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CHARACTERIZATION OF CONATHANE
EN-4 URETHANE RESIN

EP 4119681, Topical Report

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Project Team:
C. J. Camp
F. E. Meisner

Published August 1973

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CHARACTERIZATION OF CONATHANE EN-4 URETHANE RESIN

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Prepared by D. J. Caruthers, D/814, under EP 4119681

High voltage protection of electrical components is provided by Conathane EN-4 manufactured by Conap Incorporated. EN-4 is a polybutadiene based isocyanate resin cured with a polyol blend. The material has better hydrolytic stability and a lower compressive modulus than either the polyether or polyester castable urethanes.

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SUMMARY

A polybutadiene-based urethane resin cured with a polyol blend, Conathane EN-4, manufactured by Conap Incorporated is a new product offering better hydrolytic stability, better electrical breakdown, lower cure shrinkage, and improved adhesion than polyether urethane elastomer systems. Each processing step known to affect the end product is discussed. Close adherence to the Process Specification 99297083 is required if uniform repeatable results are to be effected. Specifications require that the material have a starting viscosity of under 5000 centipoise (5 Pa·s).

Physical test data show the tensile modulus of EN-4 increases by 80 percent and the dielectric strength increases by 250 percent after room temperature aging for 75 days. The data also show that three cure schedules, 24 hours at 160°F (71°C), 16 hours at 180°F (82°C), and 10 hours at 200°F (93°C) yield similar physical properties. Production cures are limited to temperatures of 160°F or 180°F. Temperatures above 205°F (95°C) can cause some catalysts to volatilize. Cure shrinkage of EN-4 is less than the amine and glycol cured polyethers. Room temperature curing of EN-4 is not possible.

The adhesion of the polybutadiene-based urethane is exceptional. Values obtained with metals are over twenty times those obtained with polyether-based urethanes. This adhesion is obtainable without the use of primers. Adhesion to polyolefin and Kynar* wire insulation is good. Both thermal cycling and humidity cycling improved the adhesion to Kynar, and better adhesion is obtainable to the Kynar than to polyolefin.

Dynamic properties of modulus are presented showing the polybutadiene material (EN-4) to be capable of absorbing more energy than the polyether urethane (Adiprene L-100 MOCA) system at room temperature.

A comparison of handling characteristics and resulting properties of EN-4 and Adiprene L-100 MOCA is presented.

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*Kynar: Pennwalt Corporation, polyvinylidene fluoride.

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DISCUSSION

SCOPE AND PURPOSE

Components in a new assembly required protection from high voltages not previously encountered. To meet this requirement a new material manufactured by Conap Incorporated, Conathane EN-4 a polybutadiene based isocyanate resin cured with a polyol blend, was evaluated. Changes in material resulting from changes in processing and aging were noted.

PRIOR WORK

Conathane EN-4 has only recently been made available. Hysol Corporation offered another system consisting of a polybutadiene resin with chlorinated aromatic amine cure but discontinued production because of environmental toxicity.¹ About the time the Hysol product was removed from the market Conap Incorporated offered their Conathane EN-4 using a similar resin with a polyol curing agent.

ACTIVITY

Description of Conathane EN-4

Conathane EN-4, manufactured by Conap Incorporated (Table 1), is a hydroxylated polybutadiene/toluene diisocyanate prepolymer cured with a mixture of polyols containing a phenyl mercuric oleate catalyst.

The catalyst acts as a steering agent to limit the urea and biuret linkage and highly favors the urethane linked hydrocarbon resulting in greater stability than is obtainable with a polyether prepolymer cured with a chemically hindered aromatic diamine (du Pont's Adiprene L-100 and MOCA).²

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¹Letter, A. J. Quant, Sandia Corporation, "Improved Castable Urethane Elastomers," April 4, 1972.

²U. S. Patent 3,419,509, J. T. Willett, Wyandotte Chemical Corporation, December 31, 1968, and U. S. Patent 3,583,945, J. Robins, Minnesota Mining and Manufacturing Company, June, 1971.

Cautions and Safety Measures

The mercuric steering agent is volatile above 205°F (96°C) even in the cured state. Cures for this compound are limited to temperatures of 200°F (93°C) or lower. Any excess hardener (Part B) shall be combined thoroughly with the required quantity of resin (Part A) prior to disposal in the Part B container. Personnel working with the resin system prior to completion of cure shall wear protective gloves thereby avoiding contact with the resins in the uncured state.

These cure temperatures are well below the melting temperature of solder therefore soldering through an EN-4 coating should be prohibited because of the generation of mercury vapors.

Additional problems related to the stress transmitted to solder joints are detailed in another report. Unless special precautions are taken, EN-4 will crack solder joints experiencing three to five thermal cycles. Techniques are presented in the above report for the satisfactory use of EN-4.

Resin and Hardener Processing Prior to Mixing

The resin component (part A) tends to crystallize during storage at and below room temperature. There is a free isocyanate in the resin which must be remelted and reconstituted within the mass inside the resin container. Heating the container to 150 ±10°F (66 ±5°C), then mixing the contents thoroughly are recommended before opening the sealed container. Since the containers are square metal cans with small screw caps covering a pressed metal seal, the contents cannot be seen to determine if the resin has crystallized. The free isocyanate will separate out and freeze in a layer on top of the remaining resin. This isocyanate is hazardous and extremely reactive with moisture in the air. Therefore all containers should be processed by heating and tumbling prior to breaking the container seal.

The hardener component (part B) contains a desiccant to absorb moisture. During storage this desiccant settles in the container and must be remixed into the curing agents. The tin liner in the hardener container can be attacked by the steering agent which corrodes the container and precipitates free mercury into the desiccant. Both of these problems will be solved when the manufacturer packages the hardener in glass containers. This way the operators can see when the desiccant is blended into the hardener and no metal corrosion can take place. One problem may still exist; however, this occurs only when the material is being used in thin, less than 0.010 inch (0.25 mm), coatings. The desiccant tends to agglomerate when it settles and may not redisperse during mixing.

Table 1. Properties of Conathane EN-4 Resin (Vendor Data)

Part A (Resin Component)	
Appearance, white to amber opaque liquid	Visual
Viscosity at 25°C, centipoise 7500 $\pm$ 2000 (7.5 $\pm$ 2 Pa·s)	Brookfield PVT
Isocyanate Content, (percent) 8.9 to 9.1	Dibutylamine titration
Part B (Curing Agent)	
Appearance, opaque amber liquid	Visual
Equivalent weight, 86	Calculation
Viscosity at 25°C, centipoise 750 $\pm$ 150 (0.75 $\pm$ 0.15 Pa·s)	Brookfield RVT
Mix Viscosity, Centipoise (Pa·s) After Mixing at Ratio 100:17.5 pbw	
Initial	5500 (5.5)
After 10 minutes	4750 (4.75)
After 20 minutes	6750 (6.75)
After 30 minutes	36500 (36.5)
After 35 minutes	93000 (93.0)

Mixing Procedures

Procedures for processing Adiprene L-100/MOCA are satisfactory for EN-4 material. To eliminate as much contamination by foreign material as possible, clean separate cup holders and mixing blades are used. This also eliminates cross-contamination with other products.

Definition of Pot Life and Exotherm

Pot life is the usable time after adding the hardener solution to the resin component until the resin mixture will no longer flow satisfactorily. Many resins such as du Pont's Adiprene L-100/MOCA start out with a viscosity less than 1000 centipoise ($1.0 \text{ Pa}\cdot\text{s}$); EN-4 resin materials start with viscosities three to five times greater. The normal method of changing the viscosity is by heating the resin component and the hardener, however, this may limit the pot life too much. The viscosity/temperature curves in Figure 1 show the changes which can occur. Although the initial viscosity is lower for the warm resins during the first 8 minutes of the cure, the material would not run between the circuit board and components of a test assembly. Increasing the resin component temperature to 90°F (32°C) can shorten the pot life from approximately 20 minutes to 15 minutes. By accepting a 10-minute pot life, the viscosity could be lowered from 4000 to 2500 centipoise (4 to $2.5 \text{ Pa}\cdot\text{s}$). Preheating the assembly to be encapsulated to 160°F (71°C) prior to encapsulation is recommended.

The exotherm should normally peak out at 160°F (71°C) which is the same as the recommended cure temperature of 160°F for 24 hours. These results were obtained using 300 gram batches of resin; exotherms obtained in production units would not be expected to be as high. One technique found useful on production units was to encapsulate the components at preheat temperature taking advantage of the short time lowering of viscosity before the heat of the component has dissipated. This practice is effective for components that are close to the circuit boards.

Modification of Material

Normal mixing procedures produced a 2000 volt per mil (0.025 mm thickness) electrical standoff on test panels. However, when the particulate and desiccant material are removed by filtering or by separation in a centrifuge plus cure in a clean atmosphere, over 4000 volts electrical standoff can be obtained with the same thickness. Along with these problems inadequate or improper cleaning of components is also a problem. Investigations of these problems are continuing.

Assembly Cleaning Methods

Most cleaning methods are acceptable if they do not add contaminants to the component surface. Vapor degreasing with trichloroethylene was the most consistently effective method. Compression molding compounds having inherent mold releases trapped into the as-molded surfaces should be vapor blasted to remove the external glaze coating containing the major portion of these release agents. This action also increases the surface area and allows the EN-4 to key into any rough exposed surface.

Figure 1. Viscosity/Temperature Versus Time Curves

Table 2. Comparison of Properties for Different Cure Schedules for EN-4

Property	Cure Schedule		
	24 Hours at 160°F (71°C)	16 Hours at 180°F (82°C)	10 Hours at 200°F (93°C)
Tensile			
Ultimate in psi (MPa)	1720 (11.86)	1830 (12.62)	1580 (10.89)
Modulus at 100 percent in psi (MPa)	1030 (7.10)	886 (6.11)	918 (6.33)
Modulus at 200 percent in psi (MPa)	1360 (9.38)	1200 (8.27)	1220 (8.41)
Percent elongation at break	270	330	380
Tear Strength in pli (kN/m)	218 (38.2)	214 (37.5)	253 (44.3)
Hardness (Shore A)	91	89	89
Specific Gravity	1.00	1.01	1.00

Filling Procedures

To make sure no unmixed material can possibly be used to fill a product the mix is transferred to a second dried container. The unmixed material adhering to the surfaces of the mixing cup is discarded. One production filling method uses atmospheric pressure to transfer the material to the unit which is under a partial pressure of 25 to 55 mm Hg (3.3 to 7.3 kPa). If closed molds were used, the EN-4 could be introduced with a Simco gun using additional pressure; however, careful consideration of the material flow pattern would be required because filling too rapidly could entrap gasses or leave voids within closed cavities. All components within the encapsulation should withstand the specified partial vacuum without outgassing or leakage. The material is usually a clear liquid prior to gellation permitting verification of workmanship prior to curing the unit. Bubbles can be worked out of the surface of the resin after the pressure is increased to atmospheric conditions. EN-4 tends to wet many materials which were not wetted by the Adiprene L-100/MOCA system. This wetting phenomena may cause EN-4 to wick inside cable bundles and to crawl over dams where wires are located too close causing the EN-4 to bridge. The increased adhesion of EN-4 to most materials makes it difficult to remove if wicking or spillage occurs.

Curing Procedures

Three cures were suggested by the vendor as equivalent cures, resulting in the physical test data described in Table 2. A separate oven is used to cure the EN-4 production assemblies after the oven has been cleaned to remove rust, scale, and spills from previous operations. Cure cycles are limited to those below 200°F (93°C) because traces of mercury vapor can be detected when the cured or uncured mixture is heated above 203°F (95°C). The two allowable cure cycles, 160°F (71°C) for 24 hours and 180°F (82°C) for 16 hours, do not fully cure this material. It requires 10 days at 160°F to achieve fully cured EN-4; however, data available indicate properties are within 70 percent of their ultimate values after 24 hours at 160°F. Foam temperature post cure continues to improve those physical values over several months. It is not known at this time if room temperature aging will continue to increase the values to approach those of a long time (10 days) oven cure.

Repair of EN-4 Encapsulation

Repair of EN-4 encapsulations damaged when malfunctioning components are replaced is possible when normal cleaning procedures are used. Repair should begin as soon after the original cure cycle as practical, thereby taking advantage of the lower shrinkage of the fresh material and any unreacted sites that would promote adhesion. No primers are required for repair work. The EN-4 system (being hydrolytically stable) does not transmit or absorb moisture while aging. High voltage ceramic capacitors have been successfully repaired by overcoating the breakdown area with approximately 10 mil (0.254 mm) of EN-4.

Comparison of Cure Temperature on Shrinkage

The cure shrinkage of EN-4 (Table 3) is less than a polyether based urethane using comparable cure temperatures. At room temperature EN-4 will not cure in a reasonable time; however, at 160°F (71°C) shrinkage is only half as much as the shrinkage of the du Pont polyether based urethane Adiprene L-100, according to Process Specification 9927076 and only one third the shrinkage of polyol cured Adiprene L-100 processed according to PS9927022. Shrinkage differences are not as noticeable at higher cure temperatures, but only two cure temperatures, 160°F (71°C) and 180°F (82°C), are being allowed for production use.

Thermal Shrinkage After Cure

Although the shrinkage of EN-4 is less than the polyether based urethanes, problems exist where short rigid leads are soldered to circuit boards and then encapsulated in the EN-4. Solder cracking has become evident after a

few -40°F (-40°C) thru 160°F (71°C) thermocycles. Although -40°F is above the second order transition temperature of EN-4, the coefficient of expansion in conjunction with EN-4's adhesion for most materials causes enough stress to cause solder joint cracking and possible failure.

Table 3. Comparison of Cure Shrinkage

Material	Cure In Hours (°F) (°C)	Percent Shrinkage at Ambient Temperature	
		24 hours	60 days
Adiprene L-100/MOCA	96 at Ambient	0	---
EN-4	24 at 160 (71°C)	0.36	0.48
Adiprene L-100/MOCA	4 at 160	0.68	0.72
Adiprene L-100/glycol	40 at 160	0.92	0.92
EN-4	16 at 180 (82°C)	0.76	0.88
EN-4	10 at 200 (93°C)	0.90	1.22
Adiprene L-100/MOCA	3 at 200	1.08	1.02
Adiprene L-100/glycol	16 at 200	1.26	1.36

Table 4 is a listing of results obtained from temperature cycling EN-4 from low to ambient and then to high temperature. The coefficients were calculated from the heating cycle from -65°F to room temperature and then from room temperature to +165°F (74°C).

To compare EN-4 with du Pont's Adiprene L-100/MOCA the data in Table 5 are presented.

This data shows that little change is caused by the different cure cycles when material is tested 3 weeks after completion of cure. Where the Adiprene L-100/MOCA system shows almost the same coefficient throughout the total range tested, the EN-4 specimens indicate a slightly larger coefficient

below room temperature. This would indicate greater stress on components and solder joints during cold cycling than during hot cycling. It may also indicate a second order transition change starting above the -65°F (-54°C) temperature. Since these two materials have nearly the same value below room temperature, there would be little difference in applied stress if the strength of the two were equal.

Table 4. Thermal Coefficient of Expansion for EN-4

Cure	Average Coefficient from -65°F (-54°C) to Room Temperature	Average Coefficient from RT to 165°F (74°C)
24 Hours at 160°F (71°C)	96.6×10^{-6} in/in/°F (113.8 $\mu\text{m}/\text{m}/^\circ\text{C}$)	113×10^{-6} in/in/°F 203 $\mu\text{m}/\text{m}/^\circ\text{C}$
16 Hours at 180°F (82°C)	97.6×10^{-6} in/in/°F (175.7 $\mu\text{m}/\text{m}/^\circ\text{C}$)	no data
10 Hours at 200°F (93°C)	97×10^{-6} in/in/°F (175 $\mu\text{m}/\text{m}/^\circ\text{C}$)	no data

Table 5. Thermal Coefficient of Expansion for Adiprene L-100 MOCA

Cure	Average Coefficient from -65°F (-54°C) to Room Temperature	Average Coefficient from RT to 165°F (74°C)
4 Hours at 160°F (71°C)	110×10^{-6} in/in/°F 198 $\mu\text{m}/\text{m}/^\circ\text{C}$	106×10^{-6} in/in/°F 191 $\mu\text{m}/\text{m}/^\circ\text{C}$
3 Hours at 200°F (93°C)	109×10^{-6} in/in/°F 196 $\mu\text{m}/\text{m}/^\circ\text{C}$	109×10^{-6} in/in/°F 196 $\mu\text{m}/\text{m}/^\circ\text{C}$

Equivalence of Cure

The ability of polyether urethanes to withstand heated environments is dependent upon the cure temperature and crosslinking mechanisms. Elevated temperature cures were compared to determine if a particular cure would exhibit a lower expansion coefficient or if any different coefficient existed between cures. This information can also be used to match the coefficients

of a resin system to an assembly as well as to determine if abrupt changes occur within an anticipated operating temperature range.

One method of determining the similarity between material cured under different conditions is to measure the expansion caused by temperature change in a small sample. When the sample dimensions are the same, direct comparisons can be made of linear swell versus temperature of exposure. If structural differences occur one would expect to see the effect in the expansion each different structure would exhibit when treated in the same environment. Care must be exercised to ensure that each specimen is tested similarly and that the temperature changes are executed in identical time intervals.

Equipment for measuring this phenomena is manufactured by du Pont as a Thermo-Mechanical Analyzer (TMA). During this test, samples of Conathane EN-4 cured at three different cure temperatures were examined: 24 hour cure at 160°F (71°C), 16 hour cure at 180°F (82°C), and 10 hour cure at 200°F (93°C). These cures provided equivalent material according to manufacturers tests.

Samples were taken from the material set used for comparative physical data reported in Table 2. These curves show two temperatures, -58°F (-50°C) and 158°F (70°C) where changes in the material occur. Both are within the extremes of the normal thermal cycling tests shown in Figure 2.

An analysis of the relative change in thickness shows the two lower cure temperatures, 160°F and 180°F cause similar changes inside the range from -58°F through 140°F (Table 2). Tests for shrinkage from mold dimensions (Table 3) indicate a lower percent shrinkage from lower temperature cures.

Physical and Electrical Test Data and Effects of Aging

The physical properties of EN-4 after a 24-hour, 160°F cure are given in Table 6. The values for tensile modulus and dielectric strength indicate considerable change takes place during a 75-day aging period. Sandia Albuquerque, using torsional modulus, has noticed similar increases during a 3 to 4 week aging period.

Adhesion of EN-4 for Laminate Materials and Acrylic

Adhesion of EN-4 to the common materials found in electronic construction shows marked improvement over values obtained with Adiprene L-100/MOCA systems to the same materials. Hydrolytic stability and better initial adhesion allows EN-4 to be used without primers.

Figure 2. Dimension Change Versus Temperature

Table 6. Properties of EN-4 After 24 Hour Cure at 160°F (71°C)

Property	Tested Within 7 Days of Molding	Tested After 75 Days of Ambient Aging
Tensile in psi (MPa)		
Ultimate	2130 (14.68)	2150 (14.81)
Modulus at 100 percent	696 (4.80)	1000 (6.89)
Modulus at 200 percent	900 (6.20)	1320 (9.10)
Hardness (Shore A)	87	89
Specific Gravity	1.00	1.01
Percent Elongation	1.75	3.25
Tear in pli* (kg/m)	269 (3.09)	280 (3.22)
Dielectric Strength		
Volt per mil 0.075 inch specimen	573	1400
(kV per mm) 1.905 mm specimen	(23.9)	(56.0)
Volume Resistivity (Ω /cm)(T Ω /m)	6.34×10^{15} (63.4)	10.5×10^{15} (105)
Surface Resistivity (Ω) (T Ω)	115×10^{15} (115000)	100×10^{15} (100000)
*Pounds per linear inch		

Specimens were prepared for shear testing by bonding 1-inch (25 mm) wide strips together with a 0.5-inch (13 mm) lap and curing them in a press for 24 hours at 160°F (71°C). The strips were pulled apart in a tensile tester at a travel rate of 0.005 inch (1.3 mm) per minute (Table 7). Cured EN-4 samples were added to determine if the material could be repaired satisfactorily. The values obtained are several magnitudes greater than those obtained with Adiprene L-100/MOCA immediately after cure and after 30 days aging at room temperature. In a 50 percent relative humidity atmosphere, the Adiprene system values drop to near zero because of moisture in the bond area.

Table 7. Adhesive Shear Values of EN-4 on Various Substrates

Material	Shear in psi (MPa)
Epoxy-glass laminate	918 (6.376)
Tin-lead plating	1025 (7.066)
Gold plating	949 (6.542)
Nickel plating	839 (5.784)
Nickel Foil	935 (6.445)
Cured EN-4	1051 (7.245)
Acrylic resin	655 (4.515)

A test was also made using 0.25-inch (6.5 mm) diameter acrylic rod. One end of the rod was potted in EN-4 to a depth of 0.375 inch (9.52 mm) and an effort was made to pull the rod free. The test was unsuccessful because the rod broke at a tensile pull of 235 pounds (1045 N) for one specimen and 240 pounds for another. These values indicated a shear bond greater than 800 psi (5.51 MPa). The discrepancy between this value and the one obtained from the lap shear test of 655 psi (4.51 MPa) might be because the lap shear specimens were 0.125-inch (3.175 mm) thick. The thickness displaced the bonded joint from the plane of direct tensile pull so that pure shear stress was impossible.

Adhesion of EN-4 for Wire Insulation

Three types of wire insulation were tested to determine the degree of adhesive bond between the insulation and Conathane EN-4 encapsulating resin. Three types were tested: clear and black polyolefin heat shrinkable sleeving,

and Kynar (polyvinylidene fluoride). Insulated wire was encapsulated into a matrix of EN-4 to a depth of 1 inch (25 mm) and the force required to pull the insulation free was determined. Three sets of six specimens each were prepared with the black polyolefin and Kynar. One set was used as a control. The second set was temperature cycled three times between 200°F (93°C) and -65°F (-53°C). The third set was subjected to ten 24 hour cycles at 95 percent RH with the temperature ranging between 77°F (25°C) and 155°F (69°C). Only one set of specimens was prepared with the clear polyolefin sleeving (Table 8).

A second test was made to establish the bond strength between Conathane EN-4 and wire insulation (Table 9). This time the insulation was a composite, consisting of polyolefin adjacent to the wire with an outer jacket of clear Kynar (Material Specification 8224005). Two sets of six specimens each were prepared. One had the Kynar jacket on and the other had the jacket stripped off. The sets were subdivided so that three of the specimens were conditioned by cycling between 200°F (93°C) and -65°F (-53°C) three times. The specimens were held at temperature for 4 hours with a maximum transfer time of 5 minutes. They were allowed to stabilize at room temperature for a minimum of 24 hours prior to testing.

Although the specific values differed, this second test confirmed data in Table 9 in that there was better adhesion to the Kynar than to the polyolefin, and temperature cycling resulted in improved bond strengths.

Bulk Modulus

Most components in an electrical assembly are stressed by the packaging material. If an intermediate material injected between components could absorb this force, or reduction in volume, then the interactions of encapsulated components would be mitigated. Ideally the intermediate material chosen would not change physical, electrical, or mechanical character during the temperature environment of the assembly or change structurally as a result of intermolecular forces.

One intermediate material used is a sponge. The compression of the encapsulant is absorbed in the compression of the gasses within the sponge transmitting little effective energy to the component. The presence of a gas void within a thin conformal coating, however, cannot be tolerated when high voltages are involved and many sponge materials are not stable throughout the environmental requirements of manufacture and intended usage.

Table 8. Degree of Adhesive Bond for Three Types of Insulation

Properties	Clear Polyolefin	Black Polyolefin	Kynar
Diameter	0.044 in (1.12 mm)	0.048 in (1.22 mm)	0.056 in (1.42 mm)
Surface bonded	0.138 in ² (89.9 mm ²)	0.151 in ² (97.4 mm ²)	0.176 in ² (113.5 mm ²)
Average pullout strength control	22.1 lb (98.2 N)	16.1 lb (71.6 N)	34.0 lb (151.2 N)
After thermal cycling		9.1 lb (40.5 N)	39.2 lb (174.4 N)
After humidity cycling		15.6 lb (69.4 N)	36.2 lb (161.0 N)
Specific pullout strength	160 psi (1103 kPa)	107 psi (737.7 kPa)	193 psi (1330 kPa)
After thermal cycling		60.3 psi (415.1 kPa)	223 psi (1537 kPa)
After humidity cycling		103 psi (710.2 kPa)	206 psi (1391 kPa)

High molecular weight polymers should have some compressibility as a solid. If techniques were developed to compare the differences between polymers plus the differences within a polymer under different environmental conditioning improved material selections could be made.

The compressibility of a solid is measured by using the bulk modulus of the material. Since most polymeric materials will move when a force is applied (Table 11), test equipment must be designed which will contain the material and contain compressibility factors much greater than those of the materials being tested. A free floating cylinder of heavy wall construction was used so a close fitting piston from each end would compress the sample. The pistons must prevent extrusion between the pistons and the cylinder wall and the sample must also be constructed to close tolerances. If the loading is slow, little heat is generated within the sample and this is mitigated by absorption to the heavy cylinder walls.

Table 9. Comparison of Bond Strength of EN-4 and a Composite Wire Insulation

Adhesive Bond	Kynar Intact Control	Kynar Removed Control	Kynar Intact Temperature Cycled	Kynar Removed Temperature Cycles
Sample 1	31 lb (137.9 N)	19 lb (84.5 N)	31 lb (137.9 N)	21 lb (93.4 N)
Sample 2	28 lb (124.5 N)	27 lb (120.1 N)	31 lb (137.9 N)	27 lb (12.01 N)
Sample 3	27 lb (120.1 N)	19 lb (84.5 N)	31 lb (137.9 N)	20 lb (89.0 N)
Average	28.7 lb (127.7 N)	21.7 lb (96.5 N)	31.0 lb (137.9 N)	22.7 lb (101.0 N)
Diameter	0.068 in. (1.72 mm)	0.059 in. (1.51 mm)	0.068 in. (1.73 mm)	0.059 in. (1.51 mm)
Area Bonded	0.213 in. ² (137.4 mm ²)	0.185 in. ² (119.3 mm ²)	0.213 in. ² (137.4 mm ²)	0.185 in. ² (119.3 mm ²)
Pull Strength	135 psi (930.7 kPa)	117 psi (806.7 kPa)	145 psi (997.7 kPa)	123 psi (848.0 kPa)

Table 10. Bulk Modulus of EN-4 Versus Length of Specimens

Specimen and Cure	Length (Inches) (mm)	Bulk Modulus (psi) (MPa)
24 Hours at 160°F (71°C)	0.5 (13.7)	463000 (3183)
	1.0 (25.4)	405000 (2784)
	1.5 (38.1)	376000 (2585)
	2.0 (50.8)	387000 (2660)
16 Hours at 180°F (82°C)	0.5 (13.7)	448000 (3080)
	1.0 (25.4)	330000 (2268)
	1.5 (38.1)	383000 (2626)
	2.0 (50.8)	376000 (2585)

Two cures of EN-4 were used to make a choice of specimen size. Specimens were constructed in rod molds having no seams and were machined into various lengths. Specimens were aged at room temperature 7 weeks after cure with the previous results (Table 10).

Table 11 compares bulk modulus of EN-4 with Adiprene L-100/MOCA cured at the same temperatures.

Table 11. Bulk Modulus of EN-4 and Adiprene L-100 Versus Cure Temperature

Cure Temperature	EN-4 (psi) (MPa)	L-100 (psi) (MPa)
160°F (71°C)	374110 (2572)	408640 (2809)
180°F (82°C)	375540 (2582)	No specimen
200°F (93°C)	389486 (2677)	371533 (2554)

Compressive Modulus

Compressive modulus, the stress required to produce a unit strain which is a change in length, and Poisson's ratio, the ratio of the transverse expansion per unit length when subjected to a compressive stress allow further examination to determine differences between materials'. The compressive modulus and Poisson's ratio were determined for the three cures of EN-4 as well as for three cures of Adiprene L-100 with the results shown in Table 12.

The data in Table 12 is the average of six individual readings. Checks were made of the room temperature aging time experienced by each specimen to determine if aging would have any effect. It is known properties change for a short time after the designated cure is completed, up to 30 days for EN-4 and 7 days for Adiprene L-100. All specimens were aged from 60 to 130 days prior to testing and no trend could be detected.

The compressive modulus of the L-100 system is double that of EN-4 except for the 200°F (93°C) cure. Therefore EN-4 would not be expected to exert or transfer as much stress under a given strain as the L-100 material which means Conathane EN-4 behaves more like a fluid at room temperature than Adiprene L-100.

Shear Modulus, Loss Modulus, Loss Tangent

A technique to study the dynamic characteristics of materials used in coating and encapsulation is being incorporated. The technique allows insight into those properties which offer protection to components. Techniques for measuring the energy stored and the energy absorbed and the resultant energy loss in metals are well known; however, little information is available on plastics. Also, little is known about how these materials change as a result of aging or when tested under different conditions. The American Society for Testing and Materials has published Dynamic Mechanical Properties of Plastics by Means of a Torsional Pendulum (D-2236-70) describing the equipment and formulas which can be used. Normally this technique is used to determine second order transitions within a plastic by measuring these moduli over critical temperature ranges. By comparing the value of shear modulus, loss modulus, and loss tangent the changes in second order transition can be determined as well as changes resulting from formulation, processing, environmental conditions, and aging. Thus far only formulation and processing have been started.

To obtain this data it was necessary to design and build a torsional pendulum according to the standard oscillating disc design. The pendulum consists of a brass disc for the inertial mass, Jacob chucks to grip rod specimens, a rotary variable differential transducer (RVDT), and a recorder for angle

Table 12. Compressive Modulus and Poisson's Ratio of EN-4 and Adiprene L-100 Tested at Room Temperature

Cure	Compressive Modulus psi (MPa)	Poisson's Ratio in Compression
<u>Conathane EN-4</u>		
24 hours at 160°F (71°C)	5595 (3857)	0.439 0.439
16 hours at 180°F (82°C)	4950 (3413)	0.478
10 hours at 200°F (93°C)	4902 (3379)	0.467
<u>Adiprene L-100/ MOCA ratio 100:11</u>		
RT cure (7 days)	10486 (7229)	0.425
4 hours at 160°F (71°C)	9147 (6306)	0.470
3 hours at 200°F (93°C)	7530 (5191)	0.413

versus time indications. The equipment will accommodate specimens from 0.25 to 0.50 inch in diameter and up to 15 inches (381 mm) long (similar to Arrangement B of ASTM-D-2236-70).

During this test a 0.50-inch-diameter (12.7 mm) specimen was gripped in the Jacob chucks and the length of the specimen between the chucks was measured. The brass disc was rotated approximately 45 degrees and released. The disc oscilated and turned the RVDT directly. A sine type curve was generated on the recorder which provided all of the information necessary to calculate the desired properties.

Three properties were calculated shear modulus, loss modulus, and loss tangent.

Equations for calculating these properties are as follows:

$$\text{Shear Modulus (G')} = \frac{2\text{Im}\omega 2h}{R^4} \left[1 + \frac{2}{4\pi^2} \right]$$

$$\text{Loss Modulus (G'')} = \frac{\Delta G'}{\pi}, \text{ and}$$

$$\text{Loss Tangent (tan)} = \frac{G''}{G'},$$

where

ω = the material frequency of the specimen in cycles/second, and

$$\Delta = \log \text{ decrement} = \ln (A_1/A_2)$$

The logarithmic decrement of damping is defined as the material logarithmic of the ratio of the amplitudes (A) of two successive oscillations.

where

Im = inertial mass of the system (sum of grip, shaft, disc, transducer),

h = length of specimen between grips, and

R = radius of specimen.

Im, h, and R are constants measured before the test. ω and Δ are calculated from the generated curve.

Two materials, EN-4 and Adiprene L-100/MOCA 100:11, were submitted for testing at room temperature after stabilization and the dynamic test values are shown in Table 13.

The dynamic shear modulus was higher for Adiprene L-100 than it was for Conathane EN-4 when both cured at 160°F (71°C). However, when the Adiprene L-100 was cured at either room temperature or at 200°F (93°C) the shear modulus was equal to EN-4 cured at 160°F (71°C) (Figure 3).

The dynamic shear modulus is a measure of the elasticity or stored energy in the material.

Figure 3. Shear Modulus Versus Cure Temperature

The loss tangent of EN-4 was much higher than Adiprene L-100 at any cure (Figure 4). This indicates that EN-4 is a better energy (shock) absorber than Adiprene L-100. The loss modulus is another measure of the energy lost to the material. Since EN-4 has a lower modulus one would expect it to have a higher energy loss as indicated (Figure 5). This test shows EN-4 cured at 180°F (82°C) contains the maximum shock absorption.

Table 13. Dynamic Mechanical Properties of EN-4 and Adiprene L-100

Material	Cure	Shear Modulus	Loss Modulus	Loss Tangent
Conathane EN-4	24 hours at 160°F (71°C)	2990 psi (20.61 MPa)	581 psi (4.00 MPa)	0.194
	16 hours at 180°F (82°C)	2880 psi (19.23 MPa)	600 psi (4.14 MPa)	0.209
	10 hours at 200°F (93°C)	2790 psi (19.23 MPa)	592 psi (4.08 MPa)	0.213
Adiprene L-100/ MOCA 100:11	Room Temperature Cure	2910 psi (20.06 MPa)	153 psi (1.05 MPa)	0.053
	4 hours at 160°F (71°C)	3310 psi (22.82 MPa)	114 psi (0.786 MPa)	0.034
	3 hours at 200°F (93°C)	2960 psi (20.40 MPa)	90 psi (0.62 MPa)	0.030
All tests were conducted at room temperature.				

Comparison of EN-4 and Adiprene L-100

A comparison was made of the properties of EN-4 and L-100/MOCA. The comparison included both raw and cured material. The results are shown in Table 14.

ACCOMPLISHMENTS

Conathane EN-4, a polybutadiene urethane prepolymer cured with a polyol mixture, was compared with a Adiprene L-100/MOCA system. The material can be processed in existing equipment used for Adiprene; however,

Figure 4. Loss Tangent Versus Cure Temperature

Figure 5. Loss Modulus Versus Cure Temperature

processing should be at room temperature at the start of mixing. Three equivalent cures using temperatures of 160°, 180°, and 200°F were used to produce similar properties. The 200°F cure was found to evolve a volatile mercury compound and the two lower temperature cures are recommended for production use. Cure shrinkage of EN-4 at 160°F is half the shrinkage found in Adiprene L-100 and is directly proportional to the cure temperature. Repair is feasible by recasting if previously cured surfaces are clean.

Electrical properties can be improved by filtering the desiccant material from the resins prior to mixing the components together. Room temperature aging improves the electrical properties.

Shear modulus for EN-4 was found to be comparable with that of Adiprene L-100/MOCA systems however loss modulus for EN-4 exhibited much higher values showing it to be desirable as a damping media over Adiprene L-100/MOCA systems. The adhesive of EN-4 for materials found in electronic assemblies shows marked improvement over the adhesion of Adiprene L-100/MOCA systems.

Table 14. Comparison of Properties of EN-4 and Adiprene L-100 in Cured State

Conathane EN-4	Adiprene L-100/MOCA
Handle at room temperature	MOCA melted at 230°F (210°C)
Viscosity after 20 minutes 8000 centipoise (8 Pa·s)	Viscosity after 20 minutes 50000 centipoise (50 Pa·s)
Free isocyanate	No free isocyanate
Strong odor of polybutadiene	No odor
300 gram batch exotherm to 150°F (65°C)	No exotherm
Viscosity 5 minutes after mix is 4000 centipoise at 95°F (35°C)	Viscosity 5 minutes after mix is 1000 centipoise at 160°F (71°C)
Available cure cycles are 24 hours at 160°F (71°C) and 16 hours at 180°F (82°C)	Available cure cycles are 48 hours at ambient temperature, 4 hours at 160°F or 3 hours at 200°F (93°C) (71°C)
Toxic curing agent	Classified as a carcinogen by OSHA
Hardness: Shore A-87	Hardness: Shore A-90
Tensile strength, 2030 psi (14 MPa)	Tensile strength, 4500 psi (31 MPa)
100 percent modulus is 1000 psi (6.9 MPa)	100 percent modulus is 1100 psi (7.6 MPa)
200 percent modulus is 1320 psi (9.1 MPa)	200 percent modulus is 2100 psi (14.5 MPa)
300 percent modulus (none)	300 percent modulus is 3600 psi (24.8 MPa)
Ultimate elongation is 275 percent	Ultimate elongation is 450 percent

Table 14 Continued. Comparison of Properties of EN-4 and Adiprene L-100 in Cured State

Conathane EN-4	Adiprene L-100/MOCA
Compression set, 55 percent after 24 hours at 125°F (52°C) and 10.0 percent deflection	Compression set, 27 percent after 22 hours at 158°F (70°C) and 50 percent deflection
Tear strength, die C, pli 269 (3.09 kglm)	Tear strength, die C, pli 400 (4.6 kglm)
Dielectric Strength, 0.075-inch thick slab is 573 volts/mil (22300 volts/mm); after 60 days aging at 40 percent RH, ambient temperature, 1400 volts/mil (54600 volts/mm)	Dielectric Strength, 0.075-inch is 600 volts/mil (23400 volts/mm); after 60 days aging at 40 percent RH, ambient temperature, 550 volts/mil (21400 volts/mm)
Coefficient of thermal expansion from -65°F (-53°C) to ambient is 97×10^{-6} in/in/°F (174 $\mu\text{m}/\text{m}/^\circ\text{C}$)	Coefficient of thermal expansion from -65°F to ambient is 110×10^{-6} in/in/°F (198 $\mu\text{m}/\text{m}/^\circ\text{C}$)
Dielectric strength doubles after 75 days at ambient temperature	No change in dielectric strength after 75 days
Leakage current at 180°F (82°C) is less than 0.01 amperes at 500 volts	Leakage current at 180°F (82°C) is 1.35 amperes at 500 volts
Hydrolytic stability test results in 30 percent reduction of modulus after 60 days at 250°F (121°C) and 15 psi steam (103 kPa)	Hydrolytic stability-extensive reversion after one day at 250°F (121°C) and 15 psi steam (103 kPa)
Good adhesion to metals and specific plastics	Poor adhesion to metals and plastics requiring primers
Suitable mold release TFE (duPont)	Suitable mold release, TFE, FEP (duPont) and DC23, DC167 (Dow Chemical)
Cure shrinkage at 160°F (71°C) is approximately 0.4 percent	Cure shrinkage at 160°F (71°C) is approximately 0.7 percent