Effect of Structure on Impact Strength of Rubber-Reinforced Polystyrene

G. CIGNA, S. MATARRESE, and G. F. BIGLIONE, *Centro Ricerche Montedison, Mantova, Italy*

Synopsis

The influence of the quantity (gel-%), the degree of crosslinking (swelling index), and the particle size (mean cord) of the elastomeric phase on Izod impact strength of rubber-reinforced polystyrene has been investigated. It has been observed that (particle size being 2–3 μ) impact strength increases almost linearly with gel content and the slope of the curves increases with decreasing degree of crosslinking. This relation proved to be no more linear for different particle sizes: small particles prove more effective than other particles in the high gel-% range and less in the low gel-% range. These results are discussed in the light of theories of rubber toughening in polystyrene and on the basis of data from Izod tests with recorded stress–time curve as well as of electron micrographs of fracture surfaces.

INTRODUCTION

In previous papers from this laboratory, the influence of structure on modulus and tensile properties of impact polystyrene has been reported. It has been shown[1] that shear modulus decreases with gel content and is practically indepotent of other structural features such as rubber particle size and grafting index. Moreover, it has been observed[2] that tensile yield strength depends on both gel content and particle size of the elastomeric phase. In the same work, a preliminary correlation between impact strength and particle size has been attempted. The aim of this paper is to investigate more completely the influence on impact strength of structural factors such as the quantity and the particle size of the dispersed elastomeric phase as well as the degree of crosslinking of the rubber particles.

EXPERIMENTAL

Materials

Several types of polybutadiene rubber-reinforced polystyrene having different structures have been prepared by mass-suspension polymerization. They were extruded as such or diluted with normal polystyrene in order to get the desired level of gel in the material

Two series of samples were obtained: one series having particle size 2.2–3.2 μ, MW about 160,000, grafting index (ratio gel-%/polybutadiene %) be-

tween 3.0 and 3.8, swelling index ranging from 9 to 17, and gel content variable in the range of 0–38% (Table I, Fig. 1); the other having MW around 180,000, swelling index about 11, grafting index between 2.2 and 3.5, particle size ranging from 1 to 4.5 μ, and gel content variable in the range of 0–43% (Table II, Fig. 2).

Another series of samples having particle size 0.9–2.5 μ, gel content variable in the range of 0–25%, and grafting index between 2.2 and 3.7 have also been taken in consideration (Table III, Fig. 3). It should be noted that these samples refer to a previous work.[2]

Structural Parameters

Determinations of structural factors such as the quantity of the gel phase (rubber + grafted and occluded polystyrene) and the particle size (mean cord) of the dispersed elastomeric phase as well as the molecular weight of the continuous matrix were carried out according to the procedures described in references 1 and 2 and shortly summarized here:

Gel determination was carried out after centrifuging a dispersion of polymer in a solvent mixture followed by washing and precipitation.

The mean cord was evaluated by the linear method of counting on micrographs in phase contrast, made on slices of 1–2 μ.

TABLE I
Results on Samples with Variable Swelling Index and Gel %
(Injection-Molded Specimens)

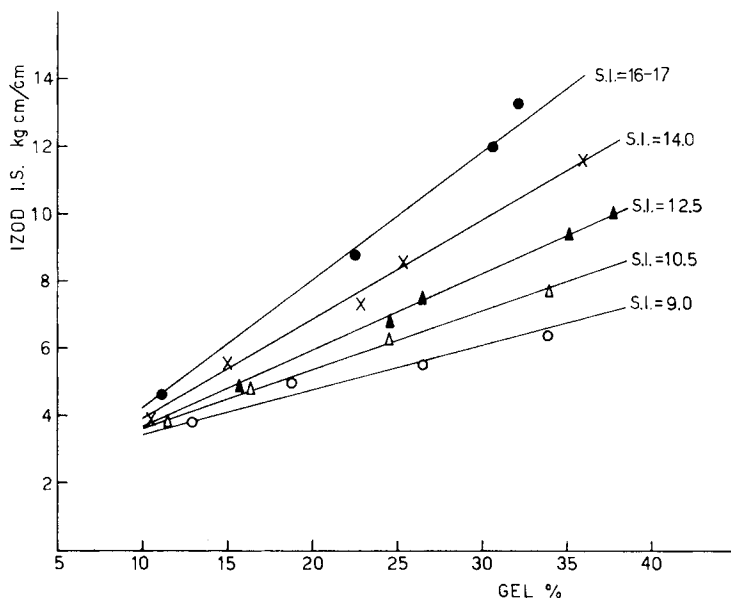| Sample no.	Gel %	Swelling Index	Tensile yield stress, kg/cm^2	Notched Izod impact strength ½″ × ½″, kg·cm/cm
A1	13.0	8.8	235	3.8
A2	18.8	9.0	220	4.5
A3	26.5	8.9	190	5.5
A4	34.0	9.0	180	6.4
B1	11.5	10.5	230	3.8
B2	16.4	10.4	220	4.8
B3	24.6	10.6	200	6.3
B4	34.0	10.5	195	7.7
C1	15.8	12.6	210	4.8
C2	24.5	12.6	200	6.8
C3	26.5	12.0	198	7.5
C4	35.1	12.6	180	9.5
C5	37.9	12.4	175	10.1
D1	10.5	13.7	220	3.9
D2	15.1	13.7	200	5.6
D3	23.0	13.8	195	7.3
D4	25.4	13.9	190	8.6
D5	36.0	13.7	190	11.6
E1	11.2	17.0	215	4.6
E2	22.5	16.5	205	8.8
E3	30.7	16.6	185	12.0
E4	32.1	16.5	180	13.3

Fig. 1. Variation of Izod impact strength with gel % at different swelling indexes.

The viscometric average molecular weight was determined in toluene following the equation

$$[\eta], \text{l./g} = 1.10 \times 10^{-5} \cdot M^{0.725}.$$

The determination of the swelling index was performed in the following way: a dispersion of polymer in toluene was at first centrifuged. Two portions of the obtained gel were put in two fritted bottom glass filters G4.

TABLE II
Results on Samples with Variable Mean Cord and Gel %
(Injection-Molded Specimens)

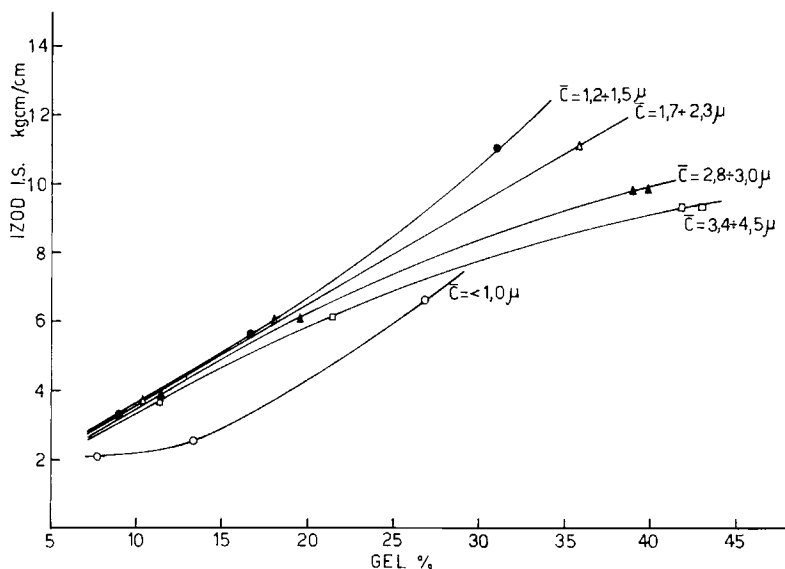| Sample no.	Gel %	Mean cord, μm	Notched Izod impact strength $\frac{1}{2}'' \times \frac{1}{2}''$, kg·cm/cm
F1	7.8	<1	2.0
F2	13.3	<1	2.5
F3	26.7	<1	7.6
G1	9.0	1.5	3.3
G2	16.6	1.4	5.6
G3	31.0	1.5	11.0
H1	10.4	1.7	3.7
H2	18.0	2.3	6.1
H3	36.0	1.7	11.1
I1	11.4	3.0	3.8
I2	19.8	2.8	6.1
I3	39.6	2.8	9.8
I4	39.0	3.0	9.8
L1	11.4	3.4	3.7
L2	21.4	4.5	6.1
L3	41.7	3.8	9.3
L4	42.8	4.5	9.3

Fig. 2. Variation of Izod impact strength with gel % at different particle sizes (mean cords μm).

Each filter was kept in a beaker (at room temperature in a closed uncharged desiccator) in such a way that the porous disks of the filters were just covered with toluene and gel could be swollen by solvent. After several hours, the swollen gel (at equilibrium) was weighed and flocculated in ethanol (taking into account the weight of the glass filter containing toluene in the pores).

The flocculated gel was dried and weighed. The swelling index was calculated by the ratio between the swollen gel and the dried gel. (For products with a high swelling index, over about 15, the described method of separating gel[1] is no longer completely effective and gives gel-% values slightly smaller than the actual dispersed-phase amount.) The higher the swelling index, the lower the degree of crosslinking.

TABLE III
Results on Samples with Variable Mean Cord and Gel %
(Compression-Molded Specimens)

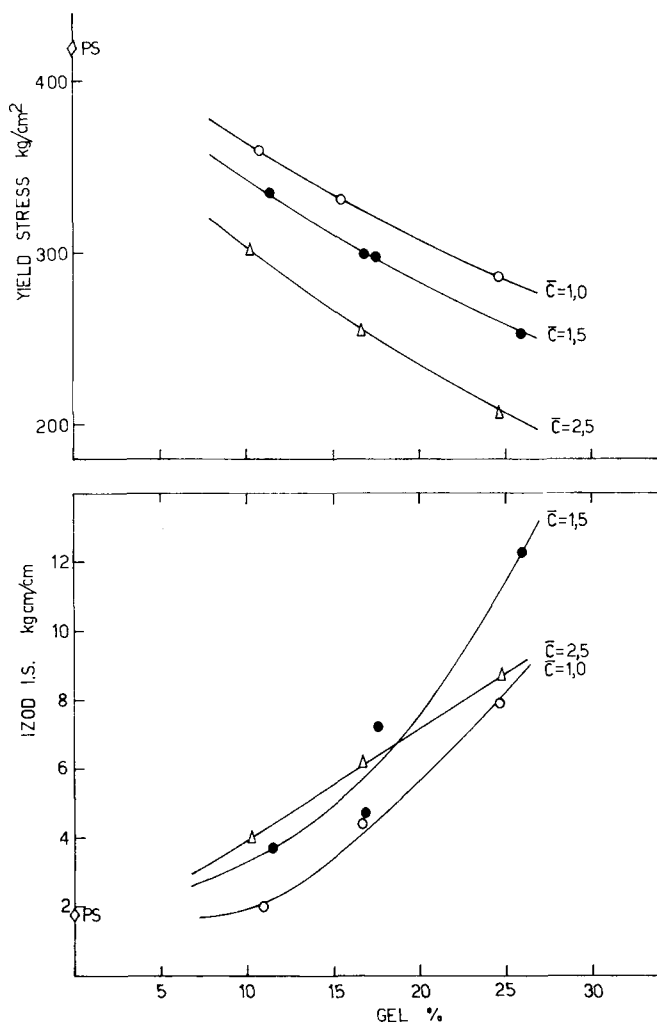| Sample no.	Gel %	Mean cord, μm	Tensile yield stress, kg/cm²	Notched Izod impact strength 1/2″ × 1/8″, kg·cm/cm
M1	11.0	0.9	367	2.0
M2	16.7	1.0	331	4.4
M3	24.7	1.0	286	7.9
N1	11.5	1.6	335	3.7
N2	16.9	1.5	299	4.7
N3	17.6	1.5	298	7.2
N4	26.0	1.5	253	12.3
O1	10.3	2.5	302	4.0
O2	16.8	2.5	255	6.2
O3	24.8	2.5	207	8.7

Fig. 3. Variation of tensile yield stress and Izod impact strength (compression-molded specimens) with gel % at different particle sizes (molecular weight 200,000).

Impact Strength

Notched Izod impact tests were carried out according to ASTM D256 on injection-molded specimens $\frac{1}{2} \times \frac{1}{2} \times 5$ in. Compression-molded specimens $\frac{1}{8} \times \frac{1}{2} \times 5$ in. were also examined.

Specimens were conditioned at $23° \pm 1°C$ for at least 48 h before testing.

In order to get more insight into the behavior of the material under stress and fracture conditions, a set of measurements of notched Izod impact strength with recorded stress–time curves were conducted on selected samples.

A proper examination of the fracture surface of broken specimens was performed under a scanning electron microscope. The micrographs were taken at corresponding points having about the same macromorphologies.

RESULTS

Figure 1 shows the change in Izod impact strength as a function of gel content for a series of samples having different swelling indexes. Izod impact strength increases almost linearly with gel content, and the slope of the lines exhibits a progressive increase with swelling index. This behavior indicates that, at a given gel content, the lower the degree of crosslinking, the higher the impact strength of the material. The relationship found refers to sample of impact polystyrene having a grafting index (gel phase %/polybutadiene %) between 3 and 3.8.

It has been reported[3] that grafting index can affect the impact strength of rubber-reinforced polystyrene in such a way that an increase in the amount of grafted and occluded polystyrene into the rubber particles up to an optimum value increases impact strength, and beyond this value impairs the deformability of the particles and depresses impact properties. Despite the probable influence of this parameter on the capacity of the material to absorb energy, it appears that in our case the small variation of grafting index does not significantly affect the impact strength values obtained for the different samples.

Figure 2 shows the variation of Izod impact strength as a function of gel content for samples having different particle size. The increase in impact strength with increasing gel content is almost linear for a mean cord particle size of 2–3 μ, but is no longer linear for particles of a different size. For small particles (1.3–2 μ), curves are obtained in which the increase in impact strength with gel content is progressively greater than for particle size 2–3 μ. The reverse occurs in the case of larger particles (3–4 μ) in which a progressively lower increase is observed. For particles smaller than 1μ, the impact strength curve proves much lower, especially at low gel content, than the one for particles 2–3 μ in size. As has been reported,[3] a variation in particle size, obtained by variation of the agitation rate during polymerization, is accompanied by a corresponding variation in the degree of grafting and rubber content of the particle, connected principally to variation in the subocclusion amount. However, this size–composition interrelation can also be changed by variation of rubber concentration and polymerization kinetics, probably realizing different thicknesses of interocclusion membranes. The ranges of grafting index of the samples of Figures 2 and 3 are 2.2–3.5 and 2.2–3.7, respectively.

DISCUSSION

In order to clarify the prominent effect of the gel content and the degree of crosslinking on impact strength of rubber-reinforced polystyrene, it is useful to consider the results of Izod impact strength with recorded stress–time curves conducted on selected samples as well as the additional information obtained from the examination of fracture surfaces under the electron microscope.

However, to establish a background for the discussion, the aspect of deformation and fracture resistance of rubber-modified thermoplastics will be briefly considered. When a load is applied to a clamped Izod specimen, the
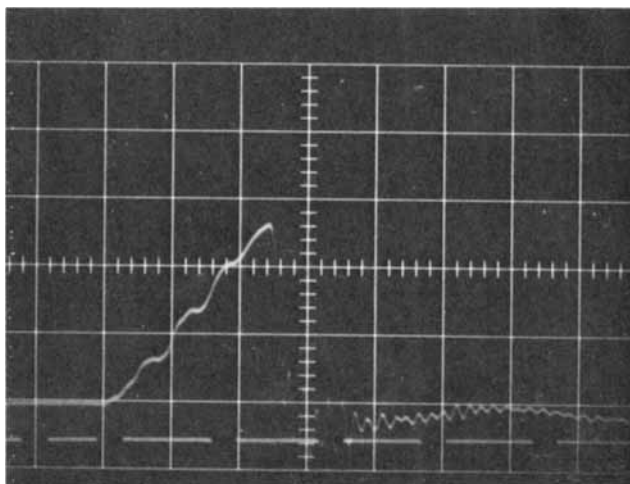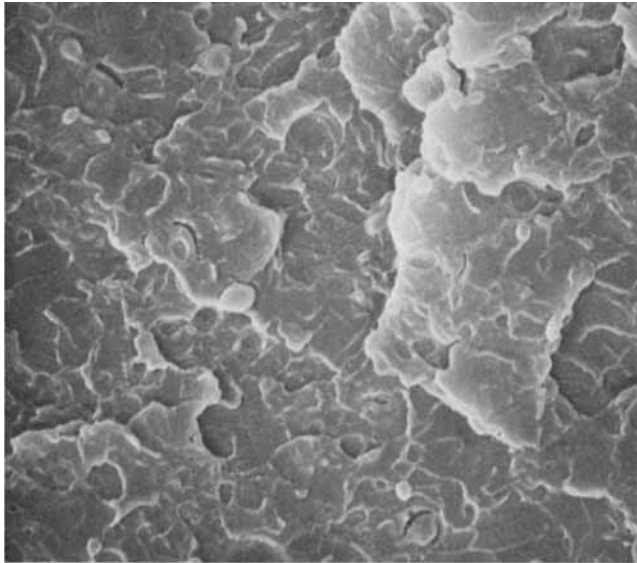
(a)
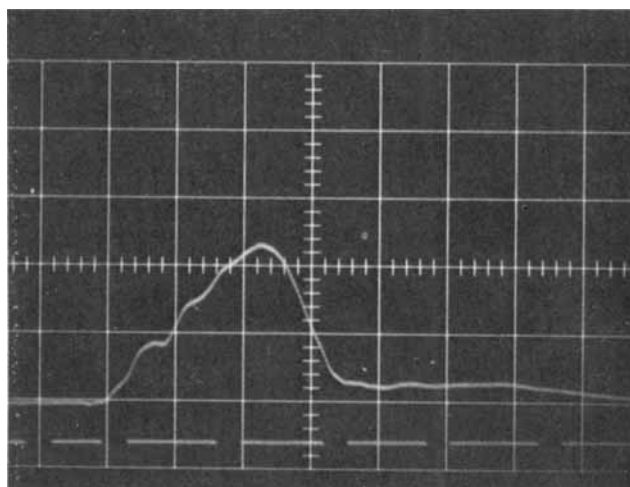
(b)

Fig. 4. Stress–time curves recorded from Izod tests for two samples with the same gel % and particle size but different swelling index: (a) sample with swelling index 10.5; (b) sample with swelling index 16.5 (x-axis, 0.15 msec/division; y-axis, 5 mV/division).

material deforms elastically and to some extent plastically[4] with stress build-up at the tip of the notch up to a critical level at which fracture develops and propagates across the specimen. The stress–time curve recorded during the impact event can then be divided in two parts: a first part in which the stress reaches a maximum with crack initiation, and a second one in which stress decreases during crack propagation. The shape of the curve depends on morphologic and structural factors of the rubber-reinforced material. Suggestions made by several authors[4–8] on the mechanism of rubber toughening in polystyrene point out that rubber particles act as stress concentrators and catalyze the formation of fine craze structures (stress whitening) in the surrounding matrix which precede crack propagation and prevent frac-

ture. Moreover, the efficiency of craze formation decreases when the stiffness of the particles rises.[5,6]

Cold drawing of matrix and craze/crack associated with abstraction of rubber particles from the adjacent matrix are other proposed mechanisms to account for energy absorption by the two-phase system.[9-11] From this it is clear that structural features of rubber particles can play a prime role in affecting the impact properties of the material.

Stress–time curves from Izod tests show that an increase in gel content of
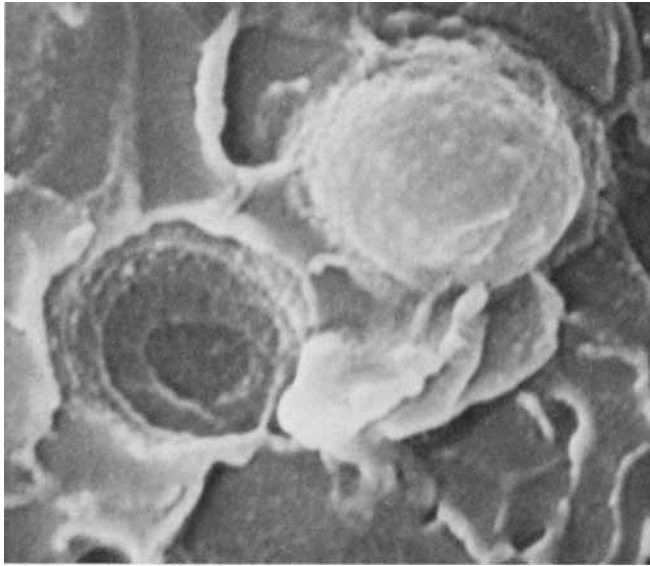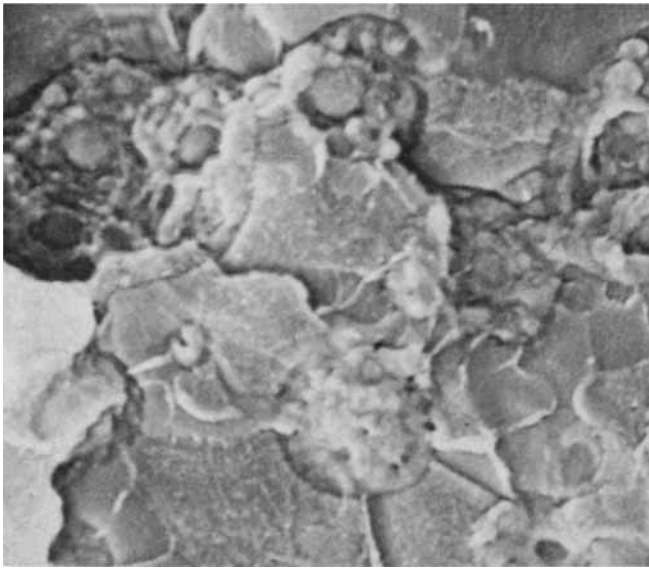

(a)
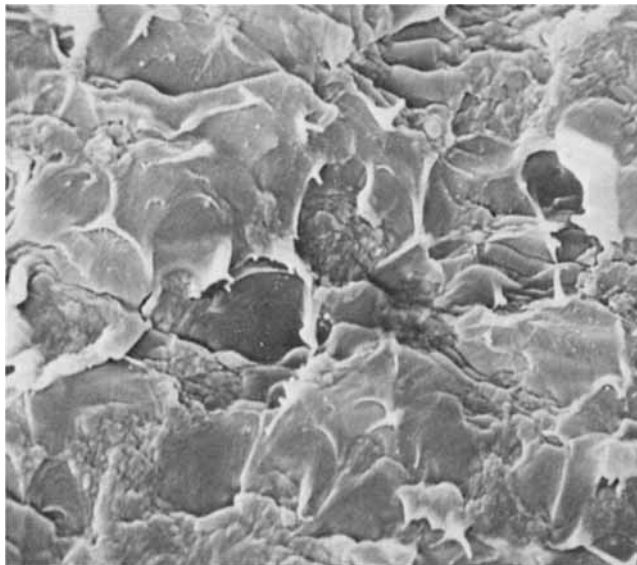
(b)

Fig. 5 (continued)

(c)

(d)

Fig. 5. Electron micrographs of two samples with the same gel % and particle size but different swelling index (S.I.) taken at points with similar macromorphology: (a) sample with S.I. 10.5 (3000×); (b) sample with S.I. 16.5 (3000×); (c) sample with S.I. 10.5 (10,000×); (d) sample with S.I. 16.5 (7500×).

the material (in the examined range) does not substantially affect the value of the peak stress but delays the time to reach it as well as the time for the decrease of stress beyond it, and this results in an increase of the area below the curve. An increase in swelling index also produces an increase of the area below the curve; however, in this case the contribution is due primarily to an

increase of the second part of the curve concerning propagation of fracture (Fig. 4). Electron micrographs (Fig. 5) illustrate that in the case of a swelling index of 16, the fracture surfaces of broken specimens are more irregular and disturbed and show a greater portion of broken particles than in the case of a swelling index of 10 in which the fracture surfaces are less disturbed and prominently show particles abstracted from the polystyrene matrix. Moreover, samples having a higher swelling index exhibit more stress whitening on the fracture surfaces.

These observations can be interpreted as follows. The increase of impact strength with increasing gel content is due to the fact that the increase of the elastomeric phase in the material improves plastic deformation before stress maximum as well as propagation resistance. The increase of impact strength with increasing swelling index is primarily due to the fact that a lower degree of crosslinking makes rubber particles more deformable and able to relax more easily in rapid forming stress field before crack initiation and during fracture propagation ahead of a traveling crack. This accounts for the formation of a more crazed matter (stress whitening) and irregular features on the fracture surface and a greater energy asorption.

However, it is worth noting that the variation of swelling index does not produce any appreciable change in the behavior of the material in tension at low loading speed. Yielding and deformation remain practically unaffected by this parameter (at least in the range of the values examined). This suggests that the degree of crosslinking of rubber particles can influence the relaxation properties of the material at a high rate of loading but plays a role of minor importance in the case of low speed of deformation as in tension, where amount and size (more than structure) of rubber particles are important.[2] A tentative intepetration of particle size on the Izod impact strength can be as follows: for the same gel content, decreasing the particle size increases the interfacial surface between rubber particles and polystyrene matrix. This can favor the formation of more crazed matter during fracture (as craze starts at the said interface) and then an increase of impact strength.

On the other hand, products with small particles, as well as those with low gel content (high modulus), reach yielding at a higher stress (probably because of the less wide stress field around the particles)[2] (Fig. 3). This can account for the fracture with little plastic deformation and with short initiation time that occurs in the Izod tests for samples with very small particles (1 μ or less) and very low gel content (highest tensile yield stress). A reduction of stress maximum is also observed in these cases.

In case of medium gel content, no appreciable differences were noted in the Izod recorded curves of samples with different particles. At high gel content, slightly longer fracture times are observed (especially propagation time) for material with small particles. In this least case, the expected negative effect on the fracture time could be overcome by the positive effect of a large interfacial surface.

The higher efficiency of the small particles at a high gel content could be also favored by the lower grafting index of these particles (as shown in Fig. 2) which can improve the particle concentration effect.[8] However, we note that the grafting index of the 3- to 4-μ particles of Figure 2 (with slope decreasing

with gel content increase) is lower (max. 3.5) than the grafting index of the 2-to 3-μ particles of Figure 1 where a decrease in slope does not appear.

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