

Preparation and Characterization of Cryogenic Adhesives. I. Glycidyl-Terminated Polyurethane Resins

DER-SHYANG CHEN,^{1,*} CHEN-CHI M. MA,² HUNG-CHUNG HSIA,²
WANG-NANG WANG,³ and SHIAW-RUEY LIN³

¹China Technical Consultants, Inc. Catalyst Research Center, Toufen, P.O. Box 88, Miaoli, Taiwan, Republic of China; ²Institute of Chemical Engineering, National Tsing Hua University, Hsin-Chu, Taiwan, 30043, Republic of China; and ³Chung Shan Institute of Science and Technology, Lung-Tan, P.O. Box 90008-17-11, Taoyuan, Taiwan, Republic of China

SYNOPSIS

Glycidol has been introduced into isocyanate-terminated polyurethane to form glycidyl-terminated polyurethane resin. A series of glycidyl-terminated polyurethanes, based on PTMEG, PPG, and polyester soft segments, having different molecular weights were synthesized and their adhesion properties on aluminum were evaluated. The effect of the soft-segment structure, soft-segment length, and temperature on adhesion were examined. It was found that the resin showed superior adhesion at cryogenic temperatures. The results coincide with the phenomenon observed in dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). In addition, the modified system also offered some distinct advantages over the commercial polyurethane adhesives, e.g., good storage stability and room-temperature curing. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Adhesives that exhibit good joint strength in cryogenic environments are playing an important role in the present space exploration, military applications, superconductivity, and handling of liquefied gases, etc. The most promising types reported are the nylon-epoxy, epoxy-polyamide, and polyurethane-type adhesives.¹⁻⁶ Among these, the polyurethane-type adhesives were found to show the highest tensile and peel strengths at cryogenic temperature and pass the thermal shock test.⁷⁻¹⁰

Although polyurethane adhesives possess the best low-temperature properties of all commercially available adhesives, commercial polyurethanes contain free NCO groups that have some limitations. Besides the usual precautions that must be followed in bonding with any adhesives, the urethanes require additional precautions: Small amounts of moisture will interfere with proper curing and the polyurethane adhesives represent a health hazard if not

handled properly. Another class of compounds are those in which the NCO groups are "blocked" or "capped" with "active hydrogen" compounds.¹¹⁻¹³ These products show little or no reaction at room temperature. Some of the disadvantages of employing blocked isocyanates are the high temperatures or long times required for unblocking, as well as the difficulty of removing the blocking agents from the two solid substrates.

This study presents a modified polyurethane-type adhesive that may overcome these disadvantages. Glycidol was used to transfer the NCO-terminated polyurethane prepolymers to glycidyl-terminated polyurethane prepolymers. Polyamines were used as the cross-linking agents. It was found that this type of adhesive not only showed excellent cryogenic adhesion strength and thermal shock resistance, but also had the advantages of room-temperature cure, good storage stability, and higher adhesion strength at higher temperatures. However, little consideration has been taken to assess the relationship between the polyurethane structure and its performance at very low temperature. In this article, the relationship between cryogenic adhesion properties and the polyurethane structure, dynamic properties, and morphology studies will also be reported.

* To whom correspondence should be addressed.

Table I Materials Used in This Study

| Designation | Description | Source |
|----------------|---|----------------------------|
| PTMEG-650 | Polytetramethylethylene glycol, MW = 650 | DuPont Co. |
| PTMEG-1000 | Polytetramethylethylene glycol, MW = 1000 | DuPont Co. |
| PTMEG-2000 | Polytetramethylethylene glycol, MW = 2000 | DuPont Co. |
| PPG-700 | Poly(propylene oxide)glycol, MW = 700 | Chiung Long Co. |
| PPG-2000 | Poly(propylene oxide)glycol, MW = 2000 | Chiung Long Co. |
| POLYESTER-1000 | Polyester, MW = 1000 | Young Shun Chem. Co. |
| POLYESTER-2000 | Polyester, MW = 2000 | Young Shun Chem. Co. |
| TDI | Toluene diisocyanate | BASF |
| | <i>m</i> -Xylylenediamine | Tokoy Kasei Org. Chem. Co. |
| DETA | Diethylenetriamine | Tokyo Kasei Org. Chem. Co. |
| IPDA | Isophoronediamine | Tokyo Kasei Org. Chem. Co. |
| D-230 | Polyoxypropyleneamines | Jefferson Chem. Co. |
| Glycidol | 2,3-Epoxy-1-propanol | Aldrich Co. |

EXPERIMENTAL

Materials

The materials used for this study are listed in Table I. The polyols (PTMEG-650, PTMEG-1000, PTMEG-2000, PPG-700, PPG-2000, POLYESTER-1000, and POLYESTER-2000) were heated at 60°C and degassed by vacuum overnight before use. The TDI, glycidol, and cross-linking agents were employed as received.

Preparation of Glycidyl-terminated Polyurethane Resins

The preparation of glycidyl-terminated polyurethane resin (samples A–G) was carried out in two steps: NCO-terminated polyurethane prepolymers were synthesized in the first step. Then, glycidol was added to prepolymers and reacted with the NCO groups through hydroxyl groups; hence, the prepolymer will be glycidyl-terminated.

The first step involved the charging of 1 equivalent of polyol into a reaction kettle, 6 equipped with a nitrogen inlet, an electric-powered mechanical stirrer, a heating mantle, and a reflux condenser. Then, 2 equivalents of TDI was added and mixed. The temperature was maintained at approximately 70°C during the reaction, which was carried out under dry nitrogen. The NCO content was determined by the di-*n*-butylamine titration method.¹⁴ When the NCO content reached the theoretical value, the reaction was stopped.

When the first step was completed, the temperature was cooled down to 40°C and 2 equivalents of glycidol was added and mixed. The temperature was increased slowly and maintained at approximately 70°C to allow the terminating reaction to take place. A sample of the reacting mixture was taken every 0.5 h for IR analysis and determined by the di-*n*-butylamine titration method¹⁴ separately. The absorption peak of the —NCO group (2270 cm⁻¹) decreased during the reaction and eventually become zero. The results indicated that the hydroxy groups in the glycidol had completely reacted with the —NCO group of the polyurethanes prepolymer as shown in Figure 1.

Testing Methods

IR spectra were recorded on a Domet DA3-002 FTIR spectrometer to detect the absorption peaks that are characteristic of the resins during the synthetic procedures. The epoxide equivalent of glycidyl-terminated polyurethanes was determined by titrating with a standard solution of HBr in acetic acid following the procedure outlined in ASTM D-1652.

The tensile shear strength properties were measured on an Instron TM-SM universal test unit. The test specimens used were made of 6016-T6 aluminum alloy. The surfaces to be bonded were etched by an sodium dichromate–sulfuric acid etching process.¹⁵ One equivalent of the glycidyl-terminated polyurethane was mixed homogeneously with 1.05 equivalent of amine curing agent. The mixtures were

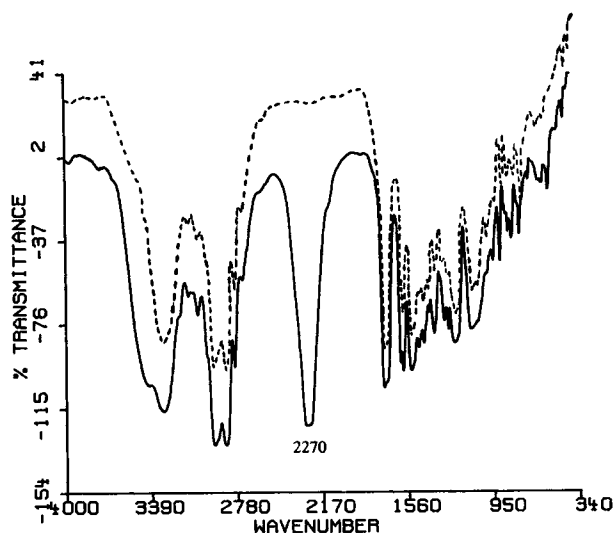


Figure 1 Infrared spectra of the reaction of isocyanate-terminated polyurethanes with glycidol: (----) start of reaction; (.....) end of reaction.

then applied to the metal within 30 min. The test panels were bonded together under the pressure of 100 psi and cured for 7 days at room temperature. The cured glue line thickness was controlled at 0.003 in. + 0.0005 in. The test procedures at elevated temperature, room temperature, and low temperature followed the methods described in ASTM D-2259, ASTM D-1002, and ASTM D-2557, respectively.

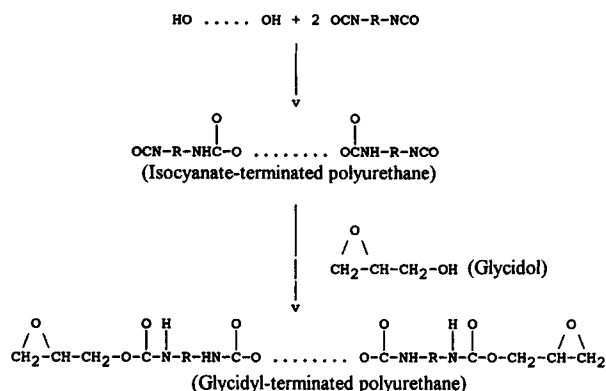
The dynamic mechanical properties of the specimens were measured using a Rheometrics dynamic spectrometer, Model RDS-7700, over a temperature range of -120 to 70°C at a heating rate of $5^{\circ}\text{C}/\text{min}$ and a frequency of 1 Hz. The dimensions of the sample were approximately $6 \times 1 \times 0.2$ cm. SEM

was taken for the fractured surface of the tensile shear strength test specimen at liquid nitrogen temperature with a Hitachi S-570 instrument.

RESULTS AND DISCUSSION

Material Characterization

A series of glycidyl-terminated polyurethanes, based on poly(tetramethylethylene glycol) (PTMEG), poly(oxypropylene glycol) (PPG), and polyester soft segments, having different molecular weights, were synthesized and are shown in Table II along with their epoxy constants. The synthesis scheme is illustrated below:



An isocyanate-terminated polyurethane prepolymer was synthesized in the first step. Then, glycidol was added to react with the isocyanate group through its hydroxyl group and the glycidyl-terminated prepolymer was formed.

In practice, many of the commercially available polyurethane adhesive systems usually contain free

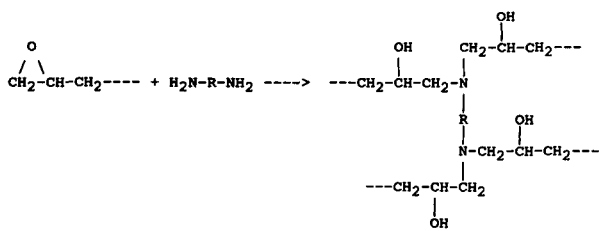
Table II Epoxide Equivalent of Synthesized Glycidyl-terminated Polyurethanes

| Sample | Soft Segment | | Epoxide Equivalent (g of Resin Containing 1 g Equivalent of Epoxide) (Actual Values) ^a | Epoxide Equivalent (Theoretical Values) |
|--------|--------------|------|--|--|
| A | PTMEG | 650 | 712 ± 18 | 573 |
| B | PTMEG | 1000 | 906 ± 20 | 748 |
| C | PTMEG | 2000 | 1450 ± 23 | 1248 |
| D | PPG | 700 | 754 ± 3 | 598 |
| E | PPG | 2000 | 1565 ± 3 | 1248 |
| F | Polyester | 1000 | 970 ± 6 | 748 |
| G | Polyester | 2000 | 1551 ± 28 | 1248 |

^a Actual values of epoxide equivalent was determined according to ASTM D-1652.

or chemically blocked isocyanates. Polyurethanes offer several distinct advantages for low-temperature adhesives; however, the high reactivity of the isocyanates toward water and the fact that the chemically blocked isocyanates cure takes place at high temperatures are limitations of conventional polyurethane adhesives.¹¹⁻¹³

This study describes a family of glycidyl-terminated polyurethanes to overcome these disadvantages. Polyurethanes containing isocyanate groups are reacted with glycidol to form glycidyl-terminated polyurethanes. Cross-linking in these cases occurs primarily through the epoxide groups, e.g.:



This modified system offers the potential for producing products that can incorporate the desirable properties of polyurethane and epoxy polymers. The glycidyl-terminated polyurethane has the advantage that it can be processed in the same manner as epoxy resins and by containing the polyurethane backbone, offers superior adhesion at cryogenic temperature.

Before the glycidyl-terminated polyurethane resins can be used for adhesive applications, they have to be converted, by means of cross-linking reactions, to form a three-dimensional infusible network held together by covalent bonds. Most of the curing agents in common use can be classified into three

Table III Tensile Shear Strength Data for Typical Curing Agents with Formulations Based on Sample A

| Curing Agent | Tensile Shear Strength on Aluminum, psi (MPa) | |
|---------------------------|---|----------------------------|
| | -320°F (-160°C) | 77°F (25°C) |
| Diethylenetriamine | 5830 ± 250 (40.2 ± 1.7) | 2050 ± 200 (14.1 ± 1.4) |
| <i>m</i> -Xylylenediamine | 6260 ± 360 (43.2 ± 2.5) | 1950 ± 150 (13.4 ± 1.0) |
| Isophoronediamine | 4720 ± 210 (32.6 ± 1.5) | 1670 ± 120 (11.5 ± 0.8) |
| Polyoxypropyleneamines | 5040 ± 225 (34.8 ± 1.6) | 1450 ± 85 (10.0 ± 0.6) |

Table IV Tensile Shear Strength Data for Various Glycidyl-terminated Polyurethane Resins with *m*-Xylylenediamine Curing Agent

| Sample | Soft Segment | | Tensile Shear Strength on Aluminum, psi (MPa) | |
|--------|--------------|------|---|----------------------------|
| | | | -320°F (-160°C) | 77°F (25°C) |
| A | PTMEG | 650 | 6260 ± 360 (43.2 ± 2.5) | 1950 ± 150 (13.4 ± 1.0) |
| B | PTMEG | 1000 | 6730 ± 325 (46.4 ± 2.2) | 1560 ± 95 (10.8 ± 0.7) |
| C | PTMEG | 2000 | 7890 ± 410 (54.4 ± 2.8) | 1200 ± 60 (8.3 ± 0.4) |
| D | PPG | 700 | 5435 ± 225 (37.5 ± 1.6) | 2180 ± 135 (15.0 ± 0.9) |
| E | PPG | 2000 | 6520 ± 190 (44.9 ± 1.3) | 1250 ± 70 (8.6 ± 0.5) |
| F | Polyester | 1000 | 4340 ± 175 (29.9 ± 1.2) | 1750 ± 105 (12.1 ± 0.7) |
| G | Polyester | 2000 | 5720 ± 220 (39.4 ± 1.5) | 1090 ± 40 (7.5 ± 0.3) |

groups, namely, amine curing agents, anhydride curing agents, and Lewis acid catalytic curing agents. Anhydrides, which are important in other areas of epoxy technology, have limited use in adhesives because of inferior properties and the high curing temperatures required.¹⁶ For room-temperature curing applications, in the formulation of glycidyl-terminated polyurethanes, the aliphatic amine curing agents are often preferred. Table III lists the data obtained for typical aliphatic amine curing agents using PTMEG-MW650 as soft segments. *m*-Xylylenediamine was selected as the curing agent in this study. The results indicate that the four amine curing agents used in glycidyl-terminated polyurethane resins exhibit good adhesion at room temperature and at cryogenic temperatures.

Effect of the Structure and Length of Soft Segment on the Adhesion Behavior

The adhesion properties of the glycidyl-terminated polyurethanes are shown in Table IV. In this study, PTMEG, PPG, and polyester-type soft segments were investigated. The PTMEG-based polyurethanes provided the most attractive capability as adhesives for use at liquid nitrogen temperature. PPG-based and polyester-based polyurethanes show acceptable performance. The above results are attributed to the degree of flexibility of the polyurethanes due to their soft-segment structures.⁸

The other important feature of these synthetic polymers is their adhesion behavior that can be varied with the soft-segment length. It was found that the tensile shear strength at room temperature decreases with increasing chain length of the soft segment for three segmented polyurethanes with PTMEG soft segment of molecular weights, 650, 1000, and 2000 (samples A, B, and C). In contrast, the tensile shear strength at liquid nitrogen temperature increases with increasing chain length of the soft-segment. The same phenomenon was observed for different soft-segment structures (i.e., PPG, polyester).

From the study on the failure behavior of the tensile shear strength test specimen, it is apparent that the failure mode of the specimen is cohesive failure, which is a property dominated by resin. When the modulus of the adhesive polymer is too low, cohesive strength and temperature resistance of the polymer decrease under mechanical stress. This means that the adhesion behavior at room temperature is attributed to the decreased modulus of the glycidyl-terminated polyurethanes due to their long chain length of soft segments. Adhesion properties are influenced by the mobility of the molecular chain structure.

The difference in adhesion behavior at cryogenic temperatures described above might be rationalized by reference to the literature.¹⁷⁻¹⁹ Segmented polyurethanes are a class of block copolymers, consisting of alternating "soft" and "hard" blocks. Soft seg-

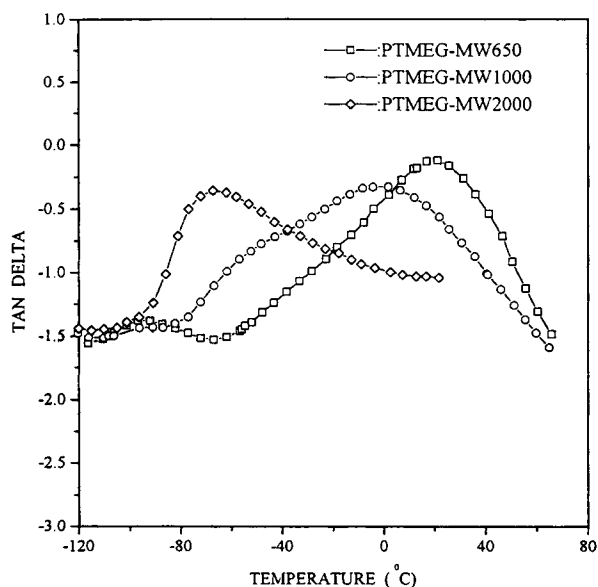


Figure 2 Temperature dependence of $\tan \delta$ for PTMEG-based polyurethanes.

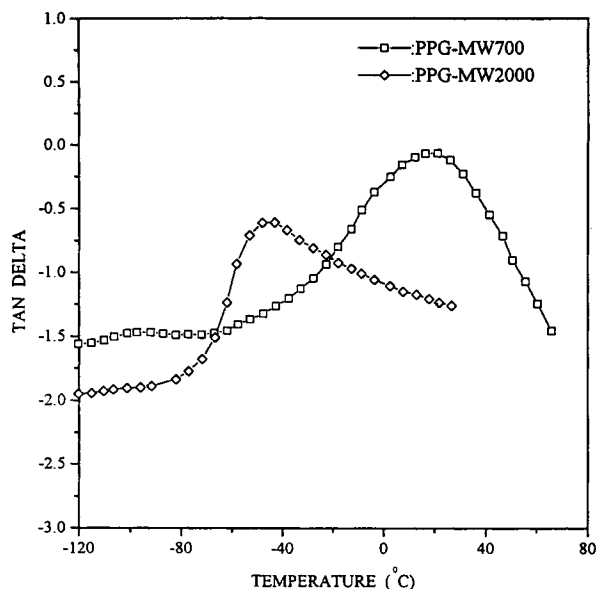


Figure 3 Temperature dependence of $\tan \delta$ for PPG-based polyurethanes.

ments are usually made of polyether or polyester chains, whereas the hard segment usually consists of a diisocyanate. The properties of segmented polyurethane can be varied across a wide range and depend on the soft-segment length, soft-segment concentration, and chemical structure of both segments. Soft segments are quite mobile and are normally present in a coiled formation. Due to the immiscibility of the two blocks, phase separation takes place. The microphase separation takes place if the length of the blocks exceed a certain value. This process continues with decreasing temperature. The existence of a two-phase morphology plays an important role in toughening polyurethane resins. It means that the long soft-chain-length-based polyurethane was tougher than the short-chain-length-based polyurethane at cryogenic temperature.

Dynamic Mechanical Behavior and Morphology

The above adhesion properties coincide with the phenomenon observed in dynamic mechanical analysis and scanning electron microscopy. Dynamic mechanical analysis (DMA) scans of the glycidyl-terminated polyurethane resins containing the soft segments of PTMEG, PPG, and polyester with different molecular weights are shown in Figures 2-7. Figures 2-4 illustrate the curves of the $\tan \delta$ vs. temperature; one can see that the resins exhibit two distinct peaks. Apparently, the α -transition peak

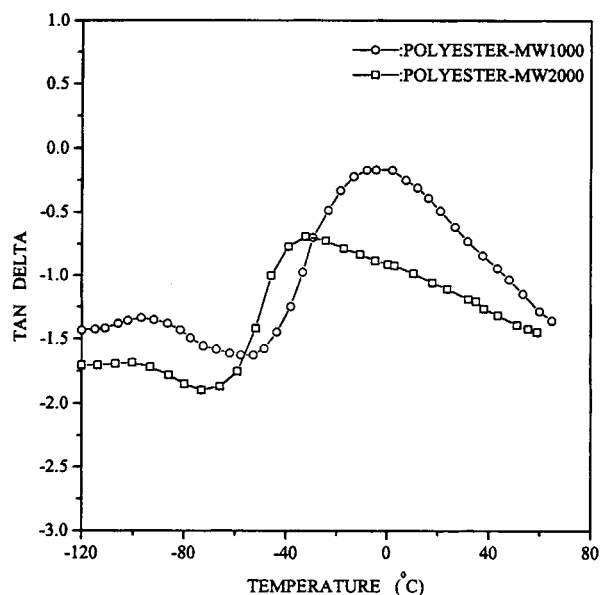


Figure 4 Temperature dependence of $\tan \delta$ for polyester-based polyurethanes.

shifts to higher temperature when the chain length of the soft segment decreases. From Figures 5–7, it can be seen that the storage modulus of resins at room temperature increases with decreasing chain length of the soft segment. One can conclude that polymers become stiffer and stronger if the molecular weight of the soft segment used in the preparation is decreased. Consequently, the cohesive fail-

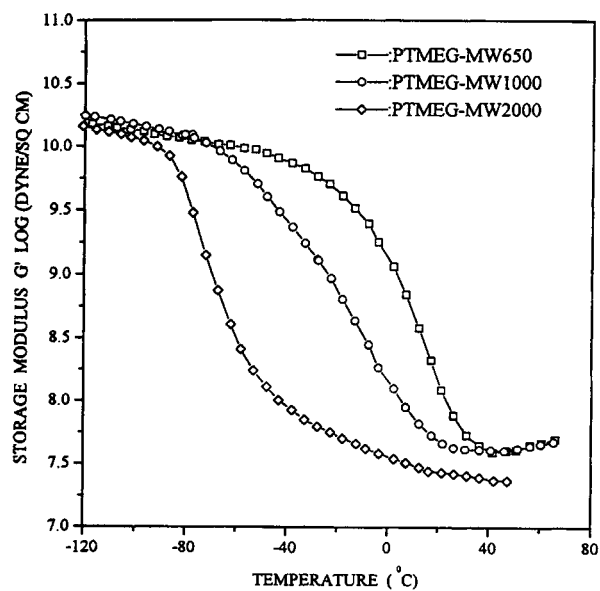


Figure 5 Temperature dependence of storage modulus (G') for PTMEG-based polyurethanes.

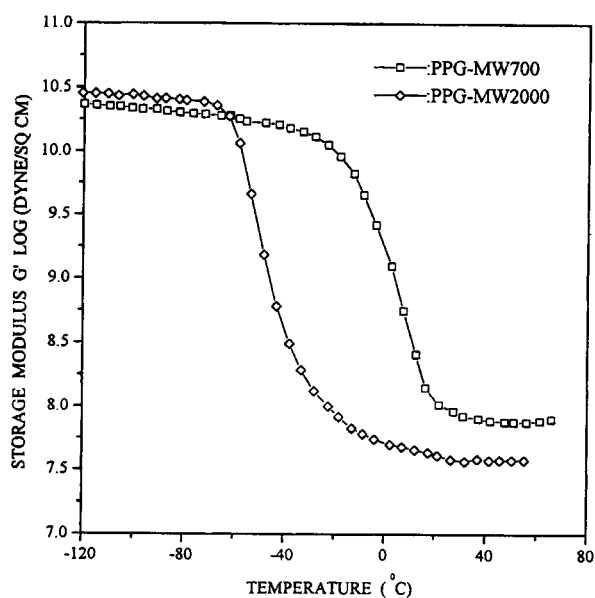


Figure 6 Temperature dependence of storage modulus (G') for PPG-based polyurethanes.

ure resistance at room temperature increases with decreasing chain length of the soft segment.

The morphology of the fractured surface of the tensile shear strength test specimen at liquid nitrogen temperature was investigated by scanning electron microscopy (SEM). The microphotographs of the glycidyl-terminated polyurethane containing the soft segments of PTMEG, PPG, and polyester, with

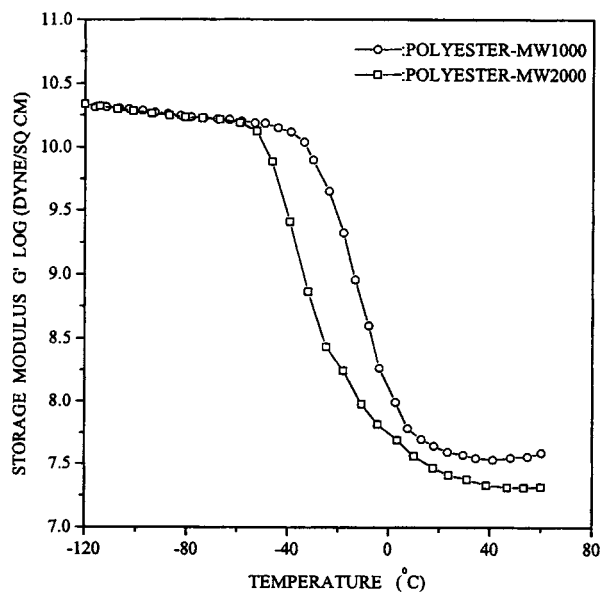


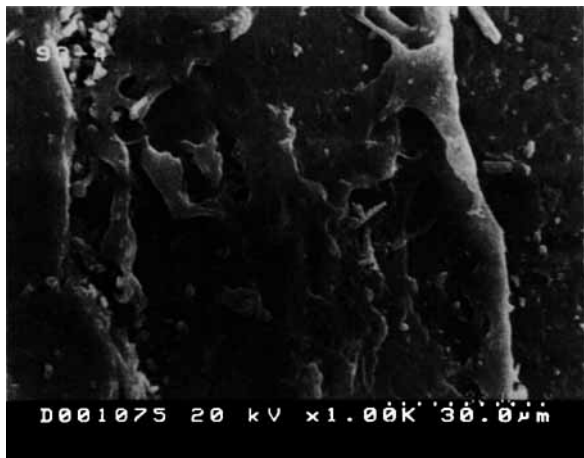
Figure 7 Temperature dependence of storage modulus (G') for polyester-based polyurethanes.



(a)



(b)



(c)

Figure 8 Scanning electron micrograph of the fractured surface of tensile shear strength test specimen of PTMEG-based polyurethane at liquid nitrogen temperature: (a) PTMEG-MW 650; (b) PTMEG-MW 1000; (c) PTMEG-MW 2000.

different molecular weights, are shown in Figure 8. Figure 8(a) shows a homogeneous structure. However, Figure 8(b) and (c) shows that the roughness of the fractured surface increased as the chain length of the soft segment increased. It was found that PTMEG-MW2000-based polyurethane was tougher than was the PTMEG MW-650-based polyurethane. The same phenomenon was observed for the PPG and polyester-based polyurethane; the long soft-chain-length-based polyurethane was tougher than the short-chain-length-based polyurethane at cryogenic temperature.

CONCLUSIONS

Glycidol was used to convert the isocyanate-terminated polyurethane prepolymer to glycidyl-terminated polyurethane prepolymer. It was found that this type of adhesive not only showed superior adhesion strength at cryogenic temperature, but also had the advantage that it can be processed in the same manner as epoxy resins. Cross-linking in this case occurs primary through the epoxide group.

The effect of the structure and length of soft segment on adhesion was examined. One of the important features of these synthetic resins is that their adhesion behavior depends on the soft-segment length. The tensile shear strength at room temperature decreases with increasing chain length of the soft segment. In contrast, the adhesion strength at liquid nitrogen temperature increases with increasing chain length of the soft segment. The same phenomenon were observed for different soft-segment structures.

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