means of Equations 1 and 5 with the values of U_0 and τ_0 [6, 7] given in Table I. Agreement can be seen to be good at rather low temperature, i.e. below about 150 K.

It is therefore concluded from the foregoing evidence that the temperature dependence of the CRSS and of the activation volume in random alloys proposed by Kratochvíl et al., agrees with experimental observations at low temperature for some unique value of the effective obstacle strength U_0, only if the flow criteria of Feltham (Equation 7) is taken into account. Further, the U_0 values (Table I) on comparison with the maximum binding energy between a solute atom and a dislocation [8, 9] show that even in dilute alloys the effective obstacles to dislocation motion are groups of solute atoms, and it is not therefore germane to consider as a model of yielding the break-away of dislocations from isolated solute atoms as, for example, in the well-known model proposed by Friedel.

References

1. P. KRATOCHVÍL, P. LUKÁČ and B. SPRUŠIL, Czech. J. Phys. B23 (1973) 621.
2. P. KRATOCHVÍL, J. Mater. Sci. 12 (1977) 1134.
3. M. Z. BUTT, Fizika 11 (1979) 65.
4. Z. S. BASINSKI, R. A. FOXALL and R. PASCUAL, Scripta Met. 6 (1972) 807.
5. P. FELTHAM, Brit. J. Appl. Phys. (J. Phys. D) 1 (1968) 303.
6. M. Z. BUTT and P. FELTHAM, Rev. Deform. Behav. Mater. 3 (1978) 99.
7. Idem, J. Nat. Sci. Math. 19 (1979) 143.
8. I. SAXL, Czech. J. Phys. B14 (1964) 381.
9. P. HAASEN, cited by F. R. N. Nabarro in "The Physics of Metals" Vol. 2 (Cambridge University, Cambridge, 1975) p. 152.

M. Z. BUTT
Department of Physics,
Government College, Lahore,
Pakistan

Dynamic mechanical properties of cross-linked poly(acrylic acid)—aluminum oxide composites

While extensive research has been conducted on polymer matrix composite materials, few studies have systematically examined the viscoelastic behaviour of cross-linked polymer composites. Recently, the effects of network formation on the physical and mechanical properties of poly-(acrylic acid) (PAA) have been reported [1, 2]. The current study presents preliminary data on the changes in the dynamic mechanical properties which occur when cross-linked PAA is combined with Al_2O_3 particles. Whereas the absolute moduli of unfilled PAA decrease with the increasing mole fractions of cross-linking agent, X, [2], present results indicate that the relative modulus is proportional to the volume fraction of filler, ϕ_2, but remains approximately constants as X increases. In addition for each composition studied, the glass transition temperature, T_g, is shifted to higher values as either ϕ_2 or X is increased.

Mixtures of acrylic acid (AA)* and the tetra-functional monomer, allyl acrylate (ALA)*, were prepared at four concentrations ($X = 0, 0.06, 0.13$ and 0.20). Each of these was subdivided into three batches: Two were combined with Al_2O_3 powder† of nominal particle size 0.05 or 1.0 μm, while the third remained unfilled. The resulting slurries were centrifuged (395 g) to obtain maximum packing of the powders, solidified via free radical polymerization (0.47 wt% benzoyl peroxide at 60° C for 24 h) and serially heat-treated to ensure complete conversion of the monomer (at 80, 100 and 120° C). The unfilled polymer was processed in identical fashion. Subsequent ash analyses indicated that $\phi_2 = 0.10$ and 0.17 for the composite materials containing the small and large filler particles, respectively. Cylindrical specimens with nominal dimensions L = 38.1 mm and r = 1.5 mm were heated under $N_{2(g)}$ at 10° C min^{-1} in a Du Pont 981 Dynamic Mechanical Analyser over a temperature range of − 50 to 225° C. The operation of this instrument and the method for converting frequency and damping data to the corre-

*Polysciences, Inc., Warrington, PA.
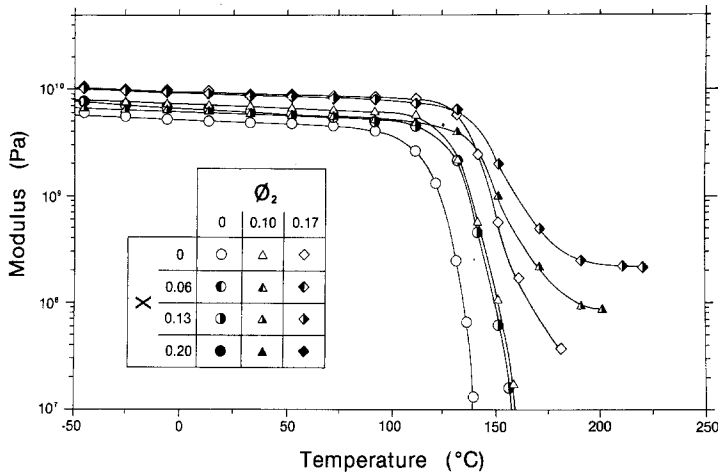†Buehler Ltd., Evanston, IL.

Figure 1 Influence of filler content and cross-linking on the dynamic mechanical modulus of poly(acrylic acid). Symbols in the inset represent the various combinations of cross-linking (X) and filler (ϕ_2) content used in all figures.

sponding modulus and tan δ values have previously been reported [3, 4].

Representative dynamic modulus values are shown (Fig. 1) for the composites and unfilled materials at two levels of X. For the uncross-linked polymer the modulus is raised over the entire temperature range as the volume fraction of Al_2O_3 is increased. As expected, this effect is most pronounced at temperatures above T_g [5]. Analogous behaviour is exhibited by the cross-linked material, although in this case the polymer and 0.05 μm composite have similar modulus values below T_g. Room temperature relative modulus values were calculated as the ratio of composite to polymer moduli at each level of X. In order to reduce the scatter of the experimental data, modulus values for the unfilled polymers were obtained from the 25° C linear regression equation previously derived for $0 \leqslant X \leqslant 1$ [2]. Although these relative modulus values may be somewhat less than those calculated by traditional extrapolation techniques [6, 7], the results (cf. Fig. 2) can be adequately represented by Nielsen's [8, 9] modified form of the Kerner [10] equation in which the Einstein coefficient, k_E, and the maximum packing fraction, ϕ_m, were assigned values of 3.5 and 0.60 [11], respectively.

The damping behaviour of the materials is illustrated in Fig. 3. Here, as in other systems, addition of filler to the uncross-linked polymer causes the curves to broaden and the maxima to shift to a higher temperature [5]. The cross-linked material behaves in a similar fashion, except that tan δ is significantly reduced with

filler content — particularly for the case of the smaller filler particles. This decrease is greater than that predicted by the law of mixtures relationship between damping behaviour and ϕ_2 and may be related to excess damping in the polymer in the vicinity of the matrix–filler interface [5, 7, 12]. Nonetheless, for all compositions examined, T_g (taken as the curve maximum) is raised as ϕ_2 is increased (cf. Fig. 4).

Although the limited data preclude a more extensive analysis, the present view-point is that the relative modulus is unaffected by changes in X. However, since specimen defects do become more extensive as X increases, the relative modulus may ultimately decrease in a manner similar to that described by Nielsen and Lee [11] for polystyrene composites containing voids. The present
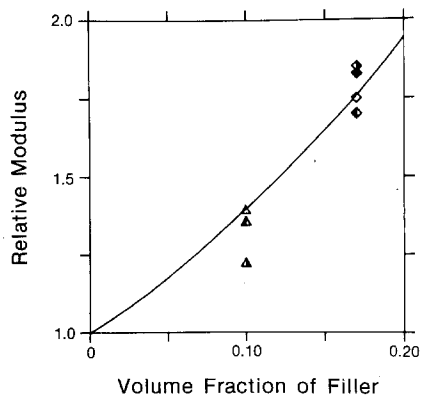

Figure 2 Relationship between relative modulus and filler content at various levels of cross-linking. Solid line: Nielsen equation with $k_E = 3.5$ and $\phi_2 = 0.60$ (compare with [8, 9, 11]).
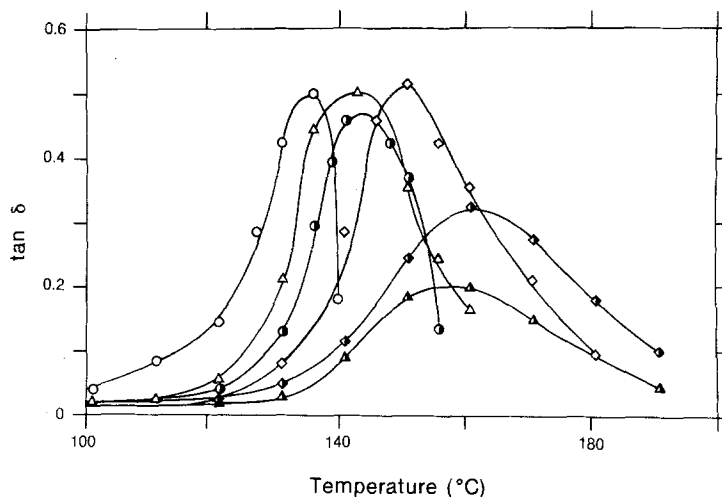
Figure 3 Influence of filler content and cross-linking on the damping behaviour of poly-(acrylic acid).

results also indicate an increase in the T_g of cross-linked PAA–Al$_2$O$_3$ composites over that expected due to increased network formation in the polymer matrix. Increases in T_g have been documented in a number of other composite systems and have been explained on the basis of reduced mobility of molecular segments in the vicinity of the filler [13–17]. Note in particular that the slopes of the T_g against ϕ_2 curves remain relatively constant with increasing X despite the fact that the hydrophilic nature of the polymer shifts as PAA is replaced by the less polar ALA. This suggests that these overall electrostatic changes do not significantly affect the polymer–filler interaction, at least to the extent that such interaction is reflected by changes in T_g.

Acknowledgement

References

1. A. R. GREENBERG and R. P. KUSY, *J. Appl. Polymer Sci.*, in press.
2. *Idem, ibid.*, in press.
3. R. P. KUSY and A. R. GREENBERG, *J. Thermal Anal., Thermochimica*, in press.
4. *Idem, Thermochimica Acta* 37 (1980) 53.
5. L. E. NIELSEN, "Mechanical Properties of Polymers and Composites" Vol. 2 (Marcel Dekker, Inc., New York, 1974) Ch. 7.
6. L. E. NIELSEN and T. B. LEWIS, *J. Polymer Sci., A-2* 1 (1969) 1705.
7. J. KOLARIK, J. JANACEK and L. NICOLAIS, *J. Appl. Polymer Sci.* 20 (1976) 841.
8. L. E. NIELSEN, Applied Polymer Symposium, No. 12 (1969) 249.
9. *Idem, J. Appl. Phys.* 41 (1970) 4626.
10. E. H. KERNER, Proceedings of the Physics Society, 69B (1956) 808.
11. L. E. NIELSEN and B. LEE, *J. Compos. Mater.* 6 (1972) 136.
12. J. R. JENNESS, Jr. and D. E. KLINE, *J. Appl. Polymer Sci.* 17 (1973) 3391.
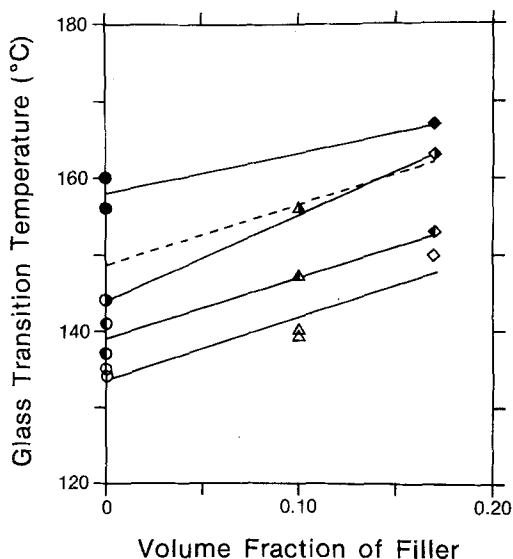13. A. YIM and L. E. ST. PIERRE, *Polymer Letters* 7 (1969) 237.

Figure 4 Relationship between glass transition temperature and filler content at four levels of cross-linking. Dashed line: Projected slope at $X = 0.13$ assuming T_g value at $\phi_2 = 0$, $X = 0$ is low (compare with [1]).

14. E. PRICE, D. M. FRENCH and A. S. TOMPA,
    J. Appl. Polymer Sci. 16 (1972) 157.
15. A. YIM, R. S. CHAHAL and L. E. ST. PIERRE,
    J. Colloid and Interface Sci. 43 (1973) 583.
16. G. K. KUZNETSOV and L. A. IRGEN, *Polymer Mech.* 9 (1973) 433.
17. J. SETO, *Polymer J.* 8 (1976) 475.

A. R. GREENBERG
R. P. KUSY
Dental Research Centre,
University of North Carolina,
Chapel Hill,
North Carolina 27514,
USA

Determination of the relative density changes in the presence of high strain gradient

During the plastic deformation of a material containing second phase particles, damage occurs either by decohesion at the interface between the particle and the matrix [1] or by fracture of the particles [2–4]. This damage can be quantified by metallurgical observations [5], measurements of Young's modulus [6], by hydrogen diffusion [7] or by relative density change measurements [8, 9]. In the present work, only metallurgical observations and relative density change measurements using a Ratcliffe's method [10] were performed. The metallurgical observations only allow very local measurements (areas of about $20 \mu m \times 20 \mu m$ were observed at a magnification of 4000 times by scanning electron microscope) but in contrast the relative density change measurements required a specimen of weight greater than 0.5 g in order to be sure of accuracy (uncertainty less than $\pm 5 \times 10^{-5}$ for the relative density measurement) [11]. The size of such a specimen compared to the size of the necking zone is important and it is a limitation to the use of this method. The aim

of this work was to assess the relative density change in the necking zone at very high strain gradients.

The results are presented for a tough pitch copper which allows very high local tensile strain,
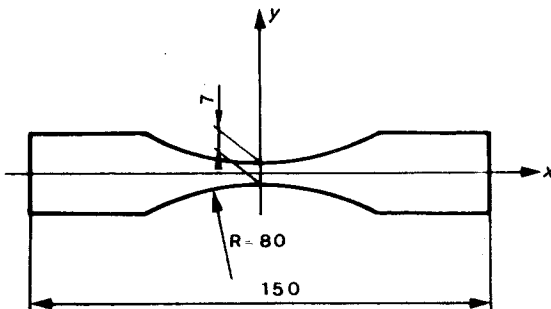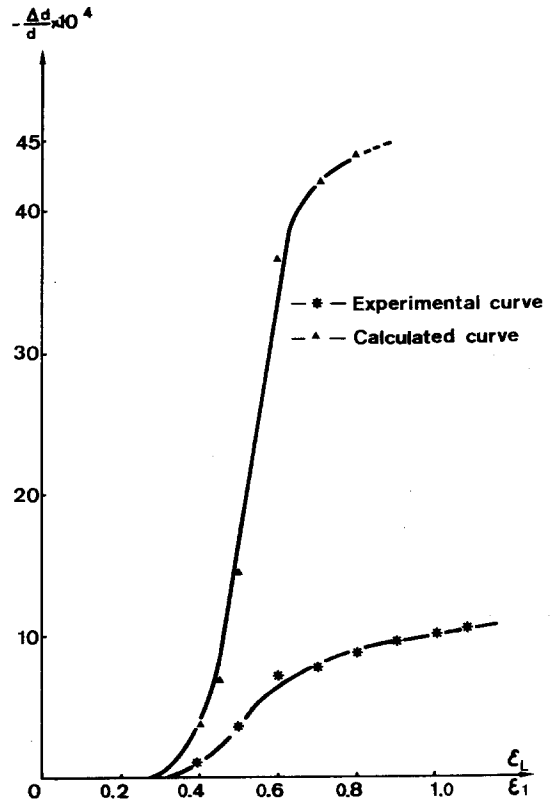

Figure 2 Relative density change curves for a tough pitch copper (experimental curve and curve calculated using a step-by-step method). The experimental curve shows the mean relative density change value on a sample 10 mm long, plotted against the tensile strain ϵ_1 measured by the strain gauge at each step of strain. The calculated curve represents the real value of the relative density at a given local strain ϵ_L on any area in the sample.

Figure 1 Shape of tensile sample (thickness: 2 mm).