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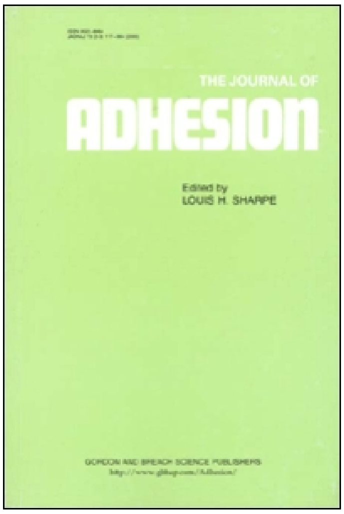

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Separation of Filler Particles from the Matrix in a Particulate-Loaded Composite Subjected to Tensile Stress[†]

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Simultaneous measurements of tensile stress, longitudinal strain, and transverse strain were obtained on particulate-filled composites. The matrix was a flexible epoxy polymer. Small glass spheres were used as filler in various volume ratios up to 0.35. The spheres were pretreated as follows: clean, coated with a parting agent, coated with either of two silane coupling agents. The volume-expansion behaviors of these four systems of composites showed differences attributed to matrix-filler separation and subsequent vacuole formation. Stress-strain behaviors were especially sensitive to this dewetting process. These two types of data, obtained simultaneously and considered together, thus provide valuable information about interface adhesion.

INTRODUCTION

If an extensible matrix material containing a particulate filler undergoes tensile stress, the matrix may start to separate from the filler particles, a process known as dewetting. Vacuoles are thus formed, and the subsequent growth of these vacuoles with increasing strain causes a marked increase in volume of this composite material. This type of volume dilation has been studied by a number of investigators.[1–4] In this paper the volume dilation effect is used in conjunction with stress-strain measurements in an attempt

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to determine how well the matrix and filler particles adhere, and to evaluate the effectiveness of various adhesion promoters or coupling agents.

MATERIALS

The matrix was a flexible epoxy resin formed from a blend of equal parts by weight of the diglycidyl ether of bisphenol A and a low molecular weight diglycidyl ether of polypropylene glycol (DER-732, Dow Chemical Co.),† and cured with 0.7 stoichiometric weight of triethylene tetramine.

The filler material consisted of glass spheres with a distribution of diameters in the range 1 to 30 μm. The glass was an optical crown glass, soda lime type, with a silica content not less than 60% (Standard Class IV Unispheres No. 4000, Cataphote Corp.). Before use the glass spheres were cleaned by passing them near the poles of a powerful permanent magnet to remove iron impurities. They were then washed twice in boiling water and refluxed in ethyl alcohol. Some of the spheres were coated with a methylchlorosilane parting agent (SC-87, General Electric Co.). Another portion was coated with the coupling agent γ-aminopropyltriethoxysilane. A third portion was coated with the coupling agent γ-glycidoxypropyltrimethoxysilane. Composite samples were made using these cleaned and coated glass spheres incorporated in volume fraction amounts between 0.05 and 0.35.

The epoxy resin ingredients were first deaerated individually in a vacuum desiccator for an hour before use. They were then combined in the proper proportions, the glass spheres added, and the resultant slurry stirred under a vacuum for 20 minutes. The mixture was carefully poured into a mold formed from glass or Teflon plates clamped on each side of a 5-mm cork gasket. The mold was sealed and the contents allowed to cure for 16 hours at room temperature. During cure the mold was rotated at 1 rpm in order to prevent the glass spheres from settling. The composite material was post cured in the mold for 16 hours at 50°C, and 8 hours at 100°C. During the latter part of the cure the clamps were removed from the mold. After post cure the composite was unmolded and stored at room temperature.

The composite tended to harden on aging. It was found, for instance, that over a period of 120 days the unfilled epoxy resin increased in Rockwell hardness[5] from an initial reading of -50R to a final reading of $+90$R, with $\frac{3}{4}$ of the increase occurring during the first 30 days. However, it was found

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† Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

that much of the flexibility could be restored to an aged composite by heating it for four hours at 150°C, and then quenching it in water or air at room temperature. A composite treated in this way retained its flexibility for about a week and then hardened slowly. In the tests reported here specimens machined from the molded slabs were heat treated at 150°C, quenched, and and allowed to rest for 2 or 3 days before testing.

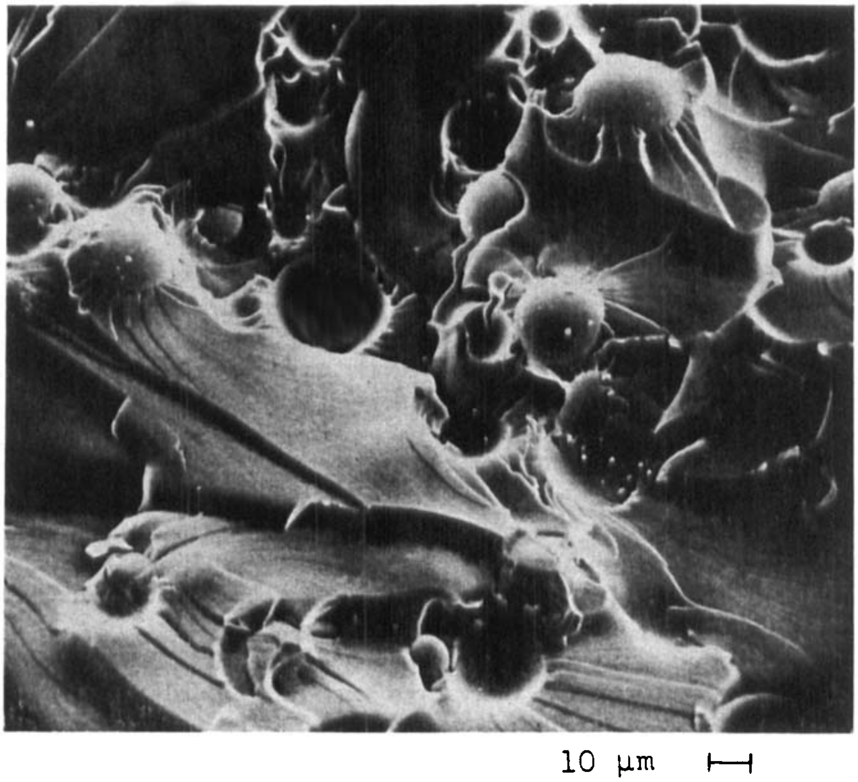
PROCEDURE

The test specimens were of dumbbell shape[6] with 5-cm gage length, 1.3-cm gage width, and 0.5-cm thickness. These specimens were tested on a tensile testing machine at 0.05-cm/min rate of extension and 11.5-cm grip separation. The state of strain in the uniform narrow portion of the specimen was monitored by recording at various instants the separation between two gage marks. Two cathetometers graduated in 0.05-mm increments were used for these measurements. A transverse extensometer employing a small linear variable differential transformer was used to obtain simultaneous measurements of the width of the specimen during test. This extensometer could detect differences in width of the order of 0.001 mm.

Over a period of ten months, tests were made on at least four specimens from each batch of material. For a given batch it was found that the initial slope of the stress-strain curve increased with increasing elapsed time between sample preparation and the heat treatment prior to testing. For purposes of comparison, therefore, the stress-strain curve selected as representative of a given composite was adjusted to correspond to an elapsed time of 150 days between sample preparation and testing. This was accomplished by multiplying the stress values by a constant factor obtained from an interpolation using data from all of the tested specimens in the same batch. Transverse contraction data was not age sensitive so data averaged from tests on the same material were used.

RESULTS OF SCANNING ELECTRON MICROSCOPY

Fracture surfaces of some of the specimens tested were examined by means of a scanning electron microscope. Representative views are shown in Figures 1, 2, and 3. Figure 1 shows the fracture surface of a specimen in which the glass spheres were clean but untreated. Here interfacial separation occurs between most of the spheres and the epoxy material, but the spheres remaining in the fracture surface appear to be well inbedded. In the specimen of Figure 2 the glass spheres were treated with aminosilane coupling agent. For this case



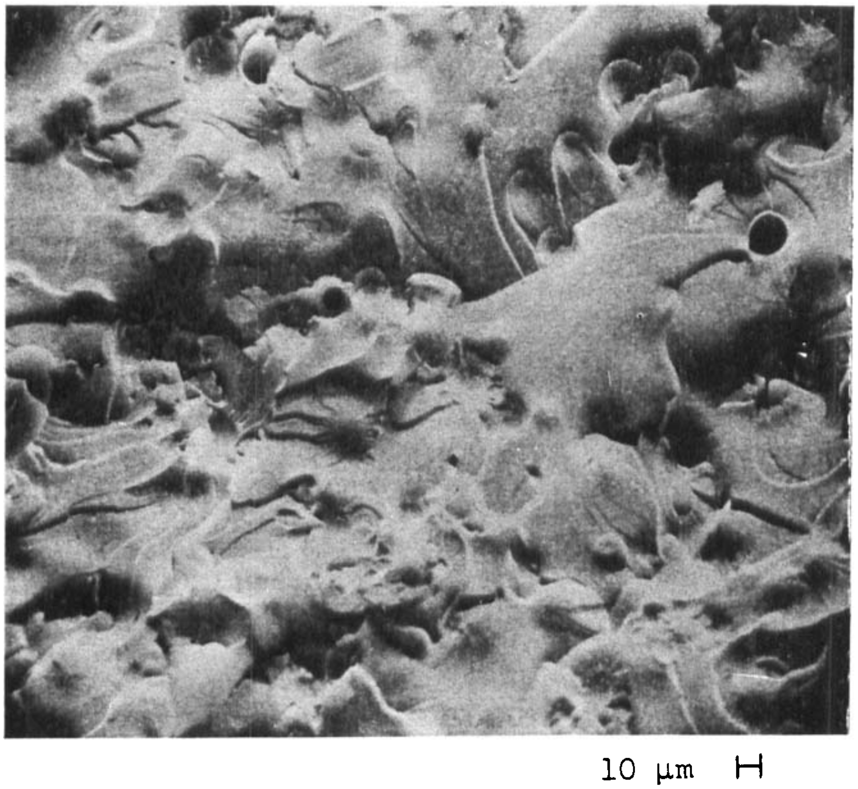
20% GLASS, UNTREATED

FIGURE 1.

fracture occurs mostly in the matrix leaving the sphere surfaces covered. For a specimen in which the glass spheres are treated with a parting agent, Figure 3 shows that a clear separation occurs between sphere and matrix, and spheres remaining in the fracture surface appear to be only loosely held. These results indicate in a qualitative way that the aminosilane coupling agent promotes adhesion between the glass spheres and the matrix material, and the parting agent prevents it, thus confirming the effects to be evaluated from stress-strain and volume expansion data.

STRESS-STRAIN CURVES, RESULTS AND DISCUSSION

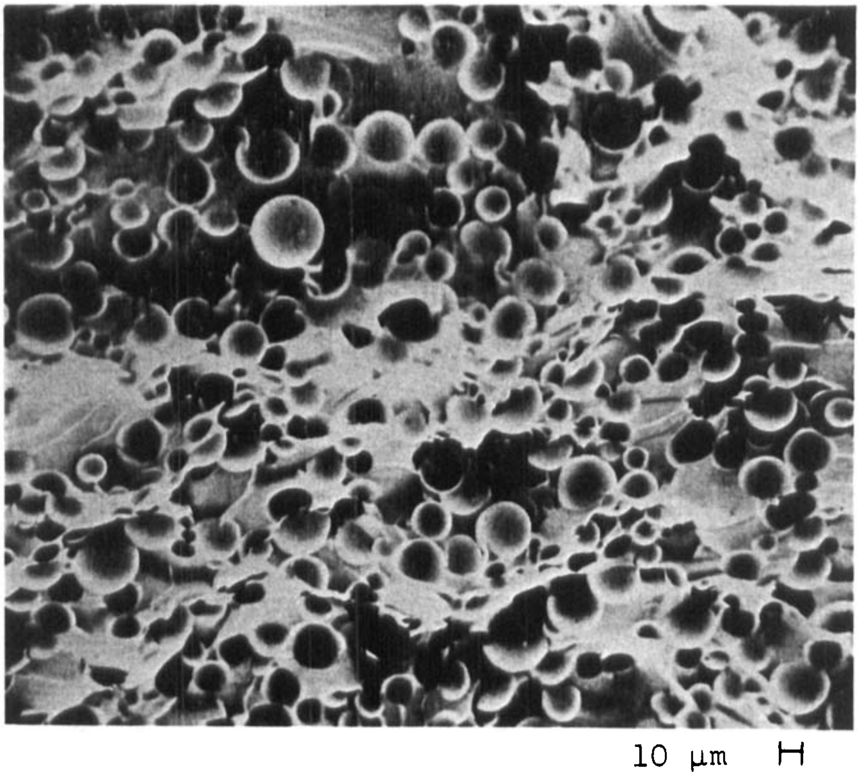
Figure 4 gives stress-strain data for composites containing clean glass spheres in volume fractions of 0.10, 0.20, and 0.30. Stress-strain data for the unfilled



20% GLASS, TREATED WITH AMINOSILANE

FIGURE 2.

epoxy resin are included for comparison. It is seen here that an increase in glass content causes an increase in stress at any given strain and a decrease in the breaking elongation. The stress-strain curve for the unfilled resin consists of two regions of constant slope and a well defined transition between them occurring at approximately 5% strain. The curves for the composites containing 10% and 20% of glass spheres have similar shapes, but the curve for the composite containing 30% of glass spheres is more rounded. This behavior suggests that for this latter material the spheres are separating from the matrix in a continuous fashion, more and more at a time as the specimen is elongated. After a separation the tensile load sustained by the specimen at a given elongation becomes less, and the slope of the stress-strain curve thus decreases. Just before break occurs the slope becomes zero indicating that a large proportion of the sphere surfaces have become separated.



25% GLASS, TREATED WITH PARTING AGENT

FIGURE 3.

Notable also is the fact that the breaking stress for each of these composite materials is greater than that for the unfilled epoxy material. Breakage in these materials occurs by brittle fracture, and evidently the presence of the glass spheres interferes with the crack propagation process.

Data for the composites containing glass spheres treated with the aminosilane coupling agent are presented in Figure 5. The stress-strain behavior is similar to that shown in Figure 4. The curves for the composites containing 10% and 20% of glass spheres are similar to that for the unfilled epoxy matrix, but the curve for the composite containing 30% of glass spheres is slightly rounded indicating that some separation of filler from matrix may be taking place.

Figure 6 presents data for the composites containing glass spheres treated with epoxy silane coupling agent. In general the behavior is similar to that

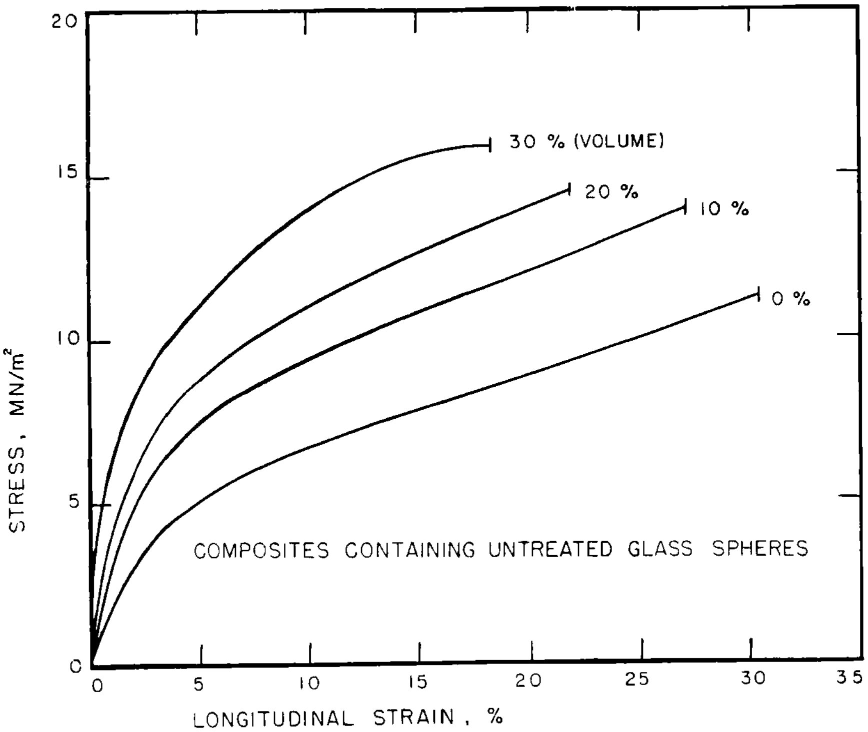


FIGURE 4.

noted for the two systems of composites discussed previously. However the curve for the material containing 25% of glass spheres seems inconsistent with the other data. It lies below the curve for the material containing only 15% of glass spheres, and does not have the well defined knee present in the 15% and 5% curves. It is possible that the spherical filler was not well dispersed in this sample and that early separation of some of the matrix and filler occurred. However it should be noted that the curve for the material containing 35% of glass spheres is also rounded, thus a transition in stress-strain behavior may be occurring at filler loadings near 25% by volume.

The stress-strain behavior of composites containing glass spheres coated with parting agent is depicted in Figure 7. For these materials an increase in the amount of glass causes an increase in the initial slope of the stress-strain curve, but at strains higher than 5% the stresses for the more highly filled materials do not increase with strain. Indeed, for a glass content of 35% the stress even decreases slightly for strains ranging between 5% and 10%. The breaking stress for each of these materials is less than that for the unfilled

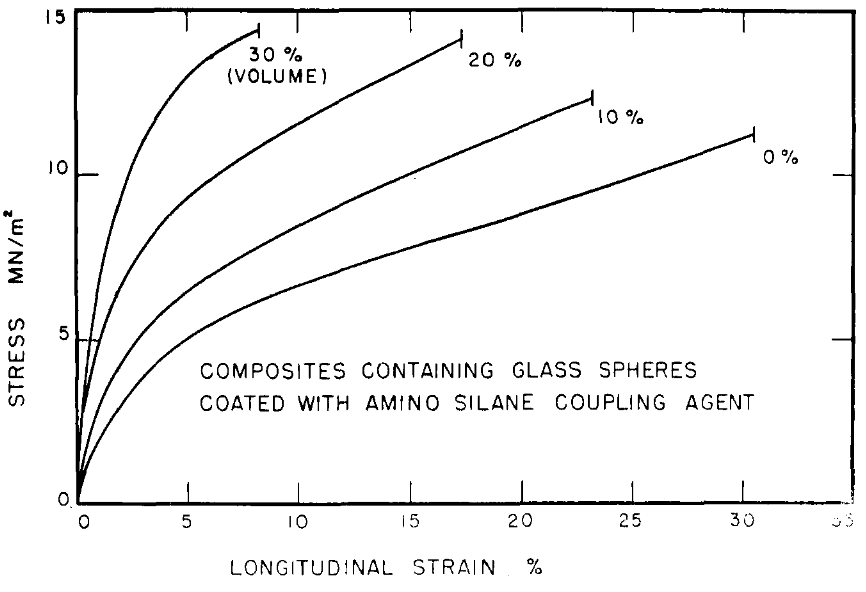


FIGURE 5.

epoxy matrix. This suggests that at break most of the sphere surfaces have separated from the matrix, and do not transmit any of the applied tensile force. For the material containing 35% volume of filler almost all of the spheres have probably become separated when the specimen has been stretched 7%. Further stretching serves only to increase the volume of vacuoles formed without significantly increasing the average tensile strain (or stress) in the epoxy matrix.

Figure 8 shows the effect of filler surface treatment on the stress-strain curves for composites containing approximately the same content (0.30 or 0.35 volume fraction) of glass spheres. These plots suggest that for perfect adhesion between filler and matrix the initial slope of the stress-strain curve is steep and is maintained to a high stress level, as exemplified by the curves for materials containing glass spheres treated with silane coupling agents. The curve for material filled with clean glass spheres does not maintain its initial slope to as high a stress level, and the curve for material containing glass spheres treated with parting agent has a lower initial slope. This is similar to the stress-strain behavior reported by Kenyon[7] for a slightly different epoxy-glass composite. It seems then that some of the clean glass spheres and many of the spheres treated with parting agent are not attached firmly to the matrix in the unstrained state, so that separation can occur at very low stress levels. Stress-strain data provide a sensitive means of detecting this effect.

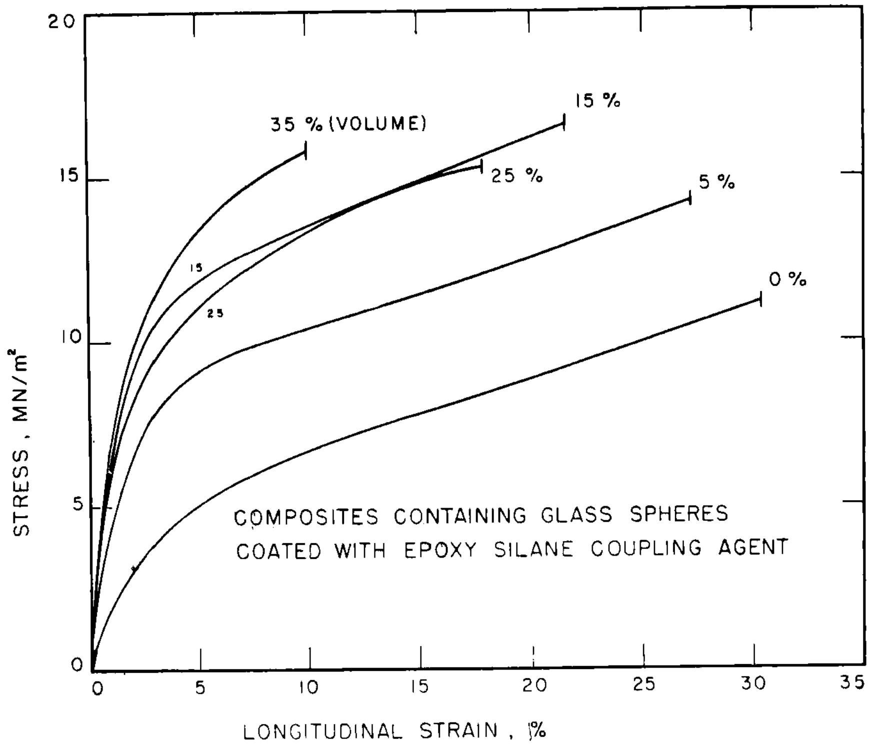


FIGURE 6.

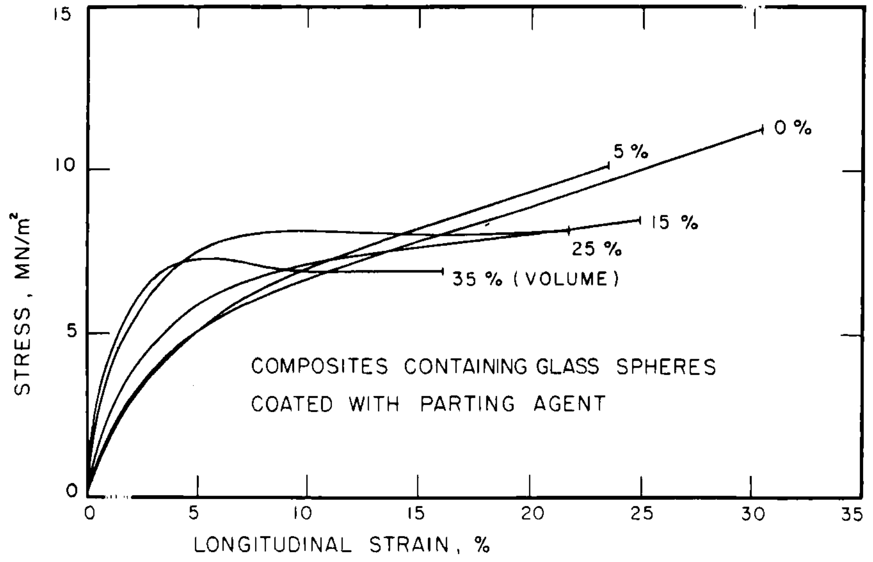


FIGURE 7.

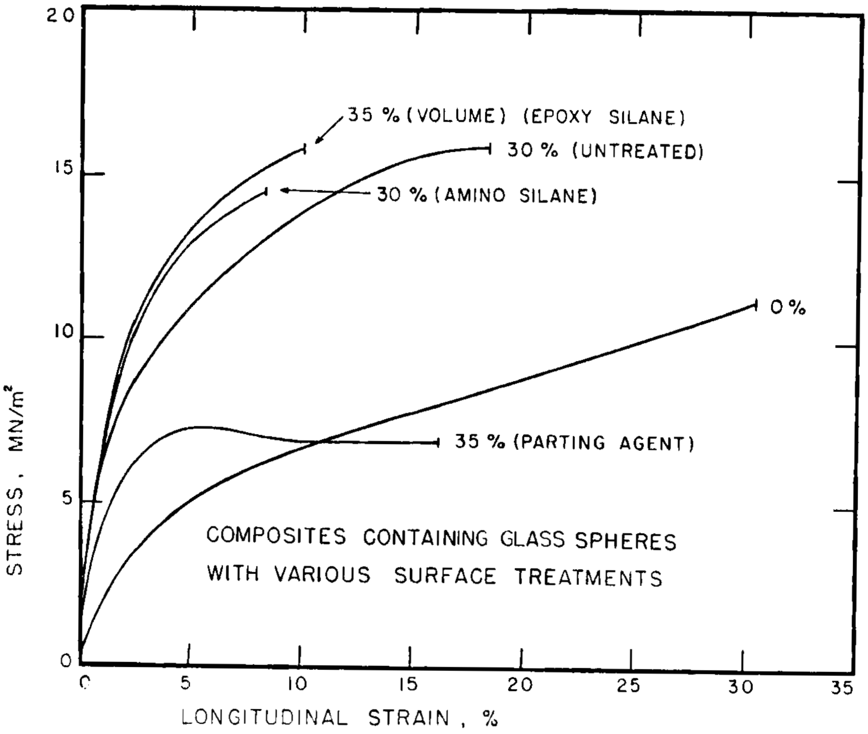


FIGURE 8

TRANSVERSE CONTRACTION DATA, RESULTS AND DISCUSSION

If λ_1 represents the longitudinal extension ratio, and λ_2 the transverse extension ratio, the volume ratio (VR), assuming that the materal is isotropic, is equal to $\lambda_1\lambda_2^2$. Thus if the volume remains constant as the specimen is subjected to successively greater uniform tensile strains, a plot of log λ_2 *vs* log λ_1 is a straight line of slope -0.5. Data for the matrix material studied here plot very close to this straight line. The transverse contraction data, therefore, can be presented compactly as a plot of $\log \lambda_2 + 0.5 \log \lambda_1$ *vs* $\log \lambda_1$; or, noting that the ordinate reduces to $0.5 \log \lambda_1\lambda_2^2$, as a plot of 0.5 log (VR) *vs* log λ_1. This is the method of representation used in Figures 9–13. The scales are graduated linearly in 0.5 log (VR) and log λ_1, but labeled in terms of the corresponding values of volume expansion and longitudinal strain.

It was found that the initial behavior of different specimens from the same slab of material exhibited considerable variation. The cause of this variation is not known, but it is not believed to result from a lack of precision in the

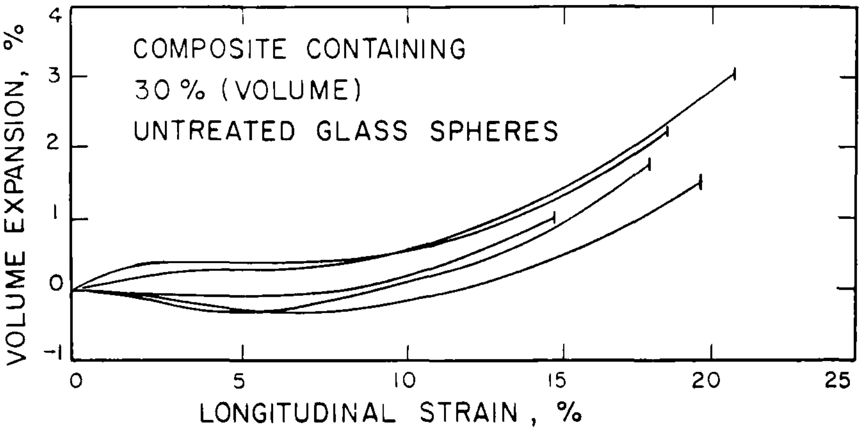


FIGURE 9

measurements. An example of the variation is given in Figure 9, where the results of tests are shown for five specimens of a composite containing 30% by volume of clean untreated glass spheres. Here the different initial behaviors of the various specimens produce an uncertainty of about ±0.5% in the absolute value of the percent volume expansion of this material. Approximately this same uncertainty was noted for each of the materials tested. Although the initial behaviors are different, the subsequent behaviors of the specimens are similar; i.e., there is a region where the volume is constant followed by a region where the volume increases with strain at the same rate for each specimen. It is interesting to note that in many of the specimens the volume decreases initially with increasing strain. This volume decrease serves

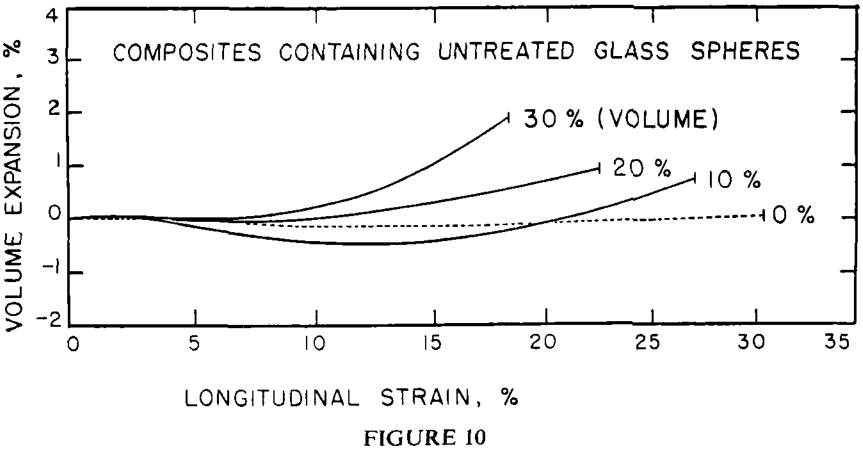


FIGURE 10

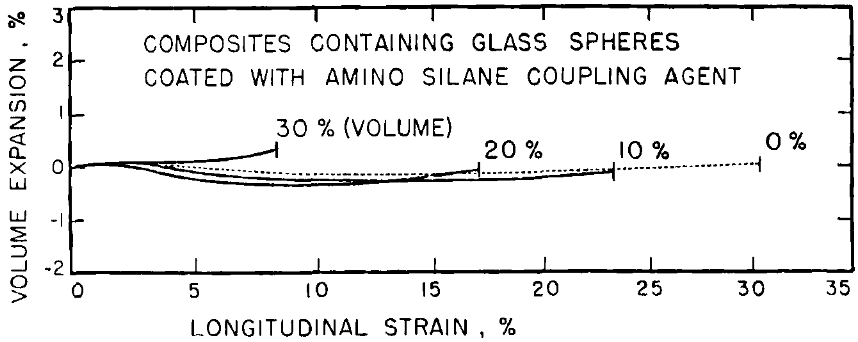


FIGURE 11

to mask some of the subsequent increase in volume of the composites due to the formation of vacuoles at the interface between matrix and filler.

Figure 10 shows the volume dilation as a function of longitudinal strain for composites loaded with 10, 20, and 30 volume percent of clean untreated glass spheres. The dotted line shows the behavior of the unfilled epoxy matrix. The composites containing 10% and 20% of glass spheres show only gradual increases in volume with increasing tensile strain, an indication that only a few of the spheres have become separated from the matrix at break. The change in volume of the composite containing 30% of spheres is more pronounced, in agreement with the inferences drawn from the stress-strain data in Figure 4.

Data for the two composite systems containing spheres treated with the silane coupling agents are given in Figures 11 and 12. Apparently the amino-silane agent provides good adhesion in the materials for each volume fraction of glass. The epoxy silane is slightly less effective. Note especially the large

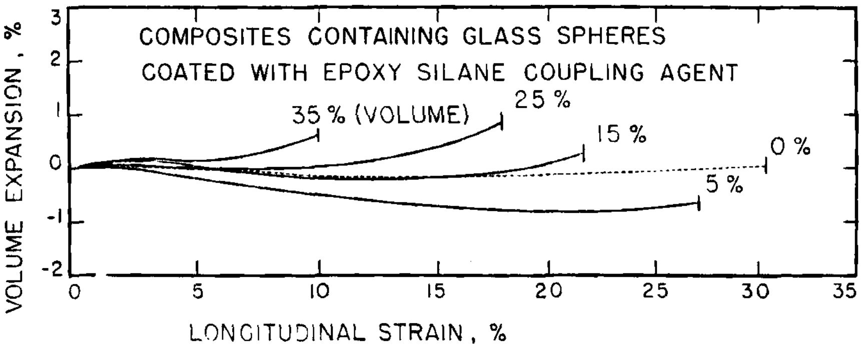


FIGURE 12

volume expansion at break for the composite containing 25% of glass spheres. This confirms the stress-strain behavior of this material shown in Figure 6.

The volume expansion behavior of the materials containing glass spheres coated with parting agent is shown in Figure 13. The volume expansions for the 15%, 25%, and 35% materials are all large. The corresponding volume expansions of materials containing either clean glass spheres or spheres coated with coupling agent are significantly less, indicating that in these latter cases many of the spheres have not separated from the matrix at break. The volume expansion behavior of the material containing 35% of glass spheres coated with parting agent is especially interesting. It consists of two regions, an early one in which the volume increases slowly with strain, and a later one in which the rate of volume increase is much greater. In the early region the spheres evidently separate from the matrix one at a time. The effect of this early separation is to decrease the initial slope of the stress-strain curve, as was noted in discussion of the stress-strain curves of Figure 8. The later region corresponds to the region of strain in which the stress is constant in this material. This agrees with the idea stated previously that in this strain range of the specimen,[1] all of the sphere surfaces have separated from the matrix. The large rate of volume expansion then is due entirely to a proportional increase in the volume of each vacuole.

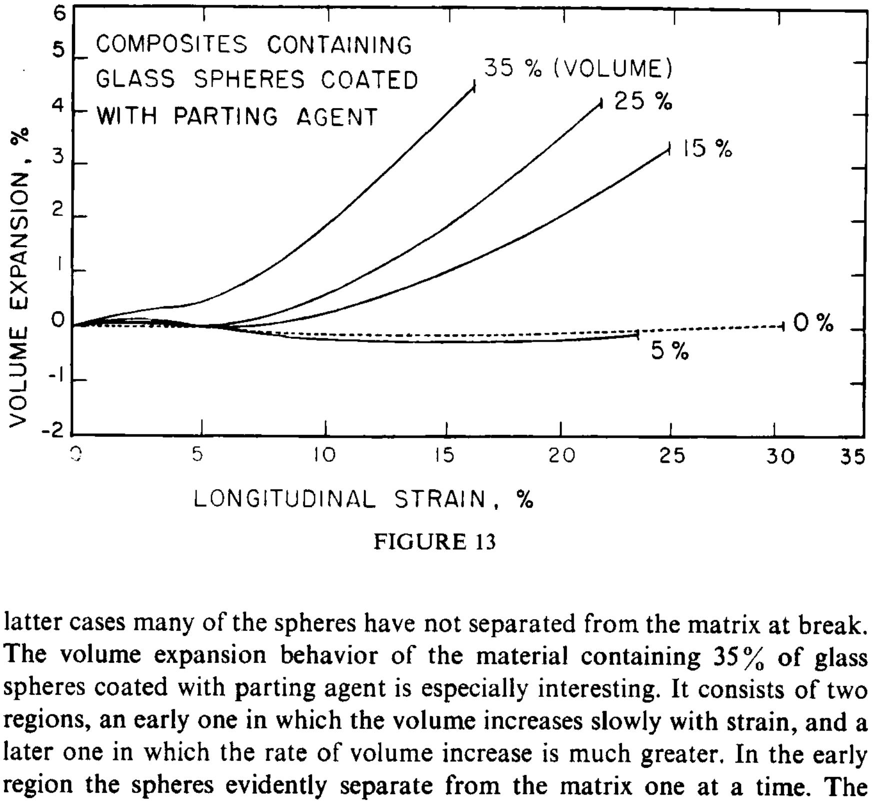


FIGURE 13

CONCLUDING REMARKS

Tests on this system of composite materials have shown that stress-strain properties are sensitively dependent on the degree of adhesion between the filler particles and the polymer matrix. The volume change properties are also influenced by adhesion but not as sensitively. These two kinds of measurements, made simultaneously and considered together, can provide information on interface adhesion during the straining process. Thus the differences in adhesive behavior between materials containing clean glass spheres, spheres treated with silane coupling agents, or spheres treated with a parting agent are easily distinguished. There is even an indication that in the system studied here the aminosilane coupling agent is slightly more effective than the epoxy silane agent as an adhesion promoter. The measurements also show that early interface separation (dewetting) can occur in a gradual process involving separation of one sphere at a time. This early sphere by sphere separation is sensitively detected by stress-strain data. It seems to occur even when the spheres are treated with silane coupling agents, if the volume fraction of the spheres exceeds 0.25.

Although stress-strain measurements provide a sensitive indication of dewetting behavior they should not be used by themselves to infer this behavior. Many of the features attributed here to dewetting are observed in the stress-strain curves of some unfilled polymers. Thus if these polymers are used as matrices, dewetting might be wrongly inferred. Inferences derived from stress-strain behavior should be corroborated by information obtained from other kinds of measurements. Transverse contraction measurements are easily obtained simultaneously on the same specimen and provide this corroborative information.

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