Effect of rubber-phase volume fraction in impact polystyrene on mechanical behaviour

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The nature and the amount of the rubber-reinforcing phase in impact polystyrene is of critical importance for a good balance of physical properties. It is difficult to change the rubber phase uniquely because of many interdependent variables in the synthesis of impact polystyrene. However, an attempt has been made to prepare rubber-modified polystyrenes with only the rubber-phase volume fraction (*RPVF*) as a variable. It was found that notched Izod impact strength increased linearly with *RPVF*, while tensile yield strength was inversely proportional (over the range covered). The area under the rubber damping peak in torsion pendulum measurements was also proportional to impact strength.

INTRODUCTION

Impact polystyrene is a two-phase material consisting of dispersed rubber particles in a continuous matrix of polystyrene. The rubber is used as a reinforcing agent to provide the impact strength that is lacking in polystyrene. The resulting impact strength is dependent upon the composition and concentration of rubber, rubber particle size and morphology, rubber-phase volume, and the levels of crosslinking and grafting, as well as on the molecular weight and molecular weight distribution of the polystyrene phase. Each one of the preceding parameters has been the subject of one or more papers published in the literature[1]. However, since each of the parameters listed above is not necessarily independent of all the others, it has not always been possible to determine whether the effects observed are due only to the parameter pertinent to the discussion.

In this paper, the rubber-phase volume fraction will be discussed. Some previous work in this area was carried out by Wagner and Robeson[2]. They polymerized 6–7% polybutadiene solution in styrene at different rates of agitation. A decreased phase volume was observed with increased agitation presumed to be caused by rupture of the rubber membranes during agitation. The best impact was achieved at 22% phase volume (6% rubber). Also, a large change in T_g of the rubber phase was observed when the rubber-phase volume was changed from 6 to 48% (−110° to −18°C). In the patent literature[3], data have been shown to indicate that with increased rate of agitation during the prepolymerization period, smaller particles are indeed obtained, giving rise to a product with reduced impact strength. With a limited period (1 h) of high rate agitation, however, a product with small particles results, but with no reduced toughness. In a recent paper, Silberberg and Han[4] also reported the effect of different agitation rates on impact and tensile strengths of impact polystyrene. Only with the highest rate of agitation were particles of less than 5 μm diameter obtained in the final polymer along with significantly reduced impact strength and slightly affected tensile strength (with SBR rubber). Based on these reports, the effect of rubber particle morphology on mechanical behaviour in impact polystyrene does not seem to be particularly clear.

In this study of the effect of rubber-phase volume fraction, an attempt was made to keep all polymerization variables as constant as possible, by only exposing the prepolymer to several brief high shear periods. The finished polymers were examined in some detail.

EXPERIMENTAL

The components of the following recipe were polymerized in a batch process: 7% Diene HD55 rubber, 1% mineral oil, 0.5% α-methylstyrene dimer, and the remainder styrene. The polymerization was carried out at 120°C through the phase inversion point to 28% solids with an agitation rate of 60 rpm. A portion of this prepolymer was removed for further polymerization in a quiescent state using the temperature profile of 2 h at 120°C, 2 h at 140°C and 40 min at 180°C. Agitation of the remainder of the master batch was then increased to 300 rpm for a period of 10 min, after which a second portion was removed for further polymerization using the same temperature profile. The agitation rate of the master batch was then increased to 600 rpm for another 10 min period. A third sample was then taken from the master batch, and further polymerization was carried out in a manner identical to the first two samples. The same finishing conditions (30 min at 220°C and 15 mmHg) were employed for each of the three samples.

Compression moulded specimens were prepared for the determination of notched Izod impact strength according to ASTM D256 and tensile strength according to ASTM D638. The dynamic shear modulus, logarithmic decrement and glass transition temperature of the rubber (taken as the temperature of the rubber damping peak) were determined using a torsion pendulum previously described[5]. The area under the rubber damping peak was measured in arbitrary units using a planimeter. Percentage gel and swelling index measurements were made using toluene as solvent. Electron

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Table 1 Percent gel and swelling index

	Agitation (rpm)	Gel (%)	*SI*
Sample A	60	34.8	8.0
Sample B	300	24.1	8.4
Sample C	600	19.6	8.9

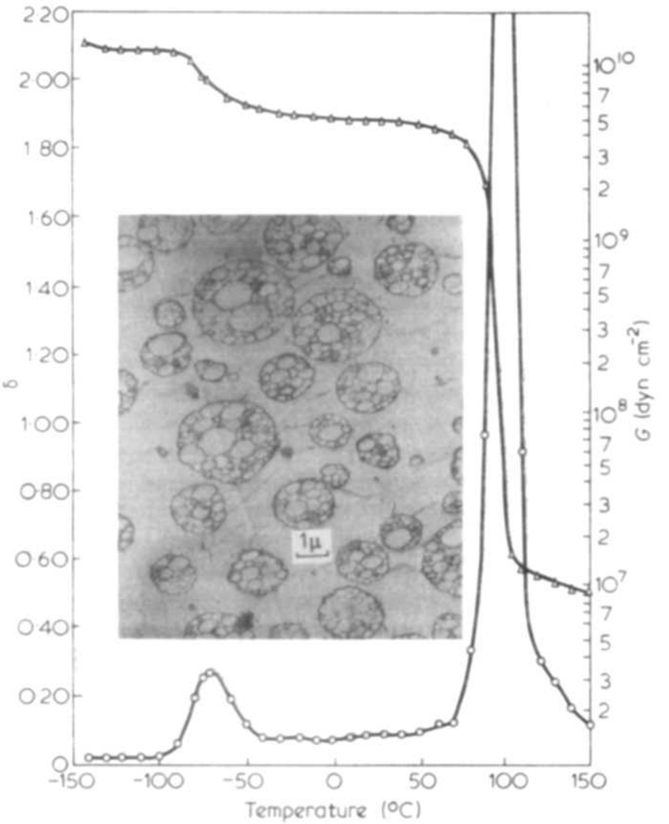

Figure 1 Dynamic shear modulus G' (Δ) and mechanical damping δ (○) for Sample A (60 rpm). Insert: Electron photomicrograph for this sample

photomicrographs were obtained from 900 Å thick sections of OsO_4-stained mouldings. The rubber-phase volume fractions (*RPVF*) were determined using a Quantimet 720 Image Analyzer.

RESULTS AND DISCUSSION

Since all three samples were made from portions of the same prepolymer master batch, the rubber contents of each sample should be the same (assuming that the same finishing step for each portion resulted in the same amount of conversion during this step). The fact that the master batch was taken to 28% solids, well past the phase inversion point, and the fact that the thermal history was nearly the same for each sample imply, with some certainty, that the molecular weight, molecular weight distribution, the grafting levels and the crosslinking levels for each sample were the same or nearly so. Some indication of similar crosslinking levels can be seen in the swelling indices (*SI*) given in *Table 1*.

The rubber-phase volume fraction, as well as the percentage gel, is shown in *Table 1* to be dependent upon the agitation level. Since the size of the rubber particles in these three samples depends on the amount of occluded polystyrene, rubber particle size is not a constant parameter. The type of morphology, that is particles with polystyrene occlusions, however, can be considered to be a constant parameter. The percentage gel, after subtracting the 7% rubber in the polymer, is a rough measure of the occluded and grafted polystyrene in the rubber particles. Since the amount of grafting can be considered to be the same in all three samples, the decrease in percentage gel can be considered to be identical to the decrease in the amount of occluded polystyrene.

The dynamic shear modulus (G') and mechanical damping were determined as functions of temperature using a freely oscillating torsion pendulum. The resulting curves are presented in *Figures 1–3*. Also included in each Figure is an electron photomicrograph depicting the size and morphology of the rubber particles in that particular polymer sample. The Figures show that as the sizes of the rubber particles decrease with decreasing amounts of occlusions (due to the higher level of agitation during the 10 min period), the drop in modulus in the vicinity of the rubber damping peak decreases and the level of the modulus curve above the rubber glass transition region increases. The damping peak height and the area under the peak also decrease with the decrease in the rubber-phase volume. The temperature of the rubber damping peak shifts to lower temperatures. These values are listed in *Table 2*, together with the rubber-phase volume fractions determined by the Quantimet 720.

The decrease in the area under the damping peak might possibly be explained by a decrease in the interfacial area between polystyrene and rubber (including that interfacial area within the occluded particle) resulting in less stress transfer from the former to the latter and, therefore, less energy dissipation. This result is similar to that found for melt-

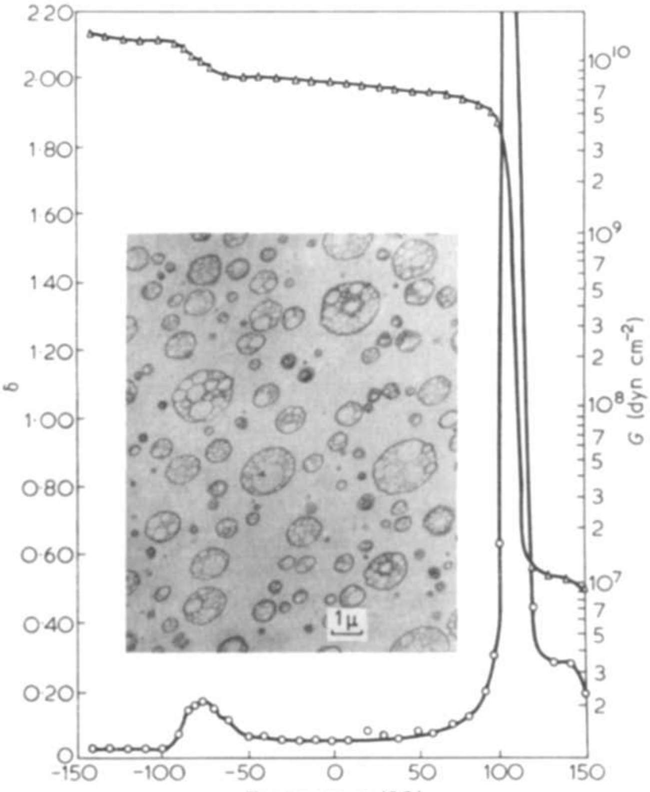

Figure 2 Dynamic shear modulus G' (Δ) and mechanical damping δ (○) for Sample B (300 rpm). Insert: Electron photomicrograph for this sample

Table 2 Dynamic properties and rubber-phase volume fractions

	Agitation (rpm)	Rubber Damping Peak Temperature (°C)	Rubber Damping Peak Area (–100° to –30°C) (arbitrary units)	G' (50°C) (dyn cm^{-2})	*RPVF*
Sample A	60	–71	1.51	4.7 x 10^9	0.442
Sample B	300	–75	0.95	7.0 x 10^9	0.303
Sample C	600	–80	0.52	8.2 x 10^9	0.221

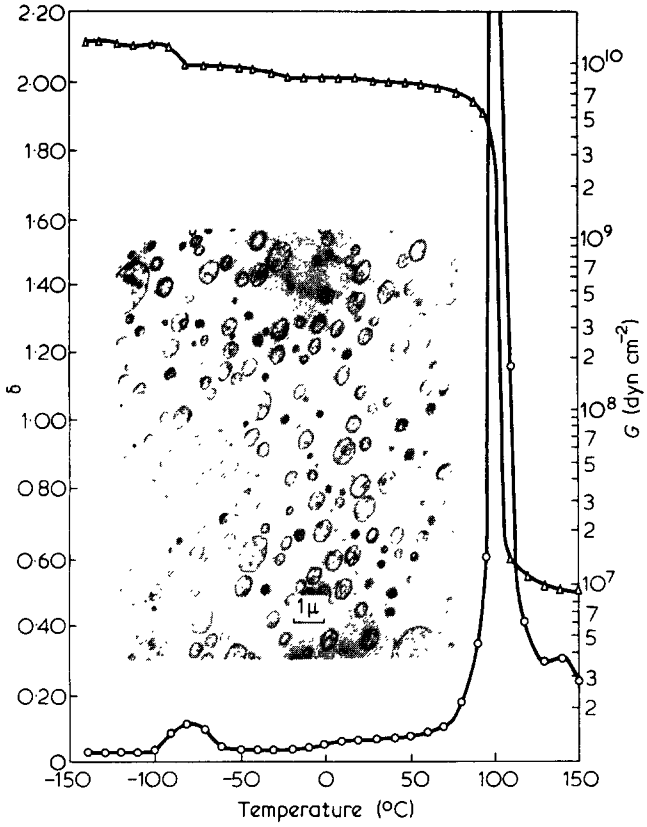

Figure 3 Dynamic shear modulus G' (Δ) and mechanical damping δ (○) for Sample C (600 rpm). Insert: Electron photomicrograph for this sample

sheared polyisoprene-modified polystyrene reported previously[6].

The modulus level above the rubber glass transition region increases with a decrease in rubber-phase volume since the volume of discontinuities in the high-modulus matrix decreases. The temperature shift could be due to the ability of the more dense rubber particles to support a more intense triaxial stress field which would lower the glass transition because of the greater free volume developed within the rubber particles[7].

The tensile strength, percentage elongation, and notched Izod impact strengths for the three samples are given in *Table 3.*

Table 3 Tensile strength, percentage elongation, and impact strength

	Tensile strength yield (p.s.i.)	Elongation (%)	Notched Izod impact (ft lb in^{-1})
Sample A	2550	12.5	1.20
Sample B	3350	0.8	0.92
Sample C	3850	0.6	0.66

As the rubber particles decrease in size due to a decrease in the amount of occluded polystyrene, the impact strength and the elongation also decrease while the tensile strength increases. The craze theory of toughening, developed for rubber-modified polystyrene[8], is based on the absorption of large amounts of energy during the initiation and propagation of crazes. Matsuo has pointed out that a smaller rubber particle is less likely to initiate a craze than a larger rubber particle[9], and Arends has pointed out that a smaller particle will initiate fewer crazes than a larger particle[10]. Bucknall[8] and Arends[10] have also stated that the dominant contribution to the elongation of a rubber-modified polystyrene test specimen is due to crazing. Therefore, it can be said that the impact strength and the elongation decrease because a smaller rubber-phase volume will not initiate as many crazes as a larger rubber-phase volume when the total rubber content is constant. The tensile strength increases due to the decrease in the volume of the softer and weaker rubber phase.

Notched Izod impact strength as well as the rubber-phase transition areas were found to increase with increasing *RPVF*. Further, tensile strength was found to be inversely proportional to the *RPVF*. A lower molecular weight polybutadiene CF-35, produced similar data in identical experiments.

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