

The Effect of Interfacial Adhesion on the Tensile Behavior of Polystyrene–Glass-Bead Composites

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Synopsis

The tensile behavior at 20°C of polystyrene–glass-bead composites has been studied at several glass concentrations. To gain insight into the role of interfacial adhesion, the bonding between glass and polystyrene was varied by using different silane coupling agents. In contrast to the elastic behavior, the crazing behavior of the composites was found to be considerably affected by the degree of interfacial adhesion. This is explained by means of the different mechanisms for craze formation at adhering and nonadhering glass beads, respectively. Furthermore, it was found that both elastic and crazing behavior of the composites are influenced by the glass bead concentration.

INTRODUCTION

When a glass-bead-filled polystyrene (PS) sample is subjected to a uniaxial tension, the crazes form at the stress concentrating glass beads. In previous papers^{1,2} it was reported that the mechanism for this craze formation is fundamentally different for adhering and nonadhering glass beads. If excellent adhesion between PS matrix and glass beads exists, the crazes form near the poles of the beads in regions of maximum dilatation and of maximum principal stress. A detail of a crazed sample with excellent interfacial adhesion is shown in Figure 1(a). On the other hand, with poor interfacial adhesion the crazes form at the interface between pole and equator [Fig. 1(b)]. The mechanism for the latter case is that the formation of crazes is preceded by dewetting along the phase boundary.

In the present work the effect of interfacial adhesion, and thus of the mechanism for craze formation, on the tensile behavior of PS–glass-bead composites is studied at several glass concentrations.

EXPERIMENTAL

The PS used was Styron 634 obtained from the Dow Chemical Co. The glass beads (Tamson 31/20) have a diameter range of 1.0×10^{-5} – 5.3×10^{-5} m and a specific gravity of 2.48. Before dispersed in PS, the glass beads were surface-treated with two different silane coupling agents: a cationic vinylbenzyl trimethoxysilane [(CH₃O)₃Si(CH₂)₃NH(CH₂)₂NHCH₂–C₆H₄–CH=CH₂·HCl] (Dow Corning Z-6032) for excellent adhesion between PS and glass, and vinyltriethoxysilane (Fluka) for poor adhesion. The silanes were applied as described previously.¹

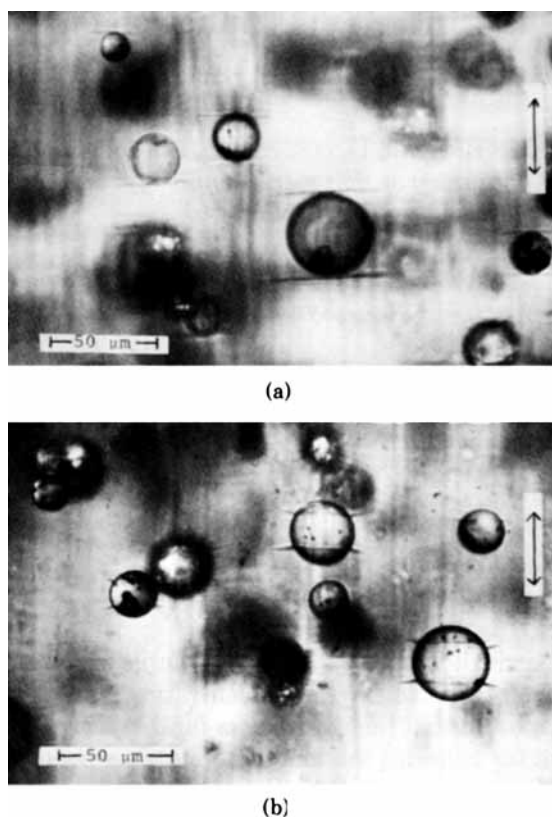


Fig. 1. Light micrographs of craze patterns around (a) excellent adhering glass beads and (b) poor adhering glass beads. The arrow indicates the direction of the applied tension.

Composites were made containing from 0 up to 25 vol % of glass beads. The composites were prepared by melt-mixing on a laboratory mill at 190°C. The total mixing time was 8 min. Tensile specimens were machined in accordance with ASTM D 638 III from compression-molded sheets. To reduce thermal stresses the specimens were annealed at 80°C for 24 h and then conditioned at 20°C and 65% relative humidity for at least 48 h before testing.

The tensile tests were performed on an Instron tensile tester at 20°C. The crosshead speed was 2×10^{-3} m/min, and the gauge length was 5×10^{-2} m. The elongation was measured with an Instron static strain gauge extensometer. At least five samples of each different glass concentration were tested.

RESULTS AND DISCUSSION

Elastic Behavior

In Figure 2 the Young's modulus is plotted as a function of glass content for both excellent and poor interfacial adhesion. It appears that at 20°C, i.e., rather far below the glass transition temperature of PS, the modulus is hardly affected by the degree of interfacial adhesion. This effect has already been reported for several other glass-bead-filled polymers.³⁻⁵

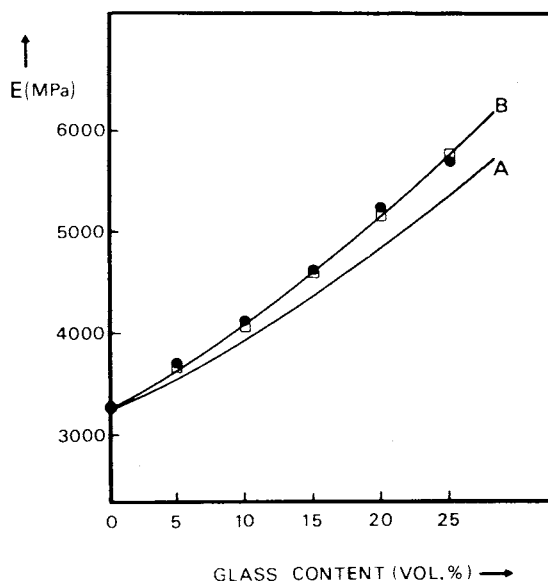


Fig. 2. The Young's modulus (E) at 20°C for PS-glass-bead composites with excellent (\square) and poor (\bullet) interfacial adhesion. The curves represent the values predicted by the original Kerner equation (A) and the modified Kerner equation (B).

The modulus increases with increasing glass content. In order to compare the experimental values with theoretical predictions, the composite moduli have been calculated using the original Kerner equation⁶ as well as the modified Kerner equation.⁷ The elastic constants used for these calculations are PS: Young's modulus = 3250 MPa, Poisson ratio = 0.34; Glass: Young's modulus = 70,000 MPa, Poisson ratio = 0.22.

In contrast with the original Kerner model, the modified model takes the maximum random close-packing fraction of the beads (0.64) into account. It appears from Figure 2 that the predictions of the modified Kerner model correspond best with experimental data.

Crazing Behavior: Effect of Interfacial Adhesion

In Figure 3 the tensile stress-strain curves for PS-glass 85/15 (vol %) composites with excellent and poor interfacial adhesion are represented. These curves only serve as an example since the stress-strain curves for the other investigated compositions show a similar course. At a certain applied stress level the curves for all examined composites (except unfilled PS) exhibit a distinct deviation of the linear elastic behavior. This must be the result of the formation and after that the growing of crazes since tensile deformation of PS occurs hardly by shear flow. Figure 3 shows that the critical stress level at which craze formation starts is considerably lower for poor adhering beads compared with excellent adhering beads: for poor adhesion the deviation of linear elastic behavior begins at about 13 MPa, and for excellent adhesion at about 20 MPa. Both stress levels were found to be practically independent of bead concentration, at least up to 25% of volume.

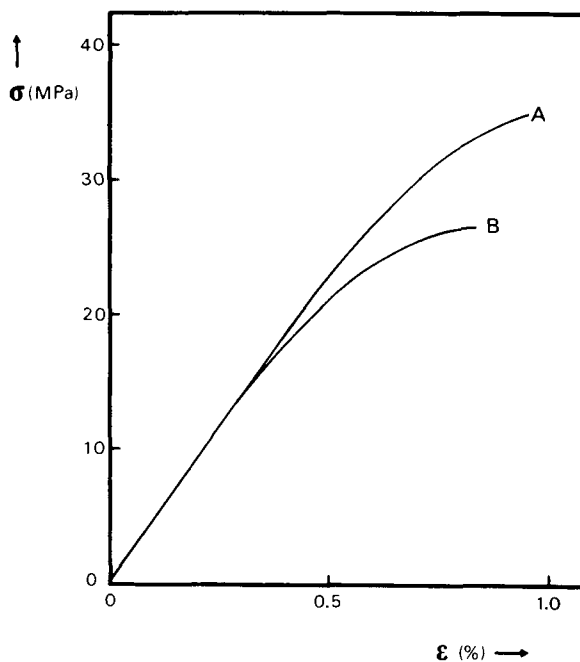


Fig. 3. Tensile stress-strain curves at 20°C for PS-glass-bead 85/15 (vol %) composites with excellent (A) and poor (B) interfacial adhesion.

The observed fact that craze formation starts at a lower applied stress for poor interfacial adhesion can be explained as follows. In contrast with excellent adhering beads, craze formation at poor adhering beads is preceded by dewetting along the phase boundary.^{1,2} During dewetting a small cap-shaped cavity is formed which lies around the top of the bead. This cavity will induce extra stress concentration especially in the vicinity of its relatively sharp edge. Because of this the craze formation (at the edge of the cavity) can occur at a lower applied stress compared with excellent interfacial adhesion, in which case no dewetting takes place as the crazes directly form near the poles of the bead. It thus appears that the mechanism for craze formation has a pronounced effect on the critical applied tensile stress required to start craze formation.

In consequence of the foregoing, the stress at break σ_B is also higher for excellent adhesion than for poor adhesion. This holds for all examined glass bead concentrations as shown in Figure 4.

Crazing Behavior: Effect of Glass Bead Concentration

Figure 4 demonstrates that for both adhesion situations the stress at break σ_B decreases with increasing glass bead concentration. As already pointed out, during the tensile experiment, craze formation starts at a critical applied stress level which is practically independent of the bead content. In samples with larger concentrations of beads, more crazes will be formed than in samples with less beads at nearly the same stress, and, consequently, more matrix material will be involved in the craze process. Now the total elongation ϵ can be assumed to be the sum of the elastic elongation of the matrix ϵ_{el} and the elongation due to

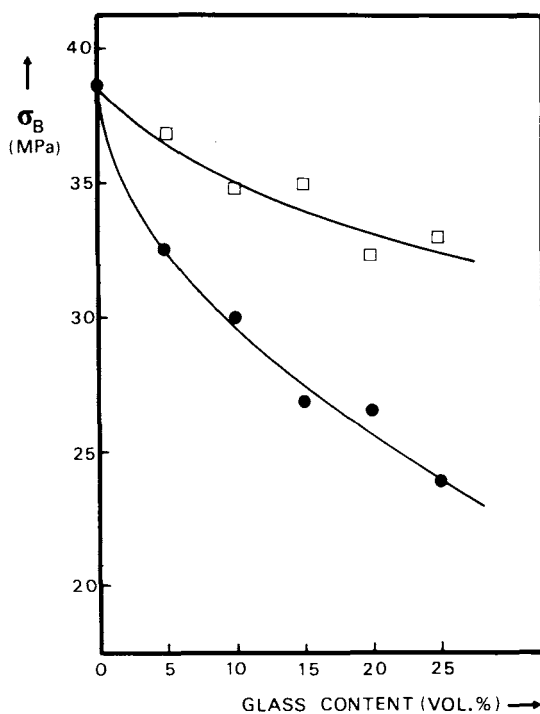


Fig. 4. Stress at break (σ_B) at 20°C for PS-glass-bead composites with excellent (\square) and poor (\bullet) interfacial adhesion.

crazing ϵ_{cr} ⁸:

$$\epsilon = \epsilon_{el} + \epsilon_{cr} \quad (1)$$

Putting $\epsilon_{el} = \sigma/E$, where σ is the applied stress and E is the Young's modulus, the stress is equal to

$$\sigma(t) = E \cdot \epsilon - E \cdot \epsilon_{cr}(\sigma, t, n) \quad (2)$$

ϵ_{cr} will depend on stress, time t , and, of course, on the number of beads n : it will increase with increasing glass bead concentration because of the increasing amount of matrix material that will be involved in the craze process. The consequence of this appears from relation (2): the stress in a constant strain rate experiment ($\epsilon = kt$, where k is a constant) will increase more slowly for samples with high than for samples with low glass bead concentration. This accounts for the decrease of the ultimate stress at break σ_B with increasing bead content.

The effect of adding increasing amounts of glass beads to PS on the ultimate elongation at break ϵ_B is illustrated in Figure 5 and is determined by several factors. First, it is likely that addition of small amounts of beads will result in an increase of ϵ_B because of the promoted crazing at lower stresses compared with unfilled PS. But beyond a certain bead content the craze density will become so high that, since glass beads are unable to control craze growth effectively,⁹ the crazes will run into each other and prompt fracture will result. So beyond a certain bead content, a decrease of ϵ_B with increasing glass bead concentration

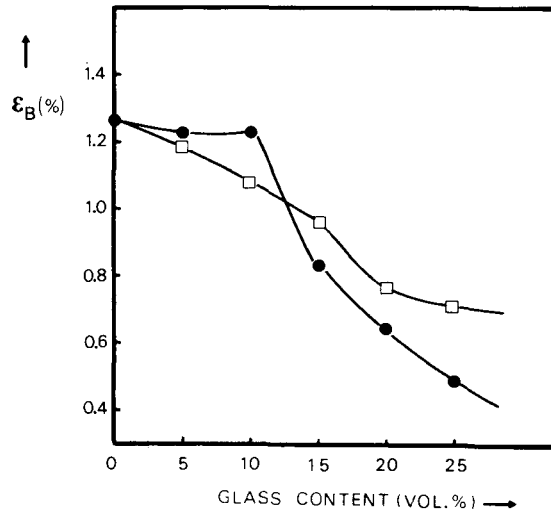


Fig. 5. Elongation at break (ϵ_B) at 20°C for PS-glass-bead composites with excellent (\square) and poor (\bullet) interfacial adhesion.

can be expected. The expected behavior, indeed, is found experimentally in case of poor interfacial adhesion, as demonstrated by the shoulder in the curve of Figure 5. However, in case of excellent interfacial adhesion, where the stress level at which crazing and fracture take place is considerably higher than for poor adhesion, ϵ_B decreases over the whole bead concentration region. From this it appears that the elongation at break, and thus the stability of the crazing material, is not only determined by the number of crazes, but also by the stress prevailing at the crazes.

CONCLUSION

A remarkable result of the present study is that the critical applied tensile stress required to start craze formation at the glass beads is determined by the degree of interfacial adhesion and thus by the mechanism for craze formation. In case of poor interfacial adhesion the dewetting along the phase boundary is supposed to cause extra stress concentration. Therefore, crazes can form at a lower applied stress compared with excellent adhesion in which case no dewetting takes place as the crazes directly form near the poles of the beads.

From the present study it also appears that neither variation of interfacial adhesion nor variation of glass bead concentration has a significant toughening effect. This indicates that even excellent interfacial adhesion does not enable the glass beads to control craze growth effectively. Obviously a more drastic modification near the glass beads' surfaces is required in order to obtain a composite both stiffer and tougher than the matrix material PS. This could be, for instance, encapsulation of the glass beads within a layer of low modulus material, as suggested on theoretical grounds by Matonis and Small,¹⁰ or the introduction of other secondary local deformation mechanisms.

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