ADD422103

UCRL-52044

PROPERTIES OF THREE ADIPRENE-BASED ADHESIVES

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
PICATINNY ARSENAL, DOVER, N. J.

H. George Hammon
Norriss Hetherington

April 1, 1976

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Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

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PLASTEC 25405

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $; Microfiche $2.25

Page Range	Domestic Price	Page Range	Domestic Price
001–025	$ 3.50	326–350	10.00
026–050	4.00	351–375	10.50
051–075	4.50	376–400	10.75
076–100	5.00	401–425	11.00
101–125	5.25	426–450	11.75
126–150	5.50	451–475	12.00
151–175	6.00	476–500	12.50
176–200	7.50	501–525	12.75
201–225	7.75	526–550	13.00
226–250	8.00	551–575	13.50
251–275	9.00	576–600	13.75
276–300	9.25	601–up	*
301–325	9.75		

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MS. date: April 1, 1976

Contents

Summary 1

Introduction 2

Characterization of Adiprene Resins 3

  Characterization of Adiprene L-100 3

  Adiprene L-100 Curing Studies 4

  Characterization of Adiprene L-315 5

  Formulation of L-315/Polyol 5

  Characterization of Adiprene LW-520 6

  Curing of Adiprene LW-520 6

Precautions for Handling Adhesive Components 7

Curing Rates and Strengths of Adhesive Bonds to Aluminum Substrates 8

  Cure Rates at Room Temperature 8

  Adhesion Properties 9

  Tensile Properties 10

  Correlation of Tensile Properties with Temperature and Shear Rate 11

  Permeability to Gas and Water Vapor of Adhesive Compositions 12

  Linear Coefficient of Thermal Expansion 13

  Glass-Transition Temperatures 13

  Density 14

  Elemental Analyses 14

  Tensile Failure Envelope 15

  Dynamic Shear Modulus of Adiprene Polymers 15

Acknowledgments 17

References 18

Appendix A Supplemental Tables and Figures 19

Appendix B Mathematical Correlations of Bulk Tensile Properties of Adiprene Adhesives with Testing Temperature and Strain Rate 31

Appendix C A Hypothetical Model Relating the Stress-Strain Behavior of Cured Urethane Adhesives to Their Structure 36

PROPERTIES OF THREE ADIPRENE-BASED ADHESIVES

Summary

This report, which replaces UCRL-75591, summarizes the properties of three Adiprene-based adhesives used in weapons applications.*

The preferred adhesive has been Adiprene L-100 polyurethane cured with methylenebis-(2-chloroaniline) (MOCA), but its use has been curtailed by Occupational Safety and Health Administration toxicity regulations. Two substitute compositions are Adiprene L-315 cured with a mixture of 1,4-butanediol, trimethylolpropane, and ferric acetylacetonate (L-315/polyol/FAA) and Adiprene LW-520 cured with methylenedianiline (LW-520/MDA).

When all the known properties are considered, the L-315/polyol composition should be as satisfactory as L-100/MOCA in most applications. A good second choice is LW-520/MDA, if its high viscosity and limited working life can be tolerated. The LW-520/MDA may be preferred if a low modulus at low temperature is important.

Table 1 compares typical bulk properties of the three Adiprene adhesives cured at room temperature. Though many properties of the three adhesives are similar when measured at room temperature, cured L-315/polyol is distinctly harder at low temperatures and softer at high temperatures. This behavior should be considered if the L-315/polyol is selected for use.

The ultimate tensile strengths of adhesive bonds to metal substrates are nearly the same for all three adhesives. However, strength develops more slowly in L-315/polyol/FAA bonds than in L-100/MOCA bonds. This can be remedied by a slight change in formulation to L-315/polyol/DABCO, which cures to a high early strength--a definite advantage in subassembly operations. The peel strength of the L-315/polyol bonds is higher than that of the other two Adiprene-based adhesives.

Although the difference may not be significant in most applications, it is worth noting that the L-315/polyol is only one-third to one-half as permeable to gases and water vapor as either L-100/MOCA or LW-520/MDA.

The dynamic shear moduli, linear coefficients of expansion, and glass-transition temperatures of the three adhesives are also reported. A more complete report on the dynamic moduli will be issued at a later date.

Tensile-failure data for all three Adiprene adhesives were integrated into a common failure envelope that relates ultimate stress and strain to strain rate and temperature. The fact that all the failure data

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*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research and Development Administration to the exclusion of others that may be suitable.

Table 1. Typical bulk properties of room-temperature-cured Adiprene compositions.

Property	L-100/MOCA	L-315/polyol	LW-520/MDA
Specific gravity	1.11	1.14	1.06
Hardness:			
Shore A	90	90	92
Shore D	43	40	43
Glass-transition temperature, K	220	274-278	210
Pot life, min	60-90	90-120	30-45
Exotherm, °C	25	40	20
Viscosity at 25°C, Pa-sec	40.	15.	80.
Bulk tensile strength, MPa	85	60	36
Strain at break	4.9	3.3	2.6
Shrinkage, %	0.5-0.7	0.4-0.5	1.0-1.3
Poisson's ratio	0.49	0.48	--
Linear coefficient of thermal expansion, $°C^{-1}$	1.7×10^{-4} [a]	1.7×10^{-4}	1.7×10^{-4}

[a] Cured at 100°C.

fall in or near the same envelope suggests that the three adhesives fail by the same mechanism.

Though time was not available to complete the work, some progress has been made in finding equations that correlate the tensile properties of cured L-100/MOCA and LW-520/Tonox (polymeric methylenedianiline) adhesives with temperature and strain rate. Except at low temperatures, the equations now in hand describe the entire stress-strain curve of these compositions. The coefficients of the equations may be related to the molecular structure.

Equations have been calculated to fit the response of stress and strain at break to temperature and strain rate for two of the Adiprene formulations, L-100/MOCA and LW-520/Tonox, both cured at 100°C. These equations have been used to generate pseudo-three-dimensional response surfaces (Figs. B1 through B4 in Appendix B).

Introduction

Adiprene L-100 cured with 4,4'-methylene-bis(2-chloroaniline)(MOCA) has been used in the assembly of nuclear weapons and devices because it is compatible with the high explosive and other weapons components, and because it cures without the release of solvents or other low-molecular-weight fragments. In May 1973 the Occupational Safety and Health Administration (OSHA) published a temporary standard severely restricting the use of 14 potential carcinogens, including MOCA. In response to this new standard, production of nuclear weapons at ERDA agencies (formerly AEC agencies) was halted, and a search for replacement adhesives was started.

Because it was vital to resume the production of nuclear weapons as soon as possible, LLL reviewed a number of candidate replacement materials in August 1973 and decided to concentrate efforts on two compositions: (1) Adiprene L-315 cured with a polyol mixture catalyzed with ferric acetylacetonate and (2) Adiprene LW-520 cured with methylenedianiline (MDA). Both of these cured compositions were sufficiently like cured Adiprene L-100/MOCA for compatibility problems to be unlikely, and their room-temperature mechanical properties were fairly similar. Although it was apparent that the LW-520/MDA was a closer match to L-100/MOCA than was the L-315/polyol, L-315/polyol was chosen as the prime candidate because of concern about the acceptability of methylenedianiline to OSHA. Chemically, methylenedianiline is very similar to MOCA, and studies elsewhere have shown it to be carcinogenic when ingested by rats.

Accordingly, LLL initiated an extensive study to optimize the L-315/polyol formulation and to measure its properties. Simultaneously, other ERDA agencies conducted property and compatibility studies, and several of these agencies have issued reports about their work (see references). This report is intended to bring together and summarize the pertinent data from all sources.

A permanent federal standard covering the use of MOCA has been in effect since February 11, 1974. The standard gives some, but not much, relief from the earlier, temporary restrictive OSHA order. Though the federal standard is still in litigation, substitutes for L-100/MOCA are still urgently needed. New compositions are under intensive study.

Characterization of Adiprene Resins

CHARACTERIZATION OF ADIPRENE L-100

Adiprene L-100 is an isocyanate-terminated polyether, the reaction product of a poly(oxytetramethylene) glycol with toluene diisocyanate. The manufacturer, E. I. du Pont de Nemours & Co., Inc.,[1] claims for the material the properties given in Table 2.

Most of the LLL adhesive test specimens were prepared from one lot of Adiprene L-100 identified as lot 420N-40016960, package No. 54, which contained 4.19% isocyanate by our analyses, in agreement with manufacturer's data. The equivalent weight is thus 42/0.0419 = 1002. The polymer is bifunctional, and, assuming no free toluene diisocyanate, the number-average molecular weight is 2004.

Number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights were measured by gel-permeation chromatography, using NBS-706 polystyrene as the calibration standard and assuming a Q-factor (molecular weight of repeat unit divided by length) of 15. On this basis, $\overline{M}_n = 1851$, $\overline{M}_w = 2900$, and dispersity = 1.62.

Table 2. Typical properties of Adiprene L-100 polymer.

Physical form	Viscous liquid
Color	Honey colored
Odor	None
Specific gravity at 25°/4°C	1.06
Flash point, °C	249
Storage stability	Excellent in absence of moisture
Brookfield viscosity, cP:	
at 30°C	18,000 ± 3000
at 100°C	500-600
Available isocyanate content, %	4.10 ± 0.20
Solubility	Aromatic hydrocarbons, ketones, esters, and chlorinated hydrocarbons

ADIPRENE L-100 CURING STUDIES

For commercial applications Adiprene L-100 is normally cured with MOCA[2] at 100°C. Mixing and curing instructions, as well as the properties of the cured material, are shown in Table 3, which is reproduced from the manufacturer's literature.[1]

For use as an adhesive in weapons, however, Adiprene L-100/MOCA is usually cured at room temperature, and the properties of the cured polymer are somewhat different.[3] During the 100°C cure some allophanate crosslinks are formed, whereas little or no allophanate crosslinking occurs during room-temperature cure. These differences are reflected in the apparent initial modulus of the cured materials, as well as in some other properties. The modulus of the compositions cured at 100°C increases with increasing temperature over the test temperature range from about 20 to about 100°C. However, the modulus of room-temperature-cured material was reasonably constant at test temperatures from about 20 to about 50°C, though it declined at higher temperatures.

Table 3. Typical properties of vulcanizates.[a]

Composition	
Adiprene L-100, parts	100
MOCA, parts	12.5
Mixing and curing	
Mix temperature, °C	100
MOCA temperature, °C	121
Cured, hr/°C	1 to 3/100
Pot life at mix temperature, min	15
Demolding time for a 2- to 10-lb casting at 100°C, min	30 to 45
Physical properties[b]	
Modulus, MPa:	
100%	7.6
300%	14.5
Tensile strength, MPa	31
Elongation at break, %	450
Hardness:	
Durometer A	90
Durometer D	43
Specific gravity at 24°C	1.10
Thermal conductivity, Btu/hr-ft^2-(°F/min)	0.917
Tear strength, kg/cm:	
Split	13
Graves	89
Abrasion resistance, NBS index, %	175
Compression set, %:	
Method B, 22 hr at 70°C	27
Method A, 22 hr at 70°C	9
Linear coefficient of thermal expansion, in./in.-°F:	
-36 to 0°C	1.43×10^{-4}
0 to 24°C	1.01×10^{-4}
24 to 100°C	0.95×10^{-4}
100 to 150°C	0.90×10^{-4}
Linear shrinkage, %	1.0
Brittleness temperature (solenoid)	below -68°C

[a] Data from Ref. 1.

[b] Test specimens were conditioned for 1 week at 24°C and 50% relative humidity before testing.

The manufacturer states that optimum properties of Adiprene L-100/MOCA cured at 100°C are obtained at a MOCA concentration of 12.5 phr (parts per hundred parts resin). At LLL it was found that the room-temperature-cured adhesive exhibited optimum properties at stoichiometric quantities of L-100 and MOCA, that is, at about 13 phr. The tensile strength of the fully cured adhesive was lower at MOCA levels above or below 13 phr.

CHARACTERIZATION OF ADIPRENE L-315

Like Adiprene L-100, Adiprene L-315 is the reaction product of a poly(oxytetramethylene) glycol and toluene diisocyanate. Compared to Adiprene L-100, it is made from a lower molecular weight polyether, has a lower viscosity (about 15 Pa-sec at 30°C), and contains more free toluene diisocyanate (about 4%). Analysis by gel-permeation chromatography shows a definite bimodal distribution as well as the following properties: $\overline{M}_n = 610$, $\overline{M}_w = 1060$, and dispersity = 1.74. The available isocyanate is about 9.5%, and thus the equivalent weight is about 442.

FORMULATION OF L-315/POLYOL

The Adiprene L-315/polyol formulation is basically the same as that described in the Du Pont trade literature[4] and was selected because the room-temperature properties of the cured composition were close to those of Adiprene L-100/MOCA. Without a catalyst, however, the L-315/polyol requires a high-temperature cure. We selected ferric acetylacetonate as the catalyst because it has reasonable activity in promoting the isocyanate-hydroxyl reaction and because it had previously been used in high-explosive binder systems as a catalyst for other urethane systems. Thus its compatibility with high explosives seemed ensured.

In the polyol portion of the system, we tested compositions containing 1,4-butanediol in the range 6 to 9 parts per 100 parts L-315 and trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol, or TMP] in the range 0 to 3 parts per 100 parts L-315. The final formulation developed from the tests was as follows:

Component	Parts by weight
Adiprene L-315	100
1,4-Butanediol	7
Trimethylolpropane	2
Ferric acetylacetonate	0.03

This formulation cured reasonably well in 24 hr at room temperature and had a pot life of 90 to 120 min (100-g batch in an insulated container) with an exotherm (temperature rise) of about 40°C. Because the ferric acetylacetonate catalyst promotes the isocyanate-water reaction as well as the isocyanate-hydroxyl reaction, it is imperative that the components and the substrate be quite dry. Fortunately, 1,4-butanediol can be obtained as the anhydrous grade containing less than 500 ppm water. Trimethylolpropane can be purchased with as little as about 300 ppm water. Care must be taken, however, because both materials are hygroscopic and will absorb large quantities of water from the atmosphere if unprotected.

The polyols and catalyst should be compounded before they are mixed with the

L-315. We recommend heating the 1,4-butanediol to about 60°C, adding the ferric acetylacetonate with stirring or shaking until it dissolves, adding the trimethylolpropane at 60°C, and vacuum degassing and purging the mixture with argon prior to storing. One should avoid heating much above 60°C because this may cause the mix to turn cloudy and change the cure rate and stability of the polyol component.

Made in this manner, the polyol component is a clear, red-orange solution. At present, we recommend that its shelf life be no more than 60 days, though more prolonged storage may be possible. As noted above, the polyol mixture is hygroscopic and should be protected carefully from atmospheric moisture. If the mixture is cloudy or contains a precipitate, it should not be used.

In preparing the adhesive, 9.03 parts by weight of the polyol component are added to 100 parts by weight of the Adiprene L-315 at room temperature. We recommend mixing a 109-g batch by hand for 3 min.[5] The mixture should be vacuum degassed prior to use, or the mixing may be done *in vacuo*. A higher viscosity, quicker setting material can be made by preheating the L-315 to 50°C before adding the polyol component.

CHARACTERIZATION OF ADIPRENE LW-520

Though Adiprene LW-520 is also made from a poly(oxytetramethylene) glycol, the diisocyanate used for its manufacture is Hylene W, a mixture of aliphatic diisocyanates obtained by the hydrogenation of 4,4'-methylenebis(phenyl isocyanate) (MDI), which is much less reactive than the aromatic diisocyanates. This lower reactivity permits LW-520 to be cured with unhindered aromatic diamines, such as methylenedianiline.

Adiprene LW-520 has a higher viscosity (about 45 Pa-sec) than either L-100 or L-315. It has about 4.75% available isocyanate and contains a small amount of free diisocyanate (about 1%). Analysis by gel-permeation chromatography shows that the molecular weight distribution is essentially Gaussian ($\overline{M}_n = 3640$, $\overline{M}_w = 6440$, and dispersity = 1.8).

CURING OF ADIPRENE LW-520

Typical properties of LW-520/MDA cured at 100°C (as recommended by Du Pont) are shown in Table 4.[6] For our applications we prefer to cure at room temperature (see Appendix A, Table A4).

The biggest handling problem with LW-520/MDA is its short pot life. Commercially pure MDA melts at about 90°C, but it cannot be supercooled very much before crystallizing. For this reason the LW-520 must be heated to about 60°C or higher before the melted MDA is added. This mix will have a pot life of less than 30 min. If necessary, the pot life can be extended by incorporating polymers of MDA such as Tonox or Upjohn's Curithane 103 at lower mixing temperatures.

Most of our work has been done with Tonox, which can be supercooled without crystallizing. In our work, we have cooled the Tonox to about 30°C and mixed it with LW-520 at about 35°C to yield a composition with a pot life of about 45 min. Workers

Table 4. Physical properties of vulcanizate: Adiprene LW-520 cured with methylenedianiline.

	Typical	Range[b]
Composition		
Adiprene LW-520 (4.75% NCO), parts	100	
Methylenedianiline (95% theory), parts	10.6	
Mixing and curing		
Polymer mix temperature, °C	100	
Cured, hr/°C	16/100	
Working life, min	4-6	
Physical properties[a]		
Hardness, Durometer A	90	88-92
100% Modulus, MPa	7.8	7.1-8.5
300% Modulus, MPa	22.6	19.3-25.9
Tensile strength, MPa	32.4	25.9-39.0
Elongation at break, %	350	310-390
Tear strength, ASTM D-470, kN/m	9.6	7.9-14
Compression set,[c] %	65	60-70
Abrasion resistance, NBS Index	1200	1100-1300
Resilience, rebound, %	40	38-42
Brittleness temperature (solenoid), °C	-70	--
Specific gravity at 24°C	1.056	--
Linear shrinkage, %	1.3	--

[a] Samples were conditioned for 1 week at 24°C and 50% relative humidity before testing.

[b] Statistical range of values based on 90% confidence.

[c] Method B: 22 hr at 70°C.

at the Y-12 Plant have used a similar approach to extend the pot life of Adiprene LW-520 by curing it with a eutectic of MDA/MPDA (m-phenylenediamine); the eutectic will also supercool. The formulation preferred at LLL is the following:

Component	Parts by weight
Adiprene LW-520	100
Tonox	10.5

Precautions for Handling Adhesive Components

Adiprene L-315 contains terminal isocyanate groups as well as about 4% free toluene diisocyanate (TDI), which can react with the skin and is a known allergen. For rats, the lethal TDI concentration in air was found to be 12 ppm, and the current maximum permissible limit in air is 0.02 ppm. The Occupational Safety and Health Administration has proposed a reduction to 0.005 ppm.

LLL's Hazard Control staff exposed freshly applied L-315/polyol on an area of

$4\ ft^2$ ($0.37\ m^2$) in a chamber containing $2\ ft^3$ ($0.056\ m^3$) of air. Though the air concentration of TDI produced was only 0.016 ppm, or slightly under the threshold limit value[7], good ventilation is nevertheless recommended. Butanediol, TMP, and ferric acetylacetonate are all of low toxicity and require no special precautions.

Adiprene LW-520 contains a hydrogenated MDI [a mixture of isomers from the hydrogenation of 4,4'-methylenebis(phenyl isocyanate)], known as Hylene W. Since it has a higher molecular weight and lower volatility than TDI in normal operation, a lower concentration would be expected in the air. However, its toxicity and allergenic properties are not well known, and it should be used with good ventilation.

Methylenedianiline is a potent liver toxin and has been found to be carcinogenic when fed to rats on a protein-deficient diet. Special care should be taken to avoid breathing the dust; a filter-type respirator is recommended. Since MDA can also be absorbed through the skin, adequate protection is urged. Like MOCA, MDA should not be overheated. The following safety precautions are suggested by Du Pont:

1. A "fail-safe" mechanism for controlling the temperature of the MDA should be provided. In the event of any irregularity, the mechanism should turn off the heating system automatically.

2. The MDA vessel should be provided with a pressure-relief system that will permit pressure dissipation in the event of thermal breakdown. The relief system should be so constructed that if venting occurs, the stream of gases and hot MDA are directed away from any personnel area and, preferably, into an outside exhaust system.

3. As an added precaution, the machine operators should monitor the temperature of the MDA system regularly (e.g., every half hour).

Curing Rates and Strengths of Adhesive Bonds to Aluminum Substrates

CURE RATES AT ROOM TEMPERATURE

Since these Adiprene compositions are intended for use as room-temperature adhesives, it is important to know their cure rates. Rates were studied by several methods.

Measurements at LLL of the swelling behavior in benzyl alcohol showed that volume swell ratios of L-315/polyol specimens reached a minimum in specimens that were cured for about 60 days, but that in L-100/MOCA and LW-520/Tonox compositions complete curing required considerably longer--about 120 to 180 days.[5]

Butt-tensile strengths (aluminum-to-aluminum bonds), which are another indication of cure, were measured at both LLL and Y-12. The strengths of L-315/polyol/FAA (HGH-2) approached a maximum after 60 days at room temperature (see Fig. 1 and Appendix A, Table A1). This composition had lower strengths in Y-12 measurements, but agreement with LLL data is reasonably good. Strength data from Y-12[8] for the L-315 composition and for the L-520/MDA-MPDA eutectic are shown in Appendix A, Tables A2 and A3.

Bulk tensile strengths of these cured adhesive compositions (measured at Y-12) as a function of cure time are also available (see Appendix A, Table A4). The data lead to similar conclusions: the L-315/polyol composition takes longer to cure at room temperature (more than 28 days) than does the LW-520 composition (14 to 28 days).

In our experience, the L-315/polyol/FAA composition requires about 48 hours at room temperature to cure satisfactorily to a reasonable handling strength, whereas LW-520 compositions may attain satisfactory cure in as little as 12 hours. The L-315/polyol cures faster when catalyzed with DABCO (formulation HGH-3) (see Appendix A, Table A3), but its ultimate strength may be a little lower.

With regard to handling time, L-100/MOCA specimens are usually strong enough to be handled after 24 hours or less of room-temperature curing (see Appendix A, Figs. A1 and A2).

ADHESION PROPERTIES

Urethane adhesives are widely used because they bond to a variety of substrates; it is for this reason that they were chosen for weapons applications.

Generally, all three Adiprene compositions showed satisfactory adhesion to aluminum substrates. Though most low-modulus urethane adhesives tend to fail in a peel mode, L-315/polyol/FAA bonds with aluminum were atypical: they had unusually high peel strengths[8,9] and showed no significant loss in strength (Fig. 1) after a year's aging. Adiprene LW-520/MDA bonds behaved more conventionally, showing moderate strengths. Inexplicably, however, the LW-520/MDA formulation had lower bond strength when fully cured than when it was only partially cured.

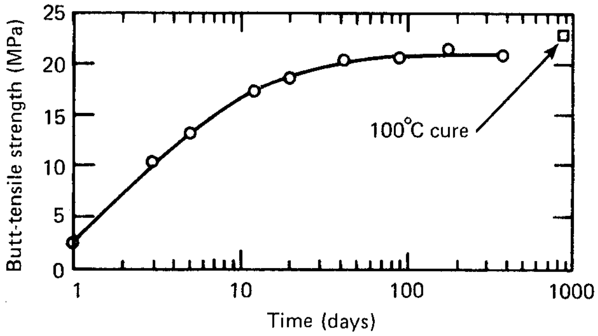


Fig. 1. Butt-tensile strength of room-temperature-cured L-315/polyol/FAA (formulation HGH-2) versus time (aluminum substrates).

All three Adiprene formulations are useful at low temperatures. The L-100/MOCA adhesive has been used at cryogenic temperatures, although its bond strength under those conditions has not been measured. The bond strength of both L-315/polyol and LW-520/MDA increased at temperatures below room temperature (see Fig. 2).

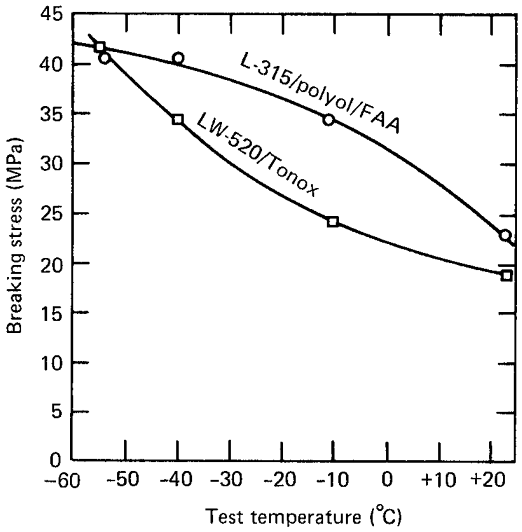


Fig. 2. Adhesive bond strength (butt-tensile test) of L-315/polyol/FAA and LW-520/Tonox versus test temperature.

TENSILE PROPERTIES

The bulk tensile properties of the three adhesive compositions were measured on ring-tensile specimens using methods developed by Smith.[10,11] Data from measurements over the temperature range 233 to 373 K (-40 to +100°C) and at strain rates from 2.8×10^{-4} to 1.4×10^{-1} sec^{-1} are listed in Appendix A (Tables A5 through A12). Tensile moduli determined at strain rates of 5.6×10^{-3} and 2.8×10^{-2} sec^{-1} are plotted against temperature in Figs. 3 and 4.

It is evident from these data that the ring-tensile properties of the cured adhesive compositions are only slightly sensitive to strain rates in the range of rates tested, especially in tests at room temperature. On the other hand, the tensile properties are strongly temperature dependent--particularly the cured L-315/polyol compositions, which become stiffer at low temperatures and softer at high temperatures than either L-100/MOCA or LW-520/Tonox. The cured L-315/polyol compositions are also weaker at higher temperatures than either the L-100 or LW-520 compositions.

The procedures used at LLL in the preparation and testing of the tensile rings have been described by Buckner et al.[12]

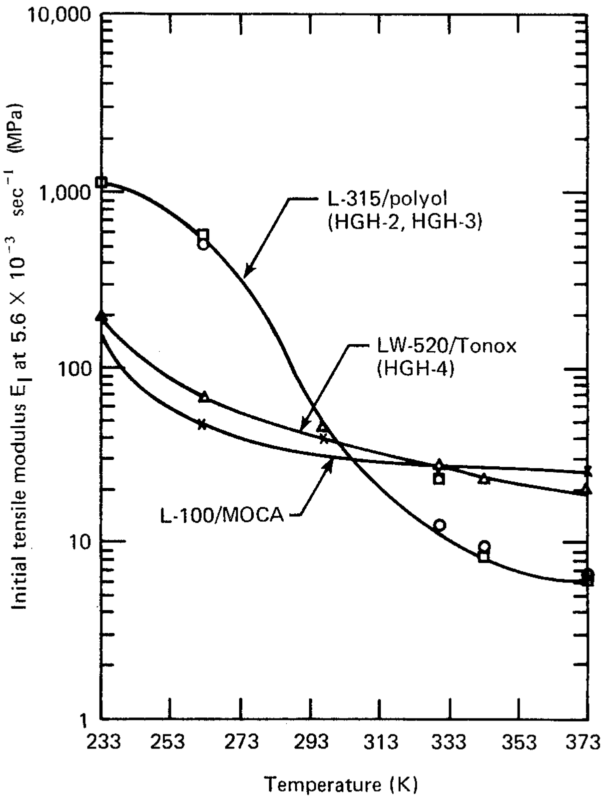


Fig. 3. Tensile modulus of L-315/polyol (compositions HGH-2 and HGH-3) and LW-520/Tonox (composition HGH-4) versus temperature at a strain rate of 5.6×10^{-3} sec^{-1}.

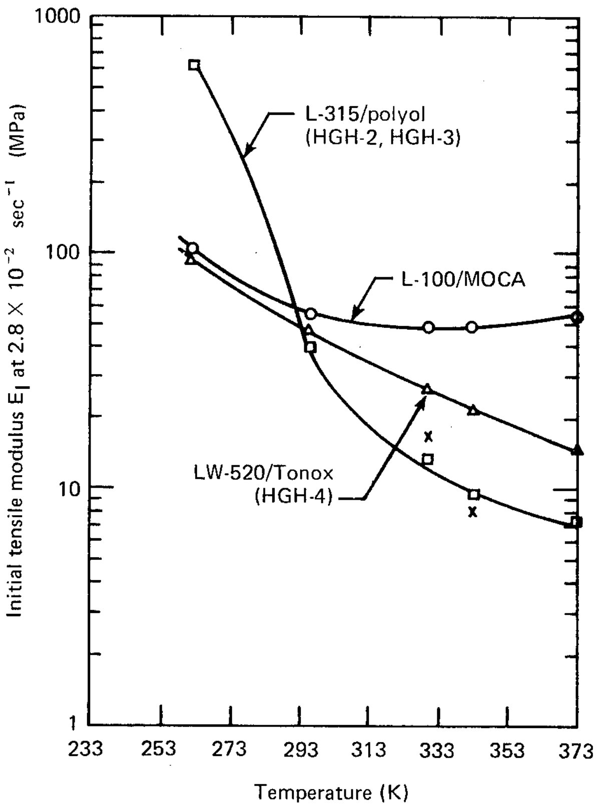


Fig. 4. Tensile modulus of L-315/polyol (compositions HGH-2 and HGH-3) and LW-520/Tonox (composition HGH-4) versus temperature at a strain rate of 2.8×10^{-2} sec^{-1}.

Briefly, a fly cutter was used to cut rings (outside diameter of 38.12 mm, inside diameter of 35.18 mm, and a thickness of about 1.8 mm) from sheets cast in standard rubber molds. Testing was done on a standard Instron testing machine, using an environmental chamber as necessary. Data were stored in digital form on magnetic tape and PDP-8 disk and processed by a computer. Nominal breaking stress and strain were taken from the nominal-stress/nominal-strain plot, extrapolating the plot for strain on the internal diameter, as suggested by Smith.[10]

Tensile moduli were taken from a true-stress/nominal-strain plot. The "initial tensile modulus" E_I determined in this manner is somewhat lower than the Young's modulus determined on thick, bonded specimens since effects at early strain are lost in straightening the ring specimen. This initial modulus is a function of the hydrogen bonding in the Adiprene polymer, whereas the midrange modulus E_M appears to be more a function of true crosslinking within the polymer.

The L-315/polyol shows rigid plastic-type, rather than rubberlike, behavior at 262 K (-11°C) and below. The stress-strain curve undergoes a definite yield point at low temperatures and then drops to a level plateau for one to two strain units before the final increase in stress to the rupture point. Thus the zero midrange moduli for formulations HGH-2 and HGH-3 have implications that differ from those of the zero midrange moduli for L-100/MOCA at 330 K (57°C) and above. In the latter case, we believe it to be indicative of little or no crosslinking.

The increased low-temperature modulus of L-315/polyol, relative to L-100/MOCA, and LW-520/Tonox, is due to the onset of glassy behavior in the soft domains of relatively low molecular weight polyether. The decreased modulus at high temperatures may be due to the disruption of hydrogen bonds in the hard domains by the trimethylolpropane crosslinking agent. Furthermore, aromatic-diamine-cured urethanes, such as L-100/MOCA and LW-520/Tonox, have been shown to have improved performance at higher temperatures than do aliphatic-diamine-cured urethanes.[13] The L-315/polyol was cured with an aliphatic diol, which may additionally disrupt the hydrogen-bond networks within the hard domains, causing hard-domain imperfections.

CORRELATION OF TENSILE PROPERTIES WITH TEMPERATURE AND SHEAR RATE

Three-dimensional representations (response surfaces) of the relationships among tensile properties, strain rates, and temperature would be useful in understanding the performance of Adiprene adhesives and in locating possible optima for future uses. These response surfaces are ordinarily generated by using a Box and Hunter[14] experimental design, from which equations that represent the experimental data are developed. The details of the application of this method to tensile data from adhesive specimens, the equations derived, and a complete discussion are given in Appendix B. Only the results are summarized here.

The response surfaces (see Appendix B, Figs. B1 through B4) for stress and elongation at break versus temperature and strain rate adequately described the data. However, surfaces calculated for initial modulus and midrange modulus were not deemed adequate. Apparently, the domain of experimental values spanned a greater range of temperature than could be handled by the quadratic surfaces generated. A logarithmic transformation of the data did not improve the fit of the data to the surfaces. Higher order surfaces are indicated. However, the very large number of experimental data points required prohibited any further research in this area.

We were successful in developing equations that describe the entire stress-strain curves of cured L-100/MOCA and LW-520/Tonox compositions, except at low temperatures, where the compositions do not behave in a rubberlike manner. The equations fit the data very well; that is, numbers generated from the equations agree with the experimental data within the accuracy of the Instron testing device and our ability to control the environmental factors during testing.

As discussed at length in Appendix C, we theorize that the coefficients of these equations are related to the structure of the cured compositions, possibly to the number and arrangement of "hard" and "soft" domains of the cured polymer chains.

PERMEABILITY TO GAS AND WATER VAPOR OF ADHESIVE COMPOSITIONS

The permeability of the cured adhesives to gases is of concern in a variety of applications. In the bonding of detonators, it is desirable that any high-explosive offgas should escape to avoid pressure buildup. In other applications, it is desirable that hydrogen or its isotopes permeate the material readily. Although requirements are not known quantitatively, design engineers and compatibility experts felt that the permeability of substitute compositions should be similar to that of L-100/MOCA.

Because of the difficulty in preparing

Table 5. Gas and water-vapor permeability coefficients of adhesive compositions.[a]

Gas	Permeability coefficient, nm^2/Pa-sec (cm^3_{STP}-cm/sec-cm^2-cm Hg)		
	L-100/MOCA	L-315/polyol	LW-520/MDA
Argon	34.5 (4.6×10^{-10})	8 (1.1×10^{-10})	83 (1.1×10^{-9})
Helium	69 (9.2×10^{-10})	42 (5.6×10^{-10})	98 (1.3×10^{-9})
Hydrogen	90 (1.2×10^{-9})	40 (5.3×10^{-10})	130 (1.7×10^{-9})
Carbon monoxide	13 (1.7×10^{-10})	2.6 (3.5×10^{-11})	24 (3.2×10^{-10})
Carbon dioxide	230 (3.1×10^{-9})	35 (4.7×10^{-10})	280 (3.7×10^{-9})
Nitrous oxide	260 (3.5×10^{-9})	49 (6.5×10^{-10})	310 (4.1×10^{-9})
Nitric oxide	44 (5.9×10^{-10})	8 (1.1×10^{-10})	57 (7.6×10^{-10})
Water vapor	1.3×10^{5} (1.75×10^{-6})	2.9×10^{4} (3.88×10^{-7})	1.3×10^{5} (1.72×10^{-6})

[a] Method: ASTM D-1434-66, Method M, in Dow cell, 23°C.

new specimens of L-100/MOCA while complying with OSHA safety regulations, we used a slab that had been made in May 1972; its age at test time was about 2 years. Its composition by weight was 100 parts L-100 and 12.1 parts MOCA, and it had been cured at room temperature and 10% relative humidity. The L-100/MOCA test specimen was cut from a slab cast in a conventional rubber mold, about 150 by 150 by 1.6 mm. The actual thickness of the specimen was 1.93 mm.

Similar specimens were prepared from the L-315/polyol composition (100 parts of L-315, 7 parts of 1,4-butanediol, 2 parts of trimethylolpropane, and 0.02 part of ferric acetylacetonate) and the Adiprene LW-520/MDA composition (100 parts of LW-520 and 10.5 parts of methylenedianiline). The thickness of the L-315/polyol and LW-520/MDA specimens was 1.33 and 1.54 mm, respectively. Both of the latter specimens were cured at 100°C for 6 hr; it is unlikely that permeability would be greatly different in room-temperature-cured specimens, and it was impractical to wait for the 6 to 9 months necessary for an equilibrium room-temperature cure.

Table 5 shows the gas permeabilities for seven gases at 23°C. Measurements were made with a Dow cell according to ASTM D-1434-66, Method M, using gases as supplied by Matheson Gas Products. The test chamber was evacuated to a pressure of less than 13 Pa (0.1 mm Hg), and the pressure of the test gas over the specimens during permeation was 133 to 200 kPa (1000 to 1500 mm Hg).

The data in Table 5 show that the permeability of L-315/polyol specimens was lower than that of L-100/MOCA by a factor of 2 to 4 and that the permeability of the LW-520/MDA films was usually 1.5 to 2 times that of the L-100/MOCA. Although we have not studied fully the precision of the experimental observations, we believe them to be valid within a factor of 2. Perturbing factors would most likely be variations in specimen thickness, lot-to-lot and specimen-to-specimen chemical variations, and instability of the recorder during tests.

We measured the water-vapor permeability at 23°C using the method of Hubbell.[15] Table 5 shows that the LW-520/MDA specimen and the L-100/MOCA specimen had about the same permeability, whereas the permeability of the L-315/polyol specimen was lower by a factor of 4.

LINEAR COEFFICIENT OF THERMAL EXPANSION

The linear coefficient of thermal expansion of cured Adiprene adhesive compositions was determined at LLL on cylinders about 12 mm in diameter and about 120 mm long. Both LW-520/Tonox and L-315/polyol specimens cured at room temperature had coefficients of 1.7×10^{-4} from -65 to +130°C.

We did not determine this property on L-100/MOCA specimens. However, the manufacturer's data over a temperature range from -36 to +150°C (Table 3, 100°C cure), indicate that the coefficient is quite dependent on temperature.

GLASS-TRANSITION TEMPERATURES

Glass-transition temperatures (below which rubbery behavior ceases) were measured by low-temperature differential thermal analysis (DTA).

We had previously found that L-100/MOCA

compositions had a glass-transition temperature of 233 ± 5 K, with no apparent dependence either on MOCA content over the range of 11 to 14 phr or on whether the material was cured at room temperature or at 100°C. The LW-520/Tonox composition showed a well-defined rubbery-to-glassy transition at about 210 K, but the transition of the L-315/polyol compositions was not as sharp.

It was initially estimated at LLL and also at Pantex that the glass-transition temperature of L-315/polyol was about 253 K. However, our tensile tests at 262 K show that the material acts as a rigid plastic at that temperature, and dynamic shear modulus tests conducted by Smith et al.[16] showed an inflection in the G' versus T curve at about 293 K. Trick[17] has shown that the torsional inflection temperature is about 15°C higher than the glass-transition temperature, which led us to assign a value of about 278 K to the glass-transition temperature for L-315/polyol. Low-temperature DTA tests using the polymer specimens without a metal container cup showed fairly sharp transitions, and we are able to assign a temperature range of 274 to 278 K for the glass-transition temperature of L-315/polyol.

We must point out, however, that the glass-transition temperature does not represent either the brittle temperature or the low-temperature use limit. For example, L-100/MOCA has a brittle temperature of about 203 K, some 20 K lower than its glass-transition temperature, yet it has been used successfully in LLL applications as an adhesive at 20 K and even at 4 K. We had no difficulty in pulling tensile rings of L-315/polyol at 233 K. Butt-tensile strengths below the glass-transition temperature were 35 to 42 MPa, higher than the room-temperature strength.

DENSITY

Figure 5 shows the change of density with temperature for L-100/MOCA and L-315/polyol/FAA.

ELEMENTAL ANALYSES

The Adiprene polymers were analyzed by gel-permeation chromatography, and all components were examined for carbon, hydrogen, nitrogen, and trace elements. Since the structure of the Adiprene prepolymers has already been well described by Smith et al.,[16] it will suffice to say that the three systems evaluated, as well as their components, contained only small amounts of elements other than carbon, hydrogen, nitrogen, and oxygen. Naturally, the L-315/polyol system catalyzed by ferric acetylacetonate contained iron, about 50 ppm. Up to 10 ppm of silicon was found in all polymers and only minor amounts of other elements.[18]

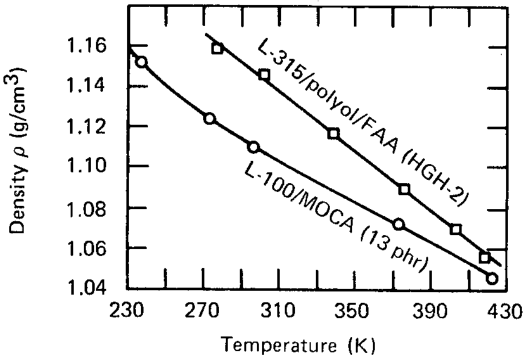


Fig. 5. Density of L-315/polyol/FAA (formulation HGH-2) and L-100/MOCA (13 phr) versus temperature.

TENSILE FAILURE ENVELOPE

The tensile failure envelope for all three urethane elastomers (Fig. 6) shows the dependence of their ultimate stress and strain on either strain rate or temperature. Presumably, the curve could be used to predict failure under monotonically increasing stress or strain.

Although the curve was originally constructed for L-100/MOCA (HGH-1), its shape was not materially changed by adding data for L-315/polyol (HGH-2, HGH-3) and LW-520/Tonox (HGH-4). Considerably more scatter was introduced, however.

Application of the failure envelope assumes that the polymer is amenable to time-temperature superposition and remains amorphous up to failure. If these assumptions are valid for the Adiprene, then the rupture properties can be predicted independently of the time-temperature history of the specimen (test conditions). The principle has been shown to be applicable to a large number of unreinforced amorphous elastomers.[22] Though the theory has not been experimentally verified with the Adiprenes, there is no reason to expect any gross deviation.

The failure envelope, then, is a way to describe ultimate properties and to relate their dependence on the topological and physical characteristics of the polymer network. That the failure envelope was not materially changed appears to indicate that all of the elastomers fail by the same mechanism.

DYNAMIC SHEAR MODULUS OF ADIPRENE POLYMERS

Dynamic shear moduli are useful in certain design and engineering calculations.

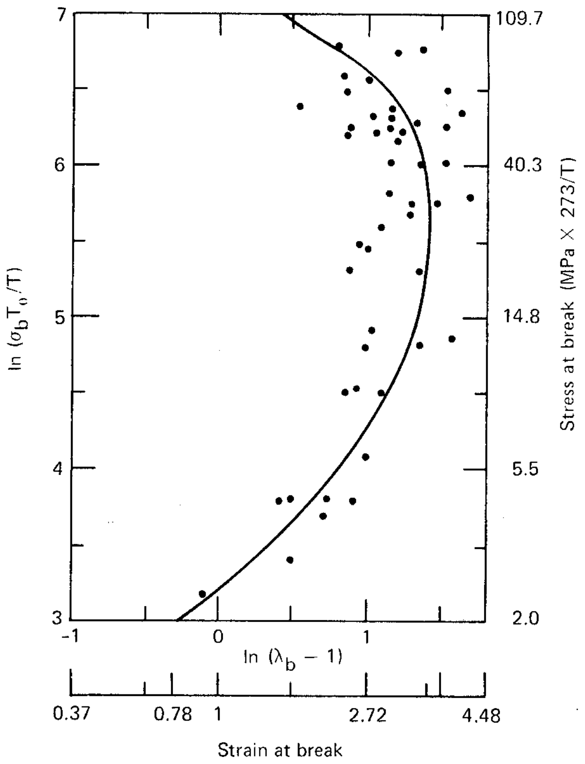


Fig. 6. Tensile failure envelope for Adiprene adhesive compositions HGH-1, HGH-2, HGH-3, and HGH-4 over test temperatures from -40 to +100°C and strain rates from 3×10^{-4} to 1.5×10^{-7} sec^{-1}.

Although a more complete report on the dynamic shear modulus (complex shear modulus) of Adiprene L-100/MOCA, L-315/polyol, and LW-520/Tonox will be issued later, we are summarizing the pertinent information in this report for immediate use. The data should be used with caution, however, until we can supplement it with data on moduli measured at high strain rates on the Hopkinson split bar or the Dynapak apparatus.

The complex shear modulus is defined as

$$G^* = G_1 + iG_2,$$

where G_1 is the shear storage modulus and G_2 is the shear loss modulus. The shear loss modulus of L-100/MOCA and LW-520/Tonox is usually less than 10% of the shear storage modulus; thus the shear storage modulus for these compositions is approximately equal to the true shear modulus. However, in the case of the L-315/polyol, this is true only at temperatures above room temperature.

The modulus test apparatus built at LLL has been described by Hamstad[19]; it is very similar to that used by Gottenberg and Christensen[20] in their "low frequency" tests. Test specimens were 25.4 mm in diameter and 50.8 mm long; they were tested over the temperature range from about -20 to +80°C and at frequencies from 0.005 to 0.5 Hz.

In Fig. 7 the shear storage modulus of these Adiprene compositions at 0.1 Hz is plotted as a function of temperature. Adiprene L-100/MOCA and LW-520/Tonox have nearly the same shear storage modulus below room temperature, but the modulus of LW-520/Tonox falls off more rapidly at elevated temperatures. Adiprene L-315/polyol compositions, however, go through a sharp transition between 0 and 30°C (273 to 303 K) and then begin to exhibit rubbery behavior as the temperature is raised still further.

Master curves of the reduced shear storage modulus of the Adiprene compositions are shown in Fig. 8 as a function of frequency and strain rate. These

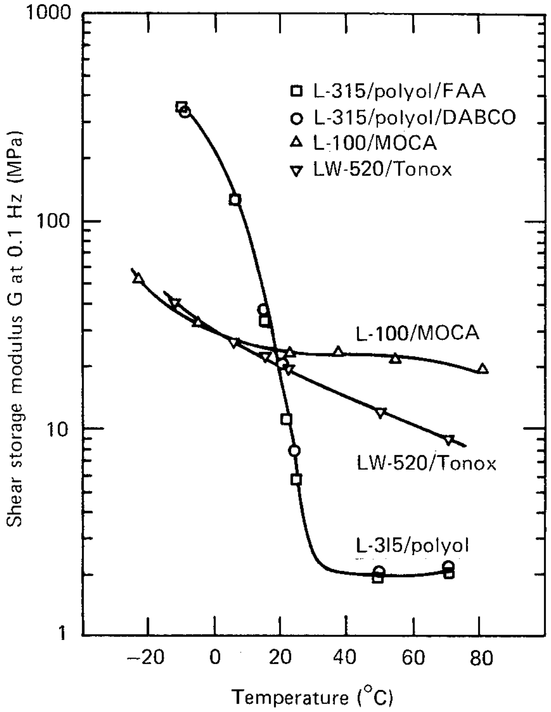
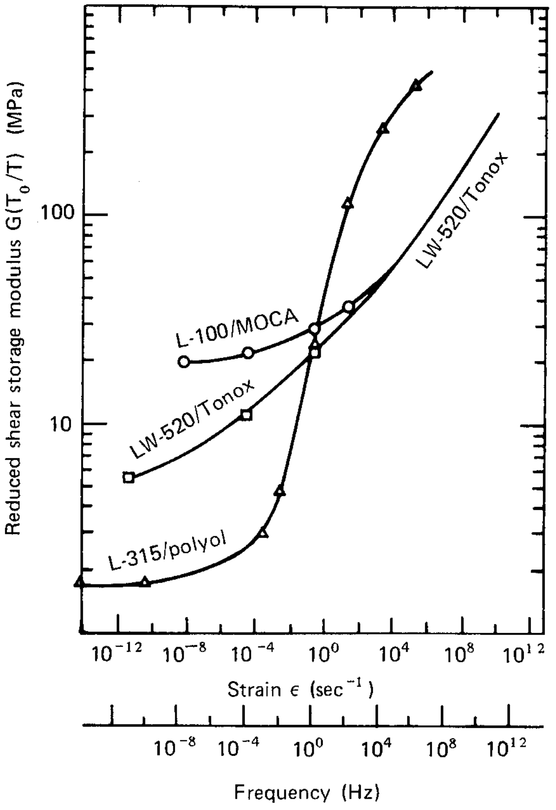


Fig. 7. Shear storage modulus of Adiprene adhesive compositions versus temperature.



LW-520/Tonox, L-100/MOCA $\Big\}$ $$\log A_T = \frac{-54(T - T_0)}{448 + (T - T_0)}$$

L-315/polyol $$\log A_T = \frac{83(T - T_0)}{-375 + (T - T_0)}$$

$$T_0 = 297.8\ \text{K}$$

Fig. 8. Master curve of reduced shear storage modulus of Adiprene adhesives.

were calculated by the method of Ferry.[21] Specific values for the needed constants of the Williams-Landel-Ferry equation were calculated; we did not use the constants for the generalized equation, as they did not fit the data well.

For Adiprene LW-520/Tonox we developed the shift equation

$$\log A_T = \frac{-54(T - T_0)}{448 + (T - T_0)} \quad T_0 = 297.8 \text{ K.}$$

The same equation fits the data for Adiprene L-100/MOCA quite well. For L-315/polyol, however, the coefficients were quite different. The shift equation in this case was found to be

$$\log A_T = \frac{83(T - T_0)}{-375 + (T - T_0)} \; .$$

Although the dynamic modulus is determined as a function of frequency, the data may be used to estimate the shear modulus as a function of strain rate at small strains. Under these conditions, the frequency in radians per second is proportional to the strain rate in reciprocal units of seconds. This is the justification for the double scale in Fig. 8.

The Williams-Landel-Ferry equation should not be used to calculate moduli for temperatures below the glass-transition temperature of the material, which for L-315/polyol is only slightly below room temperature. Our data for tensile modulus can be used to estimate the shear modulus ($G \cong E/3$). The estimated shear moduli for L-100/MOCA and LW-520/Tonox fit the master curve fairly well, but those for L-315/polyol fit only at temperatures above 23°C and at low strain rates.

Acknowledgments

We wish to thank all those who have contributed to this program, especially Albert T. Buckner and Leonard E. Caley for the preparation and testing of ring-tensile specimens, Edward S. Jessop for solvent swell measurements, Barbara McKinley for computer processing, and Jay K. Lepper for theoretical input and general support.

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Appendix A

Supplemental Tables and Figures

Table A1. Adhesive (butt-tensile) strength of Adiprene L-315/polyol/FAA, aluminum to aluminum, room-temperature cure (bond No. 442).

				Test program					
Test increment number	1	2	3	4	5	6	7	8	9
Bond subnumbers	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40	41-45
Test date	10/25/73	10/27/73	10/29/73	11/5/73	11/13/73	12/5/73	1/22/74	4/27/74	11/18/74
Bond age: days	1	3	5	12	20	42	90	185	390
Bond age: years	0	0.01	0.01	0.03	0.05	0.11	0.24	0.5	1.07
				Test results					
Mean rupture load, MPa	2.2	10.4	13.2	17.3	18.7	20.4	20.6	21.3	20.4
Range, MPa	0.36	2.90	1.06	1.83	0.91	1.22	2.44	2.14	3.4
Coefficient of variation, %	6	11	3	4	2	3	5	5	7

Table A2. Adhesive (butt-tensile) strengths of Adiprene L-315/polyol and LW-520/MDA-MPDA eutectic, room-temperature cure.[a]

L-315/polyol		LW-520/MDA-MPDA eutectic	
Cure time	Strength,[b] MPa	Cure time	Strength,[b] MPa
16 hr	0.11	16 hr	1.38
20 hr	0.17	20 hr	1.93
24 hr	0.23	24 hr	2.76
36 hr	0.42	34 hr	3.79
48 hr	0.83	48 hr	5.93
4 days	6.14	4 days	7.17
7 days	8.76	7 days	13.17
14 days	12.07	14 days	15.31
28 days	13.44	28 days	16.62
56 days	17.31	59 days	16.96
86 days	17.10	91 days	12.89

[a] Data from F. G. Childress, Urethane Adhesives--L-100/MOCA Substitutes, Y-DA-5771 (April 24, 1974).

[b] The average adhesive tensile strength was calculated on a sample population of three.

Table A3. Adhesive (butt-tensile) strengths of Adiprene L-315/polyol/DABCO (HGH-3), aluminum to aluminum, room-temperature cure (bond No. 463).

Cure time, hr	Mean rupture load	
	MPa	psi
2	0.13	19
4	0.83	120
8	2.68	389
16	8.65	1254
32	11.62	1685
64	14.81	2147
128	15.41	2235
256	15.63	2266
512	15.17	2199

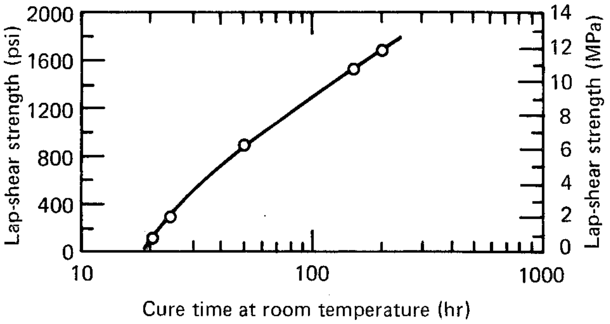

Fig. A1. Lap-shear strength of L-100-MOCA (aluminum to aluminum, room-temperature cure). Data from F. G. Childress, Urethane Adhesives--L-100/MOCA Substitutes, Y-DA-5771 (April 24, 1974).

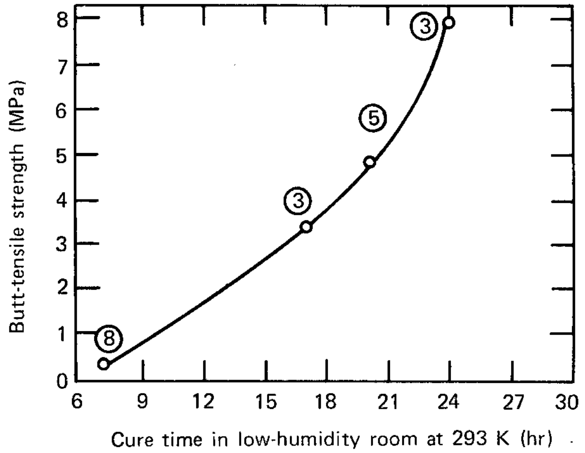

Fig. A2. Cure rate of L-100/MOCA (88.5:11.5) versus time (bond No. 367). The circled numbers indicate the coefficient of variation for each of the four butt-tensile-strength points. The average butt-tensile strength of L-100/MOCA cured for 7 days was 14.5 MPa (2100 psi).

Table A4. Bulk tensile properties of L-315/polyol and LW-520/MDA-MPDA eutectic, room-temperature cure.[a]

	L-315/polyol			LW-520/eutectic		
Cure time, days	Tensile strength, MPa	Tensile modulus, MPa	Strain at break	Tensile strength, MPa	Tensile modulus, MPa	Strain at break
4	0.25	--	7.5	5.7	16.6	3.2
7	2.2	1.2	5.1	18.0	37.2	--
14	6.1	1.5	3.7	28.5	55.9	4.5
28	13.7	11.7	2.7	27.6	52.4	3.7

[a] Data from F. G. Childress, Urethane Adhesives--L-100/MOCA Substitutes, Y-DA-5771 (April 24, 1974).

Table A5. Stress-strain properties of Adiprene L-100/MOCA at several temperatures (ring-tensile specimens, room-temperature cure).

Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C				
	-40	-11	+23	+57	+100
Initial tensile modulus E_I, MPa					
1.4×10^{-3}			48		
5.6×10^{-3}			48		
2.8×10^{-2}	351	76	49	44	29
1.4×10^{-1}			70		
Breaking stress, MPa					
1.4×10^{-3}			62		
5.6×10^{-3}			85		
2.8×10^{-2}	105	106	86	53	27
1.4×10^{-1}			65		

Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C				
	-40	-11	+23	+57	+100
Midrange tensile modulus E_M, MPa					
1.4×10^{-3}			8		
5.6×10^{-3}			9		
2.8×10^{-2}	37	21	11	6	5
1.4×10^{-1}			13		
Breaking strain					
1.4×10^{-3}			5.07		
5.6×10^{-3}			4.90		
2.8×10^{-2}	3.24	3.78	4.86	5.64	5.72
1.4×10^{-1}			2.38		

Table A6. Stress-strain properties of Adiprene L-100/MOCA at several temperatures (ring-tensile specimens, 100°C cure).

Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C -40	-11	+23	+57	+100
Initial tensile modulus E_I, MPa					
2.8×10^{-4}			52		
1.4×10^{-3}	53	53	47	51	
5.6×10^{-3}	277	53	50	51	55
2.8×10^{-2}		60	52	53	
1.4×10^{-1}			41		
Breaking stress, MPa					
2.8×10^{-4}			44		
1.4×10^{-3}		86	54	34	
5.6×10^{-3}	87	80	73	37	15
2.8×10^{-2}		64	39	30	
1.4×10^{-1}			55		

Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C -40	-11	+23	+57	+100
Midrange tensile modulus, E_M, MPa					
2.8×10^{-4}			8		
1.4×10^{-3}		16	11	12	
5.6×10^{-3}	130	18	14	12	9
2.8×10^{-2}		20	14	11	
1.4×10^{-1}			16		
Breaking strain					
2.8×10^{-4}			4.48		
1.4×10^{-3}		3.73	4.48	4.65	
5.6×10^{-3}	2.92	3.56	4.63	4.66	3.74
2.8×10^{-2}		3.15	4.3	4.83	
1.4×10^{-1}			4.52		

Table A7. Stress-strain properties of Adiprene L-315/polyol/FAA at several temperatures (ring-tensile specimens, room-temperature cure).

Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C -40	-11	+23	+57	+70	+100	Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C -40	-11	+23	+57	+70	+100
Initial tensile modulus E_I, MPa							Midrange tensile modulus E_M, MPa						
2.8×10^{-4}			5	7			2.8×10^{-4}				7		
1.4×10^{-3}			7	7			1.4×10^{-3}			6	7		
5.6×10^{-3}	899	327	8	6	6	6	5.6×10^{-3}			6	6	7	6
2.8×10^{-2}		504	13	6	6	6	2.8×10^{-2}			7	7	7	7
1.4×10^{-1}			18	5			1.4×10^{-1}			9	7		
Breaking stress, MPa							Breaking strain						
2.8×10^{-4}			40	7			2.8×10^{-4}			3.49	2.46		
1.4×10^{-3}			60	5			1.4×10^{-3}			3.48	2.08		
5.6×10^{-3}	63	47	62	7	5	3	5.6×10^{-3}	1.67	2.01	3.34	2.69	2.05	0.75
2.8×10^{2}		70	65	22	5	3	2.8×10^{-2}		2.4	3.18	3.38	2.03	1.02
1.4×10^{-1}			55	28			1.4×10^{-1}			3.07	3.42		

Table A8. Stress-strain properties of Adiprene L-315/polyol/FAA at several temperatures (ring-tensile specimens, 100°C cure).

Strain	Temperature, °C						Strain	Temperature, °C					
rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100	rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100
	Initial tensile modulus E_I, MPa							Midrange tensile modulus E_M, MPa					
2.8×10^{-4}		384	5	4			2.8×10^{-6}		13	4	5		
1.4×10^{-3}		477	7	5			1.4×10^{-3}		24	5	5		
5.6×10^{-3}	1504	436	11	6	6	5	5.6×10^{-3}		12	7	7	6	
2.8×10^{-2}		490	12	5	5	7	2.8×10^{-2}			8	6	6	7
1.4×10^{-1}		536	18				1.4×10^{-1}			9	5		
	Breaking stress, MPa							Breaking strain					
2.8×10^{-4}		50	46	5			2.8×10^{-4}		2.17	3.95	2.79		
1.4×10^{-3}		60	57	6			1.4×10^{-3}		2.59	3.80	3.05		
5.6×10^{-3}	79	65	56	38	3	3	5.6×10^{-3}	2.17	2.73	3.19	3.66	1.14	0.87
2.8×10^{-2}		69	58	30	5	3	2.8×10^{-2}		2.58	2.98	3.88	2.75	0.78
1.4×10^{-1}		55	53	26			1.4×10^{-1}		2.14	3.44	3.87		

Table A9. Stress-strain properties of Adiprene L-315/polyol/DABCO at several temperatures (ring-tensile specimens, room-temperature cure).

Strain	Temperature, °C						Strain	Temperature, °C					
rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100	rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100
Initial tensile modulus E_I, MPa							Midrange tensile modulus E_M, MPa						
2.8×10^{-4}			6				2.8×10^{-4}			6			
1.4×10^{-3}			7				1.4×10^{-3}			6			
5.6×10^{-3}	781	360	8	5	6	7	5.6×10^{-3}			6	6	7	7
2.8×10^{-2}		994	13	6	7	7	2.8×10^{-2}			7	7	7	7
1.4×10^{-1}			23	8			1.4×10^{-1}			10	6		
Breaking stress, MPa							Breaking strain						
2.8×10^{-4}			58				2.8×10^{-4}			3.65			
1.4×10^{-3}			45				1.4×10^{-3}			3.35			
5.6×10^{-3}	76	68	52	17	5	3	5.6×10^{-3}	1.96	2.40	3.29	3.29	2.01	0.84
2.8×10^{-2}		58	42	38	5	3	2.8×10^{-2}		2.10	2.92	3.48	2.02	0.73
1.4×10^{-1}			62	30			1.4×10^{-1}			3.0	3.3		

Table A10. Stress-strain properties of Adiprene L-315/polyol/DABCO at several temperatures (ring-tensile specimens, 100°C cure).

Strain	Temperature, °C					
rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100
	Initial tensile modulus E_I, MPa					
2.8×10^{-4}		370	6	6		
1.4×10^{-3}		429	8	6		
5.6×10^{-3}	1077	407	10	6	6	6
2.8×10^{-2}		713	15	6	6	6
1.4×10^{-1}		1016	19	5		
	Breaking stress, MPa					
2.8×10^{-4}		80	42	11		
1.4×10^{-3}		60	38	11		
5.6×10^{-3}	80	70	67	8	5	3
2.8×10^{-2}		78	62	35	5	3
1.4×10^{-1}		77	58	20		

Strain	Temperature, °C					
rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100
	Midrange tensile modulus E_M, MPa					
2.8×10^{-4}		18	5	7		
1.4×10^{-3}			6	6		
5.6×10^{-3}			7	6		
2.8×10^{-2}			8	6		
1.4×10^{-1}			9	6		
	Breaking strain					
2.8×10^{-4}		2.86	3.44	3.10		
1.4×10^{-3}		2.53	3.24	3.01		
5.6×10^{-3}	2.10	2.47	3.31	2.85	2.24	0.88
2.8×10^{-2}		2.58	3.20	3.63	1.98	0.93
1.4×10^{-1}		2.57	3.25	3.35		

Table A11. Stress-strain properties of Adiprene LW-520/Tonox at several temperatures (ring-tensile specimens, room-temperature cure).

Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C						Strain rate $\dot{\varepsilon}$, sec^{-1}	Temperature, °C					
	-40	-11	+23	+57	+70	+100		-40	-11	+23	+57	+70	+100
	Initial tensile modulus E_I, MPa							Midrange tensile modulus E_M, MPa					
2.8×10^{-4}			54				2.8×10^{-4}			9			
1.4×10^{-3}			71				1.4×10^{-3}			10			
5.6×10^{-3}	204	77	70	44	32	13	5.6×10^{-3}			13	9	9	7
2.8×10^{-2}		143	67	36	40	15	2.8×10^{-2}			14			8
1.4×10^{-1}			68	37			1.4×10^{-1}			12			
	Breaking stress, MPa							Breaking strain					
2.8×10^{-4}			28				2.8×10^{-4}			2.86			
1.4×10^{-3}			38				1.4×10^{-3}			3.43			
5.6×10^{-3}	63	66	32	16	11	6	5.6×10^{-3}	2.19	3.66	2.60	2.58	2.74	1.94
2.8×10^{-2}		58	36	23	16	6	2.8×10^{-2}		2.32	2.64	3.55	2.62	1.58
1.4×10^{-1}			46	22			1.4×10^{-1}		3.08	3.36			

Table A12. Stress-strain properties of Adiprene LW-520/Tonox at several temperatures (ring-tensile specimens, 100°C cure).

Strain	Temperature, °C					
rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100
Initial tensile modulus E_I, MPa						
2.8×10^{-4}		59	37	35		
1.4×10^{-3}		65	33	28		
5.6×10^{-3}	165	70	40	29	24	15
2.8×10^{-2}		83	44	31	24	17
1.4×10^{-1}		79	33	42		
Breaking stress, MPa						
2.8×10^{-4}		47	23	9		
1.4×10^{-3}		50	24	10		
5.6×10^{-3}	49	48	28	14	11	6
2.8×10^{-2}		49	36	16	12	6
1.4×10^{-1}		42	25	17		

Strain	Temperature, °C					
rate $\dot{\varepsilon}$, sec^{-1}	-40	-11	+23	+57	+70	+100
Midrange tensile modulus E_M, MPa						
2.8×10^{-4}				12		
1.4×10^{-3}		22	11	12		
5.6×10^{-3}	34	21	12	10	10	
2.8×10^{-2}		21	13	11	11	8
1.4×10^{-1}		14	14	13		
Breaking strain						
2.8×10^{-4}		2.38	2.58	1.69		
1.4×10^{-3}		2.5	2.67	1.79		
5.6×10^{-3}	1.74	2.39	2.93	2.66	2.5	1.66
2.8×10^{-2}		2.44	3.12	2.76	2.41	1.66
1.4×10^{-1}		2.18	2.51	2.18		

Appendix B

Mathematical Correlations of Bulk Tensile Properties of Adiprene Adhesives with Testing Temperature and Strain Rate

INTRODUCTION

Development of response surfaces relating three or more variables from experimental data is a well-known technique. The Box and Hunter[1] design is often used for this purpose.

The Box and Hunter technique was applied to the Adiprene adhesive stress-strain data shown in various tables in Appendix A. Table B1 shows the resultant response-surface equations relating stress-strain properties to test temperatures and strain rates for LW-520/Tonox and L-100/MOCA cured at 100°C.

The underlined coefficients in Table B1 are statistically significant at the 95% confidence level. The scaled variable X_1 represents temperature effects, and the scaled variable X_2 represents strain-rate effects. The scaled variables are calculated as follows:

$$\text{temperature} = \frac{\text{K} - 296\ \text{K}}{296\ \text{K}}$$

and

$$\text{strain rate} = \frac{\ln(\dot{\varepsilon}/2.8 \times 10^{-4})}{\ln(2.8 \times 10^{-4})}$$

where the strain rate is the crosshead speed of the Instron testing machine.

The response-surface equations in Table B1 fit the experimental data well, except at low temperatures, where the cured Adiprene adhesives do not behave in a rubberlike manner.

Table B1. Response-surface equations for LW-520/Tonox and L-100/MOCA.

LW-520/Tonox strain at break $= \underline{2.83} - \underline{0.05X_1} + \underline{0.03X_2} - \underline{0.11X_1^2} - \underline{0.02X_2^2} - 0.05X_1X_2$

L-100/MOCA strain at break $= \underline{4.44} + \underline{0.30X_1} - \underline{0.01X_2} - \underline{0.14X_1^2} - \underline{0.01X_2^2} + 0.07X_1X_2$

LW-520/Tonox stress at break $= \underline{28.3} - \underline{11.7X_1} + \underline{0.8X_2} + \underline{1.4X_1^2} - \underline{0.20X_2^2} + 0.10X_1X_2$

L-100/MOCA stress at break $= \underline{56.6} - \underline{13.3X_1} - 0.4X_2 - 0.10X_1^2 - 0.50X_2^2 + 1.5X_1X_2$

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[1] Cochran and Cox, Experimental Design (John Wiley & Sons, Inc., New York, 1957).

Table B2. Response-surface coefficients for stress at break.[a]

Composition	Strain, average level	Temperature effects		Strain-rate effects	
		Linear	Quadratic	Linear	Quadratic
L-100/MOCA	56.6	-13.3	(b)	(b)	(b)
LW-520/Tonox	28.3	-11.7	1.4	0.8	-0.2

[a] Coefficients describing synergistic effects of temperature and strain rate are statistically insignificant.

[b] Coefficients cannot be distinguished from zero and are not required to describe the response surfaces.

EQUATIONS RELATING BREAKING STRESS TO TEMPERATURE AND TO STRAIN RATE

Table B2 shows the contributions of linear and quadratic terms in the response-surface equations (Table B1) to tensile stress at break as affected by temperature and strain rate.

In agreement with experimental data, the first terms of the response-surface equations show that L-100/MOCA specimens have twice the breaking strength of LW-520/Tonox at 23°C. The larger linear coefficient (-13.3) for L-100/MOCA, in comparison to LW-520/Tonox (-11.7), describes the more rapid effect of increasing temperature on the breaking stress of L-100/MOCA. The equations correctly predict that the breaking stresses of the two adhesives are about the same at 100°C. In the equation for LW-520/Tonox the quadratic term +1.4 offsets the linear term -11.7 just enough to describe the experimental data properly at higher temperatures. Thus extrapolation beyond the domain of the data is not recommended.

It is found experimentally that at temperatures below 23°C the breaking stress of LW-520/Tonox falls faster than does that of L-100/MOCA as the temperature is lowered. This response is predicted by the presence of a linear term only in the equation for L-100/MOCA and of both linear and quadratic terms in the equation for LW-520/Tonox.

Stress at break was not very sensitive to strain rate, as is evident from the small or insignificant coefficients for the scaled variable X_2. The stress at break of L-100/MOCA was insensitive to strain rate <u>within the range of strain rates available on the Instron testing machine</u>. The breaking stresses of LW-520/Tonox showed low-level effects as strain rates varied; this can be seen from the small linear and quadratic coefficients.

That temperature and strain-rate effects are independent of each other is indicated by the insignificant synergistic coefficients (cross-product terms).

Table B3 shows nominal stresses at break calculated from the response-surface values at various strain rates. The agreement between calculated and experimental values is quite good. The fitting errors σ about the fitted surface are much smaller than those about the mean.

Table B3. Response-surface evaluations of L-100/MOCA and LW-520/Tonox nominal stress at break.

Test temperature, °C	Composition	Stress at break, MPa				
		Strain rate, $\sec^{-1}$				
		2.8×10^{-4}	1.4×10^{-3}	5.6×10^{-3}	2.8×10^{-2}	1.4×10^{-1}
-40	L-100/MOCA			92		
	LW-520/Tonox			60		
-11	L-100/MOCA		79	76	67	
	LW-520/Tonox		45	45	43	
+23	L-100/MOCA	49	56	57	53	44
	LW-520/Tonox	24	27	29	29	29
+57	L-100/MOCA		34	39	40	
	LW-520/Tonox		14	17	19	
+100	L-100/MOCA			11		
	LW-520/Tonox			12		

	Fitting errors	
Composition	σ about mean of all data	σ about mean response surface
L-100/MOCA	23	11
LW-520/Tonox	12	3

EQUATIONS RELATING STRAIN AT BREAK TO TEMPERATURE AND STRAIN RATES

Table B4 shows the contributions of linear and quadratic terms in the equations to the influence of temperature and strain rates on tensile strain at break.

In agreement with experimental data, the equations show that LW-520/Tonox specimens elongate only two-thirds as much as those of L-100/MOCA before breaking. Strain at break for LW-520/Tonox is also much less sensitive to temperature than that for L-100/MOCA, although it is considerably more sensitive to strain-rate effects (within the strain rates available from the Instron testing machine). Synergistic effects were negligible.

Table B5 compares the breaking strain of L-100/MOCA and LW-520/Tonox as calculated from the response-surface equations. Though the surface relationships of breaking strain versus strain rate and versus

Table B4. Response-surface coefficients for strain at break.[a]

Composition	Strain, average level	Temperature effects		Strain-rate effects	
		Linear	Quadratic	Linear	Quadratic
L-100/MOCA	4.44	0.30	-0.14	-0.01	-0.01
LW-520/Tonox	2.83	0.05	0.03	-0.11	-0.02

[a] Coefficients describing synergistic effects are statistically insignificant.

Table B5. Response-surface evaluations of L-100/MOCA and LW-520/Tonox strain[a] at break.

Test temperature, °C	Composition	Strain at break				
		Strain rate, sec^{-1}				
		2.8×10^{-4}	1.4×10^{-3}	5.6×10^{-3}	2.8×10^{-2}	1.4×10^{-1}
-40	L-100/MOCA			2.6		
	LW-520/Tonox			2.2		
-11	L-100/MOCA		3.9	3.7	3.5	
	LW-520/Tonox		2.7	2.7	2.4	
+23	L-100/MOCA	4.5	4.5	4.4	4.4	4.4
	LW-520/Tonox	2.3	2.7	2.8	2.8	2.4
+57	L-100/MOCA		4.5	4.6	4.8	
	LW-520/Tonox		2.3	2.6	2.6	
+100	L-100/MOCA			3.9		
	LW-520/Tonox			1.4		

Composition	Fitting errors	
	σ about mean of all data	σ about fitted response surface
L-100/MOCA	0.6	0.2
LW-520/Tonox	0.5	0.3

[a] Length at break minus gauge length divided by gauge length.

temperature do not fit the experimental data as well as the stress relationship does, the surface is adequate for our purposes.

The equations have been used in a computer program to generate pseudo-three-dimensional response surfaces of stress or strain at break versus temperature and versus strain rate (see Figs. B1 through B4).

Response-surface equations derived from Adiprene L-315/polyol data were much less reliable in predicting experimental points,

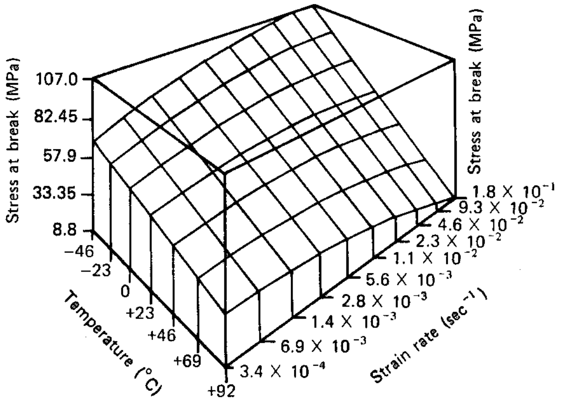


Fig. B1. Response surface of stress at break of Adiprene L-100/MOCA cured at 100°C versus temperature and strain rate.

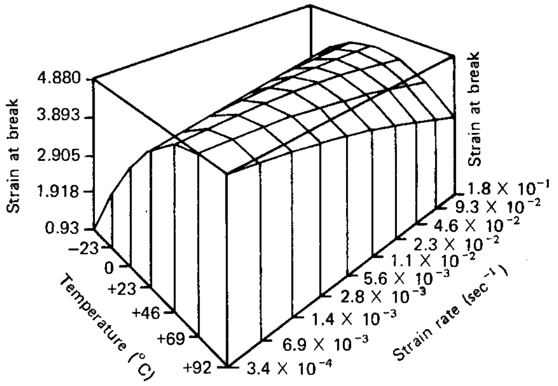


Fig. B2. Response surface of strain at break of Adiprene L-100/MOCA cured at 100°C versus temperature and strain rate.

probably because the tensile properties of this adhesive have a pronounced response to temperature.

In summary, the response-surface equations developed described well the stress-strain curves of L-100/MOCA and LW-520/Tonox (except at low temperatures) but were much less reliable in describing the behavior of L-315/polyol. The equations are limited by the highest strain rate attainable on the Instron testing machine (1.4×10^{-1} sec^{-1}). We developed other types of response surfaces relating stress-strain data to initial modulus, midrange modulus, and moduli at nominal elongations. However, these surfaces did not describe the experimental values well enough to be useful. Possibly cubic equations or equations obtained by using higher series would represent the data better.

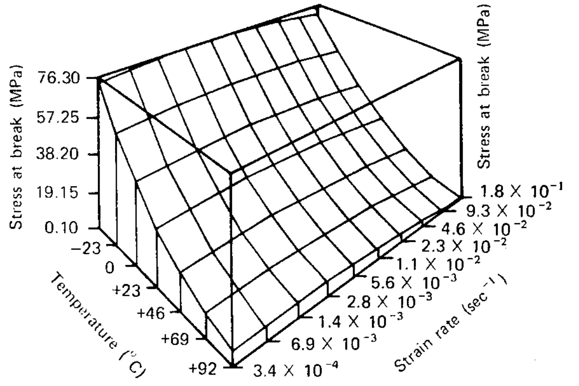


Fig. B3. Response surface of stress at break of Adiprene LW-520/Tonox cured at 100°C versus temperature and strain rate.

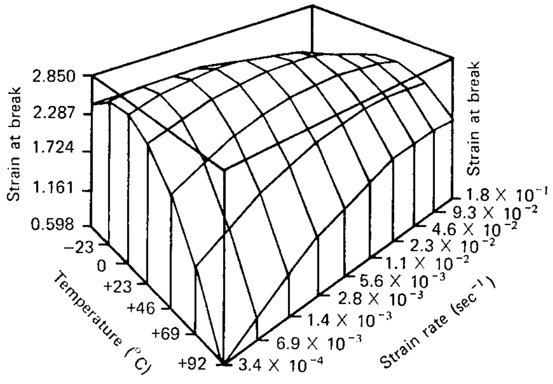


Fig. B4. Response surface of strain at break of Adiprene LW-520/Tonox cured at 100°C versus temperature and strain rate.

Appendix C

A Hypothetical Model Relating the Stress-Strain Behavior of Cured Urethane Adhesives to Their Structure

INTRODUCTION

When a polymer is stressed, its molecular conformation responds by viscous slippage, orientation, crystallization, rupture of crosslinks, changes in intermolecular forces, and other modes. The total response may be the result of several of these modes. The importance of each mode may change as the strain level changes, which implies that important molecular conformations in a polymer differ in their responses to stress. To analyze these complex relationships in a particular polymer, its entire stress-strain behavior must be studied.

The response of a single-phase, homogeneous polymer to stress should be predictable. A cured, noncrystallizing rubber, such as sulfur-cured butyl rubber, is randomly crosslinked, amorphous, and relatively homogeneous. Its response to stress is reasonably explained and predicted by the Mooney-Rivlin theory, at least in the range from 0 to 100% elongation (strain from $\lambda = 1$ to $\lambda = 2$).

However, when natural rubber is stressed in tension, crystals form at high strains and current theories about stress-strain responses do not apply. Furthermore, many new types of elastomer have appeared recently--elastomers that are nonhomogeneous, that crystallize, or that form two or more mutually insoluble domains. A more general formalism is needed to explain the elastomeric behavior of these two-phase systems.

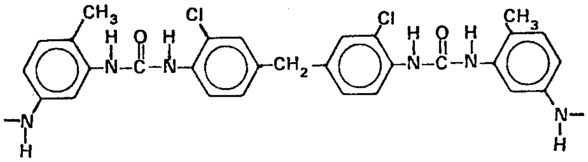
The impetus for us to extend current theories came from our need to understand the behavior of cured elastomeric urethane (Adiprene) adhesives, which are widely used in ERDA projects.

To extend the current formalism to these nonhomogeneous systems, one must find formulations for different statistical distributions of end-to-end chain lengths and/or a strain-energy function that relates stress to strain. We chose to use the formalism of Eyring,[1] who extended statistical mechanics to such diverse phenomena as the dielectric, diamagnetic, and paramagnetic properties of matter; the properties of crystals; ferromagnetism; the viscosity of polymer melts; and the steady-state theory of mutation rates.[2] The methods of Eyring and Stover[3] were recently used at LLL in connection with studies of tumor incidence.[4]

HYPOTHETICAL MODEL FOR TWO-PHASE ELASTOMERS

By applying Eyring's formalism to two-phase elastomers, we have devised a hypothetical model that permits a mathematical description of the stress-strain behavior of cured polyurethane elastomers over the entire range from zero strain to rupture. The application of Eyring's techniques here is based on the hypothesis that molecular conformational energy and molecular orientation effects are inherent in the responses of urethane adhesives to stress. These two phenomena relate to Eyring's frequency factor and his exponential factor.

In our model the two kinds of backbone segments in a cured urethane elastomer are referred to as "hard" and "soft" because one type of segment is relatively stiff and the other is flexible. As shown in the example below, the hard segments have stiff ring and polar components that reinforce themselves by intermolecular hydrogen bonding between N-H and C=0 groups and between N-H groups and the oxygen atoms of soft segments. The soft segments of the backbone chain, for example,



$$-\!\!\left[-O-CH_2-CH_2-CH_2-CH_2-\right]_n$$

$$n = 5 \text{ to } 30$$

are polyethers; they are randomly coiled and folded.

Since these two types of structures are mutually insoluble, segments of the same structure from the same molecule and/or from adjacent molecules may accumulate in microdomains in which opportunities for hydrogen bonding are considerably enhanced.

As stress is applied, the hydrogen bonds may break and reform in new positions. The hydrogen bonds to the ether oxygen atoms are weaker than those to carbonyl oxygen atoms and will therefore break first. As strain increases, hydrogen bonds are still numerous, but most of the intermolecular forces are now aligned normal to the direction of stress and are thus nonreinforcing in the same direction as stress. As elongation is increased still more, chains uncoil and entanglements are straightened and pulled out.

The basic assumptions in our hypothesis are as follows:

1. The urethane polymer chain consists of hard and soft segments. Soft segments form loops and coils in the chain, but hard segments act as stiff single units.

2. The relative axial deformation of any given polymer is proportional to the axial applied strain. The proportionality constant of a hard segment is different from that of a soft segment.

3. The hard and soft segments are noninteracting and respond differently to the applied strain. The responses are linearly additive.

4. For a given strain, a steady-state condition exists.

5. Changes in the orientation of the hard and soft domains will increase or decrease the stored energy of these individual segments because of changes in the molecular conformations of the domains.

At any strain, a certain number of hard and soft domains are contributing to the total resistance of a unit volume being stretched. That volume may be considered to be in a steady state in that the total effect of the assembly of hard and soft segments is constant.

If we apply Eyring's formalism, we can define ν as the frequency with which a segment passes over a conformational energy barrier; ν is then given by

$$\nu = \frac{Kkt}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{kT}\right),$$

where K is an adjustable parameter, k is a conversion factor (Boltzmann's constant) expressed as ergs per degree of temperature (which converts calories to ergs), h is Planck's constant, T is the absolute temperature, and $G^{\ddagger}$ is the Gibbs free energy of conformation in the strain field.

The number of domains per unit strain passing from one conformation to another is

$$\nu_1 = \frac{KkT}{h} \exp \left(-\Delta G^{\ddagger} - \frac{P_E}{2kT}\right) \qquad \text{(C1)}$$

and

$$\nu_2 = \frac{KkT}{h} \exp \left(-\Delta G^{\ddagger} + \frac{P_E}{2kT}\right), \qquad \text{(C2)}$$

where P_E is an additional energy caused by a change in elongation.

At this point we must assume that the responses of soft and hard domains in our polymeric model are each described by such an equation and that the effects are additive at each strain level since the domains are noninteracting. Further, depending on the strain level, relative rates describe the differences in the response of the hard and soft domains to strain (assumption 2 above).

The equations can be written in a form more suitable for computation and curve fitting. Utilizing the finite-difference calculus,[5] we write the relative rate of change of stress with respect to strain as

$$\begin{aligned} \Delta\sigma(t) &= F(t) \\ &= \gamma Z(1 + \gamma)^t + \overline{\gamma} Z(1 + \overline{\gamma})^t, \qquad \text{(C3)} \end{aligned}$$

where $\lambda = st + \lambda$ = elongation, λ_0 is a valid small experimental elongation, s is the equal sampling elongation interval, t = 0, 1, 2, and

$$\begin{aligned} \sigma(\lambda) &= \int_{\lambda_0}^{\lambda} \left[\frac{1}{\sigma_N(\lambda)} \frac{d\sigma_N(\lambda)}{d\lambda}\right] d\lambda \\ &= \ln \sigma_N(\lambda) - \ln \sigma_N(\lambda_0), \end{aligned}$$

σ_N being the nominal stress.

The formulation of F(t) from Eyring's theory is straightforward and is analogous to his development of the Debye equations for dielectric materials.

The statistical parameters appearing in Eqs. (C1) and (C2) have been absorbed into γ, $\overline{\gamma}$ and Z, $\overline{Z}$ coefficients. We postulate that these parameters γ', $\overline{\gamma}$, Z, $\overline{Z}$ are related to the conformation and structure of the urethane elastomers. If the F(t) equation is fitted to the experimental data in such a manner that the functional relationships are not vitiated by the fitting procedure, then the coefficients could serve as sets of figures of merit.

The summation of F(t) is the stress-strain curve:

$$\begin{aligned} \sigma(t) &= C + \overline{Z}\ (1 + \gamma)^t + Z\ (1 + \overline{\gamma})^t \\ &= \ln \frac{\sigma_N(t)}{\sigma_N(0)}. \end{aligned}$$

So far we have achieved simply a mathematical formulation of a hypothesis that relates stress and strain to the molecular properties of elastic polymers. It is of interest, as Eyring states, "...only if there is a one-to-one correspondence with experiment." We have gone part way toward satisfying Eyring's criterion by fitting the equations to data already in hand for urethane elastomers.

We succeeded in fitting the equations to data obtained by testing cured Adiprene W-520 Tonox and Adiprene L-100/MOCA specimens at many different temperatures and strain rates. The test data used for fitting are recorded in the multiple tables in Appendix A. A typical fit for about 100 different tests is shown in Table C1. Notice that the fit of $\sigma(t)$ describes the *entire* stress-strain curve from zero elongation to rupture of the specimen; this is the *first* formalism we know of that does so.

Table C1. Typical comparison of experimental and calculated values based on

$$\sigma(t) = \ln \frac{\sigma_N(t)}{\sigma_N(0)}$$

$$= C + \overline{Z}(1 + \gamma)^t + Z(1 + \overline{\gamma})^t .$$

λ	Experimental fitted values			t
	σ_N	σ	$\hat{\sigma}$	
0.1	31	0.000	0.008	0
0.3	49	0.458	0.439	1
0.5	60	0.660	0.662	2
0.7	69	0.800	0.812	3
0.9	79	0.935	0.941	4
1.1	90	1.066	1.065	5
1.3	103	1.201	1.192	6
1.5	117	1.328	1.324	7
1.7	134	1.464	1.463	8
1.9	155	1.609	1.610	9
2.1	180	1.759	1.764	10
2.3	212	1.923	1.927	11
2.5	253	2.099	2.098	12
2.7	304	2.283	2.279	13
Rupture	--	--		

Parameters

C	$\overline{Z}$	$1 + \gamma$	Z	$1 + \overline{\gamma}$
-1.237	1.770	1.054	-0.526	0.363

DISCUSSION

In our hypothesis we associate the parameters $(1 + \overline{\gamma})$ and $(1 + \gamma)$ with the hard and soft segments, respectively, of the two-phase cured-urethane adhesives. The total stress-strain curve can be thought of as the sum of two hypothetical curves contributed by the two types of segments. The responses to stress of the hard segments, whose coefficient in the equation is always less than unity (see Table C2) contribute strongly to the initial and flatter portions of the curve. The soft segments, which have a coefficient greater than unity, contribute mainly to the final parts of the total curve.

We interpret the fact that the coefficients $(1 + \overline{\gamma})$ of L-100/MOCA are always larger than those of LW-520/Tonox (see Table C2) to indicate that the hard domains of L-100/MOCA are more rigid and more resistant to stress than are the hard domains of LW-520/Tonox. This difference in magnitude was true in all but one comparison of the two adhesives (i.e., at several strain rates, in specimens cured at room temperature or at 100°C, or at several different test temperatures).

Furthermore, L-100/MOCA is more resistant to stress at low strains than is LW-520/Tonox. This is evident from the changes in the $(1 + \overline{\gamma})$ values for the two adhesives with changes in strain rate, an interpretation suggesting that still more rigid hard domains would produce adhesives having steeper initial slopes in their stress-strain curves.

Similarly, inspection of the $(1 + \overline{\gamma})$

Table C2. Parameters of $F(t) = (\gamma\bar{Z})(1 + \gamma)^t + (\bar{\gamma}Z)(1 + \bar{\gamma})^t$ for LW-520/Tonox and L-100/MOCA at various Instron crosshead speeds and test temperatures.

Test temperature, °C	Crosshead speed, cm/sec	LW-520/Tonox				L-100/MOCA			
		Soft-domain parameters		Hard-domain parameters		Soft-domain parameters		Hard-domain parameters	
		$\gamma\bar{Z}$	$1 + \gamma$	$\bar{\gamma}Z$	$1 + \bar{\gamma}$	$\gamma\bar{Z}$	$1 + \gamma$	$\bar{\gamma}Z$	$1 + \bar{\gamma}$
		Cure temperature 23°C							
23°	2.8×10^{-4}	0.058	1.145	0.202	0.313	Not available			
23°	1.4×10^{-3}	0.067	1.123	0.221	0.229	0.057	1.272	0.359	0.373
23°	5.6×10^{-3}	0.087	1.111	0.226	0.258	0.063	1.329	0.375	0.375
23°	2.8×10^{-2}	0.093	1.109	0.241	0.287	0.010	1.298	0.382	0.382
23°	1.4×10^{-1}	0.127	1.106	0.169	0.017	0.038	1.208	0.307	0.307
		Cure temperature 100°C							
23°	2.8×10^{-4}	0.068	1.102	0.305	0.325	0.014	1.219	0.135	0.496
23°	1.4×10^{-3}	0.090	1.090	0.341	0.370	0.013	1.235	0.342	0.498
23°	5.6×10^{-3}	0.087	1.060	0.360	0.360	0.018	1.244	0.357	0.512
23°	2.8×10^{-2}	0.096	1.054	0.335	0.363	0.019	1.235	0.376	0.504
23°	1.4×10^{-1}	0.183	1.068	0.285	0.308	0.031	1.199	0.363	0.417
23°	5.6×10^{-3}	0.087	1.060	0.360	0.360	0.018	1.244	0.357	0.512
57°	5.6×10^{-3}	0.098	1.027	0.408	0.301	0.026	1.138	0.315	0.447
70°	5.6×10^{-3}	0.100	1.020	0.452	0.285	Not available			
100°	5.6×10^{-3}	0.118	0.958	0.457	0.182	0.033	1.107	0.372	0.159

coefficients showed that, as the test temperature was raised, the domains of L-100/MOCA softened more readily than did the hard domains of LW-520/Tonox. Another conclusion from the coefficients was that, within the capability of the Instron test instrument, these coefficients were not sensitive to differences in the strain rate.

The responses of soft domains of the Adiprene adhesives to both strain rate and to test temperature were similar, as indicated by the sizes of the $(1 + \gamma)$ coefficients for the two adhesives (Table C2).

Comparisons of the total relative rate of change can be made by evaluating F(t) at various strains. Table C3 does this for γ = 0.1, 1.1, and 2.5. These elongations are representative of the initial, midrange, and latter portions of the stress-strain curve. Table C3 shows that the contributions of the hard domains to the relative rates of change at $\gamma = 0.1$ are of major importance. At $\gamma = 1.1$, the orientation of the hard domains in the direction of elongation makes a constant contribution to stress resistance; the hard domains thus make no contribution ot the relative rate of stress change at this elongation. The soft domain now becomes the major contributor to the relative rate of change in stress as elongation is increased.

Thus the hydrogen-bonding effects on stress, as elongation increases, are described by the mathematical model parameters when fitted to experimental data.

So far our hypothetical model has been

Table C3. Comparisons of relative rates of change of stress σ with respect to elongation λ at λ = 0.1, 0.9, and 2.5 for room-temperature and 100°C cures.[a]

		23°C cure			100°C cure		
	Elongation	Contributions to $F(\lambda)$			Contributions to $F(\lambda)$		
Composition	λ	Soft	Hard	Total	Soft	Hard	Total
LW-520/Tonox	0.1	0.087	0.226	0.313	0.087	0.360	0.447
L-100/MOCA	0.1	0.063	0.375	0.438	0.018	0.357	0.375
LW-520/Tonox	1.1	0.133	0.001	0.134	0.110	0.006	0.116
L-100/MOCA	1.1	0.196	0.010	0.206	0.043	0.025	0.068
LW-520/Tonox	2.5	0.308	<0.0001	0.308	0.175	<0.0001	0.175
L-100/MOCA	2.5	1.912	<0.0001	1.912	0.248	<0.0001	0.248

[a] Test conducted at 23°C and an Instron crosshead speed of 5.6×10^{-3} cm/sec.

used to fit the stress-strain data collected while testing certain Adiprene adhesives. We conjecture that the model has a much wider application. It should apply to block polymers, such as Shell's amorphous two- and three-phase Kratons and to the Phillips star polymers, as well as to microblock polymers like the polyurethanes Estane and Texin and to partly crystalline block polymers. The model may also be of value in describing certain commercial elastic polymers in which butyl rubber has been grafted to polyethylene and to some silicone block polymers.

At present we are planning experiments that will change the proportions of hard and soft domains in a urethane polymer (i.e., the ratio of polyether to urethane plus aromatic groups) in order to achieve greater rigidity. We would do this by adjusting the ratio of isocyanate groups in the reaction mixture to the total of all groups that can react with isocyanate as well as by selection of polyether chain length. According to our hypothesis, the increased rigidity should be detectable in the "hard" portion of the stress-strain curve and in the coefficients of our equations. In this way we hope to use the hypothesis as a tool to help tailor urethane structures to our advantage.

Furthermore, we believe that adapting this model and hypothesis to the study of compatibility and long-term aging of urethane adhesives might save valuable time, especially when the test conditions involve chemically active environments. If the effects of individual environments can be quantified by the type of parameters discussed above, aging effects on urethane adhesives could be simulated by increasing chemical concentrations in the environments or by raising the temperature and hence the rate at which the chemicals attack the urethane.

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