at 100°C. The adhesive strength also depends on NCO content. Below 60°C the adhesive strength decreased with increasing NCO content. Above 60°C the adhesive strength increased with increasing NCO content up to the optimum content (excess 1.50 mol %). However, the adhesive strength with various cure temperatures and NCO content is different for three series. The adhesive strength was higher for B6 than A6 and C6. Moreover, at a fixed NCO content and cure temperature, the adhesive strength of B series samples was higher than A and C series samples correspondingly. The adhesive strength of WBPU adhesive depends on DMPA, polyol, and chain extender content as well as polyurethane properties, such as molecular weight, tensile strength, and Young's modulus.[7,13,17] Combination of higher molecular weight and polyurethane branching increased the adhesive strength for B series samples comparing to A and C series samples with fixed residual NCO content and cure temperature.[15,17] The most interesting result was found for C series. In C series, the adhesive strength slightly increased above 80°C, even optimum NCO content (1.50 mol %) of WBPU adhesive. Only urea network formed by cure reaction of WBPU adhesive, which also suffered by less molecular weight, tensile strength, and Young's modulus due to less polyol content than B series and showed lowest adhesive strength. With optimum excess diisocyanate (1.50 mol %) and cure temperature) (100°C), the adhesive strength increased 10 and 38% for A6 and B6 comparing to A0 and B0, respectively, whereas at same condition the adhesive strength of C6 decreased rapidly comparing to C0.

CONCLUSIONS

The properties of isocyanate-reactive WBPU adhesives depend both on cure temperature and NCO content. The optimum cure temperature and excess NCO content which were independent of polyol and chain extender content found 100°C and 1.50 mol %, respectively. The molecular weight decreased with increasing excess (residual) NCO content cured at 20°C and changed to high molecular weight cured at 100°C. The tensile strength, Young's modulus, and adhesive strength increased with increasing cure temperature above 60°C up to the optimum) (100°C) and then almost leveled off. The tensile strength, Young's modulus, and adhesive strength were higher for B series comparing to A and C series with fixed excess NCO content. Among all the samples, the maximum tensile strength, Young's modulus, and adhesive strength were found with 63.22 wt % polyol, 0.93 wt % chain extender, and 1.50 mol % excess (residual) NCO content cured at 100°C.

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