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MASTER

THE STRENGTHENING AND TOUGHENING
OF BRITTLE MATERIALS

Progress Report

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Prepared by:

L. J. Broutman

B. D. Agarwal

P. K. Mallick

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF ILLUSTRATIONS.....	i
CHAPTER	
I. OBJECTIVES OF RESEARCH.....	1
II. TENSILE STATIC FATIGUE OF ALUMINUM OXIDE.....	2
A. Experimental Procedures	
B. Results	
III. THREE DIMENSIONAL ANALYSIS OF PARTICULATE COMPOSITES.....	9
A. Introduction	
B. Boundary Conditions	
C. Internal Stresses	
D. Elastic Constants	
IV. EFFECT OF A WEAK INTERFACE ON COMPOSITE PROPERTIES USING FINITE ELEMENT METHOD.....	29
V. MECHANICAL PROPERTIES OF PARTICULATE COMPOSITES.....	37
A. Introduction	
B. Constituent Materials	
C. Preparation of Glass Filled Polymer Plates	
D. Experimental Procedures	
E. Flexural Stress-Strain Curves	
F. Flexural and Tensile Strengths	
G. Area Under Stress-Strain Curves	
H. Izod Impact Energies	
VI. FUTURE WORK.....	61
VII. COMPLIANCE WITH CONTRACT REQUIREMENTS...	61
VIII. ACKNOWLEDGEMENTS.....	61
APPENDIX.....	62
REFERENCES.....	66

LIST OF ILLUSTRATIONS

Figure

1. Tensile Strength of Dry and Water Soaked Alumina Rings.
2. Static Fatigue Results for Alumina Ring Specimens.
3. Volume Packing (A) Sphere in a Cylinder, (B) Hexagonal Array, and (C) Square or Cubic Array.
4. Finite Element Types: (A) Tetrahedral Element, (B) Membrane Plane Element, and (C) Uniaxial Bar Element.
5. Octahedral Element and Degenerate Cases: (A) Basic Octahedral Element, (B) Two-tetrahedra Degenerate Case, and (C) One-tetrahedron Degenerate Case.
6. Packing of Spherical Inclusions in a Composite.
7. A Typical Three-Dimensional Region Analyzed.
8. Three-Dimensional Mesh for $r_2/r_1 = 0.870$.
9. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.357$.
10. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.714$.
11. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.870$.
12. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.952$.
13. Interfacial Stresses for Alumina-Filled Glass as a Function of Volume Percent of Alumina.
14. Comparison of Modulus of Elasticity Alumina Filled Glass as a Function of r_2/r_1 Predicted by Three-Dimensional and Axisymmetric Analyses.
15. Function of Volume Percent Alumina, Predicated by Three-Dimensional and Axisymmetric Analyses.
16. Shaded Elements Represent Finite Thickness of the Interface for $r_2/r_1 = 0.357$.
17. Shaded Elements Represent Finite Thickness of the Interface for $r_2/r_1 = 0.714$.
18. Finite Element Grid for $r_2/r_1 = 0.870$.
19. Comparison of Matrix Stresses with a Weak Interface with the Stresses Without Weak Interface for $r_2/r_1 = 0.357$.
20. Comparison of Matrix Stresses with a Weak Interface with the Stresses Without Weak Interface for $r_2/r_1 = 0.714$.

Figure

21. Photographs Showing the Distribution of Glass Spheres (CP02 Surface Treatment) in a Filled Epoxy Plate; (a) 20 volume percent glass, (b) 50 volume percent glass. The Dark Spots are Craters Resulting from Pulled Out Spheres.
22. Flexural Stress-Strain Curves of Epoxy Composites with CP02 Treated Glass Beads for Various Volume Fractions of Beads.
23. Flexural Stress-Strain Curves of Epoxy Composites with DC-20 Treated Glass Beads for Various Volume Fractions of Beads.
24. Flexural Modulus of Elasticity vs. Volume Percent Glass for Epoxy Composites.
25. Flexural Modulus of Elasticity vs. Volume Percent Glass for Polyester Composites.
26. Flexural Strength vs. Volume Percent Glass for Epoxy Composites. Solid Lines Represent Theoretical Prediction.
27. Flexural Strength vs. Volume Percent Glass for Polyester Composites. Solid Line Represents Theoretical Prediction.
28. Tensile Strength vs. Volume Percent Glass for Epoxy Composites. Solid Line Represents Theoretical Prediction.
29. Scanning Electron Microscope Photographs of Tensile Fracture Surfaces (45 tilt). Specimens Contained 20 Volume Percent Glass in Epoxy Resin.
30. Area Under Flexural Stress-Strain Curves vs. Volume Percent Glass for Epoxy Composites.
31. Area Under Flexural Stress-Strain Curves vs. Volume Percent Glass for Polyester Composites.
32. Unnotched Izod Impact Energy vs. Volume Percent Glass for Epoxy Composites.
33. Unnotched Izod Impact Energy vs. Volume Percent Glass for Polyester Composites.

I. OBJECTIVES OF RESEARCH

The objective of this study has been to investigate the influence of spherical particles on the strength and toughness of brittle materials. A finite element analysis has been used to determine the internal stresses in the matrix of a spherical particle composite as a function of interparticle spacing or volume percent. Some of the early results are presented in report COO-1794-12 and more recent results are summarized in this report. In addition to calculating internal stresses, the elastic constants can be calculated and the strength can be estimated. The mechanical properties of glass spherical particle filled polymers have been studied as a function of degree of bonding between the glass particle and matrix as well as the volume fraction of particles. It is shown that elastic constants can be predicted by the finite element analysis.

During this reporting period studies on the fatigue of alumina ceramics were completed and the results are summarized in the next section.

II. TENSILE STATIC FATIGUE OF ALUMINUM OXIDE

A. Experimental Procedures.

Both uniaxial tension tests and uniaxial static fatigue tests were performed by internal pressurization of ring specimens. The rings were 1.0 inch in height, 2.0 inches in O.D. and 0.125 inches in wall thickness $[(D/t) = 15]$.

The testing method employed, the material (Al995) studied and the ring testing equipment utilized for these tests was described in report COO-1794-9. Axial restraint of the rings was eliminated by means of three slightly oversized spacers. The uniaxial hoop tension was created in the walls of the ring specimens by internal pressurization of the ring specimens.

For the static fatigue tests, the time to failure was recorded on a Moseley 7101B Strip Chart Recorder. The pressure was read on a 0-5,000 psi thermally compensated Heise pressure gage. The rate of pressurization was approximately 5000 psi/min for all the tests.

A few specimens were tested to observe the effect of water on the tensile strength of alumina. Since the time to failure is very small in a tension test, the effect of water absorption on the tensile strength was determined by first soaking the rings in water for at least 24 hours and then measuring the tensile strength. During the tests, the rings were kept surrounded by a piece of cloth soaked in water. The rings were weighed in a Mettler balance (up to four decimal places) before and after soaking. No appreciable change in weight was observed.

B. Results.

The uniaxial tensile strength of aluminum oxide is influenced by the environment as shown by the data in tables 1 and 2 and the results plotted in Fig. 1. The dry strength (specimen tested in normal laboratory environment, approximately 40 percent relative humidity) for 50 percent probability of failure was approximately

TABLE 1
TENSILE STRENGTH DATA FOR ALUMINA RING SPECIMENS

Ring No.	Pressure (psi)	Stress (psi)	Deviation from Average Strength (psi)
1	3315	24550	-4160
2	3380	25150	-3560
3	3495	26000	-2710
4	3545	26360	-2350
5	3685	27280	-1430
6	3780	28110	- 600
7	3970	29390	+ 680
8	3990	29670	+ 960
9	4110	30430	+1720
10	4200	31100	+2390
11	4200	31230	+2520
12	4280	31690	+2980
13	4365	32320	+3610

Average Tensile Strength = 28,710 psi

Standard Deviation = 2,535 psi

Coefficient of Variation = 8.84%

TABLE 2
TENSILE STRENGTH DATA FOR ALUMINA RING SPECIMENS
SOAKED IN WATER

Ring No.	Pressure (psi)	Stress (psi)	Deviation from Average Strength (psi)
1	2240	16650	-5775
2	2730	20300	-2125
3	2900	21550	- 875
4	2980	22150	- 275
5	3020	22450	+ 25
6	3100	23050	+ 625
7	3135	23300	+ 875
8	3145	23350	+ 925
9	3170	23570	+1145
10	3180	23650	+1225
11	3585	26650	+4225

Average Tensile Strength = 22,425 psi (in water)

Standard Deviation = 2,355 psi

Coefficient of Variation = 10.5%

Figure 1. Tensile Strength of Dry and Water Soaked Alumina Rings.

23,000 psi whereas the strength for water soaked specimens was approximately 29,000 psi. From the calculated standard deviations and from the results shown in Fig. 1, the difference in strength is real and can not be attributed to scatter of the test data. Although this phenomena has been observed previously, the use of this test method which applied a pure uniaxial tensile stress to the material, makes the effect more meaningful. Furthermore it supplements our previous studies concerning the effect of cyclic stresses and environment on the strength of alumina (COO-1794-7).

The results of the static fatigue tests are shown in Fig. 2. Here, a constant internal pressure was maintained inside the rings and the time to failure was recorded. The data is presented in table 3. These specimens were not soaked in water but were left in the normal laboratory environment as mentioned above. A pronounced static fatigue effect occurs as shown in Fig. 2. Although static fatigue has certainly been observed before, as mentioned above, the use of this specimen makes the results more significant. These results allow us to better explain the previous results on cyclic fatigue of alumina.

Figure 2. Static Fatigue Results for Alumina Ring Specimens.

TABLE 3
STATIC FATIGUE DATA FOR ALUMINA RINGS

Specimen No.	Static Stress (psi)	% of Reference Stress (Avg.)*	Time to Failure		
			Hr.	Min.	Sec.
1	26950	94	00	00	48
2	27100	94.5	00	00	02
3	27150	94.5	00	00	09
1	24400	82	01	45	20
2	24400	82	00	09	00
3	24400	82	08	06	15
4	24400	82	14	31	15
5	24400	82	03	56	55
1	21150	74	15	22	04
2	21150	74	04	55	30
3	21150	74	00	39	38
4	21150	74	17	35	30
5	21150	74	25	22	30
1	18600	65	27	21	00**

*Average Tensile Strength is 28,710 psi

** Did not break.

III. THREE DIMENSIONAL ANALYSIS OF PARTICULATE COMPOSITES

A. Introduction.

It was pointed out in report COO-1794-12 that axisymmetric representation of the composite only approximates its real packing and structure. The axisymmetric cells are not an actual repetitive unit but are related in their dimensions to the inter-particle spacings. They do not account for the total volume of the composite as shown in Fig. 3. The volume fractions of filler are calculated by assuming an appropriate packing of the axisymmetric cells and each arrangement gives a different number as indicated in table 4. A computer program which analyzes three dimensional solids without restrictions enables one to overcome the apparent major limitation on the use of an axisymmetric analysis of the composite materials.

The program, SAFE-3D⁽¹⁾, for the three-dimensional elastic analysis of heterogeneous composite structures was used in the analysis discussed in this report.

This program uses the following types of finite elements:

- 1) tetrahedral elements to represent the continuum
- 2) triangular plane stress membrane elements to represent inner lines or outer case, and
- 3) uniaxial tension-compression elements to represent internal reinforcement as shown in Fig. 4.

The structure can be of arbitrary geometry and can have any desired distributions of material properties, temperatures, surface loadings, and boundary conditions. The generality of the SAFE-3D program puts a limitation on its use from an economical standpoint.

To simplify the geometric subdivision of the solids, the tetrahedral elements are placed into groups of three, which together form an octahedron (eight-sided figure). In a uniform mesh the octahedron may look like a triangular prism, as shown in Fig. 5 (a). The octahedron becomes the input element, and it is internally

$$(A) V_f = \frac{2}{3} \left(\frac{r_2}{r_1} \right)^3$$

$$(B) V_f = \frac{\pi}{36 \times 0.117} \left(\frac{r_2}{r_1} \right)^3$$

$$(C) V_f = \frac{\pi}{6} \left(\frac{r_2}{r_1} \right)^3$$

Figure 3. Volume Packing (A) Sphere in a Cylinder, (B) Hexagonal Array, and (C) Square or Cubic Array.

TABLE 4
THE RELATION BETWEEN PARTICLE SPACING
AND VOLUME FRACTION

r_2/r_1	Sphere in a Cylinder	Hexagonal Array	Square or Cubic Array
0.357	3.04	2.75	2.38
0.500	8.33	7.56	6.54
0.615	15.54	14.09	12.20
0.714	24.30	22.03	19.08
0.833	38.58	34.99	30.30
0.870	43.83	39.75	34.43
0.952	57.59	52.23	45.23

Figure 4. Finite Element Types: (A) Tetrahedral Element, (B) Membrane Plane Element, and (C) Uniaxial Bar Element.

Figure 5. Octahedral Element and Degenerate Cases: (A) Basic Octahedral Element, (B) Two-tetrahedra Degenerate Case, and (C) One-tetrahedron Degenerate Case.

subdivided by the program into three tetrahedra, as shown in Fig. 5 (a). At irregular regions in the solids, the octahedral elements may degenerate to elements of one or two tetrahedra as shown in Fig. 5 (b) and (c).

B. Boundary Conditions.

Stresses in three dimensions were calculated around spherical inclusions for various interparticle spacings. Spherical inclusions were assumed packed in a cubic array as shown in Fig. 6. As in the case of the axisymmetric analysis, the stress-strain relations of the matrix and the filler were assumed elastic and also perfect bonding was assumed between the filler and matrix.

Due to the symmetry of the problem, one needs to analyze only one eighth of the sphere embedded in a cube as shown in Fig. 7. Three dimensional meshes (subdivisions) of the solid for the cases $r_2/r_1 = 0.870$ (where r_1 and r_2 are shown in Fig. 7) are shown in Fig. 8. Three other cases with $r_2/r_1 = 0.357, 0.714$ and 0.952 were also analyzed. It was assumed that the composite is loaded by a force in the Z-direction and that no tractions are applied in the x or y direction. The following boundary conditions for the typical region (Fig. 7) have to be satisfied.

By symmetry, the shear stresses on all the faces of the cube ABCDEFGH are:

$$\tau_{xy} = \tau_{yt} = \tau_{zx} = 0$$

Thus the faces ABFE, EFGH and BCGF of the cube remain parallel to their original positions after they are displaced by the force in the z-direction whereas the faces ABCD, ADHE and DCGH remain fixed. The normal forces on the faces ABFE and BCGF must be zero so that:

$$\int_A \sigma_x dA = 0 \quad \text{on } x = r_1$$

$$\int_A \sigma_y dA = 0 \quad \text{on } y = r_1$$

where the integral is replaced by a summation in the finite element method. These

Figure 6. Packing of Spherical Inclusions in a Composite.

Figure 8. Three-Dimensional Mesh for $r_2/r_1 = 0.870$.

boundary conditions are equivalent to the ones used previously for an axisymmetric representation of the composite material.

The above boundary conditions were satisfied by a superposition method. This superposition method and subsequent calculation of composite modulus of elasticity and Poisson's ratio are discussed in Appendix I.

C. Internal Stresses.

The internal triaxial stresses were calculated throughout the volume of representative filled ceramics with filler contents up to 45.23 percent (minimum interparticle spacing = $0.096 r_2$, where r_2 = radius of spherical particles).

The following component properties were assumed:

Glass matrix	$E = 11.8 \times 10^6$ psi
	$\nu = 0.197$
Alumina filler	$E = 60.4 \times 10^6$ psi
	$\nu = 0.257$

These properties are the same as used in report COO-1794-12 and equivalent to the experimental values reported by Hasselman and Fulrath⁽²⁾.

The stresses around the spherical inclusions are shown in Figs. 9 - 12 for four different interparticle spacings ($r_2 = 0.357, 0.714, 0.870$ and 0.952). The stresses are represented as a ratio $\sigma/\bar{\sigma}_f$ where $\bar{\sigma}_f$ is the average stress applied to the composite. Thus, the ratio represents the stress concentration around the cavity. The stresses are in the elements adjacent to the inclusions and are assumed to act at the center of each of the elements.

The radial and tangential stresses obtained in the axisymmetric analysis of filled ceramics have been compared with the results of the three-dimensional analysis for three different interparticle spacings ($\frac{r_2}{r_1} = 0.357, 0.714$ and 0.870). Figs. 9 - 11 show that the two analyses give almost identical stress distributions. Minor differences at some places may be attributed to the shape and size of the finite elements. The

Figure 9. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.357$.

Figure 10. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.714$.

Figure 11. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.870$.

Figure 12. Stresses at Interface for Alumina-Filled Glass with $r_2/r_1 = 0.952$.

stresses for the case $\frac{r_2}{r_1} = 0.952$ (Fig. 12) show the same general trend of the stresses around the inclusion, and as would be expected the radial stress at $\theta = 90^\circ$ is much higher compared to that for the other three cases.

The variation of stresses at the pole ($\theta = 90^\circ$) and the equator ($\theta = 0^\circ$) of spherical particles are shown in Fig. 13 as a function of r_2/r_1 (which represents a definite interparticle spacing). The curves were extrapolated to $r_2/r_1 = 0$ which corresponds to a single inclusion in an infinite matrix. Theoretical results of Goodier⁽³⁾ applicable for $r_2/r_1 = 0$, agree quite well with the predicted values. Also shown in Fig. 13 are the stresses obtained by the axisymmetric analysis. The results of the two analyses are quite comparable in all cases except for tangential stresses at $\theta = 0^\circ$. For some unexplained reason the tangential stresses at $\theta = 0^\circ$ obtained by the three-dimensional analysis at low values of r_2/r_1 are much higher than those obtained by the axisymmetric analysis.

D. Elastic Constants.

The predicted moduli of elasticity are shown in Fig. 14 and Table 5 as a function of the ratio r_2/r_1 . The modulus of elasticity increases as the filler content increases. The moduli of elasticity values predicted by axisymmetric analysis have also been plotted in Fig. 14. It is seen, once again, that the results of the two analyses are quite close when plotted as a function of interparticle spacing.

The predicted values of moduli of elasticity have been plotted as a function of volume fraction of Al_2O_3 in Fig. 15. For the three-dimensional analysis, the volume fractions have been calculated from cubic packing of the spheres as shown in Fig. 6. In the case of the axisymmetric analysis, the volume fractions can be calculated by assuming a sphere inside a cylinder, hexagonal packing or a cubic packing of the spheres as shown in Fig. 15 and Table 4. At lower values of the ratio of r_2/r_1 the volume fractions calculated by assuming three different packings do not differ appreciably but at $r_2/r_1 = 0.87$, the volume fraction may be assumed to be

Figure 13. Interfacial Stresses for Alumina-Filled Glass as a Function of Volume Percent of Alumina.

TABLE 5
PREDICTED MODULUS OF ELASTICITY
OF ALUMINA FILLED GLASS

r_2/r_1	Modulus of Elasticity (10^6 psi)
0.357	12.30
0.714	16.05
0.870	20.57
0.952	24.96

Figure 14. Comparison of Modulus of Elasticity Alumina Filled Glass as a Function of r_2/r_1 . Predicted by Three-Dimensional and Axisymmetric Analyses.

Figure 15. Function of Volume Percent Alumina, Predicted by Three-Dimensional and Axisymmetric Analyses.

34.43 or 43.83 depending upon the assumed packing. The values of modulus of elasticity predicted by the axisymmetric analysis have been plotted against the three volume fractions in Fig. 15. At lower volume fractions all the values compare satisfactorily with the three-dimensional stress analysis. However, at higher r_2/r_1 ratio the values plotted against volume fractions calculated by assuming a hexagonal packing agree very well with the results of the three-dimensional analysis, which lie in between the other two cases.

The present results strongly suggest that the interparticle spacing is a more significant parameter than volume fraction for presenting the internal stress distributions in a composite material. The results of the axisymmetric analysis and the three dimensional analysis agree very well when presented as a function of interparticle spacing (which is uniquely determined by the ratio r_2/r_1). The axisymmetric analysis may be used without much loss of accuracy in place of a relatively complicated and much more costly three-dimensional analysis of composite materials. It may be mentioned here that the cost of obtaining information from the SAFE-3D⁽¹⁾ program is about 20 times that of obtaining the same information from Wilson's⁽⁴⁾ program for the analysis of axisymmetric solids.

IV. EFFECT OF A WEAK INTERFACE ON COMPOSITE PROPERTIES USING FINITE ELEMENT METHOD

In an actual composite material, the properties of the material at the interface may be different from those of the filler and matrix. Continuous displacements at the interface imply perfect bonding between the filler particles and the matrix. When perfect bonding does not exist between the filler and the matrix, behavior of the interface should be simulated by assigning different property values to the material at the interface. This is very easily accomplished using the axisymmetric finite element method discussed in COO-1794-12. The shaded elements in Figs. 16 and 17 have been assumed to represent the finite thicknesses of the interface for filler contents of 3.04 and 24.30 percents respectively. The shaded elements account for 0.48 percent of the total volume in the former case and 3.02 percent in the latter case. A close examination of the finite elements in Fig. 18 reveals that a much finer grid is needed to study the effect of the interface at a high volume fraction of the filler. The modulus of elasticity assigned to the elements at the interface was 1000 psi which is very small compared to that of the matrix ($E = 11.8 \times 10^6$ psi) or the filler ($E = 60.4 \times 10^6$ psi). This represents the case of a very weak interface.

The weak interface as described above completely changes the stress distribution around the interface. The stresses in the elements (in the matrix) adjacent to the interface have been plotted in Figs. 19 and 20. A very small magnitude of radial stress around the interface indicates a free boundary. The curves for tangential stresses with finite interface are very similar to the ones obtained for stresses around the cavity as shown report COO-1794-12. Due to very low modulus, the interface is not able to transfer any stress from the matrix to the hard inclusions and therefore represents a case of the filler particles completely debonded from the matrix. The hard inclusions with weak interface carry very low stresses and hence do not contribute to the enhancement of the modulus of the composite. This is similar to what Stett and

Figure 16. Shaded Elements Represent Finite Thickness of the Interface for $r_2/r_1 = 0.357$.

Figure 17. Shaded Elements Represent Finite Thickness of the Interface for $r_2/r_1 = 0.714$.

Figure 18. Finite Element Grid for $r_2/r_1 = 0.870$.

Figure 19. Comparison of Matrix Stresses with a Weak Interface with the Stresses Without Weak Interface for $r_2/r_1 = 0.357$.

Figure 20. Comparison of Matrix Stresses with a Weak Interface with the Stresses Without Weak Interface for $r_2/r_1 = 0.714$.

Fulrath⁽⁵⁾ have described as pseudoporosity which results in the weakening of the composite. The modulus of elasticity of the composite decreases with higher filler contents as indicated in Table 6.

TABLE 6
EFFECT OF INTERFACE ON MODULUS
OF ELASTICITY OF COMPOSITE

Volume Fraction Filler	Composite Modulus	
	Without Interface	With Interface
3.04	12.3×10^6	11.05×10^6
24.30	16.7×10^6	6.97×10^6
43.83	22.4×10^6	3.84×10^6

V. MECHANICAL PROPERTIES OF PARTICULATE COMPOSITES

A. Introduction.

Spherically shaped glass particles or beads have been in existence for many years, but it is only recently that they have been used to fill polymers to form a useful composite⁽⁶⁾. Both thermoplastic and thermosetting polymers have been considered as matrix materials. Recent studies have been published on the elastic constants⁽⁷⁻⁹⁾ strength and toughness^(7, 10, 11) of particulate polymer composites. Theoretical expressions also exist to predict the modulus of elasticity of particulate composites^(8, 12-14) although they do not all agree with experimental data particularly at filler contents above 30 volume percent.

In the study described here the mechanical properties of spherical glass filled polymers have been studied as a function of filler content and the degree of interfacial bonding between the glass filler and the polymer matrix. Of particular importance is the change in Young's modulus, ultimate strength and elongation, strain energy to fracture and the unnotched Izod impact energy. The modulus of elasticity and strength have been theoretically calculated utilizing a finite element analysis^(15, 16) and compared to experimental results.

B. Constituent Materials.

Two polymeric materials were selected for matrix materials. An epoxy resin (Shell Chemical Co., Epon 828 tradename) and a polyester resin (Interplastic Corp., CoRezyn-1808-2, tradename) which are typical matrix materials for glass fiber reinforced plastics were selected. The reinforcing "A" glass is in the form of spherical beads (-325 U.S. Screen) manufactured by Potters Brothers, Inc. The average particle size was determined to be 30 microns (diameter). The specific gravity determined for the beads by a pycnometer was 2.30.

The epoxy resin was cured with 14 parts by weight of meta-phenylene

diamine. The room temperature properties determined for the resin are the following:

Tensile strength	10,800 psi
Tensile modulus	3.90×10^5 psi
Flexural strength	18,900 psi
Flexural modulus	4.60×10^5 psi
Specific gravity	1.202

The properties of the polyester resin cured with methylethylketone peroxide (0.5%) are as follows:

Flexural strength	10,800 psi
Flexural modulus	3.75×10^5 psi
Specific gravity	1.205

C. Preparation of Glass Filled Polymer Plates.

For the epoxy resin, fourteen parts of molten (150°F) curing agent were mixed with 15 parts of resin warmed to 150°F . This mixture was then added to 85 parts of the epoxy resin kept at room temperature. The entire mass was then stirred with a spatula for two minutes. A predetermined quantity of glass beads was then poured into the resin with constant stirring. The weight of glass is dependent on final glass concentration (by volume) desired in the composite.

The resin and glass beads were mixed under vacuum for 10 to 20 minutes depending upon the volume percentage of glass. The mixture was poured into an aluminum mold with a cavity $10 \times 10 \times 1/8$ inches in size. The resin was covered with a Mylar film taking care to avoid any air entrapment. The mold was then covered with a $1/8$ inch thick steel plate. The aluminum mold and the steel plate were fastened together between steel strips. The mold was then turned upside down for approximately the same time as used for the preparation of the casting to account for settlement of the glass spheres. The mold was then placed in a rotation fixture and rotated at 3 rpm for approximately 20 hours until the resin solidified to prevent

settlement of the particles. The mold was then removed from the rotation fixture and the steel strips removed. The following post cure schedule was followed after placing the mold and the cover plate on the platen of a hydraulic press.

<u>Temperature, °F</u>	<u>Time, hours</u>
130	2
250	1
350	2

A pressure of 30 psi was maintained to force the viscous mass to attain a uniform thickness. It should be noted that the resin first hardens without fully curing (B-stage) after 30 hours and when heated again in the press softens and becomes viscous at about 130°F before it becomes finally cured. The composite plate was slowly cooled under pressure to room temperature before removing from the press.

For the polyester resin, methylethylketone peroxide (0.5%) was first mixed with the polyester resin and the glass beads were then added. The mixture was stirred under vacuum for 5 to 10 minutes. The mixed mass was then poured into the mold using the same procedure developed for the epoxy resin and rotated in the rotation fixture for 30 minutes. The mold was removed and placed in the press to ensure uniform thickness during gelling of the resin. After allowing 4 hours at room temperature the plate was post-cured for 2 hours at 200°F in the press. Fig. 21 shows the distribution of glass beads through the thickness for two different glass contents. It should be noted that 1) the distribution of glass beads inside the resin is quite uniform, 2) air voids are negligible and a large particle size distribution exists. The nominal volume percentage of glass beads in the resin was varied from 10 to 50. The actual weight percentage was determined by resin burn-off tests and volume percentage was calculated from the measured density of the glass beads. Glass beads with the following surface treatments* were incorporated into an epoxy resin.

* Surface treatments were applied by the Dow Corning Corp., Midland, Michigan

Figure 21. Photographs Showing the Distribution of Glass Spheres (CP02 Surface Treatment) in a Filled Epoxy Plate; (a) 20 volume percent glass, (b) 50 volume percent glass. The Dark Spots are Craters Resulting from Pulled Out Spheres.

1. DC-20: Glass spheres were treated with 0.2% toluene solution of a resinous silicone containing a high proportion of dimethylsiloxane (Dow Corning). A commercial mold release treatment.
2. No treatment: used as received from Potters Brothers, Inc.
3. Z-6076: Spheres were treated with 0.2% aqueous solution of technical grade γ -chloropropyltrimethoxysilane (Dow Corning).
4. CPO2: Proprietary epoxy coupling agent (Potters Brothers, Inc.)

For polyester resin composites only two surface treatments were considered.

1. No treatment
2. CPO1: Proprietary polyester coupling agent (Potters Brothers, Inc.)

D. Experimental Procedures.

The tensile properties of the unfilled polymers were measured on an Instron testing machine at a crosshead speed of 0.05" per minute. Ten specimens were tested to establish the average values. Strain was measured using an Instron strain gage extensometer having 1" gage length. For the filled polymers only 5 specimens were tested of each material. Flexural properties (single point center load) of unfilled and filled epoxy and polyester resins were measured on the Instron using a crosshead speed of 0.05" per minute. Ten specimens for unfilled resins and five specimens for filled resins were tested to establish an average value. Flexural modulus, strength and ultimate elongation were calculated. Flexural strength of the unfilled epoxy was found to be 18.9 ksi which is about 60% greater than tensile strength. Modulus and ultimate strain also are greater than the corresponding tensile values.

Unnotched Izod specimens were used for measuring impact energies. As above, ten specimens were used for the unfilled resin and five specimens for filled resins. The materials were very brittle and thus accurate values could not be established with notched specimens. A TMI (Testing Machine Inc.) impact machine with a 2 ft-lb. hammer was used for measuring impact energies.

E. Flexural Stress-Strain Curves.

Flexural tests were performed on specimens containing up to 50 volume percent glass. Experimental flexural stress-strain curves for two surface treatments (epoxy matrix), namely, CPO2 and DC-20 are shown in Figs. 22 and 23. These figures demonstrate how the modulus, strength and ultimate strain vary with glass content of the composite and interface surface treatment.

Flexural modulus for filled (-325 mesh glass) epoxy composites has been plotted in Fig. 24. Each point is an average of five measurements. As expected the modulus of the composite increases monotonically with the glass content. Up to 30 volume percent glass all four treatments give, within experimental error, the same value of flexural modulus compared to the other three treatments, the values for which may be considered to lie within their own scatter band and thus are indistinguishable. These results are not unexpected. The modulus is measured at low strains and the influence of the interface will not be pronounced at these strains. However, as the volume percent of particles increases and thus the amount of interfacial area increases the contribution of the interface becomes more significant. The DC-20 surface treatment which is a commercial mold release agent, used to prevent bonding, produces interfaces with virtually no strength. Thus, the stiffness or modulus is less for composites having low interfacial strengths.

The flexural modulus for the glass filled polyesters has been plotted in Fig. 25. In this case the range of values for the modulus at each volume percent has also been shown. As is the case with the epoxy composites, the modulus increases with the glass content and at high volume percents of glass the weakest surface treatment results in the lowest modulus of elasticity.

The solid curves shown in Figs. 24 and 25 are the prediction of composite modulus based on a finite element analysis of internal stresses which is discussed in report COO-1794-12 and in more detail elsewhere⁽¹⁶⁾. The following assumptions

Figure 22. Flexural Stress-Strain Curves of Epoxy Composites with CPO2 Treated Glass Beads for Various Volume Fractions of Beads.

Figure 23. Flexural Stress-Strain Curves of Epoxy Composites with DC-20 Treated Glass Beads for Various Volume Fractions of Beads.

Figure 24. Flexural Modulus of Elasticity vs. Volume Percent Glass for Epoxy Composites.

Figure 25. Flexural Modulus of Elasticity vs. Volume Percent Glass for Polyester Composites.

have been made in the finite element analysis:

- 1) perfect adhesion between glass filler and matrix
- 2) uniform size spherical particle packed in hexagonal array
- 3) elastic behavior for matrix and filler

Other modulus predictions based on Hashin's⁽¹²⁾ Kerner's⁽¹⁴⁾ and Ishai's⁽⁸⁾ theories are compared in Table 7. These theories also approximate the experimental data particularly at low volume fractions of particles. Excellent agreement with the experimental values is obtained with the finite element analysis at all volume fractions. Ishai's and Kerner's theories coincide with the finite element analysis with only 2 to 3 percent maximum difference for glass volumes up to 40 percent. After 50 volume percent glass the finite element analysis gives a higher value of modulus than Kerner's and Ishai's theories. If one examines Ishai's experimental results⁽⁸⁾ one finds that the experimental points lie much above the theoretical curve especially for the tension case. Since the value given by the finite element analysis is greater than that of Ishai's theory, there would be better agreement between Ishai's experimental points and the values predicted by the finite element analysis presented here.

F. Flexural and Tensile Strengths.

Flexural strengths for the epoxy composites are plotted as a function of volume percent of filler (Fig. 26). The strength decreases with increase in volume fraction of glass. The mold release (DC-20) treatment is most severe in decreasing the flexural strength. At 50 percent glass content the strength is reduced by more than 60 percent. Both CPO2 and Z-6076 treatments are effective in retaining the strength. At 50 percent glass content the composite retains about 70 percent of the strength of the pure resin. However, the strength properties for the untreated glass composites are nearly identical to the surface treated glasses indicating that the epoxy resin by itself is capable of good bonding to the glass.

The flexural strength of filled polyester (Fig. 27) shows a different trend

Table 7. Comparison of Composite Modulus Predictions by Various Theories

Volume Fractions of Glass	Ratio of Composite Modulus to Matrix Modulus, E_c/E_m .			
	Finite Element Analysis	Ishai	Kerner	Hashin and Shtrikman*
0.2	1.46	1.43	1.47	1.45
0.4	2.31	2.30	2.25	2.11
0.6	4.15	3.98	3.80	3.37

* Lower Bound

Figure 26. Flexural Strength vs. Volume Percent Glass for Epoxy Composites. Solid Lines Represent Theoretical Prediction.

Figure 27. Flexural Strength vs. Volume Percent Glass for Polyester Composites. Solid Line Represents Theoretical Prediction.

than that of filled epoxy. The average strengths as well as the ranges are plotted in Fig. 27. The strength shows a minimum at 10 to 20 percent glass. A similar trend was found by Wambach et al.⁽¹⁰⁾ for polyphenylene oxide filled with silane treated glass. There exists some theoretical justification for such behavior of the material⁽¹⁷⁾. It should be noted that the flexural strength for treated glass exceeds that of the pure polyester at higher volume percents. In addition, the treated glass gives better strength than untreated glass at higher volume fractions. Polyester resins do not bond to glass as well as epoxy resins and the lower strength of the untreated glass is a result of poorer interfacial bonding.

Tensile strengths of filled epoxy specimens have been plotted in Fig. 28. Curves for all treatments, except DC-20, show a minimum at 10 to 20 percent glass content. The DC-20 mold release treatment, as was the case for flexural strengths, produces the lowest strengths. Above 20 percent glass content, the CPO2 treatment gives tensile strengths equal to that of pure resin. Scanning electron microscope photographs of tensile fracture surfaces for epoxy composites are shown in Fig. 29. From these views it appears that the untreated and DC-20 treated glass debond more than the CPO2 treated glass as evidenced by the more obvious pullout of the glass spheres.

The finite element analysis has also been used to predict the strength of the glass spheres filled composites as explained in COO-1794-12 and reference 16. The results of this analysis are shown by the solid lines in Figs. 26 and 27. The two extremes of interfacial bonding assumed in the analysis are perfect bonding and no bonding. The latter is simulated by assuming that the glass spheres are replaced by holes or voids and by then applying the appropriate boundary conditions in the mechanics analysis. It can be seen from Fig. 26 that the strength prediction for no bonding (voids) closely simulates the results obtained for the composites made with the DC-20 (mold release) treated glass spheres. The experimental strength results are

Figure 28. Tensile Strength vs. Volume Percent Glass for Epoxy Composites.
Solid Line Represents Theoretical Prediction.

(a) DC 20
Treatment

↑
50 μ
↓

(b) CPO2
Treatment

↑
50 μ
↓

Figure 29. Scanning Electron Microscope Photographs of Tensile Fracture Surfaces (45 tilt). Specimens Contained 20 Volume Percent Glass in Epoxy Resin.

(c) Untreated

← 50 μ →

greater which can be a result of the presence of residual stresses which have been neglected in the finite element analysis and also as a result of physical contact and frictional forces resulting between the matrix and filler which have been neglected by our assumption of voids replacing solid spheres. The strength analysis assuming perfect bonding very closely simulates strength results particularly for the flexural strength of epoxy composites (Fig. 26). The fact that the experimental strength values are usually greater than the theoretical values may have another explanation. As indicated in reference 18, it is assumed in the finite element analysis that composite failure occurs when the first element fails. A more realistic assumption would be that composite failure doesn't occur until several of the highly stressed elements fail, thus allowing for crack arrest by neighboring inclusions and also allowing for statistical increase in strength for the small volume of material subjected to the stress concentration. The result of this averaging technique would be to raise the theoretical strength thus corresponding more closely to the experimental strengths.

G. Area Under Stress-Strain Curves.

Traditionally, the area under the stress-strain ($\sigma - \epsilon$) curve has been regarded as a measure of toughness since it represents the strain energy stored by the material at fracture for the particular strain rate of the test. For a ductile material the percentage reduction in area at failure is a better measure of fracture toughness⁽¹⁹⁾. For a brittle material where there is uniform elongation to fracture the area under the stress-strain curve gives a measure of fracture resistance. For epoxy composites, this area is plotted in Fig. 30 as a function of the glass content. In Fig. 30 all the data points at a given volume percent are quite close and the ranges might overlap; however, some trends can be observed. The CPO2 treatment consistently gives the highest and Z-6076 treatment the lowest value of area under the $\sigma - \epsilon$ curve. It is significant to note that even for the case of the DC-20 treated glass, the area under the stress-strain curves is approximately equal to the composites with much greater interfacial

Figure 30. Area Under Flexural Stress-Strain Curves vs. Volume Percent Glass for Epoxy Composites.

strengths.

The area under the stress-strain curves for polyester composites as a function of volume percent of filler behave differently (Fig. 31). There is a rapid initial decrease with the first addition of glass. The curve then increases slowly up to 40 volume percent glass and then decreases slightly. The effect of surface treatment is not clear from this data.

H. Izod Impact Energies.

As mentioned earlier impact energies were measured using unnotched specimens. The final value of energy absorbed was corrected for toss-out energy. (The energy absorbed was extremely low for notched specimens; this made it difficult to distinguish between energies absorbed by specimens containing different percents of glass). Fig. 32 shows the results of impact energy measurements for epoxy composites. The impact energy decreases almost linearly with the glass content. It is difficult to distinguish between treatments. At 50 volume percent glass the energy absorbed is about 40 percent of the energy absorbed by the pure resin. The scatter of the data for absorbed energy are not shown in the figure but can be found in reference 18.

The impact energies for polyester composites are plotted in Fig. 33. The behavior here is different from that of the epoxy composites. The impact energy first decreases sharply with the first addition of glass and then increases slightly. It can be observed that there is an excellent correspondence between the unnotched Izod impact energy and the measured area under the stress-strain curves for these composites.

Figure 31. Area Under Flexural Stress-Strain Curves vs. Volume Percent Glass for Polyester Composites.

Figure 32. Unnotched Izod Impact Energy vs. Volume Percent Glass for Epoxy Composites.

Figure 33. Unnotched Izod Impact Energy vs. Volume Percent Glass for Polyester Composites.

VI. FUTURE WORK

The work to be accomplished in the remaining three months of the current contract period is described here.

Additional scanning electron microscopy of the fracture surfaces of spherical particle reinforced polymers will be performed. Also, smaller particle size glass beads will be used in order to obtain composites with smaller mean free paths between particles. The mechanical properties of these composites will be investigated. The fracture energies of these composites will be measured utilizing a tapered double cantilever cleavage specimen. Finite element studies will be completed with additional studies of the influence of the interface on composite properties.

VII. COMPLIANCE WITH CONTRACT REQUIREMENTS

The principal investigator has devoted 2 summer months full time and 20% of his time during the academic year. Approximately 20% of his time will be devoted to the remainder of this current contract. Three graduate assistants, Mr. Agarwal, Mr. Gaggar and Mr. Mallick have participated in this research. Mr. Gaggar has submitted an M.S. thesis utilizing this research and Mr. Agarwal and Mr. Mallick are working towards their Ph.D. degrees.

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APPENDIX I

THREE DIMENSIONAL ANALYSIS

In the three-dimensional analysis, three solutions are needed to be superposed to get the desired boundary conditions as stated in the report. Otherwise, the procedure is quite similar to that for the axisymmetric analysis. The following steps are used with reference to Fig. 7.

- (1) The stress and displacement distribution (No. 1) is found such that:

$$(U_{x1})_{ABFE} = 1 \text{ (arbitrarily specified unit displacement)}$$

$$(U_{x1})_{DCGH} = 0 \text{ (symmetry)}$$

$$(U_{y1})_{BCGF} = 0 \text{ (specified displacement condition)}$$

$$(U_{y1})_{ADHE} = 0 \text{ (symmetry)}$$

$$(U_{z1})_{EFGH} = 0 \text{ (specified displacement condition)}$$

$$(U_{z2})_{ABCD} = 0 \text{ (symmetry)}$$

and $\tau_{xy} = \tau_{yz} = \tau_{zx} = 0$ (on all faces of the cube)

From these boundary conditions, stresses σ_{x1} , σ_{y1} and σ_{z1} in all the elements and displacements U_{x1} , U_{y1} and U_{z1} at all the nodal points are determined.

- (2) The stress and displacement distribution (No. 2) is found such that:

$$(U_{x2})_{ABFE} = 0 \text{ (specified displacement condition)}$$

$$(U_{x2})_{DCGH} = 0 \text{ (symmetry)}$$

$$(U_{y2})_{BCGF} = 1 \text{ (arbitrarily specified unit displacement)}$$

$$(U_{y2})_{ADHE} = 0 \text{ (symmetry)}$$

$$(U_{z2})_{EFGH} = 0 \text{ (specified displacement condition)}$$

$$(U_{z2})_{ABCD} = 0 \text{ (symmetry)}$$

and $\tau_{xy} = \tau_{yz} = \tau_{zx} = 0$ (on all faces of the cube)

(3) The stresses and displacement distribution (No. 3) is found such that:

$$(U_{x3})_{ABFE} = 0 \text{ (specified displacement condition)}$$

$$(U_{x3})_{DCGH} = 0 \text{ (symmetry)}$$

$$(U_{y3})_{BCGF} = 0 \text{ (specified displacement condition)}$$

$$(U_{y3})_{ADHE} = 0 \text{ (symmetry)}$$

$$(U_{z3})_{EFGH} = 1 \text{ (arbitrarily specified unit displacement)}$$

$$(U_{z3})_{ABCD} = 0 \text{ (symmetry)}$$

and $\tau_{xy} = \tau_{yz} = \tau_{zx} = 0$ (on all faces of the cube)

(4) These stress and displacement distributions are superimposed to obtain:

$$\sigma = k_1 \sigma_1 + k_2 \sigma_2 + \sigma_3$$

$$U = k_1 U_1 + k_2 U_2 + U_3$$

where k_1 and k_2 are determined such that net normal forces on the faces ABFE and BCGF are zero. Thus $(F_x)_{ABFE} = \int_{ABFE} (k_1 \sigma_{x1} + k_2 \sigma_{x2} + \sigma_{x3}) dA =$

$$A (k_1 \bar{\sigma}_{x1} + k_2 \bar{\sigma}_{x2} + \bar{\sigma}_{x3}) = 0$$

where A is the area of face of the cube. Therefore $k_1 \bar{\sigma}_{x1} + k_2 \bar{\sigma}_{x2} + \bar{\sigma}_{x3} = 0$.

Summation of the force in y-direction on the face BCGF leads to another equation:

$$k_1 \bar{\sigma}_{y1} + k_2 \bar{\sigma}_{y2} + \bar{\sigma}_{y3} = 0$$

Solution of these equations gives

$$k_1 = -\frac{\bar{\sigma}_{y2} \bar{\sigma}_{x3} - \bar{\sigma}_{x2} \bar{\sigma}_{y3}}{\bar{\sigma}_{x1} \bar{\sigma}_{y2} - \bar{\sigma}_{y1} \bar{\sigma}_{x2}}$$

and

$$k_2 = - \frac{\bar{\sigma}_{x1} \bar{\sigma}_{y3} - \bar{\sigma}_{y1} \bar{\sigma}_{x3}}{\bar{\sigma}_{x1} \bar{\sigma}_{y2} - \bar{\sigma}_{y1} \bar{\sigma}_{x2}}$$

The average normal stress on face EFGH is thus

$$(\bar{\sigma}_z)_{EFGH} = (\bar{\sigma}_{z3})_{EFGH} + k_1 (\bar{\sigma}_{z1})_{EFGH} + k_2 (\bar{\sigma}_{z2})_{EFGH}$$

Average stress, σ_z , for a stress distribution is calculated as:

$$\bar{\sigma}_z = \frac{\int_A \sigma_z dA}{A}$$

where the integral is replaced by a summation as follows:

$$\int_A \sigma_z dA = \sum_{i=1}^n \sigma_z A_i$$

where σ_z is the stress in an element and A_i the area of the element on the face under consideration and n is the total number of such elements.

The modulus of elasticity is calculated from the average stress

$$E = \frac{\bar{\sigma}_z}{\bar{\epsilon}_z}$$

where the strain used is calculated from the specified boundary displacement

$$\bar{\epsilon}_z = \frac{(U_z)_{EFGH}}{|AE|}$$

$(U_z)_{EFGH}$ is the net normal displacement of the boundary as follows:

$$(U_z)_{EFGH} = k_1 (U_{z1})_{EFGH} + k_2 (U_{z2})_{EFGH} + (U_{z3})_{EFGH}$$

$$\text{but } (U_{z1})_{EFGH} = (U_{z2})_{EFGH} = 0$$

$$\text{thus } (U_z)_{EFGH} = (U_{z3})_{EFGH}$$

The normal displacement of the faces ABFE and BCGF are found to be:

$$(U_{x1})_{ABFE} = k_1 (U_{x1})_{ABFE}$$

$$(U_y)_{BCGE} = k_2 (U_{y2})_{BCGE}$$

Poisson's ratios ν_{zx} and ν_{zy} are calculated from these displacements:

$$\nu_{zx} = \frac{\left| (U_x)_{ABFE} \right| / \overline{AD}}{\left| (U_z)_{EFGH} \right| / \overline{AE}} = \frac{\left| k_1 \right| (U_{x1})_{ABFE} \overline{AE}}{(U_{z3})_{EFGH} \overline{AD}}$$

since $(U_{x1})_{ABFE} = (U_{z3})_{EFGH}$ and $\overline{AE} = \overline{AD}$

$$\nu_{zx} = k_1$$

Similarly

$$\nu_{zy} = k_2$$

Due to the symmetry of the problem ν_{zx} and ν_{zy} should be the same.

However, the size and the orientation of the elements near the surface may cause some difference in the values of k_1 and k_2 . Here also the modulus of elasticity and Poisson's ratio are calculated in the process of combining the solutions.

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