

Graded Styrene–Butadiene Rubber Vulcanizates

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ABSTRACT: Styrene–butadiene rubber (SBR) vulcanizates with graded network chain densities were prepared by a conventional method of rubber science and technology. The characteristics of the gradient and gradient direction of the network chain density were examined from the perspective of the mechanical properties of the graded SBR vulcanizates. In the matrix of the graded SBR vulcanizates, silica

particles were generated in situ, and the tensile properties were investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 61–67, 2003

Key words: rubber; gradient; network chain density; mechanical properties; silica

INTRODUCTION

Recently, graded materials have been studied as functional materials in both inorganic and organic materials science because graded structures are often observed in nature and give very reasonable functions for living. For example, the structures of bamboo¹ and bivalves^{2,3} are graded, and their special characteristics were reported to be attributable to their graded structures. Some old statues in Japan were also built with graded structures, and they are still tough and beautiful.³

In rubber science and technology, the gradient of the network chain density is not special because heat diffusion during curing is not homogeneous in many cases for the production of rubber vulcanizates. Generally, the larger the mold is for processing, the more heterogeneous the formed structure is. In particular, the surface layers of produced rubber vulcanizates become hard from the direct contact of the rubber compound with a heated metal mold. Many technologists and scientists have empirically detected these phenomena. However, few reports have been published on the relationship between the graded network chain density and the mechanical properties. A few studies on the relationship between the inhomogeneous network structure and the properties of rub-

ber vulcanizates have been reported.^{4,5} Therefore, we thought it attractive to investigate the effect of the gradient of the network chain density of the rubber vulcanizates on their mechanical properties.

So far, we have published preliminary results on graded rubber vulcanizates.^{6,7} Ono⁸ investigated the diffusion of curing reagents into a rubber matrix from solution and prepared graded rubber vulcanizates. Vallat⁹ also researched the effect of the gradient on the curing of rubbers. However, studies on graded rubber vulcanizates prepared by conventional mixing have been limited to our studies. In this study, the effect of network chain density of styrene–butadiene rubber (SBR) vulcanizates on the tensile properties and dynamic mechanical properties was investigated in detail. Additionally, in situ silica generation was first conducted with graded SBR vulcanizates to prepare a new graded material.

EXPERIMENTAL

Materials

SBR was supplied from JSR Co. (Japan). The product number was SBR1502 (a nonstaining, cold type), its Mooney viscosity (ML_{1+4}) at 100°C was 52, and the content of bound styrene was 23.5 mass %. The crosslinking reagent was sulfur, and *N*-oxydiethylene-2-benzothiazoylsulfenamide was used as an accelerating agent. Stearic acid and ZnO were also used for the vulcanization. The tetraethoxysilane (TEOS) used was Shin-etu LS-2430 (Japan). The catalyst for the sol–gel reaction was *n*-butylamine, which was reagent-grade in purity. All reagents were commercially available and were used as received.

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TABLE I
Layering of the Compounding Sheets for the Preparation of Graded SBR Vulcanizates and Their Overall Network Chain Density

Sample code	Layered compound sheets	ν_s (10^{-4} mol/cm ³)
SBR-2V	SBR-2	0.15
SBR-3V	SBR-3	1.2
SBR-4V	SBR-4	2.0
SBR-6V	SBR-6	2.9
SBR-8V	SBR-8	3.9
FGR-6V	SBR-2/SBR-8	2.0
FGR-7V	SBR-2/SBR-4/SBR-8	1.7
FGR-8V	SBR-2/SBR-3/SBR-4/SBR-6/SBR-8	1.9
FGR-11V	SBR-2/SBR-8/SBR-2	1.7

Preparation of the graded SBR vulcanizates

Graded SBR vulcanizates were prepared via heat pressing at 150°C for 40 min after the layering of the compounding sheets, as shown in Table I. These compounds were prepared by conventional mixing on a two-roll mill according to the compounding recipes shown in Table II. The amounts of sulfur and accelerator were varied to change the network chain density of the vulcanizates. The temperature of the mold for curing was strictly controlled, and the size of the mold was 25.0 cm × 20.5 cm × 4.5 cm. Here, FGR-V means the graded vulcanizate. For example, the preparation of the graded SBR vulcanizates (FGR-7V) is illustrated in Figure 1. The thickness of the vulcanizates was approximately 2 mm. The control samples were SBR vulcanizates prepared from the homogeneous compounds, which are abbreviated SBR-V.

In situ silica generation in the vulcanizate

The graded SBR vulcanizate was immersed in TEOS for 48 h at 30°C and soaked in a 10% aqueous solution of *n*-butylamine at 30°C for 24 h to follow the sol-gel reaction of TEOS at 50°C for 72 h in the desiccator. Then, the sample was dried at 50°C in vacuo.^{10–12}

Material characterization

The overall network chain densities (ν_s) of the vulcanizates were determined by a swelling test and are summarized in Table I. The specimen (0.2–0.3 g) was soaked in benzene at 30°C for 72 h, and ν_s was calculated with the Flory–Rehner equation.¹³ The network chain density in the thickness direction of the SBR vulcanizates was evaluated by the measurement of the hardness of the thickness direction with 0.05-mm portions with an MD-1 microhardness tester from Kobunshi Keiki Co. (Japan) at room temperature. The values reported were the averages of three mea-

surements for each sample. This evaluation was based on the good relationship between ν_s and hardness, as shown in Figure 2, which clearly gave a straight line. In other words, the hardness of the SBR vulcanizates varied in proportion to their ν_s values when no fillers were added.

An alternative swelling was carried out in toluene at room temperature for 48 h for a qualitative evaluation of the difference in the network chain densities of the vulcanizates.

The tensile properties of the vulcanizates were measured on a tensile tester (Autograph AGS-1 kNG) at room temperature, at a strain rate of 10 mm/min, with dumbbell-type specimens (length = 60 mm, width = 3.18 mm). The length between the benchmarks was 20 mm.

The temperature dispersions of the storage modulus (E') and loss tangent ($\tan \delta$) were measured with a Rheospectolar DVE-4 instrument (Rheology Co.) at a frequency of 10 Hz and at a heating rate of 2°C/min. The tensile mode was used, and the size of the specimen was 30 mm × 5 mm × 2 mm.

A thermogravimetric analysis was carried out with a Shimadzu TGA-50 for the measurement of the in situ silica content. A sample (ca. 100 mg) was placed in a platinum pan and heated under air to 1000°C at a rate of 10°C/min.

The morphology of the samples was observed by transmission electron microscopy (TEM) with a JEOL TEM-100 U instrument from Hitachi, Ltd. The accelerating voltage was 80 kV. Ultrathin films of the samples were prepared with a microtome (KLB 4800A Ultratome) in liquid nitrogen from an LKB 14800 Cryokit. The specimen was placed on a copper grid, which was coated in advance with Folmvar and evaporated carbon.

RESULTS AND DISCUSSION

Preparation of the graded SBR vulcanizates

The curing of the layered compounding sheets produced the graded SBR vulcanizates. For example, the swollen SBR vulcanizate with a graded network chain density (FGR-7) in toluene is displayed in Figure 3. A

TABLE II
Compounding Recipes (phr^a)

Sample code	SBR	ZnO	Stearic acid	Sulfur	MSA ^b
SBR-2	100	5.0	1.5	1.0	1.0
SBR-3	100	5.0	1.5	1.5	1.5
SBR-4	100	5.0	1.5	2.0	2.0
SBR-6	100	5.0	1.5	3.0	3.0
SBR-8	100	5.0	1.5	4.0	4.0

^a Parts per hundred of rubber by weight.

^b *N*-Oxydiethylene-2-benzothiazolylsulfenamide.

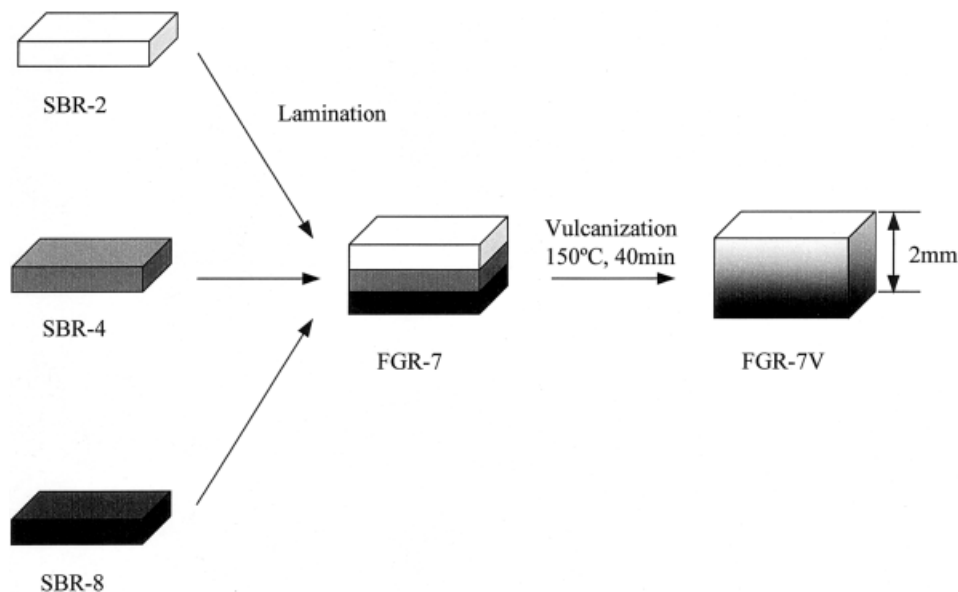


Figure 1 Preparation of the graded SBR vulcanizate.

vulcanizate with a sandwich-type gradient was also prepared by this method. The hardness of the thickness direction for the graded SBR vulcanizates is shown in Figure 4. FGR-6V, that is, a two-layered vulcanizate, gave a wider degree of the gradient in the thickness direction than FGR-8 (a five-layered vulcanizate). This observation was attributable to the competitive effects between the crosslinking reaction and the diffusion of crosslinking reagents into the layered rubber matrixes. That is, the rubber became a lower viscous liquid at 150°C than at room temperature, and so the mixed reagents for curing were diffused be-

tween the neighboring rubber matrixes at 150°C before crosslinking. Therefore, the interfacial region in the graded SBR vulcanizates was estimated as shown in Figure 5.

As a reference, the hardness of SBR-4V is also displayed in Figure 4. The network chain density of the surface of SBR-4V was slightly larger than that of the interior. Other SBR-Vs were also vulcanizates slightly graded like SBR-4V. These observations suggest that homogeneous vulcanization was not achieved even in the curing of a homogeneous compound approximately 2 mm thick under the conditions of this study. This may be a very rare result elucidating the degree of the gradient of the network chain density quantitatively.

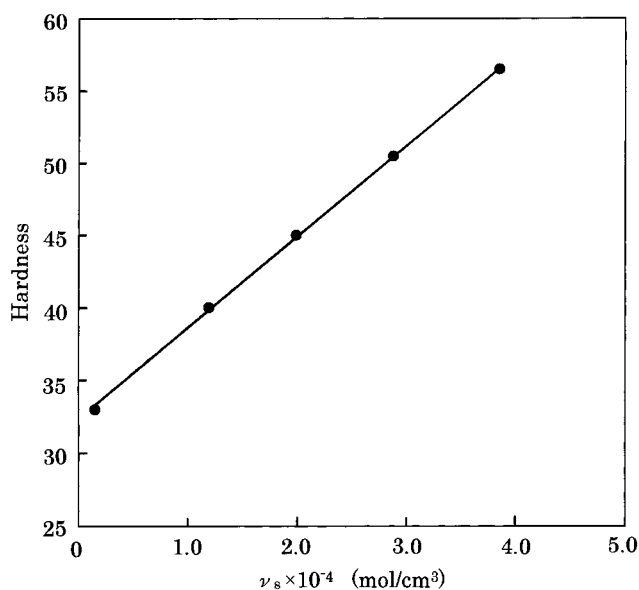


Figure 2 Relationship between the network chain density and the hardness of the SBR vulcanizates.

Tensile properties of the graded SBR vulcanizates

The stress-strain curves of SBR-Vs are illustrated in Figure 6. The larger the network chain density was,

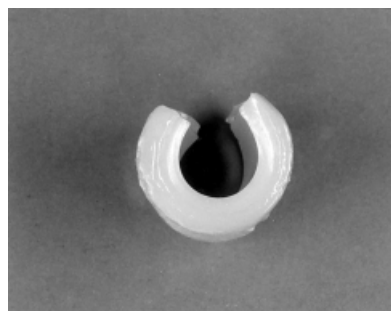


Figure 3 Swollen SBR vulcanizate with a graded network chain density.

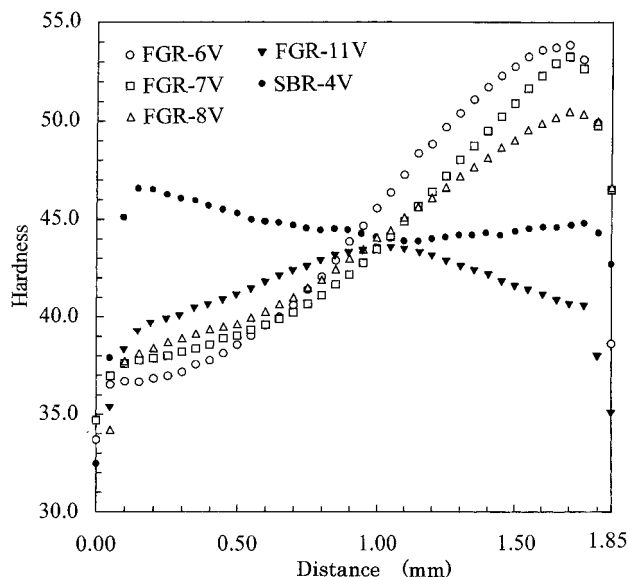


Figure 4 Gradient of hardness of the SBR vulcanizates.

the higher the modulus was and the lower the elongation became. For an investigation of the effect of the gradient of the network chain density on the properties of rubber vulcanizates, samples with similar overall network chain densities should be prepared because the network chain density significantly influences the physical properties of rubber vulcanizates in general. In this study, comparisons of SBR-4V, FGR-6, and FGR-8V and of FGR-7V and FGR-11 were conducted because the network chain densities of FGR-6V, FGR-8V, and SBR-4V were 2.0×10^{-4} , 1.9×10^{-4} , and 2.0×10^{-4} mol/cm³, respectively, and those of FGR-7V and FGR-11V were 1.7×10^{-4} mol/cm³. The stress-strain curves of these graded SBR vulcanizates are shown in Figure 6 along with those of SBR-Vs. The tensile properties of FGR-6V and FGR-8V were similar to those of SBR-4V. A close inspection showed a tendency for the stresses of FGR-6V and FGR-8V to become a little greater than that of SBR-4V. The short chains between the crosslinking points in FGR-6V and FGR-8V increased their stress. In addition, this phenomenon was remarkably detected in the graded SBR vulcanizate with a high degree of the gradient in the network chain density. The gradient seemed to reduce the strength at break (T_B) and the elongation at break (E_B). The heterogeneity of the network structure by the gradient of the network chain density in the thickness direction is considered to influence the tensile properties at break.

An ABA-type graded SBR vulcanizate (FGR-11V) showed interesting characteristics for its tensile properties: the network chain density of A was lower than that of B. Both T_B and E_B of a sandwich-type vulcanizate were larger than those of FGR-7, and its stress

was lower than that of FGR-7. In other words, the ABA-type graded SBR vulcanizate was a tough material. In the processing of rubber products via heat pressing, BAB-type graded rubber vulcanizates are generally produced, as shown by SBR-4V. Therefore, the preparation of ABA-type graded rubber vulcanizates by control of the crosslinking reagents may bring about a new area for rubber science and technology.

Dynamic mechanical properties of the graded SBR vulcanizates

The effect of the gradient of the network chain density was clearly observed in the dynamic mechanical analysis. In Figure 7, the temperature dispersions of E' and $\tan \delta$ of FGR-6V, FGR-8V, and SBR-4V are displayed. The gradient of the network chain density in the thickness direction brought about a broader $\tan \delta$ curve and a lower $\tan \delta$ height with respect to SBR-4V. The broadness and height of the $\tan \delta$ curve tended to become wide and low, respectively, with an increasing degree of the gradient. It was also observed that the temperature of the $\tan \delta$ peak top, which corresponded to the glass-transition temperature, shifted to the high-temperature region by giving the gradient in the network chain density of the SBR vulcanizate. E' at room temperature for the graded SBR vulcanizates became slightly larger than that for SBR-4V. However, no distinct difference in E' was observed between FGR-6V and FGR-8V, and this was ascribed to the low strain in the dynamic mechanical analysis.

The dynamic mechanical properties of FGR-11 were relatively similar to those of SBR-4V rather than to those of FGR-Vs because the degree of the gradient for the network chain density of FGR-11 was low. For example, the temperature dispersions of E' and $\tan \delta$ of FGR-11 and FGR-7 are illustrated in Figure 8.

In situ silica reinforcement for the graded SBR vulcanizate

The network chain density, that is, the size of the network of diene-type rubber vulcanizates, has been

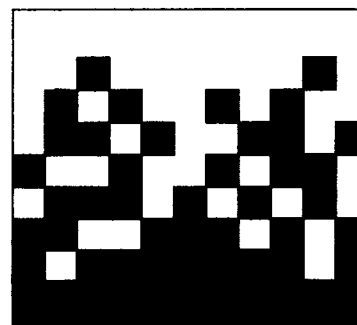


Figure 5 Interfacial region of the graded SBR vulcanizates.

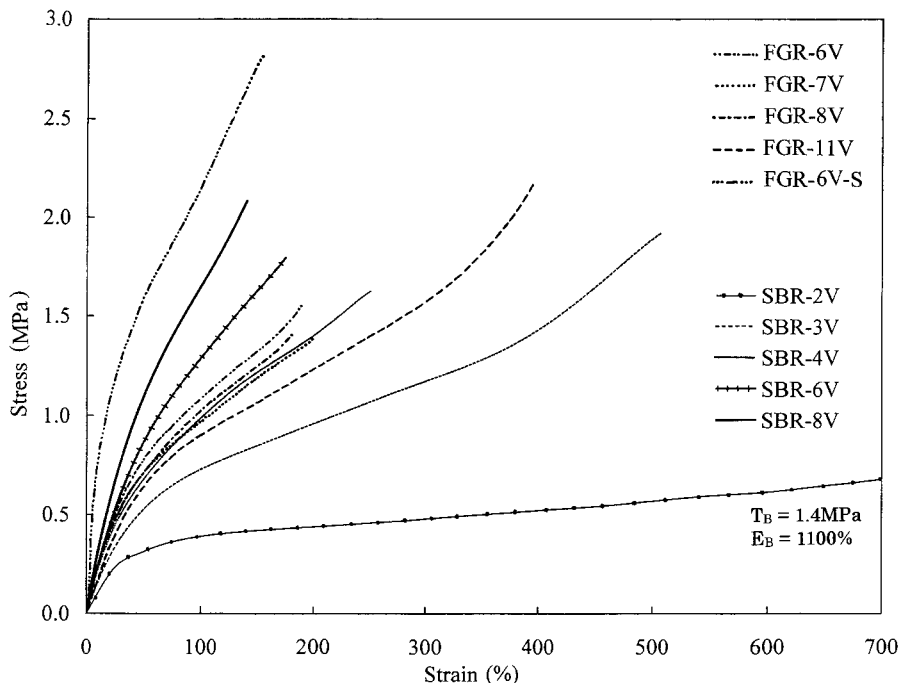


Figure 6 Stress-strain curves of the SBR vulcanizates.

reported to influence the size of in situ silica particles.^{11,12} Therefore, using FGR-V as a matrix for generating silica in situ may produce a new graded SBR vulcanizate reinforced by graded in situ silica particles. Figure 9(a-c) displays TEM photographs of in situ silica-reinforced FGR-6V (FGR-6V-S), showing the side of low network chain density, the middle, and the side of high network chain density of FGR-6V-S, re-

spectively. It is clear that the silica particles of the first were larger than those of the last, depending on the network chain densities. The size of in situ silica particles in the middle, however, was comparable to or a little smaller than those of the last. Because the thickness of the vulcanizate was approximately 2 mm, the homogeneous generation of in situ silica seemed to be difficult under the reaction conditions of this study.

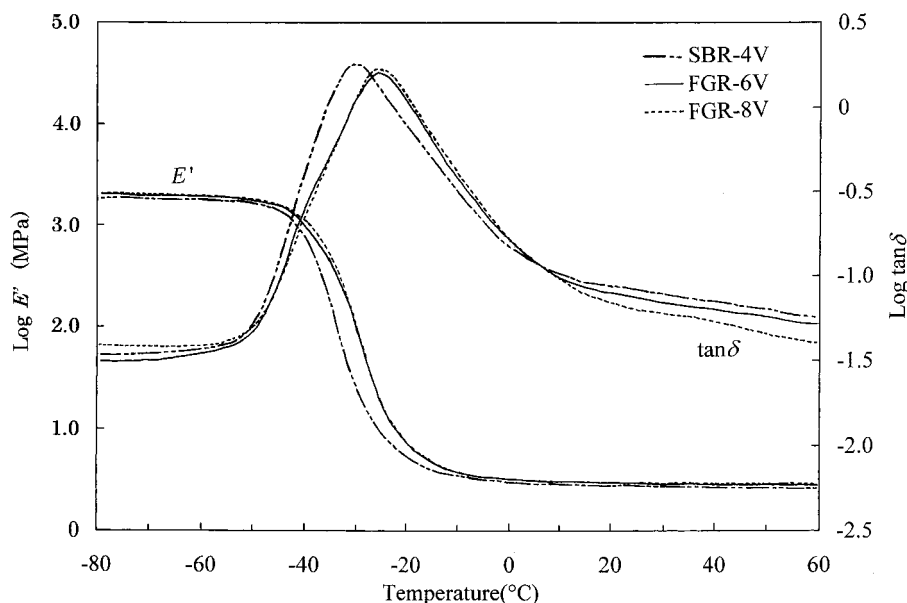


Figure 7 Temperature dispersions of E' and $\tan \delta$ of FGR-6V, FGR-8V, and SBR-4V.

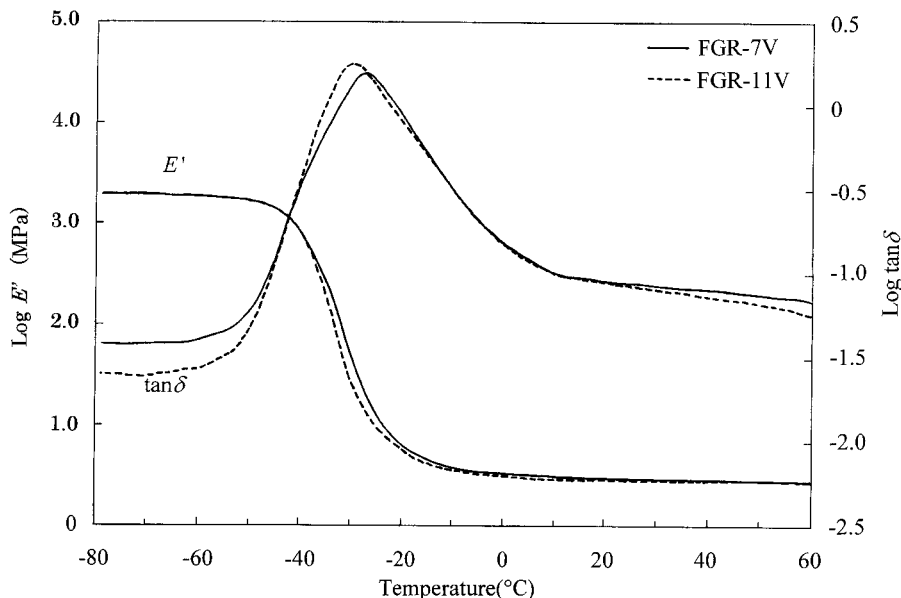


Figure 8 Temperature dispersions of E' and $\tan \delta$ of FGR-7V and FGR-11V.

Adding approximately 16% in situ silica approximately doubled the stress at 150% strain, as shown in Figure 6. The control of the sol-gel reaction of TEOS for the in situ silica reinforcement of graded rubber vulcanizates is a continuing subject for us in our quest to obtain highly functional rubber materials.

CONCLUSIONS

SBR vulcanizates with graded network chain density were prepared by the layering and heat pressing of compounding sheets containing different amounts of sulfur and accelerator. The layering of two compounding sheets brought about a wider gradient for the net-

work chain density than the multilayering of compounding sheets in the preparation of graded SBR vulcanizates approximately 2 mm thick. The gradient in the thickness direction of the network chain density slightly increased the stress and reduced the properties at break. The $\tan \delta$ peak of SBR vulcanizates with the gradient in the thickness direction became broader and shifted to a higher temperature region than that of SBR vulcanizates prepared from the homogeneous compounding sheets. A sandwich-type graded SBR vulcanizate was found to be tough, for which the network chain density outside was lower than that inside. The in situ silica generation in the graded SBR vulcanizate produced a new graded material. The unique characteristics of graded SBR vulcani-

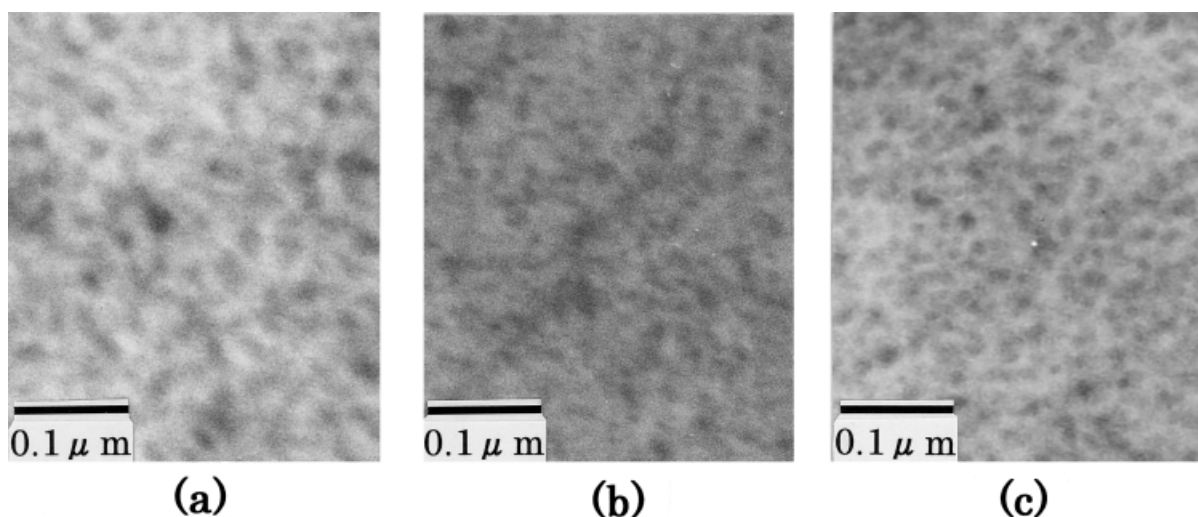


Figure 9 TEM photographs of in situ silica-generated FGR-6V: (a) the matrix with low network chain density, (b) the middle matrix, and (c) the matrix with high network chain density.

zates will be useful for the preparation of functional rubber products.

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