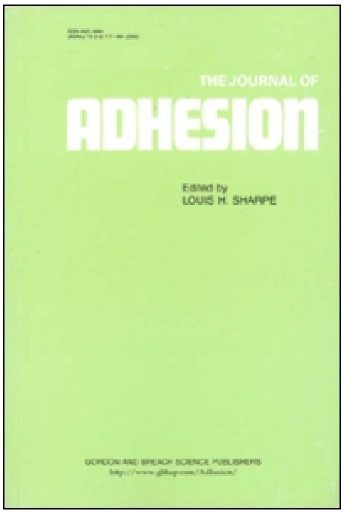

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P. Dreyfuss[a]; D. E. Larive[a]
[a] Michigan Molecular Institute, Midland, MI, U.S.A.

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Effect of Chemical $\bar{M}_c$ of Polyurethanes on Adhesion to Glass†

P. DREYFUSS and D. E. LARIVE

Michigan Molecular Institute, 1910 W. St. Andrews Road, Midland, MI 48640, U.S.A.

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Three polyether polyols of different polarity were fabricated into polyurethanes with different average molecular weights between chemical crosslinks, $\bar{M}_c$, and their adhesion to glass was related to their chemical constitution. The polyols that comprised the soft segment were hydroxylated polybutadiene, poly(tetramethylether) glycol (α,ω-hydroxypolytetrahydrofuran) and a glycol from 3,3-*bis*-azidomethyl oxetane and tetrahydrofuran copolymer. The hard segment was derived from toluene diisocyanate, 1,4-butanediol and trimethylolpropane. The length of the hard segment was varied using variable amounts of free NCO. The length of the soft segment was varied using poly(tetramethyl ether) glycols of different average molecular weight. $\bar{M}_c$ was also varied using chain extension reactions. In general, the adhesion increased or remained nearly constant as $\bar{M}_c$'s increased but there were some anomalies at the highest and lowest values of $\bar{M}_c$. Increasing the polarity of the polyurethane increased its adhesion to glass. Possible reasons for the observed behavior are discussed.

KEY WORDS Adhesion; polyurethanes; molecular weight between crosslinks; polybutadiene polyol; polytetrahydrofuran glycol; poly(tetramethylene ether) glycol.

INTRODUCTION

In earlier investigations of the adhesion of polyurethane coatings to glass and various metal substrates, it was reported that the work of adhesion *increased* as the crosslink density of the polymer increased,[1–3] i.e. as the average molecular weight between chemical crosslinks decreased. In these investigations the crosslink density was varied by changing the ratio of trimethylolpropane to NCO concentration, while maintaining the total concentration of urethane groups at a constant value. This conclusion contrasts with work in elastomeric systems where the strength of adhesion decreased with increasing crosslinking, if the elastomer was chemically bonded to the surface or was *independent* of the degree of crosslinking in the absence of chemical bonding.[4] It also contrasts with fracture studies in a variety of other polymeric systems where it was clearly demonstrated

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that threshold tear strengths of elastomers are proportional to the square root of the average molecular weight $\bar{M}_c$ of the network strands,[5] as predicted by the theory of Lake and Thomas.[6] The latter work is applicable to adhesion studies if it is presumed that the same forces are active in adhesion as in fracture. The present study was undertaken to find out if this seeming disagreement between the effects of $\bar{M}_c$ in polyurethane systems and in the other systems is real and to gain greater insight into the chemical factors which govern adhesion of polyurethanes to substrates.

The paper focusses on the contributions made by different chemical structures found in the bulk of model polyurethane adhesives and on the effects of changing the molecular weight of the segments constituting the polyurethane. The polyurethanes considered are of the type that might be used in solid rocket propellant binders. The primary variables are chemical in nature and the objective of the study was to relate the chemical constitution of the polyurethanes to the strength of resulting adhesive bonds. Ultimate tensile strength, elongation at break, swelling ratios, percent sol, and sometimes also hardness and glass transition temperatures were determined for each of the polyurethanes. Wide angle X-ray patterns were recorded in instances when crystallization of one of the polyurethane segments was deemed possible.

EXPERIMENTAL

Materials

Three different kinds of polymeric polyols were used in this study. One kind was hydroxy-terminated polybutadiene (R-45HT) from ARCO Chemical Co. This polymer was 60% *trans*-1,4, 20% *cis*-1,4 and 20% vinyl-1,2 and had the other properties listed in Table I. The second kind was poly(tetramethyl ether) glycols from The Quaker Oats Co. (the QO series) and from E. I. duPont de Nemours

TABLE I
Properties of glycols

Polymer	Hydroxyl value meq/g	M.W. No. Avg.	OH functionality
R-45HT	0.83	2800	2.4
Tc 650	3.04	650	2.0
QO 1000	2.01	1000	2.0
Tc 1000	2.03	1000	2.0
QO 2000	1.00	2000	2.0
Tc 2000	0.97	2000	2.0
Tc 2900	0.69	2900	2.0
Tn 5750[a]	0.35	5750	2.0
BAMO/THF-	0.82	2400	2.0

[a] Tn 5750 is a Terathane specially synthesized for this project and provided by G. Pruckmayr of du Pont.

& Co. (the Teracol, T_c, series and Terathane 5750) of the molecular weights and other properties given in Table I. The third was a glycol copolymer of 35% 3,3-*bis*-azidomethyloxetane (BAMO) and 65% tetrahydrofuran (THF) with the properties given in Table I. Other materials included TDI (80/20 mixture of 2,4 and 2,6 isomers of toluene diisocyanates) from BASF Wyandotte Corporation, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, $99^{+}\%$ (triol, trimethylolpropane), 1,4-butandiol (diol) from Aldrich Chemical Co., Inc., and *p*-dioxane from Eastman Kodak Co. Precleaned Opticlear soda lime microscope slides (75 × 25 × 0.6 mm) from KIMBLE were used as model substrates for adhesion tests.

Purification and characterization of polyols

Most of the polyols were used as received. The copolymer from BAMO and THF was received as a solution in methylene chloride. Before use the methylene chloride was removed with the aid of a rotary evaporator, and the polymer was precipitated into methanol, stirred for one hour, and refrigerated overnight. The polymer was collected by decanting and then dried 24 hrs in a vacuum oven at 80°C.

Hydroxyl numbers of the polybutadiene and the poly(tetramethylene ether) glycols were determined by titration procedures recommended by ARCO[7] and Quaker Oats,[8] respectively. Agreement with the values supplied by the manufacturers was excellent. Hydroxyl numbers for some poly(tetramethylene ether) glycols and for the copolymer of BAMO and THF were determined by a slightly modified NMR procedure of Baum, *et al.*[9] using a Bruker WM360 NMR spectrometer.

Preparation of polyurethane

The polyurethanes were prepared from the glycols, TDI, diol, and triol using a two-stage procedure. Typically, the glycol was degassed at 110°C and 5 mm Hg for 30 min., the glycol was cooled to 60°C, TDI was added, the isocyanate endcapping reaction was continued for 2 hrs at 60°C and 50 mm Hg, the pressure was lowered to 5 mm for 30 min., diol was added and the reaction mixture was stirred 10 min., triol was added and the reaction mixture was stirred for 5–15 min. before pouring into the mold. The exact charge for each of the polymers prepared is given in Table II. The ratio ([–NCO]/[total OH]) was kept constant and equal to 1.0 but the ratio [–NCO] to hydroxyl number of glycol was varied in some experiments. Where not otherwise specified, a 6% excess [–NCO] to hydroxyl number of glycol was used.

Application of elastomer layer and curing

For adhesion studies, glass slides were placed in a Teflon-coated compression mold. Prior to molding, both the mold and slides were stored at least overnight in an air oven at 130°C until used. About two hours before the polyurethane

TABLE II
Charges for preparation of polyurethanes

Polyol[a]	Polymer[b]	TDI g	% Free NCO	Moles diol OH / Moles triol OH	Diol g	Triol g
R-45HT	PB	18.4	6	100/0	7.886	0.
R-45HT	PB	18.4	6	80/20	6.308	1.565
R-45HT	PB	18.4	6	60/40	4.731	3.131
R-45HT	PB	18.4	6	40/60	3.154	4.696
R-45HT	PB	18.4	6	20/80	1.577	6.262
R-45HT	PB	18.4	6	0/100	0.	7.827
Tc 650	PTHF	44.40	6	20/80	1.856	7.380
Tc 1000	PTHF	34.38	6	20/80	1.730	6.866
QO 1000	PTHF	28.08	4	20/80	1.099	4.365
QO 1000	PTHF	34.14	6	20/80	1.726	6.857
QO 1000	PTHF	40.81	8	20/80	2.417	9.597
QO 1000	PTHF	48.18	10	20/80	3.407	12.624
QO 1000	PTHF	104.50	20.5	20/80	9.007	35.763
Tc 2000	PTHF	23.86	6	20/80	1.595	6.329
QO 2000	PTHF	24.17	6	20/80	1.600	6.342
Tc 2900	PTHF	21.06	6	20/80	1.559	6.186
Tn 5750	PTHF	17.66	6	20/80	1.514	6.011
BAMO/THF[b]	BAMO/THF	22.40	6	20/80	1.575	6.255
BAMO/THF[b]	BAMO/THF	22.40	6	80/20	6.301	1.564

[a] Charges are based on 100 g polyol.

[b] PB is polybutadiene; PTHF is polytetrahydrofuran; BAMO/THF is the copolymer of BAMO and THF.

synthesis was complete, the top of the mold was covered with a sheet of washed, dried and pressed cotton cloth, and the assembly was transferred to a vacuum oven at 60°C and 2 mm Hg. When the mixing of the polyurethane was complete, the polyurethane was poured into the mold and the samples were cured in a PHI press first for 0.5 hrs at 60°C and 25,000 pounds ram force on a four-inch ram and then at 100°C for 3.5 hrs at the same pressure. Curing was completed under nitrogen in an oven at 100°C.

Polyurethane sheets were cured in a vertical mold in a vacuum oven under nitrogen at atmospheric pressure first at 60°C for 2 hrs and then at 100°C for times that varied with the polyol. Before being placed under nitrogen, the samples were degassed at 60°C in the mold for about 20 min at 20 mm Hg, and 30 min at 2 mm Hg. Samples of 80/20 BAMO/THF copolymer cured faster and were degassed at 60°C for 10 min at 20 mm Hg and 5 min at 2 mm Hg. Curing time was continued until the samples were no longer tacky and a constant set of properties were achieved. In general, samples from the polybutadiene polyol required at least one and sometimes several days to cure completely, samples from the polytetrahydrofuran glycols were completely cured in 17–18 hrs, and samples from the glycol of the BAMO/THF copolymer were cured in 24 hrs. Swelling ratios suggested that the polybutadiene glycol sample prepared with 100% triol and the polyurethane prepared from Teracol 650 may not have cured completely under any conditions tried. Possibly, diffusion and mobility of the short chains in these polyurethanes is too low to allow complete reaction. Alternatively, the swelling ratios may be dominated by, for example, the soft segment, or to the extent that some hard segment/soft segment phase mixing occurs at low hard segment length, the measured swelling ratios may not be an accurate reflection of $\bar{M}_c$. These results are discussed further below. Specimens from some recipes were further aged at room temperature in air or in nitrogen or at 0°C in air before testing to make certain that representative properties were achieved in the times given above.

Measurement of work of adhesion

180° peel tests were carried out at room temperature ($23 \pm 2°C$) on strips of cloth-backed polyurethane layer after trimming to a uniform width of 2 cm on the substrate. The cloth-backed polyurethane layer was peeled off the substrate at a constant rate of 0.5 cm/min. The same slow rate was used for all measurements. The work of adhesion per unit area of interface was calculated from the time average of the peel force P per unit width of the detaching layer: $W_a = 2P$. The thickness of the adhesive layer was 0.39 ± 0.09 mm. All samples were prepared in the same mold and from the same bolt of cloth. Values quoted for W_a are the average of at least six specimens.

Tensile tests

Tensile tests were carried out at room temperature on a table model 1102 Instron using a crosshead speed of 50 cm/min and dumbbell specimens. Breaking elongation was calculated from the ratio $(L_b - L_0)/L_0$, where L_0 and L_b were the initial length and the length at break, respectively. A minimum of seven specimens were measured for each polyurethane.

Swelling ratio measurements

Duplicate samples were cut from molded rod or sheet. The weight of samples approximately 5 cm long and 1 cm wide was obtained before, W_0, and every 24 hrs after immersion in dioxane solvent at room temperature. Usually two to three days were required to achieve constant weight, W_f. The swelling ratio, q, was calculated from the relationship $(W_f - W_0)/W_0$. The swollen samples were dried first in air and then in a vacuum oven at 60°C and 2 mm Hg until constant weight, W_d, was achieved. The % sol was calculated from the relationship $[(W_0 - W_d)(100)]/W_0$.

X-ray diffraction and optical microscopy

Wide angle X-ray diffraction patterns were recorded with a Phillips XRG-3000. Optical microscopy was carried out with a Leitz Dialux-Pol polarizing microscope.

Glass transition temperatures and hardness determination

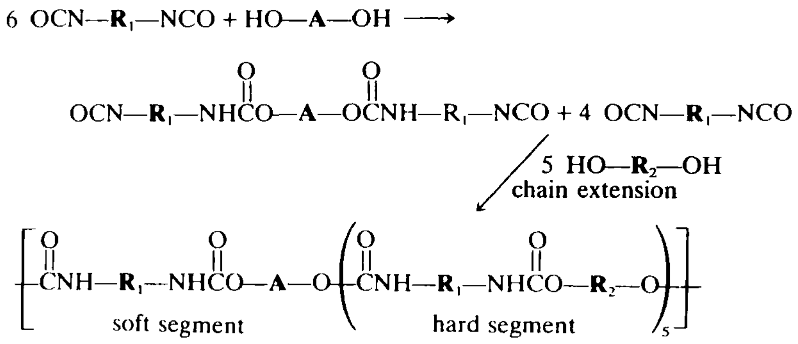
Preliminary DSC traces were recorded on a du Pont Instruments 1090B Thermal Analyzer. A PTC Instruments durometer, model 306L (A-scale), was used for all hardness tests.

RESULTS AND DISCUSSION

The objective of the studies reported in this paper was to determine the effect of the chemical constitution and chemical $\bar{M}_c$ of polyurethanes on their adhesion to substrates. Polyurethanes are a very complex system for which to try to make these determinations. They are also very important commercial adhesives[10] and binders[11,12] about which greater fundamental understanding is needed. The factors that have been considered in the present study are chemical in nature. They include the chemical reactions that can occur, the effect of changing the length of the hard segment while keeping the length of the soft segment constant, the effect of changing the length of the soft segment while keeping the length of the hard segment constant, the effect of chain extension reactions on $\bar{M}_c$, and the effect of changing the polarity of the soft segment. These factors have been considered from a literature point of view and experiments have been carried out to determine how well the properties that are obtained for the present system agree with literature results. The model systems chosen consist of polybutadiene- or polyether-based soft segments, a hard segment derived from TDI and 1,4-butanediol, and crosslinking controlled by the addition of triol. As will be described below, other crosslinking reactions governed by the reactivity of the isocyanate group also occur spontaneously and are difficult to control at will.[10] In order to make this study it was assumed that controllable reactions are overwhelmingly more important for the properties being studied. We recognize that changes in chemical constitution of polyurethanes also can affect physical features of the polyurethanes such as phase mixing, the degree of internal hydrogen bonding and overall morphology; see for example, References 13–16. The interpretations given in this paper assume that the physical features are a reproducible function of the chemical constitution under the conditions of our experiments. We will attempt to point out where chemical constitution changes may have induced changes in physical features. Such changes were not examined in the present study, but might offer an alternative explanation or make an additional contribution to explanations relying on chemical changes alone.

The chemical reactions that can occur

The polyurethanes in this study were prepared by a two stage method of synthesis. In the first stage the polyol, HO—A—OH, was reacted with excess TDI, OCN—R_1—NCO, to form a diisocyanate. In the second stage the stoichiometric amount of hydroxyl from diol and triol needed to react with unreacted isocyanate groups was added and the reaction was carried to completion. If six moles of isocyanate per mole of glycol are used and for purposes of illustration only diol, $HO-R_2-OH$, is used, the primary reactions would be:



$$6\ OCN-\mathbf{R}_1-NCO + HO-\mathbf{A}-OH \longrightarrow$$

$$OCN-\mathbf{R}_1-NH\overset{O}{\overset{\|}{C}}O-\mathbf{A}-O\overset{O}{\overset{\|}{C}}NH-R_1-NCO + 4\ OCN-\mathbf{R}_1-NCO$$

$$\xrightarrow{5\ HO-\mathbf{R}_2-OH \text{ chain extension}}$$

$$\left[-\underbrace{\overset{O}{\overset{\|}{C}}NH-\mathbf{R}_1-NH\overset{O}{\overset{\|}{C}}O-\mathbf{A}-O}_{\text{soft segment}}\underbrace{\left(-\overset{O}{\overset{\|}{C}}NH-\mathbf{R}_1-NH\overset{O}{\overset{\|}{C}}O-\mathbf{R}_2-O-\right)_5}_{\text{hard segment}}-\right]$$

Triol leads to the same reactions as diol except that a network instead of a linear polymer forms. These network bonds are true covalent bonds, which are stable once formed and contribute permanently to the strength of the material. They are different from the physical crosslinks in the hard segment that are formed as a result of hydrogen bonding. Hydrogen bonds can be broken, for example, by raising the temperature, and will reform again on cooling but will not necessarily reform in exactly the same way. Dumais, *et al.* have suggested that in interfacial areas of polyurethanes, the life span of interurethane H-bonds is short ("Interfacial hard segments undergo nearly isotropic motion on a time scale of 10^7/s.").[16] We, therefore, expect that the contribution of the chemical crosslinks to adhesion to surfaces will be greater and more permanent than that of physical crosslinks. If the polyol has a functionality greater than 2, as is the case with the polybutadiene polyol used in this study, additional covalent crosslinks form from this source also. The isocyanate group can react with any adventitious water present in the reaction mixture or on a surface to form amine and carbon dioxide. The isocyanate group can also react with the amine to form a urea, and with urethane groups to form allophanates.

The question of whether there are chemical bonds to the surface also needs to be considered. One report states that isocyanates react with hydrated oxide layers on surfaces, thus producing an *in situ* clean surface, and therein most probably allowing the urea groups of the polyurethane to form chemical bonds with the residual valencies of the surface.[10] Other reports state that values of the molecular weight between crosslinks, $\bar{M}_c$, were different when polyurethane films were crosslinked away from or close to surfaces, but attribute the difference to the formation of physical bonds between the polar (NCO and OH) groups of the polyurethane and the surface.[17,18]

The extent to which side reactions occur, of course, upsets the careful balance of reactants used in the preparation of the polyurethane. In order to make this analysis it was assumed that the effects of the crosslinks deliberately introduced was overwhelmingly greater than those from the many side reactions that are possible.

Changing the length of the hard segment

Changing the length of the hard segment of a polyurethane can be achieved by varying the % free NCO in the charge, while maintaining the ratio of equivalents of diol OH to triol OH constant. Percent free NCO is defined as the ratio [-NCO] to hydroxyl number of polyol and is calculated as follows:

$$\%\text{ free NCO} = \frac{\text{wt. NCO unreacted in first stage} \times 100}{\text{total wt.}}$$

where the wt. NCO unreacted is the number of equivalents of TDI used in excess of the number of equivalents required to react with the polyol multiplied by the equivalent weight of NCO, 42, and the total wt. is the weight of polyol, usually 100 g, plus the weight of TDI given in Table II for the given polymer.

Increasing the % free NCO increases the length of the hard segment because more diol must be added to maintain the balance between NCO and OH. This in turn increases $\bar{M}_c$ but it has other effects also. In one study by Liang and Dreyfuss[19] the effect of changing the % free NCO was examined using polybutadiene polyol and a modified recipe in which the diol was *N,N-bis*-2-hydroxypropylaniline instead of 1,4-butanediol. The results indicated that the work of adhesion increased initially, reached a maximum at about 6% free NCO content and then decreased with further increases in —NCO. Elongation showed similar behavior, tensile strength increased continuously to about 6% free NCO and then remained constant, and shore A hardness increased continuously with % free NCO. It was argued that increasing the —NCO content increases the concentration of urethane groups and thus also increases the polarity and rigidity of the resin. This results in increased intermolecular attractive forces between the adhesive and the surface and accounts for the initial increase in the work of adhesion. Further increase in the —NCO content increased the rigidity so much that the work of adhesion and the elongation at break decreased. Reegen and Ilkka[3] saw a similar increase in adhesion with increasing concentration of urethane groups in a polyurethane prepared from sorbitol, propylene oxide, and TDI. They concluded that there were two reasons for the increased adhesion; namely, an increase in true adhesion due to increased polarity and increased rigidity which required more force to bend the specimen. Reegen and Ilkka were able to distinguish between the effects of intrinsic adhesion and of rigidity in one case where they prepared two series of similar polyurethanes of different rigidity, each at different thicknesses, and extrapolated the observed peel strength to zero thickness. They found that although the more rigid polyurethane showed higher peel forces at every thickness tested, data from both polymers extrapolated to the same intrinsic adhesion.

As can be seen from Table II, in the present study the % free NCO was most commonly kept constant and equal to 6% but in one series of polymers using QO 1000, the ratio was varied from 4 to 20.5%. From a chemical constitution point of view, the increase in NCO percentage results in a greater concentration of isocyanate groups as the hard segment grow longer, more possibilities of hydrogen bonding, and an overall more polar molecule. As in the previous studies, the polyurethanes became increasingly rigid as the % free NCO was increased. The hardness of the samples increased from 52.6 at 4% free NCO to 98.0 at 20.5% free NCO. Peeling occurred predominantly adhesively. Examination of the peeled specimens by eye, by optical microscopy, and by electron microscopy did not reveal areas showing significant cohesive failure. This an indication that covalent bonds are absent or at least low in concentration. Other results are shown in Figure 1. Work of adhesion, ultimate tensile strength, and elongation at break decreased from 4% to 6% free NCO and then increased to 10% free NCO. Work of adhesion and ultimate tensile strength then continued to increase slowly to 20.5%, the highest % free NCO studied, while elongation at break decreased. Simultaneously, the swelling ratios decreased steadily. The decreasing swelling ratios suggest a decreasing $\bar{M}_c$ even though the chemistry should lead to an increasing $\bar{M}_c$. Some explanation is needed. One possibility is that the soft segment swells relatively more than the hard segment in the dioxane solvent used. If so, as the proportion of hard segment increases, swelling ratios would decrease due to changes in composition, and the relationship to $\bar{M}_c$ would be lost. Another possibility is that the swelling ratios do indeed measure the effective crosslink density, but that, as already suggested by Sergeyeva, *et al.*,[18] there is no similarity between the experimentally determined effective crosslink density and the

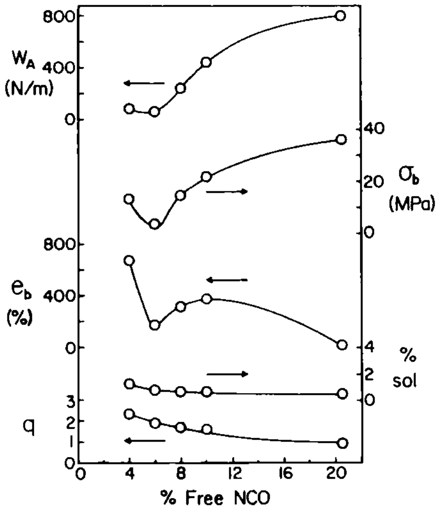


FIGURE 1 Effect of % free NCO content of poly(tetramethylene ether) isocyanate prepolymer on physical properties of polyurethanes.

chemical crosslink density characterized by the ratio NCO/OH groups. Sergeyeva, *et al.* found effective crosslink densities of polyurethanes were smaller than chemical crosslink densities and attributed the decrease to the presence of stable physical crosslinks.[18] We have calculated apparent $\bar{M}_c$ values from our swelling ratios using the Flory-Rehner equation[20] and reasonable polymer-solvent interaction parameters based on those determined by the latter authors and also find that the calculated values are significantly smaller than the chemical crosslink density based on the quantities of reagents charged. Another possibility is that the concept of phase mixing might explain the transition in adhesion, tensile strength, and elongation to break seen in Figure 1 as the hard segment length was varied. Some hard segment/soft segment phase mixing could be occurring at low hard segment length. But as hard segment length increases, phase separation and thus physical crosslink contributions to decreasing $\bar{M}_c$ could be taking place. Our results neither support nor contradict such an explanation. Preliminary T_g measurements were inconclusive with regard to systematic changes in degree of phase mixing as the percent of NCO changed. No direct measurements of degree of phase mixing were made. The combination of earlier results and these new results leads to the conclusion that in polar systems like polyurethanes, where hydrogen bonding within a sample and with a surface is a possibility, adhesion is a function of both the flexibility of the chains between crosslinks and the attractions between the surface and the adhesive; the number of urethane linkages in the hard segment, *i.e.* the length of the hard segment, seems to be an important factor in controlling its adhesion to surfaces.

Changing the length of the soft segment

Changing the length of the polyol segment of a polyurethane without introducing substantial additional polarity in the form of urethane or urea groups can be accomplished by using polyols of different molecular weight. Few such studies have been reported, probably because a sufficiently broad range of molecular weights is not available for most polyols. Kuksin, *et al.*[2] compared the adhesive behavior of polyurethane coatings based on oligodiethylene adipate with molecular weights of 600 and 1200 after reaction with a TDI/triol adduct. They observed that in comparable recipes the decrease in the molecular weight of the starting oligoester led to as much as a six-fold *increase* in adhesion to glass or metals. One difficulty with these results is that the polyols are still rather short and polar. Again the concept of phase mixing can be used to argue that more hard segment/soft segment phase mixing is occurring with the lower molecular weight. Also the proportional number of urethane groups in the polyurethane from the 600 molecular weight species is double the number in the polyurethane from the 1200 molecular weight species. As was shown above, increasing the number of urethane groups increases the adhesion. More data covering a broader range and higher molecular weights of a less polar soft segment is needed to reach a convincing conclusion.

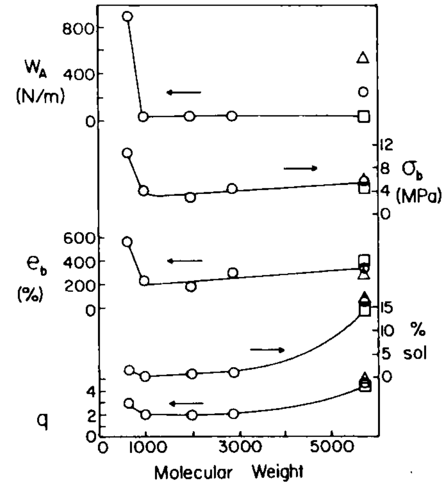


FIGURE 2 Effect of molecular weight of poly(tetramethylene ether) glycols on physical properties of polyurethanes. □ Aged 1.75 hr; ○ aged 24 hr; △ aged 48 hrs. For isocyanate endcapping these glycols were degassed at 100°C, the TDI was added at 60°C as before, but the isocyanate endcapping reaction was continued at 70–80°C instead of 60°C. Otherwise the procedure was the same as the typical reaction given above in the experimental section.

In the present study, as shown in Table I, poly(tetramethylene ether) polyols ranging in molecular weight from 650 to 5750 were used to prepare polyurethanes. The results are summarized in Figure 2. The work of adhesion showed a small to insignificant *decrease* in adhesion to glass as the molecular weight of the starting polyol decreased from 5750 to 1000 followed by a large increase in the work of adhesion of the polyurethane derived from the 650 molecular weight polyol. As stated in the experimental section, the increase might arise from several different causes. It could be attributed to incomplete curing of the sample, evidenced by the higher q and % sol values for this sample. Tensile and elongation behavior were also consistent with this interpretation. At this low molecular weight, diffusion could be too slow and/or the chains might be too short for complete curing to occur. In addition, in this case, there is some evidence for phase mixing in the DSC traces. The low temperature T_g found for the polyurethanes from polyols of 650 and 1000 molecular weight were significantly higher than those for polyurethanes from polyols of higher molecular weight, −20°C and −35°C, respectively, compared to −62°C and lower for the polyols of higher molecular weight. (The T_g's of the pure polyols are 10 or more degrees lower than those found in the polyurethanes.)

Poly(tetramethylene ether) can crystallize, so it was of interest to determine if there was evidence of soft segment crystallization in the polyurethanes derived from these polyols. Some samples were aged at room temperature and others at 5°C and then examined for evidence of crystallinity by wide angle X-ray diffraction and by polarizing microscopy. Tn 5750 was the only sample that

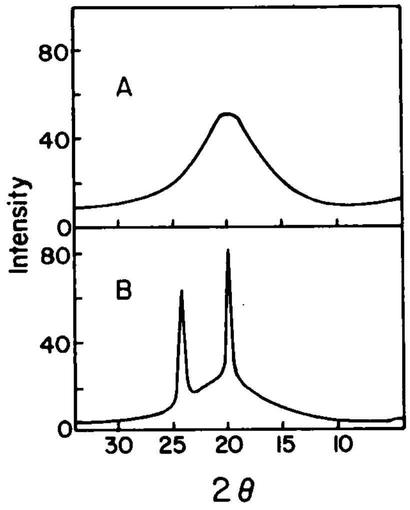


FIGURE 3 X-ray diffraction patterns of polyurethanes from poly(tetramethyl ether) glycols. A from Tc 2900; B from Tn 5750.

showed evidence of crystallinity by either method. (See Figure 3.) It is noteworthy that, as shown in Figure 2, the observed peel force increased more than tenfold as crystallization proceeded. This observation could be due to a genuine increase in the forces bonding the two surfaces or it could arise from an increase in stiffness of the polyurethane and a consequent increase in the force needed to bend the specimen. Perhaps phase separation is occurring. Further study of the effect of crystallization on adhesion is needed. The combined results from glycols of various molecular weights lead to the conclusion that in the absence of chemical bonding, adhesion to substrates decreases or stays constant as the molecular weight of a relatively nonpolar soft segment decreases. At very low molecular weights (~600 for the polymers examined by Kuksin, *et al.*[2] and by us) adhesion seems to increase markedly.

Effect of chain extension

Chain extension of a polyurethane prepolymer occurs when additional diol, usually in the form of a monomeric diol but occasionally in the form of polyol, reacts with the free NCO in the system. In the adhesion studies reported to date triol has most commonly been used as the crosslinking agent and diol OH has been increased at the expense of triol OH, while maintaining the NCO to total OH ratio constant and equal to 1. The $\bar{M}_c$ is increased by segments of hard segment if a monomeric diol is used or by multiples of the polyol if only polyol is used. In one such study Liang and Dreyfuss[19] observed remarkable changes in the work of adhesion as the diol, again in the polybutadiene system with *N,N-bis*-(2-hydroxypropyl)aniline as the diol, and triol concentration were varied at 6% excess NCO. Polymers with the greater percentage of diol gave stronger bonds and their swelling ratios were higher. The observed increase was attributed to two factors; namely, the increase in $\bar{M}_c$ as the relative concentration of diol increased and to the probable presence of additional ionic bonds, formed between the aniline and silanol groups of the glass substrate used, as diol concentration increased.

In another study, Reegen and Ilkka[3] varied the triol/ethylene glycol ratio in polyurethanes prepared from adipic acid, and a constant amount of TDI and studied adhesion of the polyurethanes to nickel and cadmium panels. They argue that rigidity of the films increases with increasing crosslink density (lower $\bar{M}_c$) and observed that the peel strength increases by a factor of two to three when the amount of triol is increased from 10% to 40% of the diol/triol mixture. The effects were attributed to the lower $\bar{M}_c$ but the increased peel forces could also result from increased forces required to bend the stiffer specimens.

Kuksin, *et al.*[2] also noted that the adhesion of polyurethanes is determined by their crosslink density and reported that the highest adhesion was found at the lowest $\bar{M}_c$. They studied polyurethanes prepared from an oligodiethylene adipate with molecular weight of 1200 and TDI/triol adducts. They state that the crosslink density was controlled by "changing the NCO/OH ratio" and plot their results in terms of the latter ratio. Unfortunately, insufficient data are given to determine exactly what this ratio means in terms of concentration of reactants. $\bar{M}_c$ values are calculated from swelling ratios. Typical $\bar{M}_c$ values of 120–300 are given for NCO/OH ratios ranging from 1.25:1 to 4:1 and it is assumed that adhesion is dependent on the value of the overall effective crosslink density, including both chemical and physical nodes.

As can be seen from Table II, in this study polyurethanes have been prepared from polybutadiene glycol using a constant amount of TDI and a variable ratio of diol/triol. The constant amount of TDI means that the $\bar{M}_c$ was varied at constant urethane concentration. The hydrocarbon backbone was chosen to avoid polar effects that might obscure or overwhelm the effect of changes in $\bar{M}_c$. The results are shown in Figure 4. It is apparent from the comparatively high q values that the samples with 80% and 100% triol (20% and 0% diol) were difficult to cure completely, again probably due to poor diffusion and even steric hindrance in such potentially tightly crosslinked systems. From 40% to 100% diol the work of adhesion and other properties, including q, increase as the % diol increases and $\bar{M}_c$ increases. The decrease in the work of adhesion for the polyurethane from 100% diol to the polyurethane from 80% diol was almost 82%, 207 N/m. In the polyurethane from 100% diol, only the residual crosslinking due to the 2.4 functionality of the R-45HT and any allophanates adventitiously formed remain. The work of adhesion for the remaining samples in the series stayed fairly constant with a decrease of 21 N/m over the entire range. As shown in Table III the trend with BAMO/THF glycols was similar. These results are in agreement with those of Liang and Dreyfuss.[19] Why they differ from the conclusions of Reegen and Ilkka[3] and of Kuksin, *et al.*[2] is unresolved at the present time. Perhaps, as suggested above, the polyurethanes in the latter two studies are very

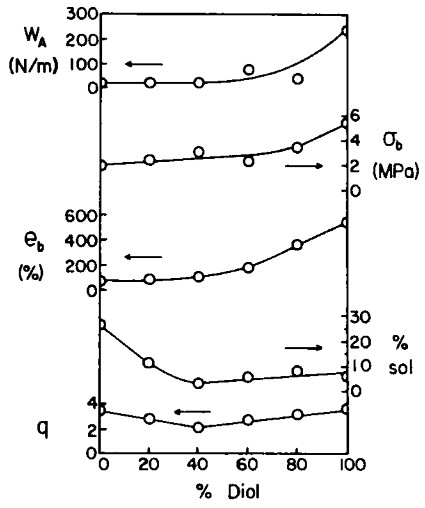


FIGURE 4 Effect of % diol on physical properties of polyurethanes from polybutadiene polyols.

stiff and the higher values of W_a at low $\bar{M}_c$ are due to high bending forces rather than to higher intrinsic adhesion.

Changing the polarity of the polyol

The glycol from the copolymer of BAMO and THF has pendant polar azido side groups as well as oxygen atoms along its backbone. The oxygen atoms occur after every three carbon atoms in the units from BAMO and after every four carbon atoms in the units from THF. The copolymer is therefore more polar than poly(tetramethylene ether) glycol, which is unsubstituted and has an oxygen atom after every four CH_2 groups. Polybutadiene polyol has a hydrocarbon backbone and is the least polar of the polyols. The order of polarity of polyurethanes from these polyols is therefore BAMO/THF > PTHF > PB. Table III shows the effects

TABLE III
Effect of polarity of glycol on properties of polyurethanes

Eq. diol OH / Eq. triol OH	Polymer	W_a (N/m)	σ_b (MPa)	e_b (%)	q	% sol
20/80	BAMO/THF[a]	92	5.2	106	2.79	10.4
	PTHF[b]	54	4.5	282	1.92	1.3
	PB[c]	25	2.3	103	2.88	11.3
80/20	BAMO/THF[a]	143	4.5	224	3.33	7.6

[a] BAMO/THF is the copolymer of BAMO and THF with $\bar{M}_n$ of 2400.
[b] PTHF is Tc 2900 with $\bar{M}_n$ of 2900.
[c] PB is R-45HT with $\bar{M}_n$ of 2800.

of changes in polarity of the glycol on the properties of the resulting polyurethanes. Three polyols of similar number average molecular weight were compared in order to minimize the effects of differences in chain length. On the basis of chain length alone, from the data with poly(tetramethyl ether) glycols presented above, the BAMO/THF polyurethane would be expected to have the smallest adhesion if it differed at all because it has the lowest number average molecular weight, $\bar{M}_n$, of the group. Yet just as increases in polarity due to a greater concentration of urethane groups led to increases in adhesion to surfaces, so increases in polarity of the starting glycol also lead to increases in the work of adhesion. The order of decreasing work of adhesion is BAMO/THF > PTHF > PB for both the 20/80 and the 80/20 ratios of equivalents of diol OH to triol OH studied. Other properties show supporting trends.

CONCLUSIONS

It is difficult to design experiments to test the isolated effect of chemical $\bar{M}_c$ on the adhesion of polyurethanes to substrates. Changes in chemical constitution are likely to lead to physical changes as well. Among the possibilities are compatibility changes, different levels of phase mixing, and morphology changes. The overall effect on adhesion is probably a composite effect of several different factors originating with the chemical constitutional change rather than just an effect of changing $\bar{M}_c$. Bearing this in mind, we suggest that our reexamination of the effect of the $\bar{M}_c$ of polyurethanes on adhesion to glass surfaces supports the following conclusions:

1. Increasing the polarity of a polyurethane increases its adhesion to glass surfaces. The manner of increase of polarity is not important. Polarity can be increased by increasing the number of urethane groups. (One way to achieve this is to increase the length of the hard segment.) Or polarity can be increased by increasing the polarity of the starting glycol. The effect is best demonstrated by changing polarity at constant $\bar{M}_c$. This conclusion is in agreement with the earlier work of Reegen and Ilkka[3], who studied adhesion of polyester polyurethanes to metals, and found that greater urethane content increases adhesion, that a more polar monomeric isocyanate increases adhesion, and that increasing the polarity of the polyester segment increases adhesion. The conclusion is also in agreement with the earlier work of Lipatov, *et al.*,[1,2,17,18] who studied the adhesion of polyurethane coatings to metals and glass and demonstrated that increasing the concentration of polar groups per unit volume of polyurethane improves their adhesion to surfaces. Other physical consequences of changes in polarity of components of polyurethanes are probably differences in degrees of compatibility and phase mixing of the hard and soft segments, plus a magnified effect on properties as a result.
2. Increasing the initial molecular weight of the soft segment at constant urethane concentration may increase adhesion to glass slightly but the effect is

not great. This conclusion is in agreement with the work of Ahagon and Gent,[4] who found that adhesion increases with $\bar{M}_c$ when chemical bonds to the surface are formed, but remains constant if no bonds are present. (The present work shows no direct evidence of chemical bond formation with the surface. It is in agreement with earlier work that indicates physical or polar bond formation of polyurethanes with surfaces.[2]) Tensile strength shows the same trends as adhesion. At very low molecular weight of starting oligopolyether glycol (650) adhesion seems to increase. The latter observation is in agreement with earlier work on oligopolyester glycols.[2]

3. The effect of chain extension at constant concentration of urethane groups was real but not very large in magnitude in the present study. At smaller $\bar{M}_c$, adhesion to glass was smaller. This is consistent with other work on elastomers.[4,5] The difficulty with increasing the $\bar{M}_c$ of a polyurethane by this method is that adding triol changes the linearity of the polymer and thereby alters some of the intermolecular and intramolecular interactions so that the effect on adhesion is probably a composite effect of several different factors rather than just an effect of changing $\bar{M}_c$.

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