

Characterization of Crosslinked Polystyrene Beads and Their Composite in SBR Matrix

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SYNOPSIS

Monodisperse crosslinked polystyrene (PS) beads were prepared by a reaction of semibatch emulsion polymerization with styrene monomer, divinylbenzene (DVB) crosslinking agent, and potassium persulfate ($K_2S_2O_8$) initiator in the absence of emulsifier. The glass transition temperature (T_g) and the mean diameter of the beads were increased from 100 to 135°C and from 402 to 532 nm, respectively, for an incorporation of 2–10 mol % DVB. Crosslinking density was also linearly increased with DVB content. Scanning electron microscopy (SEM) photographs of styrene–butadiene rubber (SBR) composite filled with various contents of PS beads revealed that PS beads are relatively well dispersed without changing the spherical shape of the beads in all ranges of compositions. In stress–strain analysis, elongation at break and tensile strength of SBR composite were increased with the bead content. Applicability of the PS beads as a filler in SBR matrix is tested by plotting Mooney–Rivlin or Guth–Smallwood equations. However, mechanical properties of the composite with the beads were not so excellent as those of the composite with carbon black. Crosslinked PS beads are still tentative as a white color reinforcing filler on the SBR matrix. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, rubber composite in engineering plastics is widely applied in various fields of automobile bumpers, interior, and so forth. Natural or synthetic rubber in its original state is not suitable for engineering applications since it is hard and brittle at low temperature and too soft at high temperature. An incorporation of reinforcing filler gives improved properties or processability of rubber composite, and thereby it can be used for industrial applications.¹ Fine particle sized carbon black is used as the most useful reinforcing filler on rubber based on low cost of production and improved mechanical properties. However, this system has a critical drawback owing to the black color of carbon black.² If rubber composite is possibly produced with improved properties, low cost of production and good colorability with reinforcing filler giving excellent

mechanical properties such as carbon black, the applied area of rubber composite would be much expanded.

Recently, Aklonis and Salovey synthesized monodisperse crosslinked polystyrene (PS) and poly(methylmethacrylate) (PMMA) beads by an emulsion polymerization of the monomer and crosslinking agents, in the absence of emulsifier. They suggested that these beads having various size and crosslinking density could be used as a filler in matrix of rubber composite.^{3–6}

In this article, monodisperse crosslinked PS beads were synthesized by a reaction of semibatch emulsion polymerization with styrene monomer, divinylbenzene (DVB) and potassium persulfate in the absence of emulsifier, and studied for an application as a filler. Styrene–butadiene rubber (SBR) composite filled with the beads was cured with sulfur and other fillers such as antioxidant or accelerator and characterized in terms of thermal properties and morphology. Mechanical properties of SBR composite filled with the beads and carbon black were extensively investigated for a comparison.

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Table I Curing Recipe by Weight (phr)

SBR	100
Filler ^a	Various ratio
Stearic acid	2
Zinc oxide	5
BHT	1
Accelerator	1.5
Sulfur	2

^a PS beads synthesized with various amounts of DVB.

EXPERIMENTAL

Materials

SBR was produced by Kumho Tire Company, Kwang-Joo, Korea, and compounded with various contents of PS beads. Technical-grade styrene monomer, divinylbenzene (DVB, 55% para- and meta-divinylbenzene, 42% ethyl-vinylbenzene, 3% diethylbenzene) and potassium persulfate were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, and used without further purification. Sodium hydroxide obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, was used to remove an inhibitor in the styrene monomer and DVB. Tetrahydrofuran (THF) purchased from EM Science, Gibbstown, New Jersey, for dynamic light scattering (DLS) was used without further purification. Sulfur powder was purchased from Shinyo Chemical Co., Osaka, Japan.

Synthesis of Crosslinked Monodisperse PS Beads

Crosslinked PS microbeads were prepared by a semibatch emulsion polymerization using styrene monomer and DVB crosslinking agent in the ab-

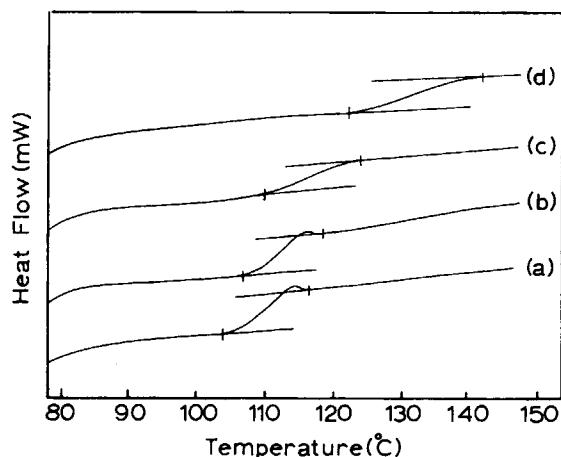


Figure 1 DSC thermograms of PS beads crosslinked with different DVB mol %: (a) 2, (b) 3, (c) 5, and (d) 10.

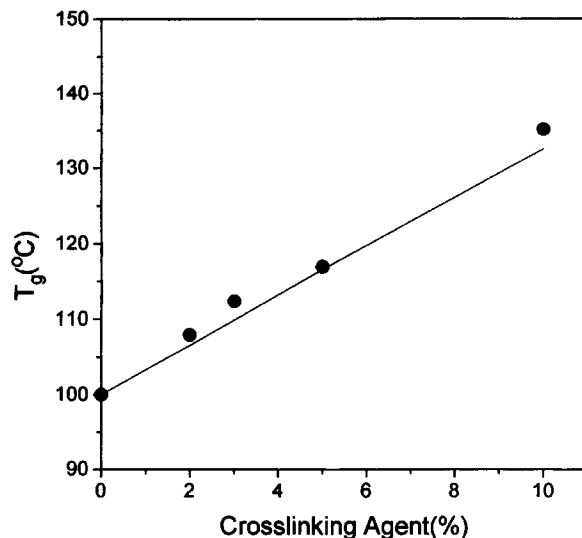


Figure 2 Dependence of the glass transition temperature on the content of DVB in PS beads. Solid line is calculated by Eq. (1).

sence of emulsifier. The synthetic process is modified in this laboratory from Ref. 3–6 and is as follows. Polymerization was conducted in a 600-mL reaction flask by stirring. In the beginning of the reaction, 0.3 g sodium chloride was added to control the ionic strength. After 15 min, prewashed styrene monomer was added to the flask and allowed to mix for 20 min to equilibrate. The ratio of DVB to monomer was controlled to 2–10 mol % and DVB was added dropwise into the flask, following the addition of 0.25 g of potassium persulfate dissolved in 50 g of distilled water. Polymerization was performed under constant conditions, at 350 rpm, 80°C for about 8 h. After reaction, the flask was removed from the water bath, latex of PS beads in water was emptied

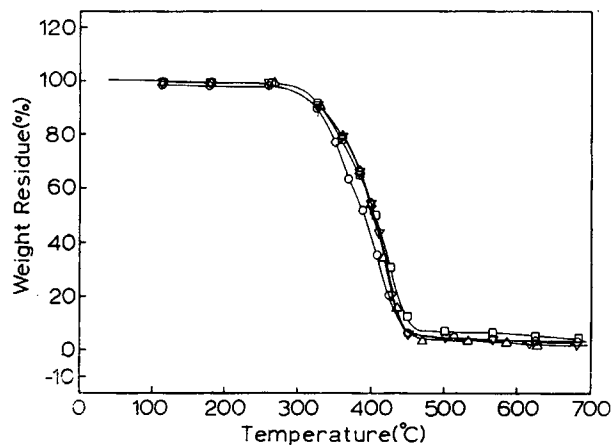


Figure 3 TGA thermograms of crosslinked PS bead in nitrogen atmosphere. DVB mol %: (O) 2, (∇) 3, (Δ) 5, and (□) 10.

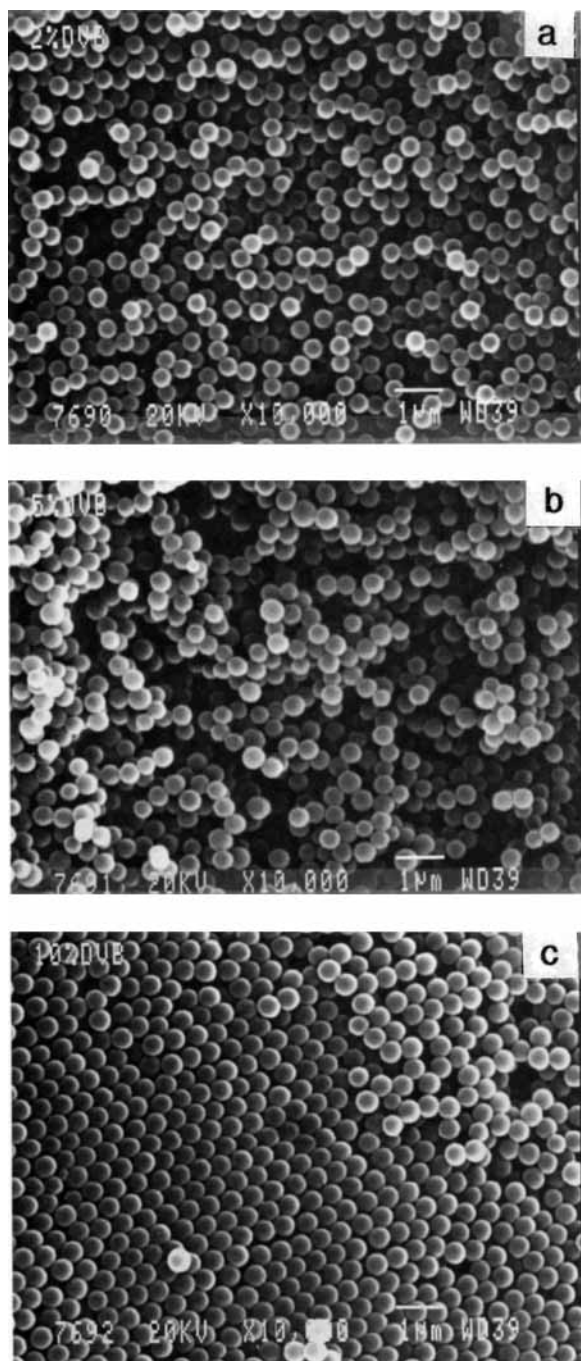


Figure 4 SEM microphotographs of synthetic PS beads crosslinked with DVB mol %: (a) 2, (b) 5, and (c) 10.

into a bottle and cooled to -15°C for 8 h. The cooled latex was melted at room temperature and then separated into two phases. Solid crosslinked PS beads were settled in the bottom, isolated by filtration through glass filter, and washed repeatedly with distilled water. In order to remove moisture and unreacted monomer, the wet solid was dried in a vac-

uum oven at 80°C for 24 h, yielding a fine white powder.

Compounding of SBR Composite

SBR composite with PS beads crosslinked with 10 mol % DVB was cured by the recipe given in Table I for consulting various sulfur systems.^{7,8} Compounding was conducted with twin-screw extruder. SBR was blended with stearic acid, zinc oxide, and 2,6-di-tert-butyl-4-methylphenol (BHT) antioxidant in order to avoid mechanical and thermal degradation of polymer beads in twin-screw extruder at $60\text{--}65^{\circ}\text{C}$ with 50 rpm for 10 min. Then appropriate amounts of fillers, 2,2'-dithiobis benzothiazole and sulfur were added for another 15 min at 100 rpm. After compounding, a composite specimen was formed to dimension in $1.2 \times 7.5 \times 78$ mm by compression molding under $200 \text{ kg}_f/\text{cm}^2$ pressure for 30 min in hot press which was preheated at 160°C . In addition, to compare the two different filler systems, SBR composite filled with carbon black was also prepared by the same recipe and procedure as the SBR with the beads.

Analysis

Differential scanning calorimetry (DSC) experiments were carried out using a Perkin-Elmer DSC-7 controlled by 7500 PC. PS beads were heated from 30 to 150°C at a heating rate of $20^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere, annealed for 5 min at 150°C and quenched to room temperature. The second scan was recorded out at the same heating rate as the previous scan up to 150°C and the glass transition temperature (T_g) was collected as a midpoint of the endothermic displacement between linear baselines.

A Polymer-Laboratories TGA-1000 was used to measure thermal stability of PS beads with various contents of DVB and SBR composite filled with various contents of the beads, under nitrogen atmosphere at a heating rate of $20^{\circ}\text{C}/\text{min}$ over a temperature range from 40 to 700°C .

In order to study the size and morphology of the dry beads, a drop of PS beads diluted with an equal volume of methanol was placed on a cover glass and dried with clean air at room temperature. Dried beads were coated with gold and palladium using a sputter coater, and the morphology of the beads was studied using a Phillips SEM-515. Fractured surface of SBR composite filled with 532-nm beads which was crosslinked with 10 mol % DVB was also coated using the same procedure as the previous one and used for a degree of dispersion of the beads.

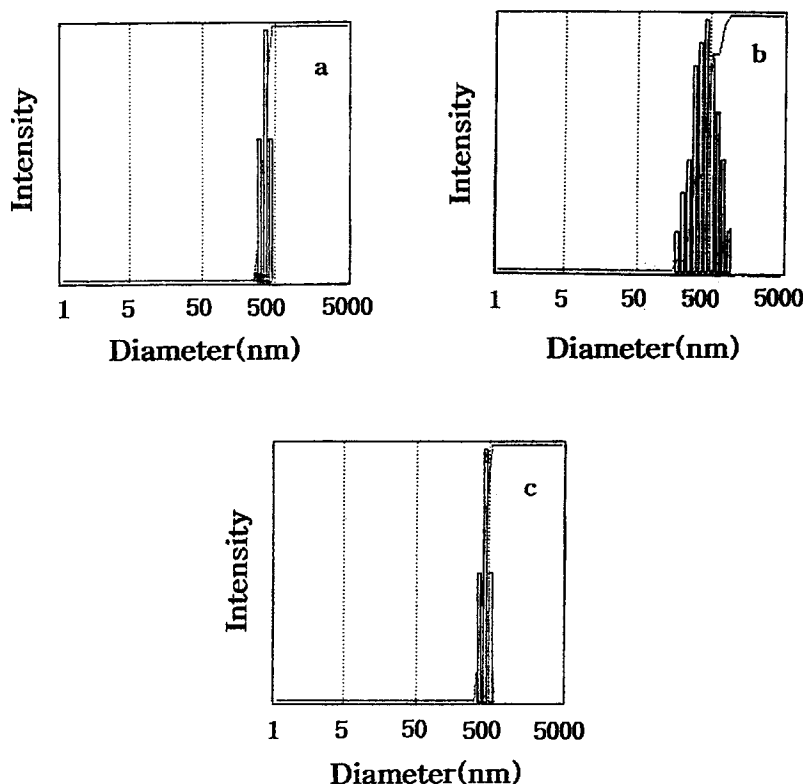


Figure 5 Particle size and its distribution of PS beads crosslinked with DVB mol %: (a) 2, (b) 5, and (c) 10.

The size and distribution of the swollen beads were also measured by DLS by the next procedure. A test tube was washed and soaked in H_2SO_4 for 2 days, dried in a vacuum oven and again soaked in liquid soap. Subsequently, it was washed with distilled water four times and dried in a vacuum oven at $100^\circ C$. Synthetic PS beads were dissolved in 0.005 wt % THF solution at a low stirring speed at room temperature for 24 h. DLS measurements for the swollen beads in THF was accomplished by using a BI 8000 AT (Brookhaven Instrument Corp.) with a He-Neon laser beam and a goniometer fixed at $90^\circ C$. Individual measurement was performed every 2 s for about 34 min total. The particle size of the swol-

len beads was determined and compared with that of the dry beads by SEM.

Crosslinking density (q) of the beads was calculated by the following measurement. In order to correct the solvent, which was absorbed in the beads surface or which was contained within the voids between beads prior to swelling, crosslinked PS beads dissolved in solvent were extracted; 0.2 g of the crosslinked beads was swollen in toluene ($d = 0.866$) for 24 h at $25^\circ C$. Subsequently, ultrafiltration membrane was weighed, and after filtration of the swollen solution for 2 min, it was immediately weighed. The ultrafiltration membrane was reweighed after vacuum drying at $80^\circ C$ until constant weight was ob-

Table II Crosslinking Density of PS Beads^a

DVB Content (mol %)	ρ_p	ψ_p	χ_{12}	\bar{M}_c	q (mol %)
2	1.0907	0.229	0.3578	5.190×10^3	2.004
3	1.0920	0.277	0.3422	3.128×10^3	3.32
5	1.0954	0.327	0.3255	1.982×10^3	5.25
10	1.0972	0.401	0.3005	1.036×10^3	10.04

^a Swelling temperature, $25^\circ C$; solvent, toluene.

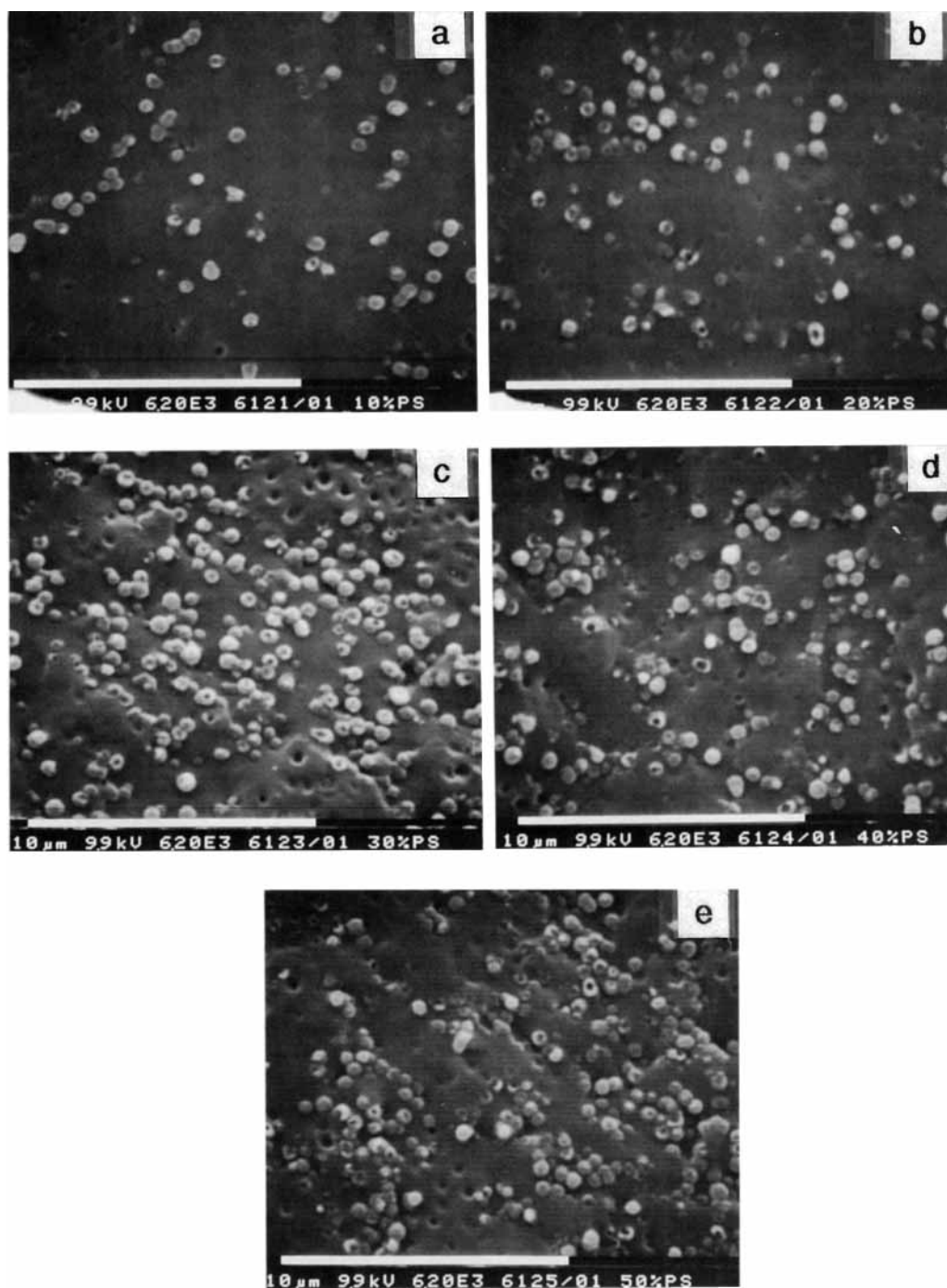


Figure 6 SEM microphotographs of fractured surface of SBR composite filled with PS beads crosslinked with 10 mol % DVB. PS bead content: (a) 10 phr, (b) 20 phr, (c) 30 phr, (d) 40 phr, and (e) 50 phr.

tained. Thus, the weight of the dry beads, m_p , and that of the beads including solvent at equilibrium, $m_{p,a}$, were measured. These values were used to calculate the volume fraction of polymer beads (φ_p), polymer-solvent interaction parameter (χ_{12}), and

average molecular weight between crosslinking networks (\bar{M}_c), followed by crosslinking density (q).

Dynamic mechanical thermal analysis (DMTA) of SBR composite filled with the beads and carbon black was carried out by using a Polymer-Labora-

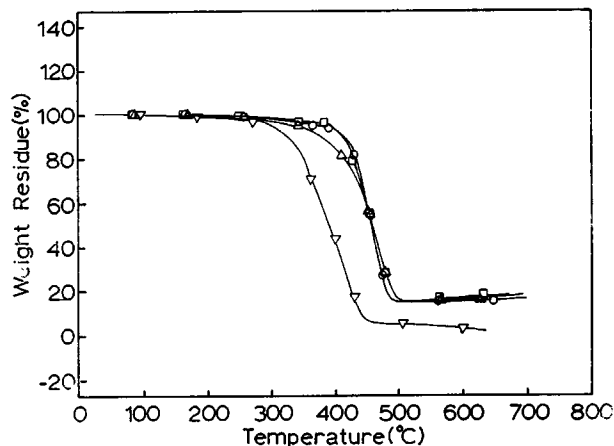


Figure 7 TGA thermograms for (∇) pure PS beads and SBR composite filled with PS beads in nitrogen atmosphere: PS bead content: (\square) 0 phr, (\circ) 20 phr, and (\triangle) 40 phr.

tories DMTA MK-III. The experiment was performed in a tensile mode from -70 to 30°C at a frequency of 4 Hz with a heating rate of $4^\circ\text{C}/\text{min}$. The dynamic storage and loss modulus and damping factor $\tan \delta$ of the specimens were measured as a function of temperature.

Tensile properties of the composite were measured using an ASTM-882 type specimen on a table model Instron 4200 at room temperature with a crosshead speed of 100 mm/min. The stress-strain data were averages of 10 measurements.

RESULTS AND DISCUSSION

Thermal Analysis of the Beads

A DSC thermogram of the synthetic PS beads with various contents of DVB is shown in Figure 1. For example, the T_g of the beads crosslinked with 5 mol % DVB is 117°C , while that of the beads with 10 mol % DVB is 135°C . The higher the DVB content, the higher the T_g observed. It is believed that the limited macromolecular relaxation by crosslinks in network reduces a chain flexibility and elevates the T_g of the beads. Fox and Loshaek suggested that the T_g of crosslinked polymers may be plotted as a function of crosslinking density.⁹ They reported that networks from vinyl-divinyl copolymer at low crosslinking density were consistent with their theory.

DiBenedetto reported that Eq. (1), which is modified from the Fox and Loshaek equation, gives better agreement at higher crosslinking density:¹⁰

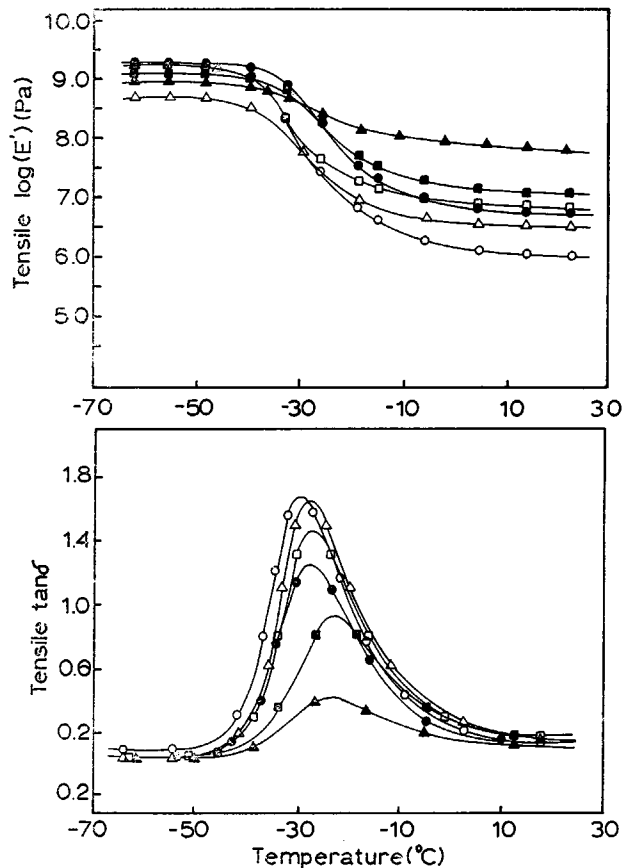


Figure 8 Dynamic storage modulus and damping $\tan \delta$ peak of SBR filled with various contents of PS beads. PS bead content: (\circ) 0 phr, (\triangle) 10 phr, (\square) 20 phr, (\bullet) 30 phr, (\blacksquare) 40 phr, and (\blacktriangle) 50 phr.

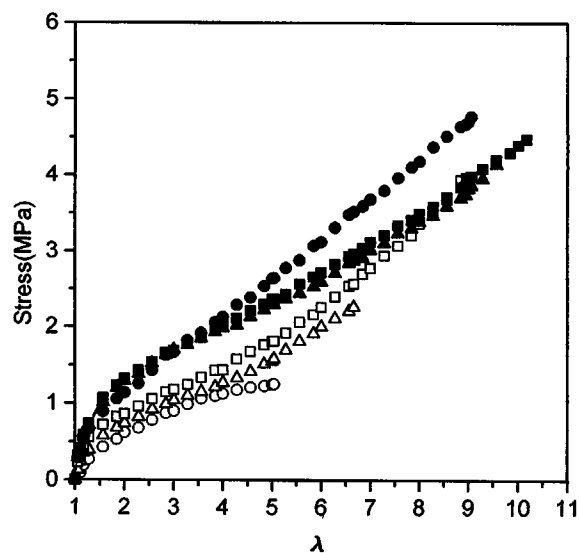


Figure 9 Stress-strain curves for SBR filled with various contents of PS beads with 10% DVB. Symbols are the same as in Figure 8.

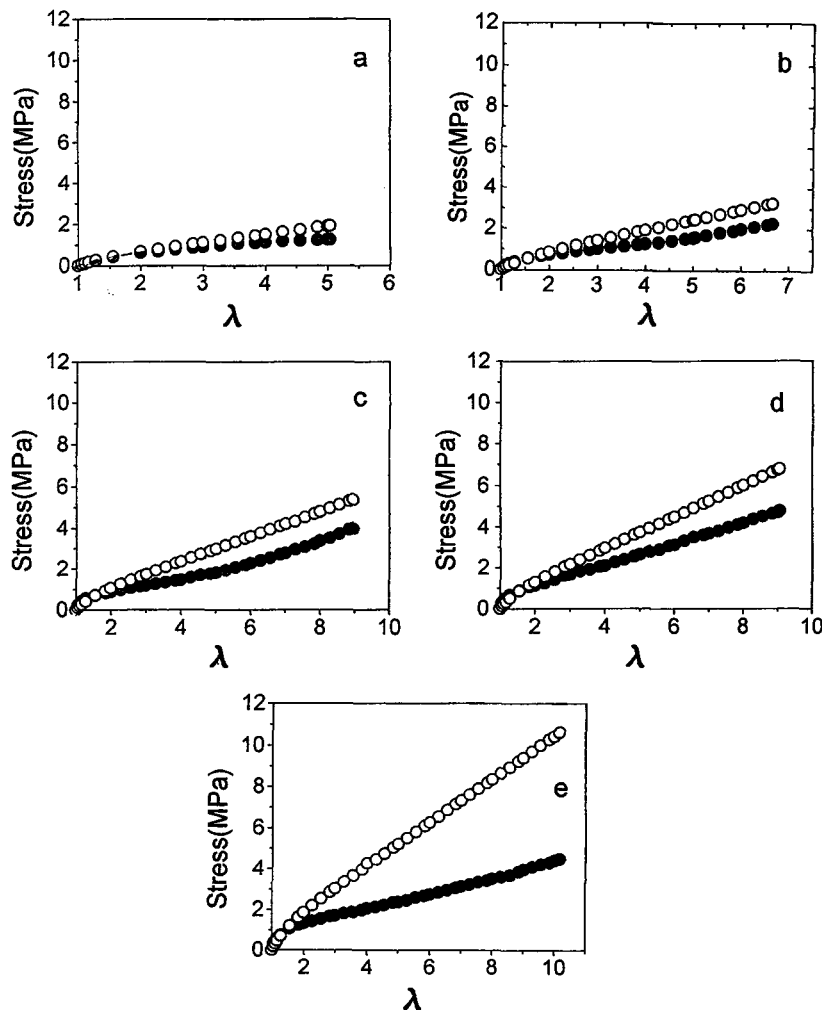


Figure 10 (●) Experimental and (○) theoretical stress–strain curves for SBR composite. PS bead content: (a) 0 phr, (b) 10 phr, (c) 20 phr, (d) 30 phr, and (e) 40 phr.

$$T_g = T_g + T_g \left(K_2 \frac{X_c}{1 - X_c} \right) \quad (1)$$

where T_g is the glass transition temperature of uncrosslinked polymer, X_c is the crosslinking density, and K_2 is a constant which was estimated to be 1.2 for styrene–divinylbenzene copolymer. An increase in T_g as a function of DVB content is plotted in Figure 2 and the experimental values are in good agreement with the calculated value by using Eq. (1).

Thermal stability of PS beads crosslinked with various contents of DVB is illustrated in Figure 3. For PS beads crosslinked with 10 mol % DVB, 5% weight loss was observed at about 317°C while that of the beads crosslinked with 2, 3, and 5 mol % DVB was observed at 302, 304, and 311°C, respectively.

Thermal stability of the beads was not significantly increased with DVB contents.

Morphology and DLS Measurements of PS Beads

SEM microphotographs of PS beads show that the size of the beads with 5 and 10 mol % DVB is fairly monodisperse than that of the beads with 2 mol % DVB (Fig. 4). Moreover, their spherical dimension is gradually increased from about 390 to 505 nm by an incorporation of DVB up to 10 mol %.

Particle size and its distribution of the swollen beads by DLS are shown in Figure 5. The distribution is narrow, as shown in this figure, and the calculated mean diameters of the beads with 2, 5, and 10 mol % DVB were 402, 509, and 532 nm, re-

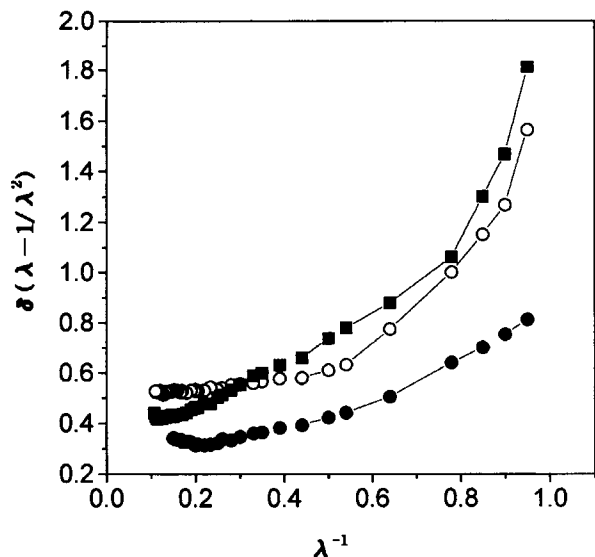


Figure 11 Mooney-Rivlin plots of SBR composite filled with PS beads with 10% DVB. PS bead content: (●) 10 phr, (○) 30 phr, and (■) 50 phr.

spectively. The slightly larger dimension of the beads characterized by DLS is consistent with that observed by SEM.

Crosslinking Density of PS Beads

The crosslinking density was derived by the several methods.¹¹⁻¹³ To obtain this, volume fraction (φ_p) of the beads is calculated by

$$\varphi_p = \frac{m_p/\rho_p}{m_p/\rho_p + (m_{p,a} - m_p)\rho_s} \quad (2)$$

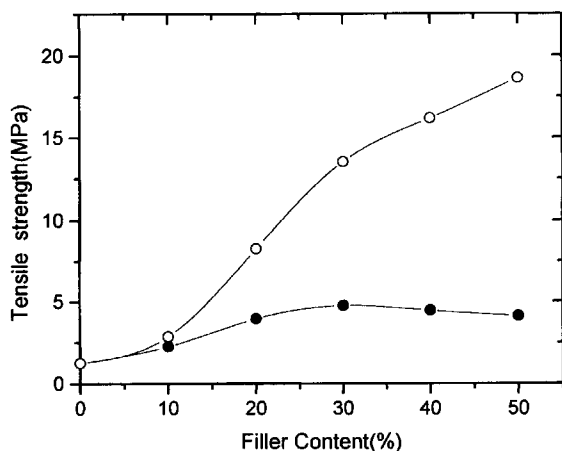


Figure 12 Tensile strength for SBR composite filled with (●) PS beads and (○) carbon black.

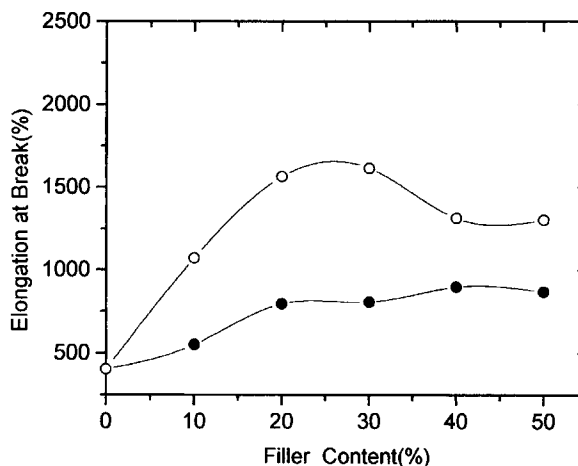


Figure 13 Elongation at break for SBR composite filled with PS beads and carbon black. Symbols are the same as in Figure 12.

where, ρ_s and ρ_p are the densities of solvent and polymer, respectively, m_p is the weight of dry beads, and $m_{p,a}$ is that of the beads including solvent at equilibrium.

For the PS system, the polymer-solvent interaction parameter (χ_{12}) was calculated by the following formula:¹⁴

$$\chi_{12} = 0.431 - 0.311\varphi_p - 0.036\varphi_p^2 \quad (3)$$

One of the most important structural parameters characterizing crosslinking density is \bar{M}_c , the average molecular weight between crosslinking networks. According to the theory of Flory and Rehner,¹⁵

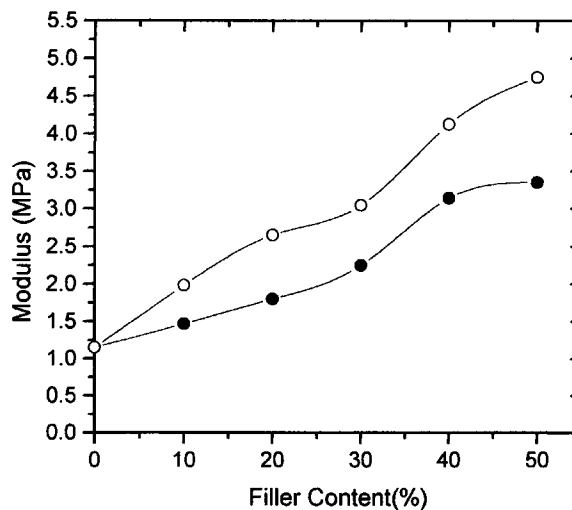


Figure 14 Tensile modulus for SBR composite filled with PS beads and carbon black. Symbols are the same as in Figure 12.

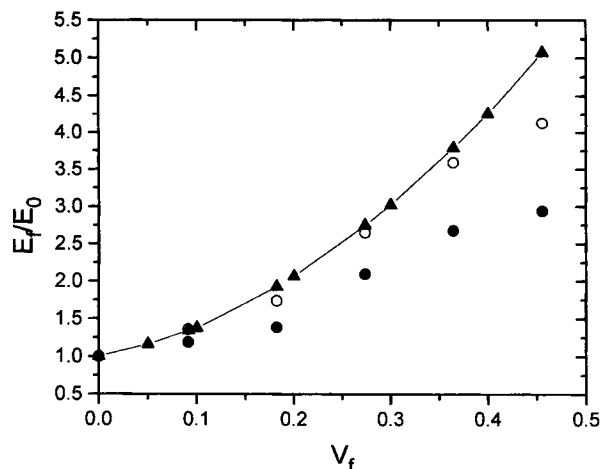


Figure 15 Effect of filler on moduli of SBR composite: (●) PS beads, (○) carbon black, and (▲) theoretical data by Guth–Smallwood equation.

$$\bar{M}_c = -V_s \rho_p \frac{\varphi_p^{1/3} - \varphi_p/2}{\ln(1 - \varphi_p) + \varphi_p + \chi_{12} \varphi_p^2} \quad (4)$$

where V_s is the molar volume of the solvent.

Here the crosslinking density q is defined as the mole fraction of crosslinked units:

$$q = \frac{M_0}{\bar{M}_c} \quad (5)$$

where M_0 is the molecular weight of the repeating unit of the polymer. Crosslinking density (q) of the beads calculated by Eqs. (2)–(5) is listed in Table II. It was increased with DVB content and slightly exceeded the mole fraction of DVB added for copolymerization with styrene. Since crosslinked PS beads were extracted with toluene and acetone prior to swelling, soluble linear or branched PS beads were presumably removed. As a consequence, calculated crosslinking density of the beads may be slightly higher than the incorporated mole fraction of DVB.

Morphology and Thermal Stability of SBR Composite

Figure 6 shows SEM micrographs of the fractured surface of SBR composite filled with PS beads crosslinked with 10 mol % DVB as a function of beads content. SEM micrographs indicate that the PS beads are relatively well dispersed and retain their spherical shape despite the fracture. SBR composite filled with 30 phr PS beads exhibits better uniform dispersion than those filled with other

compositions. When the bead content is more than 40 phr, slight agglomeration takes place.

Typical TGA thermogram of SBR composite filled with PS beads crosslinked with 10 mol % DVB is shown in Figure 7. For PS beads 5% weight loss was observed at 317°C and at 394°C for vulcanized SBR (0 phr PS beads). Vulcanized SBR shows better thermal stability than PS beads and similar stability to the composite. In addition, no dependence of the beads content on SBR composite is observed. Thus, thermal stability of the composite was not improved by an incorporation of the beads into SBR.

Dynamic Mechanical Properties of SBR Composite

Figure 8 shows dynamic storage modulus (E') and damping $\tan \delta$ peaks of SBR composite filled with PS beads of 10 mol % DVB. Storage modulus in the rubbery region increases with increasing content of the beads. Although we have not measured the crosslinking density of the SBR composite, we believe that the above behavior may be associated with an increase of degree of crosslinking of SBR composite. Crosslinking is reported to induce an increased glass transition temperature, broadened transition with slow drop in modulus, and a higher modulus of plateau region.¹⁶ In general, inorganic fillers are rigid solid particles with high modulus. When filled rubber is deformed, since fillers are more rigid than rubber, they essentially remain undeformed and thereby rubbery region will reach a plateau at higher modulus.¹⁷

Damping $\tan \delta$ peak is shifted to higher temperature from -34°C for no filler to -23°C for 50 phr filler. On the other hand, the height and the width of $\tan \delta$ peak is reduced with the content of PS beads. These results suggest that PS beads act as a crosslink point tying segments of molecule together to lead a restricted motion.

Mechanical Properties of SBR Composite

Representative stress–strain curves of SBR composite filled with various contents of PS beads crosslinked with 10 mol % DVB are shown in Figure 9 as a function of extension ratio (λ) which is written $\lambda = 1 + \epsilon = L/L_0$, where ϵ is the tensile strain, L_0 is the initial length of the SBR composite, and L is the final length after stretching. Crosslinked PS beads are rigid spherical particles and pure SBR is ductile material. As the beads content is increased, gradual improvement in tensile strength and elongation at break is observed. SBR composite filled

with 30 phr PS beads exhibits the highest tensile strength. This behavior is in accord with a good dispersion of the fractured surface of SBR composite with 30 phr PS beads in the previous section.

Figure 10 compares the experimental stress-strain curves of SBR composite with theoretical values calculated under the Gaussian assumption. Theoretical value was obtained by the equation $\sigma = E_0/3(\lambda - 1/\lambda^2)$, where E_0 is the tensile modulus of the composite in the stress-strain curve. The experimental curves of SBR composite agree well with the theory for strains below about 100%, or $\lambda < 2$, in all composition of the beads, however, at higher strain, relatively low values are observed. When a rubber sample is stretched, network chains approach their finite extension and the Gaussian assumption is no longer valid. The rise in elastic stress at higher strain is described as strain-induced crystallization or finite extensibility of chains in a filled system. The behavior of increased elastic stress of the filled SBR at high strain is presumably due to a finite extensibility of the polymer chains in the network.

Figure 11 shows the Mooney-Rivlin plot of SBR composite filled with PS beads crosslinked with 10 mol % DVB. In general, at finite extension, filled rubber shows upturn behavior, indicating a dramatic increase in elastic stress. However, the SBR with PS beads exhibits slight upturn due to a lack of strain-induced crystallization.

Figures 12-14 compare tensile strength, elongation at break, and tensile modulus between SBR composite filled with PS beads and those of the SBR filled with carbon black. SBR composite filled with the beads exhibits better tensile properties than the SBR without filler. In addition, for SBR filled with carbon black, we have observed a dramatic rise in tensile strength with carbon black content. This might be an evidence of a considerable strain-induced crystallization and a finite extensibility. Relatively, the SBR filled with PS beads showing a gradual increase in tensile properties seems to be affected by a finite extensibility solely.

Figure 15 shows the effect of fillers on elastic modulus of rubber by using the Guth-Smallwood equation.^{18,19} The most commonly used expression is

$$\frac{E_f}{E_0} = 1 + 2.5V_f + 14.1V_f^2 \quad (6)$$

where V_f is the volum fraction of the filler, E is an elastic stress, and subscripts f and 0 refer to the filled and unfilled SBR, respectively. Experimental value of the SBR filled with carbon black is in good

accord with that by the Guth-Smallwood equation up to about 0.3 of V_f , however, above them, the values of the SBR filled with PS beads are relatively lower than that by the Guth-Smallwood equation.

CONCLUSION

Monodisperse crosslinked polystyrene beads were prepared by a reaction of styrene monomer, divinylbenzene (DVB) crosslinking agent and potassium persulfate initiator in the absence of emulsifier. The glass transition temperature (T_g) of the beads was increased from about 100 to 135°C. The average diameters of monodisperse beads prepared by various contents of DVB (2-10 mol %) were varied from 390 to 505 nm by SEM photographs and from 402 to 532 nm by DLS measurements. Spherical mean diameter of the swollen beads by DLS was consistent with the SEM results. SEM micrographs of the fractured surface of SBR composite filled with PS beads crosslinked with 10 mol % DVB revealed that PS beads were relatively well dispersed and retained their spherical shape. SBR composite with more than 40 phr PS beads exhibited slight agglomerate, while that with 30 phr PS beads showed better uniform dispersion. Dynamic mechanical properties of SBR composite with PS beads with 10 mol % DVB were affected by a content of PS beads. Dynamic storage modulus in the rubbery region was increased and damping $\tan \delta$ peak shifted to higher temperature indicating a crosslink effect. In tensile properties, tensile strength and elongation at break of SBR composite was increased with PS beads, however, SBR composite filled with PS beads exhibited relatively lower tensile properties than that with carbon black. Crosslinked PS beads may play a role of reinforcing filler in enhancing mechanical and tensile properties without changing the original color of SBR.

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