JOURNAL OF MATERIALS SCIENCE 21 (1986) 301–306

Rubber toughening of plastics

Part 9 *Effects of rubber particle volume fraction on deformation and fracture in HIPS*

CLIVE B. BUCKNALL, FRÉDÉRIC F. P. CÔTE, IVANA K. PARTRIDGE
School of Industrial Science, Cranfield Institute of Technology, Cranfield, Bedford MK43 0AL, UK

Electron microscopy of a high-impact polystyrene (HIPS) polymer, containing 8.5 wt% polybutadiene, shows that the volume fraction, ϕ, of composite rubber particles is 35%. The rubber particle size distribution has a median diameter of 1.6 μm. By making a series of blends between this HIPS and polystyrene, it is shown that Young's modulus decreases linearly with ϕ. Dilution with polystyrene results in a sharp drop in notched Charpy impact strength. The relevance of these data to the interpretation of structure–property relationships for a wide range of HIPS morphologies is discussed.

1. Introduction

Developments in polymerization technology and in the use of butadiene–styrene block copolymers have in recent years led to an expansion in the range of commercial HIPS polymers. Electron microscopy shows that the novel materials differ in several ways from the more traditional HIPS grades. The two most obvious differences are smaller particle size and a distinctive morphology within the rubber particle. Whereas the rubber particles in established HIPS grades have a "salami" structure, with numerous polystyrene subinclusions embedded in a continuous rubber phase, the newer types of rubber particles formed from block copolymers have either a "core–shell" or an "onion" structure. In a core–shell particle, a thin spherical shell of rubber encloses a single polystyrene inclusion; in the "onion" structure, there are several concentric spheres of rubber and polystyrene [1, 2]. The aim of the present investigation is to understand the effects of these changes in particle size and morphology upon mechanical properties.

Changes of this type inevitably affect the distribution of polystyrene between the matrix and the rubber particles. By altering the load-bearing capacity of the matrix, the redistribution results in significant changes in modulus, strength and toughness. In order to study this aspect of structure, it is convenient to use transmission electron microscopy to measure the volume fraction, ϕ, of the composite rubber particles, including all material enclosed within the outer layer of polybutadiene in each particle, but *not* including any polystyrene chains grafted to the rubber and lying outside that boundary. For the purpose of this paper, external polystyrene chains are counted as part of the matrix. In this respect, there is a difference between ϕ and the gel content measured by centrifuging a solution of HIPS in a suitable solvent. The distinction becomes important as the particle size becomes smaller, and the contribution of externally grafted polystyrene chains to the total gel content becomes significant. A typical thickness for the outer polystyrene layer is about 20 nm [3], which means that for a rubber particle diameter of 160 nm (measured to the boundary of the polybutadiene), the gel content would be twice the volume fraction of the composite particles, ϕ.

Later papers in this series will show that ϕ varies by more than a factor of 2 with morphology at constant polybutadiene content. In order to lay a basis for the wider investigation, the present paper defines the volume fraction and size distribution of rubber particles in a conventional HIPS, and correlates mechanical properties with ϕ in a series of blends made by diluting the same HIPS with polystyrene.

2. Experimental details

2.1. Materials

The parent material for the series of HIPS polymers presented here contains 8.5 wt% polybutadiene chains and 2 wt% plasticizer. The weight average molecular weight, M_w, of the polystyrene matrix, obtained after centrifuging solutions in toluene to remove the rubber particles as a gel fraction, is 196 000. Electron microscopy, which is discussed more fully later, shows that the polymer contains 35 vol% composite rubber particles.

In order to make comparisons between materials containing different volume fractions of rubber particles, but with the same rubber particle size and size distribution, the parent HIPS polymer was blended with polystyrene ($M_w = 232\,000$) at ratios resulting in particle volume fractions of 22.5, 17.5, 10.5 and 3.5%. The HIPS and PS granules were premixed in a high-speed mixer and melt-blended in a Werner-Pfleiderer ZSK 30M9 co-rotating twin-screw compounding extruder operating at 100 r.p.m. with barrel temperatures set at 180 to 200° C.

All HIPS materials were compression moulded at 200° C into 3 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 standardize the thermal history of the sheets. Specimens for tensile creep and for dynamic

0022–2461/86 $03.00 + .12

mechanical measurements were prepared by milling from the 3 mm thick sheets; Charpy impact specimens were made from the 6 mm thick sheet.

2.2. Microscopy and testing

Transmission electron micrographs of the parent HIPS polymer were prepared using the Kato osmium staining technique. Prints measuring 190 mm × 240 mm were made at a magnification of 10 000. The volume fraction of composite particles was determined by ruling a series of parallel lines at intervals of 10 mm on each print and summing intercepts. The particle size distribution was obtained from direct measurements on the same micrographs. The ultramicrotome blade causes compression along the direction of travel but does not alter dimensions parallel to the knife edge, so that the particles appear elliptical in the micrographs. Particle diameters are therefore determined from the long axes of the ellipses.

Transmission electron micrographs of several of the blended HIPS materials were also prepared in order to check the volume fractions and particle sizes. There was no indication of particle breakdown resulting from the compounding process and the measured values of volume fraction were in agreement with the calculated values. The error in the volume fraction ϕ is typically ± 0.5 vol %.

Dynamic mechanical measurements were carried out between -100 and -20° C, using Polymer Laboratories (Loughborough, UK) DMTA equipment in the bending mode, at a frequency of 1 Hz and a heating rate of $4^\circ \text{C min}^{-1}$. Sample dimensions were 1 mm × 10 mm × 25 mm and the distance between supports was 12 mm.

Notched Charpy impact energy was measured using a Hounsfield impact tester with a 40 mm span. The bar dimensions were 50 mm × 12 mm × 6 mm. A 3 mm deep notch was machined across the narrow face of the bar, with a notch tip radius of 0.25 mm.

Values of Young's modulus were obtained at 20° C and 60% r.h. from 100 sec isochronous low-strain tensile creep measurements, using a method described fully in previous papers of this series [4, 5].

3. Results

A representative electron micrograph of the original HIPS polymer is shown in Fig. 1. The rubber particles have a cellular or "salami" structure, with many polystyrene subinclusions dispersed throughout the polybutadiene phase.

Determination of the volume fraction of composite particles from this type of micrograph presents few problems provided that the section thickness is small compared with the minimum particle diameter. The composition of a section is representative of the material as a whole, and can be measured either by summing areas of individual particles, or by drawing lines on the micrograph and determining the fraction of each line that lies within rubber particle boundaries: the composition of the one-dimensional sample traced by a line is also representative of the whole material. Sampling errors are of course reduced by taking a number of sections from different locations. The sections used in this work had a silver/grey interference colour, indicating a thickness of about 50 nm. The value of the volume fraction of the parent material determined by this method is 36.5%. Owing to the finite thickness of the sections, this value is an overestimate of the true volume fraction, ϕ. An adequate correction is provided by the expression [6]

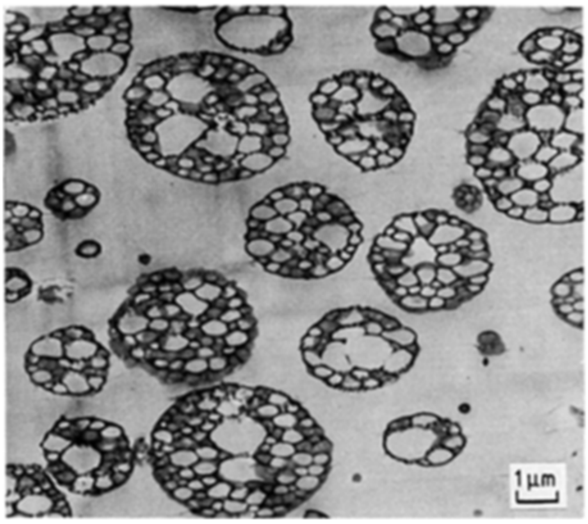

Figure 1 Transmission electron micrograph of the parent HIPS polymer. Osmium stained section. (By courtesy of Dow Chemical Co.)

$$\phi = \phi_{\text{app}}[2\bar{d}/(2\bar{d} + 3t)] \tag{1}$$

where ϕ_{app} is the apparent volume fraction, $\bar{d}$ the average particle diameter and t the thickness of section. This expression is valid for thin sections where no particle overlap can occur [6]. The corrected value for the volume fraction, ϕ, of rubber particles in the parent polymer is 35%.

By contrast, particle size determinations do present a problem, since the observed diameter, r, of any given particle is in general smaller than its true diameter, R. If R_{m} is the maximum true diameter, the real size distribution $h(R)$ is related to the observed size distribution $g(r)$ by the equation [7]

$$\frac{h(R)}{R} = \frac{-2}{\pi}\frac{\mathrm{d}}{\mathrm{d}R}\int_R^{R_{\text{m}}} \frac{g(r)\,\mathrm{d}r}{(R^2 - r^2)^{1/2}} \tag{2}$$

A full analysis of $h(R)$ based on this equation has not been attempted in the present study.

The cumulative probability plotted in Fig. 2 represents the fraction of particles that have observed diameters less than $2r$ and is defined by

$$\text{cumulative probability } (r) = \frac{\sum_{r=0}^{r} N(r)}{\sum_{r=0}^{\infty} N(r)} \tag{3}$$

where $N(r)$ is the number of particles of radius r. A plot of cumulative probability against $\log r$ would give a straight line for a material with a log-normal distribution of particles sizes as reported by Willersin [8]; however, checks show that the HIPS polymer studied here does not exhibit a log-normal distribution. The median particle diameter determined from Fig. 2 is

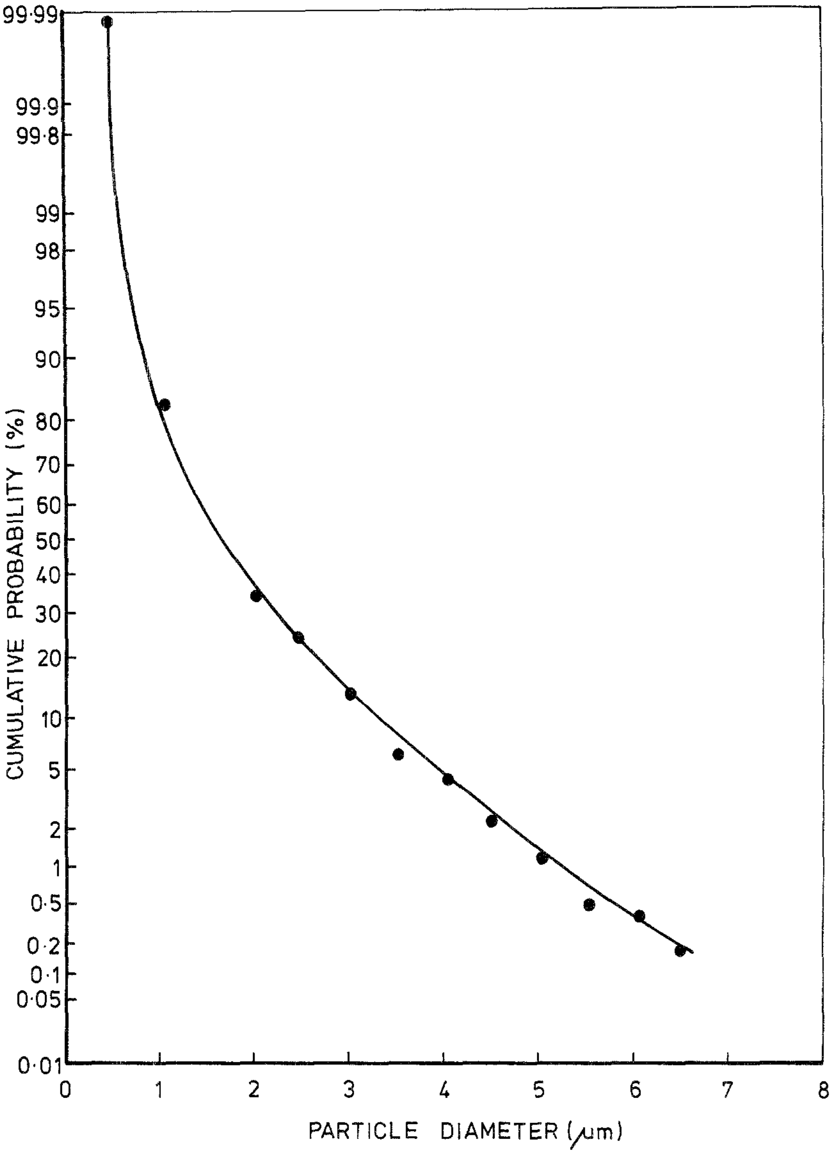

Figure 2 Gaussian plot of cumulative probability as a function of particle diameter of the parent HIPS polymer.

1.6 μm. This type of plot gives equal weighting to both the very small and the very large rubber particles present in the material. However, the larger particles make a much larger contribution than the smaller particles to the total effective rubber volume fraction, and it could be argued that cumulative probability plots expressed on a volume basis provide a better basis for correlating materials structure with mechanical properties. It is difficult to obtain reliable data for such a plot from transmission electron micrographs, as this would require the exact evaluation of the integral in Equation 2 and the conversion of the real linear size distribution $h(R)$ into a volume distribution, with the inevitable escalation in the relative error of the determination.

In assessing electron micrographs visually, there is a tendency to estimate proportions on a volume basis, and this is why the value of 1.6 μm might appear rather low for the morphology typified by Fig. 1.

Isochronous curves of 100 sec Young's modulus against 100 sec strain for the parent HIPS polymer, and a blend containing 22.5% volume fraction of the same composite rubber particles, are shown in Fig. 3. As expected, the modulus is higher for the material containing less rubber. As the strain increases, the moduli of HIPS materials fall, firstly because of non-linear viscoelastic behaviour, which occurs in all polymers, and secondly because of the onset of multiple crazing, which becomes more rapid as the strain increases beyond 1%. The modulus at very low strains is a linear function of the volume fraction, ϕ, as shown in Fig. 4. Each modulus value is an average of three to eight determinations, accurate to ± 0.02 GPa.

The rubber particle volume fraction also affects the dynamic loss of the material [9]. In Fig. 5, the area under the tan δ peak correlates with the rubber volume fraction in a non-linear relationship. The fact that the peak temperature is the same, within experimental error, for the blended materials as for the parent HIPS polymer confirms that the compounding process does not alter the nature of the rubber phase.

At temperatures below the glass transition of the rubber, the values of the dynamic storage modulus, E', of the materials converge as shown in Fig. 6. Similarly, below $-40°$ C, the impact resistance of the HIPS polymer is unaffected by the amount of rubber present, as illustrated in Fig. 7. The fracture surfaces at these low temperatures are smooth, and show no signs of whitening. This is because the polybutadiene is below its glass transition temperature under the conditions of test, and consequently the rubber is ineffective as a toughening agent. Above $-40°$ C, the

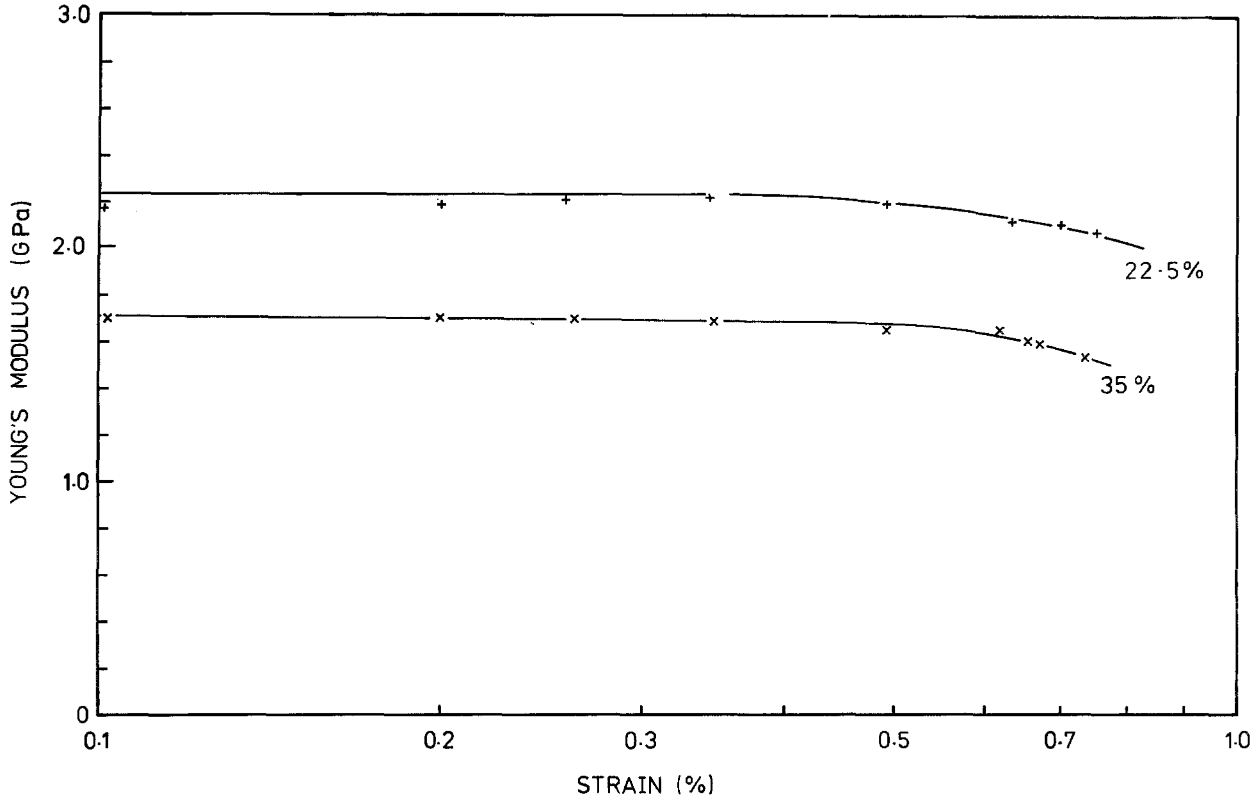

Figure 3 Isochronous curves of 100 sec Young's modulus against 100 sec tensile strain.

impact specimens show whitening at the notch tip, which spreads further with increasing temperature, until at 0° C the fracture surfaces of the materials containing a rubber volume fraction of 17.5% and above become uniformly whitened. The depth of the whitened zone is greater in the HIPS materials that have higher rubber volume fractions, reflecting the superior impact resistance of the materials. The fracture surfaces of the HIPS materials containing less than 11% volume fraction of rubber particles have a rough, speckled appearance. Observations in the scanning electron microscope suggest that the crack propagates discontinuously, on several different planes. Whitening at the back edges of the specimen is observed at 85° C.

The changes in fracture surface appearance correspond to the transitions depicted in Fig. 7. The first transition in properties is associated with the glass transition in the elastomeric region of the composite rubber particles; the second transition can also be regarded as associated with the T_g of the rubber particles, but now shifted to about 0° C in accordance with the time–temperature superposition principle as the propagating crack speeds up and the time scale of the required response is reduced [10].

4. Discussion

This study has defined the volume fraction, ϕ, and size distribution of composite rubber particles in a typical commercial HIPS, and in a series of its blends with

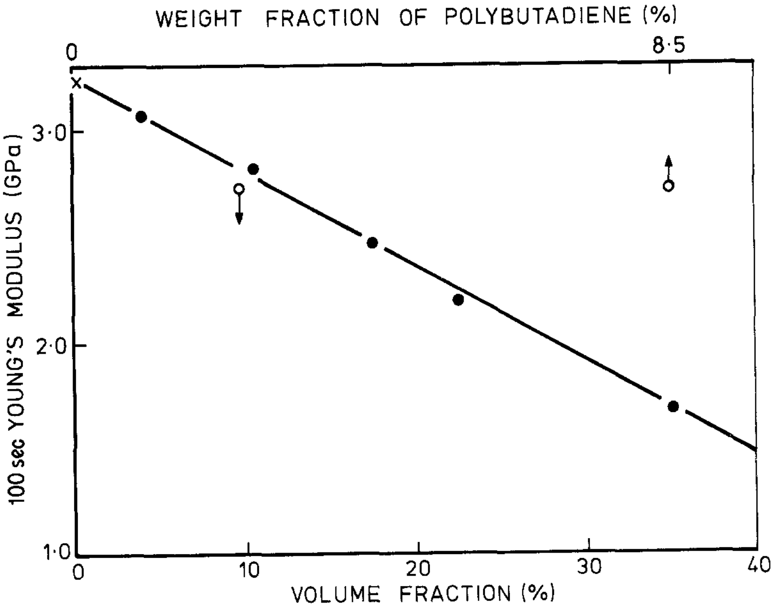

Figure 4 100 sec Young's modulus against volume fraction of rubber particles and against weight fraction of polybutadiene. ×, unmodified PS, ○, blend of PS and polybutadiene; ●, HIPS containing composite particles.

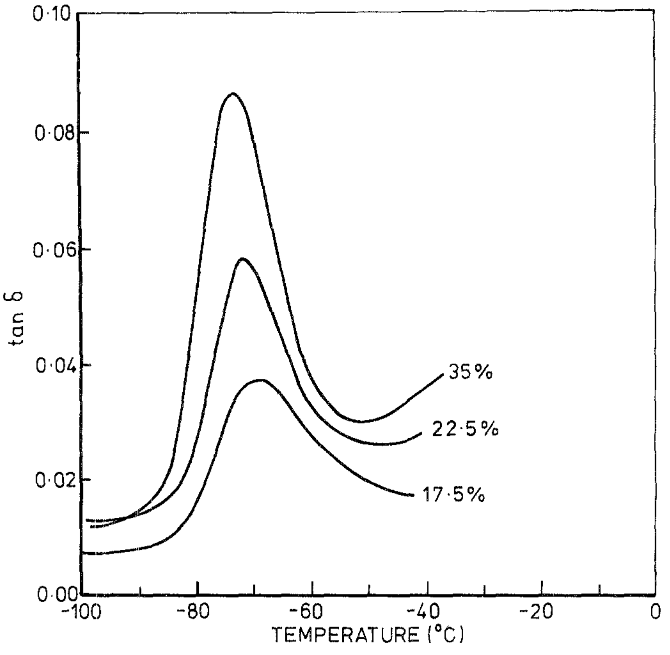

Figure 5 Plot of tan δ against temperature for the parent HIPS and two blends with polystyrene.

polystyrene. As reported by previous authors [10], a relatively small amount of polybutadiene produces a much larger amount of composite particles: in the present series of HIPS materials the ratio of polybutadiene to polystyrene in the particles is 23:77.

The enhanced volume fraction, ϕ, produced by these subinclusions causes a substantial drop in the Young's modulus of HIPS, as shown in Fig. 4. The relationship is linear. For comparison, the same diagram includes a value for the modulus of a melt blend of polystyrene with 8.5 wt % polybutadiene. In this blend there are no subinclusions: after allowing for the difference in density between the components, ϕ is 9.8%. It is clear that the factor controlling modulus is the volume fraction of particles and not the volume or weight fraction of polybutadiene.

The main purpose of this paper is to provide a set of data on the structure and mechanical properties of a standard HIPS material, which can be used as a basis for comparison with novel materials of different structure. Before reaching any conclusions about the effects of particle size, or internal morphology, it is necessary to ask whether the change in polymerization route has also affected ϕ, which may be regarded as a fundamental structural parameter. Later papers in this series will explore further the quantitative relationship between ϕ and deformation kinetics [11], and will distinguish between those changes in mechanical properties that derive from a change in ϕ, and those that are also dependent upon other factors. Previous work has shown that the mechanical properties of HIPS are controlled by the response of the polystyrene matrix to applied stress [10], and the volume fraction $(1 - \phi)$ of the matrix is clearly important. As discussed in Section 1, identification of ϕ with the gel content can lead to serious errors in interpretation, especially when the particle size is small.

Particle volume fraction, particle size distribution, and glass transition of the rubber phase, are all important factors to be considered when discussing impact properties. In addition to defining the effects of ϕ, the present work has shown how impact energy varies with temperature in a series of HIPS blends in which the glass transition temperature of the rubber has been held constant. This information is essential in distinguishing the effects of particle size and internal

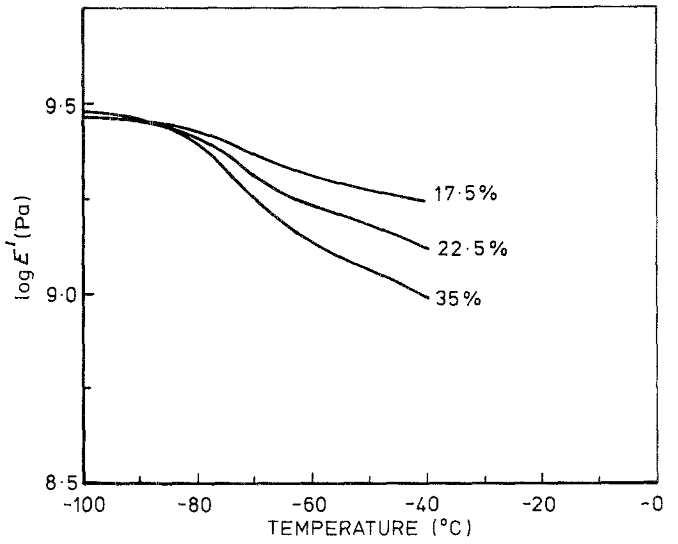

Figure 6 Plot of log E' against temperature for the parent HIPS and two blends with polystyrene.

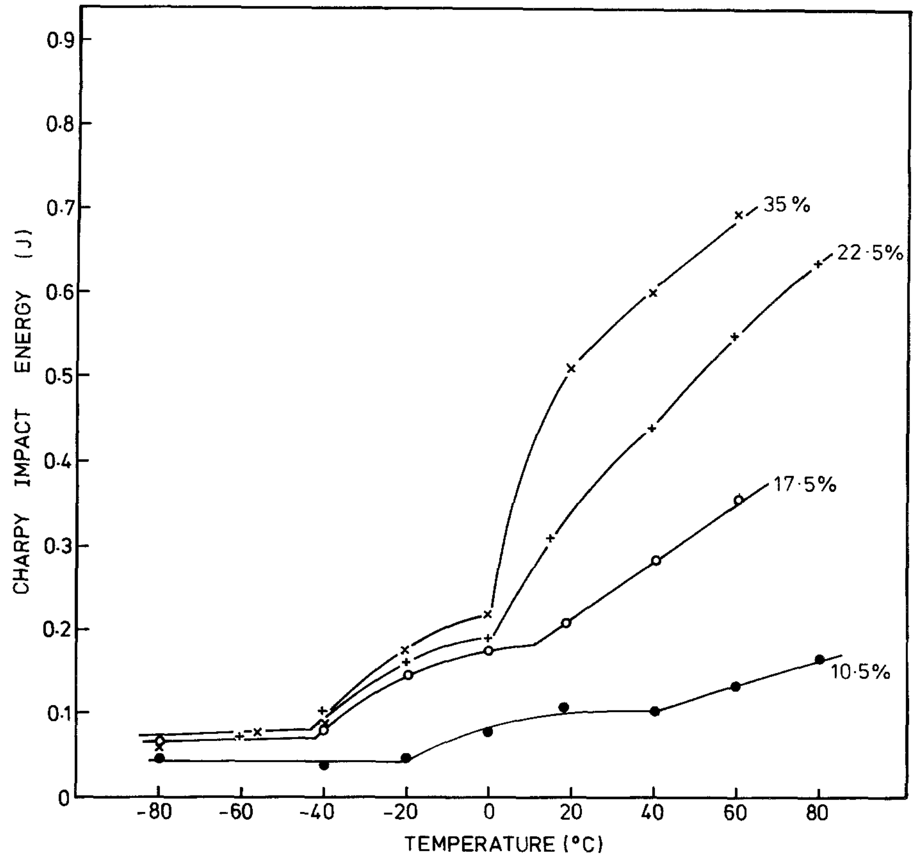

Figure 7 Plot of notched Charpy impact energy against temperature for the parent HIPS and three blends with polystyrene.

morphology from those due to variations in ϕ and T_g (rubber). Such incidental variations resulting from the polymerization route are often overlooked.

Acknowledgements

The authors thank the Science and Engineering Research Council for a grant in support of this work, Polymer Laboratories Ltd for assistance with the dynamic mechanical measurements and Dow Chemical Co, for the gift of materials.

References

1. G. RIESS, M. SCHLIENGER and S. MARTIN, *J. Macromol. Sci. (Phys.)* **B17** (1980) 355.
2. A. ECHTE, *Angew. Makromol. Chem* **58/59** (1977) 175.
3. H. KESKKULA and S. G. TURLEY, *Polym. Lett.* **7** (1969) 697.
4. C. B. BUCKNALL, D. CLAYTON and W. E. KEAST, *J. Mater. Sci.* **8** (1973) 514.
5. C. B. BUCKNALL and I. C. DRINKWATER, *ibid.* **8** (1973) 1800.
6. E. E. UNDERWOOD, "Quantitative Stereology" (Addison-Wesley, Reading, Massachusetts, 1970) p.103.
7. L. HOLLIDAY, "Composite Materials" (Elsevier, Amsterdam, 1966) p. 21.
8. H. WILLERSIN, *Macromol. Chem.* **101** (1967) 296.
9. S. G. TURLEY and H. KESKKULA, *Polymer* **21** (1980) 466.
10. C. B. BUCKNALL, "Toughened Plastics" (Applied Science, London, 1977) p. 290.
11. C. B. BUCKNALL, P. DAVIES and I. K. PARTRIDGE, *J. Mater. Sci.* **21** (1986) 307.

Received 14 February
and accepted 13 March 1985