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PREPARATION OF A REMOVABLE POLYURETHANE
ENCAPSULANT

PDO 6989246, Final Report

B. G. Parker, Project Leader

Project Team:
D. R. Jamieson

Published August 1976

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Kansas City
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PREPARATION OF A REMOVABLE POLYURETHANE ENCAPSULANT

BDX-613-1406, UNCLASSIFIED Final Report, Published August 1976

Prepared by B. G. Parker, D/814, under PDO 6989246

The preparation of polyurethane encapsulants, based on polyether diol/diisocyanate prepolymers and 1,4-butanediol, which are soluble in several organic solvents, was investigated. Since these materials can be easily removed, repair of electronic circuitry found defective in potted units can be readily accomplished. Polyether diols of varying molecular weights were reacted with toluene diisocyanate (TDI) and methylene diphenylisocyanate (MDI) to produce stable prepolymers. Several properties of both the isocyanate prepolymers and 1,4-butanediol cured polyurethane encapsulants are presented.

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SUMMARY

In order to study the feasibility of producing isocyanate prepolymers suitable for use as soluble encapsulants, this project was initiated to characterize the prepolymers by molecular weight and isocyanate content, determine their shelf life, and prepare cured specimens for testing.

Sandia Laboratories had previously prepared soluble linear polyurethane encapsulants in a one-step process using four components and was interested in developing a prepolymer to be used in a two-component system. This soluble polyurethane encapsulant could easily be removed for rework of electronic circuits.

Several prepolymers and prepolymer blends were prepared at Bendix Kansas City which yielded soluble potting material when cured with 1,4-butanediol. The Bendix prepolymers have satisfactory shelf life stability as indicated by small changes in viscosity and percent isocyanate content with time. The softening point of these urethane encapsulants is similar to the softening point of Sandia encapsulants, however, it is somewhat below that normally required for electronic potting materials.

DISCUSSION

SCOPE AND PURPOSE

Most materials used for encapsulating electronic assemblies are difficult to remove in order to repair electronic circuitry found defective after encapsulation. This project was undertaken to synthesize isocyanate terminated prepolymers which, when cured with a low molecular weight diol, would produce a soluble polyurethane encapsulant. This encapsulant could easily be removed for rework of the electronic circuitry.

PRIOR WORK

Potting materials have been prepared at Sandia Albuquerque which were a one-step or one-shot process; that is, all of the ingredients (two long chain polyether diols, one short chain diol, and toluene diisocyanate) were mixed together and reacted. These potting materials were soluble in organic solvents such as tetrahydrofuran.

ACTIVITY

Preparation of the Prepolymers

Several polyether diols covering a wide range of molecular weights were obtained from various companies (Table 1). The diols vary in average molecular weight from 300 to more than 3000 and are urethane-grade polyether diols containing less than 0.2 percent water.

The diisocyanates used were toluene diisocyanate (TDI) and methylene diphenylisocyanate (MDI). The TDI had a 80/20 isomer ratio (80 percent by weight of the 2,4-toluene diisocyanate isomer and 20 percent by weight of the 2,6-toluene diisocyanate isomer).

A ratio of two moles of diisocyanate for each mole of polyether diol was used to prepare the prepolymers.

The diisocyanate was placed in a 1 liter (dm^3) resin reactor fitted with an air-driven stirrer, reflux column, nitrogen inlet valve, and a thermometer. The reaction vessel was heated to 60°C and then the polyether diol, also preheated to 60°C , was added with stirring. The reaction was allowed to exotherm to 71°C at which point the reaction was quenched by immersing the reaction vessel in ice water.

Table 1. Materials Used in Preparing Prepolymers

Diisocyanate	Polyether Diol	Hydroxyl Number	Average Molecular Weight (Calculated)
80/20 TDI*			174
125 (M)MDI**			250
	Voranol 2103***	374	300
	Voranol 2122	56	2000
	Pluracol P-410†	259	433
	Pluracol P-710	146	769
	Pluracol P-1010	107	1049
	Pluracol P-2010	56	2022
	Pluracol 479	41	2748
	Poly-G 720P††	145	773
	Poly-G 3020P	36	3082
	Poly-GX-419PG	110	1020

*Mobay Chemical Company

**Upjohn Company

***Dow Chemical Company

†Wyandotte Chemicals Corporation

††Olin Chemicals

The prepolymer was then transferred to a glass jar and degassed in a vacuum oven until the bubbles ceased. The jars were then sealed under a nitrogen blanket. The formulations used in preparing the prepolymers are shown in Table 2.

Initial preparation of cured samples indicated that MDI based prepolymers would not yield a suitable encapsulant when cured with 1,4-butanediol. The MDI based prepolymers produced clay-like products when cured and had very low softening points. For this reason no additional investigation of polyether diol/MDI polymers was proposed.

Characterization of the Prepolymers

The viscosities of the prepolymers shown in Table 2 were determined with a viscometer (Brookfield Engineering Laboratories Incorporated) at 23.5°C. Viscosity measurements, given in Table 3, were made shortly after preparing the prepolymers and again 2 months later

Table 2. Formulations of Prepolymers

Polyether Diol	Polyether Diol (Grams)	TDI (Grams)	MDI (Grams)
Voranol 2103	431	500	
Voranol 2122	575	100	
Pluracol P-410	498	400	
Pluracol P-710	662.4	300	
Pluracol P-1010	604	200	
Pluracol P-2010	580	100	
Pluracol 479	789.7	100	
Poly-G 720P	667.2	300	
Poly-G 3020P	886	100	
Poly-GX-419PG	732.5	250	
Pluracol P-410	400		463
Pluracol P-710	400		260.2
Pluracol P-1010	400		190.7

to help indicate the shelf life stability of the prepolymer. The major change in viscosity is caused by the reaction of the prepolymer with moisture in the air when the container is opened. All prepolymers were equally exposed to atmospheric moisture. Table 3 also shows the percent increase in viscosity over a 2-month period is only slight for low molecular weight prepolymers and greater for higher molecular weight prepolymers.

The viscosity of the prepolymer formed (Figure 1) increases as the molecular weight of the polyether diol used decreases. The viscosity of the (Voranol 2103) prepolymer makes it unusable for all practical mixing purposes.

The amine equivalent of each prepolymer was determined by reacting a known weight of prepolymer with a known excess of N,N dibutyl amine, back-titrating with a one normal hydrochloric acid solution, and comparing with a blank sample. Titrations were run on a Metrohm Herisau automatic titrator (Brinkman Instruments).

To help indicate stability of the prepolymers and determine the amount of 1,4-butanediol required for curing, the amine equivalents were determined at various time intervals. Percent NCO and the average molecular weight of the prepolymers can be derived from the amine equivalent and are shown in Table 4.

Table 3. Change in Viscosity of TDI Prepolymers

Prepolymer Base	Initial Viscosity at 23.5°C (Pa·s)	Viscosity After 60 Days at 23.5°C (Pa·s)	Increase (Percent)
Voranol 2103	10,500	10,600	0.9
Pluracol P-410	761	768	0.9
Pluracol P-710	30.1	30.9	2.5
Poly-G 720P	17.5	29.9	70.8
Poly-GX-419PG	2.9	9.2	216
Pluracol P-1010	3.0	17.1	472
Voranol 2122	1	6.9	593.6
Pluracol P-2010	1.2	5.6	370.2
Poly-G 3020P	2.3	7.1	207.6
Pluracol 479	1.1	5.9	455.3

The stability of the prepolymer, as far as change in amine equivalents is concerned, decreases as the average molecular weight of the prepolymer increases.

Gel permeation chromatography analysis of the polyether diols (Figure 2) helps to show why the viscosity of the Voranol 2103 prepolymer was so high. A large portion of Voranol 2103 is composed of an amount below the 300 molecular weight average and, as shown in Figure 1, the viscosity of the prepolymer increases very rapidly as the molecular weight decreases. This large amount of lower weight polyether diol increases the viscosity above that expected for the 300 molecular weight alone.

The P-410 and P-710 polyether diols on the other hand have a much more uniform molecular weight distribution and produce prepolymers having viscosities which are usable.

Preparation and Characterization of Encapsulant Samples

Required amounts of 1,4-butanediol were mixed with preheated prepolymers (71°C) and the mixture was placed in a vacuum oven at 60°C and degassed. The encapsulant samples were then allowed to cure for 16 hours at 60°C and removed from the mold. Softening points of the cured polyurethanes were run on a Perkin Elmer thermomechanical analyzer. The results of softening point analysis are given in the following tabulation.

Figure 1. Molecular Weight/Viscosity
Characteristics of Polyether
Diol/TDI Prepolymers

<u>Prepolymer</u>	<u>Softening Point (°C)</u>
Voranol 2103	
Pluracol P-410	44.6
Pluracol P-710	6
Poly-G 720 P	5
Poly-GX-419PG	-10
Pluracol P-1010	-12
Voranol 2122	-26
Pluracol P-2010	-25
Poly-G 3020P	-30
Pluracol 479	-33

Table 4. Change in Percent of Isocyanate Content

Prepolymer Base	Initial Amine Equivalent	Amine Equivalent (30 Days)	Amine Equivalent (60 Days)	Percent NCO		
				Initial	30 Days	60 Days
Voranol 2103	352	356.6	358.2	11.9	11.8	11.7
Pluracol P-410	413	419.7	422.6	10.2	10	9.9
Pluracol P-710	588	596.6	602.9	7.1	7.1	6.9
Poly-G 720P	583	607.9	653.5	7.2	6.9	6.4
Poly-GX-419PG	678.8	715.6	733.4	6.2	5.9	5.7
Pluracol P-1010	669.9	713.1	672.4	6.3	5.9	5.5
Voranol 2122	1019.5	1108.8	1433.6	4.1	3.8	2.8
Pluracol P-2010	1003.7		1229.4	4.9		3.4
Poly-G 3020P	1275.8		1804.6	3.3		2.3
Pluracol 479	1482.9		1485.8	2.8		2.8

Figure 2. Gel Permeation Chromatograph of Polyether Diols

The softening point decreases as the molecular weight of the prepolymer increases (Figure 3). The P-410 prepolymer produced a cured polymer with the highest softening point (44.6°C), however, this polymer was very susceptible to cracking. In order to help reduce the susceptibility to cracking, an additional higher molecular weight prepolymer or diol acting as a flexibilizer must be added.

The P-710 prepolymer was chosen for use as the flexibilizer because it has the next highest softening point (6°C) and would not lower the softening point of a mixture as much as the other prepolymers would.

Gel permeation chromatography analyses were run on the P-410 and P-710 prepolymers to determine the amount of free TDI in each prepolymer (Table 5).

Figure 3. Molecular Weight/Softening Point of Cured Polyurethane

Varying ratios of P-410 and P-710 prepolymers were mixed and cured with 1,4-butanediol. The softening points and results of GPC analysis of these cured mixtures are shown (Table 6).

The following tabulation shows the formulation for an encapsulant sample prepared at Sandia Laboratories using a one-shot process, along with its softening point and molecular weights as determined by GPC analysis. GPC analysis of Sample A is very similar to that of Sandia's sample, however Sample A has a higher softening point than the Sandia material (Figure 4).

6 Parts by Weight Voranol 2103
 1 Part by Weight Voranol 2120
 0.13 Part by Weight 1,4-butanediol
 4 Parts by Weight TDI
 38.3°C Softening Point
 12,300 Weight Average Molecular Weight
 5600 Number Average Molecular Weight

Table 5. Composition of P-410 and P-710
Prepolymers by GPC

Prepolymer	Weight Percent		
	Monomer (TDI)	Dimer	Trimer
Pluracol P-410	2.3	62.5	35.2
Pluracol P-710	1.3	69	29.7

The urethane encapsulant samples are soluble in several polar organic solvents (Table 7). The solubility time could be shortened by heating the solvents or agitating the sample in the solvent. Since the encapsulant is soluble, it can easily be removed from potted parts for repair of electronic circuitry by immersion in a solvent.

ACCOMPLISHMENTS

Polyurethane prepolymers which yield a soluble polyurethane potting material when cured with 1,4-butanediol have been developed. Because of its solubility, this material can be readily removed from electrical units to allow rework of defective circuits. The prepolymers are based on Wyandotte Chemical Corporations' Pluracol P-410/TDI with varying amounts of Pluracol P-710/TDI added as a flexibilizer. Several polyurethane encapsulant samples were prepared and sent to Sandia Laboratories for additional evaluation as a potting material. With repeated opening and closing of the prepolymer containers, exposing them to atmospheric moisture, over a two month period, there was less than 2.5 percent change in percent isocyanate and viscosity of the P-410/TDI and P-710/TDI prepolymers. This indicates satisfactory shelf life stability of the prepolymers. The softening points of various ratios of P-410/TDI and P-710/TDI prepolymers when cured with 1,4-butanediol, and solubility in various organic solvents was given.

FUTURE WORK

Although the softening points of the cured prepolymers are in the same range as samples prepared at Sandia, they are, however,

Table 6. Preparation of Prepolymer Blends

Sample Number	P-410 Prepolymer (Parts by Weight)	P-710 Prepolymer (Parts by Weight)	1,4-Butanediol (Parts by Weight)	Softening Point (°C)	Molecular Weight	
					Weight (Average)	Number (Average)
A	5	0	0.56	44.6	12,200	5,500
B	6	1	0.75	41	13,000	5,400
C	5	1	0.64	40	14,300	5,300
D	4	1	0.53	37	15,300	6,500
E	3	1	0.41	29.9	23,000	8,500
F	2	1	0.30	27.5	14,000	5,400

Figure 4. Gel Permeation Chromatograph of Polyurethanes

somewhat lower than normal potting materials. Either the softening point of the cured polymer must be raised by some means (i.e. addition of fillers) or a different prepolymer needs to be developed.

Table 7. Solubility of Polyurethane Encapsulants in Various Solvents (Sample Number A, B, and C, Table 6)

Solvent	Time (Hours)
Tetrahydrofuran	1
Dichloromethane	1.08
Chloroform	1.16
Acetone	1.75
N,N-Dimethyl Acetamide	16
Methanol	*
Benzene	*
Toluene	**
Tetrachloroethylene	**
1,4-dioxane	*
O-dichlorobenzene	**
Dichloroethane	*
Water	**

*Melts to the bottom of test tube
but does not dissolve.
**Insoluble

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