

# Interaction of Polymerization Conditions, Structural Variables, and Mechanical Properties of Rubber-Modified Plastics Produced from Bulk Polymerized Styrene/Poly(butadiene-co-styrene)

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## Synopsis

Rubber-modified polystyrenes were prepared by bulk polymerization with seven different butadiene-styrene copolymers of differing chemical microstructures. The products were structurally characterized through measurement of the swell ratio, percent insolubles, intrinsic viscosity of the soluble fraction, and transmission electron microscope photomicrographs. Increasing initiator concentration or raising polymerization temperature gives lower molecular weight, higher rubber crosslink density, and decreased grafting. Increasing rubber content generally leads to aggregation. Tensile stress-strain curves and Izod impact strengths were measured. High Izod impact strength and increased elongation to break are favored by increasing matrix molecular weight, rubber content, and extent of grafting.

## INTRODUCTION

Polystyrenes containing rubber globules and substantial quantities of polystyrene-rubber graft have long been important commercial polymers because of their enhanced toughness and tensile ductility. Products of this type were first synthesized in the 1920's by Ostromyslenski,<sup>1</sup> who bulk polymerized a solution of natural rubber in styrene monomer. More extensive investigations at the Dow Chemical Company in the 1940's and '50's led to commercial products based on polystyrene and emulsion-polymerized butadiene-styrene (SBR) copolymers, which came to be called high impact polystyrene (HIPS).<sup>2,3</sup> From about 1960, the SBR's in HIPS have been replaced with polybutadienes, though in recent years there has been increased interest in rubber modification using styrene-butadiene block copolymers.<sup>4,5</sup>

There have been numerous studies of HIPS in the literature which range from investigations of the mechanism of formation of the two phase structure<sup>6-8</sup> and grafting reactions during polymerization<sup>8-11</sup> to the influence of rubber particle size on mechanical properties.<sup>8,12-14</sup> Most of these studies involve polybutadiene, and few papers have given much attention to such effects with SBR. These investigations generally indicate globular two phase morphologies with polystyrene occlusions in the rubber particles. A recent study of block SBR copolymer modified polystyrenes show these systems can possess lamellar morphologies.<sup>5</sup>

In this paper we present an experimental study of the polymerization-struc-

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ture-property relationships of rubber modified polystyrenes based on SBR's. The relationship of polymerization conditions and SBR character to the HIPS morphology, degree of grafting, and crosslink density will be examined. We will also examine the influence of the structural characteristics of the rubber-polystyrene composite on its mechanical properties. This paper is part of a series of papers by the authors<sup>15-17</sup> on the properties and processing of rubber-modified polystyrenes.

## EXPERIMENTAL

### Materials

Styrene monomer was obtained from Eastman Kodak. It was washed with a 0.2 N NaOH aqueous solution and then dried with molecular sieves before use. Dicumyl peroxide, manufactured by Pfaltz and Bauer, was used as an initiator. Several butadiene-styrene copolymers were used in this study. These SBR's differ in amount of bound styrene and chemical microstructures. They are summarized in Table I. The rubber-monomer compositions investigated are listed in Table II.

### Polymerization

The polymerization reaction was performed in a batch reactor consisting of a steel pipe 11 cm in inside diameter and with a 0.5 cm thick wall. The reactor contained a Teflon® liner. The reactor was placed in a silicone oil constant-temperature bath. Two different stirrers powered by a compressed air driven motor were used during the polymerization process. Different polymer and initiator concentrations and polymerization temperatures were used. The details of the polymerization conditions used are summarized in Table III.

The desired amount of rubber was weighed and cut into small pieces. The rubber and styrene monomer were charged into the reactor along with a measured amount of dicumyl peroxide. Nitrogen gas was bubbled into the reactor to limit

TABLE I  
Elastomers Used in This Investigation<sup>a</sup>

| Commercial name | Manufacturer       | Designation | % Bound styrene | Butadiene C <sub>is-1,4</sub> | Micro-structure 1,2 | Polymer method        |
|-----------------|--------------------|-------------|-----------------|-------------------------------|---------------------|-----------------------|
| Solprene 300    | Phillips Petroleum | SBR-A       | 25              | 18.8                          | 20.2                | alkyl lithium anionic |
| Solprene 1204   | Phillips Petroleum | SBR-B       | 25              | (18.8) <sup>b</sup>           | (20.2) <sup>b</sup> | alkyl lithium anionic |
| FRS-1502        | Firestone          | SBR-C       | 23.5            | 11.5                          | 13.0                | cold emulsion         |
| FRS-1006        | Firestone          | SBR-D       | 23.5            | 17.0                          | 14.0                | hot emulsion          |
| Solprene 303    | Phillips Petroleum | SBR-E       | 48              | 19.0                          | 14.0                | alkyl lithium anionic |
| Stereon 700     | Firestone          | SBR-F       | 20.5            | 31.8                          | 6.4                 | alkyl lithium anionic |

<sup>a</sup> Microstructures based on Kotaka and White.<sup>18</sup>

<sup>b</sup> ( ) surmised by presumed identical microstructure of solprene 1204 with solprene 300.

TABLE II  
Systems Investigated

| Type of rubber | Wt % elastomers | Designation |
|----------------|-----------------|-------------|
| SBR-A          | 6               | A-1         |
|                | 10              | A-2         |
|                | 22              | A-3         |
|                | 23              | A-4         |
|                | 32              | A-5         |
| SBR-B          | 6               | B-1         |
|                | 10              | B-2         |
|                | 11              | B-3         |
|                | 11              | B-4         |
|                | 13              | B-5         |
|                | 17              | B-6         |
|                | 17              | B-7         |
|                | 17              | B-8         |
|                | 21              | B-9         |
| SBR-C          | 9               | C-1         |
|                | 12              | C-2         |
|                | 12              | C-3         |
|                | 16              | C-4         |
|                | 18              | C-5         |
|                | 19              | C-6         |
|                | 19              | C-7         |
|                | 20              | C-8         |
| SBR-D          | 10              | D-1         |
|                | 15              | D-2         |
|                | 25              | D-3         |
| SBR-E          | 9               | E-1         |
|                | 13              | E-2         |
|                | 17              | E-3         |
| SBR-F          | 12              | F-1         |
|                | 13              | F-2         |
|                | 17              | F-3         |
|                | 22              | F-4         |

the presence of oxygen. The mixture was stirred for 2 h without heating to allow the polymer to dissolve. The temperature of the oil bath was raised to the desired temperature at a rate of about 1°C/min. Polymerization was allowed to proceed until high conversions. In some experiments we used a rotation speed of 800 rpm through the polymerization. Under such conditions the reacting mixture overheated and foamed. However, foaming could be prevented by reducing the stirring speed to 400 rpm after the phase inversion.

After removal from the reactor, the solid polymer was placed in a vacuum oven at 150°C for about 10 h to allow further polymerization and to strip off unreacted monomer.

#### Sol-Gel Content and Polystyrene Matrix Molecular Weight

The rubber-modified polystyrene was extracted in a Soxhlet extractor with toluene for a period of 24 h. A 5-mL aliquot was pipeted into an aluminum weighing dish and the solvent evaporated. The dish was weighed again and the amount of polymer determined. The ratio of this amount of polystyrene to the

TABLE III  
 Polymerization Conditions

| Systems polymerized   | Temp (°C) | Initiator concn (wt % styrene) |
|---|-----------|--------------------------------|
| A-1, <sup>a</sup> A-2, <sup>a</sup> B-1, <sup>a</sup><br>B-5, <sup>a</sup> F-1, <sup>a</sup> F-3, <sup>a</sup><br>F-4 <sup>a</sup>  | 100       | 0.20                           |
| B-8 <sup>a</sup>  | 120       | 0.20                           |
| B-2, <sup>a</sup> B-6 <sup>a</sup>  | 120       | 0.05                           |
| A-3, <sup>a</sup> A-4, <sup>a</sup> A-5, <sup>a</sup> B-4 <sup>a</sup>  | 100       | 0.02                           |
| F-2, C-1, <sup>a</sup> C-2, C-3, <sup>a</sup><br>C-4, <sup>a</sup> C-5, <sup>a</sup> C-6, C-7, <sup>a</sup><br>C-8, D-1, D-2, D-3,<br>E-1, E-2, E-3<br>B-3, <sup>a</sup> B-7, <sup>a</sup> B-9 <sup>a</sup> | 120       | 0.02                           |

<sup>a</sup> "Runaway" overheating, resulting in foaming/boiling during polymerization.

initial polymer gives the fraction soluble polymer. We take the fraction insoluble to represent rubber plus graft.

The intrinsic viscosity of the dissolved polystyrene was determined in toluene at 25°C and used to compute a viscosity average molecular weight through the relation<sup>19</sup>

$$[\eta] = KM^a \quad (1)$$

using a value of  $a = 0.69$  and  $K = 1.7 \times 10^4$ .

### Swelling Test

A polymerized HIPS sample of known mass (0.3–0.4 g) was swollen in 10 mL of toluene. A stoppered test tube of known weight was kept in darkness for 48 h and the remaining solvent then decanted. The test tube was weighed again and the swelling index determined as the ratio of the weight of the swollen gel to that of the dry gel. A 15% correction was made for the excess solvent not decanted and remaining in the bottom of the test tube. From the work of Flory and his co-workers,<sup>19</sup> the swelling index corresponds to an inverse of the cross-linking density.

### Transmission Electron Microscopy

Microtoming was carried out in a Porter-Blum Microtome made by Van Sorvall, Inc. Ultra thin sections of about 500–1000 Å were cut. These were stained with a 2% osmium tetroxide solution for 5 h.<sup>20</sup> A Philips EM 300 Transmission Electron Microscope was used to determine the morphology with 60 kV and 80 kV electron beams.

### Mechanical Testing

Tensile and Izod specimens were injection molded in a Hilliard PM-20 Injection Molding Machine with a barrel temperature of 225°C, mold temperature of 75°C, and an injection pressure of 100 psi. The mold for the tensile bars was the standard ASTM D638 bar type with a crosssection of 2.27 cm × 0.32 cm and

a gauge length of 8.9 cm. For the Izod impact bars, a standard ASTM D256 type mold with dimensions of 2.27 cm  $\times$  2.27 cm  $\times$  1.35 cm. A notch of 0.25 cm was introduced by milling.

Tensile tests were carried out in an Instron tensile tester at a crosshead velocity of 0.5 cm/min. A minimum of five samples for each condition were prepared and tested.

Izod impact tests were performed using a Galen Model 66 Plastic Testing Machine. At least five samples were prepared and tested for each condition. Average values are reported.

## STRUCTURAL CHARACTERIZATION

### Results

We summarize in Table IV all of our data for percent soluble polystyrene, the polystyrene matrix viscosity average molecular weight, and reciprocal swell ratio of the polymerized product. The TEM photomicrographs of selected morphologies are contained in Figures 1 and 2.

TABLE IV  
Structural Characterization of Polymerized Samples

| Designation | % Soluble PS | Reciprocal swell ratio | Viscosity average matrix molecular wt ( $\times 10^{-3}$ ) |
|-------------|--------------|------------------------|--|
| A-1         | 79           | 0.43                   | 142  |
| A-2         | 68           | 0.38                   | 163  |
| A-3         | 57           | 0.33                   | 237  |
| A-4         | 72           | 0.29                   | 200  |
| A-5         | 51           | 0.18                   | 254  |
| B-1         | 73           | 0.39                   | 134  |
| B-2         | 74           | 0.37                   | 161  |
| B-3         | 61           | 0.35                   | 182  |
| B-4         | 58           | 0.32                   | 213  |
| B-5         | 75           | 0.44                   | 196  |
| B-6         | 65           | 0.35                   | 263  |
| B-7         | 49           | 0.25                   | 263  |
| B-8         | 70           | 0.41                   | 165  |
| B-9         | 62           | 0.30                   | 205  |
| C-1         | 82           | 0.31                   | 315  |
| C-2         | 59           | 0.23                   | 258  |
| C-3         | 68           | 0.28                   | 185  |
| C-4         | 66           | 0.25                   | 207  |
| C-5         | 67           | 0.37                   | 213  |
| C-6         | 49           | 0.24                   | 303  |
| C-7         | 62           | 0.29                   | 161  |
| C-8         | 56           | 0.15                   | 316  |
| D-1         | 72           | 0.32                   | 422  |
| D-2         | 69           | 0.27                   | 460  |
| D-3         | 64           | 0.24                   | 310  |
| E-1         | 74           | 0.39                   | 195  |
| E-2         | 68           | 0.30                   | 207  |
| E-3         | 51           | 0.19                   | 299  |
| F-1         | 78           | 0.51                   | 107  |
| F-2         | 71           | 0.46                   | 193  |
| F-3         | 68           | 0.37                   | 162  |
| F-4         | 72           | 0.40                   | 133  |

Certain trends are readily apparent in the experimental data when the results of Table IV are compared with the polymerization conditions listed in Table III. In general with high initiator concentration and high polymerization temperature, a material with a relatively large amount of soluble polystyrene of low molecular weight and high reciprocal swell ratio (crosslink density) is usually obtained. On the other hand, lower initiator concentration and temperature more readily gives rise to a product with a higher molecular weight and lower reciprocal swell ratio. Also materials obtained from systems exhibiting thermal runaway tend to have a larger amount of soluble polystyrene of lower molecular weight and lower reciprocal swell ratio than materials which did not exhibit this response during the polymerization.

Observations of TEM photomicrographs (especially systems A-1 to A-5) (Figures 1) show a gradual change in rubber morphology as the concentration

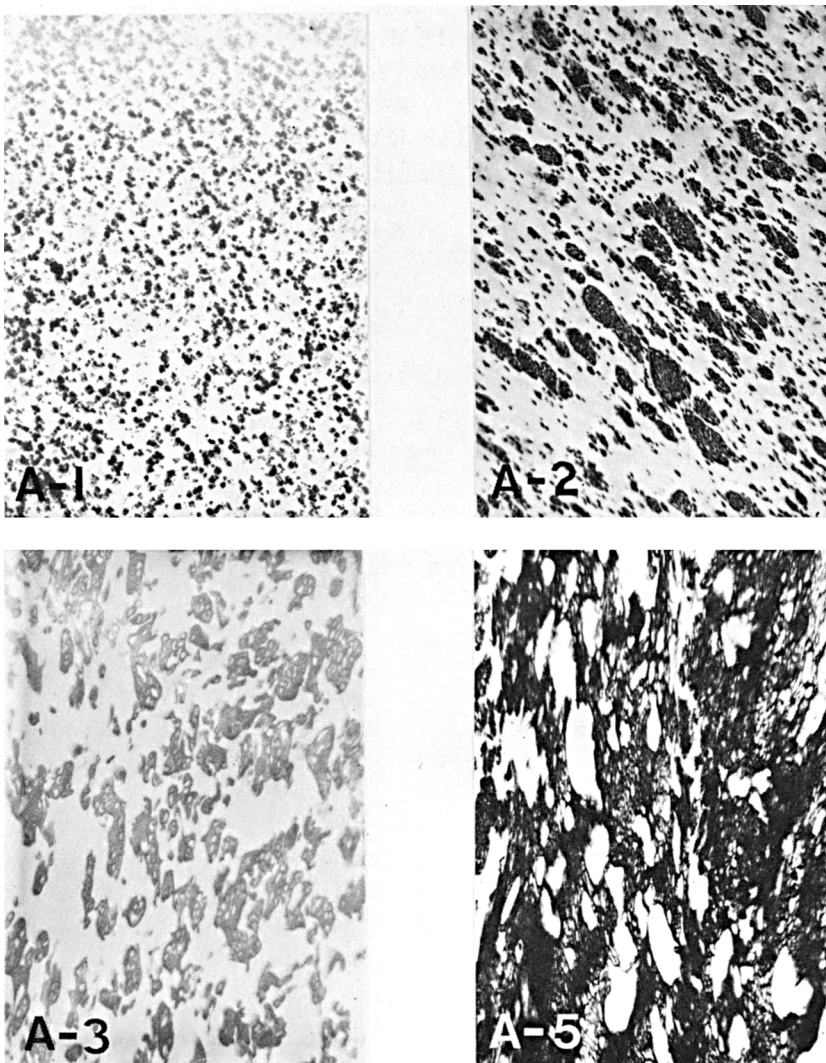


Fig. 1. TEM morphology of rubber modified polystyrenes, (a) A-1, (b) A-2, (c) A-3, (d) A-5 containing SBR-A with 6%, 10%, 22%, and 32% rubber.

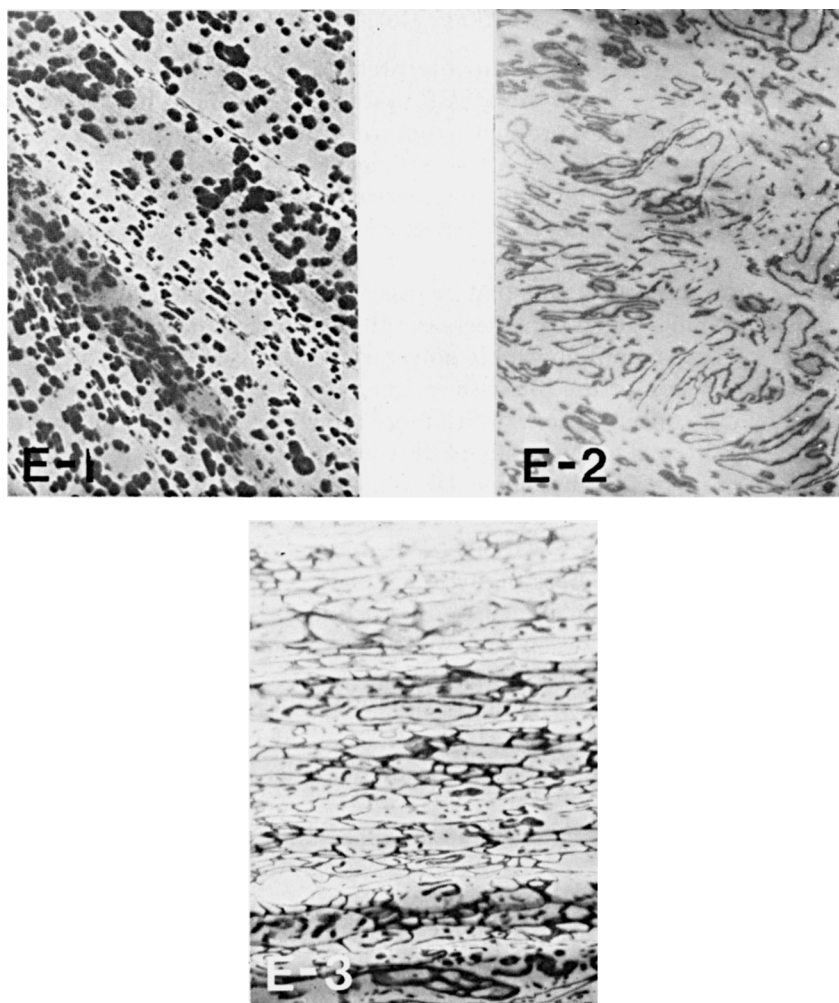


Fig. 2. TEM morphology of rubber modified polystyrenes (a) E-1, (b) E-2, (c) E-3 containing SBR-E with 9%, 13%, and 17% rubber.

of the elastomer phase is increased. With 6 wt % rubber, the rubber particles are discrete, small, and evenly distributed. The average size was about  $0.2 \mu\text{m}$ . At 10% rubber, the individual particle size is still small. However, one now starts to see larger domains with polystyrene occlusions, perhaps due to aggregation of smaller particles. These range in size from  $0.3$  to  $1.3 \mu\text{m}$ . When the rubber level goes to 22%, one finds more large domains and fewer small particles. The domains have polystyrene occlusions and seem loosely packed in the matrix. The domain size ranges from  $0.3$  to  $1.5 \mu\text{m}$  with an average size of about  $0.6 \mu\text{m}$ . At 32% rubber, the domains exhibit further increase in size and pack so tightly that they seem to interconnect with each other. Their size now ranges from  $0.4 \mu\text{m}$  to several microns. Observations on other systems (SBR's B, C) show similar variations in rubber morphology with loading.

In the case of SBR E (Fig. 2) which has a rather high styrene content (0.48) and a small styrene block, one sees an evolution from individual rubber particles to domains with polystyrene occlusions to a continuous lamellar network.

### Interpretation

In this section, we shall attempt to interpret the mechanisms operating during the polymerization of the styrene/SBR systems and explain how the several variables studied influence product structure. The key to such understanding is that styrene polymerizes by a free radical mechanism. The free radicals produced by the initiator not only polymerize the monomer but directly, or indirectly through the growing chain, crosslink the rubber globules and produce graft copolymer.

One of our key observations is that increasing initiator concentration decreases the polystyrene molecular weight, decreases the swell ratio of the rubber particles, and increases the amount of soluble polystyrene. Each of these effects can be interpreted in terms of the increase in free radical concentration due to the greater initiator concentration. With more growing chains, termination rates which are proportional to the square of the concentration of free radicals increase and average chain length and molecular weight decrease. This is a well-known result of free radical polymerization kinetics and is developed in some detail in a number of monographs.<sup>19</sup> An increased free radical concentration will also result in more extensive crosslinking reactions. The reciprocal swell ratio is proportional to the crosslink density. This explains the observed relationship between initiator concentration and swell ratio. If the number of grafting sites on the rubber is constant, the grafting process will become saturated at some free radical concentration. More polymer chains of lower molecular weight will be produced and the intensity of grafting with crosslinked particles will decrease. This should result in more soluble and lower molecular weight polystyrene which in fact is observed.

Increasing polymerization temperature will result in a more rapid breakdown of initiator and a greater free radical concentration. There will also be increased propagation and termination rates. The results of this will be essentially the same as an increase in initiator concentration. The molecular weight of the polystyrene is decreased, the extent of rubber particle crosslinking is increased, and the amount of grafted and insoluble polystyrene is decreased.

The observations of rubber morphology variation with elastomer content suggests that agglomeration of rubber particles occurs during polymerization. The extent of agglomeration increases with rubber content. Earlier investigators, notably Lee,<sup>21</sup> and Munstedt,<sup>22</sup> have called attention to the existence of yield values in shear flow of rubber modified plastics. They suggest that this is due to network structures of agglomerated rubber particles. Lee was concerned with rubber-modified polypropylene and Munstedt with ABS resins.

## MECHANICAL PROPERTIES

### Results

In Table V, we summarize the tensile modulus, yield value, and elongation to break of the tensile tests and the Izod impact strength. It can be noted that the mechanical properties are rather insensitive to SBR type used. We summarize the trends in the tensile mechanical property data with rubber level in Figures 3 and 4. In Figure 3, we plot engineering stress-strain curves for systems with SBR (B-1, B-2, B-3, B-7, B-9) and in Figure 4 for systems with SBR F (F-2,



TABLE V  
Mechanical Properties of Rubber-Modified Polystyrenes

| Designation | Youngs modulus $\times 10^{-10}$ (dynes/cm <sup>2</sup> ) | Yield value $\times 10^{-8}$ (dynes/cm <sup>2</sup> ) | % Elongation to break | Izod impact strength ( $\times 10^{-6}$ dyne-cm/cm) |
|-------------|---|---|-----------------------|---|
| A-1         | 1.39  |   | 4                     | 1.1   |
| A-2         | 1.32  | 4.71  | 8                     | 1.2   |
| A-3         | 0.97  | 3.08  | 25                    | 4.9   |
| A-4         | 0.91  | 2.98  | 34                    | 0.9 ?   |
| A-5         | 0.51  | 1.65  | 48                    | 7.2   |
| B-1         | 1.38  |   | 5                     | 1.0   |
| B-2         | 1.41  |   | 6                     | 1.3   |
| B-3         | 1.39  | 4.53  | 6                     | 1.9   |
| B-4         | 1.37  |   | 5                     | 2.0   |
| B-5         | 1.30  |   | 4                     | 0.8   |
| B-6         | 0.96  | 3.45  | 9                     | 1.1   |
| B-7         | 1.05  | 3.93  | 9                     | 5.1   |
| B-8         | 1.32  |   | 4                     | 0.9   |
| B-9         | 1.10  | 3.57  | 17                    | 10.2  |
| C-1         | 1.32  | 4.30  | 6                     | 1.9   |
| C-2         | 1.05  | 3.08  | 31                    | 9.2   |
| C-3         | 1.24  | 4.70  | 6                     | 2.1   |
| C-4         | 1.22  | 3.65  | 15                    | 2.0   |
| C-5         | 1.05  | 3.24  | 12                    | 1.7   |
| C-6         | 1.02  | 3.10  | 38                    | 16.1  |
| C-7         | 1.05  | 3.10  | 20                    | 2.2   |
| C-8         | 0.69  | 2.34  | 19                    | 12.2  |
| D-1         | 1.06  | 3.71  | 38                    | 8.5   |
| D-2         | 1.08  | 3.39  | 49                    | 8.6   |
| D-3         | 1.04  | 3.07  | 28                    | 9.8   |
| E-1         | 1.34  |   | 4                     | 1.4   |
| E-2         | 1.29  | 4.23  | 7                     | 2.0   |
| E-3         | 0.93  | 2.79  | 16                    | 7.5   |
| F-1         | 1.17  |   | 5                     | 0.7   |
| F-2         | 1.03  | 2.51  | 11                    | 2.0   |
| F-3         | 0.76  | 2.01  | 40                    | 2.8   |

F-3, F-4). Certain trends in this engineering stress-strain data are apparent. In general the samples are brittle at low rubber levels and become increasingly ductile as the rubber content increases. This is also seen in the impact strength data of Table V.

However, beyond this the influence of structural characteristics are complex. Clearly not only rubber content, but matrix molecular weight, quantity of graft, rubber particle size, and rubber crosslink density are important. It is difficult to isolate individual variables. Attempts at this are shown in Figures 5 and 6, where we plot Izod impact strength as a function of percent rubber plus graft and graft content alone. There are trends for both increasing rubber, rubber plus graft, and graft alone to increase strength. The correlation with rubber plus graft is the best.

We have tried to show the impact strength as a function of two variables in terms of surfaces in Figures 7 and 8. It can be seen in Figure 7 that increasing particle size and increasing rubber plus graft increase impact strength at fixed matrix molecular weight. In Figure 8 we show that increasing matrix molecular weight and rubber plus graft content increase impact strength.

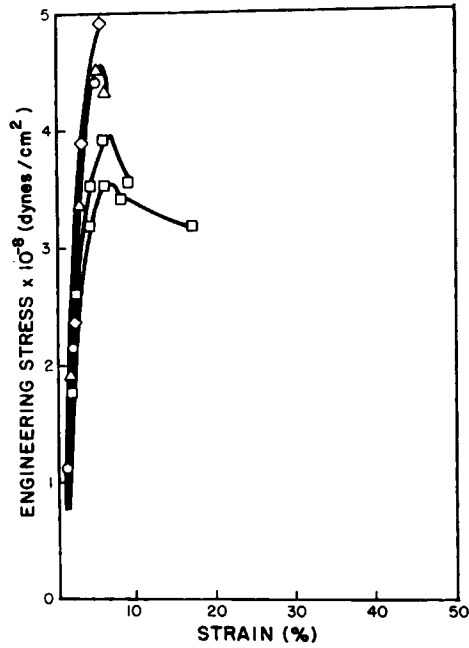


Fig. 3. Engineering stress-strain curve for SBR-B modified polystyrene with 6% (O), 10% (◇), 11% (△), 17% (□), 21% (▽) rubber.

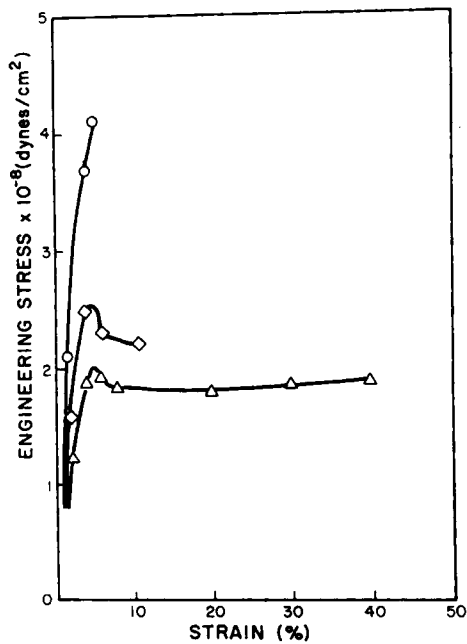


Fig. 4. Engineering stress-strain curve for SBR-F modified polystyrene with 13% (O), 17% (◇), and 22% (△) rubber.

### Interpretation

The general trends in our data agree with those of previous investigators on similar systems. Particular comparisons can be made between the present work and that reported by Wagner and Robeson<sup>8</sup> and Cigna, Matarrese, and Biglione.<sup>13</sup> One sees that impact strength and other mechanical properties can be discussed

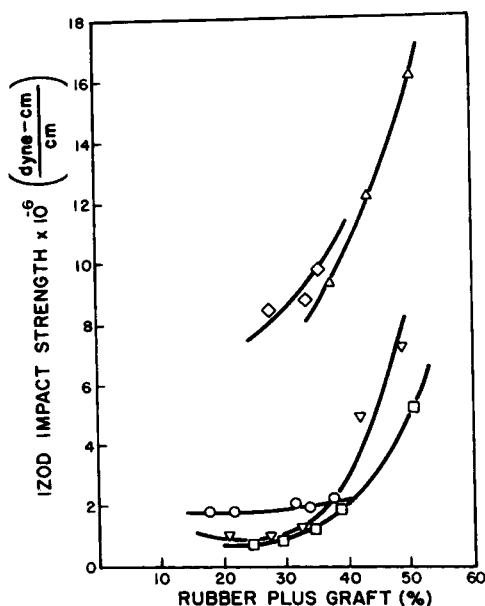


Fig. 5. Izod impact strength as a function of rubber plus graft content. Without overheating: (Δ) SBR-C; (◇) SBR-D; with overheating: (▽) SBR-A; (□) SBR-B; (○) SBR-C.

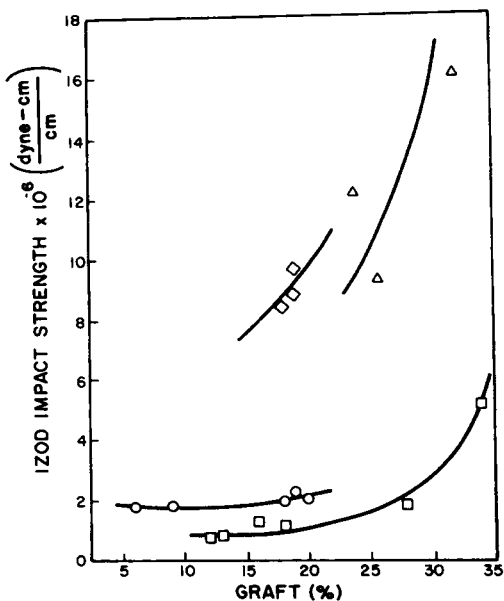


Fig. 6. Izod impact strength as a function of graft content. Without overheating: (Δ) SBR-C; (◇) SBR-D; with overheating: (□) SBR-B; (○) SBR-C.

in terms of rubber plus graft content, rubber particle size, crosslink density, and polystyrene molecular weight.

The results of the relationship between impact strength and grafting agree with the findings of Cigna and co-workers.<sup>13</sup> However, while they found a linear increasing relationship between impact strength and gel content (rubber plus graft), our findings indicate that the increase of impact strength is mild below 40% of gel content, but much greater above 40%. Wagner and Robeson<sup>8</sup> find that a "phase volume" around 20% is optimum. Our findings indicate that marked impact improvement can be achieved only if the amount of rubber plus graft is relatively high. When the amount of graft only is plotted against impact strength, the smooth correlation begins to deviate. This suggests that the important parameter is not the amount of graft, but the amount of rubber plus graft (compare Figures 5 and 6). Therefore, the total gel content improves the ten-

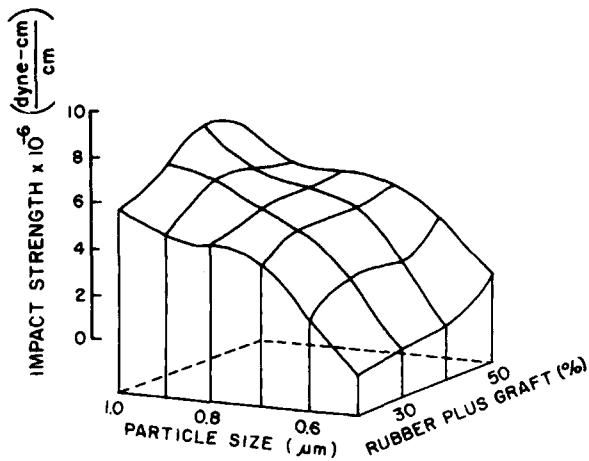


Fig. 7. Izod impact strength surface as a function of rubber particle size and rubber plus graft. The matrix molecular weight is  $230,000 \pm 30,000$ .

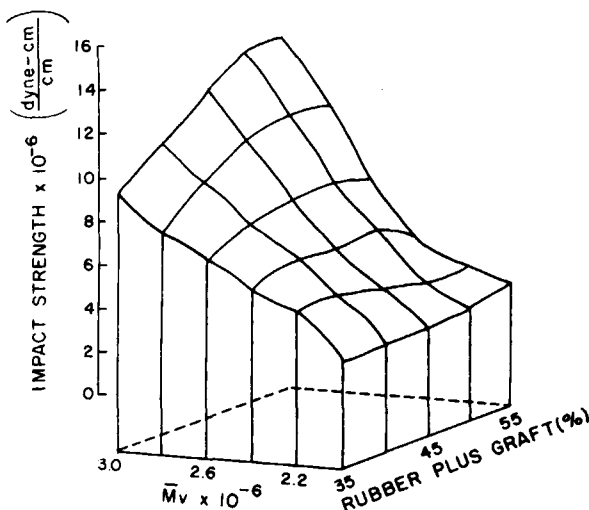


Fig. 8. Izod impact strength surface as a function of matrix molecular weight and rubber graft content.

dency to plastic deformation and absorbs impact energy, and thus increases resistance to crack propagation. The impact strength decreases with increasing reciprocal swell ratio (crosslink density). One hypothesis to explain this is that stress relaxation of highly crosslinked material is relatively slower than linear polymer and, upon sudden loading, these materials cannot relax fast enough to prevent crack initiation and propagation. Others<sup>8</sup> have interpreted this as due to hindered craze formation.

An interesting observation is the effect of overheating on the impact strength of materials made with FRS-1502. As discussed earlier, materials which experienced overheating have a large amount of soluble polystyrene and lower matrix molecular weight. The result is a manyfold lower impact strength. The effect of polystyrene molecular weight on the impact strength of HIPS is easily understood from the work of Fellers and Kee.<sup>23</sup> These authors found that the strength of polystyrene drops drastically as  $\bar{M}_n$  goes below a molecular weight equivalent to  $2M_e$ . They argue that this is due to the inability to form a network via physical entanglements. In the case of HIPS, no substantial benefit can be given by the rubber component then until the polystyrene molecular weight satisfies the above-mentioned condition.<sup>23</sup>

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