

# Toughened Polystyrene Composites by the Concentrated Emulsion Pathway

ELI RUCKENSTEIN\* and HANGQUAN LI

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

## SYNOPSIS

Rubber-styrene solutions of various compositions and containing a suitable initiator have been polymerized starting from concentrated emulsions in which the above solutions constitute the dispersed phase and solutions of sodium dodecylsulfate in water the continuous phase. Latexes of rubber-modified polystyrene composites have been thus obtained. Solutions of rubber-styrene have been also polymerized by bulk polymerization for comparison purposes. The molecular weights have been determined from intrinsic viscosity measurements, and the mechanical properties of the composites have been studied via tensile testings. Because of the lower mobility of the high-molecular radicals in the concentrated emulsions, higher molecular weights have been obtained by the concentrated emulsion polymerization than by the bulk polymerization method. The tensile properties and toughness of the composites have been determined. While the two polymerization methods provide high, comparable toughness, the concentrated emulsion method generates latexes that can be easily processed in any desirable shape. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polystyrene (PS) is one of the most important plastic materials. Since due to its brittleness it could not be employed in a number of applications, a number of attempts have been made to improve its toughness by preparing rubber-toughened polystyrene composites. PS and rubber can be blended in a number of ways. Originally the ingredients were compounded either in a two-roll mill or using a mixer or an extruder. The toughness of the products was not, however, appreciably improved compared to that of the unmodified polymer. Today's common practice<sup>1</sup> is to dissolve the rubber in styrene and then to polymerize the system. The blend thus obtained contains not only rubber and polystyrene but also a graft polymer because of the attachment of short polystyrene side chains to the rubber molecules. The toughness of this material is markedly improved compared to that of PS.

In the present investigation, the styrene-rubber solution was polymerized via the concentrated

emulsion polymerization method,<sup>2,3</sup> which was recently developed by this group. A concentrated emulsion has the appearance of a gel and differs from the conventional emulsion in that the volume fraction  $\phi$  of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of spheres of the same size), and may be as high as 0.99. The continuous phase has a low volume fraction, and for large values of  $\phi$  is in the form of a network of thin liquid films that separate polyhedral drops. The small size of the droplets of the emulsion and its gel structure restrain the mobility of the high-molecular-weight species in each of the drops. As a result of this "gel effect," the bi-radical termination is sharply decreased, the so-called self-acceleration appears from the very beginning of the polymerization process, and a high rate of polymerization and a high molecular weight is expected. Another advantage consists in the control and size uniformity of the polymer latexes, and this can be useful in many special applications.

Many kinds of rubbers have been used as PS modifiers. Styrene-butadiene rubber (SBR),<sup>4</sup> high *cis*-1,4-polybutadiene,<sup>5,6</sup> and peroxidized ethylene-propylene rubber are some examples. In the present investigation, styrene-butadiene-styrene tri-block

\* To whom correspondence should be addressed.

copolymer (SBS) and styrene-ethylene/butylene-styrene tri-block copolymer (SES, which is simply hydrogenated SBS) were used as rubber modifiers to prepare toughened PS composites. For comparison purposes, styrene-rubber solutions with the same composition were polymerized by both concentrated emulsion and bulk processes. The mechanical properties of the resultant composites were measured by tensile testing and the molecular weights were calculated from their intrinsic viscosities.

## EXPERIMENTAL

### Materials

Styrene (Aldrich) was distilled before use. Azobisisobutyronitrile (AIBN, Alfa) was recrystallized from methanol. Sodium dodecyl sulphate (SDS, Aldrich), SBS (Aldrich), and SES (Aldrich) were used as received. Water was deionized and distilled.

### Preparation Procedure

Certain amounts of SBS (or SES) and AIBN were introduced in styrene and the system was allowed to stand overnight to generate a uniform styrene-rubber solution. An aqueous solution of SDS was introduced into a single-neck 100-mL flask provided with a magnetic stirring bar. Half of the styrene-rubber solution was added dropwise with vigorous stirring into the flask with a pipette. The volume of SDS aqueous solution was one-fourth of the styrene-rubber solution. The whole addition process lasted about 15 min and took place at room temperature. The gel-like concentrated emulsion thus formed was additionally stirred for 15 min and finally was transferred to a tube of 30-mL capacity. The tube was sealed with a rubber septum and introduced into a water bath of 60°C to carry out the polymerization. Another half of the styrene-rubber solution was transferred to another tube and introduced into a Cole Parmer ultrasonic mixer, at 60°C, for 6 h. After 6 h the viscosity of the system became very high and further mixing was no longer possible. Consequently, the tube was transferred to a water bath of 60°C. Both polymerization processes lasted 96 h. The material obtained by the concentrated emulsion method was transformed in a fine powder in a blender, washed in an extractor with methyl alcohol for 48 h and dried in a vacuum oven for another 48

h. The product obtained by bulk polymerization was directly used in various testings.

### Measurement of the Intrinsic Viscosity

A small amount of toughened PS composite was dissolved in tetrahydrofuran (THF) to form a dilute solution with a concentration of about 0.5 wt %. After standing at room temperature for 24 h, the solution was filtered using a preweighed filter paper to remove any insoluble species present. The intrinsic viscosity of the filtered solution was measured with an Ubbelodhe viscometer at the temperature of  $25 \pm 0.2^\circ\text{C}$ . The filter paper was then dried in a vacuum oven and reweighed to obtain the weight of the insoluble species.

### Tensile Testing

The powder of a sample was thermopressed in a Laboratory Press (Fred S. Carver Inc.) to form a sheet, which was cut to the size required by the ASTM D.638-58T. The tensile testing was conducted with an Instron Universal Testing Instrument (Model 1000) at room temperature. The elongation speed of the instrument was 50 mm/min.

## RESULTS AND DISCUSSION

### Intrinsic Viscosity and Molecular Weight

As mentioned in the introduction, the composites obtained in this study are not simply two-component blends of polystyrene and rubber, since a third component—styrene-grafted rubber—is also formed. The SBS-modified composites contain also a small amount of THF insoluble gel that is believed to be a crosslinked species. The insoluble gel can be readily removed by filtering, but the amount of grafted rubber is difficult to determine. For the intrinsic viscosity measurements and the further calculation of the molecular weight of the PS homopolymer, the grafting will be neglected in a first approximation. The intrinsic viscosity of the polystyrene homopolymer contained in each of the samples can be therefore calculated by using the following relation:<sup>7</sup>

$$[\eta] = W_1[\eta]_1 + W_2[\eta]_2 \quad (1)$$

where  $[\eta]$ ,  $[\eta]_1$ , and  $[\eta]_2$  are the intrinsic viscosities of the composite, PS homopolymer and rubber, and

**Table I Intrinsic Viscosities and Molecular Weights for SBS-Toughened Composites**

Sample <sup>a</sup>	Concentrated Emulsion			Bulk		
	Intrinsic Viscosity of Composite (mL/g)	Intrinsic Viscosity of PS (mL/g)	Mol. Weight of PS	Intrinsic Viscosity of Composite (mL/g)	Intrinsic Viscosity of PS (mL/g)	Mol. Weight of PS
SBS 0	—	132.0	423,000	—	99.6	287,000
SBS 10	250.1	267.6	1,121,000	199.9	212.5	816,000
SBS 15	214.7	235.0	937,000	160.2	173.1	615,000
SBS 20	196.4	220.4	858,000	125.4	135.7	436,000
SBS 25	178.3	204.1	771,000	101.3	108.1	321,000
SBS 30	137.3	155.9	532,000	93.0	98.7	283,000

<sup>a</sup> SBS $x$  (with  $x = 0, 10, 15, 20, 25, 30$ ) stands for  $x$  weight parts of SBS to 100 weight parts of styrene.

$W_1$  and  $W_2$  are the weight fractions of PS homopolymer and rubber, respectively. The molecular weight of PS homopolymer can be obtained using the Mark-Houwink relation:<sup>7</sup>

$$[\eta]_1 = KM^\alpha \quad (2)$$

where  $M$  stands for the molecular weight, and  $K = 0.011$  mL/g and  $\alpha = 0.725$  are the Mark-Houwink constants.<sup>8</sup>

Tables I and II (in which SBS $x$  and SES $x$  mean that the samples were prepared from the solutions containing  $x$  weight parts of SBS or SES to 100 weight parts of styrene) list the intrinsic viscosities of both composites and PS homopolymer and the molecular weight of PS homopolymer. Even though the intrinsic viscosities and molecular weights of the PS homopolymers were determined in an approximate manner, they are useful for comparative purposes. One may notice that high molecular weights of PS were achieved in both polymerizations, some being higher than  $10^6$ . In the common bulk poly-

merization of styrene, the molecular weight of the product is hardly higher than  $3 \times 10^5$ . Tables I and II show that the molecular weight of the PS homopolymer passes through a maximum as the rubber content increases, remaining, however, up to 30 weight parts to 100 parts of styrene greater than that of the product of homopolymerization. The high molecular weights obtained could be attributed to the presence of the rubber molecules in the monomer, which increase the viscosity of the system and thus decrease the bi-radical termination rate. The decrease of the molecular weight after the maximum can not be, however, explained in this manner. Possible explanations are: (i) the viscosity is responsible not only for the gel effect, but has also a negative effect upon the growth of the chains, and (ii) Eq. (1) employed in the calculations is not completely accurate, perhaps because increasing grafting takes place as the content of rubber increases.

The gel effect stimulated by the concentrated emulsion is reflected in the viscosities and molecular weights of Tables I and II. As expected, all the vis-

**Table II Intrinsic Viscosities and Molecular Weights for SES-Toughened Composites**

Sample <sup>a</sup>	Concentrated Emulsion			Bulk		
	Intrinsic Viscosity of Composite (mL/g)	Intrinsic Viscosity of PS (mL/g)	Mol. Weight of PS	Intrinsic Viscosity of Composite (mL/g)	Intrinsic Viscosity of PS (mL/g)	Mol. Weight of PS
SES 0	—	132.0	423,000	—	99.6	287,000
SES 10	238.6	254.0	1,044,000	187.4	198.0	740,000
SES 15	159.0	171.3	606,000	135.3	143.7	476,000
SES 20	132.2	142.9	472,000	103.8	108.0	320,000
SES 25	106.0	113.2	342,000	88.0	90.7	252,000

<sup>a</sup> SES $x$  (with  $x = 0, 10, 15, 20, 25$ ) stands for  $x$  weight parts of SES to 100 weight parts of styrene.

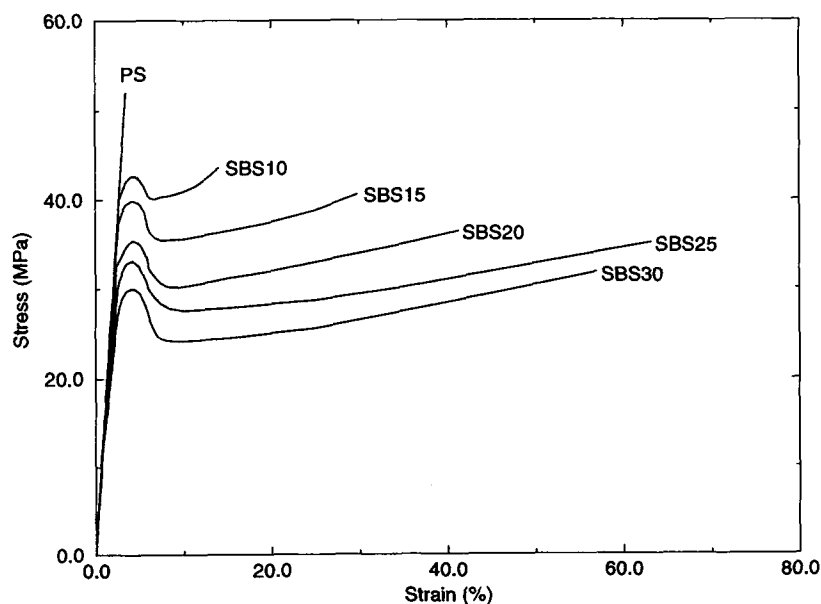
cosities (and hence the molecular weights) of the samples prepared via the concentrated emulsion are higher than those prepared via bulk polymerization.

Since the intrinsic viscosity of pure SES (77.4 mL/g) is somewhat higher than that of pure SBS (74.1 mL/g), it appears a paradox that the molecular weights of the specimens containing SES are lower than those of the specimens containing SBS. This may be due to the formation of grafted and crosslinked species. Because of the presence of double bonds in the main chain, SBS interacts more easily with the initiator and hence can be more easily grafted and crosslinked. Indeed, a small amount of an insoluble gel due probably to crosslinking was detected in the SBS but not in the SES-modified specimens. As a result, the SBS-based composites have higher intrinsic viscosities than those based on SES, and hence higher molecular weights.

### Stress-Strain Curves

Figure 1 presents some of the stress-strain curves of the rubber-modified PS composites and shows that the shapes of these curves are similar and have the following three characteristics. First, each has a yield point that is typical for tough plastic materials. One may notice that even the sample containing as much as 30 weight parts rubber to 100 weight parts styrene still exhibits a pronounced yield point and not a rubberlike behavior. The yield strength decreases, however, as the rubber content increases.

Second, after stress softening, large deformations occur for small stress increases. The higher the rubber content, the larger are the deformations achieved. Third, the ultimate fracture stress (which is a measure of the tensile strength of the material) is just a little higher than the yield stress. When the sample bars were subjected to tension near the yield point, both tilt shear bands and stress whitening appeared. The stress whitening became stronger as the strain became larger till the sample broke. These phenomena indicate that the PS composites are toughened by two mechanisms:<sup>9</sup> shear yielding and crazing. However, the contributions of the two mechanisms are different for different rubber contents. The shear bands on the sample bars with a lower rubber content (say, 10–15 weight parts to 100 weight parts styrene) are more pronounced than on those with higher rubber content. This suggests that in the systems with lower rubber content the shear yielding is dominant. On the other hand, the higher the rubber content, the stronger is the stress whitening. This indicates that the crazing near the rubber particles plays an increasingly important role. The third feature mentioned above supports the point of view<sup>10-13</sup> that the rubber particles bear the load and provide the ductility and that they are involved in stopping the crack propagation and in stimulating craze initiation. The stress-strain curves of Figure 1 are in contrast to that of the unmodified PS, which is a very brittle material with no yield point and a very small deformation, below 4%.



**Figure 1** Stress-strain curves of SBS-toughened PS composites prepared via the concentrated emulsion pathway.

**Table III Mechanical Properties for SBS-Toughened Composites**

Sample	Concentrated Emulsion			Bulk		
	Tensile Strength (MPa)	Elongation (%)	Break Energy (MJ/m <sup>3</sup> )	Tensile Strength (MPa)	Elongation (%)	Break Energy (MJ/m <sup>3</sup> )
SBS 10	43.6	14.0	5.2	56.5	8.7	4.4
SBS 15	40.6	29.8	10.9	51.1	26.0	12.6
SBS 20	36.4	41.3	15.0	47.5	34.0	16.2
SBS 25	35.1	63.2	26.6	41.0	61.8	27.9
SBS 30	31.8	56.9	23.5	36.5	64.9	28.4

### Tensile Strength and Elongation

Tensile data are listed in Tables III and IV and illustrated in Figures 2 and 3 where the mechanical properties of the samples prepared via the concentrated emulsion and via the bulk polymerization are compared. The bulk polymerization was carried out by us under ultrasonic mixing. Consequently, the results can be considered close to those obtained in the industrial process, which employs mechanical stirring. One can see that for the same composition, the results for both types of polymerization are comparable and show similar trends: the higher the content of rubber, the higher the elongation and the lower the tensile strength. This can be easily explained: The presence of a large number of flexible rubber segments in the system impedes the packing of the stiff PS segments, thus generating a greater free volume. As a result, the segments of PS have more space to change their conformation (i.e., can have larger elongation) with less energy. However, the diluted densities of the segments and lateral groups provide smaller intermolecular interactions, hence a lower tensile strength.

The composites toughened with SBS show some differences compared to those toughened with SES when the results based on concentrated emulsion and bulk polymerizations are compared. For those toughened with SBS, the concentrated-emulsion-

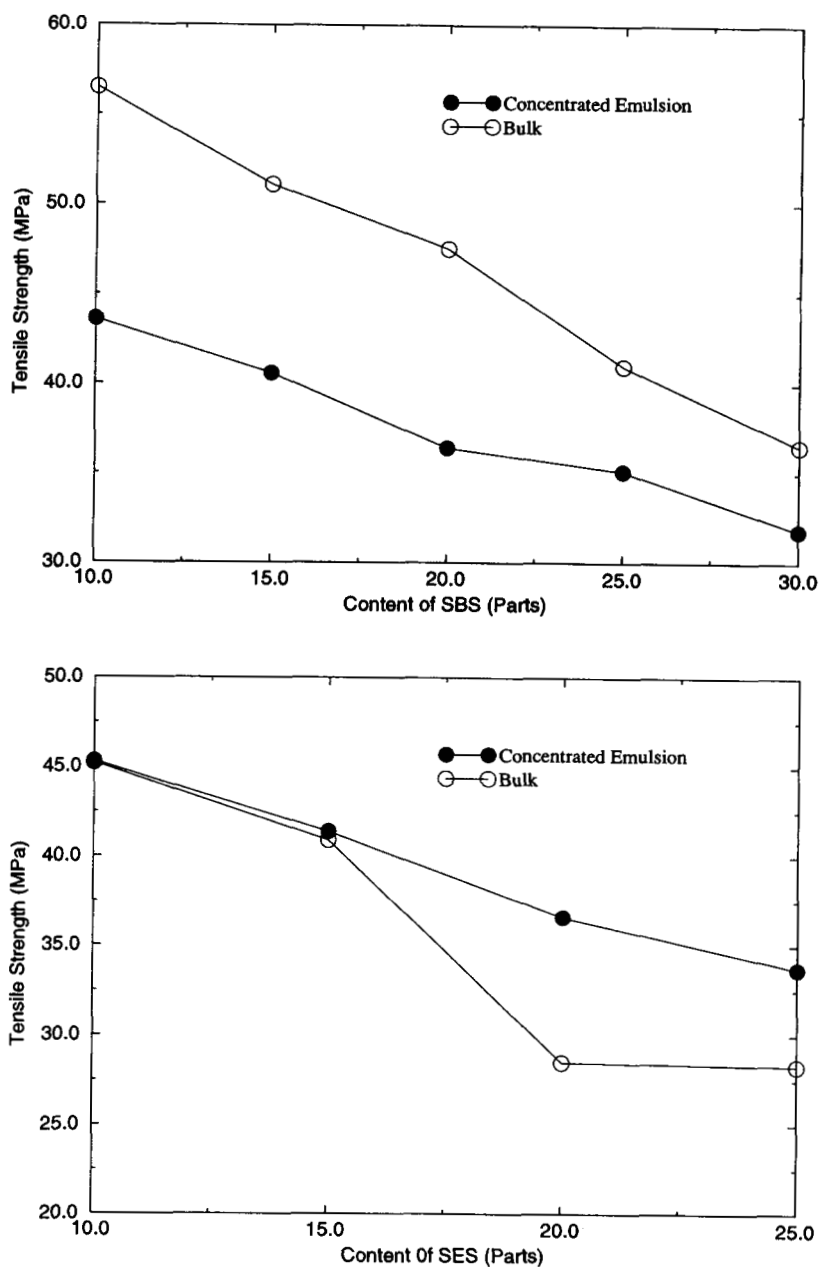
based composites exhibit lower tensile strengths but somewhat higher elongations, while for those toughened with SES, the concentrated-emulsion-based specimens exhibit higher tensile strengths but lower elongations. When the concentrated emulsion method is employed, the rates of the termination, grafting, and crosslinking reactions are decreased in both SBS and SES containing systems, because of the gel effect. While the grafting increases the flexibility, because a larger free volume is generated, in contrast, the crosslinking decreases the flexibility. The different behaviors of SBS and SES containing systems are due to the presence of crosslinking in the former and its absence in the latter system. Since less grafting occurs in the concentrated emulsion polymerization, the polymers obtained in the SBS containing systems will have a higher elongation and a smaller tensile strength than those obtained by bulk polymerization. In contrast, in the SES containing system, less flexibility should occur in the polymers prepared via the concentrated emulsion methodology, because of reduced grafting.

### Evaluation of Toughness

The toughness of the specimen is estimated from the area under the stress-strain curve by graphical integration, which represents the work done in order to tensile a sample bar till it breaks. From Tables

**Table IV Mechanical Properties for SES-Toughened Composites**

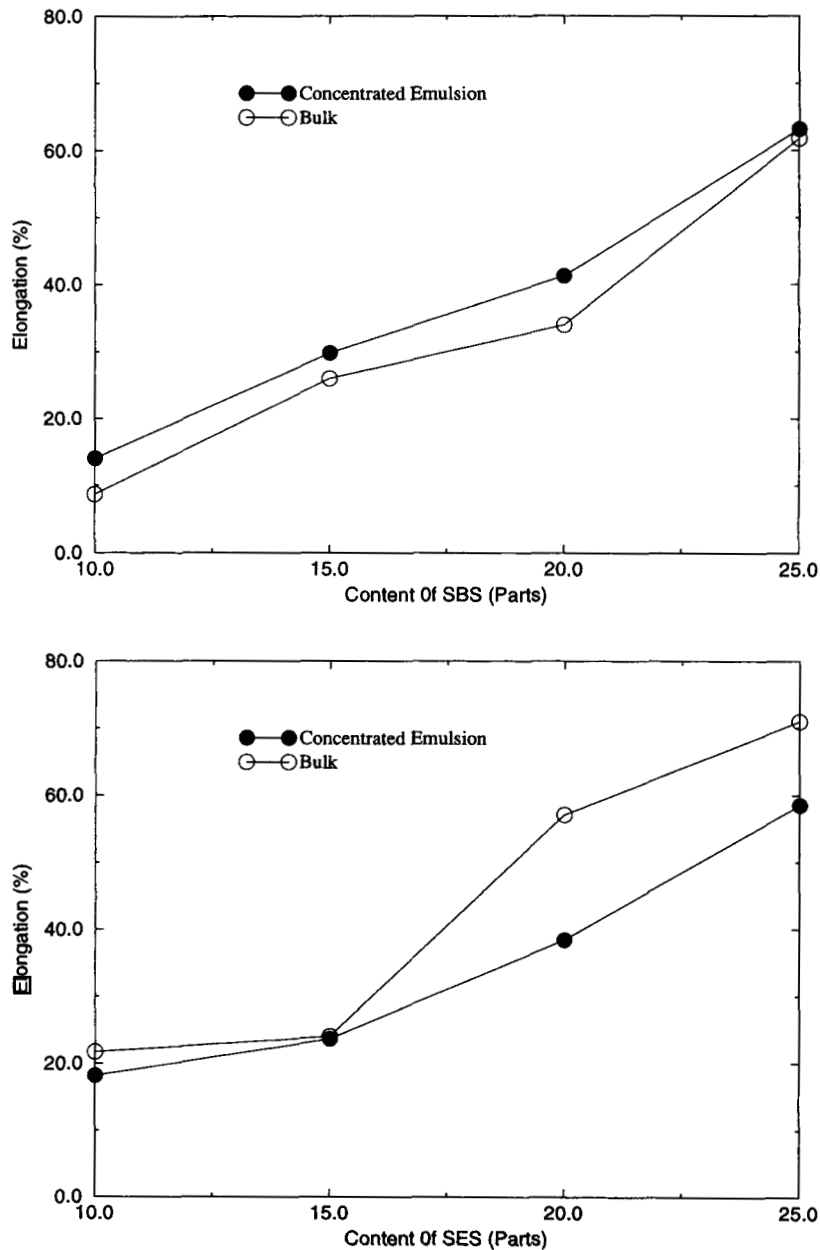
Sample	Concentrated Emulsion			Bulk		
	Tensile Strength (MPa)	Elongation (%)	Break Energy (MJ/m <sup>3</sup> )	Tensile Strength (MPa)	Elongation (%)	Break Energy (MJ/m <sup>3</sup> )
SES 10	45.3	18.2	7.4	45.2	21.7	8.8
SES 15	41.4	23.6	9.3	40.9	24.0	9.3
SES 20	36.6	38.4	14.1	28.5	57.1	16.2
SES 25	33.7	58.5	21.7	28.3	71.0	22.1



**Figure 2** (a) Tensile strength of SBS-toughened PS composites: (●) concentrated emulsion, (○) bulk. (b) Tensile strength of SES-toughened PS composites: (●) concentrated emulsion, (○) bulk.

III and IV one can see that the toughnesses of the composites prepared via both types of polymerization are comparable and have similar trends: the greater the amount of rubber blended, the higher is the toughness. When the SBS content becomes higher than 30 weight parts or the SES content higher than 25 weight parts for 100 weight parts styrene, the styrene-rubber solution becomes too

viscous to be handled. For this reason the rubber content used in this study was kept below these levels. One can also notice that the toughnesses of the SBS containing composites are somewhat higher than those of SES containing ones. This is because of the presence of some crosslinking in the structure of the former composites. It was reported<sup>1</sup> that a rubber with 5–20 wt % insoluble species provides



**Figure 3** (a) Elongation of SBS-toughened PS composites: (●) concentrated emulsion, (○) bulk. (b) Elongation of SES-toughened PS composites: (●) concentrated emulsion, (○) bulk.

the highest toughness. In the section regarding the intrinsic viscosity measurements we noted that the amount of the insoluble species (gel content) of SBS-based composites falls into that favorable range, while for SES-based composites no insoluble species were detected. Hence the SBS-toughened composites should be tougher than the SES-toughened ones.

### Influence of Surfactant

Generally speaking, the conventional emulsion polymerization method is seldom used for producing polystyrene because of the large amounts of surfactant left in the polymers, which adversely affect the mechanical properties and other characteristics, and because of difficulties that appear during agitation

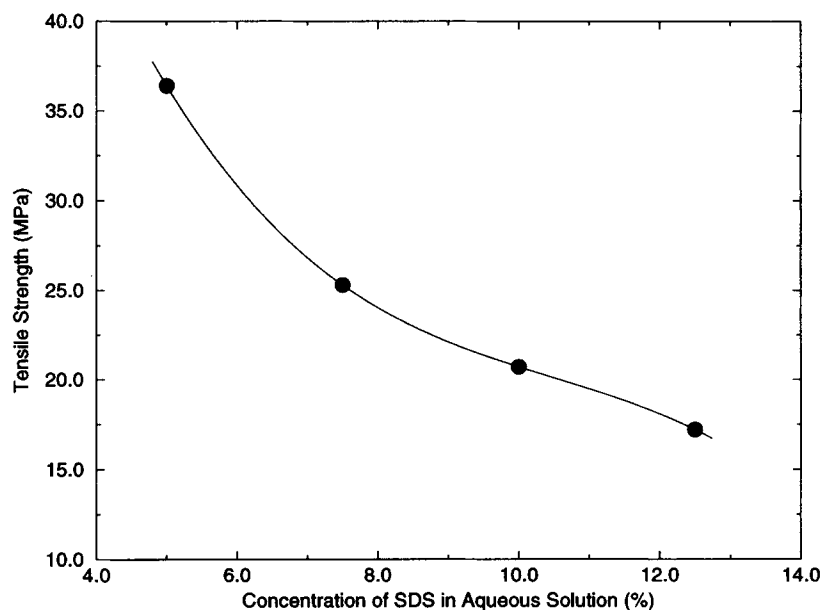


Figure 4 Effect of surfactant on tensile strength (for sample SBS20).

and densification. In contrast, in the concentrated emulsion polymerization, a very small amount of surfactant is used, only 1 wt %, based on the styrene-rubber solution. This means that for 100 mL of solution, only 20 mL of 5 wt % aqueous solution of SDS is employed. For the styrene-rubber solution, the 5 wt % is the lowest concentration of the aqueous

solution that allows to obtain a stable concentrated emulsion; below this value, phase separation occurs. Higher concentrations of SDS result in higher amounts of surfactant left in the resultant polymers, which affect adversely the mechanical properties. In Figures 4 and 5 the tensile strength and elongation are plotted against the concentration of SDS in the

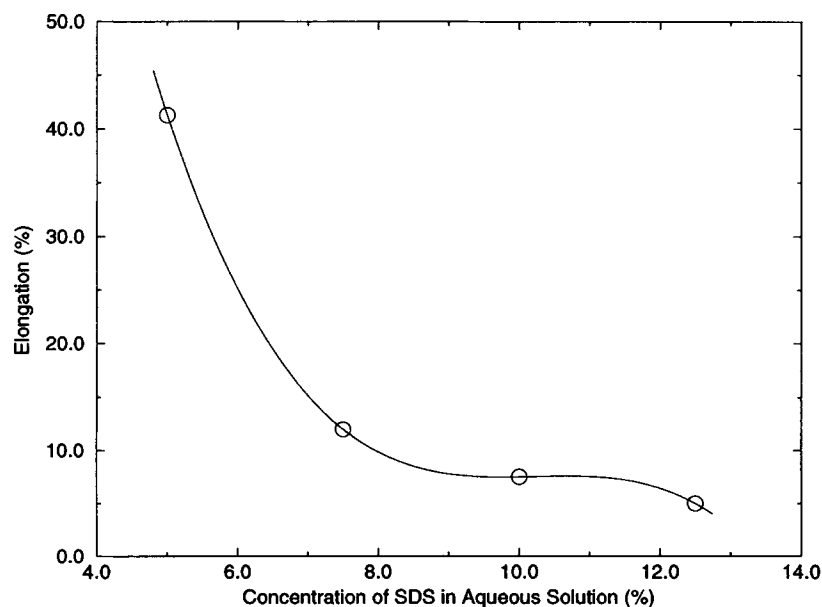


Figure 5 Effect of surfactant on elongation (for sample SBS20).



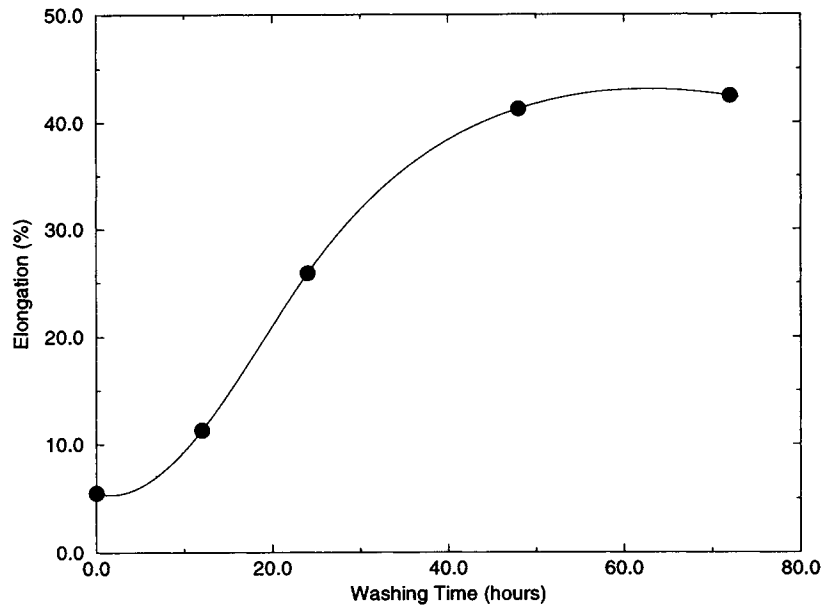


Figure 6 Effect of washing time on elongation (for sample SBS20).

aqueous solution. One can see that the surfactant left in the polymers has a stronger influence on the elongation than on the tensile strength. Even for SDS concentration in the aqueous phase as low as 5 wt %, long washing times are needed to ensure good mechanical properties. One can see from Figure 6 that 48 h of washing can remove most of the surfactant.

#### Advantages of the Concentrated Emulsion Polymerization

The present investigation demonstrates that composites prepared via the concentrated emulsion polymerization possess comparable toughness and other mechanical properties as those prepared via the bulk polymerization. The concentrated emulsion methodology, however, has the advantage of providing a fine powder, which can be easily employed in many applications, while the bulk polymerization produces a bulk material, which must be further pelletized with an extruder. Besides, the concentrated emulsion polymerization provides a means of increasing the polymer molecular weight without decreasing the polymerization rate. As shown by the results of this investigation, higher molecular weights can be obtained by the concentrated emulsion polymerization process than by the bulk polymerization.

#### CONCLUSION

1. Polymerization of styrene-rubber solutions by the concentrated emulsion method provides higher molecular weights than the bulk polymerization.
2. Rubber-toughened polystyrene composites prepared via the concentrated emulsion polymerization have comparable toughness and other mechanical properties as those prepared via the bulk polymerization.
3. Polystyrene toughened with rubber via the concentrated emulsion method can have an elongation 16 times larger than the ordinary polystyrene, while decreasing with only 33% the tensile strength. The toughness of toughened composites can be 15 times higher when measured by the area under the stress-strain curves than that of ordinary polystyrene.

#### REFERENCES

1. N. E. Davenport, L. W. Hubbard, and M. R. Pettit, *Brit. Plastics*, **32**, 549 (1959).
2. E. Ruckenstein and J. S. Park, *J. Polym. Sci., Chem. Lett. Ed.*, **26**, 529 (1988).
3. E. Ruckenstein and K. J. Kim, *J. Appl. Polym. Sci.*, **36**, 907 (1988).

4. C. B. Bucknall, *Trans. Instn. Rubber Ind.*, **39**, 221 (1963).
5. M. E. Fowler, H. Keskkula, and D. R. Paul, *J. Appl. Polym. Sci.* **37**, 225 (1989).
6. N. G. Podosenva and V. P. Budtov, *Vysokomol Soedin, Ser. A*, **30**, 2275 (1988).
7. Hans-Georg Elias, *Macromolecules*, Chapter 9, Plenum Press, New York, 1977.
8. A. L. Sparatorico and B. Coulter, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1139 (1973).
9. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum Press, New York, 1976.
10. C. G. Bragaw, in *Multicompound Polymer Systems*, American Chemical Society, Washington, D.C., 1971.
11. C. B. Bucknall, *Brit. Plastics*, **40**(11), 118 (1967); **40**(12), 84 (1967).
12. C. B. Bucknall and R. R. Smith, *Polymer*, **6**, 437 (1965).
13. H. Keskkula, "Rubber Modified Styrene Polymers," in *Polyblends and Composites*, P. F. Bruins, ed., Interscience, New York, 1970.

Received November 1, 1993

Accepted January 17, 1994