

Physical Aging in Particulate-Filled Composites with an Amorphous Glassy Matrix

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Synopsis

Physical aging was studied on particulate-filled glassy network polymers by means of mechanical-dilatational, differential scanning calorimetry (DSC) and density measurements on specimens that were aged at room temperature. The composites aged for 0.5 day fractured in a brittle manner at a constant ultimate stress, which is close to the tensile strength of the unfilled material, regardless of the filler content and the presence of a coupling agent. This type of mechanical behavior is caused by the compressive residual stresses that are present due to curing and differential thermal shrinkage. As aging takes place, the compressive residual stresses are relieved; as a result the ultimate tensile strengths of the composites decrease. The 120-day-old untreated glass bead containing composites exhibited dilatation and yield in mechanical-dilatational testing. This type of behavior is described as "having no adhesion" between the filler and the matrix. The 120-day-old composites with coupling agent-treated glass beads fractured at a tensile stress which is equal to 1/1.6 the tensile strength of the unfilled material. These materials did not exhibit dilatation and yield in mechanical-dilatational testing. Density and DSC data indicate densification and enthalpy relaxation upon aging and support the hypothesis presented for the observed change in the mechanical-dilatational behavior.

INTRODUCTION

Polymeric glasses undergo physical aging when stored below their glass transition temperature.¹ The relatively immobile chains pack with time, resulting in volume and enthalpy relaxation. The density, tensile and flexural yield strengths, and elastic modulus increase; impact strength, fracture energy, ultimate elongation, and creep rate decrease upon aging, and a transition from ductile to brittle fracture may occur.²

In contrast to the extensive studies made on aging of polymeric glasses,¹ composites with glassy polymeric matrices have not received as much attention. Nicolais and Narkis³ studied the stress-strain behavior of styrene-acrylonitrile (SAN)/glass bead composites in the glassy region and observed yield when unannealed composites were stretched. However, annealing resulted in smooth stress-strain curves with no discontinuities. It was also stated that Young's modulus of the 21.3% filled composite was 20% higher after annealing. In Ref. 4 stress-strain-dilatational behavior of a flexible epoxy/glass bead composite was investigated. It was mentioned that the composites hardened on aging. The unfilled epoxy resin increased in Rockwell hardness from -50R to +90R in 120 days, with 75% of the increase taking place in the first 30 days. Flexibility was restored by heating and quenching. It was found that Young's modulus of these composites increased upon aging in contrast to the findings in Ref. 3. Smith⁵ reports similar increase in Young's modulus with aging time in rigid epoxy/glass

TABLE I
 Materials Studied^a

Crosslink density (g mol/g matrix)	Vol % of filler					
	0	10	20	30	40	50
1.5×10^{-3}	†				A	
1.75×10^{-3}	†			A,A*		
2.0×10^{-3}	†	A,A*	A,A*	A,A*	A,A*	A,A*
2.18×10^{-3}	†				A	

^a † = unfilled materials. The letter A denotes untreated glass beads having an average diameter of 25 μm . The symbol A* denotes treated glass beads having an average diameter of 25 μm .

bead composites. In that study⁵ Young's modulus was affected by aging time, but was not affected by the relative humidity of the environment.

In this study, glass bead/network polyurethane composites were prepared in order to study the effects of aging on mechanical behavior. The volume fraction of the filler, crosslink density of the matrix and the degree of coupling between the matrix were studied as material properties. Materials were characterized by mechanical-dilatational, differential scanning calorimetry (DSC) and density measurements after aging for various time intervals at room temperature and humidity, as well as room temperature and 0% relative humidity.

MATERIALS

The materials were synthesized by reacting a polyoxypropylene diol of 1050 g/g mol molecular weight and a polyoxypropylene triol of 425 g/g mol molecular weight with TDI. The TDI was a mixture of 80% 2,4-, 20% 2,6-tolylene diiso-

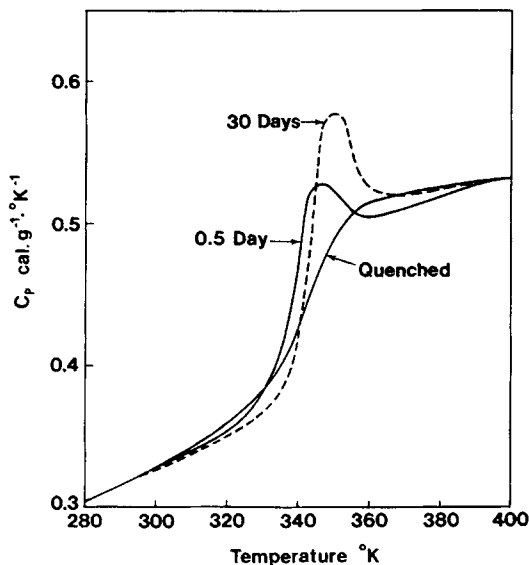


Fig. 1. Specific heat of the unfilled polymer with a crosslink density of 2×10^{-3} (g mol crosslinks/g matrix) after various periods of aging.

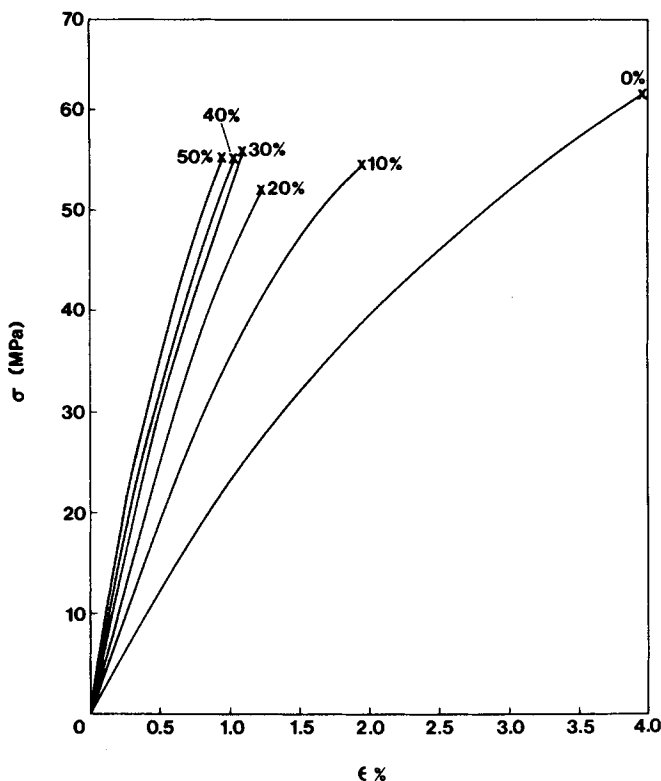


Fig. 2. The stress-strain behavior of untreated glass-bead-filled composites after 0.5 day of aging. No dilatation is observed.

cyanate. Glass beads of 25 μm average diameter were used with no surface treatment and also with an amino functionality silane coupling agent surface treatment. The crosslink density of the matrix was controlled by using stoichiometric amounts of glycols and TDI, but varying the diol-triol ratio. Ferric acetyl acetonate was used at 0.01 wt % of reactive components as a catalyst.

The glycols were dehumidified, degassed, and transferred into a vacuum reaction kettle equipped with a mechanical stirrer. Previously dehumidified glass beads and the catalyst were added, and the mixture was cooled down to room temperature while stirring under vacuum. Then the stoichiometric amount of TDI was added. The reaction mixture was further stirred under vacuum for 1–2 min and poured into a Teflon-coated glass mold which was preheated to 100°C. Rapid solidification of the mixture under these conditions prevented settling of the glass beads. The composite was further cured for 16 h at 100°C. The thickness of the plates prepared were approximately 2.3 mm.

Specimens for all tests were cut with dies at 70–100°C and then annealed at 100°C for 4 h, followed by slow cooling overnight inside the hot oven. Materials were then aged for various time intervals at room temperature and humidity, as well as room temperature and 0% relative humidity.

Materials studied are shown in Table I. The filler fractions discussed in this

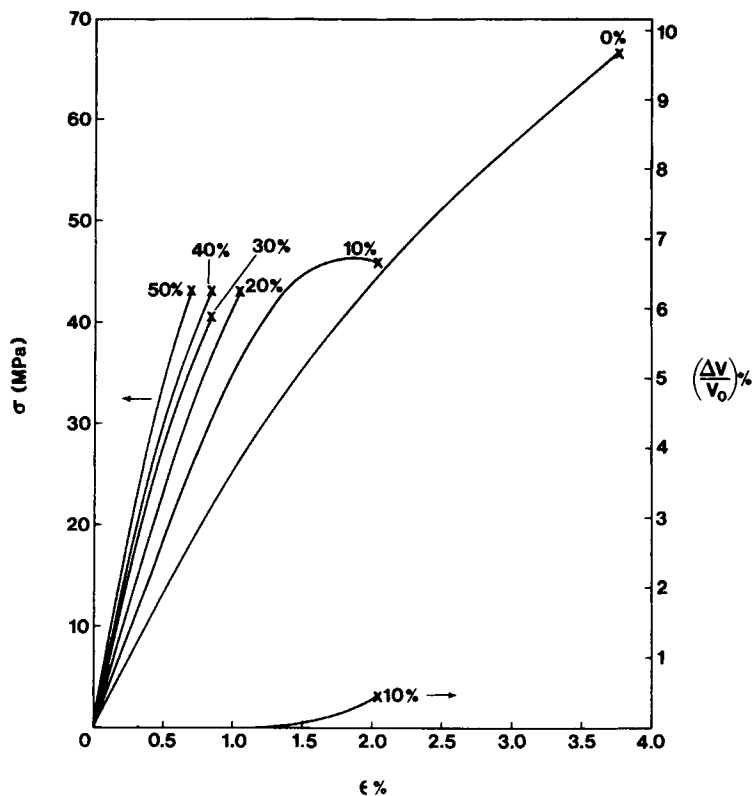


Fig. 3. The stress-strain-dilatational behavior of untreated glass-bead-filled composites after 15 days of aging.

paper are based on volume. Materials have a matrix crosslink density of 2×10^{-3} (g mol crosslinks/g matrix) whenever not specified.

EXPERIMENTAL AND DISCUSSION

Differential Scanning Calorimetry

Previously cut and annealed samples were investigated by DSC. It was found that the materials were amorphous with glass transition temperatures of 35, 50.5, 66, and 72°C for crosslink densities of 1.5×10^{-3} , 1.75×10^{-3} , 2.0×10^{-3} , and 2.18×10^{-3} (g mol/g matrix). The glass transition temperatures increase linearly with increasing crosslink density. No systematic changes of T_g were observed with different filler contents and coupling agents.

DSC data were taken with a Perkin-Elmer DSC 2. Two runs were made on each sample. The glass transition temperatures mentioned are determined from the inversion points of the second run. The first run was performed at 20 K/min heating rate up to 400 K. Then the sample was quenched at 80 K/min cooling rate to 270 K, and the second heating run was started at 20 K/min heating rate. The second run is referred to as the quenched run. A sample of the DSC data

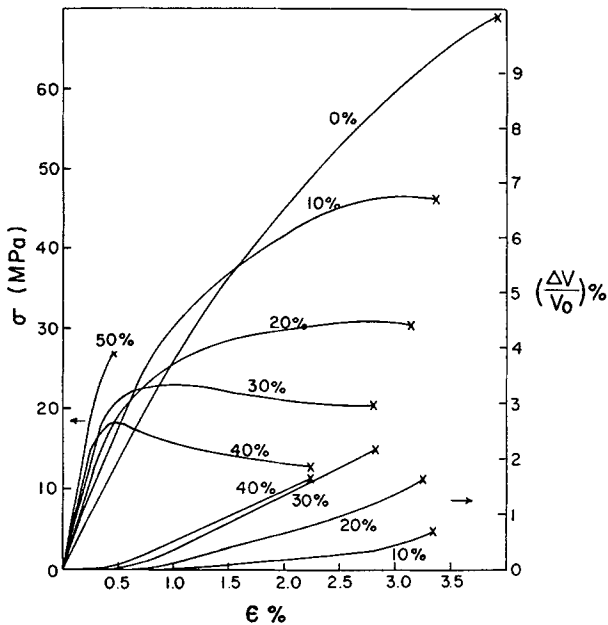


Fig. 4. The stress-strain-dilatational behavior of untreated glass-bead-filled composites after 120 days of aging.

is shown in Figure 1 for the unfilled material having a crosslink density of 2.0×10^{-3} (g mol/g matrix). The results are similar to literature data.⁶ An increasing enthalpy recovery is seen with increasing age. Even the sample tested after 0.5 day is significantly different from the quenched sample. It is known that the process of enthalpy recovery is logarithmic with time; thus significant relaxation takes place during slow cooling and in the following 12 h of aging. Similar data were obtained at other crosslink densities and for filled specimens. However a quantitative comparison as in Figure 1 cannot be made in composites without correcting for the exact amount of filler in the specimen.

Density

For density measurements approximately 5 cm³ of samples were cut and heat-treated as outlined earlier. Densities were obtained by the hydrostatic weighing technique. A sample was hung and weighed in air, as well as in controlled temperature, distilled water enabling a determination of the volume. The density of the *same* sample was followed over a period of 120 days, since the density variation among seemingly identical samples can be quite large due to uneven distribution of the filler. Density measurements were made on unfilled, 30% untreated glass-bead-filled and 30% treated glass-bead-filled materials having matrix crosslink density of 2.0×10^{-3} (g mol/g matrix).

The average densities of five specimens obtained after 0.5 day of aging were 1.1641 g/cm³ for the unfilled material, 1.5749 g/cm³ for the untreated glass bead filled material, and 1.5720 g/cm³ for the treated glass-bead-filled material. The

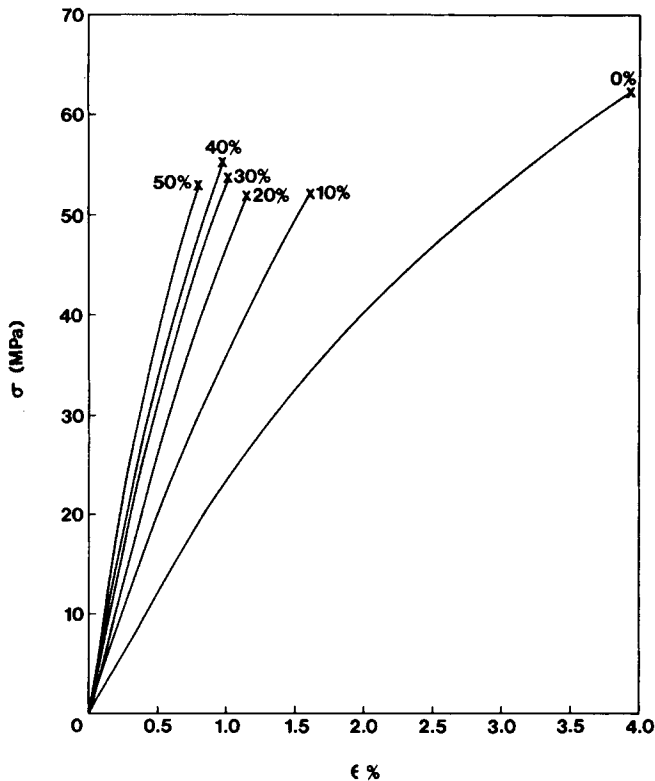


Fig. 5. The stress-strain behavior of treated glass-bead-filled composites after 0.5 day of aging. No dilatation is observed.

density of the unfilled material increased 0.27% and the densities of the 30% filled materials increased approximately 0.2% after 15 days of aging. The densities remained constant within the accuracy of the experiments for the following 105 days.

The magnitude and the nonlinear increase of density with time is similar to data obtained on PMMA.⁷

Mechanical-Dilatational Measurements

Mechanical-dilatational measurements were made on ASTM D638-Type I samples cut with a die and heat treated as outlined earlier. The gas dilatometer of Ref. 8 was used in obtaining the mechanical-dilatational data.

Dilatational measurements provide information on the mode of the deformation and the degree of adhesion between the filler and the matrix.⁸⁻¹⁰

Materials were tested at 23°C, at a strain rate of 0.1 min⁻¹. The strain rate is based upon the total gage length in between grips. The stresses in this report are based on the original cross-sectional area of the specimen.

Mechanical dilatational response of composites with indicated amounts of untreated filler are shown in Figures 2-4. Materials in Figures 2, 3, and 4 were aged at room temperature and humidity for the indicated periods of time.

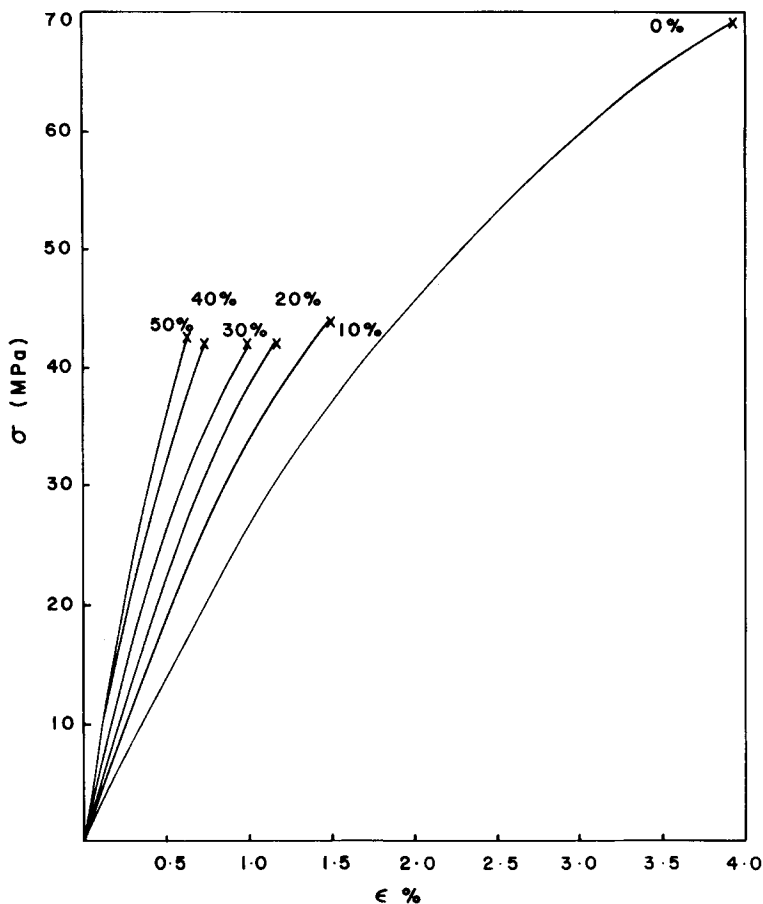


Fig. 6. The stress-strain behavior of treated glass-bead-filled composites after 120 days of aging. No dilatation is observed.

Similar data are presented in Figures 5 and 6 for treated filler containing composites that were aged under similar conditions. The crosslink density of the matrix in Figures 2-8 is 2×10^{-3} (g mol crosslinks/g matrix). The ultimate stresses of composites with untreated glass beads are shown in Figure 7, the ultimate stresses of composites with treated glass beads are shown in Figure 8.

It is seen in Figures 7 and 8 that the ultimate stresses of the composites aged for 0.5 day are all the same regardless of the filler content and the presence of the coupling agent. The tensile strength of these relatively unaged composites are close to the tensile strength of the unfilled material. The tensile strengths drop when the composites are aged as shown in Figures 7 and 8.

The mechanical response of the unfilled material in Figures 2-4 is in qualitative agreement with other polymeric glasses, i.e., the modulus and the tensile strength increases and the ultimate elongation decreases upon aging. The mechanical response of the composites are in apparent contrast to the mechanical response of the unfilled polymer, but consistent with the annealing experiments of Ref.

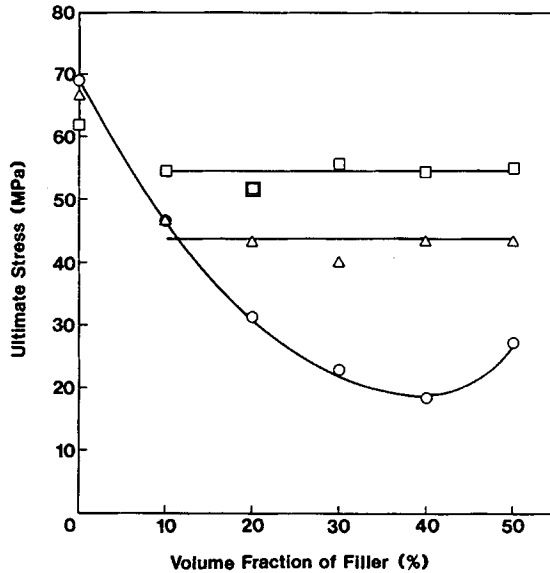


Fig. 7. Ultimate stress of untreated glass-bead-filled composites as a function of the aging time (after annealing): (□) 0.5 day; (Δ) 15 days; (○) 4 months.

3. The moduli of the composites decreased approximately 10% upon aging for 120 days, the tensile strengths dropped, and the ultimate elongations increased in some cases.

All unaged composites fractured in a brittle manner without undergoing dilatation and yield. It is known^{8,11} that dilatation in particulate-filled glassy thermosets is caused by dewetting of the filler particles from the matrix. Dewetting results in yield and gives rise to ductile behavior. Dilatation was observed in the 10% untreated glass-bead-filled composite that was aged for 15 days and in the 10, 20, 30, and 40% untreated glass-bead-filled composites that were aged for 120 days. Dilatation was not encountered in treated glass-filled composites.

In view of the DSC and density data, the following mechanism is proposed for the effect of aging on the mechanical-dilatational properties. Residual stresses form as a result of cure shrinkage, as well as the differential thermal shrinkage between the filler and matrix when the composite is cooled from above its glass transition temperature. The thermal expansion coefficients of polymers¹² are much larger than the thermal expansion coefficient of glass, resulting in compressive residual stresses on the filler particles.

It is also known that when a particulate-filled composite is subjected to external load, the stresses near the interface are not equal to the "far field" applied stress.¹³ For rigid spherical inclusions Goodier¹³ calculated a stress concentration factor of 1.8 at the poles. Sahu and Broutman¹⁴ calculated stress concentration factors of 1.8-2.8, depending on the filler content.

Thus when a composite of the type studied is subjected to external loading, there are two types of competing stresses at the polymer-filler interface. There exist compressive residual radial stresses and the tensile stresses which are multiplied by a stress concentration factor. The actual stress field is determined

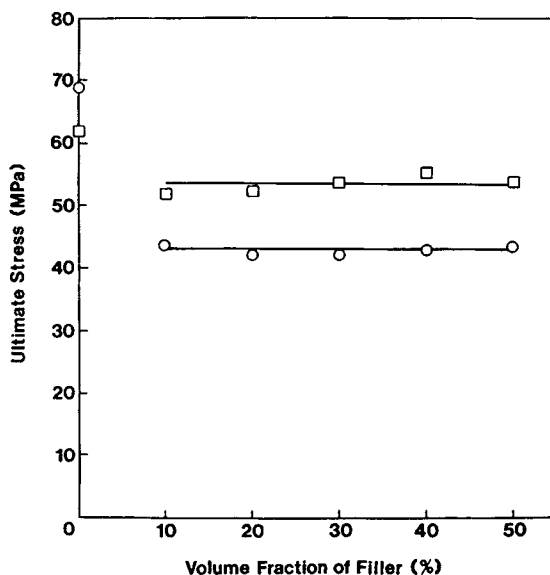


Fig. 8. Ultimate stress of treated glass-bead-filled composites as a function of the aging time (after annealing): (\square) 0.5 day; (\circ) 4 months.

by the superposition of the two fields. Thus when an unaged specimen having compressive residual stresses is loaded in tension, the true tensile stress at the polymer-filler surface can be smaller than the average "far field" stress in the matrix. In this case fracture takes place in the matrix without dewetting. The tensile strengths of the unaged composites may then be independent of the filler content and the presence of the coupling agent as demonstrated in Figures 2 and 5. In the extreme case, e.g., when a sample is quenched as opposed to slow cooling as it is done here, the tensile strength of the composite can be equal to the tensile strength of the unfilled material. This type of failure is referred as "good adhesion" failure in the literature.¹⁵

As aging takes place, volume and enthalpy relaxations occur, compressive residual radial stresses diminish, and the apparent adhesion between the matrix and the filler becomes poor. In aged composites with uncoated filler particles, failure takes place between the matrix and the filler. These composites exhibit dewetting and yield prior to fracture. This type of mechanical-dilatational behavior is observed in 120-day-old untreated glass-bead-filled composites of Figure 4. The corresponding tensile strength data of these composites seen in Figure 7 is very similar to those in Refs. 16 and 17, where the tensile strength is a decreasing function of the filler content. This type of behavior is referred as "no adhesion" behavior.¹⁵

In the intermediate case the compressive residual stresses are partially relaxed. When a specimen of this type is loaded in tension, the fracture stress of the unfilled polymer may be reached in the "far field" matrix phase, before dewetting can occur. Then the material fractures without dewetting, but now at an observed stress which is smaller than the tensile strength of the unfilled polymer due to partial relaxation of the compressive residual stresses upon aging. This type of response is observed in the 20–50% filled composites of Figure 3 and the 50% filled composite of Figure 4. The stress concentrations may overlap at higher

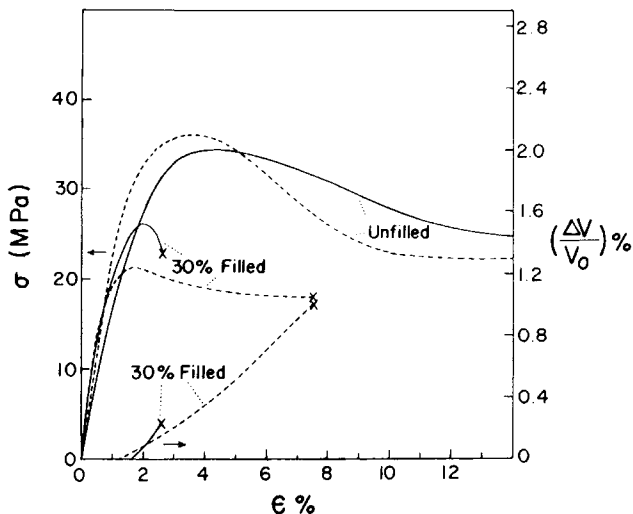


Fig. 9. Stress-strain-dilatational behavior of untreated glass-bead-filled composites after 0.5 (—) and 60 (---) days of aging. The matrix crosslink density is 1.75×10^{-3} (g mol crosslinks/g matrix). No dilatation is observed in the unfilled material.

filler contents; thus brittle behavior may be encountered at high filler loadings. At high filler contents, the stress at far field can become greater than the tensile strength of the polymer before the polymer-filler separation can take place at the interface.

The same process of relaxation takes place in coated-filler-containing composites, except now the polymer chains are chemically bound to glass beads; therefore, there exists some adhesion between the filler and the matrix. Composites with coated filler fractured without any dilatation and yield, as observed in Figures 5 and 6. However, the tensile strength of the composites dropped to (1/1.6) the tensile strength of the unfilled polymer upon aging. This type of behavior can be predicted quite well by the finite-element analysis of Sahu and Broutman, where materials were assumed to have perfect adhesion, but no residual stresses.¹⁴

The slight decrease in the modulus of the composites upon aging in contrast to the increase in the modulus of the unfilled material can also be explained in the same way. It is believed that in aged composites very few particles dewet even at very low stresses, causing a greater extension than in the case of no dewetting, and thus giving rise to lower moduli.

The transition of the brittle to ductile fracture of composites upon aging is a rather sensitive function of the crosslink density, extensibility, and T_g of the matrix as well as the filler content. The mechanical-dilatational response of 30% untreated glass-bead-filled composite with a matrix crosslink density of 1.75×10^{-3} (g mol crosslinks/g matrix) is shown in Figure 9. The glass transition temperature at this crosslink density is 50.5°C . This matrix had a large extensibility, and the composite exhibited dewetting, dilatation, and yield even after only 0.5 day of aging. In the unfilled material, aging increased the tensile

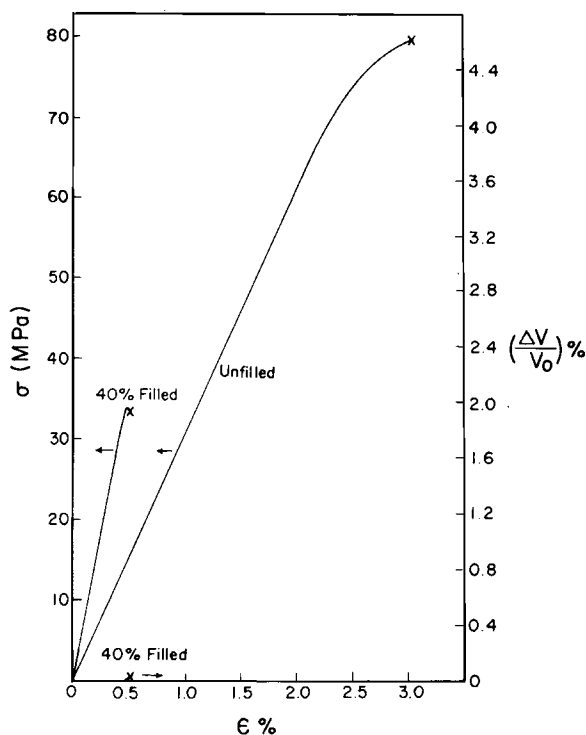


Fig. 10. Stress-strain behavior of untreated glass-bead-filled composites after 120 days of aging. The matrix crosslink density is 2.18×10^{-3} (g mol crosslinks/g matrix). No dilatation is observed in the unfilled material.

strength and the elastic modulus, but decreased the strain at yield, as observed in other glassy polymeric materials. However, in the filled material yield is primarily caused by dewetting of the filler particles from the matrix. As the filled material aged and the compressive residual stresses were relieved, the strain at the initiation of dewetting decreased; consequently, the yield stress also decreased.

On the other hand, a composite having 40% untreated filler and a matrix of 2.18×10^{-3} (g mol crosslinks/g matrix) crosslink density, fractured in a brittle manner even after 120 days of aging. This composite shown in Figure 10 had a lower extensibility and a higher T_g of 72°C .

It was found that the mechanical-dilatational response of the composites aged at room humidity and 0% humidity were the same. Also aging was found to be of a physical nature. The composites aged for 120 days behaved as unaged materials when the heat treatment was repeated.

Finally the absence of dilatation in unfilled materials as well as treated glass-filled materials imply that dilatation is the result of dewetting rather than crazing. The unfilled materials either fracture in a brittle manner or by shear yielding. Neither of these result in dilatation. However, the 120-day-old, untreated filler-containing composites yield and then elongate by growth of vacuoles in a direction perpendicular to the applied stress.⁸

CONCLUSIONS

Unaged composites fracture at a stress level close to the tensile strength of the unfilled material regardless of the filler content and the degree of coupling studied here. The unfilled material has a greater modulus and tensile strength, but a smaller ultimate elongation after aging. The untreated filler containing materials lose their tensile strength and may undergo a brittle to ductile transition caused by dewetting of the filler particles from the matrix in tensile testing. The treated filler-containing composites lose their tensile strengths to the point determined by the chemical bond between the matrix and the treated glass. The observed phenomena can be explained in terms of the initially present thermal residual stresses which are relieved by relaxation upon aging. DSC and density data confirm these findings.

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References

1. For a recent review on this subject the reader is referred to M. R. Tant and G. L. Wilkes, *Polym. Eng. Sci.*, **14**, 874 (1981).
2. S. E. B. Petrie, in "Polymeric Materials: Relationships between Structure and Mechanical Behavior," Am. Soc. for Metals, Metal Park, OH, 1975.
3. L. Nicolais and M. Narkis, *Polym. Eng. Sci.*, **11**, 194 (1971).
4. J. C. Smith, G. A. Kermish, and C. A. Fenstermaker, *Recent Advances in Adhesion*, Gordon and Breach, London, 1973, p. 333.
5. J. C. Smith, *Polym. Eng. Sci.*, **16**, 394 (1976).
6. S. Matsuoka, *Polym. Eng. Sci.*, **14**, 907 (1981).
7. M. Cizmecioglu, R. F. Fedors, S. D. Hong, and J. Mocanin, *Polym. Eng. Sci.*, **14**, 940 (1981).
8. U. Yilmazer and R. J. Farris, *Polym. Eng. Sci.*, to appear.
9. H. F. Schippel, *Ind. Eng. Chem.*, **12**, 33 (1920).
10. L. C. Cessna, *Polym. Eng. Sci.*, **14**, 696 (1974).
11. U. Yilmazer and R. J. Farris, Proceedings of IUPAC MACRO '82, Amherst, MA, p. 501.
12. J. Brandrup and E. H. Immergut, *Polymer Handbook*, Wiley-Interscience, New York, 1967.
13. J. N. Goodier, *Trans. ASME*, **55**, A39 (1933).
14. S. Sahu and L. J. Broutman, *Polym. Eng. Sci.*, **12**, 91 (1972).
15. L. Nicolais and L. Nicodemo, *Polym. Eng. Sci.*, **13**, 469 (1973).
16. A. S. Kenyon and H. J. Duffey, *Polym. Eng. Sci.*, **7**, 189 (1967).
17. L. Nicolais and R. A. Mashelkar, *J. Appl. Polym. Sci.*, **20**, 561 (1976).

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