

Novel Method for Toughening of Polystyrene Based on Natural Rubber Latex

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ABSTRACT: γ -Radiation vulcanized natural rubber latex/phase transfer/bulk polymerization is a novel process for the preparation of toughened polystyrene based on natural rubber latex. The negatively charged γ -radiation vulcanized natural rubber latex was first titrated with benzyltrimethylhexadecylammonium chloride in the presence of a styrene monomer. At a critical transfer concentration, the crosslinked rubber particles transferred from the aqueous phase into the styrene phase in which they swelled, depending on the irradiation dose used. By bulk polymerization of the styrene phase containing transferred particles, the polymer blends exhibited two-phase morphology similar to that of commercial high-impact polystyrene that was microscopically obtained. The final product showed an increase in the unnotched Izod impact energy over the unmodified polystyrene. The effect of irradiation dose, rubber content, and initiator concentration on the impact property and morphology of toughened polystyrene prepared was investigated. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 1333–1345, 1999

Key words: high-impact polystyrene; natural rubber latex; phase transfer

INTRODUCTION

Rubber-toughened plastics are materials designed for good impact resistant property. The discovery that brittle plastics can be toughened by the addition of a minor portion of rubber has aroused paramount interest in research that led to the commercialization of high-impact thermoplastics.^{1–5} One of the leading commodity thermoplastic materials is high-impact polystyrene (HIPS).

Several methods for incorporating rubber into polystyrene (PS) matrix are known. Besides the melt blending technology, the *in situ* polymerization technique has been well proven to be an attractive method for producing HIPS.^{1,2,6} In this process, polymerization of styrene containing 5–10% of dissolved butadiene-based rubber takes

place thermally under shearing agitation. While PS is forming, phase separation occurs that finally produces multiphase morphology (i.e., the discrete rubber particles having a complex structure containing numerous PS occlusions disperse in the PS matrix). The proposed mechanisms for toughening rely mainly on the dispersion of rubber particles within the glassy matrix that results in energy absorption by the rubber particles, debonding at the rubber–matrix interface and crazing. Many factors (i.e., amount of rubber added, type of rubber, size and morphology of the rubber particles, rubber phase volume, degree of adhesion of the rubber to the matrix, relaxation behavior of rubber, and composition of matrix) are believed to play a significant role in the improved impact performance of HIPS.^{1,2,7–13}

Emulsion polymerization has been widely used for producing rubber particles that was further applied to toughen the glassy plastics. Polymers in the form of emulsion or latex are usually easy to handle and, moreover, the morphology of each latex parti-

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cle can initially be designed.^{10–18} The multilayer latex particles are prepared by sequential emulsion polymerization in which seed particles are first formed and then grown in either two or three stages. This can increase not only the particle size of the rubber latex (which is normally too small) for effective toughening, but also the adhesion of the rubber phase to the matrix for satisfactory stress transfer. However, the overall process of coagulation by the addition of precipitating agent, filtration of the precipitate, wash with water, and then dry prior to blending with solid polymer matrix by using extruder and finally compression-molding^{10–14} has proved to be cumbersome. Therefore, a more convenient method was required; one that involved the emulsion polymerization/phase transfer/suspension polymerization process for the preparation of high-impact poly(methyl methacrylate) (HIPMMA).¹⁵ In the phase transfer technique, the negatively charged crosslinked synthetic rubber particles are titrated with an aqueous solution of cationic surfactant in the presence of a MMA monomer. At a critical transfer concentration (CTC), the hydrophobic layer is formed and the rubber particles transfer from the aqueous phase into the MMA phase. HIPMMA was obtained by using the suspension process for polymerizing the MMA monomer containing transferred rubber particles. It was noted that many stages normally required for the preparation of toughened particles from rubber latex (such as coagulation, filtration, washing and drying or dissolving rubber solid in monomer) were omitted.

Natural rubber (NR) latex was also studied for its use as an impact modifier of several polymers.^{16–18} Due to its broad particle size distribution, the existence of large size and high molecular weight,¹⁹ the NR latex particle might be suitable for the improvement of toughness of glassy polymers, including PS. However, in previous works,^{16–18} many steps for the preparation of the HIPS incorporated with the composite NR-based latex particles were required (e.g., the PS subinclusions within NR latex particles were synthesized by multistages and the hard shell encapsulating the soft rubber core was needed for the continuous blending process in a twin screw extruder). We now report the investigation of an attractive method for the preparation of HIPS based on NR. The key steps involve the use of γ -radiation vulcanized natural rubber (RVNR) latex/phase transfer/bulk polymerization. The phase transfer technique has been successfully used to transfer noncrosslinked, γ -radiation vul-

canized and deproteinized NR latex particles from the aqueous phase into the styrene monomer phase.^{20–22} Not only the easily transfer behavior, but the RVNR latex also exhibits an ingredient-free nature and the unaltered rubber phase morphology and particle size due to the crosslinked structure; hence, it was selected for our study. The styrene monomer containing transferred RVNR particles was polymerized in bulk form. Major factors (such as total irradiation dose, rubber content, and initiator concentration affecting the polymerization process, properties, and morphology of rubber-toughened PS prepared) are presented.

EXPERIMENTAL

Reagents Used

Styrene (Fluka, puriss) and *n*-butyl acrylate (Fluka, purum) monomers were purified by passing through an aluminum oxide column. Carbon tetrachloride (Merck, GR), toluene (Merck, GR), benzyldimethylhexadecylammonium chloride (Fluka, purum), and other reagents were used without special purification.

RVNR Latex

Irradiation of NR Latex

Concentrated high ammonia preserved NR latex having ~ 60% dry rubber content, purchased from Rayong Bangkok Rubber Co. Ltd. (Rayong, Thailand), was first filtered with 250 mesh aluminum screen and diluted with 1% (w/w) ammonia solution to 50% dry rubber content. The 10% aqueous potassium hydroxide solution (4 parts per hundred of rubber; phr) was then added to enhance latex stability. After 10–15 min, the sensitizers (i.e., *n*-butyl acrylate and carbon tetrachloride) were gradually added with gentle stirring for 2 h. The mixture in a 250 mL glass bottle was finally left overnight before being subjected to radiation from ⁶⁰Co γ -ray source (Gammacell 220). The irradiation vulcanized conditions are given in Table I.

Particle Size Measurement

The particle size distribution of RVNR latex was measured by using a laser particle size analyzer (Mastersizer S, Malvern).

Table I Irradiation Conditions Used for Vulcanization of NR Latex

NR latex	Concentrated HA
Radiation source	^{60}Co , 5.47×10^{14} Bq
Temperature ($^{\circ}\text{C}$)	25
Dose rate (kGy h^{-1})	9.6
Total dose (kGy)	Vary
Sensitizers	(a) <i>n</i> -butyl acrylate (10 phr) (b) CCl_4 (1 phr)

Determination of Swelling Ratio

Dried rubber sheets were prepared by spreading the RVNR latex on glass plates at room temperature. The thin sheets were cut into small pieces (1 g) and then immersed in toluene (150 mL) until the swelling reaches equilibrium. The swelling ratio of crosslinked rubber was calculated from

$$\% \text{ Swelling ratio} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weights of the sheets before and after swelling, respectively.

Phase Transfer Procedure

RVNR latex (15 g) having 6% solid content was diluted with distilled water (45 g) in an Erlenmeyer flask. A styrene monomer (30 g) was added, and the mixture was then titrated with an aqueous solution of benzyldimethylhexadecylammonium chloride (5 gL^{-1}), according to the method previously described in detail.²¹ The CTC (which is the number of moles of surfactant used per gram of dry latex) of RVNR latex was subsequently determined by the following equation

$$\text{CTC} = \frac{V \times C}{10 \times \text{TSC} \times m} \quad (2)$$

where V is the quantity of used cationic surfactant at titration endpoint (mL), C is surfactant concentration (mol L^{-1}), TSC is the total solid content of latex (%), and m is the weight of the latex sample (g).

Bulk Polymerization

A known amount of RVNR latex was transferred into the styrene monomer and allowed to swell for 24 h at room temperature. The styrene containing swollen transferred rubber particles was gently

centrifuged by using a Supraspeed Centrifuge (Sorvall RC 28S, Du Pont) to eliminate trace of water before the addition of a benzoyl peroxide (BPO). The mixture was poured into a Teflon-coated steel mold ($10.4 \times 10.4 \times 2.6$ cm) and then heated in an oven at 70°C . The mixture was also poured into closed test tubes for determination of polymerization of the styrene monomer in the presence of transferred rubber at various time intervals. The % conversion of PS was calculated from,

$$\% \text{ Conversion} = \frac{W}{W_t} \times 100 \quad (3)$$

where W_t is the weight of sample collected at time t and W is the constant weight of the sample after removing the remaining monomer by evacuation at room temperature.

Determination of Properties and Morphology

Impact resistance of unnotched sample ($63.5 \times 12.7 \times 3.2$ mm) according to ASTM D4812-93 was measured by using an Izod apparatus (Zwick 5102) while hardness (Zwick DIN 53505) was measured in accordance with ASTM D2240-95. The average value of 10 specimens was reported for each measurement.

Morphology of rubber-toughened PS was conducted on a transmission electron microscope model H 300 (Hitachi). Specimens were prepared according to the osmium staining principle.

RESULTS AND DISCUSSION

Characterizations of RVNR Latex

From particle size measurements, the volume distribution curve of the RVNR latex (14 kGy) is shown in Figure 1.

As expected, the histogram in Figure 1 indicates a broad particle size distribution of the RVNR latex. The volume diameter of the latex ranges from 0.2 to $1.4 \mu\text{m}$ where the volume average particle size is $0.7 \mu\text{m}$. Data obtained agreed with the typical data that indicated the naturally polydispersed rubber particles in the NR latex.¹⁹ Concerning the size of rubber for toughening of PS, several works reported that there is an optimum size in the range of $1\text{--}4 \mu\text{m}$ for maximum impact resistance of HIPS prepared by solution polymerization.^{11,23} However, by using this

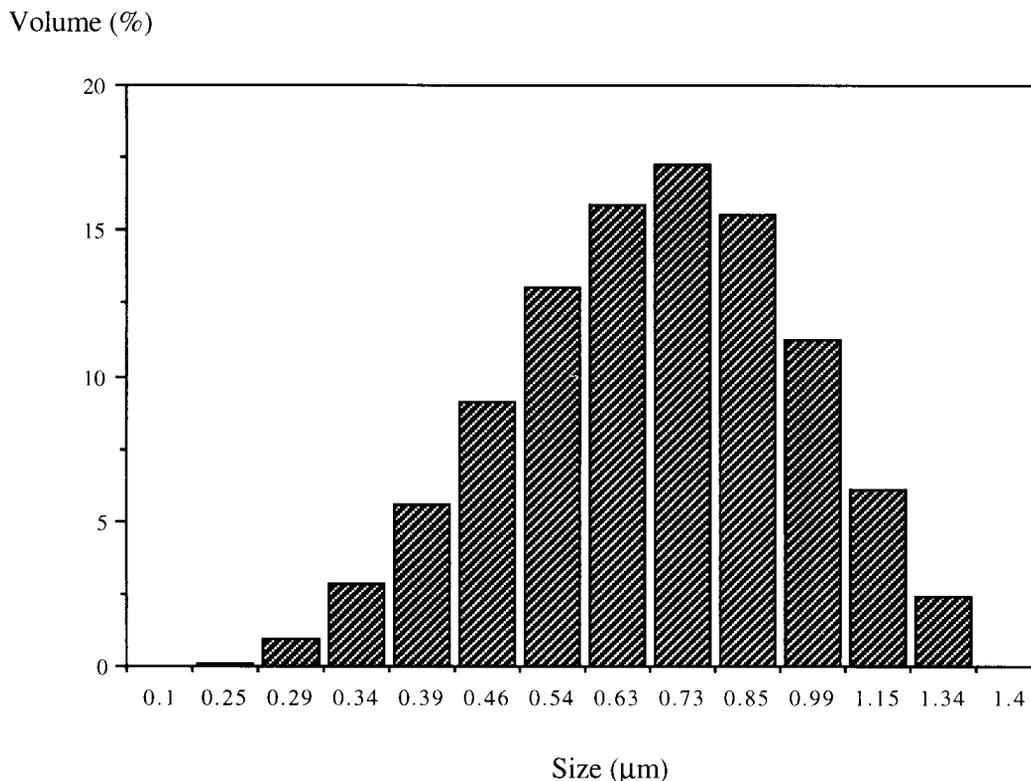


Figure 1 Particle size distribution, by volume, of RVNR latex (14 kGy).

method, HIPS has a broad distribution of rubber phase and the internal particle morphology often changes with size. When using emulsion polymerization, it was found that monodisperse particles in the 2- to 3- μm diameter range gave optimum impact toughness.¹¹ Recently, a bimodal rubber parti-

cle distribution with a population of small and large particles in HIPS has been shown to be more effective than a monomodal distribution.²⁴ It has

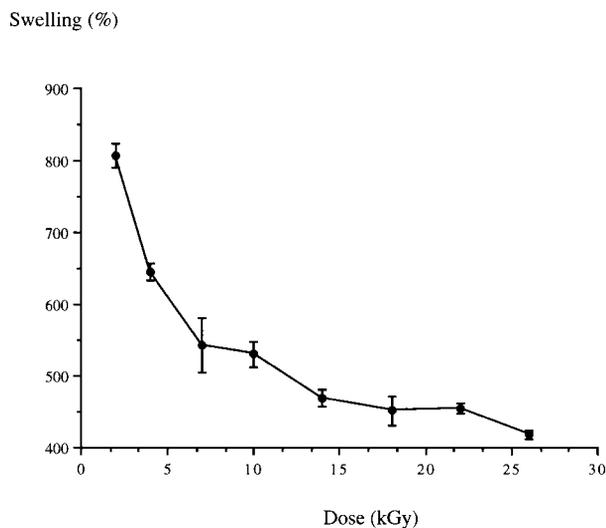


Figure 2 Effect of irradiation dose on swelling ratio of rubber sheet prepared from RVNR latex.

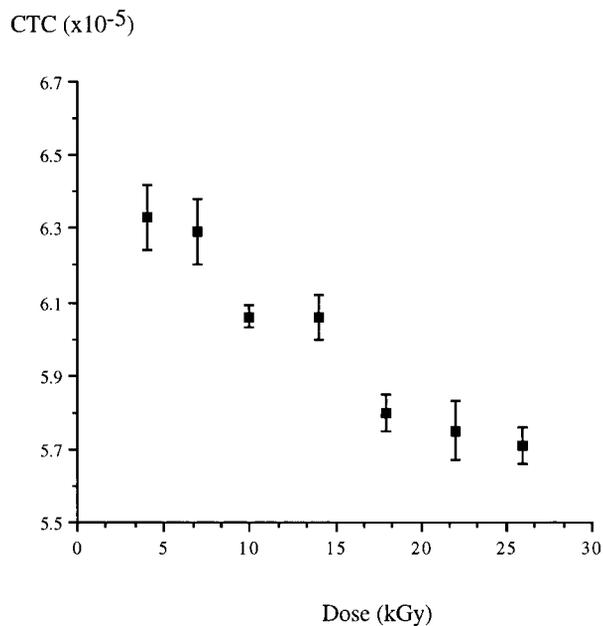


Figure 3 CTC values of RVNR latex irradiated with various doses.

Table II Effect of Quantity of Transferred Rubber on the CTC Values (mol of Surfactant Per g of Dried Latex) of the RVNR Latex (14 kGy)

Rubber in Styrene (% w/w)	CTC ($\times 10^{-5}$)
3	5.55 ± 0.03
4	5.57 ± 0.01
5	5.53 ± 0.02
6	5.56 ± 0.03

been explained that the small particles (below $1 \mu\text{m}$) initiate crazes and the large ($> 1 \mu\text{m}$) stop and control the propagation of damage.

In our work, it was noticed that the range of rubber particles in the RVNR latex was slightly too small to effect toughening of PS. It should be mentioned that, when the phase transfer technique was adapted in the next step, the size of crosslinked particles would increase after swelling in the styrene. The increase in swollen RVNR particles should normally depend on the crosslinking density of the rubber. Therefore, the swelling ratio of the dried rubber sheet prepared from the RVNR latex irradiated with various doses was measured. The swelling ratio of the rubber sheet was plotted as a function of irradiation dose in Figure 2.

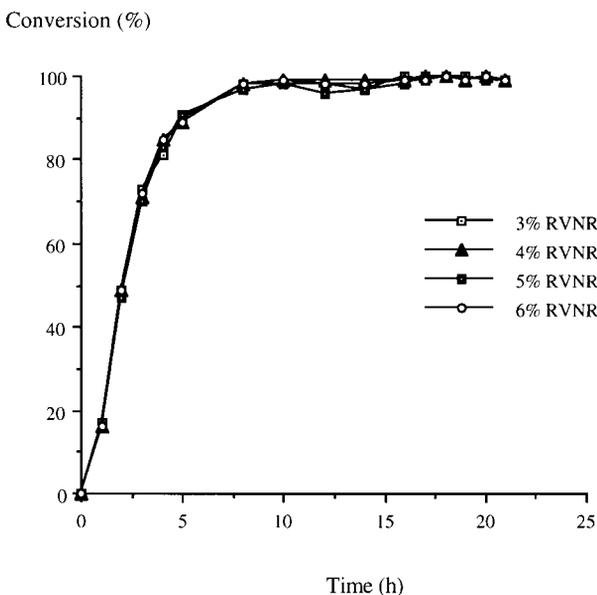


Figure 4 Effect of quantity of transferred RVNR (14 kGy) on % conversion of styrene polymerized at 70°C using 1% of BPO as an initiator.

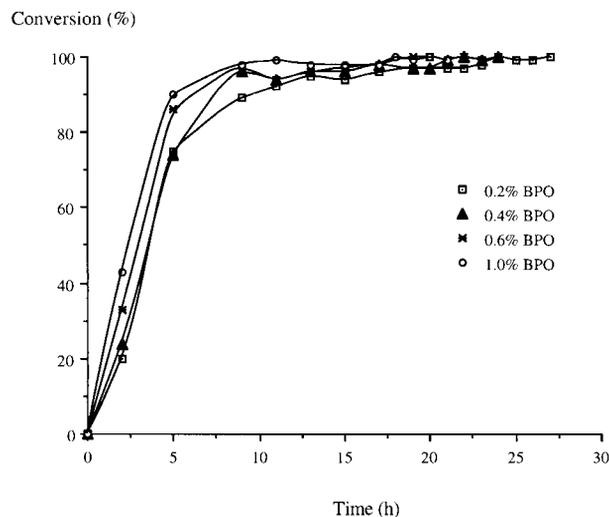


Figure 5 Effect of concentration of initiator (BPO) on % conversion of styrene containing 3% of transferred RVNR (14 kGy) polymerized at 70°C .

It can be seen that the equilibrium swelling ratio, which is inversely proportional to crosslinking density, of the RVNR sheets abruptly decreased with increasing dose from 2 to 14 kGy. Above 14 kGy, a relatively small change in the swelling ratio was found (i.e., the maximum crosslinking of NR latex would be attained). The radiation-induced crosslinking rubber may be expected to have different effects on the toughening mechanism.

Effect of Irradiation Dose and Rubber Content on CTC Values

In a previous paper,²¹ the phase transfer technique has been used to characterize the surface of RVNR latex. The optimum conditions of the tech-

Table III Effect of Irradiation Dose of RVNR Latex on Unnotched Izod Impact Resistance and Indentation Hardness of the Rubber-Toughened PS (Using 3% RVNR, 1% BPO at 70°C)

Irradiation Dose (kGy)	Impact Resistance (kJ m^{-2})	Hardness (Shore D)
10	1.9 ± 0.2	82.1 ± 0.4
14	2.4 ± 0.6	82.4 ± 0.4
18	2.1 ± 0.7	81.9 ± 0.4
26	2.0 ± 0.3	82.4 ± 0.7

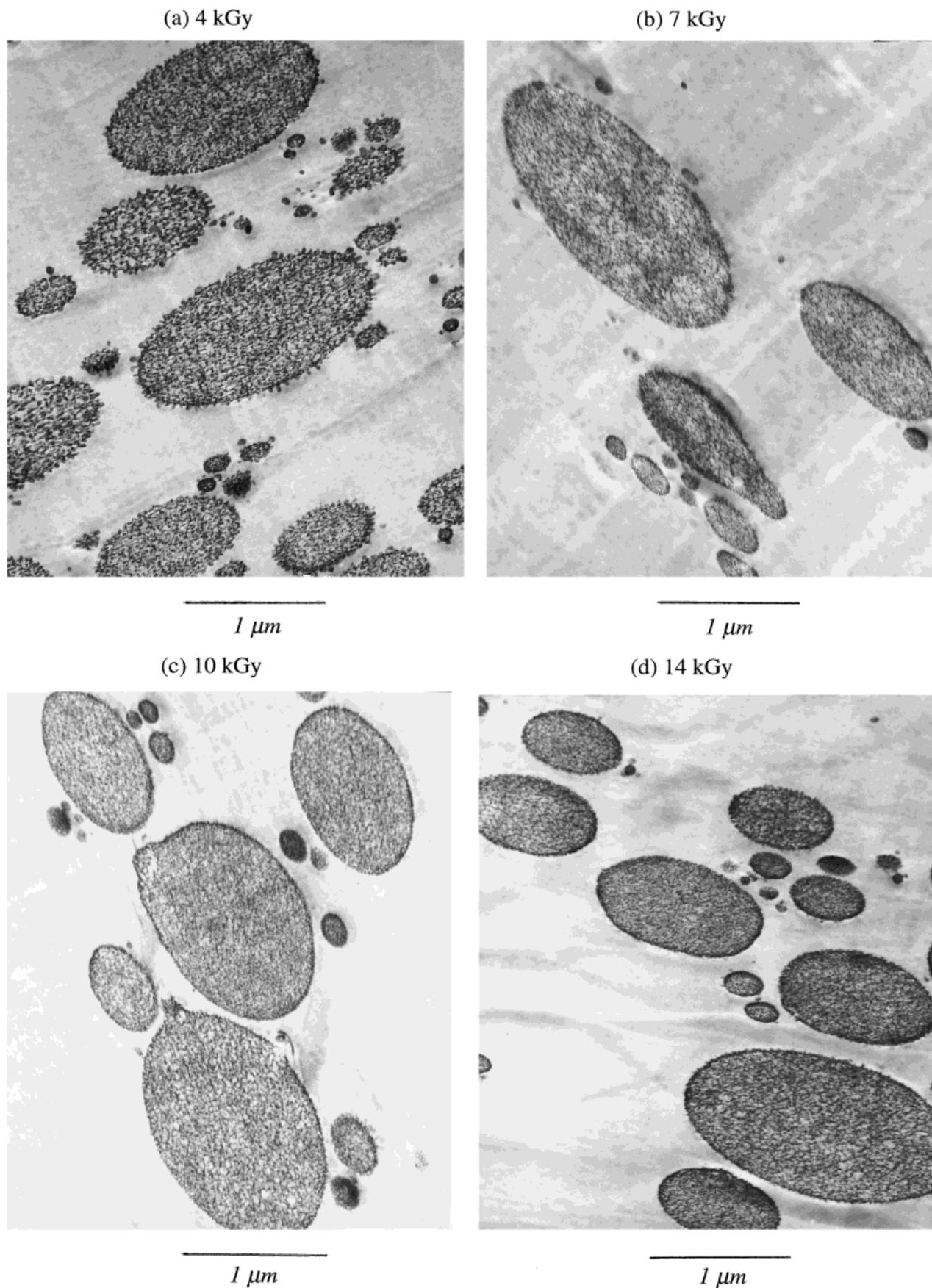


Figure 6 TEM of toughened PS based on RVNR irradiated with: (a) 4 kGy, (b) 7 kGy, (c) 10 kGy, (d) 14 kGy, (e) 18 kGy, and (f) 26 kGy.

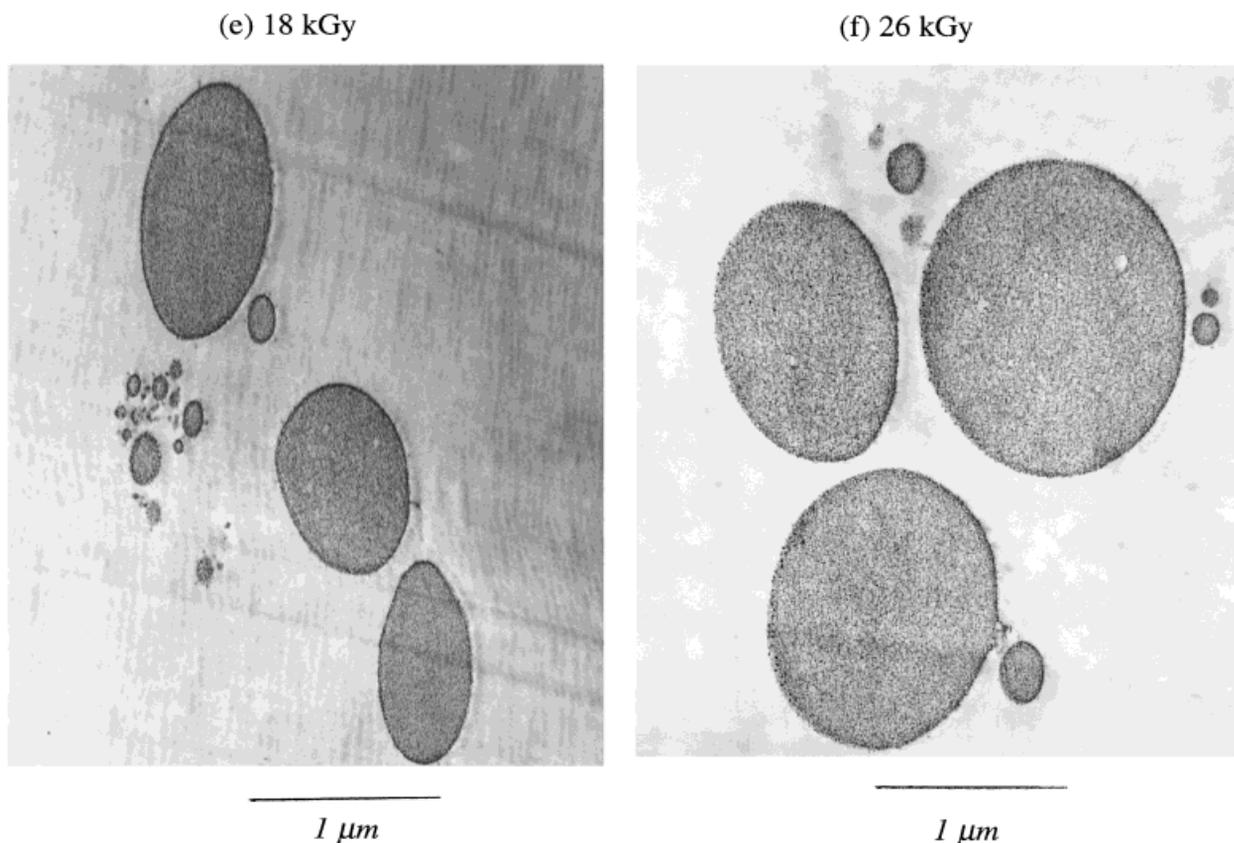


Figure 6 (Continued from the previous page)

nique (i.e., effect of organic solvents, including styrene monomer, solid content of the NR latex, and volume fraction of the organic phase) have already been studied. In this work, this technique was applied for the preparation of toughened PS based on RVNR latex. Other factors (i.e., the amount of dose used for irradiation of rubber and the rubber content that may have direct influence on the CTC values of the latex) were investigated. Latex samples were titrated at pH 9, with an aqueous solution of benzyldimethylhexadecylammonium chloride by using styrene as the organic phase. The effect of irradiation dose used on the CTC values of RVNR latex (3%) is shown in Figure 3.

The results from Figure 3 indicated that the CTC values of the RVNR latex depended on the irradiation dose used. The CTC values decreased when increasing of the irradiation dose corresponding to an increase in the crosslinking density of rubber. It can be explained that the highly crosslinked rubber particles would slightly swell in the styrene monomer and, consequently, expose less surface charges than those in the case of

the lightly crosslinked. The higher the irradiation dose used, the lower the quantity of the added cationic surfactant for neutralization of the negative charge on the surface of RVNR particles required and, hence, the decrease in CTC values.²⁰

The effect of rubber content on the CTC values of RVNR latex irradiated with 14 kGy is shown in Table II. These values are reproducible and do not depend on the quantity of rubber transferred (3–6% w/w).

Bulk Polymerization of Styrene-Containing Transferred RVNR

The styrene monomer containing 3, 4, 5, or 6% transferred RVNR latex (14 kGy) was polymerized at 70°C using 1% BPO as an initiator. The % conversion of these samples at different polymerization times was determined to find the suitable conditions for further preparation of toughened PS. The effect of rubber content on the amount of polystyrene formed is shown in Figure 4.

It can be seen that the % conversion of the styrene promptly increased in the initial periods

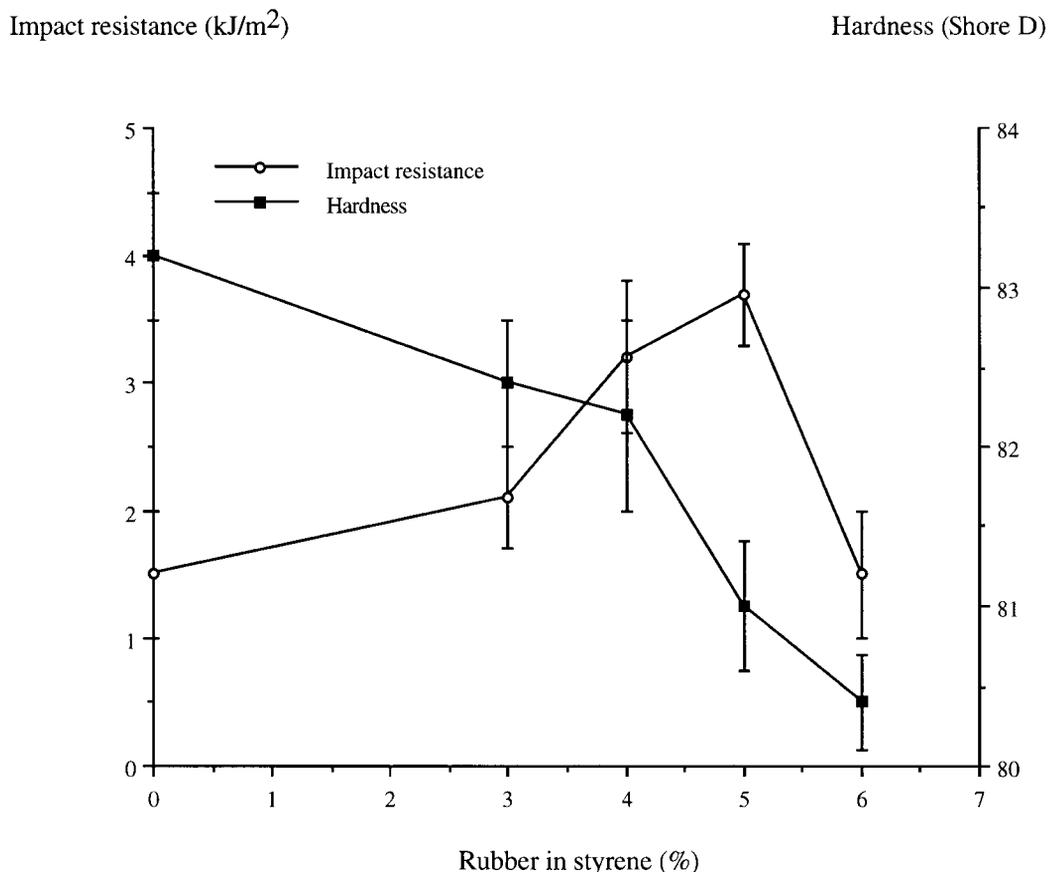


Figure 7 Unnotched Izod impact resistance and hardness (Shore D) of toughened PS based on RVNR latex (14 kGy) as a function of the rubber content.

of polymerization until it approached a constant value of 100% within ~ 16 h. It is apparent that the polymerization rate of PS was relatively insensitive to the observed rubber content.

The effect of initiator concentration (0.2, 0.4, 0.6, or 1% of BPO) on the % conversion of the styrene containing 3% of RVNR (14 kGy) at various polymerization times is displayed in Figure 5. It was found that, when the amount of BPO increased, the polymerization rate slightly increased. However, for all initiator concentrations, 100% conversion of PS was obtained within ~ 16 h.

Properties and Morphological Studies

The unnotched specimens placing a greater emphasis on ductility before crack initiation having the advantages of being easily and rapidly performed were tested in our experiments. This rudimentary approach allows only the comparison of different materials.

Because the properties and morphology of the toughened PS based on RVNR obtained from the latex/phase transfer/bulk polymerization process has never been studied, many factors influencing the impact property and also indentation hardness of the materials prepared were, therefore, investigated. The morphology of specimens was also studied under transmission electron micrograph (TEM).

Effect of Crosslinking Density of Rubber Particles

From the results in Figure 2, the crosslinking density of rubber was directly proportional to the amount of irradiation dose used. After transfer, the difference in the ability of styrene monomer to swell the rubber particles crosslinked with various irradiation doses might cause the difference in rubber volume phase and the amount of PS occlusions in the final toughened PS.

Because it was practically difficult to separate clearly the styrene phase containing the highly

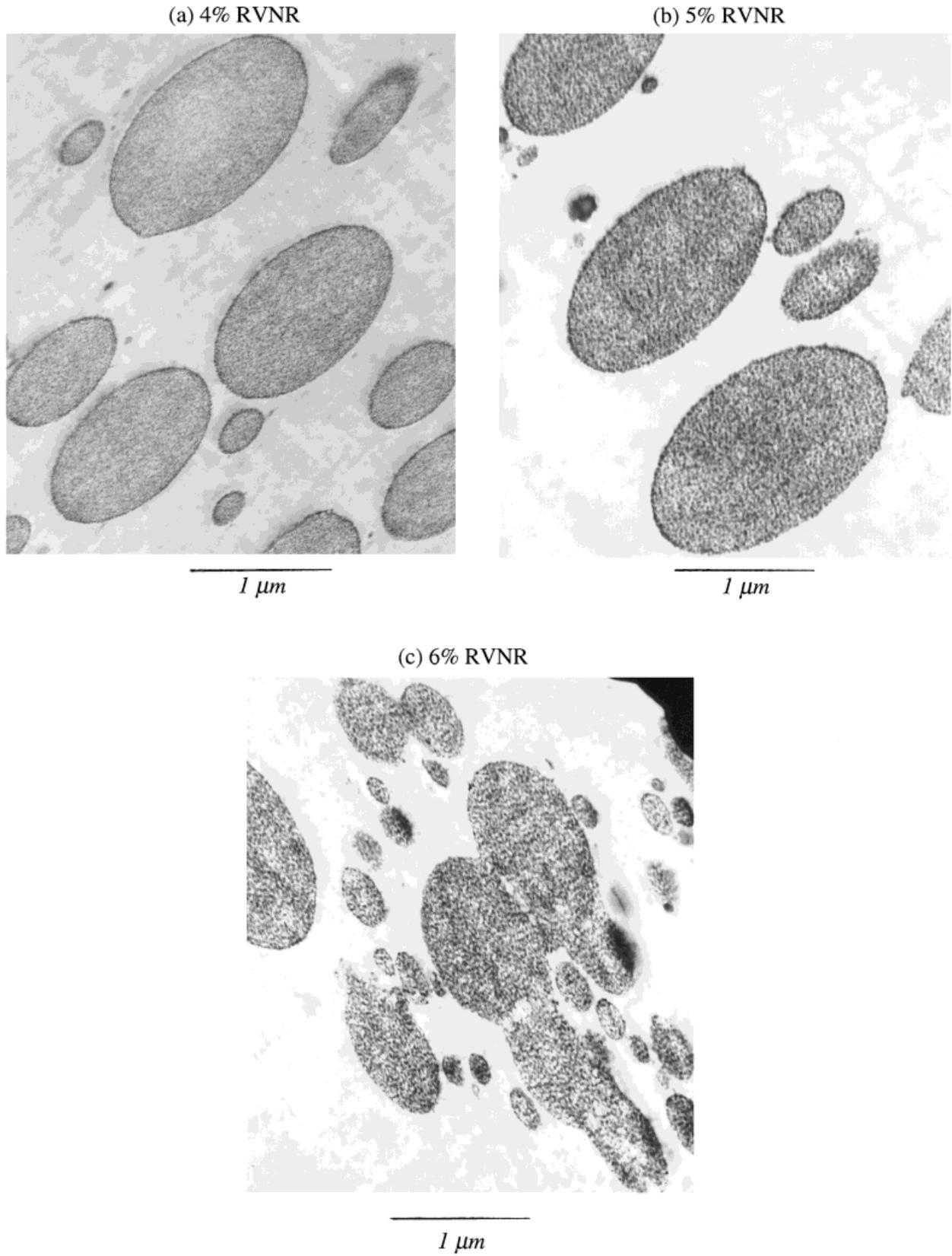


Figure 8 TEM of toughened PS based on RVNR: (a) 4%, (b) 5%, and (c) 6%.

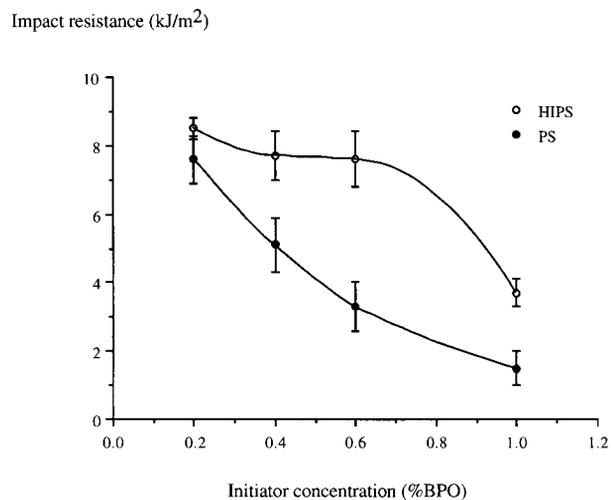


Figure 9 Effect of concentration of BPO on unnotched Izod impact resistance of unmodified PS and toughened PS (5% of RVNR, 14 kGy) polymerized at 70°C.

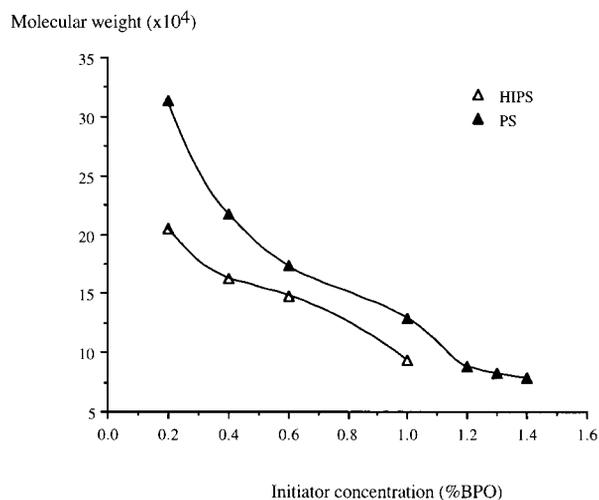


Figure 10 Molecular weight, determined by gel permeation chromatography, of dissolved modified PS and PS extracted from toughened PS prepared by using various concentrations of BPO.

(a) 0.2% BPO



(b) 0.4% BPO

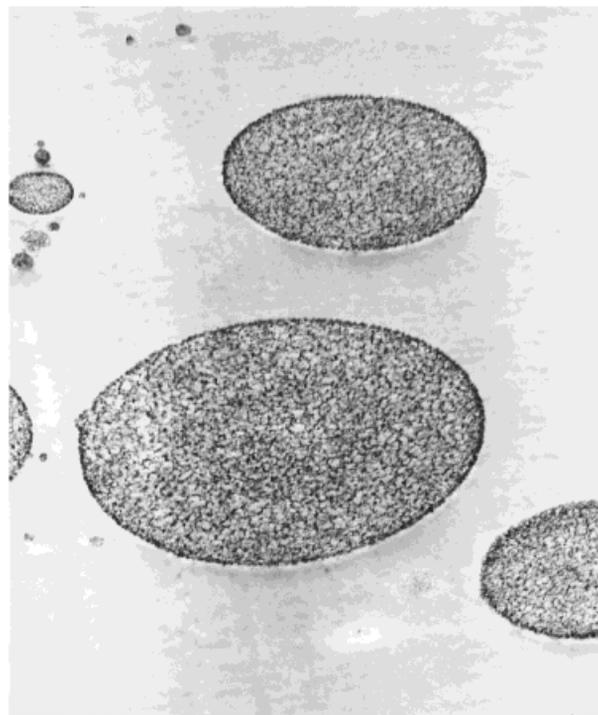
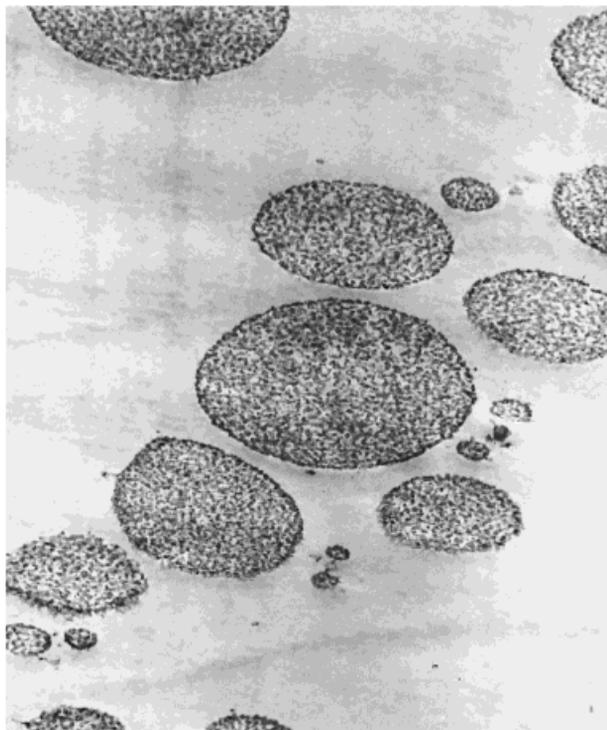


Figure 11 TEM of toughened PS based on RVNR using BPO: (a) 0.2%, (b) 0.4%, and (c) 0.6%.

(c) 0.6% BPO

1 μm **Figure 11** (Continued from the previous page)

swollen rubber particles obtained by irradiation dose below 10 kGy, we therefore used RVNR latex irradiated with 10, 14, 18, and 26 kGy for the preparation of the rubber-toughened PS. Data of the unnotched Izod impact resistance and indentation hardness are presented in Table III.

Table III shows the insignificant effect of irradiation doses used on both properties. It was believed that the fully crosslinked of rubber particles was obtained when the irradiation dose was >10 kGy, as observed in Figure 2. Consequently, the rubber volume phase and the amount of PS occlusions in the toughened PS prepared using RVNR latex in the dose range (10–26 kGy) might be similar. The impact resistance obtained seemed to be low, which might be due to the low content of rubber incorporated. However, it is noted that the use of 14 kGy produced the highest impact of materials and, therefore, this dose was used for subsequent experiments in this investigation.

The TEMs showing contrast between PS (light) and rubber (dark) of toughened PS based on RVNR

(3%) irradiated with various doses are illustrated in Figure 6. Two-phase morphology of rubber-toughened PS prepared from the emulsion/phase transfer/bulk polymerization process in our study was similar to that of commercial HIPS.²⁵ The broad distribution of size and shape of NR particles containing occluded PS, dispersed in PS matrix, was clearly seen. Figure 6(c–e) indicated the existence of membrane layer around particles, derived from the protein–lipid complex,^{19,26} whereas the boundary of membrane seemed to be relatively undetermined in Figure 6(a,b). This may be due to the fact that the use of 4 and 7 kGy produced lightly crosslinked rubber that greatly swelled in the styrene monomer and, hence, the membrane was partially broken. Furthermore, by comparing Figure 6(a) with Figure 6(e,f), it can be noted that the high crosslinking density of rubber particles occurred when irradiated with high dose. The results showed the similar trend to those of swelling ratio in Figure 2. It should be noted that the characteristics of the crosslinked rubber network determined the domain size of occluded PS, which is, in turn, responsible for the impact property of those normally found in the interpenetrating polymer networks technique.²⁷

Effect of Rubber Content

Figure 7 plots the unnotched Izod impact resistance and hardness of the toughened PS based on RVNR latex (14 kGy) as a function of the rubber concentration.

An increase in the impact energy of the toughened PS prepared over the unmodified PS was generally observed. As presented in Figure 7, there existed an optimum rubber content at 4–5% of rubber for maximum impact resistance attainable. Besides this concentration, the unnotched Izod impact resistance slightly improved over the base matrix. A possible reason for this behavior was that, at lower rubber contents, the energy abstracted from the crack during propagation was not sufficient to withstand the complete fracture of the specimen,¹ whereas the higher rubber loadings might affect the interparticle spacing in the matrix. Consequently, the 5% RVNR was further used to prepare toughened PS in our study.

The micrographs of toughened PS, based on 3, 4, 5, and 6% of RVNR were illustrated in Figure 6(d) and in Figure 8(a–c), respectively, whereas the rubber particles with occluded PS embedded in the PS matrix were apparent. The fused rubber particles were only found in Figure 8(c), where 6% of rubber was used.

Figure 7 also showed the hardness values of the materials plotted against rubber concentration. As expected, the hardness was found to decrease with an increase in rubber concentration (i.e., the glass transition temperature of rubber-toughened PS could be lowered).

Effect of Initiator Concentration

The effect of initiator concentration (0.2, 0.4, 0.6, and 1% of BPO), using for polymerization of styrene containing 5% of RVNR (14 kGy) on impact resistance of unmodified PS and toughened PS, was studied. Data measured are presented in Figure 9.

From Figure 9, it can be seen that the impact resistance of both PS and toughened PS decreased with an increase in the initiator concentration. It can be explained by considering the molecular weight of PS matrix. It was reported that the molecular weight of the PS matrix is also an important parameter in improving impact strength due to its influence on the crazing mechanism in HIPS.¹⁰ A higher molecular weight polymer gives the fibrils a greater degree of stability, compared with those of lower molecular weight PS because of its greater entanglement density. It is well known that the molecular weight of the polymer formed from the free radical polymerization is inversely proportional to the initiator concentration. Therefore, we used the gel permeation chromatographic method (Millipore Water 150CV) for determination of the molecular weight of the dissolved unmodified PS and PS extracted from the toughened PS previously prepared. The results are shown in Figure 10, which indicated that the molecular weight of unmodified PS was higher than that of the PS extracted from the toughened materials. When the percentage of BPO was increased, the molecular weight of PS obtained decreased; this might attribute to the decline of impact properties of both materials.

For all initiator concentrations used, it was observed that the impact resistance of toughened PS (HIPS), based on RVNR, was higher than that of the unmodified PS. It was concluded that the RVNR could be used as a toughening agent for improving the impact resistance of PS despite the fact that the presence of RVNR reduced the length of PS chains.

The effect of concentration of BPO on the morphology of toughened PS was also studied, as illustrated in Figure 8(b) and in Figure 11(a–c).

The size of occluded PS in the rubber particles seemed to be larger in Figure 11(a) (using 0.2% BPO), compared with the other micrographs. This might be due to the fact that the polymerization rate of PS in the presence of RVNR was proportional to the BPO concentration as previously seen in Figure 5. Thus, at 0.2% of BPO used, the styrene monomer could penetrate and swell in the rubber particles for a longer period. When PS was polymerized, the network of crosslinked polyisoprene might be better separated because of incompatibility of PS formed and the rubber phase. The greater occlusion size showed in Figure 11(a) might play an important role in the higher impact of HIPS.

CONCLUSIONS

The emulsion polymerization (latex)/phase transfer/bulk polymerization process could be used as a method for preparation of toughened PS based on NR latex. The RVNR latex was transferred from the aqueous phase into the styrene monomer, and the toughened PS was obtained when the styrene monomer containing rubber-swollen particles was polymerized in bulk form. The irradiation dose is responsible for the control of the crosslinking density of the rubber particles and consequently the size of occluded PS in the PS matrix. The dose also influenced the CTC values of the RVNR latex, whereas the rubber concentration seemed to have no significant effect. The toughened PS prepared exhibited the HIPS-like morphology, and their impact energy was generally higher than that of the unmodified PS. The unnotched Izod impact resistance of the toughened PS prepared depended on the rubber content and the amount of initiator. Samples prepared from 5% of RVNR showed maximum impact resistance, whereas the use of a smaller quantity of initiator producing the higher molecular weight PS matrix provided higher impact energy.

Although it is postulated that the impact property efficiency depends on the rubber–matrix adhesion and particle size distribution, among other factors, the process presented herein is very simple and herein lies its attraction. Accordingly, it seems particularly important to continue with this work, and further results will be reported.

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