

# **Microparticle and Fiber Reinforcement of Epoxy Resins**

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# Microparticle and Fiber Reinforcement of Epoxy Resins

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Abstract: Microparticle and fiber materials have been investigated as reinforcing agents for a diglycidyl ether of bisphenol A type of epoxy resin. These materials were limited to low concentrations in order to insure retention of the resin binder properties, such as viscosity and pot life, required for glass-filament-winding processes. In general the material screened did not substantially improve the compression properties of the cast resin as compared to the best unfilled controls. The greatest improvement was achieved with colloidal boehmite alumina and Hi-Sil X303 silica, when the stoichiometric amount of amine curing agent was used. The alumina was superior to the silica in increasing the resin modulus of toughness, but the silica gave higher values for the compression yield and ultimate strengths.

The highest values for the compression properties of the unfilled resin controls were obtained when 78% of the stoichiometric amount of m-phenylene diamine (CL) curing agent and a critical "B" stage curing temperature were used.

As indicated by a limited study, "flaw sensitivity" or surface imperfections may significantly influence the compression strength of unfilled cast resin test specimens, whereas these effects were negligible with specimens containing Hi-Sil X303 silica.

Experiments to determine the effect on the interlaminar shear strength of glass-filament NOL rings wound with resins containing colloidal boehmite alumina and Hi-Sil X303 silica were inconclusive because of the high void content of state-of-the-art wound NOL rings.

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## INTRODUCTION

Glass reinforced plastics are promising structural materials for the fabrication of deep submergence vehicles because of their high strength-to-weight ratios. However, in order to compete in this service they will be required (a) to sustain high compressive loads for long periods of time, (b) to sustain repeated stress cycling, both in tension and compression, (c) to have high shock resistance, and (d) to be highly resistant to the environmental conditions encountered at sea. These broad general requirements indicate that for the most part the composite structure must meet even more stringent and diverse specifications than those required for large internal pressure vessels, such as the glass-filament-wound Polaris motor case. The latter vessel is subjected primarily to tensile stresses, and the glass-filament reinforcement carries the bulk of the load, with the resin acting essentially as a binder and as a medium for transmitting stresses to the glass-filament reinforcement. Evidence has accumulated, however, that for external pressure vessels

the full compressive load must be transmitted and distributed more uniformly throughout the structure on both the reinforcement and resin alike. Consequently, the strength of the resin system becomes an important factor in determining the ultimate strength of the composite, even though the resin content is low compared to that of the glass filament reinforcement.

For example, Prosen, Mureller, and Barnet (1) have shown that the resin system is probably one of the most important parameters in establishing interlaminar shear and compressive strength levels in glass-reinforced-plastic (G.R.P.) composites. Data obtained by Fried and Kaminetsky (2), in studying the influence of material variables on the compressive properties of simple parallel reinforced plastics, indicate that the point at which the resin "yields" or flows determines to a large extent the load carrying capacity of the composite, since support of the low compressive strength glass filament reinforcement is reduced and buckling ensues, resulting in catastrophic failure of the composite.

Research directed toward the synthesis of stronger resins suitable for the filament-winding process is being vigorously pursued at several laboratories as one approach to maximizing the

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NRL Problem C03-19; Project SR 007-03-04-1008. This is an interim report on one phase of the problem; work on the problem is continuing. Manuscript submitted March 1, 1966.

strength of G.R.P. composite vessels. At this Laboratory, efforts are being directed toward increasing the strength of the resin matrix by the prewinding reinforcement of the present state-of-the-art resin binders with materials having fine particle or fiber structure and/or materials capable of reacting with the resin molecules. The concentration of these materials in the resin are such that those properties of the liquid resin system required for the filament winding or pre-preg processes are reasonably retained. In particular the relatively low resin viscosities required for the proper impregnation of the glass filaments limits the maximum quantity of reinforcement material which can be incorporated. Another limiting factor is that the pot life of the resin be unaffected by the additive, or at least not decreased appreciably.

#### EPOXY AND CURING SYSTEMS USED FOR FILLER EVALUATIONS

The epoxy compound selected for the reinforcement studies was the diglycidyl ether of bisphenol A, DER332LC.\* This is a low-chlorine-content compound. Two batches were used in the course of this study, one analyzing for an epoxide equivalent weight of 174 and the other for 169. The compounds were filtered prior to use through a No. 40 Whatman filter paper, which removed a small amount of filterable impurities.

Two curing systems were used: an amine, m-phenylene diamine (CL),† and an anhydride system, hexahydrophthalic anhydride (HHPA) catalyzed with benzyldimethylamine (BDMA). Most of the data contained in this report were obtained with the amine curing system.

#### TEST PROCEDURES

The compressive properties of the epoxy resins were determined according to the ASTM D695-54 procedure using an Instron testing machine and a Baldwin subpress.

The ASTM D638-60T procedure was used for measuring the few tensile properties included in the study. The tensile test specimens were axially aligned in the grips of the testing machine (Fig. 1)

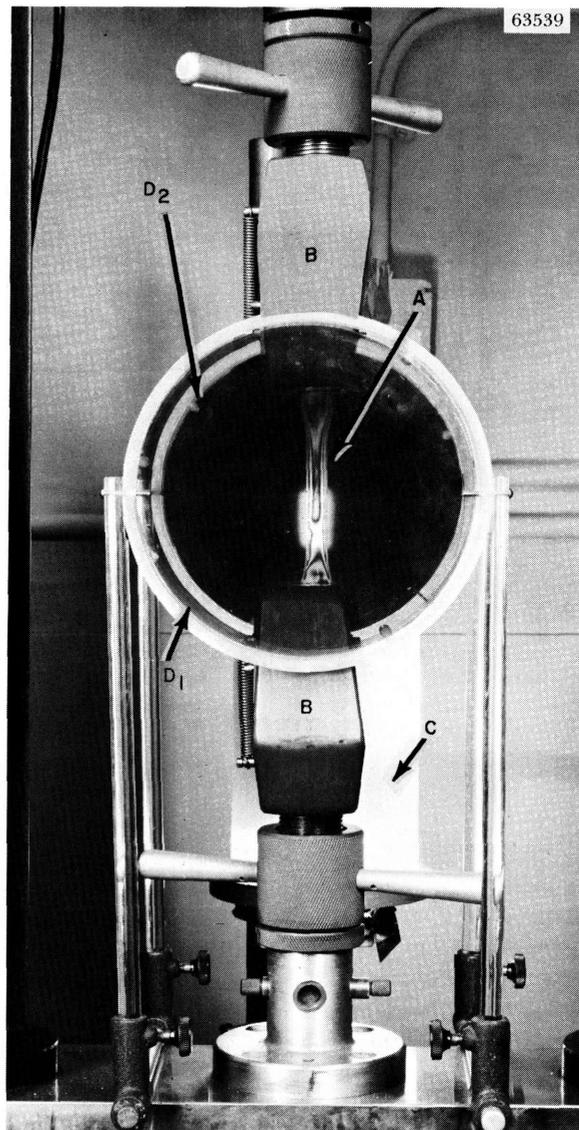


Fig. 1 - Tensile specimen alignment apparatus in an Instron testing machine: (A) tensile dumbbell test specimen showing birefringence lines; (B) testing machine tensile specimen grips; (C) sodium light source; (D<sub>1</sub>) Polaroid film and 1/4-wavelength plate forward of the test specimen, and (D<sub>2</sub>) Polaroid film and 1/4-wavelength plate back of the test specimen.

by a photoelasticity technique of placing the gripped specimen between two sets of film, each consisting of a Polaroid film and 1/4-wavelength plate, through which was passed the monochromatic light of a sodium lamp. With this arrangement the stress birefringence lines could be observed as they developed when a slight

\*Dow Chemical Company, Midland, Mich.

†Shell Chemical Corporation, New York, N.Y.

tension was applied to the specimen and the position of the specimen within the grips corrected for axial alignment.

Interlaminar shear strength was determined by the NOL horizontal shear measurement procedure (3) on segments cut from standard NOL type rings. The rings were wound directly on NOL ring winding equipment and also were cut from cylinders wound on a Lamtex\* filament-winding machine.

The modulus of toughness (4),  $E_T$ , was calculated from the stress-strain curves using a planimeter and the equation

$$E_T = \frac{\text{stress (psi)} \times \text{strain (in./in.)} \times \text{area under curve}}{\text{total area}}$$

### PREPARATION OF THE TEST SPECIMENS

The standard procedure for preparing the compression and tensile test specimens, unless other-

\*Lamtex Corporation, Farmingdale, N.Y.

wise indicated, was to add the microparticle filler to the melted epoxy compound (ca. 50°C) in an Eppenbach shear mixer and stir for 30 minutes. The curing agent was then added, first with hand mixing, and then by further mixing during vacuum deaeration in the modified Rinco High Vacuum Rotating Evaporator shown in Fig. 2. The compression or tensile specimens were cast by carefully transferring the deaerated resin mix through a stopcock arrangement in the deaeration flask to the polished steel molds shown in Fig. 3. One inch by 0.5 inch compression plugs having planar parallel ends were machined from the 2 inch by 0.5 inch rods obtained from the molds. Machining of the tensile dumbbells was required only on the open side to conform to the ASTM dimensions prescribed in D638-60T (5), Type I, for specimens with thicknesses 1/4 inch or under. The dumbbells were finished by positioning the cast specimens on the bed of a surface grinder using double-coated pressure-sensitive tape.

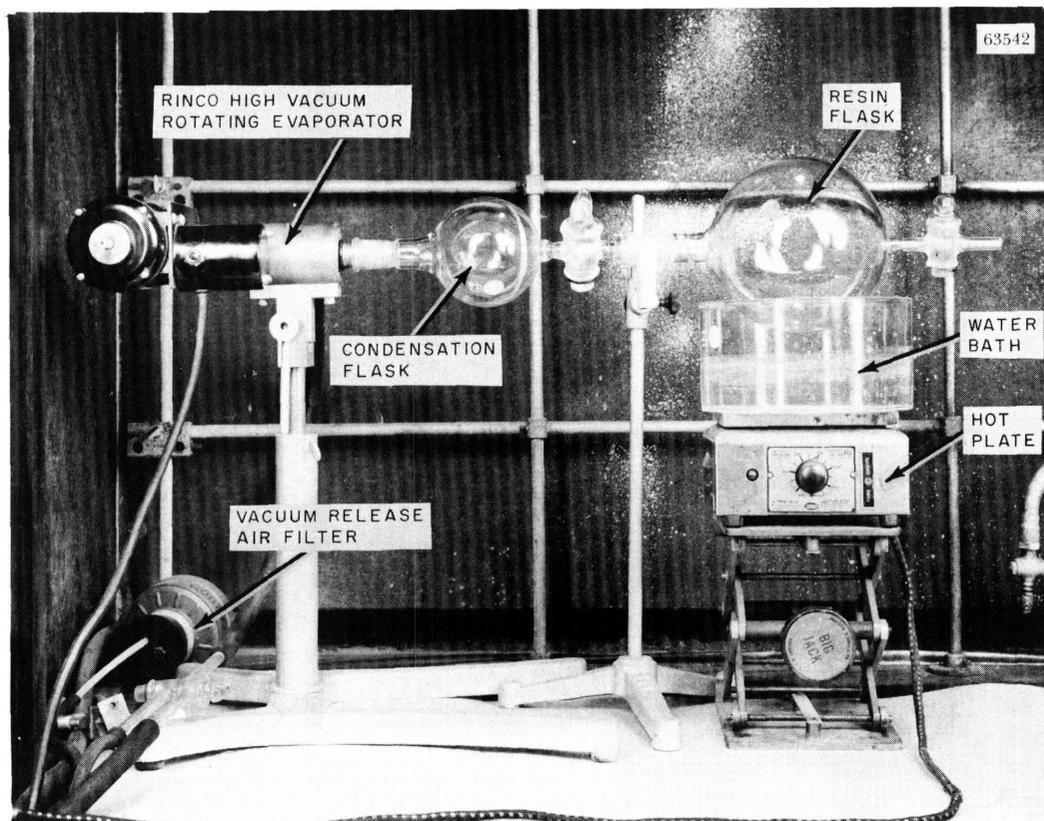


Fig. 2 - Epoxy resin deaeration and mixing apparatus

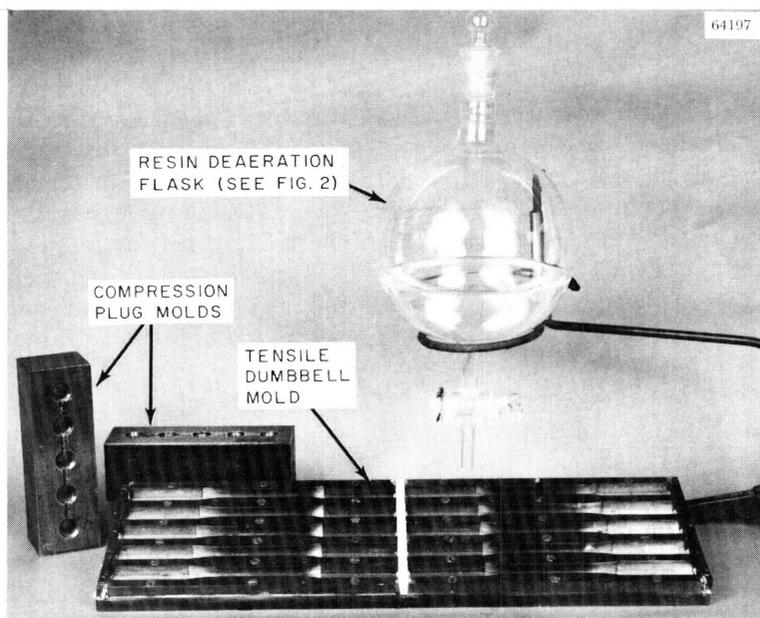


Fig. 3 — Apparatus and molds used for casting epoxy tensile test dumbbells and compression plug test specimens

### THE EFFECT OF CURING CONDITIONS ON THE COMPRESSIVE PROPERTIES OF EPOXY RESINS

In the early stages of this project the stoichiometric amount of *m*-phenylene diamine (CL) was used to cure the resin. As will be discussed later, quite substantial increases in the ultimate compressive strength of microparticle reinforced cast resins were obtained relative to the unfilled control epoxide using this curing system. Later, however, the improvements obtained with the reinforcing materials were essentially equaled merely by decreasing the ratio of curing agent to epoxy compound in unreinforced compositions. Figure 4 illustrates how changes in this ratio affect the compressive properties of the cured unfilled resin. The yield strength is varied only by a few percent, whereas the ultimate compressive strength is improved in some instances by more than 50% at a concentration of amine curing agent of 12.5 parts per hundred (phr), which is approximately 78% of the stoichiometric amount.

However, this increase in compressive strength is achieved only over a short range of "B" stage curing temperatures, as shown in Fig. 5. The effect of varying the "B" stage temperature was negligible, however, when the stoichiometric

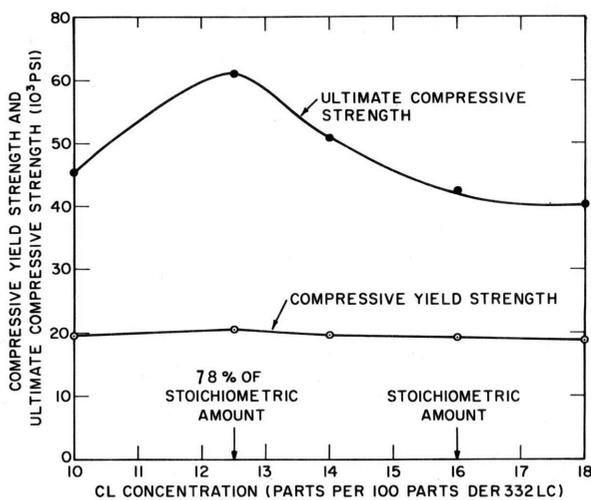


Fig. 4 — Effect of varying the concentration of the curing agent on the compressive yield strength and on the ultimate strength of DER332LC/CL epoxy resin. Cure: 16 hr at 128°F ("B" stage), 1 hr at 180°F, and then 3 hr at 340°F.

amount of CL was used for curing the resin. The reason for this was not fully understood, but under these conditions the excess of curing agent over the optimum amount, perhaps acting as a diluent, may have masked the "B" stage temperature effect. The final curing temperatures were less

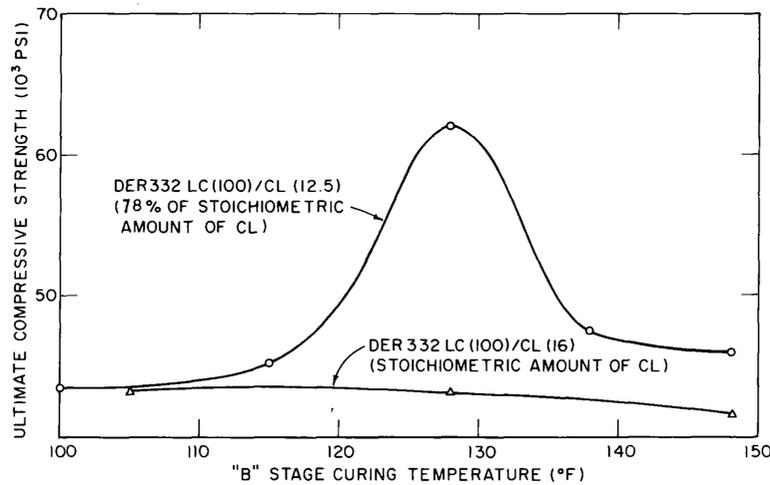


Fig. 5 — Effect of varying the "B" stage temperature on the ultimate compressive strength of two epoxy resins

critical, since variation over a relatively wide range produced little variation in the ultimate compression strength values. Using the proper "B" stage temperature is important, since it is this step in curing that the small epoxy molecules are combined into larger units having only occasional interconnections; as the temperature is raised in the second stage, the clusters are joined together at many points to form one big molecule.

Ideally, the maximum properties would be obtained when the clusters are uniform in size and distributed evenly throughout the resin before final crosslinking takes place. This is never attained, since the reaction is autocatalytic; that is, when the first hydrogen of the primary amine curing agent reacts with the epoxy group, the secondary alcohol formed catalyzes the reaction of the second amine hydrogen with another epoxy molecule, and this tends to build up at a continually faster rate until the resin begins to gel; then the rate decreases as the mobility of the reactants is reduced. Because of the decreased mobility all of the curing agent is seldom used, and any uncured areas will tend to be bunched together. These observations are cited to emphasize that the full potential of an epoxy resin may be overlooked unless cure studies are conducted to determine optimum curing conditions. In addition, these observations provide background for the discussion of the reinforcement studies detailed later.

## THE EFFECT OF MICROPARTICLE ADDITIVES ON THE MECHANICAL PROPERTIES OF CAST EPOXY RESINS

### Colloidal Boehmite Alumina

Colloidal boehmite alumina (Al00H) is a free-flowing, white powder consisting of minute rod-like fibrils clustered into aggregates or bundles. The surface of the fibrils is modified by adsorbed acetate ions, which play an important role in the colloidal behavior and the useful properties of the product when dispersed in water. It is doubtful, however, that in the dry state, as it was used in these experiments, the adsorbed acetate contributed significantly to the effectiveness of the alumina as a reinforcing material. Tables 1 and 2 list the chemical composition and physical properties of this material. The size of the aggregates is an important factor affecting the mechanical properties of the epoxy resins containing this additive. Two forms of this material were evaluated, which were processed differently according to the supplier and differed only in aggregate sizes of the bundles and slightly in the concentration of adsorbed acetate ions. The form having the larger size aggregates tended to settle out of the epoxy resin before hardening; consequently, the mechanical properties of the cured resin were much lower than those obtained with the finer

aggregate type. Ball-milling reduced the size of the aggregates to where the settling was negligible, but the aggregate size was not comparable in fineness to the other alumina and neither was it as effective in improving the mechanical properties of the cured epoxy compositions.

TABLE 1  
Typical Chemical Composition of  
Colloidal Boehmite Alumina

Component	Content (wt-%)
Major Components	
Al <sub>2</sub> O <sub>3</sub>	81.5
CH <sub>3</sub> COOH	9.5
SO <sub>4</sub>	1.8
H <sub>2</sub> O	6.6
Minor Components	
NH <sub>4</sub>	0.2
Na	0.07
Fe	0.13
SiO <sub>2</sub>	0.05

Compression strength data are shown in Table 3 for compositions containing various concentrations of the finer aggregate size colloidal boehmite alumina using the two curing systems, that is, the stoichiometric amount of CL (16 phr) and the optimum quantity (12.5 phr).

The maximum values for the compressive properties of the alumina filled epoxy were obtained with 3 phr alumina using the stoichiometric quantity of CL curing agent. The values for the ultimate compressive strength represented a substantial increase (58%) over the control for this series. However, the percent increase due to the alumina is much less when compared to the unfilled control using the optimum quantity of CL (12.5 phr). With this curing system, the alumina filler actually degrades the ultimate compressive strength of the cast resin. It is apparent from these data that one can be easily misled in interpreting results when adding reinforcing materials to an epoxy composition. Curing studies should be made to obtain optimum conditions, not only on the unfilled resin but with each type of filler evaluated as a reinforcing agent.

Figure 6 graphically presents the effect of alumina concentration on the ultimate compressive strength of the epoxy resin using the two curing systems. Since the alumina was ineffective

TABLE 2  
Typical Physical Properties of  
Colloidal Boehmite Alumina\*

Property	Value
Specific surface area	256 m <sup>2</sup> /g
Pore volume	0.46 cc/g at 120°C
Pore diameter	73 Å
Bulk density	
loose	20 lb/cu ft
packed	36 lb/cu ft
Absolute density (fibril)	2.25 g/cc
Refractive Index (fibril)	1.55 M <sub>25</sub> <sup>D</sup>
Oil Absorption	89 (ASTM method D-281-31)
Color	White
pH (4% sol.)	4.3 (KCL bridge/calomel cell)
Particle charge in sol.	Positive

\*E. I. du Pont deNemours and Co. technical literature.

TABLE 3  
 Compression Data of Cast DER332LC/CL Epoxy Resins  
 Containing Colloidal Boehmite Alumina\*

Resin Composition (parts)			Compressive Yield Strength (psi)	Ultimate Compressive Strength (psi)†	Deflection (%)	Compressive Modulus (psi)
DER332LC	CL	Alumina				
100	16	0	18,700	43,200	44.2	301,000
100	16	1	19,200	47,500	45.0	282,000
100	16	3	21,400	64,000	48.2	328,000
100	16	5	19,500	61,300	49.9	311,000
100	12.5	0	19,400	60,100	51.3	320,000
100	12.5	1	20,000	51,800	46.2	291,000
100	12.5	3	20,000	55,500	47.7	309,000
100	12.5	5	21,200	54,700	46.5	319,000
100	12.5	7	21,000	54,000	46.2	329,000

\*Cure: 16 hr at 128°F, 1 hr at 180°F, and 3 hr at 338°F.

†Plotted in Fig. 6.

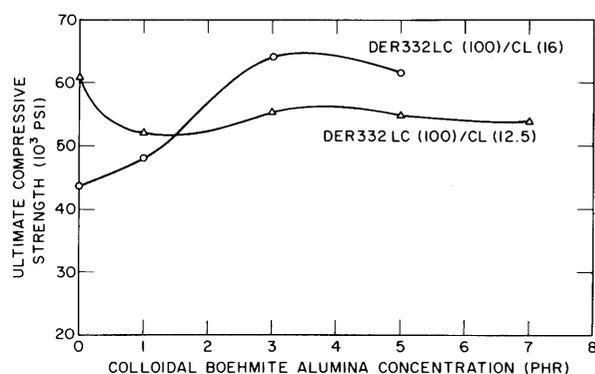


Fig. 6 - Effect of colloidal boehmite alumina on the ultimate compressive strength properties of two epoxide resins

in improving the mechanical properties in the system which produced the best unfilled resin control, the filler may have been participating in the curing process, rather than behaving as a typical reinforcing agent.

In an effort to explain the behavior of the alumina-filled resins attempts were made to determine by infrared analysis the residual  $\alpha$ -epoxy groups in cured specimens. However, because of experimental difficulties associated with sample preparation and the complexities of the spectral data, this method produced results of only limited value and was not pursued further.

Attempts were made to determine the residual  $\alpha$ -epoxy groups using a chemical analysis based on the procedure of Jungnickel *et al.* (6). This procedure depends on the hydrochlorination of the  $\alpha$ -epoxy group in a hydrochloric acid-dioxane reagent. Although this method was reliable for determining the epoxy groups of the liquid uncured epoxy compounds, erratic results were obtained with the solid cured resins. The insolubility of the cured resin presented difficulties in sample preparation. Attempts to obtain reproducible results with ground specimens were unsuccessful.

### Silicas

Two types of silicas having different structures have been studied as microparticle reinforcing agents. One is a hydrated silica (Hi-Sil X303)\* of high purity and extremely fine particle size consisting of highly porous aggregates of spheroidal shaped particles. Because of the aggregation and high porosity, much of its surface is internal. The other is a pyrogenic silica (Aerosil 2491/460)† having low porosity and extremely fine particle size; hence most of its surface is external. Table 4 lists technical data describing these two silicas.

\*Columbia-Southern Chemical Corporation, Pittsburgh, Pa.

†Degussa, Frankfurt/M., Germany.

TABLE 4  
Technical Data\* of Hi-Sil X303 and Aerosil 2491/460 Silicas

Silica	Chemical Composition (wt-% SiO <sub>2</sub> )	Primary Particle Size (m $\mu$ )	Surface Area (m <sup>2</sup> /g)	Moisture (after 105°C heating) (%)	Refractive Index	pH
Hi-Sil X303	88	22	160	—	1.45	4.5 (5% aqueous suspension)
Aerosil 2491/460	>99.8	3-15	460	<1.5	1.45	3.6-4.3 (4% aqueous suspension)

\*Data obtained from the supplier's technical literature.

TABLE 5  
Compression Data of Cast DER332LC/CL Epoxy Resins Containing Hi-Sil X303 Silica\*

Resin Composition (parts)			Compressive Yield Strength (psi)	Ultimate Compressive Strength (psi)	Deflection (%)	Compressive Modulus (psi)
DER332LC	CL	Silica				
100	16	—	18,700	43,200	44.2	301,000
100	16	1	19,100	44,200	44.0	271,000
100	16	3	19,400	47,200	45.1	276,000
100	16	5	24,500	62,000	43.9	348,000
100	16	7	21,000	60,800	46.3	303,000
100	16	9	20,300	57,700	45.5	293,000
100	12.5	—	19,400	60,100	51.3	320,000
100	12.5	5	20,600	54,000	45.2	328,000
100	12.5	7	20,800	60,100	48.6	360,000
100	12.5	10†	22,200	64,000	46.4	346,000

\*Cure: 16 hr at 128°F; 1 hr at 180°F; 3 hr at 338°F.

†Highly viscous.

*Hi-Sil X303*—The behavior of Hi-Sil X303 reinforcing material followed the same pattern as observed with the colloidal boehmite alumina. Overall the highest values for the mechanical properties were obtained with the stoichiometric amount of CL and 5 phr Hi-Sil X303, although the curing system containing less than the stoichiometric amount of CL produced the highest values for the control. Table 5 lists the compression properties of the experimental resins containing this microparticle material using both curing systems. The highest ultimate compressive strength was obtained using 10 phr silica, but the viscosity was

increased so greatly that it is doubtful it could be used in the filament winding process. More significant was a 24% increase in compressive yield strength obtained with 5 phr Hi-Sil X303 silica. This concentration and the stoichiometric amine curing system gave a resin viscosity well within the limits required for the filament-winding process. This material also gave one of the highest values (348,000 psi) for the compressive modulus of all the microparticle materials evaluated in this particular resin system. However, even though DER332LC is a relatively low modulus resin, the values obtained were lower than expected, and a

careful and exhaustive mechanical analysis of the test equipment failed to determine the reason for this discrepancy. The Hi-Sil X303 silica, using the proper curing conditions, gave the best overall results of all the materials evaluated as reinforcing additives for the epoxy resin.

*Aerosil 2491/460*—Aerosil 2491/460, a pyrogenic silica, behaved differently in the DER332LC/CL resin than the precipitated silica just described. Difficulty was encountered in casting compression plugs because of rapid thickening of the resin mix even in concentrations as low as 1 phr. By accelerating the mixing and casting procedure, compression plug specimens containing 1 and 3 phr of silica were obtained. However, flow striations were evident in the cured specimens resulting from the rapid increase in viscosity during the casting stage. This increase in viscosity appeared to result from a high exotherm which accelerated the curing process. With 5 phr silica the exotherm was so high that the resin cured to a hard, horny mass before it could be removed from the deaeration flask. This phenomena is believed to be attributable to strong adsorption of the *m*-phenylene diamine curing agent on the extremely fine particles of silica with their large external surface areas. This adsorption could increase the rate of the crosslinking reaction by lowering the activation energy of the reaction, or the high heat of adsorption could result in localized concentrations of heat, raising the temperature to where rapid crosslinking of the epoxy resin occurs. Whatever the mechanism, the addition of this silica greatly influenced the reaction rate of the curing process.

Other silicas investigated as microparticle reinforcing materials in the DER332LC/CL resin were duPont GS hydrophobic silica, Cab-O-Sil M-5, and Hi-Sil 233. None of these were effective in substantially increasing the compression properties of this resin.

### Carbon Blacks

Five carbon blacks were chosen which ranged in particle size from 360 Å to 3700 Å in area average diameter. Table 6 lists the properties of these blacks. In addition, one of the blacks, Philblack O, was attrited by ball-milling, which greatly increases the surface area and changes the chemical and structural properties of the black. All of the carbon blacks including the attrited black were deleterious to the ultimate compressive strength of the epoxy resins as compared to the unfilled control. The carbon blacks appeared to improve the yield strength slightly but not significantly. A summary of the results obtained in this series is shown in Table 7.

Numerous other microparticle and fiber materials were investigated less thoroughly, but sufficiently to indicate their lack of potential for enhancing the compressive properties of the cast epoxy resins. A list of all materials screened is contained in the Appendix.

### MICROPARTICLE ADDITIVES IN A DER332LC/ANHYDRIDE SYSTEM

A limited study was made of the microparticle reinforcement of DER332LC epoxide resins using

TABLE 6  
Technical Data of Carbon Blacks

Carbon Black	Area Average Particle Diameter (Å)	Surface Area (m <sup>2</sup> /g)	pH*
Philblack O† (HAF)	360	84	6.9
NBS Channel	445	70	3.8
Acetylene (Shawinigan)	460	69	6.5
Philblack A†	590	52	9.7
Thermax (MT)	37	8.5	7.6
Attrited Philblack O‡	—	136	3.5

\*Aqueous slurry.

†Phillips Petroleum Company, Rubber Chemicals Division.

‡Ball-milled dry, 24 hr, using 1/2-inch steel balls.

TABLE 7  
Compression Data of DER332LC/CL Epoxy Resins Containing Various Carbon Blacks\*

Carbon Black	Resin Composition (parts)		Compressive Yield Strength (psi)	Ultimate Compressive Strength (psi)	Deflection (%)	Compressive Modulus (psi)
	DER332LC	CL				
Philblack O	100	12.5	20,400	54,200	46.8	323,000
NBS Channel	100	12.5	20,000	45,400	43.6	324,000
Acetylene (Shawinigan)	100	12.5	20,500	47,000	43.5	302,000
Philblack A	100	12.5	21,500	53,900	43.8	340,000
Thermax	100	12.5	20,700	47,900	43.2	322,000
Attrited Philblack O	100	16	20,200	50,200	44.1	336,000

\*Cure: 16 hr at 128°F; 1 hr at 180°F; 3 hr at 338°F.

†Maximum concentration without excessive resin viscosity increase.

TABLE 8  
Compression and Tensile Data of Anhydride Cured DER332LC Epoxide Resins Containing Various Fillers\*

DER332LC	Resin Composition† (parts)					Compressive Yield Strength (psi)	Ultimate Compressive Strength (psi)	Deflection (%)	Compressive Modulus (psi)	Tensile Strength (psi)	Elongation (%)	Tensile Modulus (psi)
	HPHA	BDMA	Aerosil 2491/460	Alumina	Boron Carbide							
100	80	0.5	—	—	—	19,400	62,200	60.1	354,000	11,700	4.6	452,000
100	80	0.5	1	—	—	18,600	42,300	52.2	344,000	12,300	4.5	477,000
100	80	0.5	3	—	—	17,900	59,400	56.7	320,000	12,200	4.4	490,000
100	80	0.5	5	—	—	17,900	62,300	57.3	321,000	—	—	—
100	80	0.5	7.5	—	—	18,400	60,900	56.4	317,000	—	—	—
100	80	0.5	—	3	—	17,800	42,600	52.7	319,000	7,860	2.0	480,000
100	80	0.5	—	5	—	17,300	46,200	53.6	318,000	6,280	1.5	510,000
100	80	0.5	—	8	—	18,800	58,200	56.1	323,000	—	—	—
100	80	0.5	—	—	1	17,800	63,900	60.5	314,000	—	—	—
100	80	0.5	—	—	3	17,800	62,400	59.2	307,000	—	—	—

\*Cure: 16 hr at 140°F; 2 hr at 210°F; 2 hr at 256°F; 8 hr at 340°F.

†HPHA = hexahydrophthalic anhydride; BDMA = benzylidimethylamine.

the hexahydrophthalic anhydride (HHPA) plus benzyldimethylamine (BDMA) curing system. In addition to the compression data, values for the tensile properties of a few systems were determined. As shown in Table 8, none of the additives investigated produced values for these properties which were outstanding. It is interesting, however, that up to 7.5 phr of the pyrogenic silica, Aerosil 2491/460 was easily added to this system without the abnormal increase in viscosity which had been experienced previously, when even as little as 1 phr was added to the m-phenylene diamine epoxy curing system.

### MODULUS OF TOUGHNESS

The modulus of toughness in compression, which is a measure of the energy required to break the specimen and is inherent in the material, was calculated for composites containing Hi-Sil X303 silica and colloidal boehmite alumina cured with m-phenylene diamine. The values obtained for this property are listed in Table 9. The colloidal boehmite alumina at a concentration of 5 phr, using the stoichiometric curing system, was more effective in improving the toughness factor than

the silica, producing a 31% increase over the best unfilled control.

### INTERLAMINAR SHEAR STRENGTH

Standard NOL type rings were fabricated on an NOL ring winding machine using eight-end E-glass HTS finish roving. A set of rings also was cut from a cylinder wound on a Lamtex bottle-winding machine in hopes of gaining better quality control during the winding. Both Hi-Sil X303 silica and colloidal boehmite alumina were investigated to determine the effect of these materials on the horizontal shear strength of the composites.

The results obtained are summarized in Table 10. These studies produced inconclusive results, since obvious voids were present in most of the specimens. The results appear to be influenced by the void content, since shear failure usually occurred at these voids. It may be that microparticle or fiber materials will improve the interlaminar shear strength properties of filament-wound composites, but this cannot be ascertained with certainty until a process is available for winding composites (in this case, NOL rings) which are

TABLE 9  
Modulus of Toughness (Compression) of DER332LC/CL Resins  
Containing Colloidal Boehmite Alumina and Hi-Sil X303 Silica

Resin Composition (parts)				Modulus of Toughness (in.-lb/cu in.)
DER332LC	CL	Alumina	Hi-Sil X303	
100	16	0	—	9,726
100	16	1	—	10,325
100	16	3	—	11,906
100	16	5	—	17,467
100	12.5	0	—	13,308
100	12.5	1	—	11,154
100	12.5	3	—	12,424
100	12.5	5	—	12,166
100	16	—	1	9,513
100	16	—	3	10,898
100	16	—	5	13,647
100	16	—	7	12,726
100	16	—	9	12,314
100	12.5	—	5	13,227
100	12.5	—	7	13,546
100	12.5	—	10	13,609

TABLE 10  
Interlaminar Shear Data of Glass-Filament-Wound NOL Rings Using  
Epoxy Resins Containing Colloidal Boehmite Alumina and Hi-Sil X303 Silica

Resin Composition (parts)						Glass Filament Type	Glass Filament Tension	Cure Conditions	Average Interlaminar Shear (psi)
DER332LC	CL	HHPA	BDMA	Colloidal Boehmite Alumina	Hi-Sil X-303 Silica				
100	16	—	—	—	—	E-Glass-801 finish, eight-end roving	4-5 lb	16 hr at 128°F 1 hr at 160°F 3 hr at 310°F	5,100*
100	16	—	—	3	—	Same as above	Same	Same	7,330*
100	16	—	—	—	—	S-994-HTS 36 ends (Lamtex winding machine)	50g/end	Same	8,696
100	16	—	—	3	—	Same	Same	Same	9,070
100	16	—	—	—	5	Same	Same	Same	9,481
100	16	—	—	—	10	Same	Same	Same	10,110
100	12.5	—	—	—	10	Same	Same	Same	10,237
100	—	80	0.5	—	—	E-801 finish, eight-end roving	4-5 lb	16 hr at 122°F 2 hr at 200°F 2 hr at 250°F 8 hr at 300°F	10,300
100	—	80	0.5	3	—	Same	Same	Same	8,860

\*Large flaws in test specimens.

essentially free of voids (micro as well as macro). Research at this Laboratory is underway to develop techniques for winding rings with very low void content and to attempt to correlate void content with its effect on the physical properties of the composites.

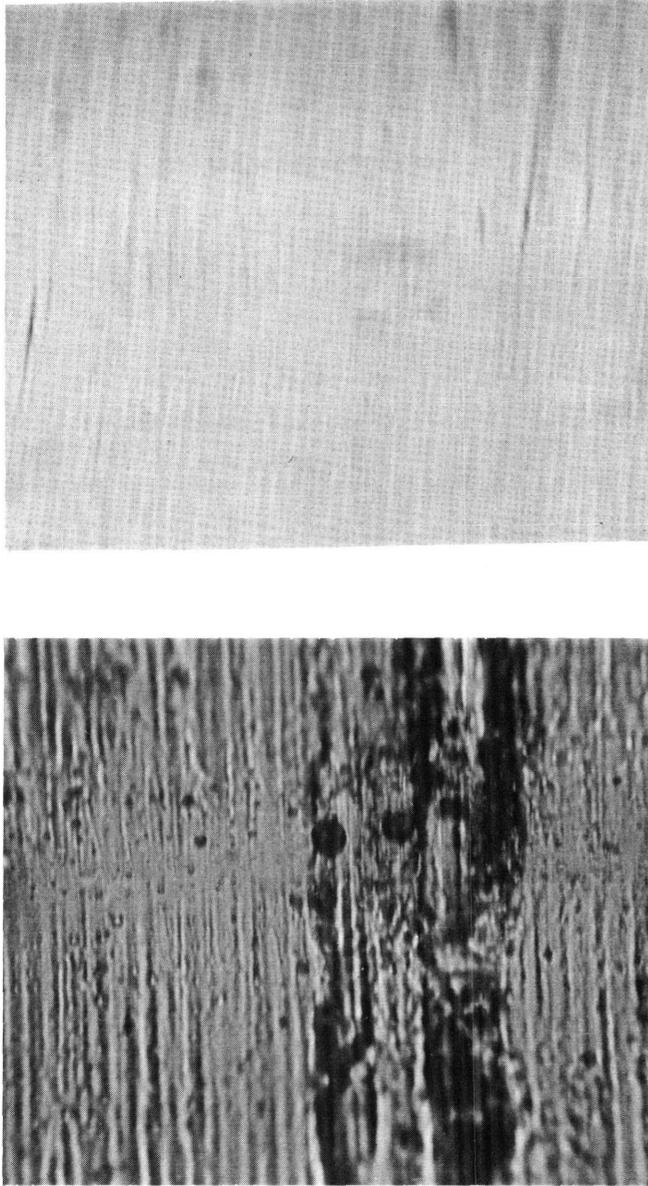
#### REDUCTION OF SURFACE SCRATCHES ON CAST EPOXY TEST SPECIMENS AND ITS EFFECT ON THE COMPRESSION STRENGTH PROPERTIES

Although polished steel molds were used to cast the epoxy compression plug test specimens, microscopic examination revealed many minute surface imperfections, as shown in Fig. 7(a), which were not readily apparent to the naked eye.

Machining, polishing, and buffing such specimens reduced the size of the flaws to those shown in Fig. 7(b). The compression strength properties were determined on sets of unpolished and polished specimens, and the data are summarized

in Table 11. A marked increase (33%) in the ultimate compressive strength was obtained by the polishing treatment, but the values for the yield strength and modulus were not changed significantly.

This behavior might be explained by the theory of Griffiths (7), who has shown quantitatively that when the yield strength of a brittle material has been exceeded, the breaking strength is proportional to the length of the cracks or flaws in the specimen. On the other hand, the increase might be attributed to a "working" of the surface which may increase the toughness of the specimen. Whatever the mechanism, when the same treatment was applied to epoxy specimens containing Hi-Sil X303 silica, the effect was much less pronounced, as shown in Table 11. Time did not permit pursuing this phase of the problem further. It emphasizes again, however, that multiple variables complicate a systematic approach to determining the mechanical properties of reinforced plastics.



(a) Before machining, polishing, and buffing (b) After machining, polishing, and buffing

Fig. 7 — Photomicrographs of the surface contours of cast epoxy resins (12.5 phr CL). (Original magnification 460X.)

TABLE 11  
Effect of Polishing on the Compressive Properties of Cast Epoxide Test Specimens

Resin Composition* (parts)	Compressive Yield Strength (psi)		Increase in Compressive Yield Strength (%)	Ultimate Compressive Strength (psi)		Increase in Ultimate Compressive Strength (%)	Compressive Modulus (psi)		Increase in Compressive Modulus (%)	Deflection (%)		Increase in Deflection (%)	
	Hi-Sil X-303 Silica	No Polish		Polished	No Polish		Polished	No Polish		Polished			
100	12.5	19,500 (602)†	19,500 (179)	0	46,900 (2,259)	62,400 (1,014)	33	324,000 (9,618)	335,600 (3,781)	3.6	46.0 (0.60)	51.1 (0.35)	11
100	16	19,360 (300)	19,500 (403)	0.7	53,000 (1,014)	57,800 (2,250)	9.0	305,000 (5,000)	315,000 (1,581)	3.3	46.4 (0.53)	47.6 (0.97)	1.0

\*Cure: 16 hr at 128°F; 1 hr at 180°F; 3 hr at 338°F.

†Figures in parentheses are standard deviations.

## CONCLUSIONS

1. Low concentrations (1 to 10 phr) of micro-particle or fiber materials, in general, do not produce substantially improved compressive properties of a cast diglycidyl ether of bisphenol A type epoxy resin (DER33LC/CL) when the optimum concentration of amine curing agent (78% of the stoichiometric amount) is employed. This concentration of curing agent produced the highest compressive property values for the unfilled resin control.

2. Colloidal boehmite alumina and Hi-Sil X303 silica produced the greatest increase in compression properties of a diglycidyl ether of bisphenol A type epoxy resin (DER332LC/CL) of all the additives investigated using the stoichiometric amount of amine curing agent.

3. The optimum concentration of amine curing agent (CL), with respect to compression properties of the unfilled, cast DER332LC/CL epoxy resin, was 78% of the stoichiometric amount as determined by curing studies. Curing studies also revealed a critical "B" stage curing temperature (128°F) for the less than stoichiometric amount of curing agent. When the stoichiometric amount was used, the "B" stage temperature effect was negligible. Final curing temperatures were less critical, and a variation over a relatively wide range of temperatures produced little variation in compression strength.

4. An increase of 26% in compressive yield strength was produced by the addition of 5 phr Hi-Sil X303 silica to the DER332LC/CL epoxy resin. This additive gave the best overall results of all the materials evaluated.

5. Colloidal boehmite alumina was superior to the silica in increasing the modulus of toughness, producing a 31% increase over the best unfilled control value.

6. "Flaw sensitivity" or surface imperfections significantly influence the compression strength of unfilled cast epoxy test specimens. A 33% increase

in ultimate compression strength was obtained by surface machining, polishing, and buffing the specimens. The values for the compression strength of specimens containing Hi-Sil X303 silica were not changed appreciably by this treatment.

7. Experiments to determine the effect on the interlaminar shear strength of NOL rings of adding colloidal boehmite alumina and Hi-Sil X303 silica to the resin binder were inconclusive because of the inability to wind rings with low void content using state-of-the-art winding techniques.

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## Appendix

### LIST OF MATERIALS INVESTIGATED AS ADDITIVES FOR THE EPOXY RESIN

<u>Material</u>	<u>Description</u>	<u>Source</u>
Colloidal boehmite alumina "F" Powder (fine aggregate form) Baymal (larger aggregate form)	Hydrated alumina oxide	E. I. du Pont deNemours and Co., Inc.
Hi-Sil X303	Precipitated silica	Pittsburgh Plate Glass Co., Chemical Division
Hydrophobic Silica GS Hi-Sil 233	Coated precipitated silica Precipitated hydrated silica	E. I. du Pont deNemours and Co., Inc. Pittsburgh Plate Glass Co., Chemical Division
Cab-O-Sil M-5 Aerosil 2941/460	Pyrogenic silica Pyrogenic silica	Cabot Corporation DeGussa, Frankfurt/M., Germany
Philblack O Philblack O, attrited Philblack A Shawinigan acetylene black Thermax NBS Channel	HAF carbon black HAF carbon black, ballmilled FEF carbon black CF carbon black MT carbon black EPC carbon black	Phillips Petroleum Co. Phillips Petroleum Co. Phillips Petroleum Co. Shawinigan Products Corporation R. T. Vanderbilt Co., Inc. National Bureau of Standards
Syl-Kem 90	1,3 bis[3(2,3-epoxy propoxy) propyl] tetramethyldisiloxane	Dow Corning Corporation
A-1100 A-172	$\gamma$ -aminopropyltriethoxysilane Vinyl tris (2-methoxyethoxy) silane	Union Carbide Corporation Union Carbide Corporation
Sylodex 351 Modified Sylodex 351 Tetraminobiphenyl Boron Carbide Crocidolite L-100 Adiprene Resorcinol	Proprietary thickening agent Proprietary thickening agent  Asbestos Polyurethane 1,3-Dihydroxybenzene	W. R. Grace and Co. W. R. Grace and Co. American Aniline Products, Inc. Fisher Scientific Company  E. I. du Pont deNemours and Co., Inc. Eastman Kodak Company
Hi-Sil X303/A-172 Hi-Sil X303/Syl-Kem 90 Chopped E Glass/Baymal	Silane treated silica Silane treated silica Colloidal boehmite alumina treated E-Glass	

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13. ABSTRACT <p>Microparticle and fiber materials have been investigated as reinforcing agents for a diglycidyl ether of bisphenol A type of epoxy resin. These materials were limited to low concentrations in order to insure retention of the resin binder properties, such as viscosity and pot life, required for glass-filament-winding processes. In general the material screened did not substantially improve the compression properties of the cast resin as compared to the best unfilled controls. The greatest improvement was achieved with colloidal boehmite alumina and Hi-Sil X303 silica, when the stoichiometric amount of amine curing agent was used. The alumina was superior to the silica in increasing the resin modulus of toughness, but the silica gave higher values for the compression yield and ultimate strengths.</p> <p>The highest values for the compression properties of the unfilled resin controls were obtained when 78% of the stoichiometric amount of m-phenylene diamine (CL) curing agent and a critical "B" stage curing temperature were used.</p> <p>As indicated by a limited study, "flaw sensitivity" or surface imperfections may significantly influence the compression strength of unfilled cast resin test specimens, whereas these effects were negligible with specimens containing Hi-Sil X303 silica.</p> <p>Experiments to determine the effect on the interlaminar shear strength of glass-filament NOL rings wound with resins containing colloidal boehmite alumina and Hi-Sil X303 silica were inconclusive because of the high void content of state-of-the-art wound NOL rings.</p>		

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