Indentation Studies in Aluminum-Filled Epoxies

P. S. THEOCARIS, S. A. PAIPETIS, and G. C. PAPANICOLAOU,
Department of Theoretical and Applied Mechanics, The National Technical University, Athens 625, Greece

Synopsis

A class of aluminum-filled epoxy composites were subjected to indentation tests over a wide temperature range. The tests were carried out under constant load and continuously varying temperature. The effect of aluminum content, applied load, and adhesion efficiency between matrix and aluminum particles on the indentation behavior was studied. Measured indentation values were found to lie within limits predicted theoretically.

INTRODUCTION

Composite materials produced from a polymeric matrix into which a suitable metal powder has been dispersed exhibit highly improved mechanical properties, better electrical and thermal conductivity, lower thermal expansivity, and improved dimensional stability and behavior at elevated temperatures. Machine parts, structural components, etc., may be successfully manufactured from such materials.[1] Epoxy resins are suitable matrices for this class of materials, and extensive research on their mechanical properties was carried out by several investigators. Particularly, the dynamic properties[2] and the thermal properties[3] of aluminum- and iron-filled epoxies were dealt with by the authors. The rheological properties of the epoxy matrix materials were extensively investigated by Theocaris[4,5] over wide ranges of plastification. Indentation studies of these latter materials were also carried out by the authors.[6]

This kind of study, that is, of the response to surface pressure, is of great importance for structural materials. They are performed by means of a rigid indenter pressed against the surface under consideration and by measuring the characteristic dimension of the resulting deformation. With tough materials, either metals or polymers, one is referred to indentation hardness, which can be determined from the size or the depth of the residual deformation created by a rigid indenter pressed against the surface with a specific force for a specific period of time. Hardness measurements cannot, in general, be directly related to any fundamental property of the material considered.

With viscoelastic materials, such as polymers or polymeric composites, particularly at high temperatures or highly plasticized, that is, close to or within their transition zone, time-dependent phenomena interfere, and the deformation caused by an indenter under load for a material exhibiting creep recovery can hardly be determined with acceptable accuracy.[7]

With elastic materials, theoretical indentation studies were carried out for ball indenters[8] or frictionless, flat-ended ones[9] pressed against material layers sufficiently thick for the indenter size. Frictional curved-profile or flat-ended indenters were considered in reference 10. Respective problems for thin material layers were considered in references 11 and 12. With viscoelastic materials, the

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correspondence principle, permitting the use of the respective elastic solutions, can be applied in limited cases only.[13]

Considerably simpler appears to be the case with incompressible materials such as rubbers, elastomers, or polymers in their rubbery state. Particular cases have been treated by several investigators.[14–16] Indentation studies by means of a thermomechanical analyzer (TMA), leading to the determination of Young's modulus of elastomeric materials, were also performed.[17]

The same instrumentation was used in the present work, in order that the depth of indentation be determined under the action of a rigid, cylindrical, flat-ended indenter of a class of aluminum-filled epoxy materials over a wide temperature range. The load applied was sufficiently small, and no plastic deformation remained after its removal. The material exhibited in fact viscoelastic behavior, and curves of indentation depth plotted against temperature displayed discretely glassy, transition, and rubbery zones.

The present materials are clearly inhomogeneous, and indentation measurements can only be reproducible if particle sizes and interparticle distances are small compared with the area of the indenter cross section. Indeed, with all the materials considered in the present work, i.e., for all volume concentrations of aluminum particles, all the results were highly reproducible. This was not the case, however, with some trial tests on iron-filled epoxies, where the particle size was of the order of a few hundred microns. At higher temperatures indentation measurements contained a respective amount due to thermal expansion, which had to be determined by a series of separate tests.

Although no accurate theoretical predictions can be expressed for the complex phenomena involved in the present work, some comparisons were attempted for particular cases, and experimental results were found to lie with reasonable approximation within expected bounds.

EXPERIMENTAL

The materials employed in the present work were derived from a basic diglycidyl ether of bisphenol A epoxy matrix (Epikote 828, Shell Co.) with an epoxy equivalent of 185–192, a molecular weight between 370 and 384, and a viscosity of 15,000 cP at 25°C. As curing agent, 8 phr by weight triethylene tetramine was employed, i.e., a highly reactive primary aliphatic amine capable of curing diglycidyl ethers at room temperature.

In the above system, while in liquid state at about 30°C, various amounts of aluminum powder were added, with 0.2% Al_2O_3, in the form of spheroidal grains with the following size distribution: +0.16 mm, traces; +0.125 mm, 0.5%; +0.04 mm, 10%–12%; −0.04 mm, 80%–90%. The procedure of preparing a mixture of the liquid matrix phases and the metal powder and of rotating it in a sealed mold in order to obtain uniform spatial distribution of aluminum particles, the curing process, etc., are described in detail elsewhere.[2]

The structural integrity of the specimens produced was checked by means of density measurements and photomicrographs. It was proved that aluminum particles of the present small size exhibited poor adhesion with the matrix material and tended to agglomerate, with detrimental effect on the mechanical properties of the resulting composite material. By means of more careful stirring and degassing, improved specimens were produced, and their properties were

compared with the respective properties of the ordinary ones. The individual specimens were characterized by the amount of aluminum particles by volume.

Specimens about 3 mm thick with a smoothly machined surface of approximately 8 mm^2 were cut from each of the above materials and tested on a du Pont 900 differential thermal analyzer combined with a du Pont 941 thermomechanical analyzer (TMA). A systematic description of the instrument can be found, for example, in reference 17. The indentation probe used for the TMA was a flat-ended quartz rod with diameter 0.833 mm, adjusted to act normally to the surface of the specimen, i.e., vertically. A constant axial load was applied to the probe, and the displacement of the probe was recorded as a function of temperature. The probe used for the TMA for measuring the linear thermal expansion coefficient was also a flat-ended quartz rod, but with diameter 2.5 mm, adjusted in the same manner and loaded with a very light weight.

RESULTS

For each particular material the test piece was loaded at ambient temperature, and subsequently the temperature was increased at a constant rate of 5°C/min. Indentation depth was then recorded as a function of temperature. The same test was then repeated with the thermal expansion probe, and values thus recorded were algebraically subtracted from the previous ones in order to obtain pure indentation depth. Indentation tests were performed with 20- and 50-g loads, while thermal expansion tests were performed with a very light weight (less than 0.1 g), just ensuring permanent contact of the probe tip with the specimen.

The recordings for each particular material were made on the same scale, and in Figures 1 and 2 they are presented for ordinary and improved specimens, respectively. Curves A on these graphs correspond to thermal expansion and curves B and C, to indentation with loads of 20 and 50 g, respectively. All three curves practically coincide in the first portion of the glassy region of the materials where, under the small loads applied, very small indentation occurs which cannot be distinguished since it is counterbalanced by thermal expansion. However, by approaching the transition zone, the curves are separated and follow individual paths. Upon entering the rubbery region, all curves become straight lines running in parallel.

With ordinary aluminum specimens (Fig. 1), one may notice the effect of aluminum content on the relative position of the three respective curves A, B, and C. Namely, for low aluminum volume fractions, the indentation curves B and C fall well below the thermal expansion curve A. But with increasing aluminum content, up to 30% by volume, the three curves tend to approach each other. This fact is an indication of the improved indentation response of the aluminum composite. For each particular curve the maximum slope corresponds to the glass transition temperature T_g of the viscoelastic composite. The latter has been determined[3] for the present materials by means of the thermal expansion curves. Respective determination through the indentation curves of ordinary specimens leads to slightly higher values, while the effect of load appears to be unimportant.

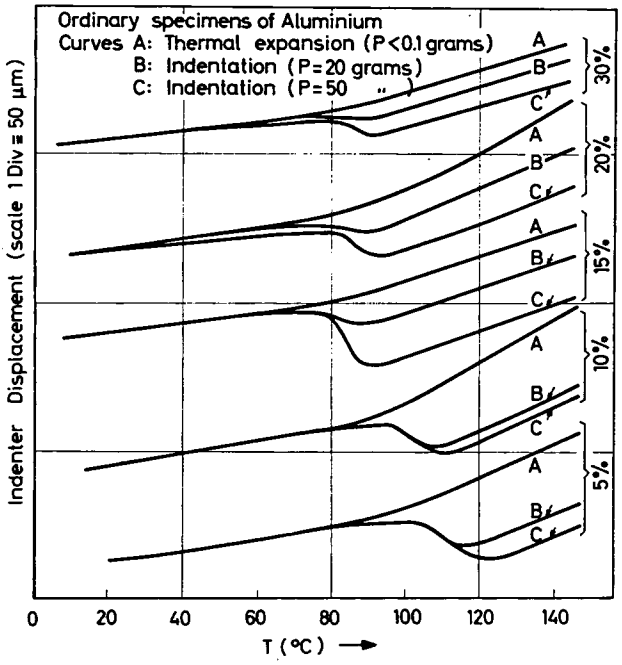


Fig. 1.

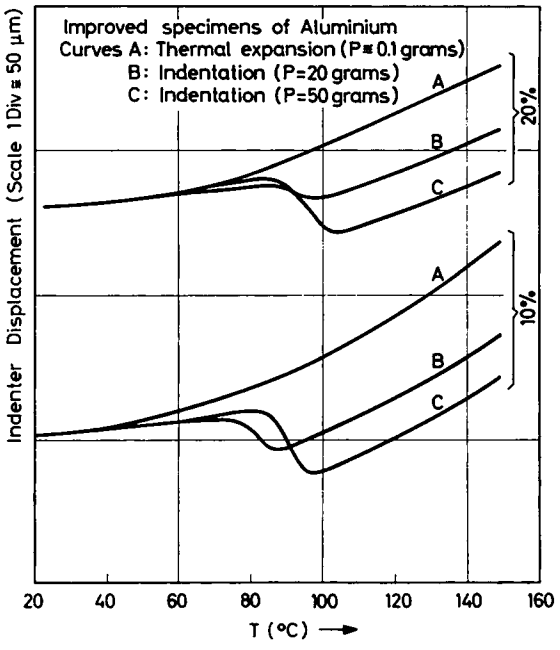


Fig. 2.

A totally different effect appears with improved aluminum specimens (Fig. 2), where 50-g curves lead to T_g higher by 10°C than the 20-g ones. This fact provides an impressive indication of how sensitive the glass transition is to the adhesion efficiency between matrix material and aluminum particles.[2,3]

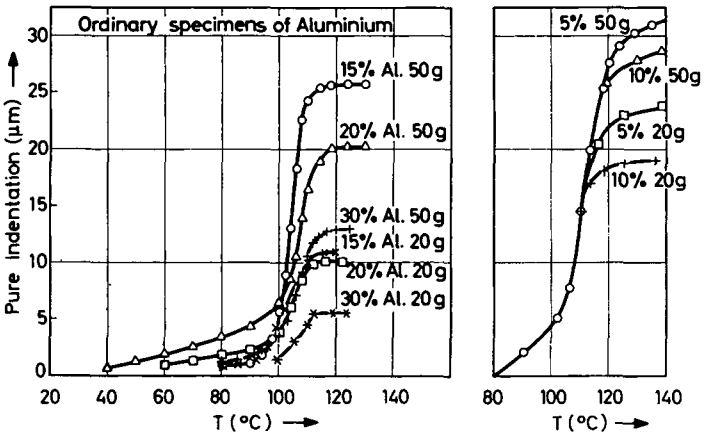


Fig. 3.

In Figure 3, pure indentation curves for ordinary specimens are given. The toughening effect of the aluminum content as well as the highly nonlinear response toward applied load are obvious. Respective curves for improved specimens are presented in Figure 4.

Even with homogeneous viscoelastic materials, existing theories fail to cover completely the complex phenomena occurring with indentation procedures, among which friction is also an important factor. As already mentioned, things are more favorable in the rubbery region of the material, for which simple expressions have been derived in several occasions, being in good agreement with experimental evidence.

As far as the matrix material of the present composites is concerned, it was found[6] that measured indentation values were predicted with good accuracy by an expression derived by Joppling and Pitts[16]:

$$P = \frac{3\pi a r_0^4 G}{2 z_0^3} \tag{1}$$

which is valid when there is no slip between the indenter and the specimen surface. This condition appears to be fulfilled for the present matrix material, as quartz probe under load adheres to the surface of the softened epoxy at elevated

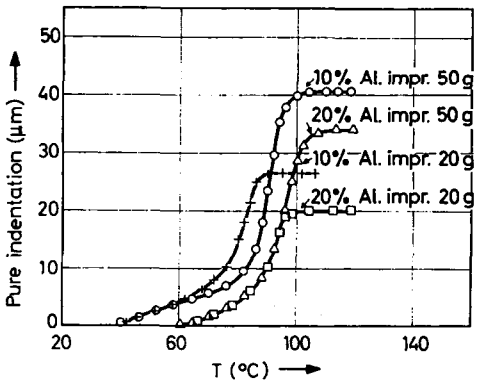


Fig. 4.

temperatures. In the above expression, P is the load in grams, a is depth of indentation, r_0 is the radius of the cylindrical indenter, G is the shear modulus of the material, and z_0 is the thickness of the test piece.

However, in order to apply this formula to the present materials, two factors should be taken into account: First, no perfect adhesion between the quartz probe and the surface of the individual specimens should be expected. On the contrary, due to the presence of aluminum particles, some kind of slip must be involved. In this case, instead of the factor 2 in the denominator of eq. (1), another factor, between 2 and 8, should be introduced.[16] Second, a suitable expression for the shear modulus G of the composite must be applied.

Such expressions can be provided, for example, by Paul's isostrain and isostress bounds[18] or by a direct approximation, as the one derived by Kerner[19]:

$$G = G_m \frac{\dfrac{v_f G_f}{(7 - 5\nu_m)G_m + (8 - 10\nu_m)G_f} + \dfrac{v_m}{15(1 - \nu_m)}}{\dfrac{v_f G_m}{(7 - 5\nu_m)G_m + (8 - 10\nu_m)G_f} + \dfrac{v_m}{15(1 - \nu_m)}} \tag{2}$$

where G, ν, and v are shear modulus, Poisson's ratio, and volume fraction, respectively, and the subscripts m and f refer to the matrix and filler material, respectively.

Theoretical indentation values, derived from the combined considered of expression (1) with either eq. (2) or Paul's bounds, are presented in Figures 5(a) and 5(b) for 20- and 50-g loads, respectively.

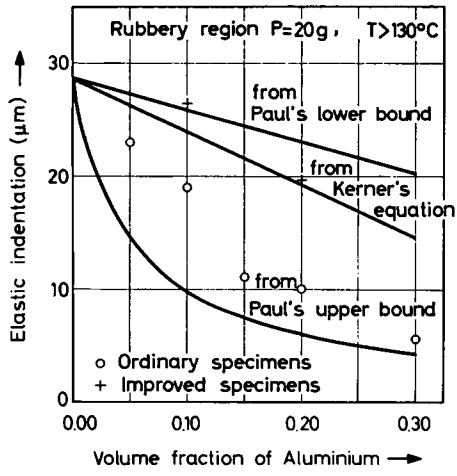
Experimental values were brought into Figures 5(a) and (b) and were found to lie within the bounds thus determined, which can be considered given the large number of uncertain factors involved in the present phenomena. The nonlinear effect of the load is again stressed.

However, the behavior of improved specimens exhibits a paradox by exhibiting at the rubbery state of the materials a higher indentation than the ordinary ones, although they are expected to possess a considerably higher shear modulus. To explain this, one should consider the microstructure of the respective materials. With ordinary specimens, voids, cracks, positions of structural discontinuity, etc., exist which, at high temperatures, are filled with matrix material as it exhibits thermal expansion. So the material becomes in fact denser and consequently more resistive toward indentation.

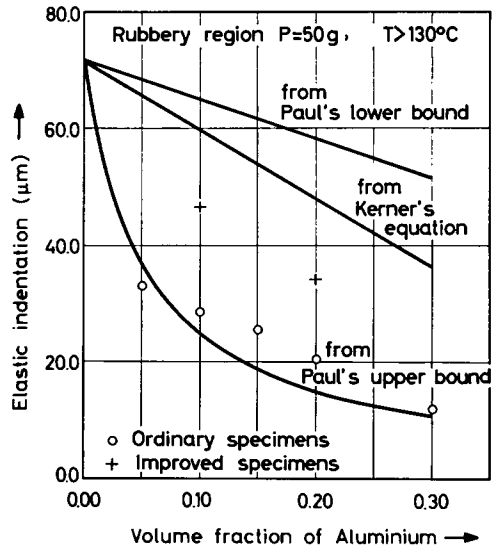
On the contrary, with improved specimen, where structural integrity more or less exists, as the matrix expands much more than the aluminum particles, the material becomes less dense and therefore more prone to indentation. To verify this assumption, indentation measurements were performed at ambient temperature with the respective materials, when a totally different behavior was observed. Namely, with 50-g loads, the improved specimens exhibited pure indentation equal to 2.25 μm while with the ordinary ones the respective figure was 3.0 μm.

CONCLUSIONS

Indentation studies were performed on a series of composites derived from an epoxy matrix in which various amounts of aluminum powder were added, over a wide range of temperature. The experimental work was carried out by means of a thermomechanical analyzer with a cylindrical, flat-ended quartz probe,



(a)



(b)

Fig. 5.

pressed vertically on the surface of the specimens. The temperature was varied at constant rate. Thermal expansion of the individual specimens was also recorded under the same condition in order that pure indentation could be assessed by subtraction. The materials could be considered as practically homogeneous for the size of quartz probe used.

During the indentation process, the materials exhibited viscoelastic behavior; and on the respective pure indentation curves one can distinguish a glassy region, a transition zone, and a rubbery region. A glass transition temperature could also be determined for each particular case. The latter was found weakly dependent on the load applied for specimens with poor adhesion between matrix and filler particles, but strongly dependent on the load for specimens with respectively good adhesion. The importance of adhesion efficiency for the response to indentation was thus demonstrated.

Comparison with theoretical predictions was attempted for the rubbery state of the individual materials by means of an expression valid with sufficient accuracy for the matrix material and various expressions for the shear modulus of the composites. Experimental values were found to lie within predicted limits, in spite of the large number of uncertainties involved in the present phenomena. A paradox was observed at the temperature of the rubbery state of the materials, where improved specimens exhibited higher indentation than ordinary ones as a result of variations of their microstructure due to thermal expansion.

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