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Rubber toughening of plastics

Part 11 *Effects of rubber particle size and structure on yield behaviour of HIPS*

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Measurements of particle size distribution, particle volume fraction ϕ, Young's modulus, tensile and compressive yield stress and Charpy impact strength were made on a series of 14 high-impact polystyrene (HIPS) polymers of widely varying structure. In materials throughout the series containing 8.5 wt% polybutadiene, it was found that ϕ varied between 0.17 and 0.44 as the mean particle size increased from 0.2 to 1.8 μm. Modulus and yield stresses depended principally upon particle volume fraction but the ratio of polybutadiene to polystyrene within the particles also appeared to have some influence upon properties. By contrast, variations in ϕ provided only a partial explanation for the observed differences in Charpy impact strength. It is concluded that impact strength is affected by rubber particle size to a much greater extent than properties measured at low strain rates.

1. Introduction

Rubber particle size is generally recognized as an important factor affecting the fracture resistance of high-impact polystyrene polymers (HIPS). Numerous studies dating back to the 1950s, have shown that the impact resistance of HIPS decreases when the average diameter of the particles falls below about one micrometre [1–6]. However, there is no general agreement concerning the causes of this particle size effect. Two possible explanations have been advanced: (a) that small particles are inefficient in initiating crazes; and (b) that small particles are ineffective in controlling the growth of crazes and their subsequent degradation to form microcracks [7].

In discussing mechanism (a), Bucknall pointed out that when the rubber particle diameter is 0.1 μm, a significant fall in stress concentration factor is to be expected in the surrounding matrix within a distance of 1 to 2 nm from the particle equator [8]. Since the diameter of the polystyrene molecule is 0.6 nm, the dimensions of the stress field might then be too small to permit the initiation of a craze. This theory received experimental support from Michler [9] and from Donald and Kramer [10], who used transmission electron microscopy (TEM) to observe crazing in thin films of HIPS and found that crazing was preferentially associated with particles above 1 μm in diameter. On the other hand, Keskkula *et al.* [11], also using TEM, have demonstrated craze initiation from a 0.2 μm particle in HIPS. These observations do not resolve the problem, because the question is not simply whether small particles *can* initiate crazes, but whether they are comparable to large ones in their rate of craze initiation.

A basic problem in studying structure–property relationships in rubber-toughened plastics is the difficulty in varying rubber particle size without at the same time introducing other significant changes in the material. In particular, reductions in particle size in HIPS are usually associated with changes in the internal morphology of the particles and with a decrease in the concentration of polystyrene sub-inclusions. These changes result in a decrease in the volume fraction ϕ of the composite rubber particles; in this paper ϕ is taken to include the whole of the rubber phase plus the included material. Control of particle size may be achieved either by varying stirring conditions or by addition of block copolymers, which behave like surfactants. Polymers made from polybutadiene usually form rubber particles with the familiar multiple-inclusion (MI) "salami" structure whereas block copolymers tend to produce single core-shell (SCS) or double core-shell (DCS) morphology [12, 13]. The effects of these different morphologies upon the mechanical properties of HIPS are far from clear at present.

The two previous papers in this series examine the relationship between particle volume fraction ϕ and a wide range of mechanical properties [14, 15]. In order to concentrate upon this aspect of the problem, a series of materials was prepared by blending a single HIPS sample in varying proportions with polystyrene (PS) so that particle sizes and morphologies were identical throughout the series. The HIPS chosen for that work was a standard commercial polymer containing MI particles of median diameter 1.6 μm. The present paper describes the properties of a set of non-standard HIPS materials of various particle sizes and

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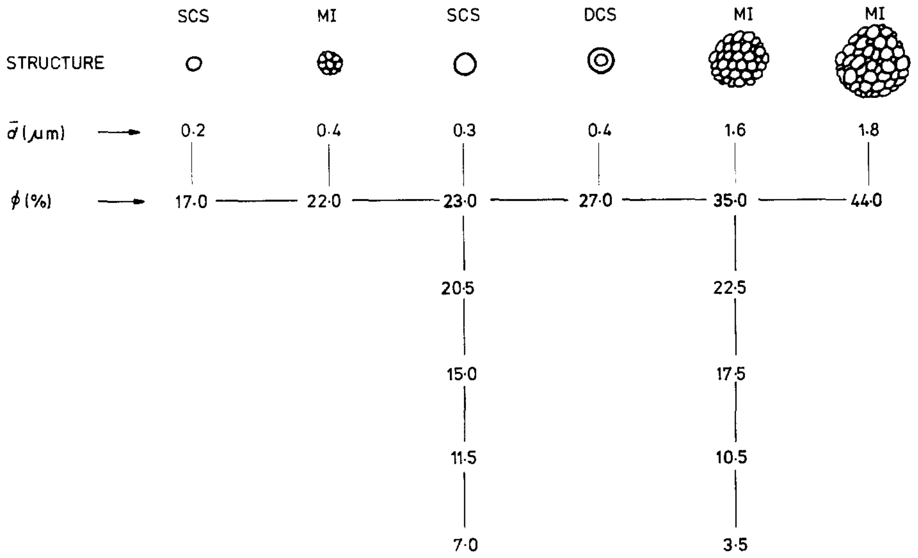

Figure 1 Schematic diagram showing rubber particle morphology, mean diameter $\bar{d}$ and volume fraction ϕ.

internal morphologies, and considers the extent to which those properties are controlled by factors other than particle volume fraction.

2. Experimental details

2.1. Materials

Six HIPS polymers, each containing 8.5 wt % of polybutadiene chains and 2 wt % of a plasticizer, were used in this study. In addition, two of these polymers were blended with polystyrene to produce materials of low rubber content. Particle morphologies, median diameters, and volume fraction of all fourteen HIPS materials are summarized in Fig. 1. Weight average molecular weights of the polystyrene matrices, obtained after centrifuging solutions of the original six HIPS polymers in toluene, to remove the crosslinked rubber, were between 187 000 and 201 000. A polystyrene of $\bar{M}_w = 269\,000$ was blended with the small-particle SCS HIPS; the PS used for blending with the large-particle MI HIPS had $\bar{M}_w = 232\,000$. Granules of PS and HIPS were premixed in a high-speed mixer being blended in a Werner-Pfleiderer ZSK 30 M9 co-rotating twin-screw extruder operating at 100 r.p.m. with barrel temperatures set at 180 to 200° C. The unmodified PS of $\bar{M}_w = 232\,000$ was chosen to provide data at zero rubber content.

Each material was compression moulded at 200° C into 3 mm and 6 mm thick sheets. At the end of each moulding cycle, the heaters were switched off and the press was allowed to cool slowly to room temperature in order to standardise the thermal history of the sheets. Specimens for mechanical testing were milled from these sheets.

2.2. Microscopy

Osmium-stained sections approximately 50 nm thick were prepared from each of the original six HIPS polymers and examined by TEM. Prints measuring 190 nm × 240 mm were made of the micrographs, at a magnification of 10 000. Particle size distributions and particle volume fractions ϕ were determined from these micrographs as described in a previous paper [14]. The procedure used in the earlier work to correct for errors in the measured value of ϕ is particularly important in the present study, because the rubber particles are small: when the particle diameters are only two or three times greater than the section thickness, viewing in transmitted illumination leads to a significant overestimate of ϕ unless the correction is applied.

2.3. Mechanical testing

Young's modulus was measured at 20° C and 60% r.h. using 100-sec isochronous low-strain tensile creep tests. The test method is described fully in previous papers [16, 17]. Yield stresses in tension and compression were measured at a crosshead speed of 0.5 mm min^{-1} and at 23° C. The parallel section of the tensile specimens was 70 mm long with a 13 mm × 3 mm cross-section. Compression was studied by means of the plane strain compression test, using 40 mm wide strips cut from the 3 mm sheet. Details of both yield measurements are given in a previous paper [15].

Notched Charpy impact energy was measured using a Hounsfield impact tester. The bar dimensions were 50 nm × 12 mm × 6 mm and the machine was set to give a 40 mm span. A 3 mm deep vee-notch was machined across the narrow face of the bar, with an angle of 45° and a notch tip radius of 0.25 mm. Specimens were conditioned in a thermostatted box and transferred rapidly to the impact machine for testing.

3. Results and discussion

3.1. Microscopy

Volume fractions of composite rubber particles were determined from the micrographs by first measuring the areas occupied by the osmium-stained regions, plus unstained inclusions, and then applying the finite thickness correction mentioned above. The results are presented in Fig. 1. They reveal a striking variation in the composition of the rubber particles with particle size. The smallest particles contain approximately 50% polybutadiene and 50% polystyrene, whilst the largest particles contain about 20% polybutadiene and 80% polystyrene. Since the polybutadiene content of the parent HIPS polymers remains constant at 8.5 wt %, the net result is that the volume fraction of

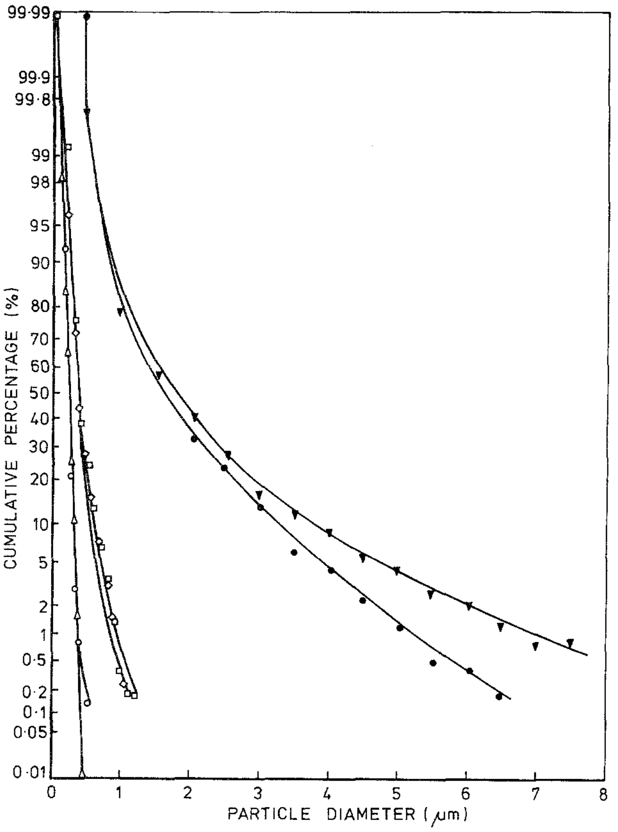

Figure 2 Gaussian plot of cumulative percentage against particle diameter for the parent HIPS polymers. (○) 17 SCS, (◇) 22 MI, (△) 23 SCS, (□) 27 DCS, (●) 35 MI, (▼) 44 MI.

composite particles increases by more than a factor of two as the particle size increases. In the discussion below, the materials are identified by their particle volume fraction and morphology; thus the material having the smallest particles is referred to as HIPS 17 SCS. The material of equivalent ϕ is HIPS 17.5 MI, which has only half the polybutadiene content.

Particle size distributions were determined as described in a previous paper [14]. Diameters observed in thin sections are, in general, less than the true diameters, but no attempt has been made to correct for this effect in the present work because a very large body of data is required for a full analysis. The results are, therefore, given in Fig. 2 in terms of the percentage of particles that have an observed diameter below a certain value.

The six HIPS materials can conveniently be divided into two categories: two contain less than 20% of particles below 1 μm in diameter, whereas the remaining four have very few particles above 1 μm in diameter. Fig. 1 gives data on the median diameter *d*, which is defined by the 50% point in Fig. 2. By giving equal weighting to very large and very small particles in a given polymer, this definition of average particle diameter tends to underestimate the influence of the larger particles, which constitute a large fraction of the total particle volume. However, because of the differences between observed and true particle diameters, it is difficult to calculate the volume fraction of composite particles that have a diameter greater than a given value.

3.2. Modulus

Fig. 3 compares modulus data for PS and all 14 HIPS materials, and shows that moduli decrease with ϕ, the effective volume fraction of composite particles, as expected. It is clear that ϕ rather than polybutadiene content is the principal factor controlling modulus.

A single line correlates the data for the large-particle HIPS materials (35 MI and its blends and 44 MI). Data for the small-particle HIPS materials (23 SCS and its blends, together with 17 SCS) lie on a separate line, which is close to Hashin's lower bound equation for this type of particulate composite [8, 18, 19], as indicated on the diagram. The lines for the two series of HIPS converge at $\phi = 0$. Continuum mechanics theories predict that there should be no effect of particle size upon modulus and it is, therefore, concluded that the divergence in the two experimental curves is due to the lower shear moduli of the smaller particles resulting from the increased proportion of polybutadiene in those particles.

3.3. Yield stress

The tensile yield stress is also controlled principally by ϕ, as shown in Fig. 4. Each point represents the average of five measurements. The solid line correlates data for the large particle HIPS materials. Most of the small-particle HIPS materials give yield stresses that are slightly above this line, but it is difficult to discern a systematic trend. Melt blending and compression moulding are both sources of batch-to-batch variations in tensile yield stress, which are sufficient to account for the observed small differences between the two sets of HIPS data.

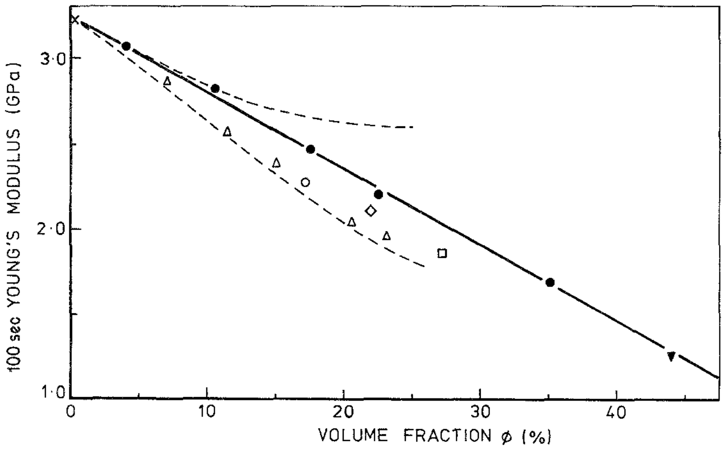

Figure 3 100-sec isochronous Young's modulus plotted against the effective rubber volume fraction. (– – –) Upper and lower bounds of Young's modulus calculated using Hashin's equations. For key see caption for Fig. 2.

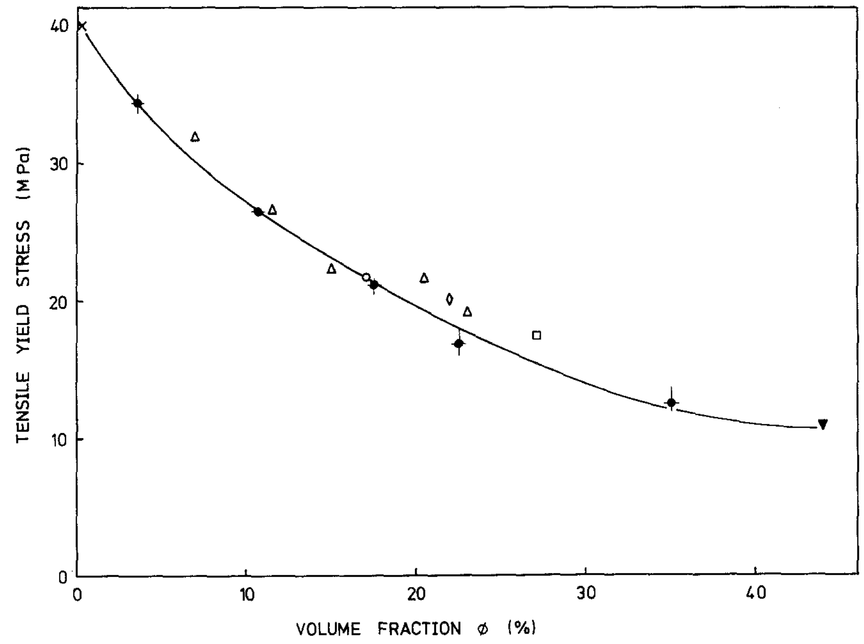

Figure 4 Tensile yield stress plotted against the effective rubber volume fraction. For key see caption for Fig. 2.

Yield stress data from the plane strain compression test are presented in Fig. 5. In these results, there is a clear separation between the large-particle HIPS materials and those having particle sizes substantially below 1 μm. At a given volume fraction, the smaller particles give a lower compressive yield stress. As in the case of modulus, the difference is unlikely to be due to particle size effects. A more satisfactory explanation is again to be found in the higher ratio of rubber to polystyrene, and therefore the lower shear moduli, of the small particles. The effects of particle size (and therefore composition) upon yield behaviour are further emphasized in Fig. 6, by plotting tensile yield stress against compressive yield stress, a procedure which eliminates any problems arising from errors in the determination of ϕ.

The mechanisms of yielding in HIPS are distinctly different in compression from those operating in tension. Under tensile loading, yielding occurs almost exclusively by multiple crazing. However, crazes cannot form under compression and the polystyrene therefore yields by forming shear bands. The stresses required for shear yielding are significantly higher than those responsible for crazing in PS and HIPS, as can be seen by comparing Figs 4 and 5. Rubber particles (a) lower the yield stress by initiating crazing or shear yielding in the surrounding PS matrix, and (b) subsequently, cooperate in the deformation of the yielded polymer. The present work indicates that these responses are relatively unaffected by the composition, internal morphology or diameter of the rubber particles when the HIPS is yielding at moderate strain rates by multiple crazing in tension, but *are* influenced by the proportion of polybutadiene in the composite particle when the polymer is yielding by shear band formation in compression.

A rubber particle can accommodate the large local tensile strains generated by crazing in the PS matrix in four possible ways: (a) by debonding from the matrix; (b) by internal cavitation; (c) by fibrillation of the rubber phase; and (d) by crazing within the sub-inclusions. The first three types of response have been reported by a number of authors [10, 11, 20, 21]. Variations between 50 and 90% in the concentration of rigid PS sub-inclusions appear to have relatively little effect upon the ability of the rubber particle to respond by mechanism (c), which is the principal mechanism operating in a well-made HIPS having

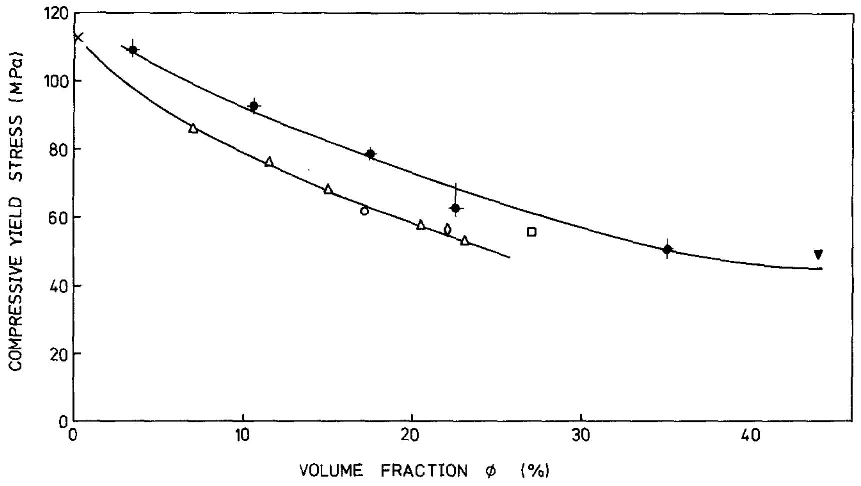

Figure 5 Compressive yield stress plotted against the effective rubber volume fraction. For key see caption for Fig. 2.

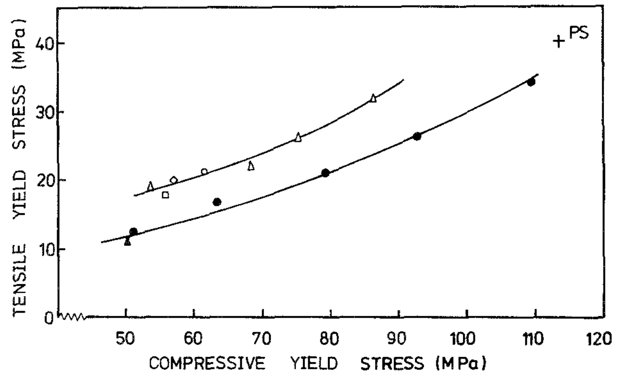

Figure 6 Tensile yield stress against compressive yield stress. (●) $\bar{d} \leqslant 0.4\,\mu\text{m}$, (○) $\bar{d} \geqslant 1.6\,\mu\text{m}$. For key see caption for Fig. 2.

good particle–matrix adhesion. However, fibrillation within the rubber particles depends upon the presence of at least some sub-inclusions: a crosslinked solid rubber particle tends to generate a single large void without fibrillation, either by forming an internal cavity, or by debonding from the matrix around the equatorial region of the particle [10]. This type of debonding, which allows the rubber particle to continue to function as a load-bearing component of the structure, must be distinguished from debonding at one of the "poles" of the particle, which is due to inadequate interfacial adhesion, and results in unloading of the particle.

The requirements placed upon the rubber particle are quite different in compressive yielding. As the PS matrix reaches large shear strains within the shear bands, the composite rubber particles are forced to deform with it. The resistance of the composite rubber particles to deformation at these high strains will obviously increase with the concentration of polystyrene sub-inclusions. This effect appears to offer the best explanation for the observed differences in compressive yield stress between the different types of HIPS studied.

3.4. Impact behaviour

The results of notched Charpy impact tests over a range of temperatures are plotted in Fig. 7 for four of the HIPS materials studied. Three of the curves refer to HIPS 35 MI and its blends with PS, and are discussed in a previous paper [14]. The fourth curve, based upon data for HIPS 17 SCS, falls well below the curve for HIPS 17.5 MI, a material that has an almost identical volume fraction of rubber particles, but exactly half the polybutadiene content. These results clearly show that factors other than ϕ affect the impact strength of HIPS, although volume fraction of rubber particles is obviously important. On the basis of this comparison, the larger particles are much more effective as toughening agents. Since modulus and yield stress correlate quite well with ϕ, it must be concluded that impact strength is more sensitive than the other properties to variations in particle size. The reasons for this increased sensitivity are now being investigated. One possibility is that the high strain rates operating during impact bring out differences in the kinetics of crazing that are not apparent in yield measurements at low rates of strain. Another possibility is that crack initiation or growth is affected by particle size. At present, there is insufficient evidence to distinguish between these alternative mechanisms.

4. Conclusions

The following conclusions can be drawn from this study:

1. The series of six HIPS polymers chosen for the programme shows a wide variation not only in particle size but also in volume fraction of composite rubber particles, ϕ, although they all have the same polybutadiene content.
2. Both tensile modulus and tensile yield stress depend principally upon ϕ.
3. At a given value of ϕ, the HIPS polymers containing smaller rubber particles have lower moduli

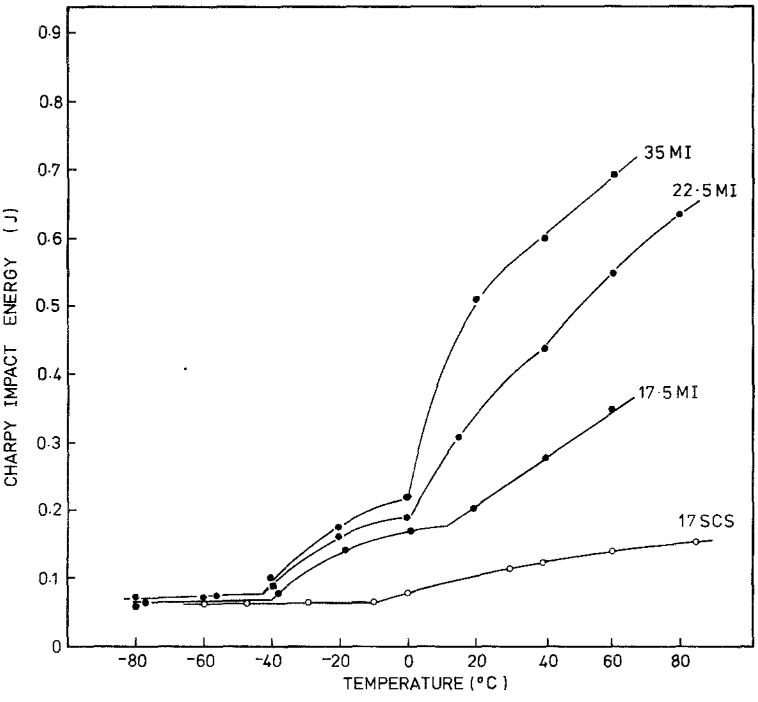

Figure 7 Dependence of Charpy impact energy upon temperature.

than those containing larger particles (over 1 μm in diameter). The difference appears to be due to the reduced fraction of PS sub-inclusions in the smaller particles.

4. Yield stresses in plane strain compression also show consistent trends with ϕ. At any given value of ϕ, smaller particles are associated with lower yield stresses. This effect can also be attributed to the smaller fraction of PS sub-inclusions and the resulting lowering of resistance to large-strain deformation in a propagating shear band.

5. There is little evidence that either particle size or internal morphology affect the tensile yield stress of HIPS.

6. The notched Charpy impact strength of HIPS is not determined solely by ϕ. After allowing for the reductions in ϕ that accompany a reduction in particle size, there is still a particle size effect: at any given ϕ, rubber particles substantially below 1 μm in diameter are less effective in toughening HIPS than particles over 1 μm in diameter. The reasons for this particle size effect remain to be established.

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