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LINEAR THERMAL EXPANSION OF FILLED EPOXY RESINS

PDO 6984742, Topical Report

H. M. McIlroy, Project Leader

Project Team:
G. L. Woodburn

Internal Distribution March 1974

Prepared for the
United States Atomic Energy Commission
Under Contract Number AT(29-1)-613 USAEC

Bendix Kansas City Division

DISCLAIMER

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Department 814

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Technical Communications

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LINEAR THERMAL EXPANSION OF FILLED EPOXY RESINS

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Prepared by H. M. McIlroy, D/814, under PDO 6984742

The coefficient of linear thermal expansion (CTE) of filled epoxies has been shown to depend upon the type of filler, the type of epoxy and curing agent, the filler concentration, the adhesion between epoxy and filler, and the filler particle size. The filler concentration has the most significant effect on the CTE of the cured mixture.

THE BENDIX CORPORATION

KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

A prime contractor for the
Atomic Energy Commission
Contract Number AT(29-1)-613 USAEC

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SUMMARY

Cured epoxy resins are widely used for the electrical, thermal, mechanical, and environmental protection of electronic components and assemblies. By varying the type of epoxy resin and curing agents, a wide range of end properties may be achieved. The addition of fillers will extend this range further. Although specific end properties may be obtained by the careful selection of all materials, the primary method of achieving these desired properties is with various fillers. Many fillers are available, and may be selected depending upon the properties desired.

Cure shrinkage, exotherm temperature during cure, thermal conductivity, mix time, viscosity, coefficient of thermal expansion (CTE), and mechanical properties are all affected by the fillers used. Fillers can reinforce an epoxy or reduce its overall mechanical properties.

Control of the thermal expansion of casting materials is one important reason for using a filler material. Encapsulated electronic assemblies may be used in environments of severe cold and mechanical shock. Many of the electrical components are glass, ceramic, or other fragile materials. Large thermal stresses can develop during temperature changes if the CTE of the casting material and the electronic assemblies are mismatched. These induced stresses must be reduced to protect both the fragile components and the casting material itself.

Many commonly used casting material formulations have CTE as high as 30 to 40 μm/m/°C. The glass, ceramic, metal components and printed circuit boards used to build electronic assemblies have CTE as low as 2 to 20 μm/m/°C. The mismatch in CTE is responsible for the thermal stresses that can cause failure of components or cracking of the potting material.

This work was done to determine and investigate the variables that influence the CTE of a casting material. The effort was divided into three major headings: the effect of epoxy resin, the effect of curing agent, and the effect of filler. Since the filler was suspected to be the greatest contributor, the filler investigation was divided into filler type, filler concentration, filler surface preparation, filler particle size, and filler size distribution.

The following conclusions were reached.

The CTE of epoxy resin and curing agent selected as the matrix material does affect the CTE of the cured mixture. At low filler concentrations the effect of the resin and curing agent is greater than at higher filler concentrations.

The CTE of the filler affects the CTE of the cured mixture. Fillers with CTE greater than the epoxy-curing agent system will increase the CTE of the cured mixture. Fillers with CTE similar to the CTE of the epoxy have little effect on the CTE of the mixture. Fillers with CTE less than the epoxy-curing agent blend will reduce the CTE of the mixture at any concentration.

The concentration of filler has the most influence on the CTE of the mixture. The processing of the mixture is the limiting factor for filler concentration. Test specimens were successfully made from mixtures with up to 70 percent-by-volume silica fillers. Beta-eucryptite fillers were used in concentrations of up to 67 percent-by-volume. At these concentrations the CTE of the mixture was about 10 μm/m/°C.

Adhesion of the epoxy to the filler will change the CTE. Non-adhesion of filler and epoxy results in greater CTE than normal adhesion. The addition of adhesion promoters did not change the CTE.

Tests to determine the effect of particle size and particle size distribution were inconclusive. Data for the silica fillers show that the smaller particle sizes have higher CTE while the beta-eucryptite fillers do not show this trend.

DISCUSSION

SCOPE AND PURPOSE

The thermal and cure stresses in a casting material can be altered by controlling the CTE of the casting material; this work was done to investigate the variables that influence the CTE of a casting resin and to determine the magnitude of that influence. An experimental rather than a theoretical approach was taken.

A casting material normally consists of a resin component, a curing agent component, and a filler. These three components were varied and the effect on the CTE was measured. Since the filler component was suspected to be the largest contributor, the filler investigation was divided into the areas of filler type, filler concentration, filler surface preparation, filler particle size, and filler size distribution.

PRIOR WORK

Casting materials have been used for many years within the AEC complex and within the general electronic industry. Several casting materials used at Bendix have been tested to measure mechanical, electrical, thermal, and environmental properties. The CTE is one of the thermal properties of interest. In the past, the characterization has been for a specific formulation and has covered many material properties. The present work concentrated on the CTE and the variables that influence the CTE of casting materials in general.

ACTIVITY

Experimental Procedure

The four epoxy resins and five curing agents used in this study are listed in Appendix A. All of these materials are commercially available and are commonly used in potting or encapsulation applications. No attempt was made to modify the base resins or curing agents. Blends of two epoxy resins were used to reduce the viscosity at room temperature or to increase the flexibility of the mixture; however, no chemical changes were made.

Only commercially available sizes and size distributions of fillers were evaluated. The fillers tested are listed in Appendix A. Blends of fillers were tested, but no attempt was made to screen materials to achieve a

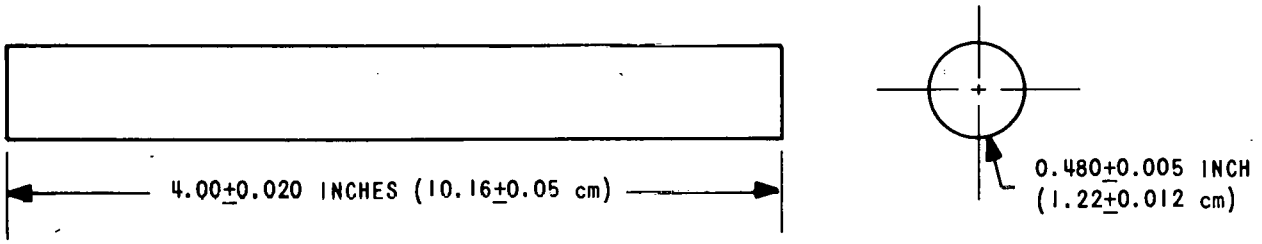
particular size distribution. All the fillers tested were carefully dried in a vacuum oven at 250°F (121°C) and 1 to 3 torr (130 to 400 Pa) for 4 hours to remove water. Some of the fillers were baked at 1100°F (593°C) to remove any organic contaminants.

For some tests, the fillers were precoated before blending with the epoxy resin and curing agent to determine the effect of filler-epoxy adhesion on the CTE of the mixture. These precoat coupling agents are listed in Appendix A. In each case, the precoat material was dissolved in dry, reagent grade toluene. A concentration of 5 grams of precoat material to 100 grams of toluene was selected. The filler was added to the toluene-precoat solution and the resulting slurry was mixed, allowed to stand for several hours, and mixed again. The toluene was removed by a vacuum of 10 torr (1300 Pa) at room temperature followed by the standard drying method mentioned previously.

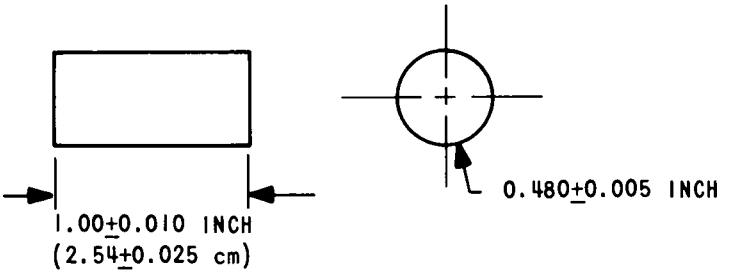
Several different methods of mixing were tried. Hand mixing in a metal container was the easiest and fastest method for small batches with low filler concentrations at low processing temperatures. The normal processing temperatures were 200 to 225°F (93 to 107°C) but the formulations with filler contents greater than 60 percent-by-volume required a processing temperature of 300°F (149°C) to reduce the viscosity. For larger batches with low filler contents an insulated Hobart mixer was used. The blending or mixing of large amounts of filler into the epoxy resin was a major problem. High shear was required to adequately mix filler loadings of greater than 60 percent-by-volume. Several high shear mixers were evaluated including a colloidal mill, a three-roll paint mill, and a two-roll rubber mill. The most effective method was the two-roll rubber mill. Loadings as high as 75 percent-by-volume were achieved with a two-roll mill at 300°F (149°C).

Coefficient of thermal expansion test specimens and compressive strength test specimens were machined from the same type casting. For filler concentrations of less than 50 percent-by-volume the test rods were made by pouring the mixture into steel or RTV silicone molds. For higher viscosity mixtures the test specimens were cast in an open face steel mold. In each case, the compressive and CTE specimens were machined to the dimensions shown in Figure 1.

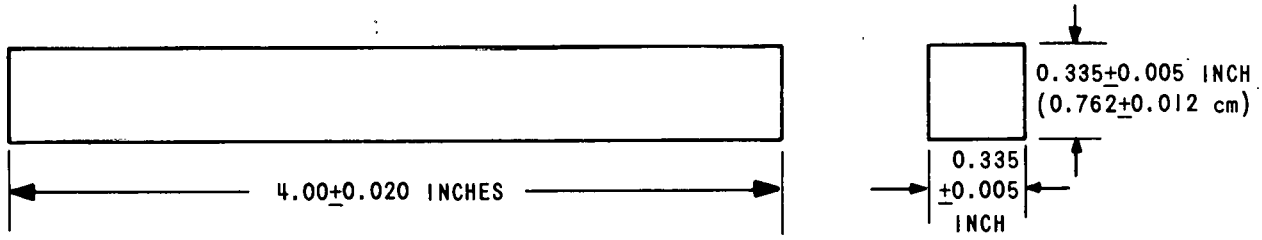
The coefficient of linear thermal expansion was tested and calculated by the procedure given in ASTM D-696 (Appendix B). This method uses a quartz tube dilatometer and measurements of the sample length are made at specific temperatures to give a CTE over a temperature range. The compressive properties were tested at room temperature according to ASTM D-695 (Appendix B).



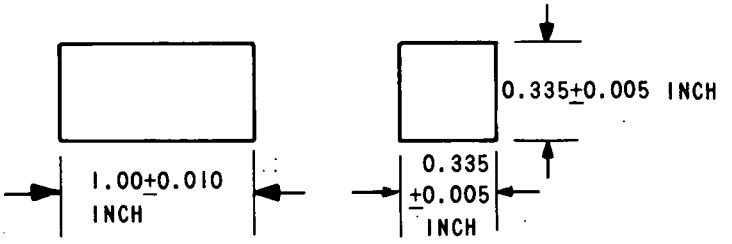
CTE ROD SPECIMEN



COMPRESSIVE ROD SPECIMEN



CTE BAR SPECIMEN



COMPRESSIVE BAR SPECIMENS

Figure 1. Test Specimen Configuration

Several tests (Appendix B) were made to characterize the fillers. Fillers with low CTE were of primary interest and were tested for average particle size, size distribution, density, and surface area.

Experimental Results

The four epoxy resins selected were tested with six curing agents. Although not all of the combinations of resins with curing agents were tested, the general purpose resin Epon 828 was tested with each of the six curing agents. The other epoxy resins were tested with Epon Z curing agent. All of the test results for linear CTE and compressive properties are listed in Table 1.

Using Epon Z hardener and adding a flexibilizer (Epon 871) to the general purpose Epon 828 increased the CTE about 14 to 20 percent over the value for Epon 828 and Epon Z alone. By using the high functionability novolac (DEN 431 diluted with RD4 to aid in processing) the CTE was reduced by about 6 percent. Six different curing agents were tested with the Epon 828 epoxy resin. At the higher temperature range of 20° to 80°C the aliphatic (DETA and Hysol 3471) and aromatic resins (Epon Z and DDS) have coefficients of thermal expansion from 62 to 65 μm/m/°C. The polyamide (Versamid 140) cured sample had a CTE of 83 μm/m/°C or about 30 percent higher than the other curing agents. At the lower temperature range of -50 to 20°C the coefficients of thermal expansions varied from a low of 43 μm/m/°C for an aromatic curing agent to a high of 61 μm/m/°C for the polyamid curing agent.

The resin and curing agent combination has a definite and significant influence on the CTE of a resin-curing agent-filler mixture. Figure 2 shows this effect for six resin-curing agent blends at two temperature ranges. At any filler loading, the CTE of the mixture is a linear function of the CTE of the resin-curing agent combination.

The type of filler will affect the processing and properties of the desired end product. The purpose described in this section was to determine the effect of filler CTE on the CTE of the epoxy-filler mixture. Fillers with CTE greater than, equal to, and less than the CTE of a cured epoxy were selected and tested. The fillers tested are given in Appendix A and the test results are listed in Table 2.

The fillers with CTE greater than or equal to the cured epoxy were all polymeric material. The filler powders selected and tested were polyethylene, polyimide, polytrifluorochloroethylene (Kel-F made by the 3-M Company), florinated ethylene propylene (Teflon made by duPont) and a phenoxy resin. All of these powders were manufactured as coating powders to be used in fluidized beds. They were selected on the basis of their reported density

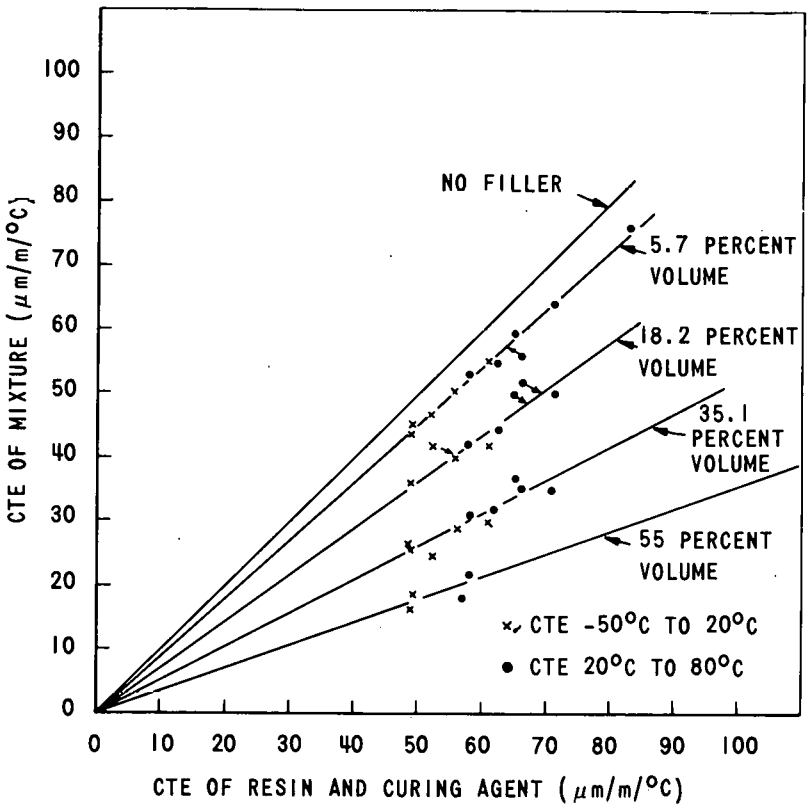


Figure 2. CTE of Mixture as a Function of the CTE of Resin and Curing Agent Blend With Increasing Silica (GP7) Concentration

Table 1. Effect of Resins and Hardeners on CTE and Compressive Properties

Resin	Hardener	Parts by Weight	Coefficient of Thermal Expansion (μm/m/°C)		Compressive Strength		Compressive Modulus		Strain (Percent)
			-50° to 20°C	20° to 80°C	(psi)	(MPa)	(psi)	(GPa)	
Epon 828	Z	100:20	49.0	02.5	13800	(129)	500000	(3.44)	8.7
Epon 828	Diamino-diphenylsulfone	100:25	43.4	62.0	21900	(151)	570000	(3.92)	6.3
Epon 828	Hysol 3471	100:29	51.1	65.5	14830	(101)	410000	(2.82)	
Epon 828	Diethlene-triamine	100:12	55.9	65.2	12087	(83)	350000	(2.41)	
Epon 828	Versamid 140	100:50	71.2	82.8	14500	(100)	370000	(2.55)	6.2
Epon 828/ Epon 871	Z	80:20:18	61.1	71.3	18500	(127)	460000	(3.17)	6.6
Epon 828	Nadicmethyl-anhydride	80:20:18	50.6	62.4	21850	(150)	500000	(3.44)	
DEN 431/ RD4	Z	100:8:23	49.2	58.2	18030	(124)	510000	(3.51)	
DEN 431/ RD4	Diethylene-thiamine	100:8:13.6	52.2	66.2					

Table 2. Effect of Fillers on CTE

Filler Resin and Catalyst		Weight Loading (Percent)	Volume Loading (Percent)	Coefficient of Thermal Expansion (μm/m/°C)	
				-50 to 20°C	20 to 80°C
Control	828/3471	0	0	51	66.5
Silica	828/3471	43.7	29.5	32	42
Polyethylene	828/3471	16.3	20.25	55	71
Polyimide	828/3471	20.4	18.09	49	65
Teflon	828/3471	33	21.9	63	79
Kel-F	828/3471	28	18	57	79
Control	828/Z	0	0	49	62.5
Phenoxy	828/Z	20	20	50.2	58.7
Mica	828/Z	20	9.74	44.1	48.2
Silica	828/Z	20	11.6	40.5	48.4
Low X	828/Z	20	10.5	40.5	47.2
Beta-Eucryptite	828/Z	20	11.1	40.5	49.5
Control	828/DETA	0	0	55.9	65.2
Teflon	828/DETA	10	5.7	58.4	68.7
Phenoxy	828/DETA	10	10	55.0	65.8
Silica	828/DETA	10	5.7	50.4	59.5
Control	828/V140	0	0	71.2	91.0
Silica	828/V140	10	5.7	64.6	76.0
Kel-F	828/V140	10	5.9	83.8	103.0

and coefficient of thermal expansion. The Teflon and polyethylene were selected as high CTE materials and the polyimide, phenoxy, and Kel-F were selected as intermediate CTE materials.

The three fillers tested to reduce the CTE of epoxy resin were mica, silica, and beta-eucryptite. The silica and mica have CTE less than 4 μm/m/°C. Beta-eucryptite is one of the few materials that will contract when heated; its CTE is a negative 6 μm/m/°C. Adding these fillers with CTE lower than the CTE of the resin catalyst system does reduce the overall CTE of the mixture. The test data are shown in Table 2.

The addition of a polymeric filler also affected the CTE of the composite material. The data in Table 2 show that the CTE was increased by adding Teflon, polyethylene, and Kel-F powders to an epoxy resin-curing agent system. For example, the addition of about 22 percent-by-volume Teflon to a mixture of Epon 828 and Hysol 3471 increased the CTE from 51 μm/m/°C (no filler) to 63 μm/m/°C for the temperature range of -55 to 20°C. The addition of the phenoxy did not change the CTE of the resin-curing agent blend.

The type of filler as well as the type of resin and catalyst used has a significant effect on the bulk properties of the composite. Table 3 lists compressive strength properties of several resin catalyst combinations with four different fillers. In each case the addition of silica filler increased the ultimate compressive strength and the modulus of the filled epoxy. The addition of a polymeric filler reduced the ultimate strength and modulus.

The effect of filler type on the CTE of resin, curing agent, and filler mixture is shown in Figures 3 and 4. Teflon (CTE of 100 μm/m/°C), phenoxy (CTE of 55 μm/m/°C), and GP7 Silica (CTE of 0.3 μm/m/°C) were tested after mixing with Epon 828/Z, Epon 828/DETA, and Epon 828/V140; the results are shown in Figure 3 for filler concentrations of 5.7 percent-by-volume. The effect of filler concentration and type of filler on CTE of the mixture is shown in Figure 4. These results show that at equal concentrations, the CTE of the epoxy curing agent and filler blend is proportional to the CTE of the filler used.

The amount or concentration of filler in an epoxy resin is a significant factor influencing the CTE of the mixture. Figures 5, 6, and 7 show CTE of the mixture as a function of filler concentration. The CTE for a temperature range of 20 to 80°C are plotted in Figure 5 for silica, mica, and beta-eucryptite fillers. Figure 6 shows the effect of filler volume on CTE over the temperature range of -50 to 20°C. At the higher temperature range, any difference between the mica, silica, and beta-eucryptite is not distinguishable. At the lower temperature range, and for high filler concentrations, the beta-eucryptite filler has a lower CTE for a given filler concentration

Table 3. Effect of Fillers on Compressive Properties

Filler	Resin and Curing Agent	Volume Loading Percent	Compressive Strength Properties			
			Stress		Modulus	
			(kpsi)	(MPa)	(Mpsi)	(GPa)
Control	828/Z	0	18.1	(124)*	0.462	(3.18)
Silica	828/Z	11.6	19.9	(137)	0.670	(4.61)
Silica	828/Z	26.2	21.7	(149)	0.950	(6.55)
Silica	828/Z	44.4	27.8	(191)	1.750	(12.06)
Phenoxy	828/Z	10	17.6	(121)**	0.467	(3.22)
Phenoxy	828/Z	10	16.3	(112)***	0.438	(3.02)
Control	828/DETA	0	14.8	(102)†	0.41	(2.82)
Silica	828/DETA	5.7	15.4	(106)†	0.50	(3.44)
Silica	828/DETA	26.2	18.0	(124)†	0.77	(5.30)
Phenoxy	828/DETA	10	14.4	(99.3)†	0.43	(3.96)
Teflon	828/DETA	5.7	13.4	(92.4)†	0.38	(2.62)
Control	828/V140	0	12.1	(83.4)	0.353	(2.43)
Silica	828/V140	5.7	12.2	(84.1)	0.397	(2.73)
Kel-F	828/V140	5.9	8.5	(58.6)	0.247	(1.70)
Control	431/RD4/DETA	0	18.0	(124)	0.507	(3.49)
Silica	431/RD4/DETA	5.7	18.3	(126)	0.585	(4.03)
Kel-F	431/RD4/DETA	5.9	11.0	(75.8)	0.311	(2.14)
Control	431/RD4/Z	0	21.8	(150)	0.595	(4.10)
Silica	431/RD4/Z	5.7	22.6	(155)	0.706	(4.86)
Kel-F	431/RD4/Z	5.9	12.8	(88.1)	0.327	(2.25)

*6.5 percent strain
**5.8 percent strain
***5.4 percent strain
†10 percent strain

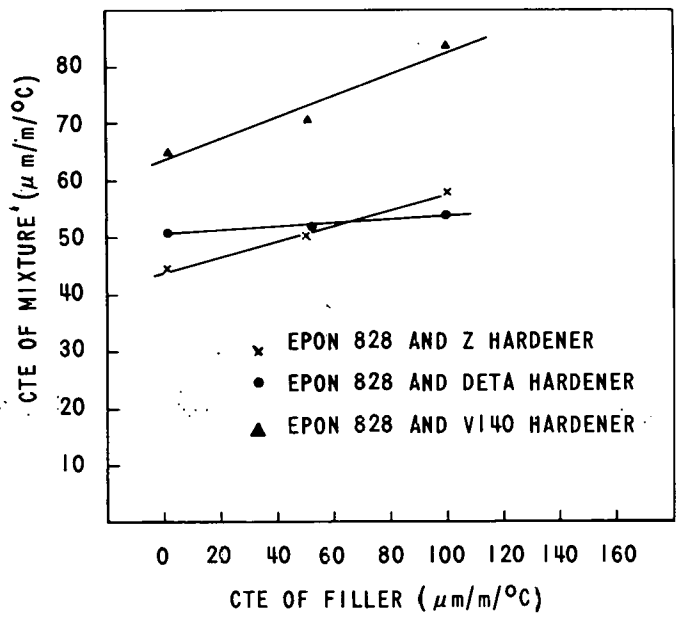


Figure 3. CTE of Mixture as a Function of CTE of Filler at 5.7 Percent Filler Concentration and Temperature Range of -55° to 20°C

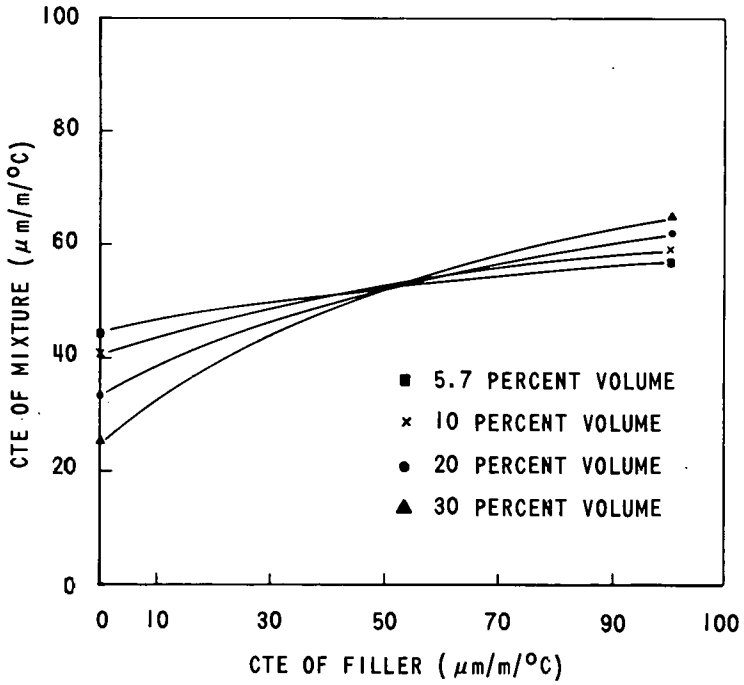


Figure 4. CTE of Mixture as a Function of CTE of Filler and Filler Concentration in Epon 828 and Z Hardener

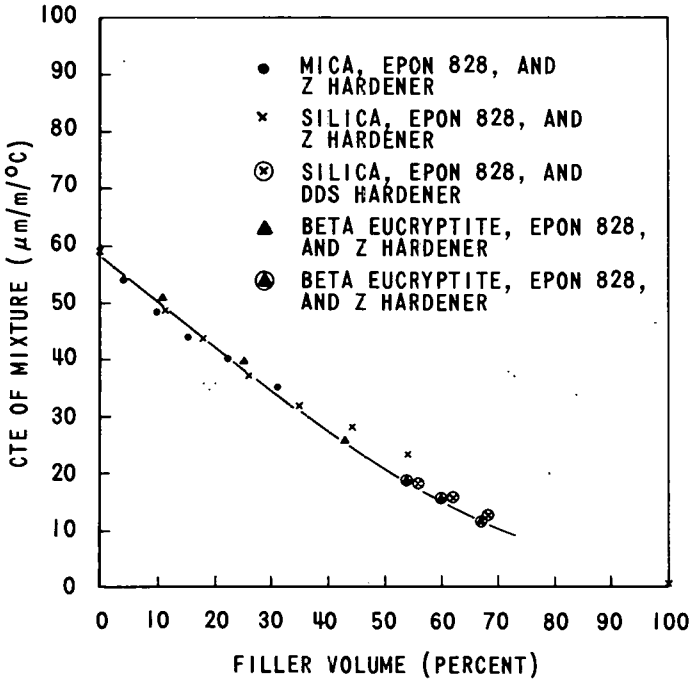


Figure 5. CTE of Mixture as a Function of Filler Concentration Over the Temperature Range of 20° to 80°C

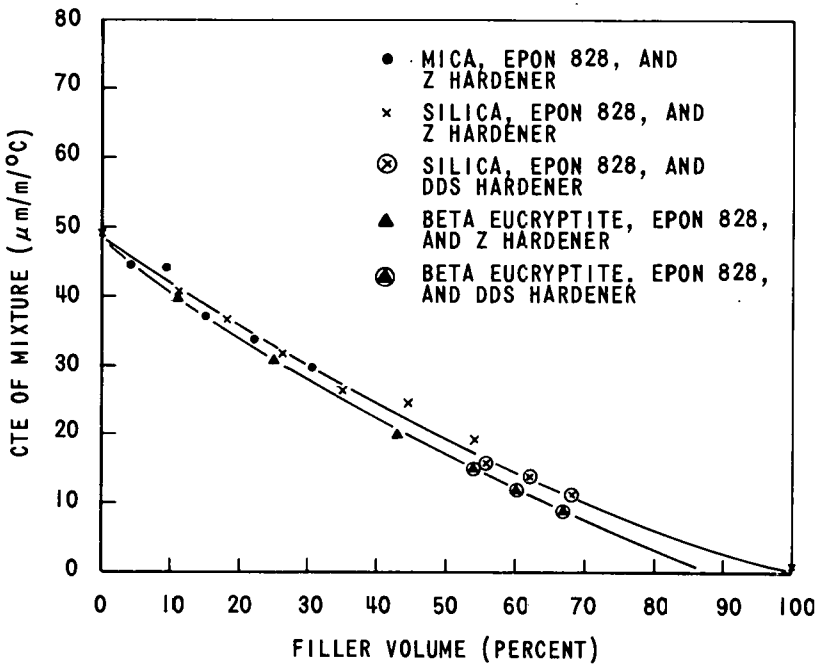


Figure 6. CTE of Mixture as a Function of Filler Concentration Over the Temperature Range of -50° to 20°C

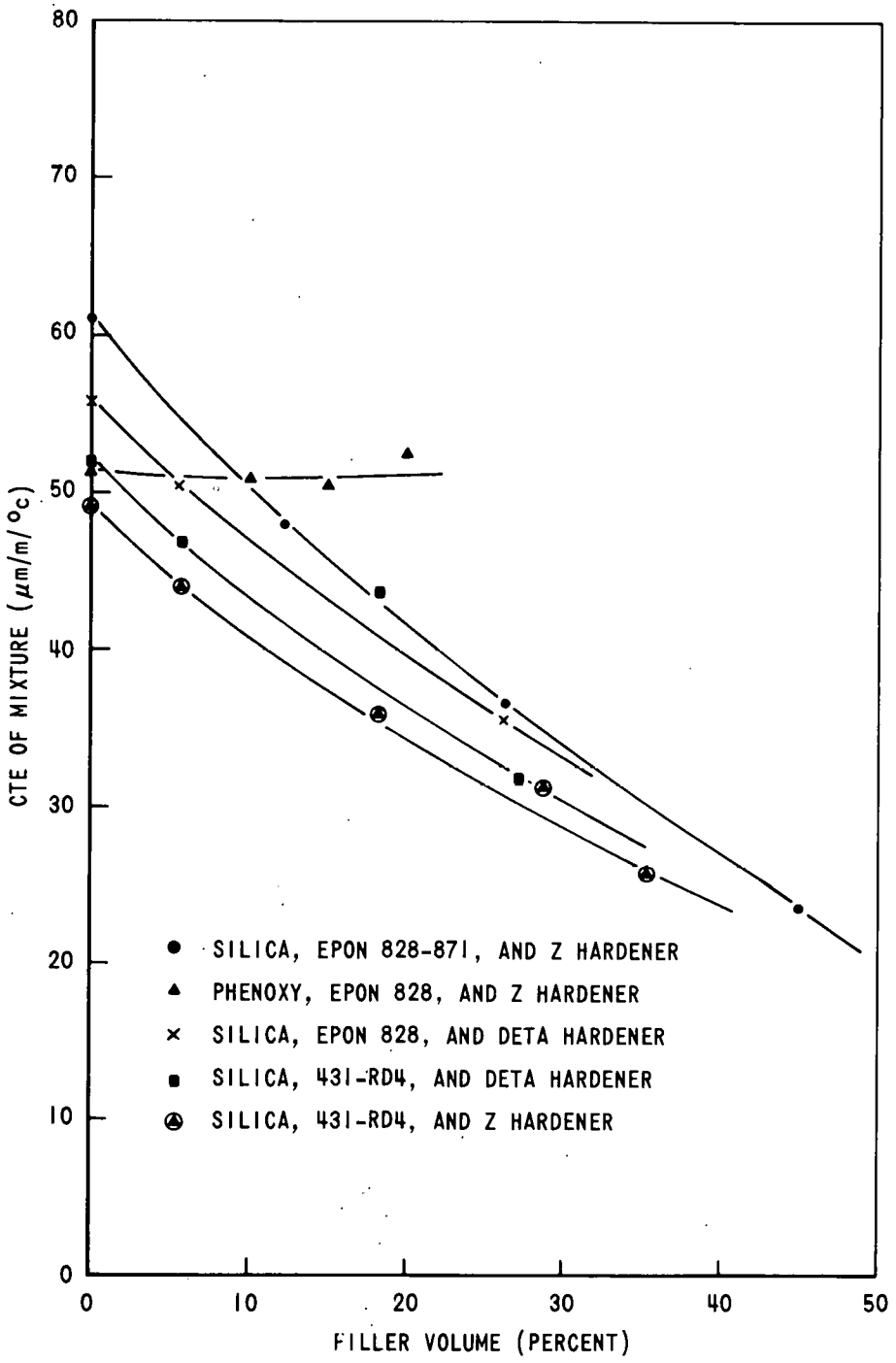


Figure 7. CTE of Mixture as a Function of Resin-Curing Agent Type and Filler Concentration Over Temperature Range of 0° to 20°C

than the silica or mica fillers. Within the processing limitations described in the procedure section, the maximum filler loading was about 68 percent with a CTE of about 10 μm/m/°C.

The data plotted in Figure 7 show the effect of epoxy resin, catalyst, and filler on the CTE of five systems at low filler concentrations. Curve 2 in Figure 7 is almost flat, indicating that the phenoxy filler has very little effect on the CTE of the composite material. The other four resin-curing agent systems are filled with varying amounts of silica. At the lower filler concentrations, the type of resin and curing agent has a considerable influence on the CTE of the mixture.

The effect of filler concentration on compressive strength properties is shown in Figures 8 and 9. The compressive yield strength versus volume filler for silica in Epon 828/Epon Z and Epon 828/DDS, and beta-eucryptite in Epon 828/DDS is shown in Figure 8. Without filler the compressive yield strength of Epon 828 with Z hardener is about 18100 psi (124 MPa) at room temperature. The compressive yield strength is directly proportional to the filler concentration for both the silica and the beta-eucryptite filler.

The compressive modulus shown in Figure 9 is also directly proportional to the filler concentration. At filler loadings of less than 50 percent the curve fits the data points without much scatter. However, at greater than 50 percent the results are not too consistent. The compressive strain (Figure 9) decreases with increasing filler concentrations.

In addition to the standard drying to remove water, a silica filler (GP7) was precoated before blending to determine the effect of filler-epoxy adhesion on the CTE of the mixture. Five precoat materials were evaluated; two precoatings were tested at a volume concentration of 35 percent and three precoatings were tested at a 50 percent filler concentration. A control sample was also tested at each concentration. Four of the precoat materials were selected to improve adhesion and one precoat was selected to reduce or prevent adhesion of the epoxy to the filler. The four precoatings to improve adhesion did not significantly change the CTE. The CTE values are similar for control specimens and the precoated specimens. However, the test specimens precoated with the DC200 silicone fluid (used to reduce adhesion) did have significantly higher CTE values than the control sample. The test results are listed in Table 4.

Figure 10 is a plot of GP7 silica concentration versus CTE with the test values for the precoated samples superimposed on the graph. The toluene control sample and the A-1100 precoat material have the same CTE as the unworked filler. The other precoats at the 50 percent-by-volume level have CTE slightly greater than the uncoated filler. The precoats to promote

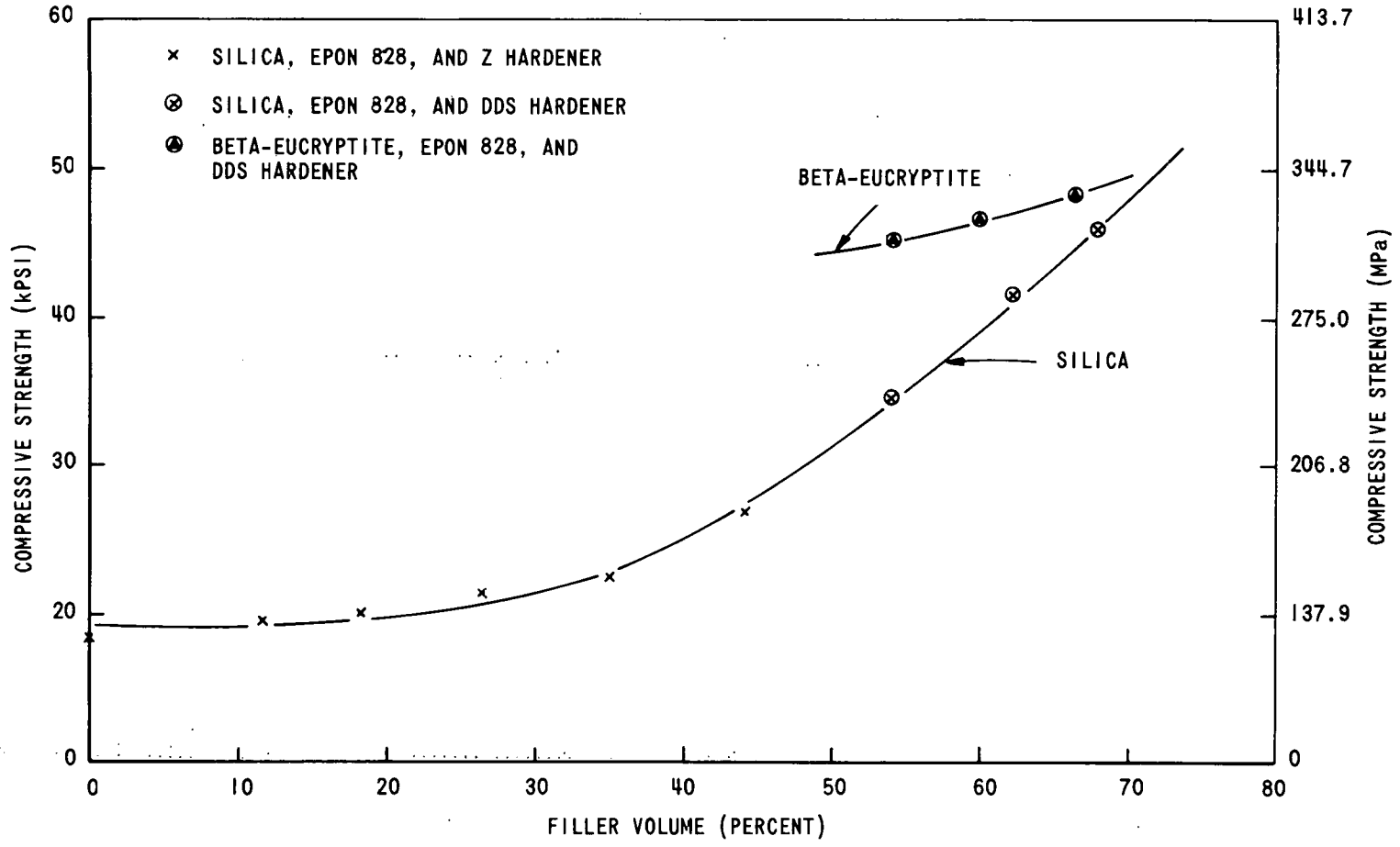


Figure 8. Room Temperature Compressive Strength Versus Filler Concentration

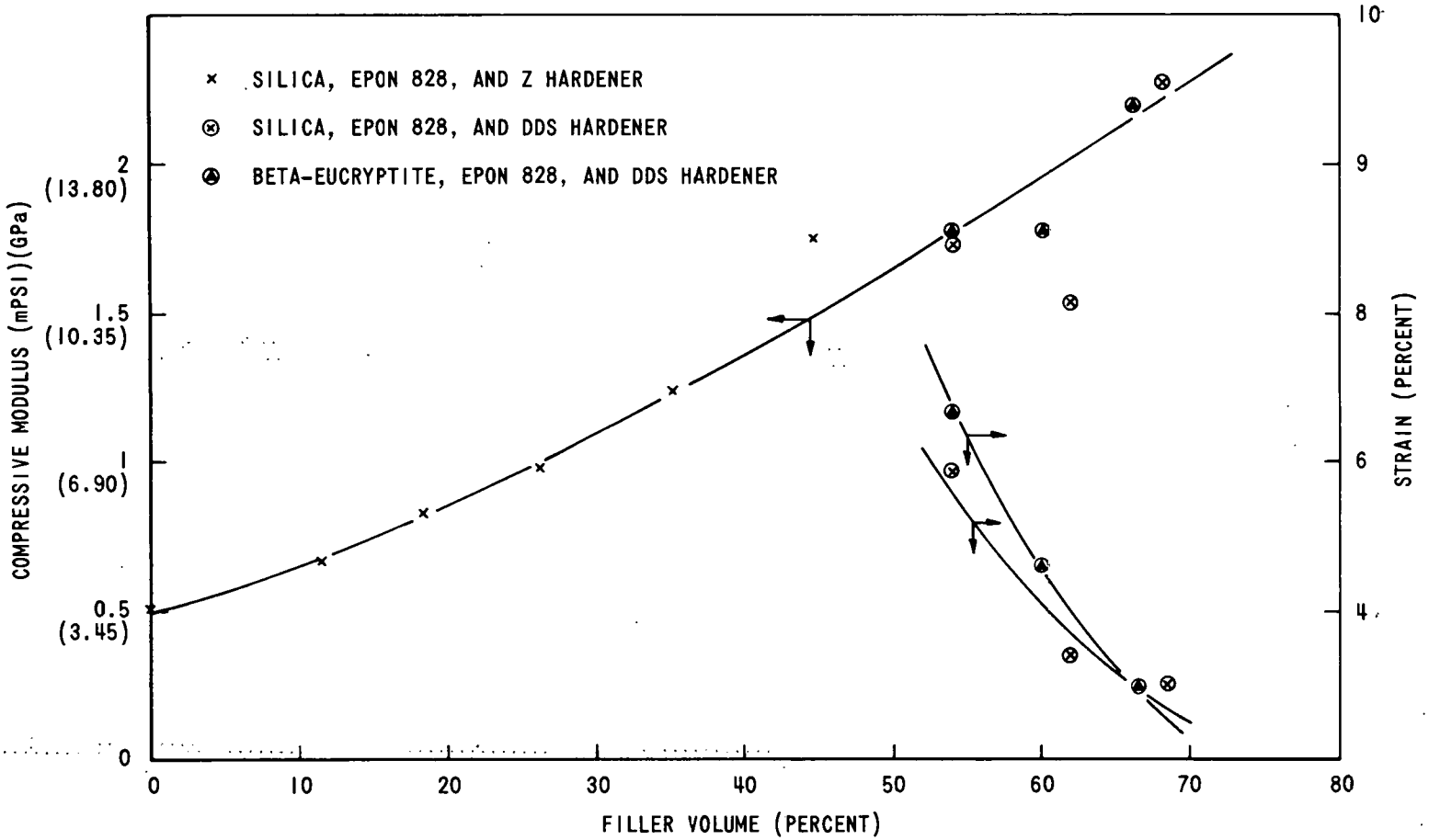


Figure 9. Room Temperature Compressive Modulus and Strain at Yield Point Versus Filler Concentration

adhesion did not reduce the overall CTE. The DC200 silicone fluid was used to prevent adhesion of the epoxy to the silica filler. The two data points for the DC200 precoat are significantly different from the base line curves.

In this study only commercially available fillers were evaluated. No attempt was made to isolate specific particle sizes of the fillers. Therefore any difference in the measured CTE of the fillers at a given concentration could be due to either the particle size or the size distributions.

Table 4. Effect of Precoating Filler on CTE

Resin and Catalyst	Volume Filler (Percent)#	Precoat	Coefficient of Thermal Comparison (μm/m/°C)	
			-55 to 20°C	20 to 80°C
828/Z	50	Control†	18.2	22.5
828/Z	50	A-187*	18.0	22.0
828/Z	50	RD4**	18.6	22.9
828/Z	50	828***	18.3	22.5
828/Z	35.1	Control†	25.9	30.5
828/Z	35.1	A-1100††	26.0	30.6
828/Z	35.1	DC200†††	28.7	34.3

*Glycidoxypropyltrimethylsilane (Reactive epoxide group)
**Vinyl cyclohexene dioxide (Epoxy diluent)
***Epon 828 Same as matrix resin
†Control (Toluene without precoat)
††Aminopropyltriethoxysilane (Reactive amine group)
†††Dimethyl silicone oil
#Silica

The test methods used to characterize the silica and eucryptitc fillers are given in Appendix B. These tests include measurements of average particle size by Fischer Sub-Sizer, size distribution by micromerograph and Coulter counter, surface area by Orr Analyzer, and density measurements by kerosene displacement and Hall flow meter. The test results are shown in Table 5 and 6 for the silica and eucryptite fillers.

The six silica fillers were tested at volume concentrations of 44.4 percent and 29.5 percent in Epon 828/Z. The three beta-eucryptite fillers used were tested in Epon 828/Z at a filler concentration of about 54 percent. The test results for the silica fillers are shown in Figure 11 and Table 7. These test data show that the particle size (or size distribution) does have an effect on the CTE of the mixture. For both concentration levels, the mixture made with the smaller particle size fillers have greater CTE than the mixtures made with larger particle size fillers.

Table 5. Properties of Silica Fillers

Test*	GP3	GP7	GP11	GP13	GP15	GP50/100
Surface Area (m^2/g)	12.254	2.592	0.154	0.076	0.592	0.066
Average Particle Size (μm)	1.2	3.5	20.5	30.8	10.4	35.0
Density (g/cm^3)	2.256	2.233	2.217	2.196	2.228	2.211
Bulk Density (g/cm^3)	0.39	0.49	0.82	0.94	0.70	0.99
Tap Density (g/cm^3)	0.6	0.8	1.2	1.2	1.3	1.2

*Tests were performed using an Orr Surface Area Analyzer, A Fisher Subsieve Sizer (particle size), kerosene displacement (density), a Hall flow meter (bulk density) and a Numeco tap density apparatus (tap density).

Table 6. Properties of Beta-Eucryptite Fillers

Test*	Standard Size	Smaller Size	Larger Size
Surface Area (m^2/g)	1.41	2.62	1.07
Average Particle Size (μm)	5.0	2.65	9.5
Density (g/cm^3)	2.40	2.40	2.39
Bulk Density (g/cm^3)	0.52	0.53	0.76
Tap Density (g/cm^3)	0.98	0.98	1.29

*Tests were performed using an Orr Surface Area Analyzer, a Fisher Subsieve Sizer (particle size), kerosene displacement (density), a Hall flow meter (bulk density), and a Numeco tap density.

Discussion of Results

The coefficient of thermal expansion is normally expressed as the linear coefficient or volume coefficient. The linear coefficient is the slope of temperature versus change in length on a single curved line. The temperature range over which the measurements are made must be specified. The volume coefficient is similar except that the change in volume (three dimensional) is used instead of the change in length (one dimension). For isotropic materials the linear coefficient is equal to one third the volume coefficient. The filled epoxies are isotropic and the linear coefficient of thermal expansion is used in this study.

Since the change in length versus temperature curve for the filled epoxies is not linear, the CTE will depend upon the temperature range selected. The data in Table 8 show the effect of temperature on the CTE of several resin, curing agent, filler combinations. Figure 12 shows the deflection

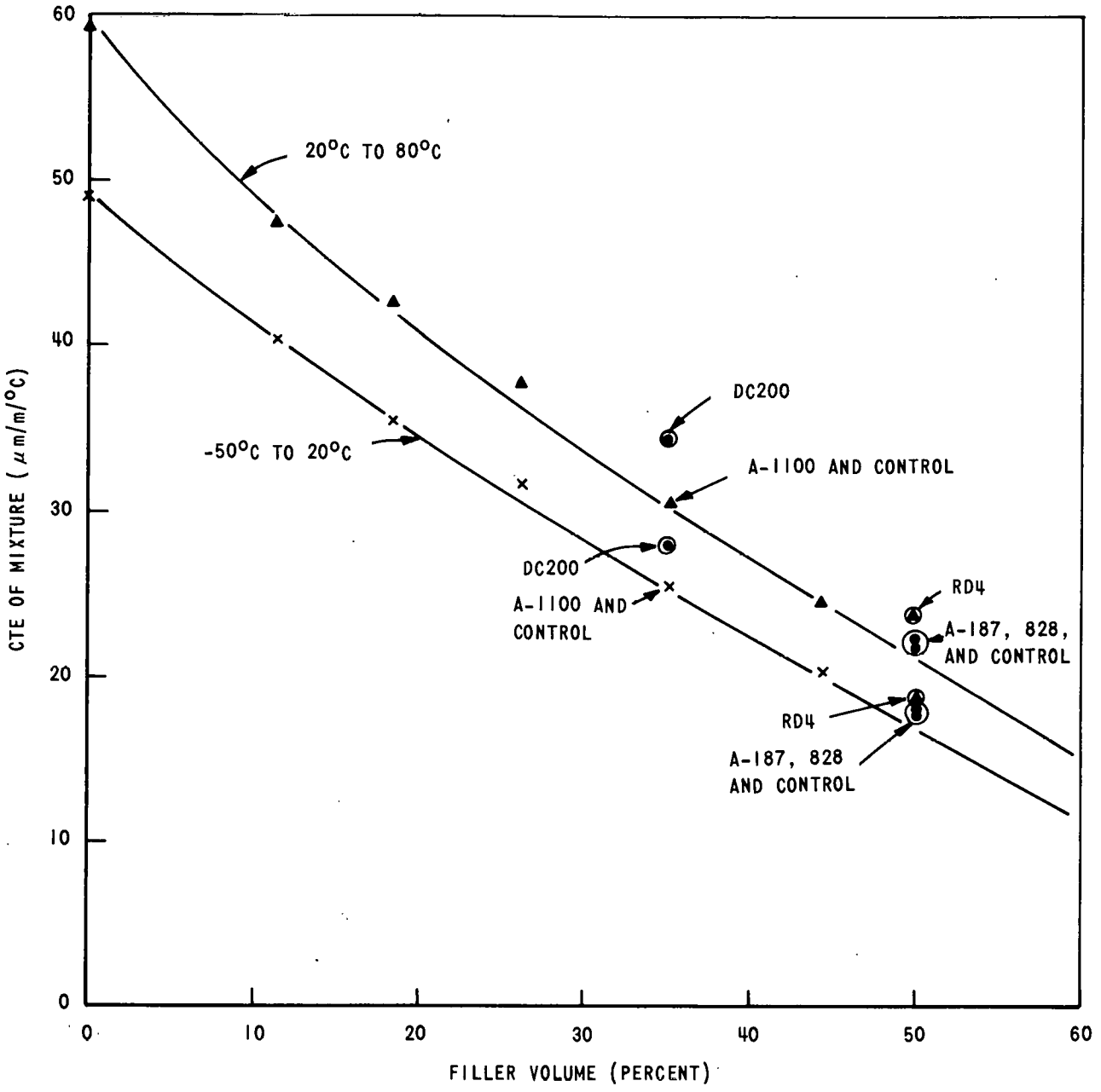


Figure 10. Effect of Adhesion Modifiers on CTE of the Mixture

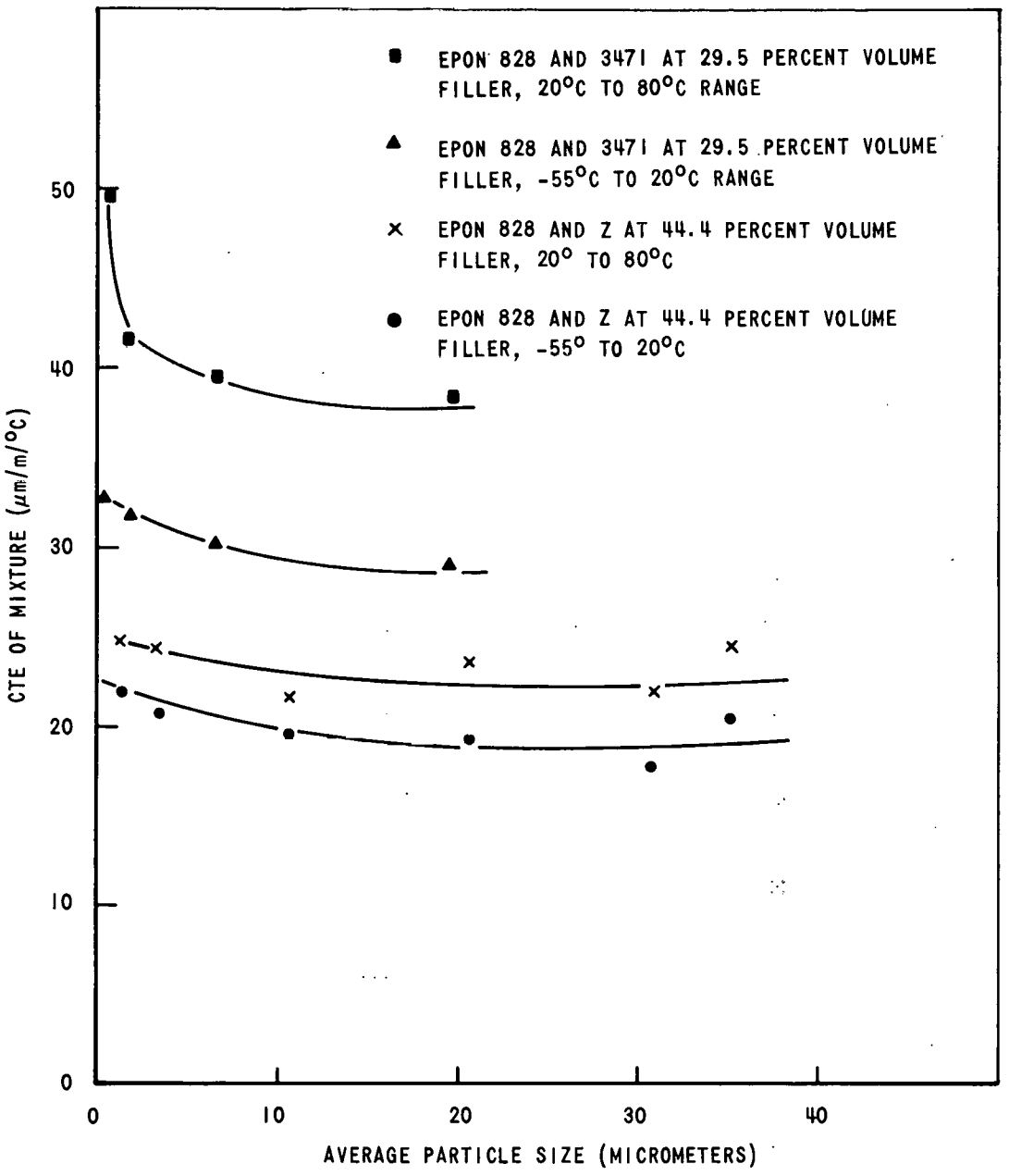


Figure 11. CTE of Mixture as a Function of Average Particle Size of Silica Fillers

Table 7. Effect of Filler Size and Size Distribution on CTE

Resin and Catalyst	Type Filler	Volume Filler Percent	Coefficient of Thermal Expansion ($\mu m/m/°C$), -55 to 20°C	20 to 40°C	40 to 60°C	60 to 80°C	20 to 80°C
828/Z	0	0	49				59.0
	GP3	44.4	22.1	23.8	25.8	25.3	24.9
	GP7		20.6	23.1	24.1	25.9	24.7
	GP11		19.2	22.5	23.9	25.4	23.9
	GP13		18.0	22.3	21.4	22.2	22.0
	GP15		19.8	19.7	22.4	22.8	21.6
	GG50/100	44.4	20.8	23.4	25.0	26.0	24.8
828/3471	0	0	51.1				65.5
	GP3	29.5	32.8				49.7
	GP7		32.0				41.8
	GP15		30.3				39.5
	GG50/100	29.5	29.0				38.5
828/DDS	71770*	52.7		17.4	22.8	37.6	
	66471*	53.9		16.3	18.9	20.1	
	66472*	56.5		12.8	15.9	18.5	
		54					
		54					
		54					

*Beta-eucryptite

Table 8. Effect of Temperature on CTE

Resin and Catalyst	Filler	Volume Filler (Percent)	Coefficient of Thermal Expansion (μm/m/°C)			
			0 to 20°C	20 to 40°C	40 to 60°C	60 to 80°C
43/RD4/Z	Silica	0	49.2	53.9	58.9	61.9
		5.7	44.1	49.1	53.4	55.8
		18.2	36.3	38.4	43.6	44.8
		35.0	25.8	28.8	31.2	32.8
828/871/Z	Silica	0	61.1	65.4	71.0	77.5
		12.0	48.0	52.8	56.4	60.6
		26.6	36.5	39.2	42.4	44.8
		45.0	23.8	24.2	27.2	28.8
828/Z	Phenoxy	0	51.8	53.3	58.0	61.4
		10	51.0	52.6	57.7	61.7
		15	50.2	53.9	60.3	62.2
		20	53.2	54.6	60.0	61.6
828/DDS	Silica	0	49.2	51.5	58.9	62.0
		55.8	16.9	17.0	17.9	18.9
		62.0	14.4	14.5	16.6	16.8
		68.3	11.6	11.6	12.6	12.4
828/DDS	Beta-Eucrydtite	0	47.2	51.5	58.9	62.0
		54.3	16.5	17.7	19.5	20.0
		60.0	13.0	14.7	10.4	20.6
		66.7	9.8	10.7	12.5	12.3

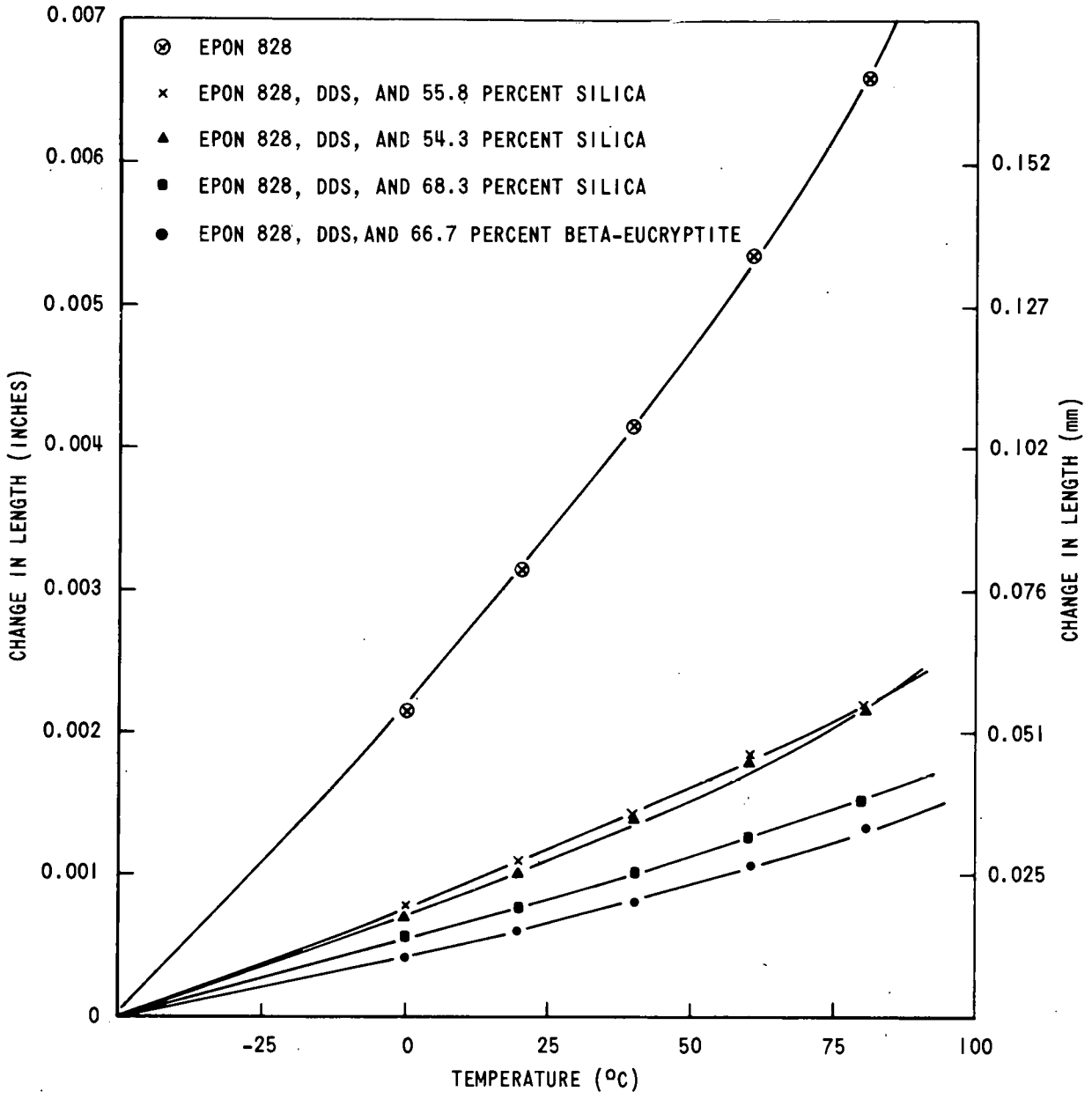


Figure 12. Effect of Temperature on the Change in Length of CTE Test Specimens

with temperature curve for 828/DDS with silica and beta-eucryptite fillers at two concentrations. As the filler concentration increases, the CTE becomes more linear for the silica and beta-eucryptite fillers. The phenoxy filler did not alter the CTE either way. The silica and beta-eucryptite are mineral fillers with CTE much lower than that of the epoxy. The mineral fillers tend to have CTE that changes little over a wide temperature range. In this study the temperature range of -50 to 80°C was of interest. Over this range the CTE of the silica and the beta-eucryptite are constant. Therefore, as the concentration of the filler is increased the CTE of the composite becomes less dependent upon the temperature.

The phenoxy is chemically similar to an epoxy and is similarly affected by temperature changes. The test data show no difference in test value for up to 20 percent-by-volume of the phenoxy. The other polymeric fillers were not tested at different concentrations. However, the CTE of the polymers tested does depend upon the temperature range and the filler concentration should not decrease the effect of temperature.

The data in Table 1 show that the type of resin and curing agent can influence the CTE of the cured mixture. The four resins and six curing agents were selected to represent different types of materials commercially available. Many material properties, including thermal expansion, are influenced by the chemical structure of the polymer. The polymers with high crosslink density and aromatic structures are, as a rule, more thermally stable than difunctional, aliphatic polymers. The test results in Table 1 show this trend.

By choosing Epon 828 with Z hardener as a standard, the CTE can be increased about 20 percent by blending with a more flexible resin (Epon 871) and decreased about 6 percent by using a more rigid resin (DEN 431). The flexible resin selected was Epon 871 which is a relatively long chain, difunctional epoxy resin. The Epon 828 is commonly added to Epon 828 to increase the flexibility of the system. The addition of the Epon 871 should and does increase the CTE of the Epon 828/Z mixture.

The novolac resin DEN 431 is a multifunctional aromatic resin commonly used in high temperature applications. All of the formulations with the DEN 431 and fillers included a small amount (about 6 percent) of a reactive diluent RD4 to help reduce the viscosity. The same amount of diluent was added to the Novolac for the measurement of CTE of the resin only. The RD4 diluent was selected because it reportedly does not alter physical properties or heat distortion temperatures of the base resin. However, no CTE measurements were made with only the DEN 431/Z system.

The small difference in the CTE of the bisphenol A type (Epon 828) and the novolac type (DEN 431) is due to the relatively low temperature of CTE

measurement. At temperatures greater than the 80°C limit, the effect of temperature will be less on the novolac, and the difference between the CTE of Epon 828 and DEN 431 will be greater.

Six curing agents were tested with Epon 828. Curing agents with both low and high functionality and aromatic and aliphatic structures were tested. Only the Versamid 140 seemed to make any significant difference in the CTE of the Epon 828. The Z hardener, diethylenetriamine, Hysol 3471, diaminodiphenylsulfane, and nadic-methyl anhydride all have similar CTE.

The cure temperature was thought to influence the CTE. To check the effect of cure time and temperature on the CTE of an epoxy resin, Epon 828 and Z hardener were cured at three temperatures with three formulations of silica (GP7) and beta-eucryptite. The temperatures were 8 hours at 160°F (71°C), 2 hours at 160°F (71°C) plus 2 hours at 200°F (93°C) and 2 hours at 160°F (71°C) plus 2 hours at 250°F (121°C). The test results are given in Table 9 and show no difference in the CTE of the filled resins at the three cure temperatures.

The choice of resin-curing agent combination has a definite and significant influence on the CTE of the filled system. Figure 2 shows this influence. Without any filler the CTE of the mixture (ordinate) is identical to the CTE of the resin-curing agent (abscissa). As filler (GP7 silica) is added the CTE of the mixture decreases. The limit is a line parallel to the abscissa and intersecting the ordinate at the CTE of the filler. Six resin-curing agent combinations are plotted for two temperature ranges.

The data in Figure 2 show that the type of resin and curing agent will significantly influence the CTE of filled epoxies. However, this effect is not as great as the effect of concentration. Data from two temperature ranges are shown in Figure 2. The curves shown depend only on the filler concentration; the CTE does change with the temperature range, but the CTE resin-curing agent versus CTE mixture relationship holds for a constant filler concentration.

The type of filler does affect the CTE of the epoxy-filler mixture (Figures 3 and 4). Figure 3 shows the CTE of the mixture as a function of filler CTE for three resin-curing agent combinations at 5.7 percent-by-volume concentration. The CTE of the mixture increases as the CTE of the filler increases. In Figure 3 the relationship looks almost linear. However, Figure 3 is a plot of data for a low concentration of filler. Figure 4 shows CTE of filler versus CTE mixture for Epon 828/Z hardener for four concentrations. The effect of the CTE of the filler is not linear, but depends upon the concentration of filler.

The fillers selected for the materials with CTE equal to and greater than the epoxy resins were polymeric fillers with physical properties of the same

Table 9. Effect of Cure Time and Cure Temperature on CTE of Epon 828 and Z Hardener With Various Fillers and Filler Volumes

Filler	Filler Volume (Percent)	Cure Time	Coefficient of Thermal Expansion (μm/m/°C)	
			-50 to 20°C	20 to 80°C
Control	0	1*	49.0	62.5
Silica	12.0	1	39.6	48.8
	26.7	1	29.9	37.4
	45.0	1	20.3	24.8
	12.0	2**	39.1	47.3
	26.7	2	29.5	38.7
	45.0	2	20.3	24.8
	12.0	2	39.1	47.3
	26.7	2	29.5	38.7
	45.0	2	20.3	24.3
	12.0	3***	38.5	48.6
	26.7	3	28.8	39.2
Silica	45.0	3	21.2	27.9
Beta-Eucryptite	11.1	1	40.5	51.0
	25.0	1	31.1	40.1
	42.9	1	20.3	25.7
	11.1	2	40.5	49.5
	25.0	2	31.6	38.5
	42.9	2	20.4	25.9
	11.1	3	39.8	49.0
	25.0	3	31.0	38.0
Beta-Eucryptite	42.9	3	20.0	36.1

*Cure time 1 is 8 hours at 160°F (71°C)
**Cure time 2 is 2 hours at 160°F followed by 2 hours at 200°F (93°C)
***Cure time 3 is 2 hours at 160°F followed by 2 hours at 250°F (121°C)

order of magnitude as the epoxies. The mineral fillers have compressive strengths and moduli much greater than the epoxy or polymeric fillers.

Increasing the amount of silica filler will reduce the CTE of the mixture. Increasing the amount of phenoxy in the Epon 828 does not change the CTE since the two materials have nearly identical expansion rates. Increasing the amount of Teflon will increase the CTE of the mixture, but not by an amount equal to the silica filler. The Teflon wants to expand, but it is restrained by the epoxy and the resulting CTE is less than expected. The lack of adhesion of the epoxy to the Teflon is also significant. Adhesion of matrix to filler is discussed below.

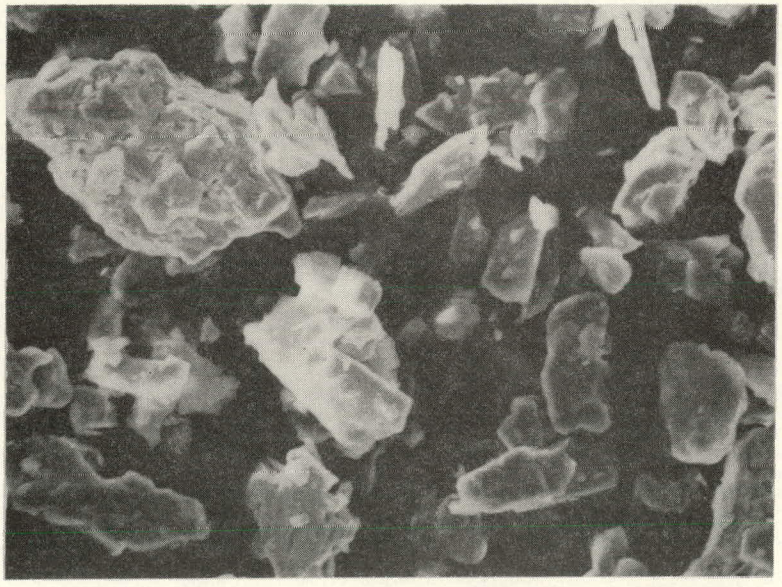
The compressive properties given in Table 3 show the same trends. The silica filler will reinforce the epoxy resin and give higher compressive strength and higher moduli to the mixture. The phenoxy does not change the compressive properties, while the Teflon tends to weaken the composite regardless of the resin and curing agent used.

The amount of filler that can be added to a resin-curing agent blend has a significant affect on the CTE. In fact, the filler concentration is the most significant variable and is easy to control. As the amount of filler is increased, the CTE of the mixture approaches that of the filler itself. The limiting factor is the processing of the mixture. High filler loadings result in extremely viscous materials that require elevated temperatures for processing. The amount of filler that can be added depends upon particle size, particle size distribution, and surface preparation. These are recognized as important variables, but no attempt was made to determine exactly how they influence the processing characteristics and maximum concentration possible.

With the silica and beta-eucryptite fillers, concentrations of almost 70 percent-by-volume with mixture CTE of 10 μm/m/°C were possible. However, with the mica filler the greatest concentration was 38 percent-by-volume. Slightly higher loadings would be possible, but for ease of processing the testing was terminated at 50 percent-by-weight. The difference in filler loading and ease of processing is caused by the particle shape of the silica, beta-eucryptite, and mica fillers. Figure 13 shows scanning electron microscope (SEM) photographs of the three fillers. The mica filler has a very definite plate-like shape while the silica and beta-eucryptite are more spherical. The surface area to volume ratio is much greater for the mica and a mixture of mica with epoxy is more viscous than the same concentration of silica or beta-eucryptite in epoxy.

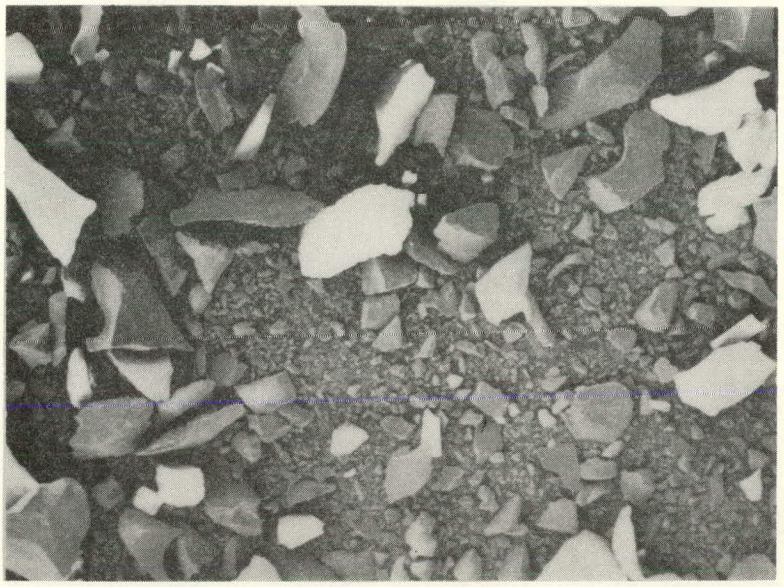
No attempt was made to find the maximum concentration of the polymeric fillers. However, the maximum amount for ease of processing was just

BETA-EUCRYPTITE (1000X)

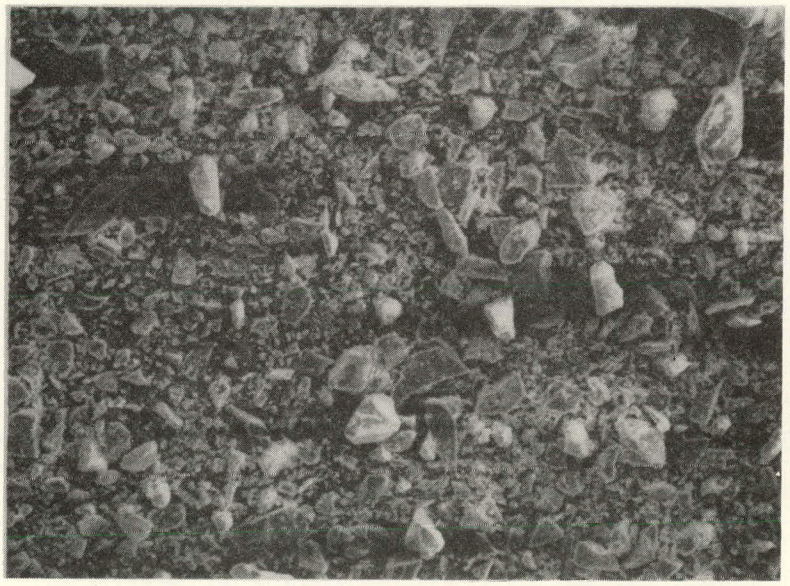


MICA (1000X)

Figure 13. Photomicrographs of Silica, Mica and Beta-Eucryptite Fillers



GP 15 (1000X)



GP 7 (300X)

Figure 13 Continued. Photomicrographs of Silica, Mica and Beta-Eucryptite Fillers

about 20 percent-by-volume for the four polymers tested. Almost 22 percent of Teflon was added to a blend of Epon 828 and Hysol 3471, while 18 percent was all the polyimide that could be incorporated. The wetting of the polymer by the epoxy is the most probable reason for the low volume of filler.

Without any filler the CTE of the mixture is equal to the CTE of the epoxy and curing agent alone; without any matrix material the CTE of the mixture is equal to the CTE of the filler alone. The relationship between the CTE of mixture and volume concentration of filler is not linear. As shown in Figures 5 and 6, the CTE of the mixture at a given concentration of filler is always somewhat less than for a linear relationship. It seems logical that the CTE of the mixture would be equal to the CTE of the epoxy times its volume fraction plus the CTE of the filler times its volume fraction. However, this relationship is not true. No reason for the nonlinear relationship is known, but the adhesion of the epoxy to the filler may alter this relationship.

At the higher temperature range of 20 to 80°C (Figure 5) the difference in the CTE of the mica, silica, and beta-eucryptite is not evident. At the lower temperature range (Figure 6) the mixture with beta-eucryptite filler definitely has a lower CTE than the mixtures with silica or mica fillers.

The silane adhesion promoters and the epoxy precoat materials did not change the CTE of the mixture. The CTE of the untreated material is the same as the treated material. At the 35 percent-by-volume concentration level the A-1100 silane and the control sample are essentially equal and fall on the same curve as earlier data. At the 50 percent-by-volume level the test values for the control, A-187 silane, Epon 828, and RD4 precoats are different from the data taken previously for the base line curve. No data was taken for the untreated GP7 silica with Epon 828/Z at greater than 44 percent-by-volume. The base line curve in Figure 10 is extrapolated to the 50 percent level. This could explain part of the difference between the base line and the precoat test values. Part of the difference could be due to experimental or testing error. In either case, the precoating to promote adhesion did not reduce the CTE of the mixture. The DC200 silicone fluid did prevent adhesion of the epoxy to the silicone. The two data points for the DC200 precoat are significantly different from the base line curves, which indicates that the lack of adhesion will increase the CTE for a given filler loading.

A considerable amount of work has been done to characterize or to understand the relationship between particle packing, particle size, and particle size distribution. Some of the properties of the six silica and three beta-eucryptite fillers are listed in Tables 5 and 6. The relationship between bulk density, tap density, and the ease of processing of maximum filler possible was not as expected. All the silica fillers have the same true density. The GP13 and GG50/100 had the highest bulk and tap densities which would

mean closer packing of the individual particles. This would logically indicate that the packing would be better in an epoxy matrix rather than air. However, the GP13 and the GG50/100 were the most difficult to process and could not be filled to the high concentrations. The GP3 and GP7 with the lowest bulk and top densities were the easiest materials to work with and the high filler loadings of 68 and 70 percent-by-volume were attained with the GP3 and GP7 fillers.

The particle size distributions by micromerograph for the six silica fillers are shown in Figure 14. The GP13 and the GG50/100 have the largest average particle sizes (30.8 microns [micrometers] and 35.0 microns) and the distribution is skewed toward the larger size particles. The GP3 and GP7 have a more normal distribution.

The three cuts of beta-eucryptite are all about the same size. The average particle size varies from 2.6 microns to 9.5 microns. The size distribution curves shown in Figure 15 for the standard beta-eucryptite and the smaller size lot are similar. The lot with the larger average size particle has a different distribution curve, but all three fillers had similar processing characteristics.

A difference in processing due to differences in surface area, and size distribution of the fillers was expected. However, the tests made to determine the effect of size and size distribution on the CTE of an epoxy show an apparent variation in CTE with the type or size of silica filler used.

The tests results are listed in Table 7 with a portion of the data shown in Figure 11. Regardless of the test temperature range and concentration, the smaller size fillers GP3 and GP7 have the highest CTE. The data for the Epon 828 and 3471 curing agent yields a smooth curve with larger particle sizes having lower CTEs. However, the data for Epon 828 and Z at 44 percent concentration shown wide variation in CTE. These data show a difference in CTE depending upon the type of silica filler used, but the effect of particle size and size distribution cannot be separated.

ACCOMPLISHMENTS

The coefficient of linear thermal expansion of epoxy casting materials has been shown to depend upon the type of filler, the type of resin and curing agent, the filler concentration, filler surface preparation, and filler particle size. The CTE of an epoxy-curing agent system can be increased or decreased by proper selection of the filler type and concentration. The addition of any filler, with a CTE different from the matrix material, will

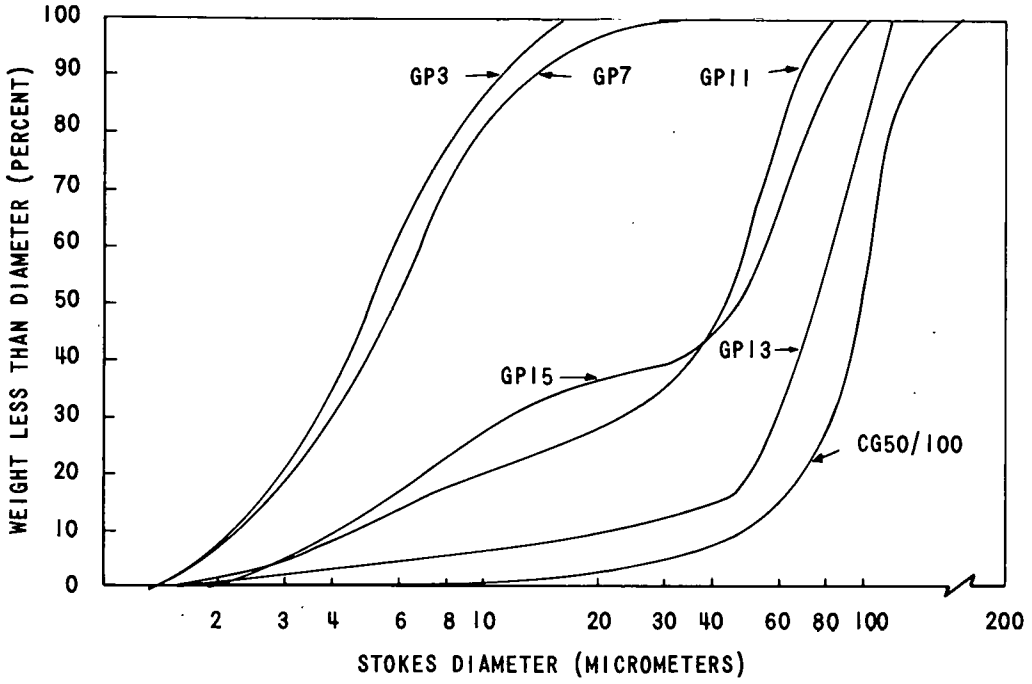


Figure 14. Particle Size Distribution of Silica Fillers by Micromerograph

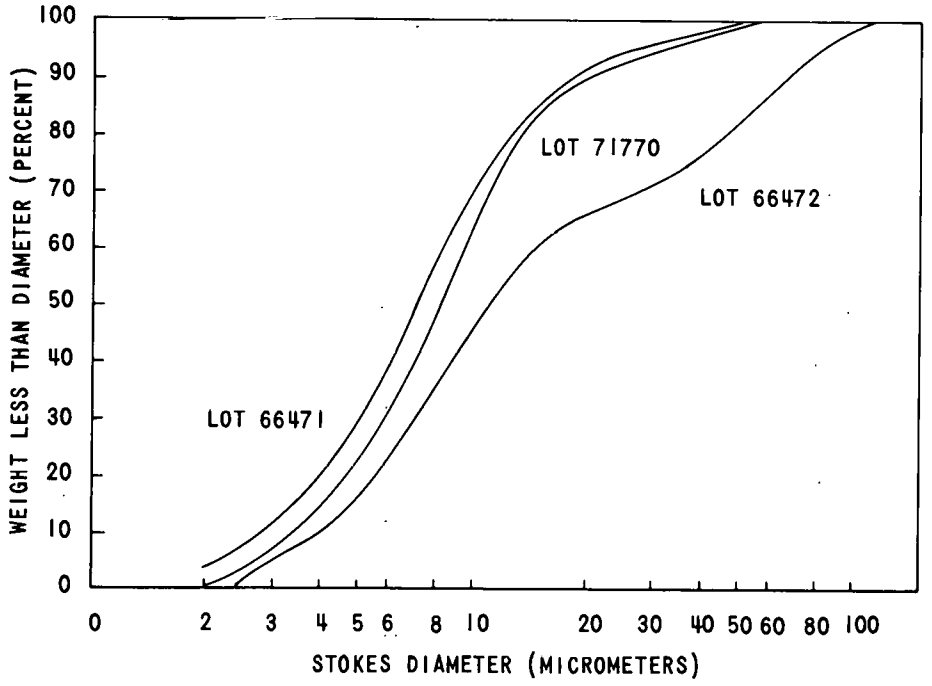


Figure 15. Particle Size Distribution of Beta-Eucryptite Fillers by Micromerograph

influence the CTE of the composite. It is possible to formulate and process a castable epoxy with a CTE between 10 and 80 $\mu m/m/^{\circ}C$ to match the CTE of encapsulated items.

FUTURE WORK

The coefficient of thermal expansion of a filled epoxy has been shown to depend primarily upon the type of filler, type of resin and curing agent and the filler concentration. The particle size and size distribution seem to have an effect upon the CTE of the mixture but the results were inconclusive. The scope of this work was limited to commercially available materials. Additional effort is needed to screen fillers into narrow particle size cuts and to blend these discrete particle sizes into distributions that theoretically will give optimum packing. By this method the effect of particle size and size distribution could be separated and evaluated.

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U. S. Patent 3,547,871, C. F. Hofman, "Highly Filled Casting Composition", December 15, 1971.

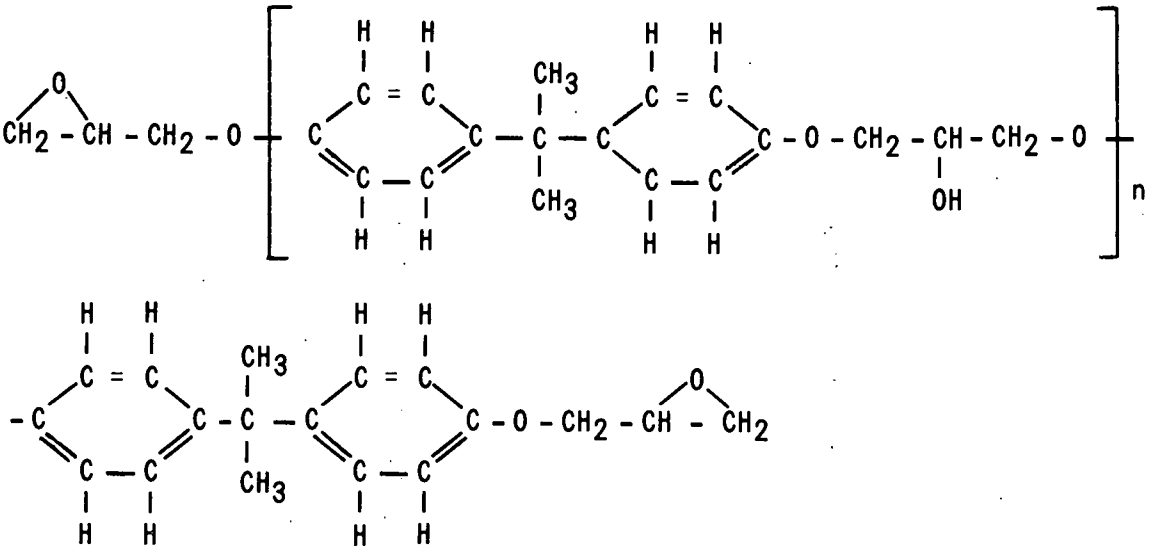
Appendix A

DESCRIPTION OF MATERIALS

EPOXY RESINS

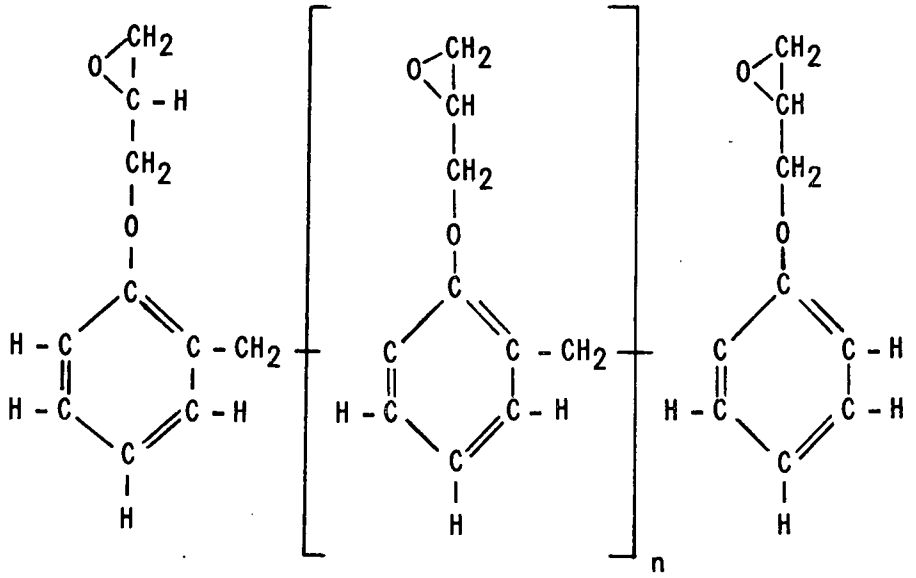
Many different epoxy resins have been synthesized and are commercially available. Four commonly used and readily available epoxy resins were tested.

The most important is Epon 828 made by Shell Chemical Company. Epon 828 is a general purpose resin made from epichlorohydrin and Bisphenol A, and has an epoxide equivalent of about 187 and a functionality of about 1.85. This means that not all the molecules have two epoxide groups attached. The ideal structure is shown below.



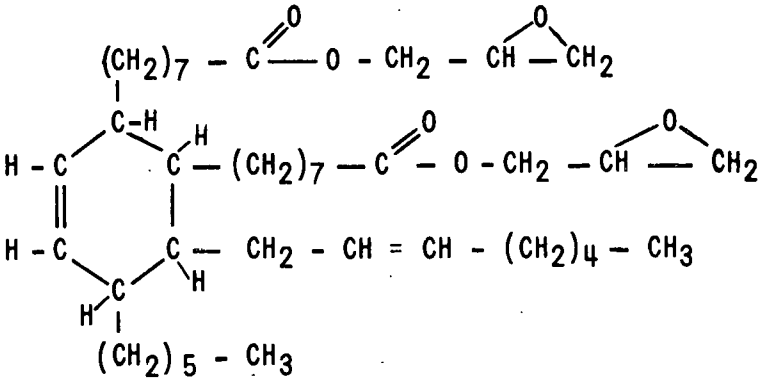
DIGLYCIDYL ETHER OF BISPHENOL A

Novolac epoxy resins are made from a novolac resin and epichlorohydrin with the ideal structure shown below. The novolac resin tested was DEN 431 made by Dow Chemical Company. DEN 431 has an equivalent weight of about 175 and a functionality of about 3.3. At room temperature the DEN 431 is a very viscous liquid.



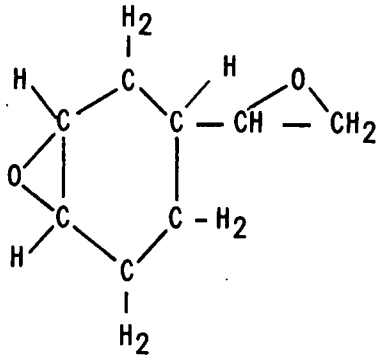
NOVOLAC EPOXY

Flexible epoxy resins are made from long chain resins. The flexible resin used in this study was Epon 871 made by Shell Chemical Company. The Epon 871 is an aliphatic polyepoxide made from diglycidal ether of linoleic dimer acid with the ideal structure given below. The viscosity of Epon 871 at room temperature is about 600 centipoise (0.6 Pa·s) and the epoxide equivalent is about 440.



DIGLYCIDYL ESTER OF LINOLEIC DIMER ACID

Diluents are used primarily to reduce the viscosity of other epoxy resins. The diluent used in this study was RD4 made by Ciba Products Company. The RD4 is vinyl cyclohexene dioxide with an equivalent weight of 77 and a functionality of 2. The ideal structure is given below.

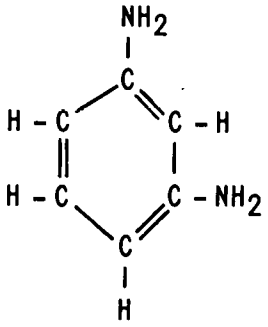


VINYL CYCLOHEXENE DIOXIDE

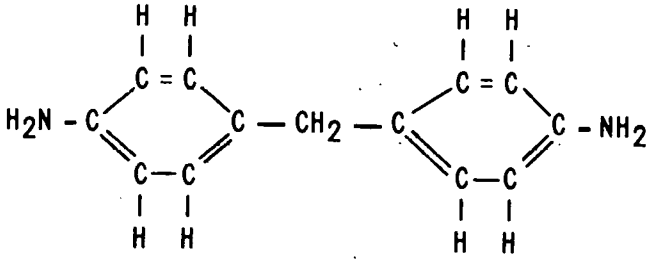
CURING AGENTS

Five different curing agents were tested. These curing agents included aliphatic and aromatic types with both room temperature and elevated temperature cures.

Shell Z is a proprietary material made by Shell Chemical Company. It is an aromatic amine made as a liquid eutectic from a blend of methylenedianiline and m-phenylenediamine. The structures of these two amine compounds are shown below.

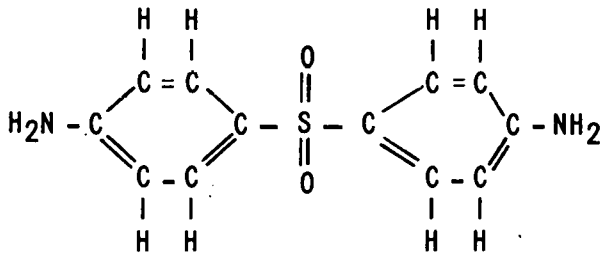


m-PHENYLENEDIAMINE



4, 4'-METHYLENEDIANILINE

Diaminodiphenylsulfone (DDS) is a solid aromatic primary amine with a melting point of 175°C.

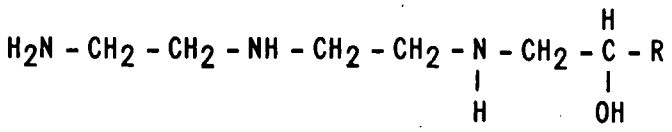


DIAMINO DIPHENYL SULFONE

Diethylene triamine (DETA) is a liquid aliphatic amine with a functionality of 5 and a chemical structure as shown below.

DIETHYLENE TRIAMINE

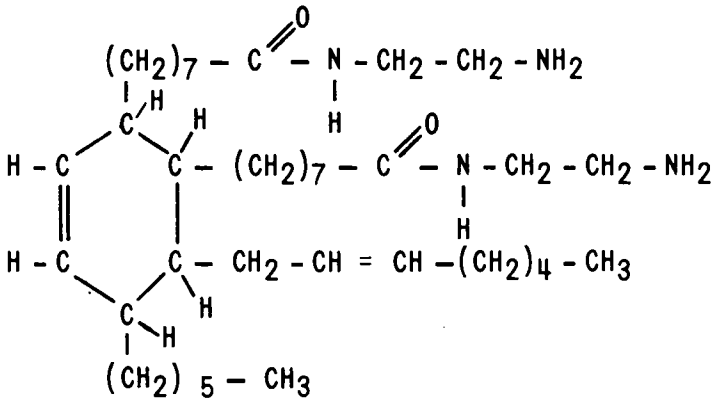
Hysol 3471 is a proprietary material made by the Hysol Company. It is an aliphatic amine made from diethylenetriamine and a low molecular weight mono-epoxy. This adduct has lower volatility and lower exotherm temperature during cure than the diethylenetriamine alone.



R = LOW MOLECULAR WEIGHT ORGANIC UNIT

DIETHYLENE TRIAMINE ADDUCT

Versamid 140 is a polyamide resin made by General Mills Company. This polyamide resin is made from a dimerized fatty acid and an aliphatic polyamine, and is a room temperature curing material used to add flexibility to an epoxy system.



FATTY POLYAMIDE

FILLERS

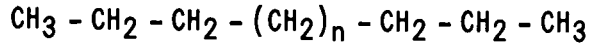
Several different types of filler were evaluated. Parts of the fillers had CTE greater than the CTE of the base epoxy-curing agent systems, while some had CTE equal to and less than the CTE of the epoxy. The bulk of this work was with fillers that have CTE much less than the CTE of the epoxy-curing agent system.

The fillers with low CTE were silica, beta-eucryptite, and mica. Six different average particle size silica fillers were tested. The silica fillers used were made by Glasrock Products Incorporated from a high purity process. The fillers were ground fused silica with a 99.6 percent silicon dioxide content. The CTE is about 0.5 to 1.0 μm/m/°C and the specific gravity is about 2.21. The six fillers evaluated had average particle sizes of 1.2 to 35 micrometers.

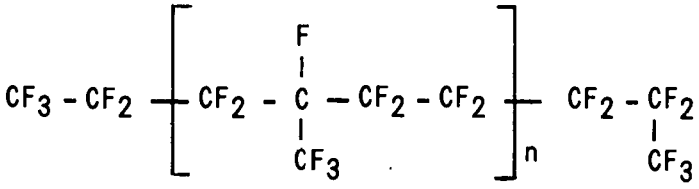
The beta-eucryptite is a crystalline lithium aluminum silicate with 95 percent of the form $Li_2O\ Al_2O_3\ SiO_2$ and with the remaining 5 percent some other form of lithium aluminum silicate. Beta-eucryptite is one of the few materials with a negative coefficient of thermal expansion. The CTE is a negative 5 to 7 μm/m/°C while the specific gravity is about 2.40.

The mica is a ground Muscovite mica of the form $KAl_2AlS_3O_{10}(H_2O)_2$. The CTE of the mica is about 3.0 μm/m/°C and the specific gravity about 2.8.

Polyethylene and fluorinated ethylene propylene (Teflon) powders were tested to determine the effect of fillers with CTE greater than the CTE of epoxy resins. The CTE of polyethylene is about 180 μm/m/°C and the specific gravity about 0.92. The CTE of Teflon is about 100 μm/m/°C and the specific gravity about 1.15.

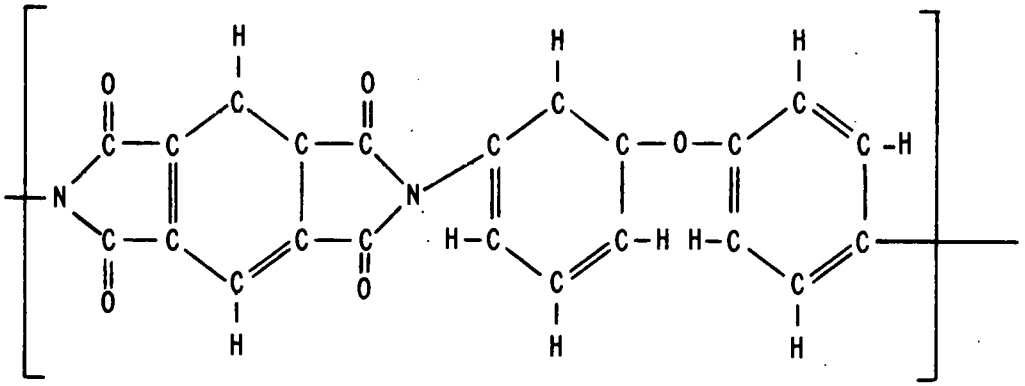


POLYETHYLENE

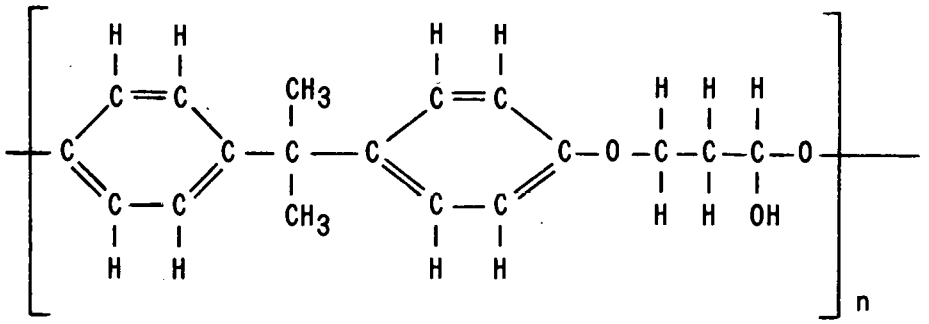


FLUORINATED ETHYLENE PROPYLENE

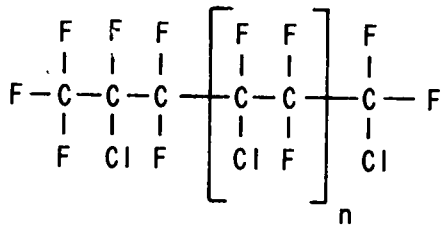
Polyimide, phenoxy, and polytrifluorochlorethylene powders have coefficients of thermal expansion of 54, 58, and 81 μm/m/°C and specific gravities of 1.47, 1.2, and 2.12, respectively. These powders were tested as fillers with CTE similar to that of the epoxy-curing agent mixture. Their structures are given below.



POLYIMIDE



PHENOXY

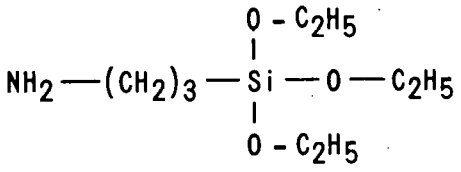


POLYTRIFLUOROCHLOROETHYLENE

COATINGS

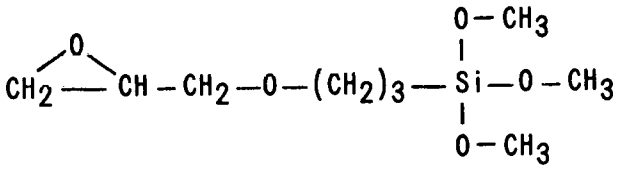
In one series of tests the dried silica fillers were coated with either a silane coupling agent or an epoxy resin to ensure wetting of the filler. The following coatings were tested.

A-1100 made by Union Carbide Corporation. The A-1100 is a gamma-aminopropyltriethoxysilane with the following structure.



GAMMA-AMINOPROPYLTRIETHYOXYSILANE

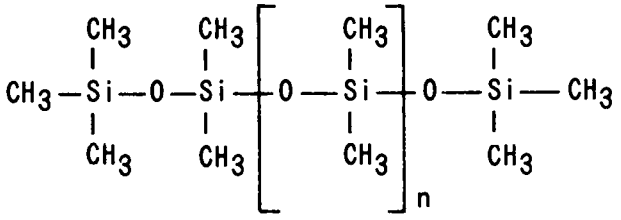
A-187 made by Union Carbide Corporation. The A-187 is a gamma-glycidoxypropyltrimethoxysilane with the following structure.



GAMMA-GLYCIDOXYPROPYLTRIMETHOXYSILANE

Epon 821 and RD4 are epoxy resins used throughout this study.

DC200 Fluid made by Dow Corning Corporation. DC200 is a dimethyl silicone fluid with the following structure.



DIMETHYL SILICONE FLUID

Appendix B

TEST METHODS

ASTM D/696, Coefficient of Linear Thermal Expansion of Plastics

ASTM D/695, Compressive Properties of Rigid Plastics

ASTM D/153, Specific Gravity of Pigments

ASTM B/212, Apparent Density of Metal Powders

ASTM B/330, Average Particle Size of Refractory Metals and Compounds by the Fisher Sub-Sieve Sizer

Surface Area by Orr Surface-Area, Pore-Volume Analyzer, Model 2100

Size distribution by Sharples Micromerograph made by Franklin Electronics

Size distribution by Coulter Counter Model T made by Coulter Electronics, Incorporated