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Prediction of the critical particle size for toughening a glassy polymer

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A bilayer specimen composed of a thin polystyrene (PS) film on a polycarbonate (PC) mini-bar was prepared for tensile test. It was observed by scanning electron microscopy that periodic cracks appeared in the PS film when the specimen was deformed in tension. From the maximum crack spacing in the PS, the ultimate shear stress at the PS/PC interface was estimated to be 49 MPa using the periodic cracking method. Based on the deformation mechanism operative in the glassy polymer and the measured crack spacing in the PS film, a new methodology was proposed and applied to predict the critical particle size for toughening a PS/PC polymer blend. © 1997 Elsevier Science Ltd.

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Polymer blends, in particular those involving one component of glassy polymers, are among the most important engineering materials used today, e.g. from consumer products to advanced aircraft, as a result of their relatively low cost and easy processing. Interface in a polymer blend plays a key role in controlling its physical, mechanical, and other properties. For example, interface is the location where crazing is initiated in a rubber-toughened glassy polymer such as high impact polystyrene (HIPS). A strong interface which shows good compatibility between components is needed to achieve effective toughening and good mechanical properties[1–3]. It is well known that particle size, morphology, chemistry, and composition of the rubber, all have profound effects on the toughness of a glassy polymer. In general, the toughness of the polymers increases with the particle size for a given particle morphology, chemistry, and composition. Large particles are more effective in initiating crazes, thereby lowering the craze flow stress to avoid early fractures of the polymers. On the other hand, if the particles are too small, they will be ineffective in initiating crazes. It is, therefore, desirable to use large particles in a polymer blend from the viewpoint of toughness. Although this practice of toughening has been quite successfully applied in industry, searching for the critical particle size is mainly based on experience.

In this paper we report a simple yet useful technique, called periodic cracking method[4,5], for measuring the ultimate shear stress at a polymer/polymer interface. The technique involves the deformation of a bilayer specimen in tension, where a thin layer of glassy polymer such as polystyrene (PS) was deposited on a ductile polymer substrate such as polycarbonate (PC). The measured ultimate shear stress at the PS/PC interface reflects the bonding strength of the PS/PC interface, while the minimum crack spacing developed in the glassy polymer during tensile test gives an insight to the critical particle size for effective toughening.

Specimens for tensile test were prepared by spin coating a thin layer of PS on a 1 mm thick PC (CALIBRE 300 polycarbonate resin by Dow Chemical Co.) mini-bar (4 mm × 40 mm). The PS has a glass transition temperature (T_g) of 102°C and number-average molecular weight (M_n) of 148 000 g mol^{-1} with polydispersity index close to 2, measured by differential scanning calorimetry and gel permeation chromatography, respectively. The coating solution was made by dissolving 2.5 g of PS pellets in 50 ml of toluene, and spin-coated on a glass slide at a speed of 2000 rpm. The PS film on the glass slide was then cut into strips with a razor blade and the slide was gradually immersed into distilled water. After the floating PS strip was picked up by the PC mini-bar, the PS-overlaid PC mini-bar was annealed in an oven at 100°C for 18 h to promote adhesion between PS and PC. The specimen was then loaded in tension and examined by a low vacuum scanning electron microscope (LVSEM).

The periodic cracking method proposed by Agrawal and Raj[4] has been applied successfully to the study of the metal/ceramic interfaces, such as SiO_2/Cu and NiO/Pt systems[4,5]. It is, however, the first time the technique is extended to study polymer/polymer interfaces, where the system involves a thin film glassy polymer on a ductile substrate. When the bilayer specimen is loaded in tension, periodic cracks perpendicular to the tensile axis will be developed in the glassy thin film. A schematic diagram illustrating the stress distribution in the thin film of the bilayer specimen is shown in *Figure 1*. The ultimate shear stress at the interface can be calculated from the maximum crack spacing. Details of the analysis can be referred to in the papers by Agrawal and Raj[4], and Shieu *et al.*[5]. According to their analysis, the ultimate shear stress, τ_{uss}, at the PS/PC interface is

$$\tau_{uss} = \frac{\pi \delta \sigma_f}{\lambda_{max}}$$

where σ_f is the fracture strength of the PS, δ is the thickness of the PS film, and λ_{max} is the maximum crack spacing in the PS film. It should be noted that the cracks mentioned here will be replaced by crazes when the failure mechanism is crazing, as in the high molecular weight glassy polymers.

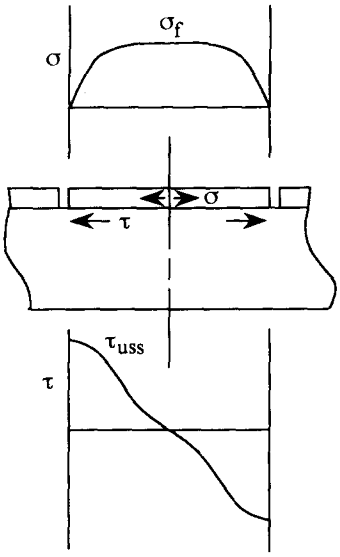

Figure 1 A schematic diagram of the stress distribution in a bilayered-specimen under applied tensile loading. The normal tensile stress σ in the thin film is coupled to the shear stress τ at the interface through a force equilibrium equation

The thickness of the PS on the PC mini-bar was measured to be 220 ± 5 nm by cross-section transmission electron microscopy. The crack density in the PS film grew rapidly when the elongation of the mini-bar reached ~2% and then stabilized. If the fracture strain of the PS is taken to be 2%, the fracture strength will be 66 MPa, using Hooke's law, where the Young's modulus of PS is 3.3 GPa[6]. A SEM micrograph of the periodic cracks in the PS film observed by LVSEM is shown in *Figure 2a*. The maximum crack spacing is measured at 936 ± 30 nm, which is about twice the magnitude of minimum crack spacing λ_{min}, 450 ± 30 nm, agreed with the prediction of the periodic cracking method quite well[4]. Given the fracture strength of the PS at 66 MPa, the ultimate shear stress at the PS/PC interface was calculated, using the above equation, to be 49 MPa.

Further deformation of the specimen up to 10% elongation does not increase the crack density in the PS film. It is, however, observed that fine and wavy short cracks, see *Figure 2b*, appeared between the previous straight cracks. Since the ductile PC can undergo shear deformation, surface steps due to shear yielding are expected to present on the PC surface at large elongation. As a result, the state of the stress at or near the interface will be different from pure shear, which presented in the early stage of the deformation and was used in the derivation of the equation.

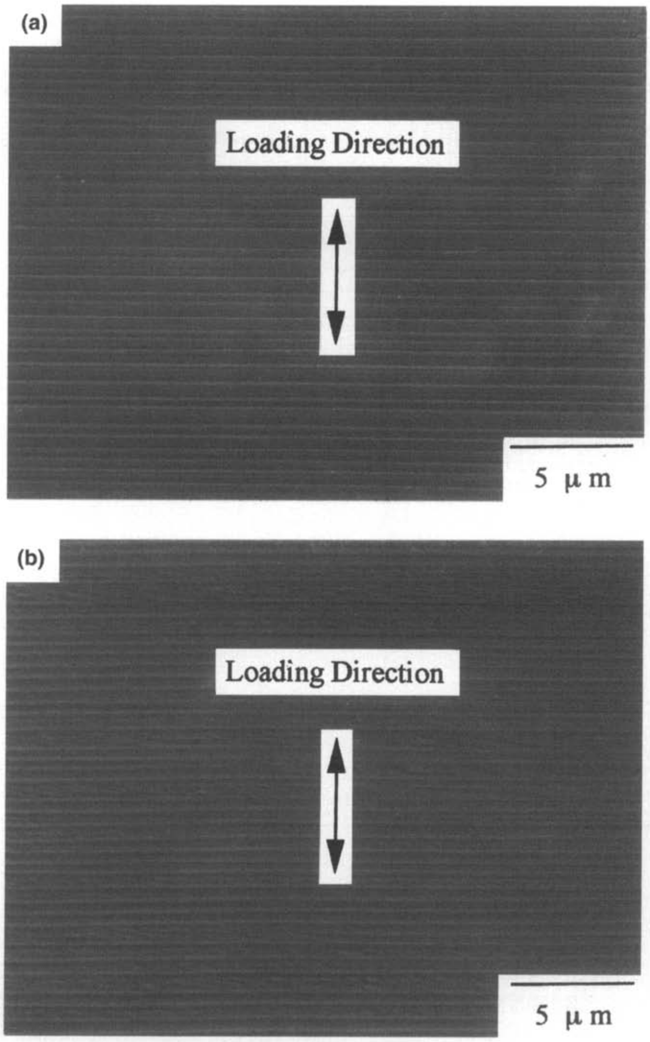

Figure 2 SEM micrographs of the periodic cracks in the PS thin film at (a) 4% and (b) 10% elongation of the PC mini-bar. The existence of fine and wavy short cracks between continuous straight cracks can be seen in (b)

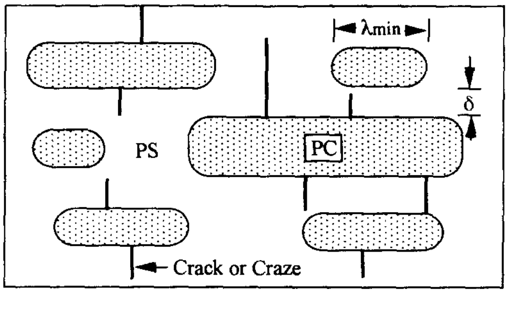

Figure 3 A simplified PS/PC (60/40) blend morphology, upon tensile loading, to illustrate the relationships among parameters obtained from the periodic cracking method and those related to the critical particle size in a polymer blend

It is seen from the tensile test result that the crack density in the PS film reached saturation above 2% elongation. In other words, cracks cannot be further induced when the strip length of the fractured PS film is smaller than the minimum crack spacing, λ_{min}. Here the effect of the fine and wavy short cracks due to shear yielding of the PC has been neglected. In a PS/PC (60/40) polymer blend produced by injection moulding, for example, a simplified morphology of the blend which contains an elongated PC phase dispersed in a PS matrix is schematically shown in *Figure 3*. According to the data obtained from the period cracking method, the critical particle size would be ~0.5 μm (the minimum crack spacing) while the particle spacing is ~0.2 μm (the thickness of the PS thin film) for the PC-toughened PS. Since the crack spacing (λ) is proportional to the thickness of the glassy film (δ) for a constant interfacial shear strength (see the above equation), the critical particle size should be normalized by the film thickness. It is therefore concluded that the optimum condition for toughening a glassy polymer is that the critical particle size is about two to three times the interparticle spacing, i.e. $\lambda_{\min}/\delta = 2 \sim 3$. The film thickness ($\delta$) corresponds to the interparticle spacing and is a function of the geometry and concentration of the ductile phase in the polymer blend. As indicated in *Figure 3*, only for those PC particles having particle size larger than $\lambda_{\min}$ can cracks or crazes be initiated in the PS and thus improve the toughness of the PS/PC (60/40) blend. It is important, however, to note that only a very simple geometry has been considered here; in reality, minor corrections, taking into account the morphology of the particle and stress concentration at the periphery of the particle, may be needed. For example, in a rubber-toughened glassy polymer such as HIPS, the apparent particle size, in which spherical glassy polymer occlusions in a topologically continuous rubber phase, should be referred.

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