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Fabrication and Evaluation of Uniform and Gradient Density Epoxies

Linda Domeier, Dawn Skala, Steve Goods, Cari Neuschwanger, Mike Tootle, and Wei-Yang Lu

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Linda A. Domeier, Dawn M. Skala, Steven H. Goods,
Cari L. Neuschwanger, Michael L. Tootle, and Wei- Yang Lu

Sandia National Laboratories
P. O. Box 969
Livermore, California 94551-0969

Abstract

Filled epoxy materials which vary in density in a designed manner have been fabricated and their mechanical properties evaluated. Density variations were produced by incorporating different volume fractions of either glass microballoons (GMB) or alumina. Several different sample types were evaluated including uniform density ($0.8\ g/cm^3 < \rho < 2.0\ g/cm^3$) samples and gradient density samples (GMB only, $0.8\ g/cm^3 < \rho < 1.2\ g/cm^3$).

The uniform density specimens were evaluated for the effects of filler type and concentration on modulus and toughness. Results indicated that addition of alumina filler significantly increased the resulting modulus while addition of GMB had little measurable effect. These differences could be understood in terms of the differing moduli of the additives relative to that of the epoxy matrix. In the former case the alumina particulates had a modulus much greater than that of the epoxy while in the latter case, the modulus of the GMB additive was only slightly greater than that of the matrix. Addition of either filler significantly degraded the toughness of the composite specimens and precluded the use of gradients to enhance toughness performance.

Discontinuous "block" gradients used for testing were fabricated by simple sequential pours of formulations with different GMB loadings and were evaluated for modulus, strength and ductility. Continuous gradients were fabricated in process studies by programmed shifts in the peristaltic pumping/mixing ratio of epoxies filled with either alumina or GMB. None of the continuous gradient materials were mechanically tested.

These results suggest that applications utilizing gradient materials containing alumina and similar high modulus fillers to provide designed stiffness rather than improved toughness are the most appropriate targets for future investigation.

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Fabrication and Evaluation of Uniform and Gradient Density Epoxies

I. Introduction

Gradient structures which vary across one or more dimensions in density and mechanical performance have been little explored and offered the potential of optimizing performance in such areas as impact resistance. Designed gradients might also be used to minimize interface CTE (coefficient of thermal expansion) mismatches within the structure and between the structure and adjoining materials. Such gradients can be fabricated via the incorporation of various fillers or filler combinations and loadings into thermoset resins such as epoxies. Fillers such as glass microballoons (GMB) and alumina are now commonly added in a homogeneous manner to epoxies to adjust density, CTE, modulus and other properties as well as cost.

Potential DP applications include support and impact mitigating structures and also shock attenuating encapsulants such as those used in neutron generators. One commercial application of a gradient filled epoxy has been reported recently in Switzerland and involved the use of varying levels of alumina in the epoxy anchor for carbon fiber reinforced polymer (CFRP) suspension bridge cables[1]. Alumina particles were pretreated with different thicknesses of epoxy coating to produce the desired filler loading. The resulting gradient modulus, designated as Load Transfer Media (LTM) technology, in the anchoring structure resulted in less damage to the carbon fiber cables than with homogeneous anchors. A literature search revealed no other significant references to gradient epoxy materials.

The work reported here covers the fabrication and testing of a variety of filler-loaded epoxy samples. Different gradient types and fabrication techniques were explored including "block" gradient samples (used for the mechanical property tests) and continuous gradient samples fabricated via co-deposition of epoxies with different filler content. More detailed background information including descriptions of the different potential types of gradient materials and the different processes which might be used to fabricate them (preform infusion, continuous co-deposition and other potential processes) are contained in Appendix A.

Samples of uniform density ($0.8\ g/cm^3 < \rho < 2.0\ g/cm^3$) were evaluated for their quasi-static, uniaxial mechanical properties. In addition, toughness of these materials was evaluated through a series of three-point bend tests conducted on notched bars at both quasi-static and impact testing rates. The properties of these uniform density specimens, in particular, the modulus, were then compared to those of gradient density specimens. Shock propagation tests, as might be relevant to neutron generator applications, were not carried out on any specimens due to both the relative complexity of the test and the lack of any existing correlations to neutron generator performance or other guidance on desirable improvements.

II. Experimental

Formulation and Processing of Uniform and Gradient Density Specimens

Fabrication Processes:

A range of both gradient types and fabrication processes were explored including "block" gradients via sequential pours and continuous gradients via co-deposition of epoxies with different filler content. Detailed descriptions of the different potential types of gradient designs and the different processes which might be used to fabricate them are contained in Appendix A along with experimental studies on block gradients, continuous co-deposition, preform infusion and other potential processes.

For mechanical testing, a variety of cylindrical, rectangular and notched bar specimens were fabricated with uniform densities ranging from 0.8 to 2.0 g/cm^3. Either GMB or alumina fillers were used and the material response with different fillers and filler levels was evaluated. In addition to the uniform density samples, cylindrical block gradient density specimens were evaluated in both compression and impact tests.

Epoxy Matrix Formulation:

Epon 862, a Bisphenol F epoxy, was chosen as the base epoxy due to its low viscosity and good engineering properties. A second more flexible polyglycol diepoxy, DER 736, was added to improve toughness in the notched bar specimens and the rectangular compression specimens cut from those notched bars. All formulations were cured with Jeffamine D-230, a low viscosity polyglycol diamine, expected to provide toughness. An accelerator (A399) was used to increase cure speed and reduce filler migration. Cab-O-Sil (TS-720) was also added to formulations with low filler levels to minimize filler migration and several drops of a degassing aid, KF-105, were typically added. Detailed descriptions of the resin components are given in Appendix C. The two primary formulations used in the study are shown in Table 1 below:

Table 1. Epoxy Matrix Formulations.

Resin Component	Resin 1 (one epoxy)	Resin 2 (two epoxies)
Epon 862 (Shell)	100	80
DER 736 (Dow)		20
Jeffamine D-230 (Huntsman)	32.5	32.5
A399 accelerator (Huntsman)	5.0	5.0
KF-105 surfactant (Shin-Etsu)	~ 3 drops	~ 3 drops

Uniform Density Specimens:

The tougher formulation, Resin 2, was used to fabricate all the uniform density notched bar and rectangular specimens as well as a limited number of cylindrical impact specimens. The degassed resin, with appropriate quantities of either GMB or alumina filler, was poured into aluminum molds and cured, yielding 12.7 mm x 12.7 mm x 127 mm rectangular blocks from which the mechanical test specimens were machined. After pouring at room temperature, the specimens were gelled and cured overnight at room temperature and then further cured 24 hours at 66°C (150°F). Formulation details are given in Table C-1 in Appendix C.

Gradient Density Specimens:
Using Resin 1, discontinuous or "block" gradient cylindrical samples 63 mm in length x 38 mm in diameter (2.5 in. x 1.5 in.), with GMB filler (no alumina) were prepared either by sequential pours into a single cylinder of formulations with different GMB levels or by stacking five disks cut from homogeneous cylinders with different densities. These homogeneous cylinders were also used as control test specimens. After degassing, pouring and gelling at room temperature, the samples were cured at 74°C (165°F) for a minimum of 8 hours, usually overnight. Multiple pour cylinders were left at room temperature 15 min., cured at 74°C for 15 min., and then cooled for 30 minutes prior to the next pour. These formulations are detailed in Table C-2 in Appendix C. Most of the formulations also contained trace amounts of dye to designate their density.

Mechanical Property Measurements

Uniform density specimens:
The influence of particulate loading on elastic modulus and notch toughness was assessed through a series of tests performed on specimens ranging in density from 0.8 g/cm^3 to 2.0 g/cm^3. Moduli were determined from stress versus strain curves for rectangular specimens (12.7 mm x 12.7 mm x 20.0 mm) tested in compression. These tests were conducted using a Instron Model 1125 test machine with an imposed strain rate of 6.67 x 10^{-4} sec^{-1}. Moduli were then calculated as the slope of the linear portion of the loading curve.

For the notch toughness measurements, quasi-static three point bend tests were performed at a displacement rate of 0.004 mm/sec using the same equipment. These tests were conducted according to ASTM E399 with the noted exception that specimens were not fatigue cracked (fatigue pre-cracking is typically recommended in the testing of metallic specimens where machining damage and variability in the notch root radius are more important issues than is the case for relatively brittle epoxies). Specimens had an unsupported length (L = 40 mm) with a square cross section (W, B =12.7 mm). A schematic illustration of the bend specimen and loading stage is shown in Figure 1.

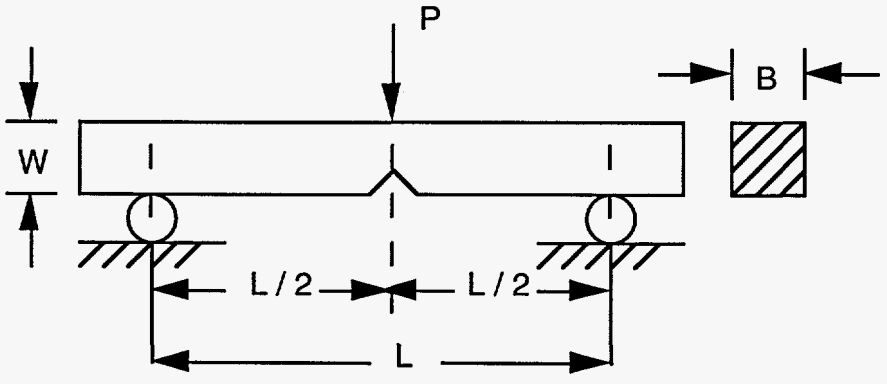

Figure 1. Schematic of bend test specimen and loading stage.

These tests yielded load versus displacement traces which were integrated to provide toughness values as illustrated in Figure 2 on the next page. In every case loading was nearly linear until the point of failure.

Charpy impact tests were also conducted on a Dynatup® Model 8250 drop weight impact tester coupled to a digital data acquisition and analysis system. The test frame can be operated in either gravity mode or with pneumatic assist. In the former case up to 300 J of energy can be delivered

to a test specimen while in the latter case up to 840 J can be delivered with impact velocities of up to 13.4 m/s. The high speed data acquisition system, which records the output of an instrumented tup (load cell), has 1 μs resolution and can acquire a complete loading (impact) event in as little as 4 ms. The software analyzes the deceleration of the crosshead between successive data points from which it determines the instantaneous velocity. Toughness of a test specimen is then calculated by knowing the instantaneous force (from the tup) as the specimen is being deflected and the integration of the time rate of change of the velocity of the crosshead as the specimen is deformed to the point of failure.

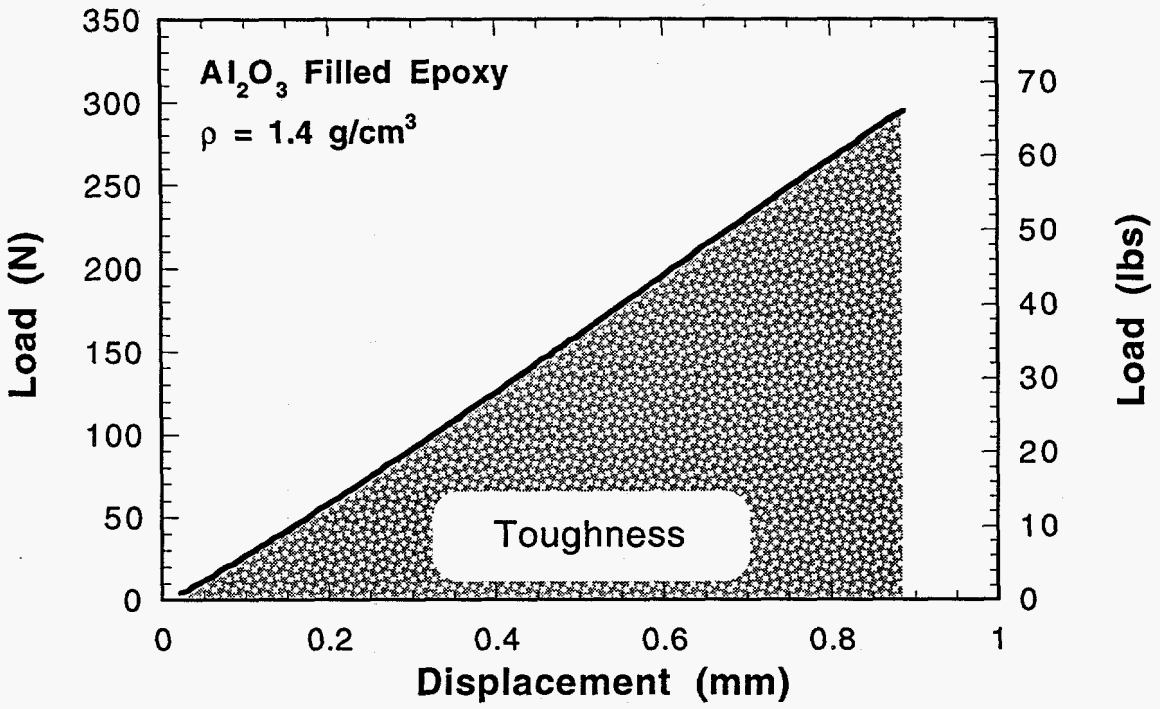

Figure 2. Typical load vs. displacement trace illustrating uniaxial notch toughness calculations

These impact tests were performed according to ASTM D256 with some modifications to the specimen dimensions and loading stage. For the tests reported here, the unsupported span between the notch was 40 mm rather than 60.3 mm as specified by D256. The physical geometry of the specimens and the specimen stage were the same as that for the above described quasi-static tests. The impact velocity for these tests was 825 mm/sec resulting in a loading rate $\approx 2 \times 10^5$ times greater than that for the quasi-static tests.

An additional series of impact tests were attempted in order to determine a different toughness characteristic of these filled epoxy materials. These tests consisted of impacting free-standing right circular cylinders (end on) using the Dynatup tester[2]. The intent was to assess the effect of particle loading on energy absorption-to-failure. Unfortunately, the stochastic nature of fracture in these relatively brittle materials, compounded with mechanical resonances induced in the instrumentation, rendered these tests unsuccessful.

Gradient Density Specimens:
Compression moduli were also measured on 63 x 38 mm cylinders with both gradient and uniform densities using standard fixtures and at a strain rate of 6.67×10^4 sec^{-1}. As noted in the preceding section, these "block-density" specimens were prepared by either stacking of cut disks of different densities or by using sequential pours of formulations of different densities in a single mold. High

densities or by using sequential pours of formulations of different densities in a single mold. High rate impact tests on these specimens were also carried out with unsatisfactory results as noted in the discussion section.

III. Results and Discussion

Elastic Moduli of Uniform Density Specimens

Experimentally determined compressive moduli for the uniform density specimens fabricated from the Resin 2 formulation are presented in Table 2.

Table 2. Measured Moduli for Particulate (Al_2O_3 and GMB) Filled Epoxy.

Density (g/cm^3)	Nominal Volume Fraction Filler	Modulus (GPa*)
0.8	0.4 GMB	3.59
0.9	0.3 GMB	3.45
1.0	0.2 GMB	3.24
1.2	no filler	3.38
1.4	0.07 Al_2O_3	4.96
1.6	0.14 Al_2O_3	6.55
1.8	0.21 Al_2O_3	7.79
2.0	0.29 Al_2O_3	9.24

* 1 GPa = 1.45×10^2 ksi

The data indicate that the specimen moduli increased rapidly with increasing volume fraction of the Al_2O_3 filler. However, GMB loading resulted in only a small effect on the modulus of the specimens. This dependence of modulus on density can be seen more clearly in Figure 3.

There exist in the literature numerous models that relate the modulus of a particulate loaded composite to the moduli of the individual constituents. These are discussed in depth in Appendix B, from which equations 12 and 13 below are taken. A straightforward mechanics approach to the problem yields the following governing equation [3]:

$$\frac{E}{E_m} = \frac{E_m + (E_d - E_m)V_d^{2/3}}{E_m + (E_d - E_m)V_d^{2/3}\left(1 - V_d^{1/3}\right)} \qquad (12)$$

where E, E_m and E_d are the moduli of the composite, the polymer matrix and the filler, respectively, and V_d is the volume fraction of the filler. The derivation of this equation is found in Appendix B-1.

An alternative approach yields a somewhat different relationship [4,5].

$$\frac{E}{E_m} = \frac{1 + ABV_d}{1 - B\Psi V_d} \qquad (13)$$

The terms A, B and Ψ are defined in Appendix B-1.

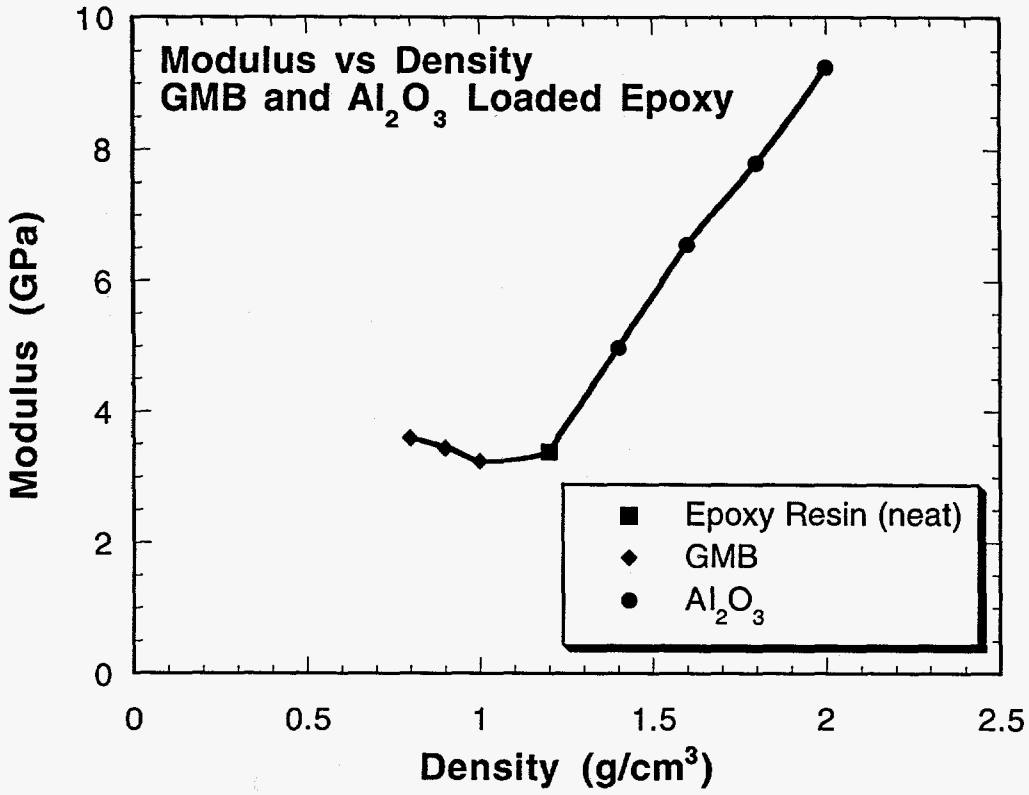

Figure 3. Dependence of compressive modulus vs. density. Alumina acts as a stiffening agent while GMB has little effect on modulus.

A comparison of these two approaches as they relate to the experimentally determined moduli is illustrated in Figure 4. The data are the same as that presented in Figure 3 although presented on a somewhat different scale to better show the predicted relationship between sample density and modulus. While both models predict the correct trend in modulus with respect to density for the alumina loaded epoxy, it is clear that the approach taken by Paul[3] is more representative of the experimental data. For the GMB loaded specimens, both models predict a small decrease in modulus with increasing fraction of GMB. However, the data show that the modulus increases slightly. The discrepancy probably lies in the assumption of a monodispersed GMB size and wall thickness (see Appendix, B-2).

Elastic Moduli of Gradient Density Specimens

Compressive moduli, strength and ductility were measured on GMB-filled "block" gradient density specimens fabricated with the Resin 1 formulation. Results from these tests are shown in Table 3. The table shows results for both the sequential pour and stacked disk specimens. For the uniform density control specimens, the strength is not significantly affected by the increasing volume fraction of the GMB filler (lower density samples). Fracture strain was found to decrease with increasing volume fraction of GMB suggesting that microballoons are acting as flaw sites enhancing fracture. The modulus measurements for these specimens agree closely with those reported above indicating that the change in the resin formulation had little effect on modulus. Results for the stacked disks were similar except for slightly lower moduli probably due to a lack of constraint or imperfect contact at the interfaces. The table also shows the results for block

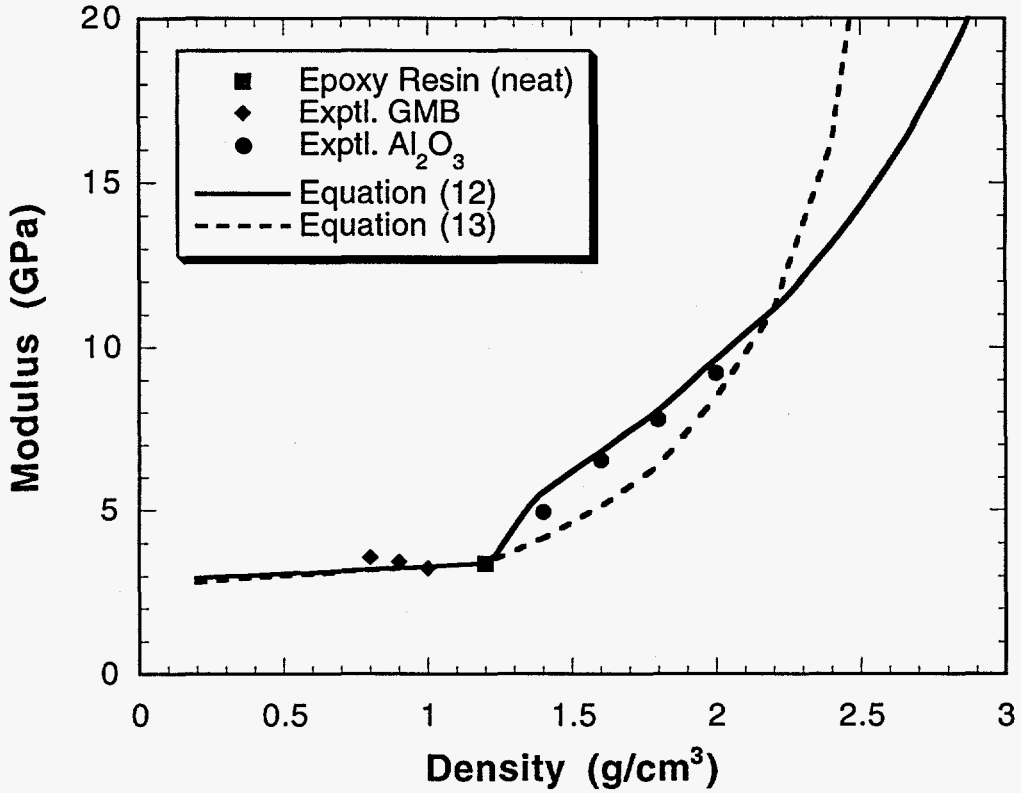

Figure 4. Comparison of measured moduli to composite moduli predicted by Equations 12 and 13.

gradient density specimens. Because the average density of the gradient specimens is 1 g/cm^3, it is most meaningful to compare these findings to the 1 g/cm^3 uniform density sample. Making this specific comparison, the block gradient density specimens show very similar behavior to that of the uniform density specimens with regard to both modulus and strength. Strain at fracture moreclosely corresponds to that for the lowest density specimens, suggesting that it is the local, rather than the aggregate, volume fraction of filler that controls ductility.

Table 3. Compression Test Results: GMB-Filled Cylinders

Sample Type and Density	Sequential Pour Cylinders			Stacked Disks		
	Maximum Stress (MPa**)	Maximum Strain (%)	Modulus (GPa***)	Maximum Stress (MPa)	Maximum Strain (%)	Modulus (GPa)
Uniform Controls:						
0.8	88.9±0.7	4.1 ± 0.1	3.08±0.01	88.9±3.4	4.1 ± 2.0	2.74±0.12
0.9	92.4±2.1	6.9 ± 0.1	3.10±0.01	92.4±2.1	4.8 ± 0.2	2.80±0.03
1.0	94.5±0.7	8.2 ± 0.1*	3.15±0.03	91.0±0.7	9.2 ± 1.1	2.99±0.06
1.1	95.2±2.1	9.1 ± 0.2*	3.10±0.08	97.2±4.8	10.3 ± 1.8	2.97±0.07
1.2	97.8±0.7	8.2 ± 0.1*	3.25±0.14	97.2±0.7	11.9 ± 0.7*	2.82±0.06
Block Gradients: Top High	92.4	4.9	2.99	91.7±0.7	4.3 ± 0.2	2.93±0.03
Top Low	93.8 ± 1.4	4.6 ± 1.1	3.05±0.03	90.3±2.1	4.2 ± 0.3	2.90±0.03
Middle Low	68.9 (large voids!)	3.8	2.93	93.8±1.4	4.1 ± 0.2	2.93±0.03

* Test terminated when sample bulged, giving non-uniform deformation (not tested to fracture).
** 1 MPa = 0.145 ksi *** 1 GPa = 1.45 x 10^2 ksi

Toughness

The toughness values derived from the notch specimen measurements described in the previous section are given in Table 4 and shown in Figure 5. All of these measurements were performed on specimens of uniform density. It is apparent that both the GMB and Al_2O_3 particulates decrease the toughness values relative to that of the unloaded epoxy resin. Numerous mechanisms of toughening of polymer matrices by rubbery or rigid inorganic fillers have been proposed and include branching, shear yielding, cavitation, and crack pinning[6-11]. The current data indicates that neither of these additives act in any way to toughen the epoxy matrix. Indeed, these fillers act as embrittling agents. It is possible that the observed behavior results from poor bonding of the matrix to the filler, allowing the filler sites to act as pre-existing flaws. Rather than inhibiting crack propagation, these flaws form an easy path for crack growth and thus, lower toughness.

Table 4. Charpy toughness results for quasi-static (0.004 mm/sec) and high rate (825 mm/sec) impact testing.

Density (g/cm^3)	Filler Volume Fraction	Quasi-static Toughness (J)	High Rate Toughness (J)
0.8	0.4 GMB	0.13	0.10
0.9	0.3 GMB	0.19	0.10
1.0	0.2 GMB	0.24	0.10
1.2	0.0	0.46	0.18
1.4	0.07 Al_2O_3	0.18	0.08
1.6	0.14 Al_2O_3	0.12	0.10
1.8	0.21 Al_2O_3	0.10	0.11
2.0	0.29 Al_2O_3	0.13	N/A

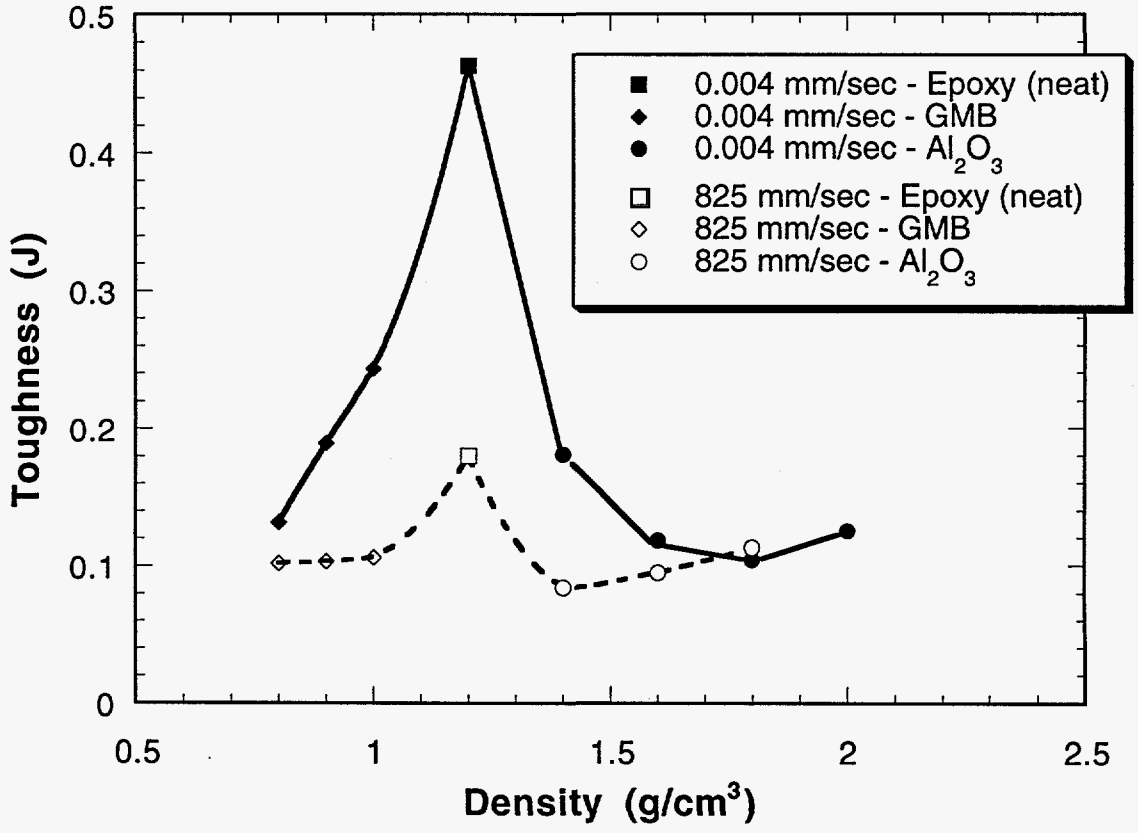

Figure 5. Toughness dependence on density for quasi-static (0.004 mm/sec) and high rate (825 mm/sec) Charpy impact testing.

Toughness values were clearly sensitive to testing rate as those derived from impact testing were less than those derived from the quasi-static tests. The largest difference was observed for the neat epoxy. With increasing loading fraction of either filler the difference in toughness between the two

different test techniques decreased. As seen from Figure 5, the data at the highest loading fractions nearly overlay. This suggests that the effect can be found in the rate sensitivity of the epoxy matrix rather than in any effect having to due with the filler constituents or the particle/matrix interface.

IV. Summary

Evaluations of modulus and notch toughness in filled epoxies showed increasing modulus with higher alumina loadings but also showed extreme brittleness with either GMB or alumina fillers. The observed changes in modulus with alumina loading agreed well with those predicted by models as did the lack of modulus changes in GMB filled materials. The dramatic loss in notch toughness at both quasi-static and impact testing rates in alumina or GMB-loaded materials suggests little possibility of realizing any improvement in this property through the use of gradient density structures.

This loss of toughness (with only modest gains in stiffness) and the identification of serious fabrication challenges on very small structures precluded known DP shock/impact mitigating applications. Applications utilizing gradients to provide a modified modulus such as the reported cable anchor, would probably be more appropriate and productive in future work.

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APPENDIX A

A-1: Background Information: Filler Gradient Types

Three general schemes exist for creating material gradients based on filler content. As shown in Figure A-1, gradients may result from simple variations in the volume loading level of a single filler or from variations in the type and mix ratio of different fillers used at more uniform total volume loadings. The LTM technology mentioned in the Introduction relied on different volume loadings of a single filler, alumina. When more than one filler type is used, a gradient can be established by gradually changing the mix ratio of two very dissimilar fillers, such as GMB and alumina, or by more abruptly changing the filler type while using more numerous fillers to cover the range of desired densities. The first of these filler type gradients, using only two fillers, is more readily processed and was used in the co-deposition process evaluation discussed later in the report. More complex hybrid gradients might utilize both varying volume loadings of the fillers plus varying mix ratios of two or more fillers.

All of the samples fabricated in this study contained only GMB and/or alumina as fillers. Most of the samples tested contained single fillers loaded to various volume fractions to produce several different, but uniform densities.

All of the gradient samples tested as part of this program, because of their relative ease of preparation, relied on "block" or "step" gradients rather than more continuous gradients. Simple test cylinders were prepared by either stacking separate cut disks of different densities or by pouring resins with different filler loadings sequentially into a single cylinder mold prior to final cure. The subsequent pour technique eliminated questions of slippage between simple stacked disks. Dyes were typically added to different densities for coding and to allow uniformity and flow effects to be evaluated.

A-2: Background Information: Gradient Processing Options

Depending of the type of resin and/or amount of resin used, two basic types of filled materials can be fabricated. Two phase (resin and filler) non-porous solids result from simply blending a liquid resin with fillers to the limits of processibility. Three phase (resin, fillers and voids) porous solids are typically prepared using solid resins which melt and coat the filler during processing. This resin provides only a binder for the filler particles and not a void-free matrix resin as shown in Figure A-2. A three phase material might also result if minimal amounts of a high viscosity, low flow, liquid resin were used to coat the filler particles. Both two or three phase materials might be fabricated into continuous or block gradients as described in the preceding section and might contain one, two or several filler types.

All of the test samples evaluated here were two phase, non-porous materials fabricated from liquid resins containing various levels of either glass microballoons or alumina. The high viscosity of heavily loaded resins limits the density range available with GMB fillers to a minimum of about 0.7 g/cm^3 and with alumina fillers to a maximum of about 2.4 g/cm^3. Neat (unfilled) epoxy resins typically have a density of about 1.1-1.2 g/cm^3.

Three phase or porous syntactic foams can provide lower densities to about 0.3 g/cm^3. (Note that blown polyurethane foams can achieve even lower densities.) Fabrication of such syntactic foams requires the deposition and consolidation of microballoons, typically made of glass or carbon, plus a binder resin into a billet or net shape configuration. Powdered resins used as binders include the powdered bismaleimide (APO-BMI) used to fabricate certain weapon forward supports as well as commercial epoxy materials such as 3M's Scotchcast 5068. These porous syntactics are generally brittle, friable materials due to the low level of binder used.

Such porous syntactics can also be used as preforms which are later infused with a second liquid resin in an RTM (resin transfer molding) type process. Fabrication and infusion of a gradient, porous preform was considered as an alternative method of preparing gradients with lower density limits while avoiding the very high processing viscosities of heavily filled liquid resins. Un-infused porous preforms would provide gradient three-phase syntactics with even lower density minimums.

Infusion of a non-gradient porous preform with a second liquid resin was demonstrated using the commercial Scotchcast material. The powdered epoxy used in the Scotchcast system was identified as a solid Bisphenol A epoxy cured with dicyandiamide (Dicy) and a catalyst, 2,4,6-tris(dimethylamino-methyl)phenol. Figure A-3 shows a Scotchcast syntactic before and after infusion with a low viscosity epoxy resin (Resin 2: Epon 862/DER 736/Jeffamine D-230/A399). The preform was fabricated by simply packing the binder/GMB mixed powder into a rectangular mold measuring 13 mm x 38 mm x 127 mm (0.5 x 1.5 x 5 inch) and curing at 107°C (225°F). The preform was then infused either by filling a reservoir above the preform with the liquid resin, placing the mold in an evacuation chamber and alternately lowering and raising the pressure to force the resin into the preform or by using a Semco gun to introduce the liquid resin into the mold through an injection port on the 13 mm x 38 mm face. The latter method provided better control of the infusion process since one could determine when the preform was completely infused. The infused samples were cured at room temperature for 4 hours and at 74°C (165°F) overnight. Fabrication of gradient porous preforms was not attempted as the focus shifted to simpler, single step fabrication processes.

Whether using liquid or solid resins, a key concern in fabricating density gradients was insuring the reproducible and precise distribution of filler particles within the cured material. As noted in the preceding section, a simple method of preparing compression test samples was the use of block gradients which were fabricated by stacking disks of different densities cut from homogeneous cast cylinders. To eliminate slippage effects, this was replaced by small hand-pours of different density formulations into a single cylinder with a brief gel cure between pours.

A continuous process to form filler gradients was demonstrated using peristaltic pumps but was not used to fabricate any of the samples tested. That continuous process is described below in A-3.

Preliminary tests to evaluate gradient processes found that, at other than very low filler loadings, GMB and/or alumina fillers, even in low viscosity resins, showed little tendency to segregate via settling and/or rising. Significant gradients could not be obtained by such spontaneous filler movement. Slight mixing and migrations, especially along mold walls, were noted, however, which would be detrimental to the gradient uniformity if not controlled by resin viscosity and curing. Small amounts of Cab-O-Sil were added to some of the lightly filled formulations to prevent such minor filler rising or settling.

A recent report (K. Tsuda et al, Powder Metallurgy, 39, pp. 296-300, 1996) suggests that gradient cermet/metal materials were prepared by free migration of TiCN particles to the surface during sintering of a TiCN/40WC/10Co/5Ni blend. These "functionally graded materials" were compared to homogeneous cermets and carbide coated metal and showed reduced cracking and spalling. The observed compositional gradients were largely near the surface with little variation in the bulk metal composition.

Whether by sequential hand pours or a continuous pumping, significant process challenges remain in fabricating reproducible filled epoxy gradients, especially over large surface areas and thin cross-sections. Fabrication of such gradients in encapsulation processes rather than in simple billets would pose additional difficulties. Larger engineering applications such as the bridge cable anchor discussed in the Introduction are clearly more suitable for current gradient processes. The

development of robust processes for fabricating small scale gradients may require technologies similar to those used in stereolithography or further refinement of the processes used in this study.

A-3: Continuous Gradient Fabrication

Initial work on a continuous gradient process was carried out with the mixing and deposition of two epoxy formulations, one filled with GMB and one filled with alumina. Continuous adjustment of the ratio of these two formulations would allow the density to be varied across the broad range of GMB and alumina filled materials.

Peristaltic pumps (Masterflex Model 7550-90 with Quickload heads) were used to separately feed the two formulations into a disposable 2.5 inch static mixing head (TAH Industries, Inc. model 160-416). The GMB and alumina formulations were held in Semco tubes with tubing attached to the bottom mounted outlet and running through the pump heads. The two incoming tubes and mixing head were all clamped to a Y-joint. Various tubing sizes were used with Masterflex L/S 16 being the most successful. Transparent plastic cylinders, 0.5 to 1 inch in diameter and about 6 inches high, were mounted in silicone or clay and served as the receiving mold.

The epoxies were cured with ~ 5 phr dicyandiamide, a latent hardener, to preclude potlife issues during these initial evaluations and Epon 815 was used as the epoxy. Dye was added to one of the formulations to provide a visual guide to the mix ratio and uniformity. Various GMB and alumina filler loadings were used, primarily about 30 phr GMB and 250 phr alumina.

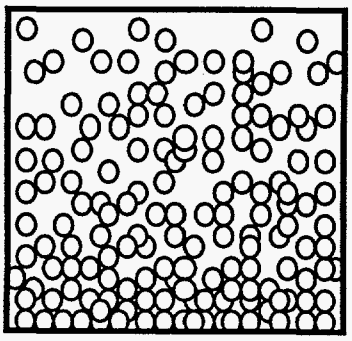
After various runs to determine the required purge/lag time of the mixing head, pumping speeds and other parameters, a series of tube molds were successfully filled with gradient filled epoxies ranging from 100% alumina filler in the bottom to 100% GMB filler in the top. The pumps could be programmed to continuously adjust the ratio of materials reaching the mixing head.

Issues requiring further refinement beyond this demonstration of feasibility included the non-uniform flow of material from the centered deposition point to the edges of the cylinder mold and uneven back-pressure at the mixing head from the two formulations. These might be addressed through robotic manipulation of the deposition point and more sophisticated plumbing. The reproducible fabrication of steep gradients over very short height changes and/or large cross-sections would clearly pose processing challenges.

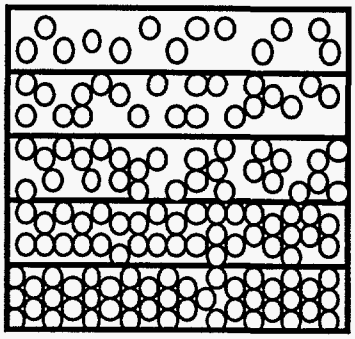
Figure A-1. Gradient Types

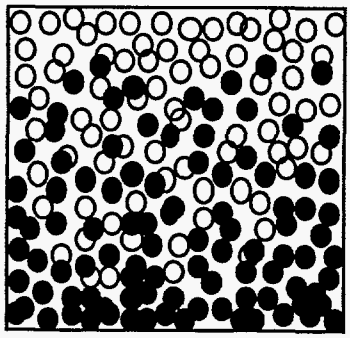
Continuous gradients

Block gradients

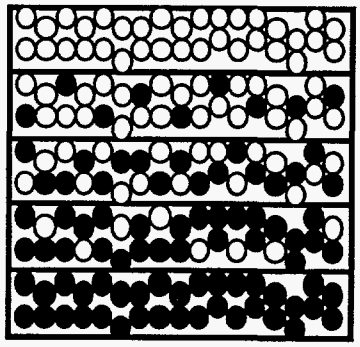


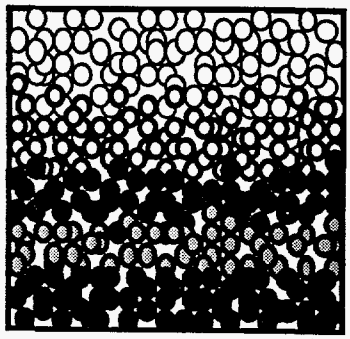
Filler level gradient:
A single type of filler is provided at different concertrations. Higher levels of a hollow filler such as glass microballoons reduce the density while higher levels of solid fillers such as alumina increase the density.





Dual-Filler gradient:
Two fillers of very different densities, such as GMB's and alumina are provided in different ratios.





Multi-Filler gradient:
Different types of fillers, such as GMBs of various densities and solid fillers such as alumina are provided in similar total concentrations.

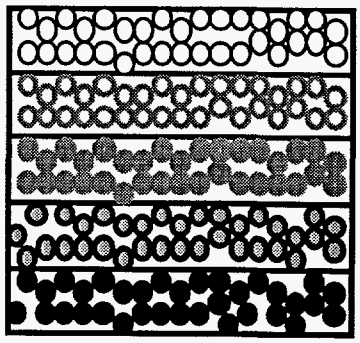
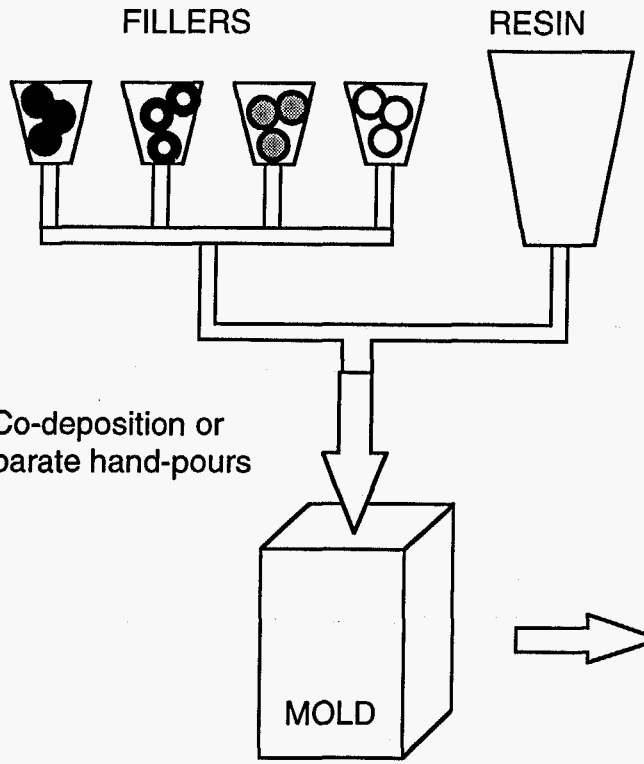
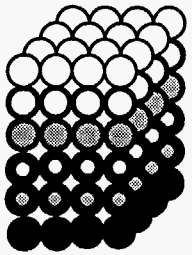


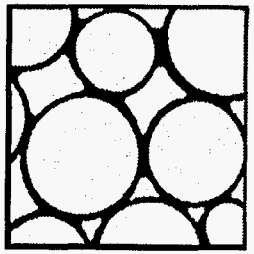
Figure A-2. Gradient Foam Fabrication Technology



using powdered resin:

porous foam "preform" similar to stacked hollow marbles (three phase foam)

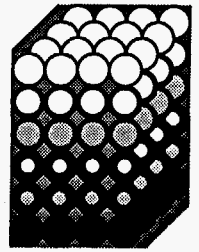


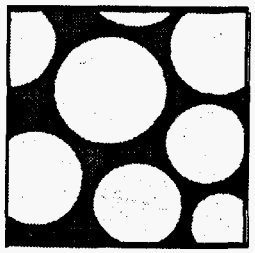


OR

using liquid resin:

non-porous foam with resin occupying intra-filler volume (two phase foam)

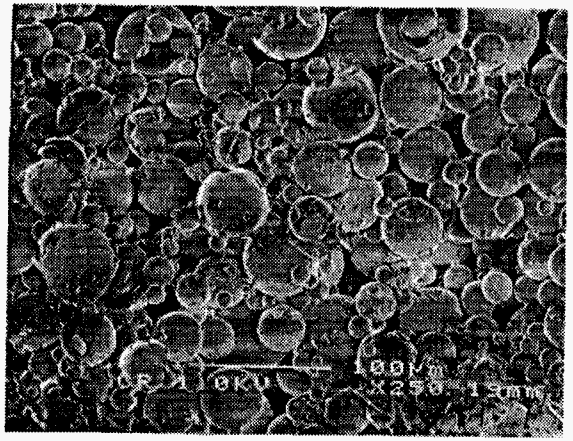




A two step process can be used to infuse the "preform" with a second liquid resin in an RTM type process. This two step process would avoid the very high viscosities sometimes found with highly filled liquid resins.

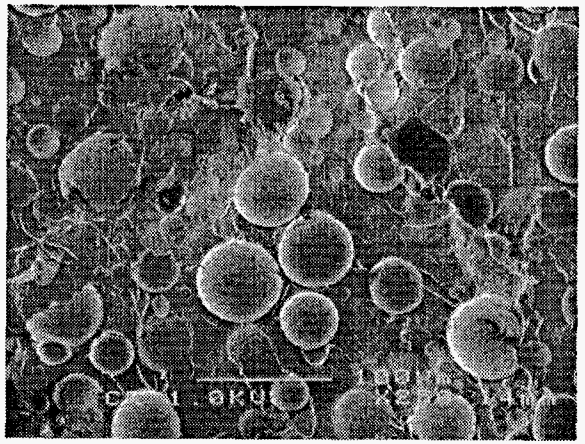
Figure A-3. Infusion of Epoxy Resin into Porous Epoxy/GMB Preform

3M Scotchcast 5068 porous syntactic was vacuum infused with liquid epoxy formulation containing Epon 862/DER 736/Jeffamine D-230/Accelerator 399.

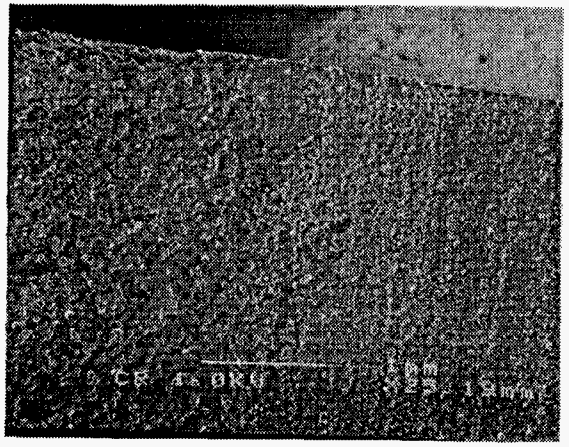


Scotchcast porous syntactic, 250X
density = 0.3 g/cc

liquid infusion



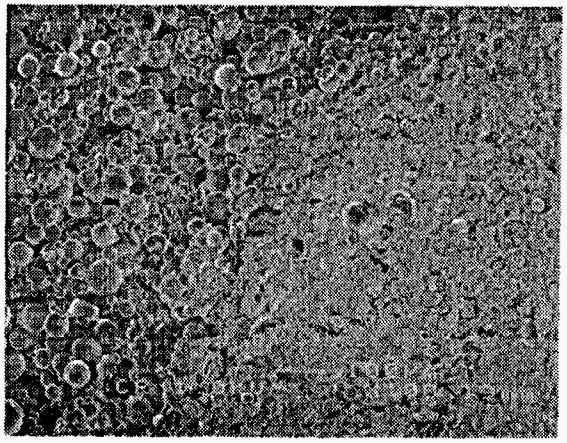
Infused non-porous syntactic, 250X
infused density = 0.7 g/cc



infusion
interface

25X

100X



APPENDIX B

B-1: Predictions of Moduli in Filled Materials

Various expressions have been derived for relating the modulus of a dispersion stiffened material to the properties, geometries and loading fractions of its constituents. A basic mechanics of materials approach can be utilized to determine the modulus of a composite material containing an inclusion of arbitrary shape[3]. If, for the unit solid shown in Figure B-1, one assumes continuity of strain across the filler and the matrix:

$$\varepsilon = \varepsilon_m = \varepsilon_d \tag{1}$$

and assuming an overall force balance:

$$F = F_m + F_d \tag{2}$$

a relationship for the aggregate modulus can be derived expressed solely in terms of the moduli of the constituent phases and their volume fractions.

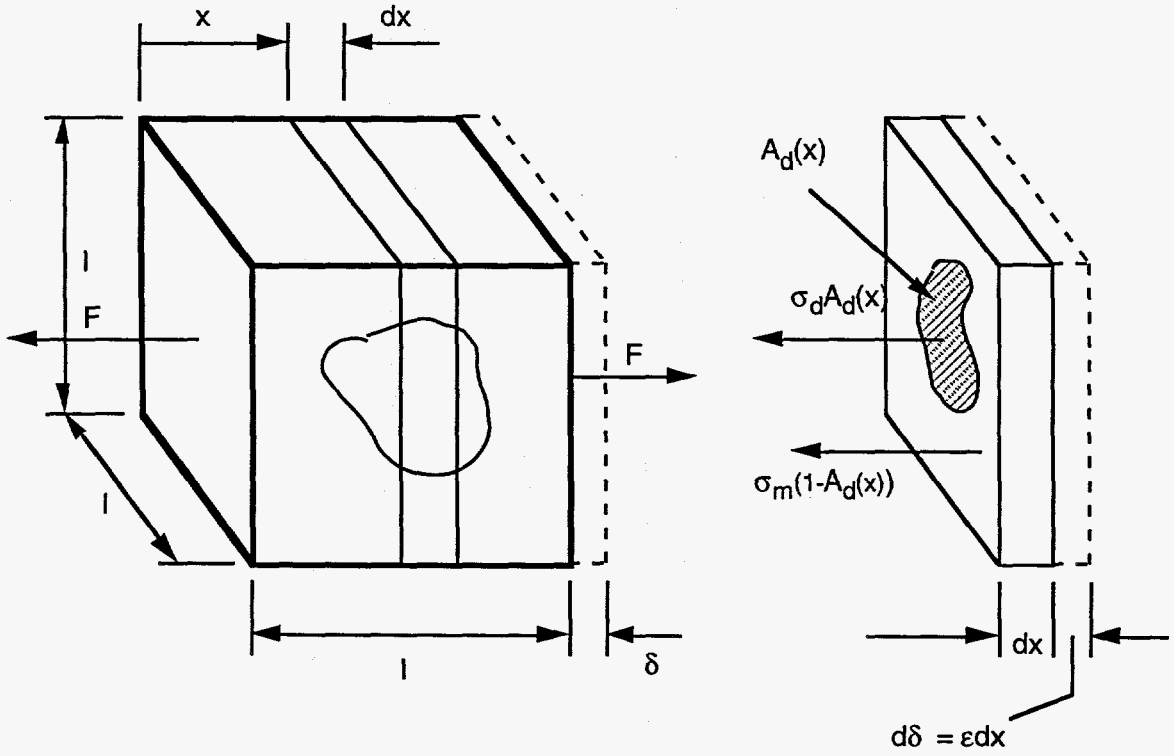


Figure B-1. Unit solid under an applied load F containing an inclusion of arbitrary shape.

where:

$\varepsilon, \sigma, E, F$	= strain, stress, modulus, force in composite
$\varepsilon_m, \sigma_m, E_m, F_m$	= strain, stress, modulus, force in matrix
$\varepsilon_d, \sigma_d, E_d, F_d$	= strain, stress, modulus, force in filler
V_d	= volume fraction filler
$A_d(x)$	= areal function of filler

Applying Hooke's law and the relevant force balance equations, the matrix strain in the differential volume is given as:

$$\varepsilon_m = \frac{\sigma_m}{E_m} = \frac{F_m}{[1 - A_d(x)]E_m} \tag{3a}$$

or

$$F_m = \varepsilon_m[1 - A_d(x)]E_m \tag{3b}$$

Similarly, the strain in the filler is:

$$\varepsilon_d = \frac{F_d}{[A_d(x)]E_d} \tag{4}$$

From Equation (1):

$$\frac{F_m}{[1 - A_d(x)]E_m} = \frac{F_d}{[A_d(x)]E_d} \tag{5a}$$

or

$$F_d = F_m\left[\frac{[A_d(x)]E_d}{[1 - A_d(x)]E_m}\right] \tag{5b}$$

Substituting into Equation (2):

$$F = F_m + F_m\left[\frac{[A_d(x)]E_d}{[1 - A_d(x)]E_m}\right] \tag{6}$$

which is simplified as:

$$F = F_m\left[1 + \frac{[A_d(x)]E_d}{[1 - A_d(x)]E_m}\right] \tag{7}$$

Substituting from Equation (3b):

$$F = \varepsilon_m[1 - A_d(x)]E_m\left[1 + \frac{[A_d(x)]E_d}{[1 - A_d(x)]E_m}\right] \tag{8}$$

Upon rearranging:

$$F = \varepsilon_m[[1 - A_d(x)]E_m + [A_d(x)]E_d] \tag{9a}$$

or recalling equation (1)

$$F = \varepsilon[E_m + (E_d - E_m)A_d(x)] \tag{9b}$$

From linear elasticity:

$$\frac{F}{E} = \delta = \int_0^1 \varepsilon dx \tag{10}$$

Substituting Equation (9b) yields:

$$\frac{1}{E} = \int_0^1 \frac{dx}{E_m + (E_d - E_m)A_d(x)} \tag{11}$$

Equation 11 is difficult to solve for arbitrarily shaped or even spherical particles but is solved straightforwardly for randomly distributed cuboidal particles:

$$\frac{E}{E_m} = \frac{E_m + (E_d - E_m)V_d^{2/3}}{E_m + (E_d - E_m)V_d^{2/3}\left(1 - V_d^{1/3}\right)} \tag{12}$$

We will use Equation (12) as an approximation to the effect of the spherical GMB and the irregular Al_2O_3 fillers of interest here.

Many other models have been put forth to predict the effect of particulate loading on the moduli of composites. The most commonly cited approach to calculating a composite modulus was taken by Nielson and Landel[4] in which the Halpin and Tsai[5] equations for fiber composites were modified for particulate reinforcement. The derivation of their model is not presented here but yields the following expression:

$$\frac{E}{E_m} = \frac{1 + ABV_d}{1 - B\Psi V_d} \tag{13}$$

where the constant A accounts for the geometry of the particulate (A = 2.0 for an aspect ratio = 1) and the constant B is defined as:

$$B = \frac{(E_d/E_m) - 1}{(E_d/E_m) + A} \tag{14}$$

Ψ is dependent upon the maximum packing fraction of the particulate, Φ_m, and is defined as:

$$\Psi = 1 + \frac{1 - \Phi_m}{\Phi_m^2} V_d \tag{15}$$

where : Φ_m = 0.6 for random loose packing of non-agglomerated particles (2)

Solving equations (12) and (13) is straight forward for Al_2O_3 filled epoxy as values for E_m and E_d can be obtained from literature such as Mallick[12] and Van Vlack[13]. For alumina and epoxy, the moduli were found to be 390.04 and 3.38 GPa, respectively. However, determining E_d for a glass microballoon is more complicated since it is the stiffness of the hollow spheres that are of interest rather than the modulus of glass itself.

B-2: Estimate of Modulus of Glass Microballoon

Figure B-2 shows the relevant dimensions of the GMB phase. The glass microballoons used had a median diameter of 35 μm and a wall thickness of 0.77 μm (l).

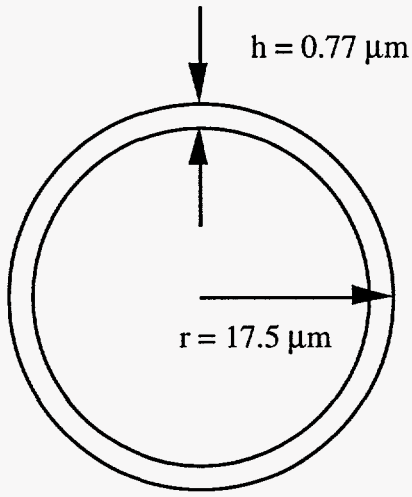


Figure B-2. A schematic cross-section of a GMB with radius r = 17.5 μm and wall thickness h = 0.77 μm.

The relatively large ratio of radius to wall thickness (17.5 μm / 0.77 μm) allows the GMB to be modeled as a thin-walled spherical shell subjected to a uniform pressure, p. Once again from basic mechanics of materials, the circumferential stress at any point in the shell is given by:

$$\sigma = \frac{pr}{2h} \tag{16}$$

and the circumferential strain is given by:

$$\varepsilon = \frac{1}{E}[\sigma - \upsilon\sigma] \tag{17}$$

where: ν = Poisson's ratio
E = modulus of glass = 69 GPa.

Note that the pressure can be either internal (p) or in the present case of interest, external (-p).

The change in the circumference can be written as:

$$\delta c = \varepsilon(2\pi r) \tag{18a}$$

substituting equations (16) and (17)

$$\delta c = (2\pi r)\left[\frac{-pr}{2Eh}\right](1-\upsilon) \tag{18b}$$

The radius of the spherical shell subjected to an external pressure (-p) is given by:

$$R = r - r(\varepsilon) \tag{19a}$$

also substituting equation (17):

$$R = r - \left[\frac{pr^2}{2Eh}\right](1-\upsilon) \tag{19b}$$

The volume of the externally loaded sphere is then calculated:

$$V = \frac{4}{3}\pi\left[r - \frac{pr^2}{2Eh}\right](1-\upsilon) \tag{20}$$

The volumetric decrease due to external hydrostatic loading is given by:

$$\Delta V = V - V_0 \tag{21a}$$

After substituting equation (20) and neglecting terms of (p/E) which are small:

$$\Delta V = \frac{-2\pi p r^4}{Eh}(1-\upsilon) \tag{21b}$$

Therefore, the volumetric strain can be written as:

$$\varepsilon_v = \frac{\Delta V}{V} = \frac{-p}{Eh}(1-\upsilon)\frac{3}{4}\frac{2\pi r^4}{\pi r^3} \tag{22a}$$

simplifying

$$\varepsilon_v = \frac{-p}{Eh}(1-\upsilon)\frac{3r}{2} \tag{22b}$$

From linear elasticity it is known that:

$$\frac{\Delta V}{V} = \frac{-p}{\kappa_s} \tag{23}$$

where: κ_s = bulk modulus of the GMB

Therefore, from equations (22b) and (23):

$$\frac{-p}{Eh}(1-\upsilon)\frac{3r}{2} = \frac{-p}{\kappa_s} \tag{24a}$$

rearranging:

$$E = \kappa_s(1-\upsilon)\left[\frac{3r}{2h}\right] \tag{24b}$$

Also from linear elasticity, the bulk modulus can be related to Young's modulus by:

$$\kappa_s = \frac{E_s}{3(1-2\upsilon)} \tag{25}$$

substituting equation (24b):

$$E = E_s\left[\frac{r}{2h}\right]\frac{(1-\upsilon)}{(1-2\upsilon)} \tag{26a}$$

solving for the GMB modulus:

$$E_s = E\left[\frac{2h}{r}\right]\frac{(1-2\upsilon)}{(1-\upsilon)} \tag{26b}$$

The modulus of glass is about 20 times greater than that of epoxy or: $E \approx 20 \times E_m$. Substituting into equation (26b), the modulus of the GMB becomes:

$$E_s = 20E_m\left[\frac{2h}{r}\right]\frac{(1-2\upsilon)}{(1-\upsilon)} \tag{27a}$$

Also noting that $r = 22.73 \times h$ for the GMB of interest and $\nu = 0.33$ for the epoxy matrix:

$$E_s = \frac{20}{22.73}E_m \tag{28}$$

The composite modulus for GMB filled epoxy is now determined by the solution of equations (12) and (13) and is shown in Figure 4 in the main text.

APPENDIX C: Epoxy Formulation Details and Components

Table C-1. Compositions for Uniform Density Notched Bar and Rectangular Specimens

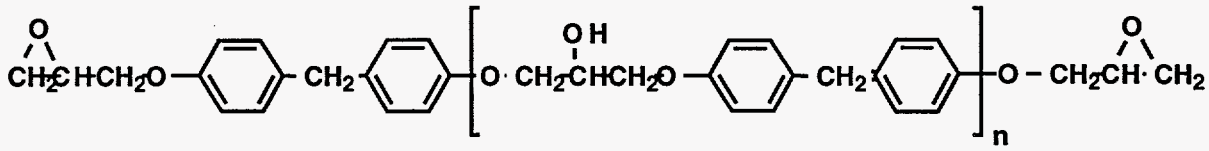
Nominal Sample Density (g/cm^3)	0.8	0.9	1.0	1.2	1.4	1.6	1.8	2.0
Epon 862	80	80	80	80	80	80	80	80
DER 736	20	20	20	20	20	20	20	20
Jeffamine D-230	32.5	32.5	32.5	32.5	32.5	32.5	32.5	32.5
Accelerator 399	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Total Parts Resin	137.5	137.5	137.5	137.5	137.5	137.5	137.5	137.5
Cab-O-Sil (TS-720)	1.0	1.0	2.0	-	1.0	-	-	-
GMB (32/4500)	30.1	17.3	9.7	-	-	-	-	-
Alumina	-	-	-	-	38.5	78.8	130.4	188.8
phr filler	21.9	12.6	7.1	-	28.0	57.3	94.8	137
Weight percent filler	18.0	11.2	6.6	-	21.9	36.4	48.7	57.9
Volume percent filler	44.7	31.7	20.6	-	7.7	14.6	22.0	29.0

Table C-2. Compositions for Uniform and Gradient Density Cylindrical Specimens

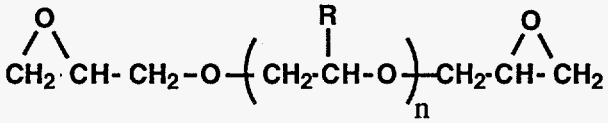
Nominal Sample Density (g/cm^3)	0.8	0.9	1.0	1.1	1.2 (neat resin)
Epon 862	100	100	100	100	100
Jeffamine D-230	32.5	32.5	32.5	32.5	32.5
Accelerator 399	5.0	5.0	5.0	5.0	5.0
Total Parts Resin	137.5	137.5	137.5	137.5	137.5
Cab-O-Sil (TS-720)	-	-	0.9	2.0	-
GMB (D32/5400)	30.1	17.7	9.9	3.6	-
phr GMB	21.9	12.9	7.2	2.6	-
Weight percent GMB	18.0	11.4	6.7	2.6	-
Volume percent GMB	44.2	32.6	20.9	9.3	-
Measured Density:					
number of samples	41	46	52	41	60
density range	0.76-0.80	0.87-0.93	0.97-1.06	1.08-1.12	1.16-1.21
density average	0.78	0.90	1.01	1.10	1.18

Figure C-1. Structures of Epoxy Formulation Components

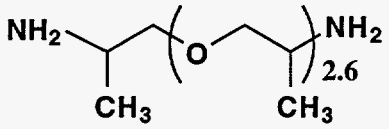
Epon 862 (Shell) Bisphenol F epoxy. Epoxy equivalent weight 166-177. Viscosity 30-45 poise.



DER 736 (Dow) polyglycol diepoxide. Epoxy equivalent weight 175-205. Viscosity 30-60 cps.

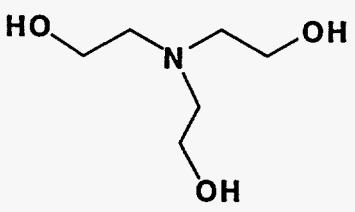


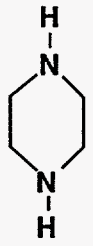
Jeffamine D-230 (Huntsman, formerly Texaco) polyglycol diamine. Amine equivalent weight 60. Viscosity 9 cps.

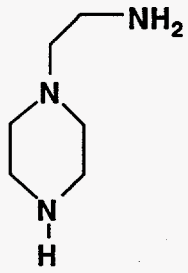


Accelerator 399 (Huntsman). Blend of:
Viscosity 880 cps.

65-80%	triethanolamine
20-35%	piperazine
4-11%	N-aminoethylpiperazine







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