LONG-TERM STRENGTH CHARACTERISTICS OF CONDUCTIVE EPOXIES

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ABSTRACT

Reliability requirements imposed on aerospace hardware together with increasing use of conductive epoxies in electronic components have resulted in the need for a better understanding of the long-term strength characteristics of conductive epoxies. Thus the objectives of this study are: 1) to determine the viscoelastic behavior of several types of conductive epoxies and 2) to provide a method of predicting operational (load-bearing) life time of these epoxy systems. Investigative results reveal creep rates to be greater at or above the glass transition temperature (T_g) of the material, and at stress levels exceeding 0.7 to $0.8\tau_F$ (fracture strength). Prediction of load-bearing life time is possible by plotting creep data, obtained at several temperatures, in an Arrhenius fashion (log time versus the inverse of absolute temperature). This information can, in turn, be used as one variable in predicting reliability of components utilizing conductive epoxies, assuming stress and environmental conditions are known.

INTRODUCTION

New uses and applications of conductive epoxies in the electronics industry have resulted in the need for a better understanding of the long-term strength characteristics of these materials. Conductive epoxies serve two equally important functions: they must possess good electrical properties while serving as structural adhesives. In the past decade, the area of conductivity has received considerable attention, while long-term strength characteristics have received limited emphasis. Consequently, the objectives of this study are: 1) to determine creep behavior of several types of conductive epoxies (one and two component) and 2) to provide a method of predicting operational (load-bearing) life time of these epoxy systems.

In this investigation, four conductive epoxy systems have been chosen for evaluation on the basis of past usage in the field of microelectronics. The adhesives evaluated include: 1) Bondmaster 640, 2) Dupont 5504, 3) Epo Tec H21D and 4) Epo Tec H20E. These systems have been characterized according to chemical structure, filler (amount, size and shape) and porosity.

Strength and creep measurements have been performed on lap shear specimens having a bond thickness of 0.010 to 0.012 inch. Both strength and creep rates were determined as a function of temperature. Creep rates of the Bondmaster system were determined over a temperature range of 60 to 100°C, and used in an Arrhenius plot (log time to fracture vs. 1/T°K). The Arrhenius plot was in turn used for predicting operational life time as a function of temperature. Creep rates of the remaining three adhesives were determined at 100°C, and in some instances, test runs were aborted prior to specimen rupture, due to the time factor involved. This resulted in insufficient data for construction of Arrhenius plots for these systems. However, data obtained from the Bondmaster Arrhenius plot together with information from other investigations [1, 2, 3] were used in approximating stresses required for causing unstable creep (rupture time less than 24 hours) to occur.

BACKGROUND

Mechanical and Electrical Characteristics

Particulate filled polymers have been in use as structural materials for several decades. As a consequence, many theoretical and experimental investigations concerning mechanical and thermal properties have been conducted and published [4, 5, 6]. Mechanical properties of filled resins have been observed to vary as a function of volume fraction filler, particle shape and size, particle agglomeration, dispersion, and interfacial adhesion. The strength of filled systems increases as a function of volume fraction filler when good adhesion between filler particles and polymer matrix exists. However, in the absence of adhesion between the two phases, the strength of the composite decreases as a function of volume fraction filler. A plot of relative strength vs. volume fraction filler for systems having both good and no adhesion is shown in Figure 1. These curves were obtained from theoretical equations proposed by Nielson [6]. Although theoretical equations of this type have been found to be valid and quite useful for some materials, experimental investigations have shown that excessive amounts of filler (>35 volume %) will usually result in a system having poor adhesion between the particles and matrix due to insufficient resin available for wetting the entire filler. Therefore, most filled systems will reach maximum strengths at volume fractions of 0.30 to 0.40 filler, depending on the viscosity of the uncured resin. However, for a nonconductive epoxy resin to become conductive, large amounts (>30 volume %) of conductive particles are required. As a consequence, highly filled conductive epoxies having low electrical resistivities will generally tend to have limited capabilities as structural adhesives. Therefore, specific epoxy applications should be considered, and compromises between strength and conductivity should be made, by adjustment of volume fraction of filler.

Creep

Creep is studied by subjecting a sample to a constant load and measuring its deformation as a function of time. In most polymeric materials there is a measurable recovery when the load is removed. This indicates that creep has both a viscous and an elastic component with the elastic component being recoverable. Polymeric chain entanglement and cross-linking contribute to the elastic component of creep. The mechanical properties and creep behavior of a polymer are very dependent upon temperature. At temperatures below the glass transition (T_g) the polymer is rigid (high modulus, low elongation) and limited creep will take place even after long periods of time. However, at temperatures above T_g the polymer softens and the rate of creep increases rapidly. Past studies conducted on filled epoxies have shown creep rates to be highly dependent on stress levels [3]. Unstable creep rates (rupture time less than 24 hours) have been observed at stress levels exceeding $0.7\tau_F$ where τ_F is the fracture stress. The fracture stress of polymeric materials however, decreases with increasing temperature to an extent which is governed by the T_g of the material. Thus, both strength and creep rate are T_g dependent.

Since creep rate is highly temperature-sensitive, it can be related to temperature by the same type of Arrhenius equation as viscosity and diffusion.

$$k = A_o \quad e^{-E/RT} \qquad (1)$$

where k can either be time to rupture or creep rate, A is a constant, E is the activation energy which is influenced by the creep mechanism, R is the gas constant and T is the absolute temperature A plot of logarithm k versus $^1/T$ will result in a straight line assuming the activation energy (E) is constant. However, the creep mechanisms operating above and below T_g are different, causing a change in activation energy. As a result, a change in slope will occur at T_g.

EXPERIMENTAL

Materials Characterization

The conductive epoxies investigated have been characterized with respect to chemical structure, filler and porosity. This characterization study was accomplished by the use of infrared spectroscopy, metallography and scanning electron microscopy.

The composition and cure schedule of the adhesive systems investigated are as follows:

1) The Bondmaster 640 is a one component solid powder melt adhesive which produces high strength bonds when unfilled. However, this powder has been used in the past by several device manufacturers as the epoxy constituant in a 3 part conductive adhesive system consisting of 85 weight percent silver (~42 v/o) and 15 weight percent Bondmaster with several parts cellosolve acetate added to develop consistency for use. The epoxy phase is a one part high molecular weight solid containing a dicyandiamide curing agent. The mixture which is made into a slurry paste by the addition of cellosolve acetate is cured at 210°C for three hours, evolving the cellosolve thinner during cure.

2) Dupont 5504 is a single component epoxy requiring low temperature storage, and containing approximately 78 weight percent silver (31 v/o). This adhesive which contains small amounts of solvent in the uncured state, was found to be cure sensitive, with respect to strength. The properties reported in this study are for specimens cured at 180°C for 16 hours. Specimens cured at higher temperatures were found to exhibit higher strength values.

3) Epo Tec H21D and H20E are both two component systems, containing approximately 78 weight percent silver (31 v/o) and no solvents or thinners. These adhesives have a lower cure temperature (100 to 80°C) than the one component systems. The major physical difference between H21D and H20E in the uncured state are reduced viscosity and increased pot life of the H20E.

Testing

Experimental testing consisted of determining thermal properties, shear strength and creep behavior of the subject epoxy systems. Thermal properties consisting of T_g, degradation temperature, and weight loss after 16 hours at 150°C were obtained by the use of a Dupont Model 900 thermal analyzing unit.

Shear strengths of the conductive epoxies were obtained at several temperatures by testing in an oven equipped Instron tensile testing machine. Lap shear specimens consisting of 1 x 4 inch etched aluminum strips and overlapped 0.5 inch had a controlled bond thickness of 0.010 to 0.012 inch The specimens were pulled at a rate of 0.2 inches per minute.

Creep experiments were conducted on lap shear specimens similar to those tested for shear strength. The creep testing apparatus consisted of an extensiometer, dial micrometer and oven. The oven temperature is controllable to ± 2°C, and the micrometer can be read to 1×10^{-5} inch. A deflection of 1×10^{-5} inch in a sample having a bond thickness of 0.010 inch is representative of a 0.10% shear strain. Although shear strains of 0.10% are large for certain metals, alloys and ceramics, a strain of this magnitude is quite small for polymeric materials. Thus, the creep apparatus used was adequate for determining long-term creep behavior of the adhesives studied.

DISCUSSION OF RESULTS

Materials Characterization

The conductive adhesives have been characterized according to chemical structure, filler (amount, particle size and particle shape) and porosity (amount and size), with results given in Table 1. Since the exact chemical structure of these epoxy systems is considered proprietary information by some of the adhesive manufacturers involved, only general classes of resin type and curing agents have been referred to. However, the importance of the chemical structure should not be overlooked, since it is a controlling factor in the T_g, viscosity and pot-life of the adhesives.

The amount of silver filler contained in the Bondmaster adhesive system is approximately 85% weight percent (~42 v/o) as compared to 78 weight percent (31 v/o) in the remaining adhesive systems. The size and shape of the particles in the four systems evaluated which are shown in Figure 2 are quite similar. The particles range from 1 to 10μ in size, and appear to be flat platelets.

The amount of porosity and average pore size in each conductive epoxy system has been determined. The average volume fraction porosity has been determined by a theoretical and bulk density relationship, while the size of the pores were determined from photomicrograph of cross-sectioned samples as shown in Figure 3. The size of pores range from 20μ to 400μ with the Bondmaster and Dupont systems having the greatest amounts of porosity as well as the larger size pores. This is due to the large amounts of solvent in these systems, which is evolved during cure, as compared to the solvent free Epo Tec systems.

Many investigations have been conducted on the effects of porosity on the mechanical properties of materials [7, 8, 9]. As a result, semi-emperical equations based on fracture mechanics [10] and on reduction of cross-sectional area [11] have been proposed, and found valid for many different classes (ceramics, alloys, composites) of materials. Two such equations are:

$$\tau_c \propto \frac{1}{\sqrt{C}} \qquad (2)$$

where τ_c is the shear strength, and C is half the crack length

$$\tau = \tau_o \, e^{-bP} \qquad (3)$$

where τ_o is the shear strength at zero porosity, b is a constant which is dependent on pore size and shape and P is the volume fraction porosity. Based on these two equations, the Bondmaster and Dupont adhesive systems should (and in fact do) have the lower strength values of the four systems evaluated.

Thermal Properties

Thermal properties consisting of T_g, degradation temperature and weight loss after 16 hours at 150°C have been determined, and are reported in Table 2. The T_gs range from 60 to 117°C with the highest strength material (Epo Tec H21D) also having the highest T_g value. The Bondmaster and Epo Tec H20E systems had similar T_g values of 75°C. The degradation temperatures range from 330° to 365°C. These relatively high degradation temperatures are typical of epoxy systems. The percent weight loss after 16 hours at the relatively low temperature of 150°C is 1.4, 0.66, 0.45, and 0.32 for Epo Tec H20E, Epo Tec H21D, Bondmaster and Dupont 5504 respectively.

Lap Shear Strength

Tensile shear strengths of the conductive epoxies were determined at the following temperatures: ambient, 50°, 100° and 150°C. This temperature range overlaps the materials T_g. The strength values obtained, which range from 300 to 1600 psi at ambient, and 100 to 1000 psi at 150°C, have been graphed (strength vs. temperature) and are shown in Figure 4.

The 300 psi room temperature strength of the Bondmaster system, which was the lowest value obtained, is relatively poor when compared to the other adhesive systems. This can be attributed to the following conditions: 1) high volume fraction filler (0.42) resulting in poor adhesion between phases and 2) high volume fraction porosity and large pores.

Creep

The viscoelastic behavior of the conductive adhesive systems were studied over a temperature range of 60° to 100°C and a stress level of 68 psi. This temperature range and low stress level approximates actual conditions experienced by conductive adhesives used in some electronic components.

Strain rate curves of the Bondmaster system, have been obtained at the following temperatures, 60, 70, 80, 90 and 100°C and are plotted in Figure 5. The time required for specimen rupture ranges from 30 seconds at 100°C to approximately 4 days at 70°C. The specimen tested at 60°C exhibited limited creep after 3.9×10^4 minutes (~26 days) at which time the test was discontinued. The specimens tested at 80°C and above exhibit signs of an unstable creep process (rupture occurs in less than 1 day). This is in fair agreement with past studies in which stresses exceeding 0.7 to $0.8\tau_F$ were observed to cause rapid specimen rupture. However, the 68 psi stress level is approximately 40% of the fracture strength at 80°C and about 70% of the fracture strength at 100°C. Thus, it appears that materials having inherent flaws such as poor interfacial adhesion and large amounts of porosity will exhibit unstable creep at much lower stress values.

Test temperature and time to rupture data obtained from the strain rate curves shown in Figure 5 have been fitted to an Arrhenius type equation, which are plotted in Figure 6 as log time to rupture versus 1/T, where T is the absolute temperature in degrees Kelvin. This Arrhenius plot can be used for predicting the operational life time of the adhesive, subjected to a constant stress level of 68 psi, as a function of temperature. For example, a Bondmaster sample requiring a life time of 5 years should not be subjected to a continuous temperature of greater than 55°C. However, a sample subjected to a temperature of 65°C would be expected to fail after 14 days. However, the reliability of this curve is questionable at temperatures below T_g since creep will occur by a different mechanism, producing a change in activation energy resulting in a change in slope.

The creep rates of the Dupont and Epo Tec adhesives were only investigated at 100°C due to time limitations. As a consequence, insufficient data was available for Arrhenius type plots. Strain-rate curves of the four adhesive systems obtained at 68 psi and 100°C are shown in Figure 7. The Bondmaster specimen ruptured after 30 seconds, and the Dupont specimen after approximately 4 days. The two Epo Tec systems however exhibited limited creep after 30 days.

The stresses required to cause unstable creep and rupture in the Dupont and Epo Tec adhesives at ambient, 100 and 150°C have been approximated by using $0.7\tau_F$, and are listed in Table 3. The τ_F values for this temperature were obtained from Figure 4. The stresses calculated for unstable creep to occur at ambient conditions range from ~1000 psi to ~450 psi for the Epo Tec H21D and Dupont system respectively. The value calculated for the Epo Tec H20E was ~750 psi, which is slightly lower than the H21D.

CONCLUSIONS

Viscoelastic behavior of conductive epoxies appears to be a direct function of 1) percent filler, 2) porosity and 3) glass transition temperature. Strain rates and creep process are highly dependent on stress levels. Stress levels of 0.4 to $0.7\tau_F$ have been observed to cause an unstable creep process in inherently weak (large amounts of porosity and poor interfacial adhesion) materials. In comparison, stress levels of 0.7 to $0.8\tau_F$ are required for unstable creep to occur in structurally sound materials.

Arrhenius type plots of log time to rupture versus inverse of absolute temperature appear to be a reliable method of predicting the operational life time of these materials under constant load. However, experimental strain rates should be obtained at temperatures below and above the T_g, since different creep mechanism will be active preventing a straight line extrapolation.

In summary, the two component solvent free systems contain less porosity, and have superior strength and creep resistance than the one component systems. However, these two component systems exhibit greater weight loss when exposed to 150°C fo 16 hours, an indication of outgassing which is als an important parameter to be considered when choosing adhesives for hybrid and component applications.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to Dr. D. Demeo and Mr. D. Smith for their assistance in determining the thermal properties and chemical structure of the adhesives evaluated.

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BIOGRAPHIES

Gilbert W. Brassell received his B. S. Degree in Chemistry from New Mexico Highlands University in 1969 and his M. S. Degree in Materials Science and Engineering from the University of New Mexico in 1972. While working on his Masters degree, Mr. Brassell was employed by Sandia Laboratories and participated in research projects in the areas of polymers, adhesives and composites. Upon completion of his Masters, Mr. Brassell accepted a position with IBM Research in the Organic Solids Department where he participated in studies on photoconduction properties of organic charge transfer complexes which involved ultra purification and crystal growth of these systems. Mr. Brassell is presently a Member of the Technical Staff in the Electrical Materials Group at Hughes Aircraft Company and is involved in materials evaluation and failure analysis of hybrids and electrical components.

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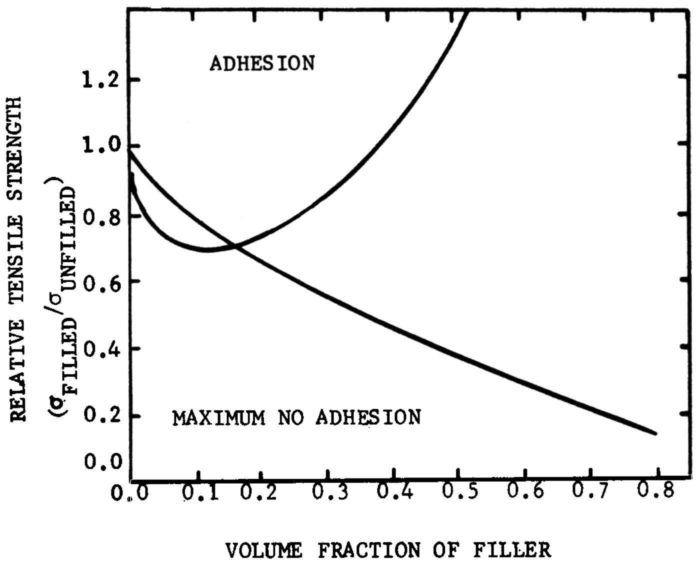
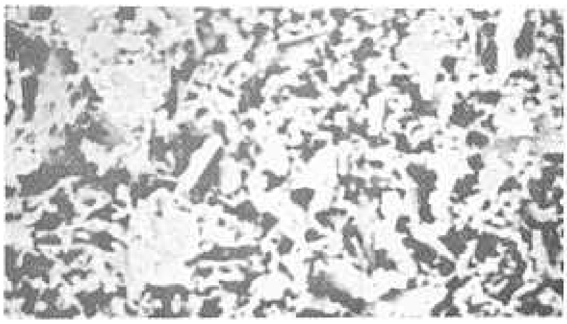


FIGURE 1

THEORETICAL CURVES FOR TENSILE STRENGTH FOR THE CASE OF GOOD ADHESION AND NO ADHESION BETWEEN FILLER AND POLYMER MATRIX [6].

FIGURE 2
S.E.M. PHOTOMICROGRAPHS OF ADHESIVE SAMPLES
SHOWING PARTICLE SIZE. ~2000X

BONDMASTER 640

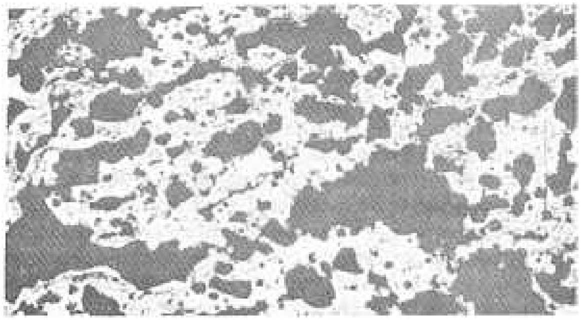


DUPONT 5504

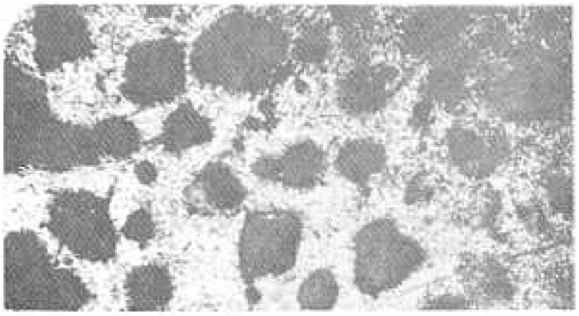
EPO TEC H21D

EPO TEC H20E

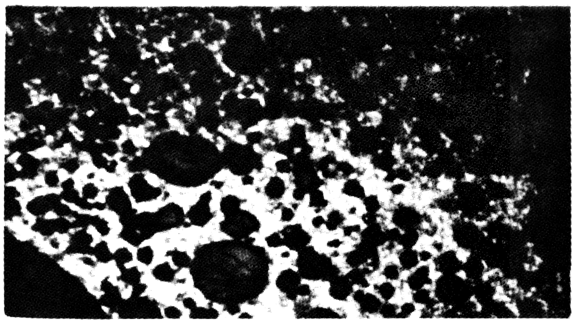
FIGURE 3-A
PHOTOMICROGRAPHS OF CROSS-SECTIONED ADHESIVE
SAMPLES DEPICTING POROSITY. ~ 25X



BONDMASTER 640



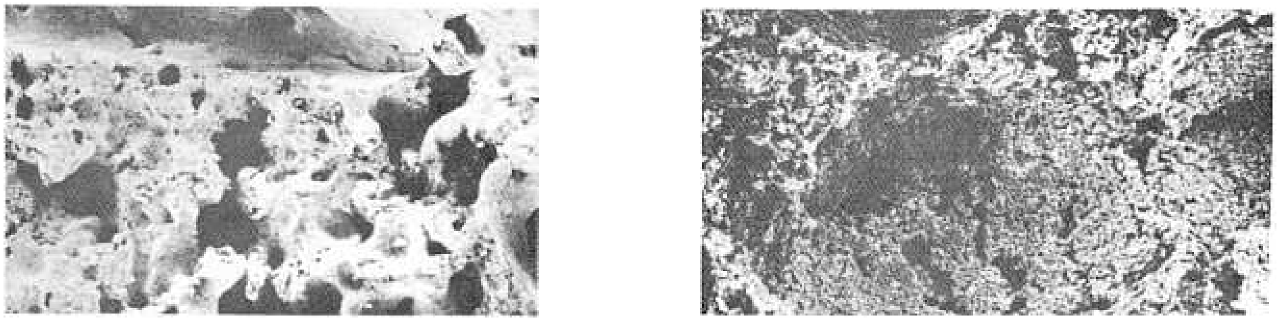
DUPONT 5504



EPO TEC H21D

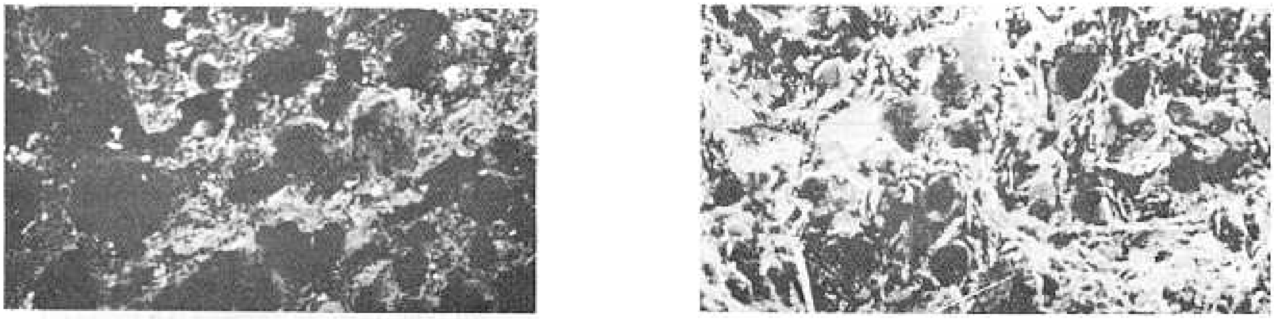
EPO TEC H20E

FIGURE 3-B
S.E.M. PHOTOMICROGRAPHS OF ADHESIVE SAMPLES SHOWING TYPICAL PORE SIZE.



BONDMASTER 640 ~50X

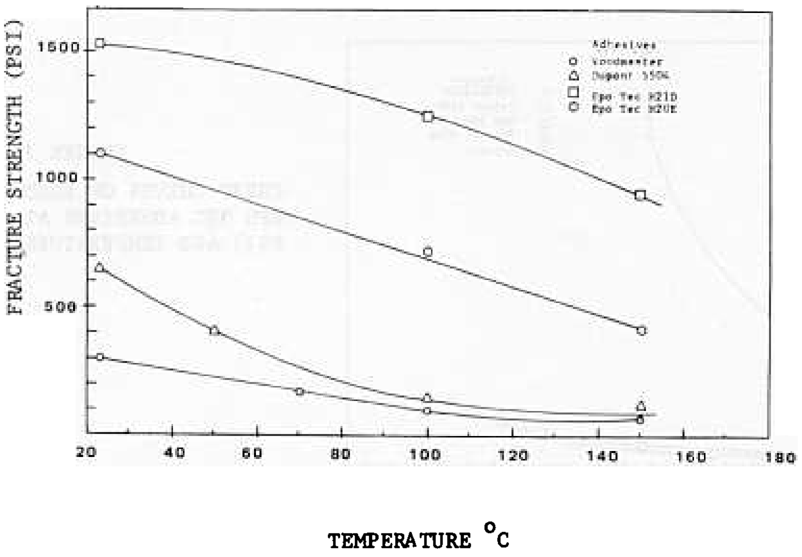
DUPONT 5504 ~200X



EPO TEC H21D ~100X

EPO TEC H20E ~500X

FIGURE 4
LAP SHEAR STRENGTH OF CONDUCTIVE EPOXIES AS A FUNCTION OF TEMPERATURE.



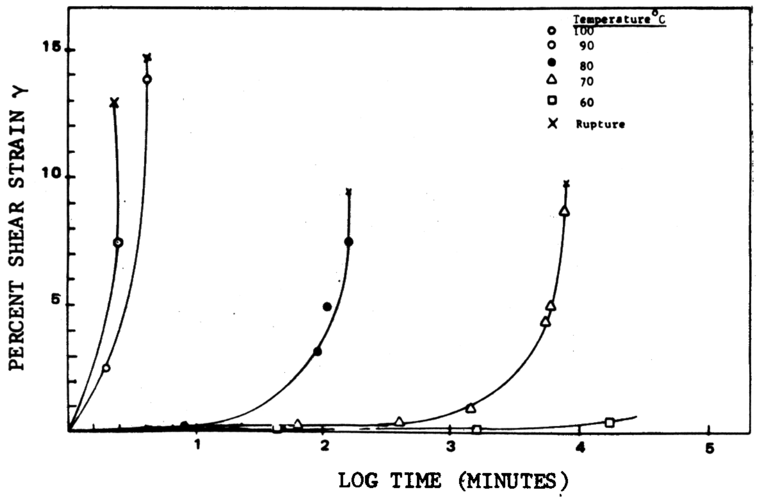
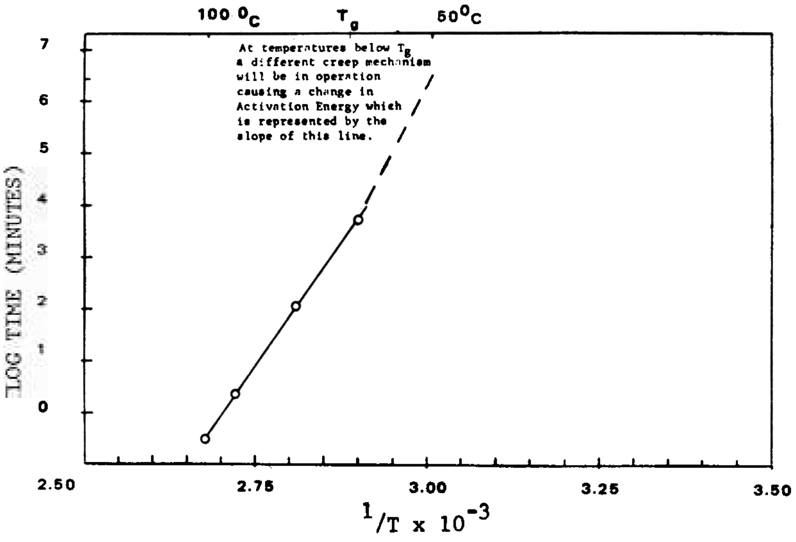


FIGURE 5

CREEP CURVES OF BONDMASTER ADHESIVE SYSTEM AT 68 PSI AND VARIOUS TEMPERATURES.



At temperatures below T_g a different creep mechanism will be in operation causing a change in Activation Energy which is represented by the slope of this line.

FIGURE 6

RUPTURE TIME OF BONDMASTER ADHESIVE VERSUS $^1/T^{\circ}K$.

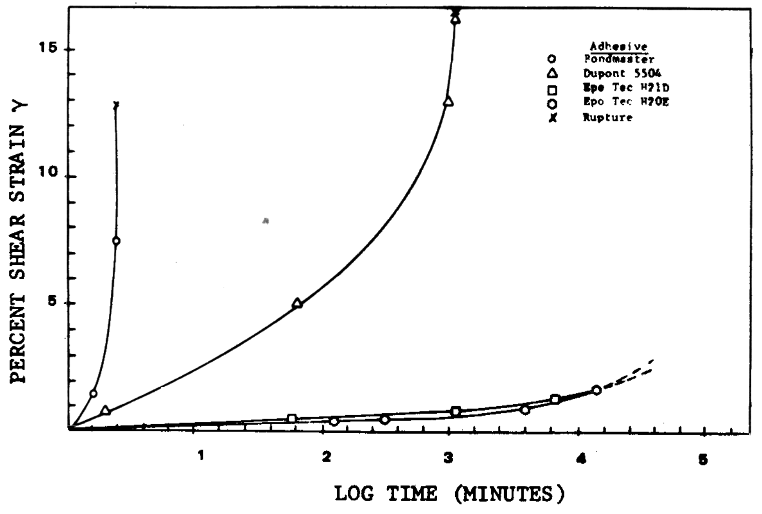


FIGURE 7

CREEP CURVES OF BONDMASTER, DUPONT AND EPO TEC ADHESIVES AT CONSTANT LOAD (68 PSI) AND TEMPERATURE (100°C).

TABLE 1

Adhesive Characterization

	Bondmaster	Dupont 5504	Epo Tec H21D	Epo Tec H20E
Resin Type	of Bisphenol A Diglycidyl Ether	of Bisphenol A Diglycidyl Ether	of Resoreinal Glycidyl Ether	of Novalac Glycidyl Ether
Curing Agent Class	Dicyandiamide	Not Available	Amine	Amine
Type of Filler	Silver	Silver	Silver	Silver
Amount of Filler (w/o)	~85	~78	~78	~78
Amount of Filler (v/o)	~42	~31	~31	~31
Particle Shape	Platelet	Platelet	Platelet	Platelet
Particle Size	1 - 5μ	1 - 5μ	3 - 10μ	1 - 10μ
Amount of Porosity (v/o)	~17%	~15%	~8%	~4%
Pore Size	100 - 400μ	100 - 300μ	50 - 100μ	5 - 20μ

TABLE 2

Thermal Properties of the Adhesive Systems

Tg	75°C	60°C	117°C	75°C
Degradation Temperature	335	330	365	355
Wt. Loss after 16 hrs. of 150°C	0.45%	0.32%	0.66%	1.50%

TABLE 3

Stresses necessary for causing unstable creep (fracture time less than 10 minutes) computed on $.70\sigma_F$.

TEMP. °C				
23°	204 psi	448 psi	1,020 psi	748 psi
100°	78 psi	102 psi	850 psi	490 psi
150°		48 psi	646 psi	286 psi