

Aqueous carbon fibre composites: effect of matrix shrinkage on toughness

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Carbon fibre pultrusions were made using as matrices frozen aqueous solutions of very soluble solids and infinitely miscible liquids. The solutes decreased the volume change on freezing, and it was possible by varying the amount of solute to cover a range of volume changes from about 8½% increase to about 9% decrease. In this way internal stresses in the composites could be controlled over a wide range. The volume change on freezing, and hence the magnitude and sign of the internal stresses, did not appear to affect the shear strength of the composites directly, although there were changes in shear strength (both increases and decreases) which were attributable to other factors. The toughness of the composites on the other hand was strongly influenced by shrinkage stresses, and had a peak when there was a very slight positive pressure at the fibre-matrix interface.

1. Introduction

Although fibre composites are widely employed, their safe use in load bearing situations requires stringent safeguards because of their lack of ductility. In addition, they are not very tough; laminates split very easily, and aligned carbon fibre composites can be broken very easily across the grain, so that the fibres are broken [1]. An analysis of this type of failure suggests that it is governed, to some extent at least, by matrix shrinkage [2]: for maximum toughness across the grain the elastic shrinkage strain the matrix should be made as nearly equal as possible to the fibre Poisson's shrinkage strain at the breaking point of the fibre. This process has led to a patent [3], and appears to be the first convincing explanation for the observation that carbon and glass fibres which are both very brittle, impart very different toughnesses to composites.

Recent work with carbon-epoxies, using special expanding monomers to control shrinkage, have indicated that toughness can be increased significantly (about 100%) without any loss in shear strength [4]. At the same time there was an increase in fatigue endurance [5] and a reduction in water absorption [6, 7]. However, only limited matrix shrinkage control was possible using expanding monomers, while much greater variations in shrinkage and expansion are possible using, as matrix, frozen aqueous solutions. The work described here is an attempt to determine the effect of matrix shrinkage on composite toughness using these matrices.

2. Experimental method

Three solids and two liquids were added to distilled water, after boiling it, to make solutions of different concentrations up to the saturation level. The higher concentrations of the solids, i.e. sodium chloride

(reagent grade) glucose (95% pure α - D(+); non-ionic) and poly(vinyl alcohol) (PVA; molecular weight M about 14 000) required dissolution at elevated temperature using a high speed mixer. They were cooled after mixing to 10°C before use as a matrix. The liquids, reagent grade glacial acetic acid, and 99% pure 2,5-hexanedione (acetonyl acetone) are freely miscible with water, and were therefore used at concentrations from 0 to 100% in steps of 5%.

Aligned carbon fibre rods about 300 mm long were made using the pultrusion method. Thornel P55 VSB 32 carbon fibre tows were wound onto a mandrel until there was sufficient thickness of fibre on the mandrel to make a composite with a fibre volume fraction of 0.40. String was tied around the fibres at one point on the circumference of the mandrel. The fibres were then cut at the diametrically opposite point, removed from the mandrel, and immersed in the solution which was kept at a temperature close to its freezing point (as indicated by the first indication of crystals). After remaining immersed for at least 15 min to ensure good impregnation, the fibres were removed from the solution, and, using the string to manipulate them, were pulled inside a glass tube with a flared end. The tube was then sealed and placed in a dry ice-acetone mixture for freezing.

When well frozen, the pultrusions were removed from the tubes, after slight warming of the tubes to release them. They were 6.9 ± 0.3 mm diameter, and were cut into 60 ± 2 mm lengths and notched at their centres to a depth of 2.2 ± 0.5 mm using a diamond cutter for the Izod test so that the area that had to be fractured was about 27 mm². Specimens for shear testing were cut into 40 ± 2 mm lengths. After preparation the specimens were stored at -78°C for at least one hour before testing.

The Izod test was carried out using a Tinius Olsen

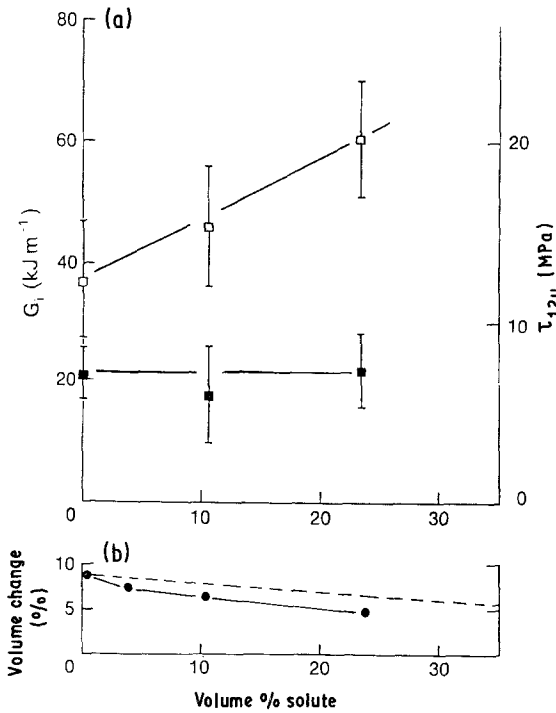


Figure 1 (a) Toughness (\square) (G) shear strength (\blacksquare) (τ) and (b) volume change (\bullet) for sodium chloride aqueous matrix composites.

Impact Tester with a 28 J maximum capacity. The test was done as quickly as possible to minimize warming of the specimen. At least five specimens were tested for each data point.

For the shear strength the specimens were tested in three-point bending using a span of 30 mm in a Table Model Instron machine at a cross head speed of 5 mm min^{-1} . The shear strength τ_{12u} was estimated from the failure load F and the diameter of the specimens D according to the approximate formula

$$\tau_{12u} \approx 0.9F/D^2 \quad (1)$$

(This is obtained from the standard result as given for example by Timoshenko and Goodier [8]: $\tau_{12u} = (3 + 2\nu)F/(1 + \nu)\pi D^2$ with Poisson's ratio ν given approximately by 0.3). Again, at least five tests were carried out for each data point.

The volume changes of the liquids on freezing were measured using a release agent coated glass pipette. This was partly filled with about 10 ml of the solution at about the freezing point, and topped by about 2 ml of a non-miscible silicone oil. The change in level of the silicone meniscus was noted as the liquid was frozen to -78°C in a dry ice-acetone mixture.

3. Experimental results

Figs 1, 2 and 3 show the results obtained when the solutions of solids were frozen to make the matrices for the pultrusions. In the upper graphs are the works of fracture and shear strengths and the lower graph shows the corresponding volume changes. The sodium chloride and glucose (Figs 1 and 2) produced composites with shear strengths of about 7 MPa which were not significantly affected by the amount of solute up to the saturation value (about 23% and 30% respectively). The works of fracture on the other hand increased significantly. (The error bars here and in later graphs all indicate \pm one standard deviation.)

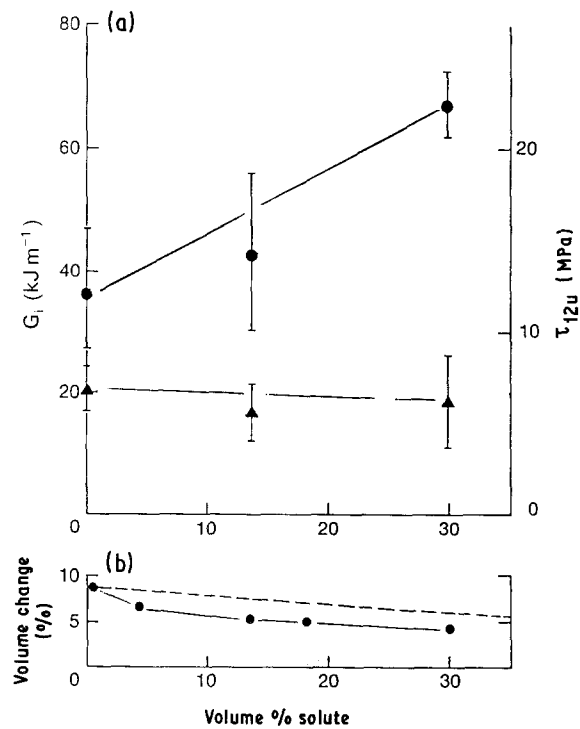


Figure 2 (a) Toughness (\bullet) (G) shear strength (\blacktriangle) (τ) and (b) volume change (\bullet) for glucose aqueous matrix composites.

PVA, on the other hand, increased the shear strength markedly but had no significant effect on the work of fracture (Fig. 3). The volume expansions decreased monotonically with increasing solute content, but in all cases were below the value expected on a Rule of Mixture basis (the dashed line). The deviation was most marked with the PVA. All the solutes had curved plots.

With the completely miscible liquids, Figs 4 and 5,

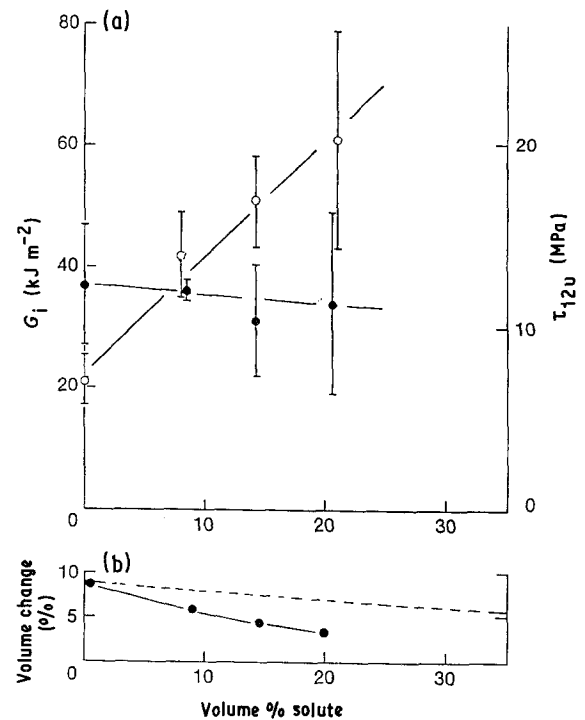


Figure 3 (a) Toughness (\bullet) (G) shear strength (\circ) (τ) and (b) volume change (\bullet) for polyvinyl alcohol aqueous matrix composites.

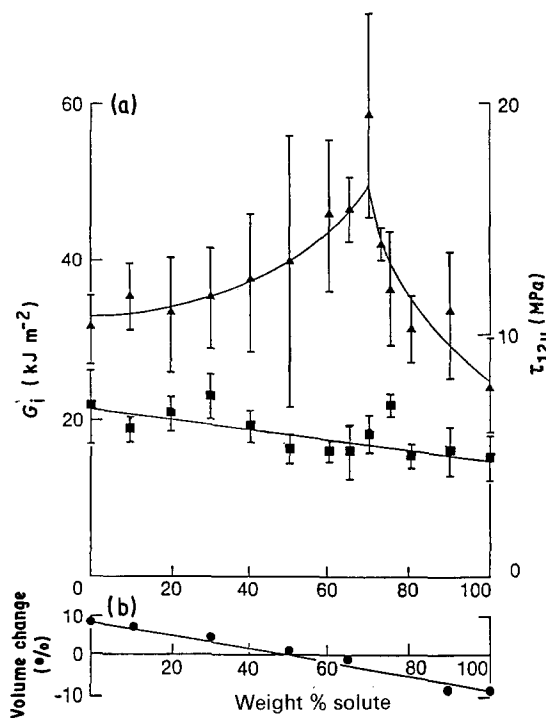


Figure 4 (a) Toughness (\blacktriangle) (G) shear strength (\blacksquare) (τ) and (b) volume change (\bullet) for acetic acid aqueous matrix composites.

both expansion and contraction could be obtained on freezing. The shear strengths appeared to decline with increasing solute in both cases, and the works of fracture had peaks when the volume changes were close to their minima, but still with significant shrinkage.

With all specimens except the PVA the composites tended to split during the Izod test, Fig. 6, although more than 50% of the fibres broke, as revealed by spreading them out after the specimens thawed, Fig. 7. In many cases, very long pulled out fibre lengths could be observed by separating the thawed out specimens manually, Fig. 8. In the case of the PVA, the specimens separated into two pieces during the Izod test.

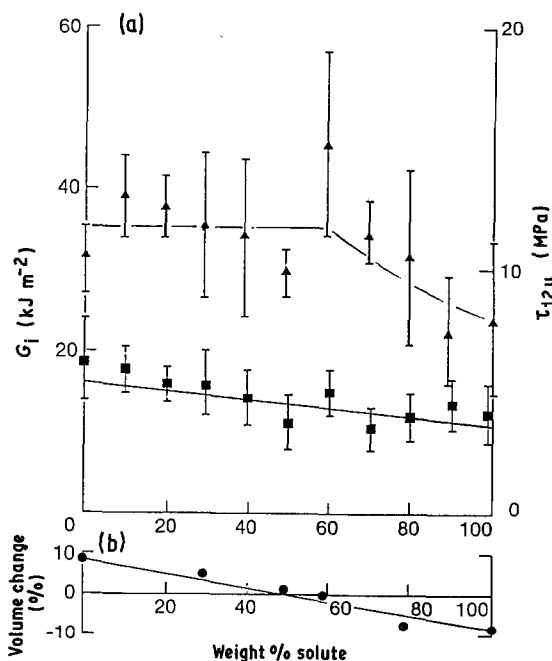


Figure 5 (a) Toughness (\blacktriangle) (G) shear strength (\blacksquare) (τ) and (b) volume change (\bullet) for 2,5-hexanedione aqueous matrix composites.

A test in which the PVA solution was spread on a flat thin strip of steel (0.01 mm thick) and then frozen, confirmed that expansion stresses were generated on freezing, i.e. the strip was convex upward with the solution on top, after freezing. The test was ineffective with the other solutions because of fracture of the frozen material and debonding.

4. Discussion

Since in most cases more than 50% of the fibres were fractured in the Izod test, the test was measuring the across-the-grain fracture resistance, rather than the resistance to splitting. However, since complete fracture was not always observed, the fracture resistance in the across-the-grain mode was probably somewhat higher than the measured value. The results obtained here are thus indicative of trends rather than absolute values.

The composites made with solidified sodium chloride and glucose solutions had shear strengths which were almost independent of the composition of the matrix (Figs 1 and 2) and two to three times higher than that of pure ice [9]. The expansion on freezing was reduced with increasing amounts of solute, and at the same time the work of fracture increased. Thus there appeared to be a direct correlation between shrinkage stress and work of fracture, with no interference from other effects, such as changes in matrix or interface strength.

In marked contrast to this, the composites made with PVA showed a substantial increase in shear strength with increasing solute content (Fig. 3). At the same time, the expansion on freezing decreased markedly: more so than for sodium chloride and glucose (compare Fig. 3 with Figs 1 and 2). This anomalously large effect indicates the formation of a hydrated species, perhaps through hydrogen bonding. Such hydration could reduce the amount of water available for expansion on freezing by a quantity greater than that expected on the basis of a simple mixture rule, and hence give the anomalously large effect.

The work of fracture was not significantly affected. This is not surprising. The frozen PVA solution did not apparently behave like ice, was probably less brittle, and probably did not permit debonding with the same facility as ice did. Hence fibre pull out could have been inhibited, thus counteracting the effect of the reduction in volume change on freezing. The relatively high shear strengths at the higher PVA contents indicates that the PVA formed some sort of extended structure in the water before freezing, and the structure was not completely disrupted by the freezing.

Since the volume change on freezing was expansive in all these cases, the toughness could not arise from the normal pull out against frictional forces resulting from positive pressure generated at the interface by matrix shrinkage. (Note: we expect matrix shrinkage to give overall a positive pressure at the interface, even if there may, in exceptional circumstances, be some tensile stress at the interface at some points around the figure circumference [9].) However, in an imperfect composite, other factors can play a part. For example,

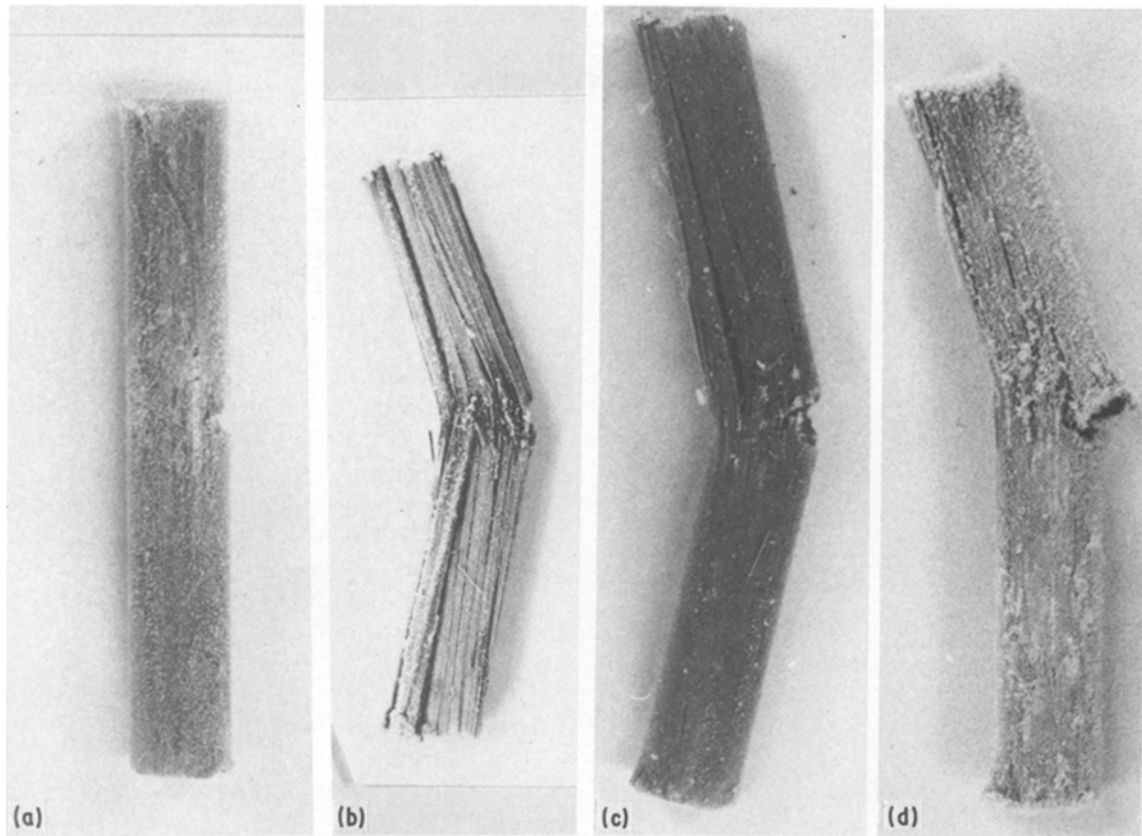


Figure 6 Aqueous matrix composite impact specimens: (a) before impact, (b) ice matrix, after impact, (c) 75% acetic acid matrix, after impact and (d) 100% acetic acid matrix, after impact.

if the fibres were not straight, pull out forces would be generated during fracture due to the fibres being pulled around bends in their sockets.

In addition long fibre pull out lengths are necessarily associated with large areas of debonding, and give a work of fracture, G_{db} , which may be estimated from

$$G_{db} = 4LG_i V_f / d \quad (2)$$

for an average pulled out length L with fibres having diameter d and volume fraction V_f . The interface has a work of fracture G_i . (Equation 2 is derived from the interface work for each fibre, which has an average value given by $\pi d L G_i$, multiplied by the number of fibres per unit area N . Since $V_f = N \pi d^2 / 4$ we replace N by $4V_f / \pi d^2$ to get Equation 2.)

From work with reinforced epoxies we expect G_i to

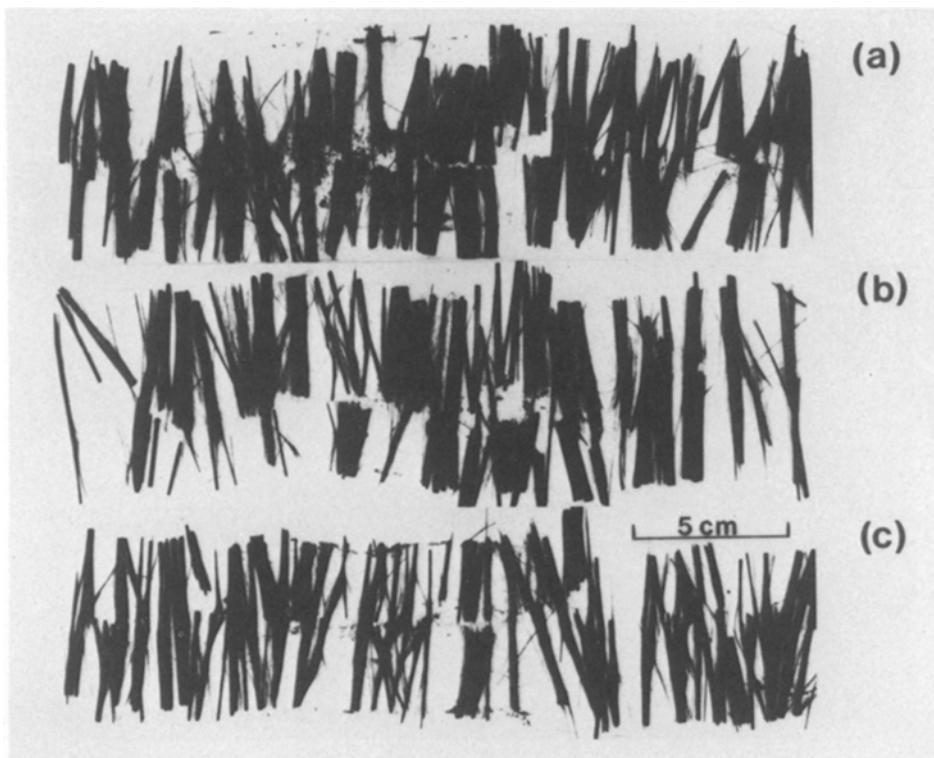


Figure 7 Thawed-out specimen after impact testing spread out to reveal the extent of fibre breakage. Specimen using (a) water, (b) acetic acid and (c) 2,5-hexanedione.

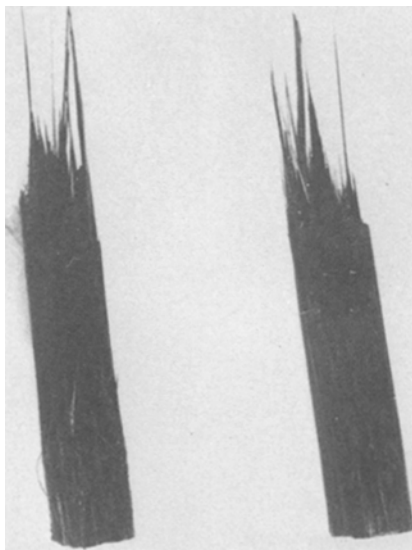


Figure 8 Thawed-out specimen separated in tension (75% acetic acid matrix).

be quite low compared with the work of fracture of the matrix [11]. (With carbon-epoxies the interface can have a work of fracture of 20 J m^{-2} with an epoxy having an Izod value of $1\text{--}2 \text{ kJ m}^{-2}$.) For carbon reinforced ice, interface data are not available, and works of fracture of the ice itself only appear to have been measured on unnotched specimens, and these appear to give large ($\times 10$) variations with size of specimens [9]. However, since frictional work in fibre pull out is likely to be vanishingly small (arising only from lack of straightness in the matrix passages through which the fibres were pulled) it is worth estimating G_{db} from Equation 2 using the best available value for G_i , i.e. the work of fracture for the ice. This comes to about 0.4 kJ m^{-2} . So for an average pulled out length of 0.5 mm (plausible, based on Fig. 7) and $V_f = 0.4$, we get $G_{db} \approx 40 \text{ kJ m}^{-2}$ which is consistent with the results. The work of splitting (see Fig. 6) could also be a major component, however. For a work of fracture of 40 kJ m^{-2} , the total work is about 1.1 J . One diametral split along the whole specimen length, if taking place wholly in the ice, could absorb about 10% of this.

The results with the completely miscible liquids spanned volume changes from 9% shrinkage to $8\frac{1}{2}\%$ expansion. The work of fracture had its maximum

when the volume change was slightly negative, i.e. a positive shrinkage pressure existed at the fibre surface. This was the case both for acetic acid and hexanedione solutions (Figs 4 and 5), and lends excellent support to the concept that shrinkage control is beneficial for composite toughness. The slight loss in shear strength at the higher solute levels is probably due to the acetic acid and hexanedione being a little weaker than water, since the shear strength of composites is controlled to a major extent by matrix strength.

5. Conclusion

The experiments using frozen aqueous solutions as matrices for carbon fibre composites show that across the grain toughness in carbon fibre composites is dependent on matrix shrinkage, and under ideal conditions can be increased substantially, without any significant loss of shear strength, by reduction of the shrinkage stresses (or expansive stresses). The toughness has a maximum when the interface is under slight compression.

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