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# Particle-size effect in craze plasticity of high-impact polystyrene

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To explore the particle-size effect on craze plasticity and on the level of toughening of high-impact polystyrene (HIPS), a commercial grade HIPS (Mobil PS 4600) with a composite particle fraction of 0.217 and average particle size of 2.51 $\mu$m was used. The matrix fractions of the material were dissolved in toluene and the unaffected particles were harvested as a gel fraction which was levitated in fresh toluene as a dilute suspension. This dilute particle suspension was centrifuged to separate the particles into two non-overlapping small and large particle populations of average size 1.03 and 3.97 $\mu$m, respectively. With these separated particles, two new blends of HIPS-type material with narrow particle distributions were reconstituted using commercial grade Lustrex HH-104 PS, together with a reconstituted blend of HIPS made up of the original broad particle-size distribution to be used as a standard for comparison. All three blends had the same volume fraction as the original HIPS. Stress–strain experiments performed on the reconstituted blends showed that the mechanical properties and toughness levels of the reconstituted HIPS were nearly identical to the properties of the original HIPS. While the toughness of the reconstituted material with larger particles was roughly halved at the same flow stress level, the flow stress of the reconstituted blend with small particles had a craze flow stress 5% higher than that of the other two reconstituted blends, and a very severely reduced level of toughness. The behaviour of these blends was analysed with the aid of a theoretical model developed by Piorkowska *et al.* and furnished additional support for the correctness of the particle-size effect based on the principle of 'stress-induced displacement misfit' proposed by Argon *et al.* previously.

**(Keywords: particle size effect; craze plasticity; high impact polystyrene)**

## INTRODUCTION

The well known particle-size effect in high-impact polystyrene (HIPS) has been discussed in the literature by numerous authors and a variety of explanations have been advanced[1–16]. Piorkowska *et al.*[17] have used data obtained on model HIPS-like materials containing carefully harvested concentric spherical shell (CSS) particles to develop a quantitative expression for the craze flow stress in terms of particle size, size distribution, volume fraction and the physical properties of the compliant particles. While comparison of the theoretical predictions of this work with the observed stress–strain behaviour of these model materials was quite good, it was nevertheless hampered by uncertainties surrounding some of the necessary steps in the preparation and harvesting of the CSS particles. Through more recent research carried out by Argon, Cohen and their co-workers, more is now known about the role of soluble low molecular weight homopolymers[18] and electron beam irradiation[19], both of which played an important part in the experimental protocols of the previous study[17].

For these reasons, a study was carried out of a commercially available HIPS which contained a broad distribution of particle sizes. From this material it was possible to harvest two distinct sets of particles for incorporation, at the same volume concentration of 0.217, into a homopolystyrene matrix and construct blends that were free of the objections cited above. Mechanical and morphological characterizations of these reconstituted HIPS materials are reported here and these results are used to re-examine the utility of our previously derived expression for the particle-size effect on the craze flow stress.

## EXPERIMENTAL

### *Materials*

Mobil PS 4600, an extrusion grade HIPS, was chosen for the present study. Dynamic mechanical measurements were carried out at 11 Hz between −126 and 113°C using a Rheovibron model DDII viscoelastometer. The mechanical damping (tan $\delta$) curve showed two distinct peaks, one at −88°C and the other at 98°C, corresponding to the glass transition temperatures of rubber and polystyrene (PS), respectively. Transmission electron micrographs of the Mobil PS 4600 HIPS were prepared using Kato's[20] osmium staining principle. A representative micrograph is shown in *Figure 1*. The freshly cut glass ultramicrotome knife caused noticeable compression along the direction of travel but did not substantially alter dimensions parallel to the knife edge; particles appeared elliptical because of these effects. Distinct and

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characteristic PS occlusions in rubber particles were observed. The gel phase was separated (see below) from the soluble PS matrix and examined in a scanning electron microscope. *Figure 2* shows the spherical composite rubber particles which were obtained.

Toluene used in the particle separation and recovery steps of this study was passed through 1 $\mu$m pore Teflon filters to eliminate any dust or particulate impurities prior to use. Once the particles were separated and sorted according to size, they were reincorporated into fresh PS Lustrex HH-101 (Monsanto Corporation). The properties of this PS have been documented by Gebizlioglu *et al.*[18].

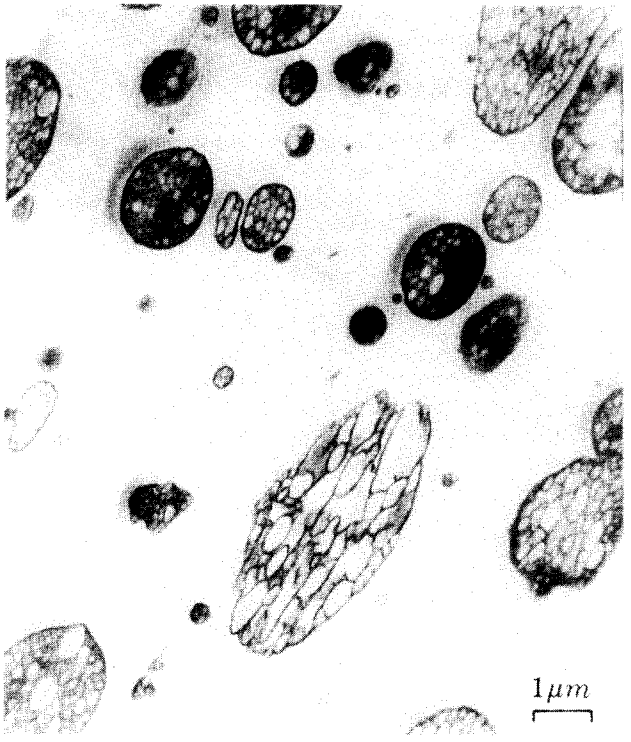


**Figure 1** Transmission electron micrograph of Mobil PS 4600 HIPS in as-received form

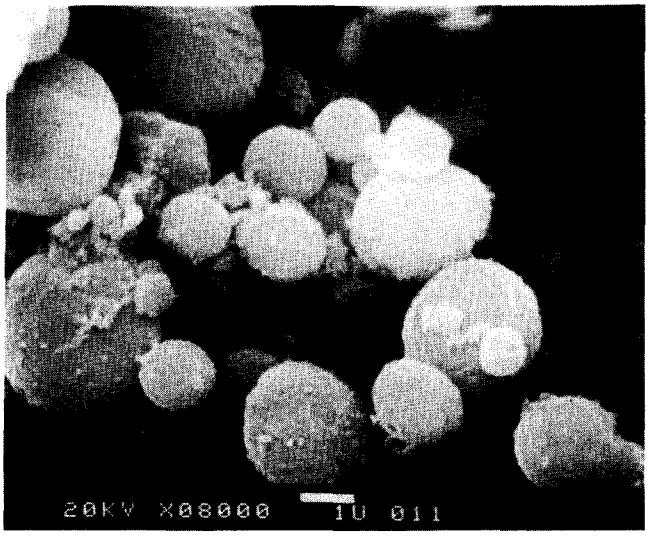


**Figure 2** Scanning electron micrograph of the gel phase of Mobil PS 4600 HIPS

*Sample preparation*

First, an attempt was made to separate the particles of HIPS by filtration. For this purpose, Millipore polytetrafluoroethylene filters with different pore sizes (10, 5, 3 and 1 $\mu$m) were used; however, even at very low concentrations of HIPS in toluene, the membranes became quickly clogged and particles settled on top of each other. Next, free settling (Stokes) column experiments were tried. The column was filled with toluene and the particles, separated from HIPS by centrifugation and resuspended in toluene, were poured on top of the toluene column very slowly to restrict the initial travel of particles as much as possible. However, owing to the very small density difference between the particles and the toluene medium, it required exceedingly long times for the particles to settle down and to give a reasonable separation according to their sizes. This method was also abandoned. In order to accelerate the separation and to avoid any Brownian motion (so that the very small particles did not agglomorate with large ones) centrifugation was chosen as the preferred method.

In the procedure that was finally adopted, Mobil PS 4600 HIPS was dissolved in toluene. The solution was centrifuged at 300 rev min$^{-1}$ for 2 h in a Beckman model J-6B centrifuge with an average radius of 184 cm. The supernatant liquid consisting of toluene and dissolved PS was carefully removed with an aspirator. Fresh toluene was then added to the gel and this mixture was placed into an ultrasonic bath until complete dispersion of the gel in the toluene was accomplished. Then it was centrifuged under the same conditions and again the supernatant liquid was removed. The process was repeated once more and the final gel obtained was dispersed in fresh toluene. For those studies described below which involve particles having the original size distribution, specimens were prepared from the gel obtained at this stage.

To obtain a large particle fraction from the gel, test tubes 2.5 cm in diameter were filled with 40 ml toluene (7.6 cm inside the tubes) and 1 ml of the gel in toluene (approximately 5 wt%) was injected very slowly onto the top of the toluene in the tubes. The tubes were centrifuged at 1000 rev min$^{-1}$ for about 10 min. The supernatant liquid was aspirated off very carefully and saved for later 'small' particle separation. The above steps were repeated twice more and the particles obtained at the end were used for studies carried out with 'large' particles.

The supernatant liquids after each of the three centrifugations were mixed together. A 30 ml sample of solution was centrifuged for about 15 min at 2000 rev min$^{-1}$. The supernatant liquid was removed and saved in clean test tubes. Gel concentration was approximately 0.6 wt% at this stage. The above procedure was repeated twice more, each time using the supernatant liquid of the previous run. Then the supernatant liquid obtained at the end was concentrated by centrifuging at 3000 rev min$^{-1}$ for 2.5 to 3 h and removing the toluene supernatant at this stage. The particles collected at this stage were used for studies carried out with 'small' particles.

*Characterization and testing*

For the particle size distribution analyses, an AMR-100 scanning electron microscope and a Magiscan II Image Analysing Computer manufactured by Joyce-Loebl were used. In the preparation of samples for scanning electron

microscopy (SEM), the method of Keskkula and Traylor[21] was adopted with some modifications. About 2 ml of the particles in toluene were stained with 1 wt% aqueous $OsO_4$. They were centrifuged for about 30 min at 2000 rev $min^{-1}$. Sedimented particles (gel phase) were dispersed in isopropyl alcohol and a drop of this mixture was placed on the sample holder. Isopropyl alcohol was evaporated and stained rubber particles then were coated with gold/palladium to avoid charging. The scanning electron microscope was operated at a beam voltage of 20 kV.

In the specimen preparation steps for mechanical testing, PS Lustrex HH-101 was dissolved in prefiltered toluene and mixed with particles suspended in toluene, at a ratio that would give 21.7 wt% particles in the PS matrix. The mixture was stirred and poured into the specimen boats, which in turn were placed onto a level surface in a desiccator. Nitrogen gas was purged continuously and the temperature was increased to 45–50°C. When the cast sample became rigid, it was transferred to a vacuum oven where the temperature was raised slowly to 100°C. Samples were held at 100°C for 20 h to promote trace solvent evaporation. After a slow cooling to room temperature, tensile specimens were cut using a metal template as a guide[22]. The gauge length was 6.35 mm and the width was 3.18 mm. Specimens were annealed for 24 h at 100°C. Tensile experiments were conducted with an Instron model 1122 testing machine. The strain rate was always $1.3 \times 10^{-4} s^{-1}$.

The microstructures and spatial arrangements of particles in the PS matrix were examined by transmission electron microscopy (TEM) in a Philips 300 instrument at an accelerating voltage of 80 kV. Small pieces from the cast film specimens were stained with 1 wt% aqueous $OsO_4$. Sections of thickness in the range of 200–400 Å were prepared with an LKB 8-800 ultramicrotome III, using glass knifes. For the examination of craze microstructure, specimens were crazed first in an Instron machine and transferred to a jig that maintained the sample strain during staining. Micrographs of the fractured specimens were obtained; in this case the microtoming was done in a direction approximately 45° to the principal tensile axis and perpendicular to the craze planes.

## RESULTS

Typical scanning electron micrographs of the 'original', 'large' and 'small' particle size distributions are shown in *Figure 3*. Owing to the long contact time (longer than 3 days) of the particles with toluene, some rubber membranes were ruptured and some occluded PS was exposed to toluene. Therefore, occasional holes are observed on the particle surfaces. The differences in the sizes of the particles are clearly observable from the micrographs, which are all presented at the same magnification. More precise definitions of the particle size distributions were determined using an image analysing computer. The experimentally measured particle size distributions for the original HIPS and for the small and the large particle populations were first converted into smoothed cumulative distributions of particle diameters. These smoothed cumulative distributions were differentiated to obtain the frequency distributions $g(D)$ of particle diameters of these three populations. These frequency distributions are all

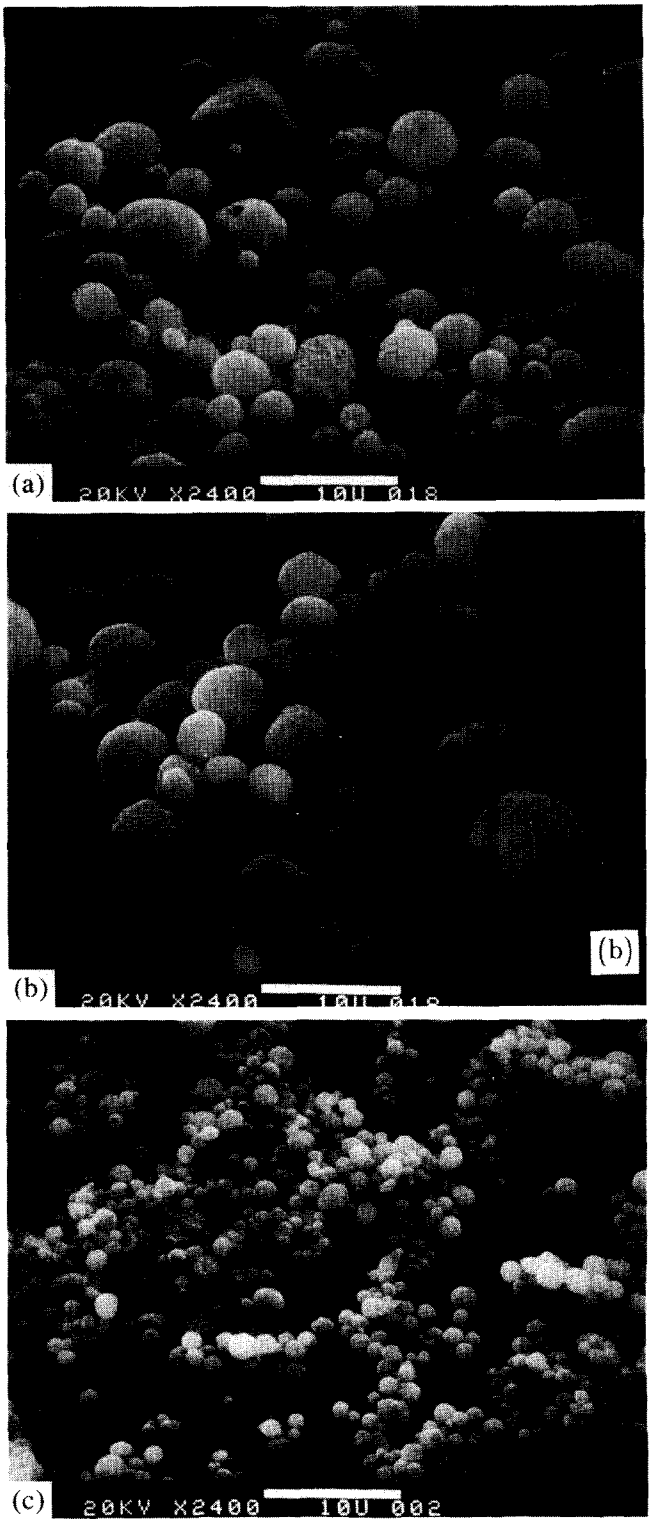


**Figure 3** Scanning electron micrographs of the separated rubber particles of: (a) the original HIPS; (b) population of large particles; (c) population of small particles

shown together in *Figure 4* for ready comparison. *Figure 4* shows that the population average diameter of particles in the original HIPS was 2.51 $\mu$m, and 3.97 $\mu$m, respectively. The figure also shows that there is very little overlap in the distributions of the small and the large diameter particles.

Transmission electron micrographs of the reconstituted samples (cut from the films prepared for mechanical tests

prior to testing), shown in *Figures 5a–5c*, revealed that particles were well dispersed and, with few exceptions, did not agglomerate during the casting process. These observations demonstrate that HIPS particles can be separated from a matrix and reconstituted in another matrix without particle agglomeration and without much particle distortion or rupture. Tensile stress–strain behaviour of these samples is shown in *Figures 6a–6d*. *Table 1* summarizes the principal parameters of these curves.

In all cases, crazes initiated from the edges of samples and from surface imperfections and initially concentrated around those areas. As the samples were stretched further, whitening spread throughout the entire gauge length in a manner identical to that in the original HIPS. The crazes were perpendicular to the tensile axis and all the samples broke within the whitened sections. In the reconstituted material with large particles, crazes were also perpendicular to the tensile axis and all the samples broke within the whitened sections. In the reconstituted material with large particles, as well as in the original HIPS samples, there was profuse crazing and whitening. In contrast, there was little whitening in samples with small particles, which broke at early stages of deformation. The different distributions of whitening in the original HIPS and the reconstituted samples with large and small particles are shown in *Figure 7*. The thicknesses and the widths of the samples were measured before and after testing; there was no observable change in width or thickness as a result of stretching, confirming that plastic deformation was due to crazing only. In *Figures 8a* and *8b*, transmission electron micrographs of the crazed samples can be seen for the large particle and small particle samples, respectively. When examined under higher magnification it was found that crazes had the typical microstructures of PS crazes, with the same internal detail of drawn fibrils.

Taken all together, the observations lead to the conclusion that only a fraction of the largest diameter HIPS particles in the small particle population initiate crazes by themselves, and for this they require a measurable elevation of the applied stress. Clearly, the large particles are crucial for initiating a profusion of crazes in HIPS.

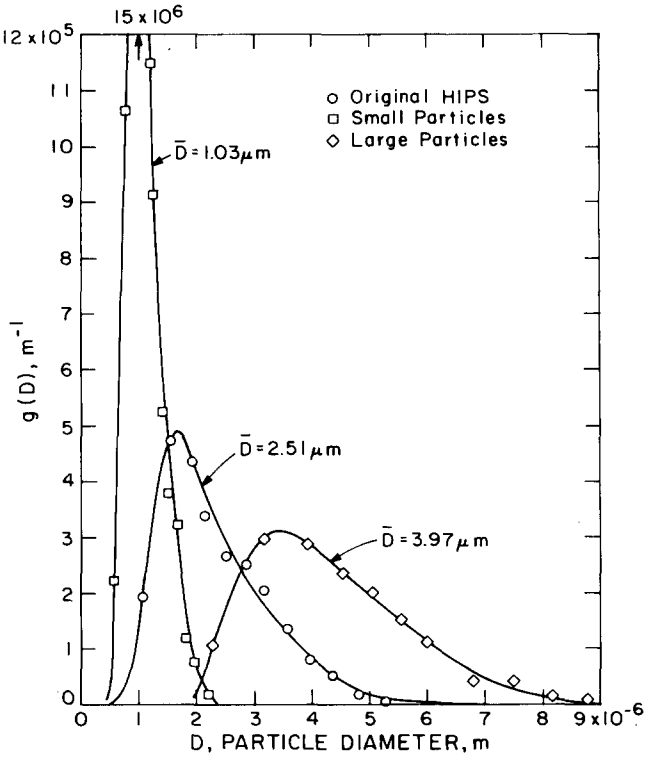


**Figure 4** Three normalized particle-size distributions for the original HIPS material (○), for the large particle fraction (◇) and for the small particle fraction (□)

## DISCUSSION

There have been many explanations of the particle size effect in HIPS-type materials influencing their craze plasticity and their level of toughness[7–9]. In some early blending experiments on PS to create composite particles with different internal morphology, Gebizlioglu *et al.*[23] found that the critical particle size below which crazes are no longer initiated in blends with different types of particles, decreases with increasing particle compliance. On the basis of this, Argon *et al.*[24] proposed a criterion for the critical particle size that states that 'a particle becomes too small to initiate even a single craze when under full load it has a stress induced displacement misfit across it that is smaller than the thickness of a mature craze'. This proposal, which is qualitatively similar to an earlier explanation advanced by Bragaw[7], has all the elements required to explain the observed effects. This principle was later made fully quantitative by Piorkowska *et al.*[17] through the use of Goodier's[25] classical solution of the stress-concentrating properties of spherical elastic heterogeneities in an isotropic elastic medium, under arbitrary distant stress. In this development, the critical particle size $D_c$ in a given distant tensile stress field $\sigma_\infty$,

**Table 1** Mechanical properties of the tensile specimens with HIPS-type particles

| Sample | Yield strength (MPa) | Yield strength eqn (2) (MPa) | Tensile strength (MPa) | Plastic strain to fracture (%) | Relative elastic modulus[a] |
|---|---|---|---|---|---|
| PS | 37.6 | | 37.1 | 1.8 | 1.0 |
| HIPS with original particles[b] | 21.8 | 20.2 | 23.6 | 44 | 0.52 |
| HIPS with large particles[b] | 19.1 | 20.2 | 21.3 | 19.2 | 0.44 |
| HIPS with small particles[b] | 23.8 | 21.2 | 20.7 | 3.6 | 0.58 |

[a] Relative to the Young's modulus of pure homoPS
[b] Containing a particle volume fraction of about 0.22

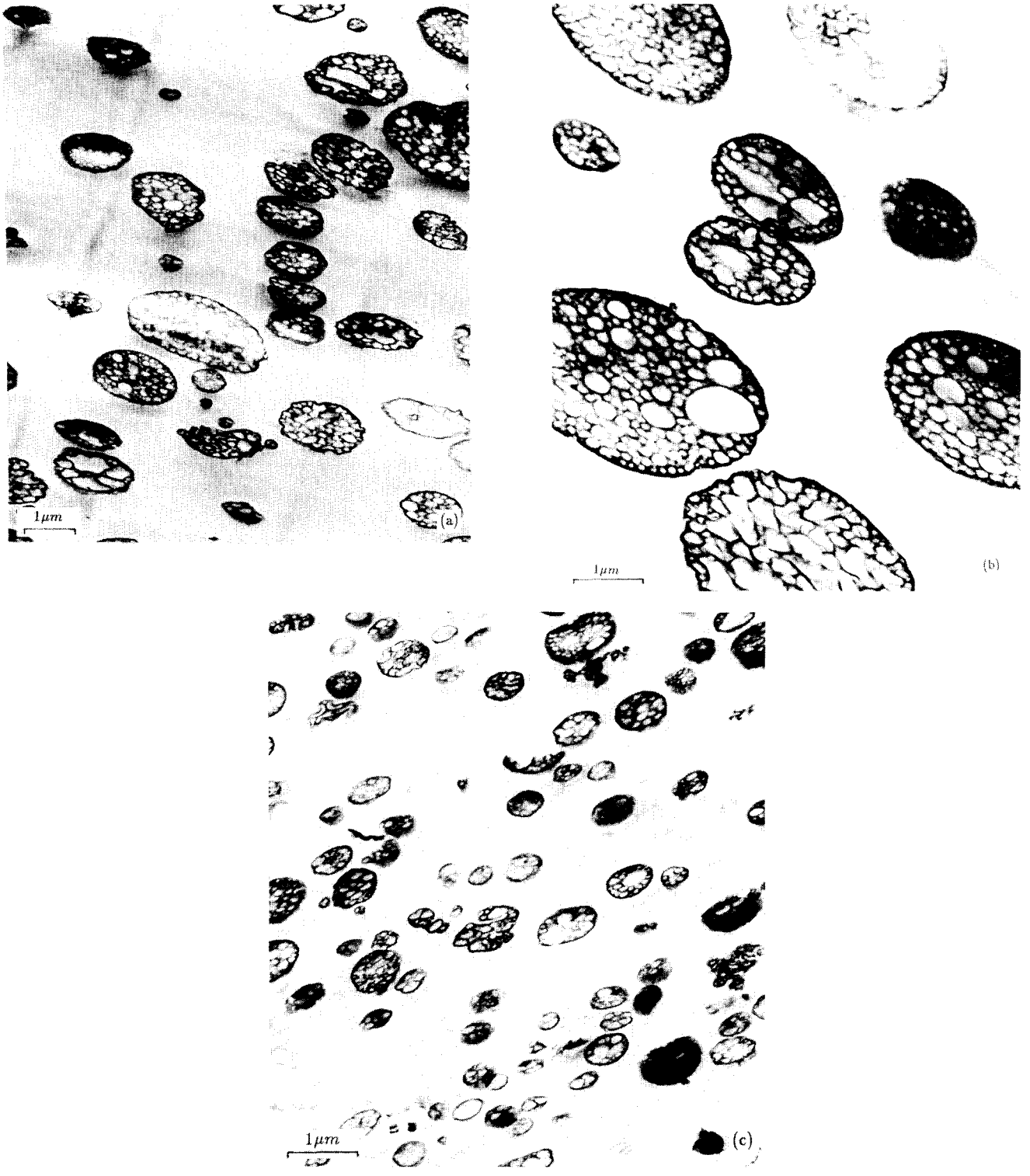


**Figure 5** Transmission electron micrographs of the reconstituted samples of heterogeneous blends: (a) original HIPS; (b) blend with large particles; (c) blend with small particles

below which crazing is no longer found, is given as:

$$D_c = \frac{h_c}{\sigma_\infty(1+B)} \frac{(1-A)}{A} [2\mu(1+\nu)] \qquad (1)$$

where $\mu$ and $\nu$ are the shear modulus and Poisson's ratio, respectively, of the background homopolymer (PS in the present case), $h_c$ is the thinnest mature craze in the homopolymer (estimated to be $1.36 \times 10^{-6}$ cm by Piorkowska *et al.*), and $A$ and $B$ are complex expressions of the relative elastic properties of the particle and its surrounding matrix, involving the ratio of their shear moduli and the Poisson's ratios of both the matrix and the particle. These specific material constants in a uniaxial tensile field were given in detail by Piorkowska *et al.*[17], where specific evaluations of their magnitudes were presented and critical values of $D_c$ were calculated for a variety of particle-bearing polymers, under their typical levels of

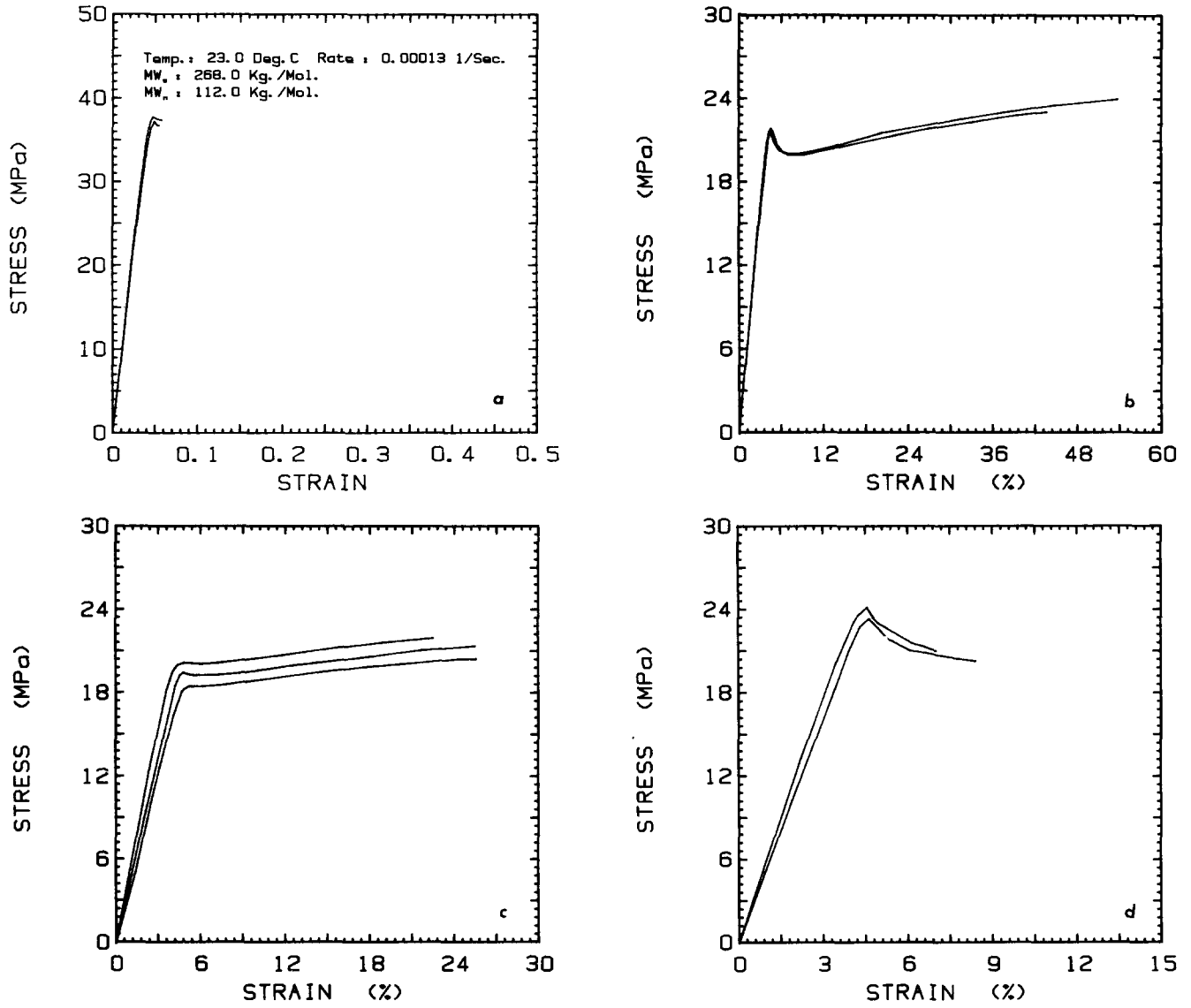


**Figure 6** Tensile stress–strain curves of: (a) unmodified homoPS; (b) reconstituted original HIPS; (c) blend with large particles; (d) blend with small particles

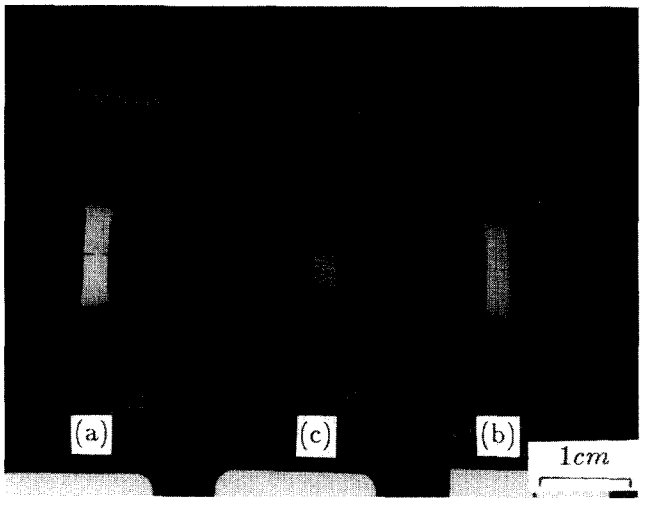


**Figure 7** Photographs showing the level of whitening in the tensile specimens after fracture: (a) blend with original HIPS particles; (b) reconstituted blend with large particles; (c) reconstituted blend with small particles

craze flow stresses. For HIPS, best estimates of $A$ and $B$ were obtained to be 0.571 and 0.665, respectively, giving an estimate for the critical particle radius of $D_c = 0.875\,\mu$m, which compares quite favourably with most of the reported observations. Piorkowska *et al.*[17] have proceeded further and provided a detailed theory for the craze flow stress, $\sigma_{\lambda_c}$, of such modified polymers. Their resulting expression for the flow stress is:

$$\sigma_{\lambda_c} = \frac{\hat{Y}}{\lambda_n'}\left\{1 - \frac{kT}{\Delta G^*}\ln\left[\frac{8\alpha v_0 \varepsilon^T f A(1+B)\hat{Y} I(D_c)}{\pi(1-A)h_c\dot{\varepsilon}_p E}\right]\right\}^{6/5} \quad (2)$$

where $\hat{Y} = 0.133\mu/(1-\nu)$ is the athermal tensile plastic resistance of the homopolymer matrix; $\alpha v_0$, $\Delta G^*$ and $\lambda_n'$ are, respectively, a pre-exponential constant, an activation free energy factor, and an effective craze matter extension ratio in a semiquantitative model for the plastic resistance of a glassy polymer, subjected to a tensile plastic strain rate of $\dot{\varepsilon}_p$; $f$ is the volume fraction of particles; $\varepsilon^T$ is the tensile transformation strain inside crazes ($=\lambda - 1$); $E$ is the Young's modulus of the homopolymer matrix; and $I(D_c)$ is an integral which gives the fraction of the particle

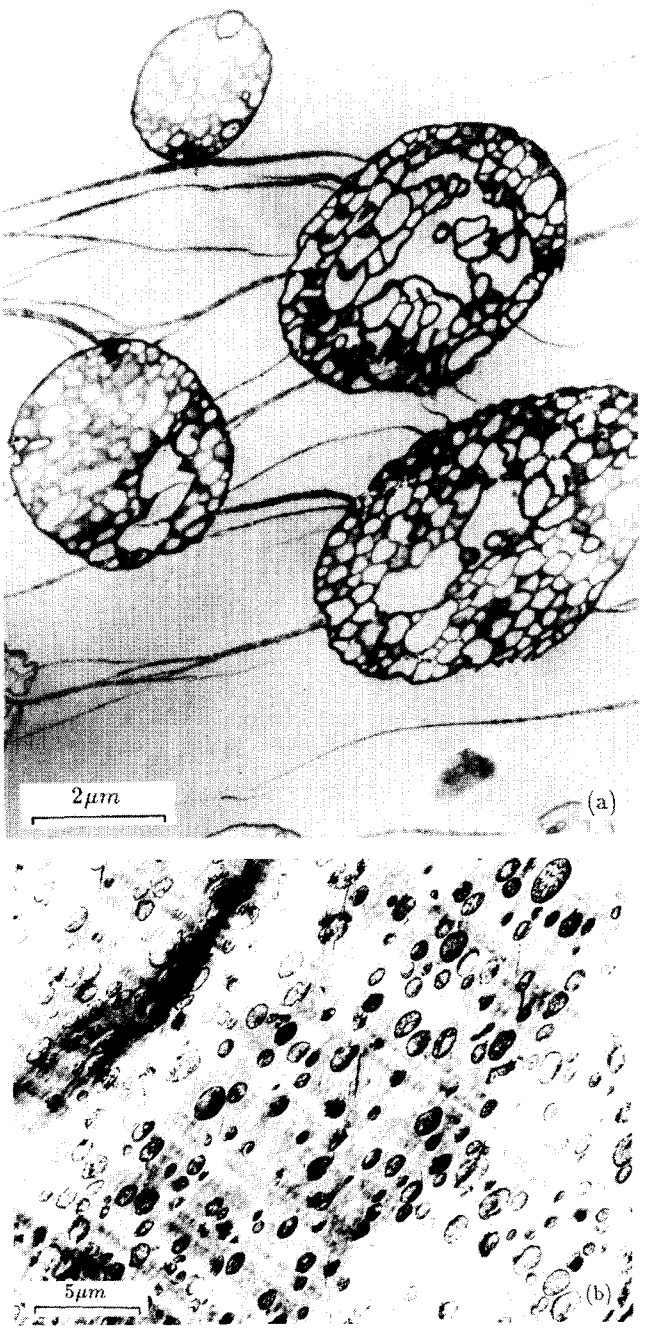


**Figure 8** Transmission electron micrographs of crazed samples: (a) blend with large particles; (b) blend with small particles

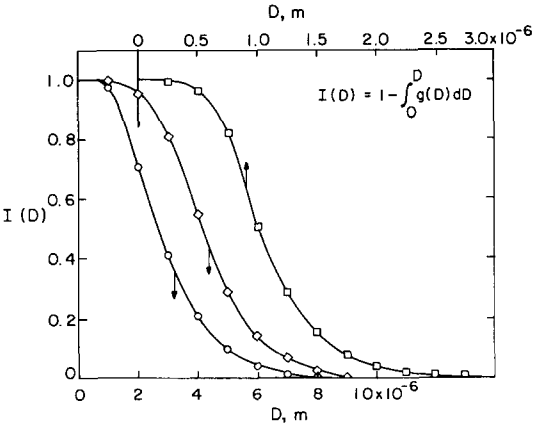


**Figure 9** Calculated distribution of particles with size equal to or exceeding a given value $D$ for original HIPS material (○), material with large particle fraction (◇) and material with small particle fraction (□)

population having a diameter equal to or greater than the threshold size $D_c$ (for the present case these integrals were obtained for the three particle populations from the distributions given in *Figure 4* and are plotted in *Figure 9*).

Based on the specific evaluations of these material constants by Piorkowska *et al.*[17], the following values for the HIPS system are appropriate at room temperature: $\hat{Y}/E = 0.133/2(1-\nu^2) = 7.31 \times 10^{-2}$; $\hat{Y} = 218$ MPa; $\nu = 0.3$; $\lambda_n' = 1.853$; $\alpha v_0 = 3.47 \times 10^5$ cm s$^{-1}$; $\Delta G^*/kT = 44.72$; $f = 0.217$; $I(D_c) = 1.0$ for original HIPS and large particle populations; $I(D_c) = 0.66$ for small particle population (see *Figure 9*); $\varepsilon^T = (\lambda - 1) = 4.0$ ($\lambda$ actual natural draw ratio of craze tufts); and $\dot{\varepsilon}_p = 1.3 \times 10^{-4}$ s$^{-1}$. Further details on the origin of these values are discussed by Piorkowska *et al.*[17].

It is clear, on the basis of equation (2) and the values of the parameters given above, that the particle populations for the original HIPS and for the large particles are nearly fully effective, i.e. almost the entire population of particles have diameters equal to or larger than the critical threshold particle size of 0.875 μm. The situation for the blends with small particles is different. In these, only two-thirds ($I(D_c) = 0.66$) of the particles have diameters exceeding the critical value, making them behave as if they contained a volume fraction of only 0.178 of particles. Thus, this blend is less effective and according to equation (2) its flow stress at 21.2 MPa is 5% higher than the flow stresses for the unmodified HIPS and the blend with large particles. These calculated craze flow stresses have been entered in *Table 1*. While the calculated levels of flow stresses do not compare too well with the experimentally measured flow stresses, they are in the correct order, and the differences between them are not too different from the calculated values, considering that all specimens are subject to a certain level of scatter. This manifests itself most in the strain to fracture, where extrinsic imperfections and non-uniform particle distributions all play an important role.

Parenthetically, we note according to equation (2) that the craze flow stress should increase progressively with decreasing volume fraction of particles, and that formally with a volume fraction of $2.5 \times 10^{-4}$ the craze flow stress of the blends should reach the craze flow stress of the unmodified PS. Actually, the approach should be less rapid since the critical particle size depends inversely on the craze flow stress, as is evident from equation (1). Since the craze flow stress of homoPS is controlled by surface flaws and not by heterogeneities, the reduced effectiveness of decreasing volume fractions of particles should manifest itself much earlier, as it usually does.

Finally, from our experimental measurements of the properties of the blends and our theoretical model, we conclude that commercial HIPS with its usual particle size distribution is a very effectively toughened material.

In all of these considerations of toughness, the important aspect that heterogeneities govern only the plastic resistance while the actual strain to fracture and the tensile toughness are affected by other non-characteristic inorganic inclusions and imperfections must not be

overlooked. Clearly, the effect of these depends rather sensitively on the stress level.

In our present study and in the earlier work of Piorkowska *et al.*[17]. we have demonstrated that definitive experimentation with regard to particles is possible by decomposing commercial and experimental heterogeneous blends and reconstituting them in new forms to create model materials of tighter distributions, without important adverse effects.

## CONCLUSIONS

The present experimental results are fully consistent with our previously proposed criterion for the critical particle size required to develop craze plasticity in heterogeneous blends of normally brittle polymers.

Starting with commercial HIPS, special blends having narrow particle-size distributions can be prepared as materials to test models for particle-size effect for craze-induced toughening, of the type proposed by Piorkowska *et al.*[17].

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