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Modification of polymer properties to minimize thermal stresses in adhesive joints

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The adhesive behaviour of epoxy–glass microballoon composites was studied at 25 and 75° C for plate and tubular lap joints of various combinations. It was found that the adhesive bond for various joints is enhanced through addition of microballoons. High adhesive force is observed at higher temperatures for various joints combinations where the thermal stresses are lowered and the bond is strengthened. The obtained results for various joint combinations demonstrate that high strength can be achieved when significant thermal stresses do not exist. The filler effect on some physical properties such as density, glass transition temperature, thermal expansion and Poisson's ratio of the epoxy composites is also investigated. Simple analysis indicates the differential thermal expansion coefficient between the adhesive and metallic joints and bulk modulus of the adhesive dictates the stress state.

1. Introduction

Many applications of engineering materials require consideration of their properties such as thermal stresses and expansion behaviour. Thermal stresses arise from either temperature gradients or differential thermal expansions in a solid body [1]. Hence, an essential requirement for the use of any solid in technological applications such as nuclear reactors and adhesion applications as a function of temperature is a knowledge of its thermal characteristics and how they function under different thermal environments. Furthermore, modification of a structural material's properties to minimize the effect of thermal stresses can result in improved performance. Thermal stresses are generally compressive (or negative) on heating and tensile (or positive) on cooling in adhesive joints. They are determined by the geometry of the body and its elastic and thermal parameters such as Young's modulus and thermal expansion coefficient in addition to the Poisson's ratio and temperature distribution effects.

The emphasis of this research work is to determine to what extent thermal stresses dominate the apparent adhesion in tubular structures. These joints are different from lap joints in that in lap joints two plates are bonded together by an adhesive and when the joint is thin, there exists a two-dimensional constraint where stresses develop in the plane of joints, but none through the thickness. In a tubular joint where the gap between telescoping tubes of different diameters is filled with an adhesive, a three-dimensional constraint exists and thermal stresses exist in the plane and in the thickness direction. This situation can be greatly modified by using tubes of different thermal expansion characteristics for the inner and outer members. During the past few years a few publications have appeared on the behaviour of composite materials containing hollow glass microspheres [2–5]. Those composites are called syntactic foams when the microballoons are embedded in an epoxy matrix [2]. But as far as we know, no studies have been performed on the adhesion behaviour of these composites with metallic surfaces. In the present study the thermal and mechanical behaviour of epoxy composite–metallic joints is investigated at room temperature and near the glass transition (curing) temperature. An attempt to determine the sensitivity of the joints to thermal stresses and to modify the composite properties to enhance the joint adhesion by adding hollow quartz microballoons to the adhesive was undertaken. Microballoons lower the bulk modulus and the thermal expansion coefficient, thereby lowering the thermal stresses and strengthening the bond.

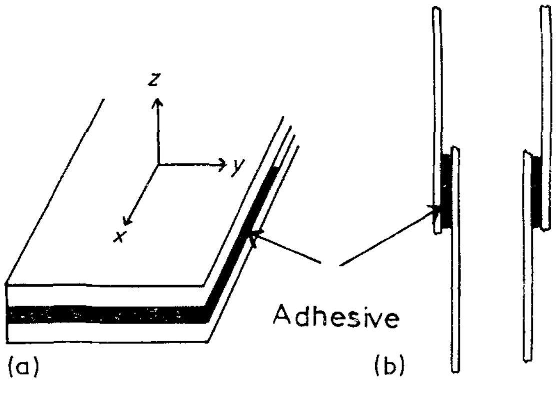

Figure 1 Schematic diagrams of adhesive joints: (a) plate system (b) tubular system.

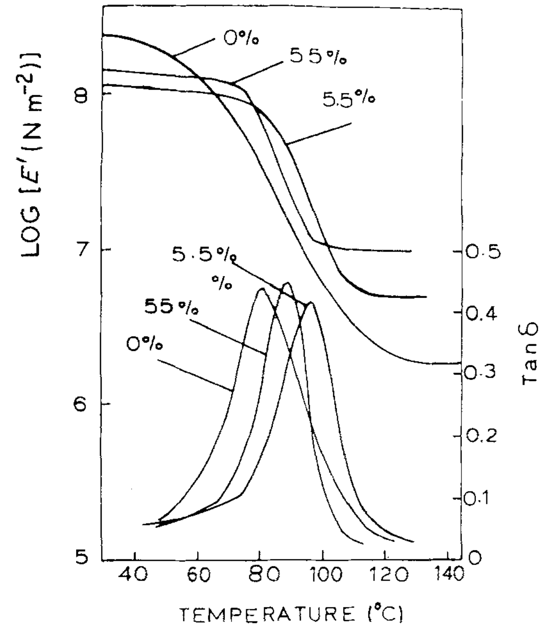

Figure 2 Dynamic storage modulus and loss tangent against temperature for three epoxy composites: 0%, 5.5% and 55% filler content. (Curing temperature 80° C).

2. Experimental procedure

2.1. Materials

The materials used in the present work are steel (ST) and aluminium (Al) plates and tubes, epoxy and hollow microspheres. The plates dimensions are 78 mm × 25 mm × 4 mm, the tubes outside diameters are 25.2 mm and 19.2 mm and both tubes had a wall thickness of 2 mm and the gap thickness in the telescoping tubes is 1 mm. The adhesive used was epoxy resin Epon 828 from Shell with polyamide curing agent V-40. The microballoons particle size is in the range of 10–180 μm and typical effective density 0.21 g cm^{-3}.

2.2. Test specimens, preparation

Test specimens of the adhesive composites were prepared by mixing the epoxy resin, curing agent and the microballoons. The mixture was stirred completely and placed into the plate and cylinder systems as shown in Fig. 1. The surface area of the adhesive filling the gaps in both plates and cylinders was the same and equals 625 mm^2. The adhesive thickness between the plates was 0.5 mm and between the cylinders was 1.0 mm. Various methods of alignment of the plates and cylinders were followed to cure the adhesive between two well-cleaned plates and cylinders to assure that the adhesive layer has a uniform thickness. Parafilm bands of equal thickness were wrapped about as spacers to ensure a uniform adhesive thickness. The adhesive test samples were allowed to react at 25° C for 24 h and cured at 80° C for 3 h in an oven. The final step was to post cure the test specimens at 150° C for 2 h. Specimens were slowly cooled in the oven to room temperature. From the same mixtures, sheet form composite specimens were prepared by casting on teflon boats for dynamic and thermal expansion coefficient measurements. A third set of rod-shape composite specimens were prepared for dilatation tests.

2.3. Tensile tests

Composite specimens, plates and cylinders shown in Fig. 1, were held to grips built for tensile deformation. The grips and specimens were coupled to an Instron universal testing machine fitted with an evironmental chamber. Tensile tests on epoxy filled-metallic joints were conducted on a constant rate of deformation of 0.1 cm min^{-1} at room temperatures (25° C) and slightly below the curing temperature (70–75° C). Temperatures were measured by placing a mercury thermometer near the test sample. Tests were carried out until joints were broken and the adhesive load was read from the load–elongation curve drawn on the Instron chart.

2.4. Dynamic mechanical and thermal expansion measurements

Dynamic mechanical and thermal analysis of epoxy–microballoons composites was carried out by using a PL-DMT Analyser manufactured by Polymer Laboratories, England. The dynamic storage moculus (E') and the damping factor (tan δ) of composite flat strips were measured as a function of temperature at 1 Hz with an ascending rate of temperature of 5° C min^{-1}. Thermal expansion measurements on composite samples of dimensions 2 mm × 3 mm × 6 mm were made on a Perkin-Elmer thermomechanical analyser TMS II at a heating rate of 10° C min^{-1}.

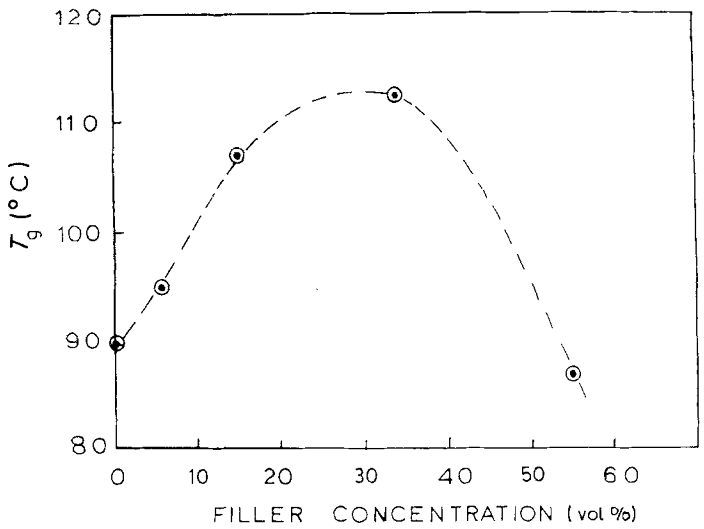

Figure 3 The glass transition temperature of epoxy composites as a function of filler content. (Curing temperature 80° C).

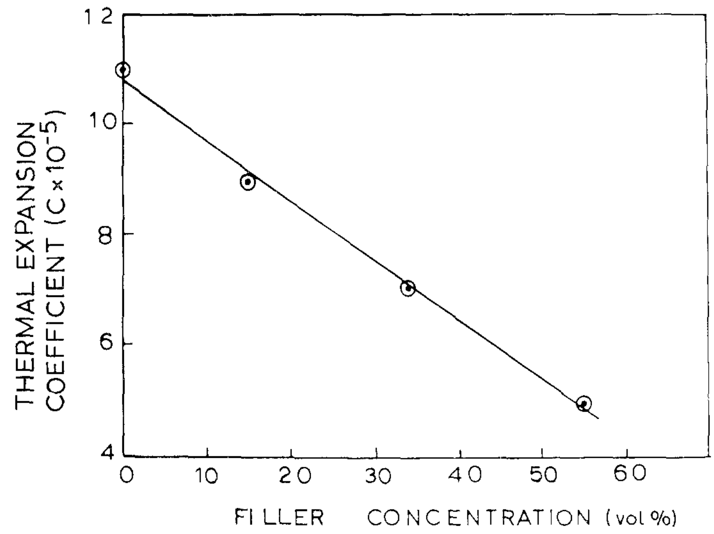

Figure 4 The thermal expansion coefficient of composite as a function of filler content. (Epoxy cured at 80° C). T = 75° C.

2.5. Poisson's ratio measurements

Mechanical-dilatation measurements were conducted in a modified gas dilalatomer [6, 7]. Rather than determining the volume-strain behaviour, measurements of the deviatoric axial stress as a function of hydrostatic pressure were obtained while the sample was maintained at constant length. Mathematically the slope of the resulting force–pressure relation is equal to $(1-2\nu)$, where ν is Poisson's ratio. These measurements were made while pressurizing to 1000 p.s.i. and were quite reproducible.

3. Results and discussion

Flat plates and tube lap joints were prepared using combinations of Al/Al, ST/ST, Al/ST and ST/Al. The filler content by volume was 0, 5, 15, 35, and 55 vol % microballoons. The temperature dependence of visco-elastic properties of microballoon filled epoxy is shown in Fig. 2. The storage modulus E' decreases with increasing temperature and filler concentration. Epoxy composites showed a pronounced peak temperature in the mecahnical tan δ which shifts with temperature and filler content. The peak temperature, should correspond to the glass transition. Fig. 3 shows the glass transition temperature (T_g) as a function of the filler volume concentration. The glass transition first increases with increasing the microballoon concentration. At filler concentration above 35 vol %, it was observed the T_g drops sharply to a lowest value. The change of T_g with increasing hollow microspheres volume fraction may be due to a free volume effect caused by residual stresses [8]. Similar data obtained by Migliaresi *et al.* [9] showed an increase of the glass transition temperature in the glass bead–epoxy system as a result of filler presence.

Figure 4 shows the thermal expansion coefficient measurements for the composite as a function of the filler concentration. The expansion coefficient decreases linearly with the composite volume concentration. Reduction of the expansion coefficient of the composite can be attributed to the large difference between the expansion behaviour of glass microspheres and the epoxy matrix. Thermal expansion coefficients of glasses are usually very low compared to that of the polymers [10]. Typical glasses have expansion coefficients about $0.9 \times 10^{-5}\,C^{-1}$ and plastics about $6 \times 10^{-5}\,C^{-1}$. Hence the decrease of the expansion coefficient for the epoxy–glass system with increasing the balloon filler content is expected.

The elastic properties of filled epoxy are of great interest. The effect of filler content on the dilational characteristics was investigated in [11]. Richard [12] studied Poisson's ratio in glass filled polyester by measuring the axial and transverse strains

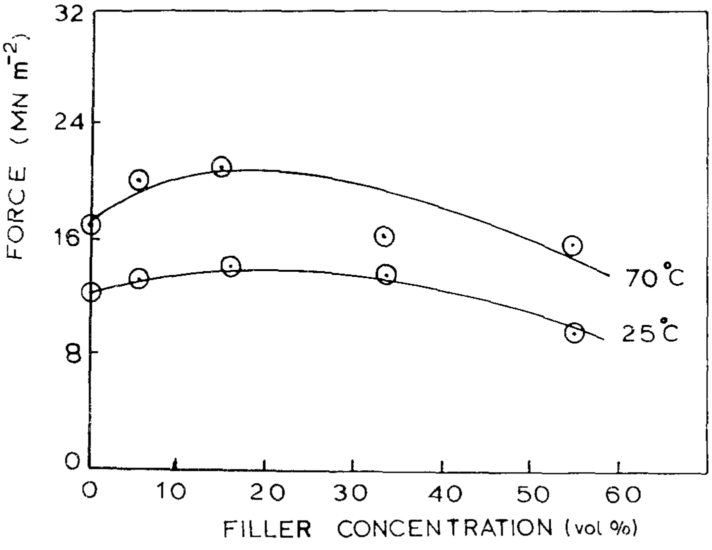

Figure 5 Bond strength against filler content for steel plate joint measured at 25° C and 70° C. (Epoxy adhesive cured at 75° C).

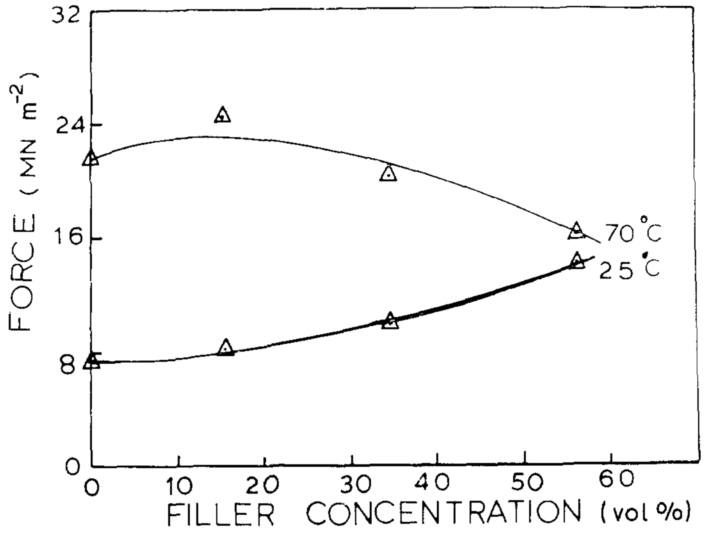

Figure 6 Bond strength against filler content for aluminium plate joints measured at 25° C and 70° C.

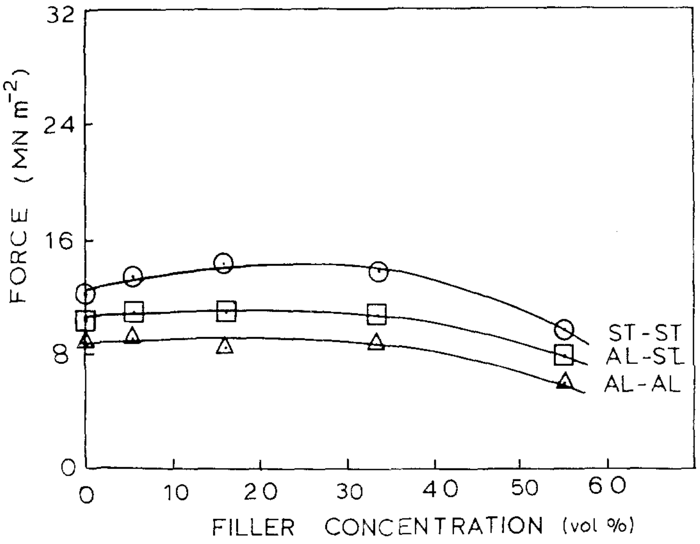

Figure 7 Bond strength against filler content for various combinations of plate joints tested at 25° C. ST = steel, Al = aluminium.

simultaneously with extensometers. In the present study the Poisson's ratio is reported as a function of microballoons volume concentration through pressure–force measurements. The experimental technique will be reported in a future communication [13]. Table I shows the obtained values of Poisson's ratio ν for an epoxy sample of different microballoon concentration.

Figure 5 through 8 illustrates the behaviour of lap shear joints as a function of microballoon content. The joints are made of steel and aluminium plates in various combinations and tested at 25 and 70° C. The strength is lower at 25° C because the residual stresses are higher at 25° C than at 70° C. The stresses in these joints are

$$\sigma_{xx} = \sigma_{yy} \cong \int_{T_g}^{T} \frac{E(T')[\alpha(T') - \alpha_m(T')]\,dT'}{1 - \nu(T')}, \tag{1}$$

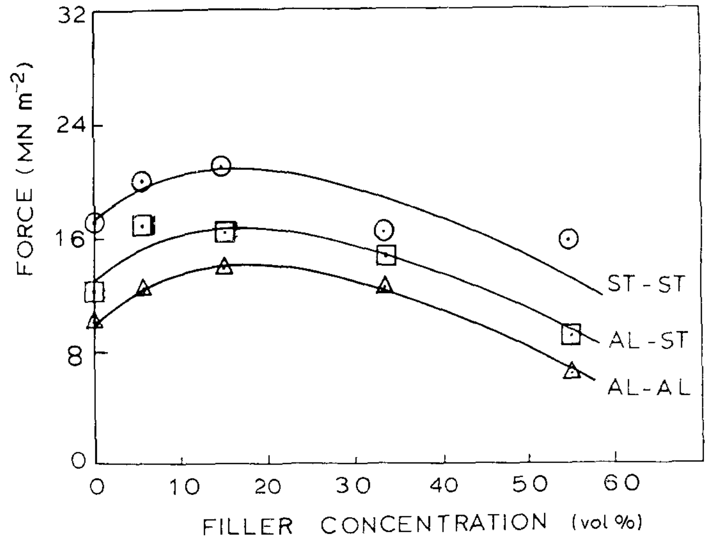

Figure 8 Bond strength against filler content for various combinations of plate joints tested at 70° C. ST = steel, Al = aluminium.

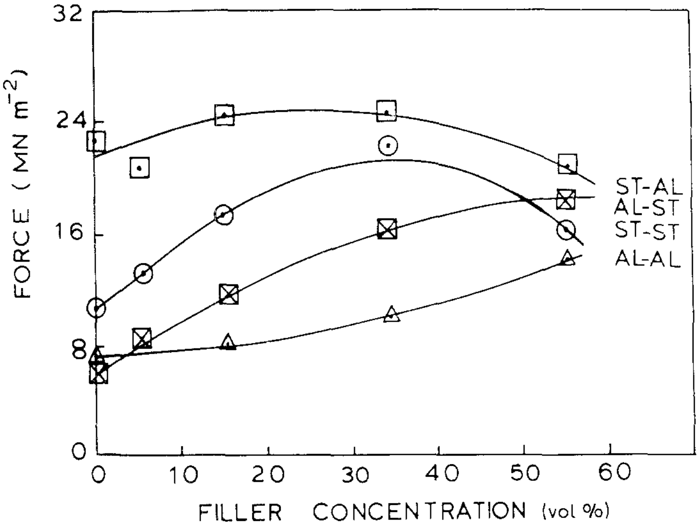

Figure 9 Bond strength as a function of filler content for various combinations of tubular joint tested at 25° C. (Epoxy adhesive cured at 80° C). ST = steel, Al = aluminium. The combinations are given as inner–outer.

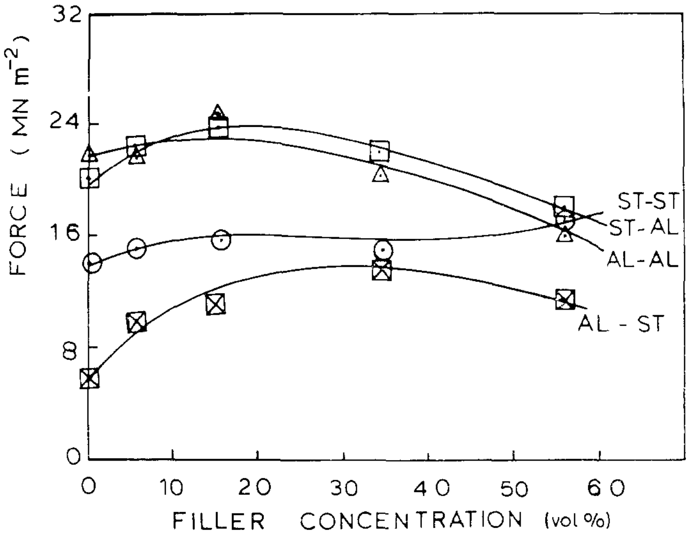

Figure 10 Bond strength against filler content for various combinations of tubular joints tested at 75° C. ST = steel, Al = aluminium. The combinations are given as inner–outer.

and

$$\sigma_{zz} = 0 \qquad (2)$$

where σ_{zz} is normal to the plates. E, ν and α and the Young's modulus, Poisson's ratio and thermal expansion coefficient for the adhesive, respectively, and α_m is the expansion coefficient for the metal.

Figures 9 and 10 illustrate the behaviour of tubular joints. In this situation

$$\sigma_{rr} = \sigma_{xx} = \sigma_{yy} \cong \int_{T_g}^{T} \frac{E(T')[\alpha(T') - \alpha_m(T')]\,\mathrm{d}T'}{1 - 2\nu(T')}, \qquad (3)$$

when the inner and outer tubes are made of the same material. These figures also illustrate the interesting results of using steel for the inner tube and aluminium for the outer tube. Because the outer aluminium tube shrinks faster than the steel tube, the thermal radial stress is compressive rather than tensile as in the first two cases. This case should be essentially unaffected by thermal stresses and in fact no bond is required to have adhesion of some value since this is similar to a shrink fit. The bond strength for this case is very high as expected and again demonstrates high strength can be achieved when significant thermal stresses do not exist. Also this case does not show any significant temperature dependence. The figures also illustrate the data when the situation is reversed using steel outside and aluminium inside. This case should have the highest thermal stresses as evidenced by the poor strength at 0% filler. The behaviour even for this extreme situation was enhanced through the addition of microballoons. As indicated earlier, part of the effect of the filler is to lower the thermal expansion coefficient and part is to lower the bulk modulus.

TABLE I Poisson's ratios at various filler concentrations

Filler concentration (vol %)	Poisson's ratio
0.0	0.41
5	0.41
15	0.39
35	0.38
55	0.32

As these data clearly indicate there can be considerable enhancement of apparent adhesion by adding microballoons to an adhesive and what remains is to perform mathematical analysis and obtain more data on the mechanical properties of the composite adhesives.

4. Conclusions

The adhesive behaviour of epoxy–glass microballoon composites was studied at 25 and 75° C for plate and tubular lap joints of various combinations. The following conclusion can be drawn from the observed results,

1. Addition of hollow microballoons lightens the epoxy polymer.
2. Presence of a glass microballoon filler shifts the apparent glass transition temperature of the cured adhesive to higher values.
3. Filler lowers the thermal expansion behaviour of the adhesive.
4. Filler lowers the Poisson's ratios of the epoxy composite.
5. The adhesive bond for various joints is enhanced through addition of microballoons.
6. Simple analysis indicated the differential thermal expansion coefficient between the adhesive and the metallic joints and the bulk modulus of the adhesive dictates the stress state.
7. High adhesive force is observed at higher temperatures for various joint combinations where the thermal stresses are lowered and the bond is strengthened.
8. The obtained data for various joint combinations demonstrate that high strength can be achieved when significant thermal stresses do not exist.

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