The boundary layer and its influence on the mechanical behaviour of composites

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The properties of an epoxy composite filled with china clay, CaF_2 and glass beads were investigated. It was found that a boundary layer formed when fillers were added to the epoxy matrix. The properties of the boundary layer are different from those of the matrix. The density, modulus and tensile strength of the boundary layer were obtained and the influence of the boundary layer on the properties of composites was discussed.

(**Keywords: boundary layer; composite; mechanical properties; epoxy; filler**)

INTRODUCTION

A large number of studies indicate that the boundary layer, with properties differing from those of the filler and the matrix, is formed as a result of the interaction of the solid fillers with the matrix. The properties and the volume of the boundary layer depend on the properties and the volume of the components, the technological process involved and other factors[1]. For an inorganic active filler, its surface influences the rate of crosslinking, the chain activity and the molecular conformations of the polymer matrix[2]. As a result, the boundary layer is formed and it has a certain thickness which depends on the cohesion energy, the chain flexibility of the matrix and the free surface energy of the solid filler.

In fact, the properties of the boundary layer vary with the distance from the filler surface and there is no obvious interface between the boundary layer and the matrix. Sagalav[3] dealt with the boundary layer as an independent phase. That is to say, the composite is composed of three phases: filler, boundary layer and matrix. Considering the variation of the composite density with the filler volume fraction, Sagalav[3] obtained the thickness and the volume fraction of the boundary layer, and proposed the idea of 'the critical volume fraction' – when the filler volume fraction reaches the filler critical volume fraction, the polymer matrix changes into the boundary layer and the properties of the composite reflect those of the filler and the boundary layer.

In engineering, it is important to estimate the properties of the composite by considering the properties of the component phases. In order to do this many models have been proposed[4,5]. However, in these models the existence and influence of the boundary layer are hardly considered. In this paper, the boundary layer of a composite filled with inorganic particles and its influence on the modulus and tensile strength of the composite are studied.

EXPERIMENTAL

Epoxy resin and triethylenetetramine were used in a weight ratio of 10:1. The fillers were china clay*, CaF_2 and glass beads. The filler volume fraction varied from 5 to 40%. The properties of the filler are given in *Table 1*. The samples were prepared in the following way: the resin was degasified at 60–70°C for 30 min under vacuum, and then cooled to room temperature. The fillers and solidifying agent were then added to the resin and mixed for 5 min under vacuum, and finally the mixture was put into the sample mould and cured for 24 h at room temperature and for 2 h at 100°C. In this way, samples in which the filler particles were well dispersed were obtained. The tensile sample is shown in *Figure 1*. The tensile experiments were carried out with a loading speed of 10 mm min^{-1} in a 250 kg test machine.

RESULTS AND DISCUSSION

The boundary layer of the composite

Figure 2 shows the relationship between the filler volume fraction and the composite density. With an increase in the filler volume fraction the composite density is obviously different from the theoretical prediction obtained by the rule of mixtures. This shows the influence of the boundary layer which increases with the filler volume fraction.

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*China clay with other minerals and impurities with approximate composition of $3Al_2O_3 \cdot 2SiO_2$

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Table 1 Physical properties of the filler

Filler	China clay	CaF_2	Glass bead
Density (g cm^{-3})	3.10	2.77	2.40
Modulus (kg cm^{-2})	381 000	401 000	701 000

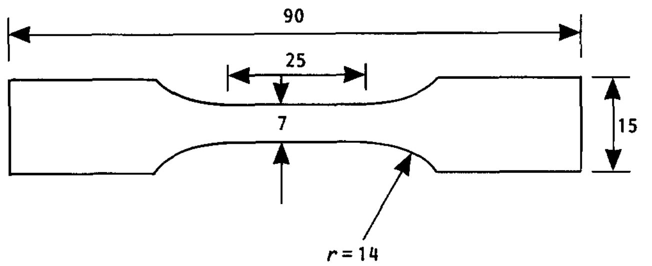

Figure 1 The tensile sample (measurements in mm)

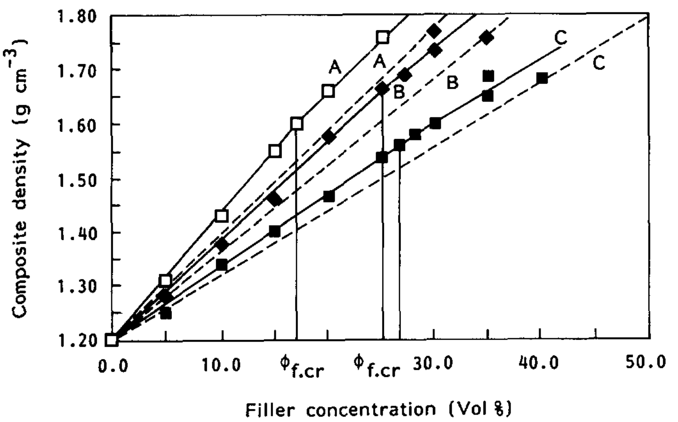

Figure 2 Relationship between composite density and the filler volume fraction: (A) china clay; (B) CaF_2; (C) glass beads; (- - -) prediction by the rule of mixtures; (——) prediction by equation (4)

In general, the density of the inorganic filler does not change, therefore the density of the resin (including the boundary layer and the matrix) can be calculated from:

$$\rho_r = \frac{\rho_c - \rho_f \phi_f}{1 - \phi_f} \qquad (1)$$

where ρ_r, ρ_f and ρ_c are the density of the resin, the filler and the composite, respectively, and ϕ_f is the filler volume fraction.

Figure 3 shows the relationship between the apparent density of the resin and the filler volume fraction. It is worth noting that initially the density of the resin increases with the filler volume fraction, then when the filler volume reaches a certain volume, all of the resin changes into the boundary layer and the density of the resin does not change further with continuing increase in filler. This filler volume fraction is determined as 'the filler critical volume fraction ($\phi_{f.cr}$)'. Obviously, at $\phi_{f.cr}$ the composite consists only of the boundary layer and the filler, and the density of the boundary layer (ρ_i) can be obtained:

$$\rho_i = \frac{\rho_c - \rho_f \phi_{f.cr}}{1 - \phi_{f.cr}} \qquad (2)$$

When the filler volume fractions are inferior to the filler critical volume fraction, for the same fillers (same type and size) the volume fraction of the boundary layer (ϕ_i) can be obtained from the following equation:

$$\phi_i = \frac{\phi_f (1 - \phi_{f.cr})}{\phi_{f.cr}} \qquad (3)$$

The structure of the composites is known: when $\phi_f < \phi_{f.cr}$, it is composed of three phases – the matrix, the boundary layer and the filler; when $\phi_f \geqslant \phi_{f.cr}$, it is composed of two phases – the boundary layer and the filler. When considering the influence of the boundary layer, the density of the composite can be expressed by the rule of mixtures:

$$\rho_c = \rho_i \phi_i + \rho_m \phi_m + \rho_f \phi_f \qquad (4)$$

where ρ is the density, ϕ is the volume fraction, and i, m, f and c are, respectively, the boundary layer, the matrix, the filler and the composite.

Using equation (4), the density of the composites has been calculated (*Figure 2*). The close agreement between the experimental data and the theoretical prediction indicates that the above assumptions are reasonable. At very high filler content, the density of the composite deviates from the prediction by the three-phase model because of the increase in porosity in the composite, which is not considered in this situation.

Influence of the boundary layer on tensile strength

For the composites filled with particles, the tensile strength depends on that of the resin, which is the continuous phase. However, the filler particles also influence the tensile strength of the resin. On the other hand, the dense boundary layer, which is formed in the composites, increases the strength of the resin; on the other hand, because of the filler's influence, the defects and the stress concentration increase and the volume fraction of the resin decreases, which brings about a decrease in the tensile strength of the composite.

Figure 4 shows the relationship between tensile strength of the composite and the filler volume fraction. Three different zones can be defined: in the first zone (before point a), the tensile strength of the composite decreases with increase in the filler volume fraction; in the second zone (between points a and b), the tensile strength of the composite increases with increase in the filler volume fraction; in the third zone, the tensile strength decreases again if the quantity of filler is increased. Point b is nearly the filler critical volume

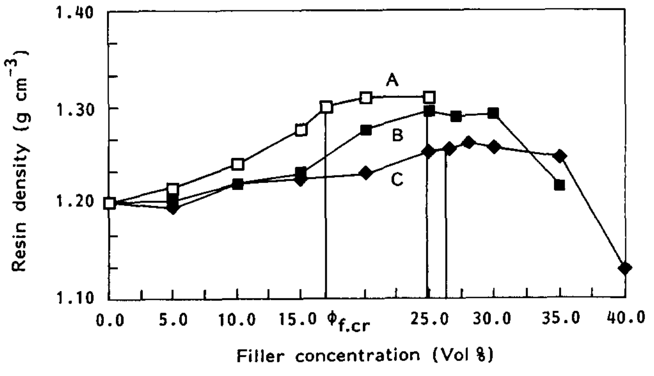

Figure 3 Relationship between resin density and the filler volume fraction: (A) china clay; (B) CaF_2; (C) glass beads

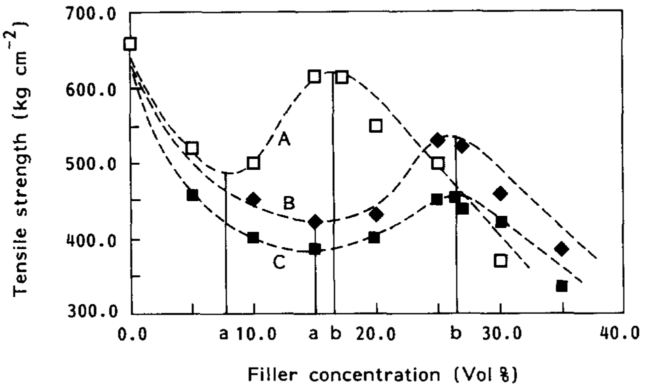

Figure 4 Variation of tensile strength with the filler volume fraction: (A) china clay; (B) CaF$_2$; (C) glass beads; (– – –) theoretical prediction; (□, ◆, ■) experimental data

fraction, where all of the resin has changed into the boundary layer. At point a, the addition of filler and the boundary layer in the composite is nearly the maximum for the bead, that is to say, the boundary layer begins to form a continuous phase at this filler content. According to these results, the role of the boundary layer in the composite can be summarized as follows: before point a, the boundary layer does not form a continuous phase and its reinforcement is not evident. The increase of the stress concentration and the decrease in the resin volume fraction with increase in filler causes the tensile strength of the composite to decrease. When the filler volume fraction is increased beyond point a, the boundary layer begins to form the continuous phase. On the one hand, the boundary layer and the continuous degree of the boundary layer is increased with increase of fillers, which increases the tensile strength of the composite; on the other hand, the increase in stress concentration and the decrease in resin volume fraction with increase in filler causes the tensile strength of the composite to decrease. The result of the interaction of these two factors is that, when the influence of boundary layer is more important than that of the stress concentration and the decrease of the resin volume fraction, the tensile strength of the composite begins to increase. After the filler critical volume fraction (point b), all the matrix has changed into the boundary layer. When the filler continuously increases, the resin volume fraction decreases, and the stress concentration and the contact between the filler particles increase, therefore the strength of the composite decreases again.

According to the above discussion, the tensile strength of the composite filled with particles can be expressed by:

$$\sigma_c = (\sigma_i s_i a_i + \sigma_m s_m)\eta \qquad (5)$$

where σ_c, σ_i and σ_m are the tensile strength of the composite, the boundary layer and the matrix, a_i and η are coefficients about the continuous degree of the boundary layer and the stress concentration in the composite, respectively, and s_i and s_m are the surface fractions of the boundary layer and the matrix. The term in parentheses expresses the tensile strength of the resin, which consists of two parts: one is the contribution from the matrix ($\sigma_m s_m$) and the other is from the boundary layer ($\sigma_i s_i a_i$).

Supposing the fillers are like beads with the same diameter, the maximum filler content (s_f) can be given by:

$$s_f = 1.21\phi_f^{2/3} \qquad (6)$$

and

$$s_i = (1 - 1.21\phi_{f.cr}^{2/3})(\phi_f/\phi_{f.cr})^{2/3} \qquad (7)$$

$$s_f + s_m + s_i = 1 \qquad (8)$$

When $\phi_f < \phi_{f.cr}$, we suppose that $a_i = [\phi_i/(1 - \phi_{f.cr})]$; when $\phi_f \geqslant \phi_{f.cr}$, the composite consists of the filler and the boundary layer. The boundary layer is the only continuous phase in the composite and therefore $a_i = 1$. The tensile strength of the composite can be expressed by:

$$\sigma_c = \sigma_i s_i \eta \; (\phi_f > \phi_{f.cr}) \qquad (9)$$

Because η is a coefficient describing the stress concentration caused by the existence of the filler, it is influenced only by the fillers and can be expressed as a function of the volume fraction and the diameter of the filler. When $\phi_f * D = 0$, $\eta = 1$ (where D is the diameter of the filler). In our experiments, it is assumed that there is a linear relationship between $\sigma_i\eta$ and $\phi_f * D$ ($\phi_f > \phi_{f.cr}$), as in *Figure 5*. The following relationship is obtained and σ_i can be obtained when $\phi_f * D = 0$:

$$\eta = 1 - 0.0107\phi_f * D \qquad (10)$$

Using the above equations, the tensile strength can be calculated (*Figure 4*), and the theoretical predictions prove to be in close agreement with the experimental data.

Influence of the boundary layer on modulus

According to the three-phase model[6,7], the modulus of the composite can be expressed by:

$$E_c = \frac{E_i E_f E_m}{E_i E_f \phi_m + E_f E_m \phi_i + E_i E_m \phi_f} \qquad (11)$$

where E is Young's modulus. When $\phi_f > \phi_{f.cr}$ equation (11) can be expressed as:

$$E_c = \frac{E_i E_f}{E_f \phi_i + E_i \phi_f} \qquad (12)$$

Considering the maximum close-packed effect, ϕ_f' replaces ϕ_f:

$$\phi_f' = \phi_f/\phi_z \qquad (13)$$

where ϕ_z is the maximum close-packed coefficient. In

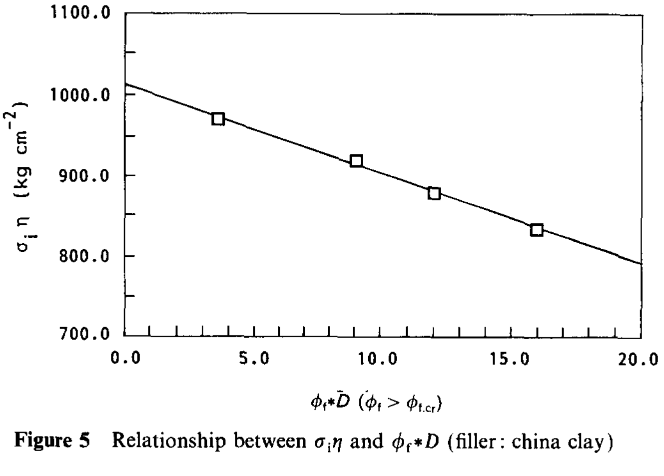

Figure 5 Relationship between $\sigma_i\eta$ and $\phi_f * D$ (filler: china clay)

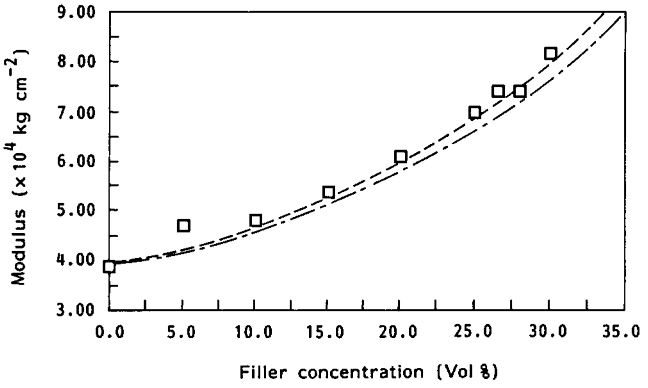

Figure 6 Experimental data and the prediction of the composite modulus (CaF_2): (□) experimental data; (–·–) prediction by Kerner's equation; (– – –) prediction by equation (14)

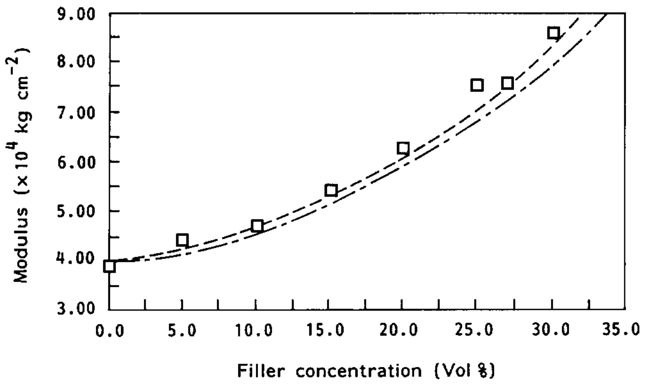

Figure 7 Experimental data and the prediction of the composite modulus (glass bead): (□) experimental data; (–·–) prediction by Kerner's equation; (– – –) prediction by equation (14)

general, for the bead filler, $\phi_z = 0.60$. Therefore equations (11) and (12) can be expressed as:

$$E_c = \frac{E_i E_f E_m}{E_i E_f \phi'_m + E_f E_m \phi'_i + E_i E_m \phi'_f} \qquad (14)$$

$$E_c = \frac{E_i E_f}{E_f \phi'_i + E_i \phi'_f} \qquad (15)$$

where ϕ'_m, ϕ'_f and ϕ'_i are the effective volume fractions of the matrix, the filler and the boundary layer, respectively. The modulus of the boundary layer can be obtained by equation (15). *Figures 6* and *7* show the experimental data and the theoretical predictions by equation (14) and Kerner's equation[8]. When the filler volume fraction increases, the volume fraction of the boundary layer increases, and Kerner's equation prediction deviates from the experimental data. This shows that the boundary layer influences the modulus of the composites.

CONCLUSIONS

In the epoxy composites filled with china clay, CaF_2 and glass beads, there is a dense boundary layer. It is possible that the boundary layer can be considered as an independent phase and that the physical properties of the boundary layer can be obtained. The influence of the boundary layer is important and from its influence the density, Young's modulus and the tensile strength of the composite can be estimated from the component phases.

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