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Cavitation of Rubber Particles in High-Impact Polystyrene

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Rubber is incorporated into plastics in order to enhance their toughness. The resulting multiphase polymeric systems are generally termed toughened plastics. Rubber particles dispersed in the polymer matrix act as stress concentration spots. They are able to initiate crazes or shear bands in the matrix as well as to prevent them from premature cracking. Thus, a large quantity of energy is dissipated during the deformation process and the toughness of the plastics is enhanced.[1] Crazing is the dominant deformation mechanism for brittle polymers such as polystyrene (PS) and polymethyl methacrylate (PMMA). Accordingly, shear yielding is the dominant deformation mechanism for ductile polymers such as polyamide (PA) and polycarbonate (PC). Massive yielding in the matrix was believed to be the main mechanism for toughness improvement. Therefore, it was naturally accepted to quantify the yielding zone in the matrix in order to estimate the polymer toughness by finite element method (FEM). The role of rubber particles played in deformation was often neglected. The only request for rubber particles to satisfy is good adhesion to the surrounding matrix. Poor adhesion leads to debonding of the particles from the matrix and holes were believed to be ineffective to initiate crazes or shear bands.

Pearson and Yee[2] studied the toughening mechanisms of elastomer-modified epoxies by microscopy. They reported the cavitation of rubber particles and shear bands generated from the cavitated particles. They also suggested that cavitation and shear yielding are the two major deformation mechanisms. Afterwards, a new toughening mechanism was suggested for the PPO/PA/rubber system by some researchers.[3–5] They proposed the importance of rubber cavitation; that either cavitation or void formation within the rubber particles or the interface plays an important role in the toughening process. Okamoto *et al.*[6] further confirmed the cavitation in rubber particles by the light scattering experiment and TEM observation in PBT/PC/rubber system. At present, cavitation together with crazing and shear yielding are well-known toughening mechanisms in rubber-toughened plastics.

Through cavitation, a part of energy can be transformed into the energy for new surface formation within the rubber particles. Especially, cavitation relieves the triaxial tension in the matrix surrounding the rubber particles. The stress condition is then transformed from plane strain to plane stress, which facilitates the creation of large plastic zone.

The structure of rubber particles is an important factor for cavitation. Generally, there are two kinds of particles: the solid rubber particles or salami-type rubber particles. The later are observed easily in poly(acrylonitrile-butadiene-styrene) (ABS) and high-impact polystyrene (HIPS) with occlusions within them under transmission electron microscope. Most of the cavitation examples occurred in the solid rubber particles. The cavitation of salami-type particles was less reported. Jar *et al.*[7] reported that cavitation did occur in both kinds of rubber particles in ABS, but much less extensively in salami-type particles than that in solid ones. Okamoto *et al.*[8] observed the cavitation in modified HIPS but cavitation was found to occur in the core-shell particles added. This paper provides evidence to show that cavitation can occur in salami-structured rubber particles alone and crazing is not necessary for void formation within the particles.

Material used for the study was high-impact polystyrene (HIPS), 492J, manufactured by Yanshan Petrol Chemical Co., Beijing, China. The HIPS contained butadiene rubber of 7 wt%. Weight-average molecular weight of the PS matrix was 197200, mea-

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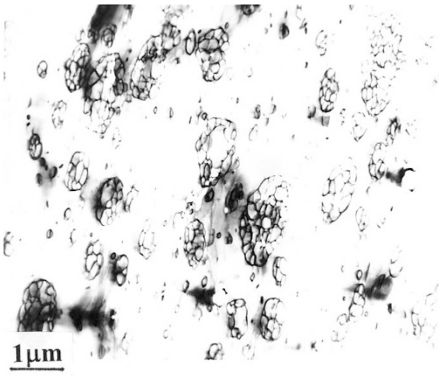

Figure 1. TEM micrograph of an undeformed HIPS specimen.

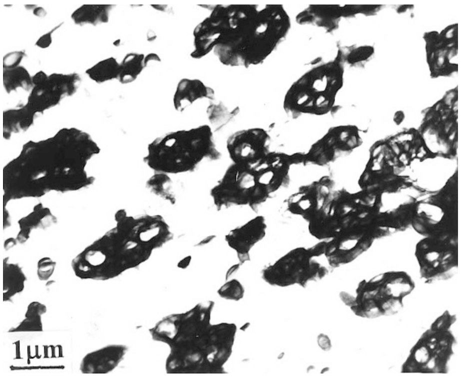

Figure 2. TEM micrograph of a fractured HIPS specimen in the region beneath the fracture surface.

sured by GPC after purification and elimination of the gel by filtering. HIPS pellets were injection-molded to prepare the samples for Izod notched impact tests with an injection moulding machine at 200°C. V-shaped single-edge notches were machined according to GB1451-83. The remaining thickness at the root of the notch was 10.16 ± 0.05 mm. The impact tests were performed on a JJ-20 instrumented impact machine[9] at room temperature. The specimen dimensions were: 63.5 mm × 12.7 mm × 6.0 mm. The region about 1.0 mm beneath the fracture surface was selected for the TEM study.

A JEM-2010 TEM (Japan) was employed to observe the morphology of the fractured specimen. An ultramicrotome was used to obtain thin sections of approximately 100 nm in thickness. The microtoming was carried out at the temperature of liquid nitrogen, to avoid the flowing of rubber. No obvious artifacts, such as holes, were introduced by microtoming as observed before staining. The sections were then stained in the vapor of 2 wt% O_sO_4 aqueous solution for 48 h before observation.

A TEM micrograph of undeformed HIPS specimens is given in Figure 1. Rubber particles of different sizes (dark region) are well dispersed in the matrix of polystyrene (white region). Within the particles, one can find many PS occlusions isolated by rubber layers between them. These are the typical salami-structured rubber particles in HIPS. The particles are easy to initiate crazes in the surrounding matrix and thus the toughness of polystyrene is improved significantly.

Figure 2 shows the TEM micrograph of fractured HIPS specimens in regions beneath the fracture surface. In comparison with Figure 1, sizes of the particles are almost unchanged and the PS occlusions also exist. The boundaries between the particles and the matrix are clear. No crazes can be observed. However, within each of the particles, only a few PS occlusions are found. The occlusions are relatively larger in size than those in undeformed HIPS. In addition, the dark area is enlarged. The results indicate that the fine salami structure in the original HIPS was destroyed after deformation. This may be attributed to the cavitation process within the salami-type rubber particles of HIPS.

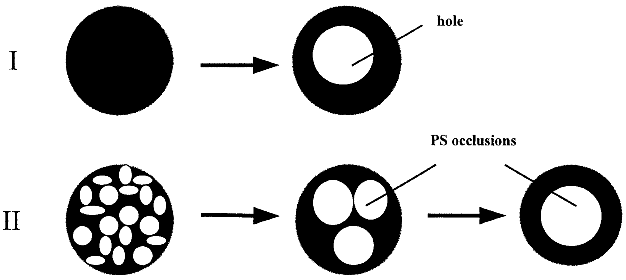

Figure 3. Schematic diagram of cavitation in rubber particles: [I] solid rubber particles; [II] salami-type rubber particles. Dark region represents the rubber phase, white region represents hole or PS occlusions.

Figure 3 gives the schematic diagram of morphological changes of rubber particles before and after cavitation. The cavitation of solid rubber particles leads to holes generated within them (Figure 3I). In salami-type rubber particles, PS occlusions are trapped in the rubber network and separated by rubber layers. Hence the cavitation in this kind of particles is to destroy these layers between PS occlusions. When part of the layers are disappeared, some small PS occlusions connect with each other to form one bigger occlusion. Therefore, the number of occlusions is decreased and the volume of each occlusion is enlarged. When all the layers are destroyed, the salami-type rubber particles transformed into core-shell rubber particles (Figure 3II).

Poisson's ratio of the rubber particles is considered to be an important factor affecting their cavitation behaviors.[10] Under the same external stress, the rubber particles with a larger Poisson's ratio should be under a higher dilatational stress, rendering a higher tendency to cavitation. The rigid SAN occlusions within the salami-type rubber particle in ABS were expected to decrease its Poisson's ratio, which leads to the less cavitation in these particles.[7]

We found that cavitation did occur in the salami-type rubber particles in HIPS and no crazes accompanied. The results support the suggestions of Jar *et al.*,[7] that matrix crazing and rubber particle cavitation are two independent deformation mechanisms that are not necessarily related in the sequence of occurrence. Though salami-type particles might have a smaller Poisson's ratio than the solid ones, they still have the capability of cavitation.

The original purpose of incorporation of the PS occlusions into rubber particles in HIPS was to increase the shear modulus of the particles. Thus, the stress concentration around the particles would be enhanced and large scale of plastic deformation would occur. Therefore, external energy is exhausted and the toughness increased. Cavitation of rubber particles consumed only a small quantity of the energy. From the point of view, the PS occlusions depressed the cavitation of rubber particles. This may interpret most of the cavitation phenomena occurred in the solid particles instead of the salami-type ones.

It should be pointed out that the white part in the rubber particles as shown in Figure 2 are not real holes. They are PS occlusions connected together. Only because of the disability to be stained by O_sO_4, the occlusions appear the characteristics of holes. If they were artifacts by microtoming, they would be observed in the particles as well as the matrix.

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