Fly Ash Particles and Precipitated Silica as Fillers in Rubbers. I. Untreated Fillers in Natural Rubber and Styrene–Butadiene Rubber Compounds

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ABSTRACT: In this study, we investigated the effects of untreated precipitated silica (PSi) and fly ash silica (FASi) as fillers on the properties of natural rubber (NR) and styrene–butadiene rubber (SBR) compounds. The cure characteristics and the final properties of the NR and SBR compounds were considered separately and comparatively with regard to the effect of the loading of the fillers, which ranged from 0 to 80 phr. In the NR system, the cure time and minimum and maximum torques of the NR compounds progressively increased at PSi loadings of 30–75 phr. A relatively low cure time and low viscosity of the NR compounds were achieved throughout the FASi loadings used. The vulcanizate properties of the FASi-filled vulcanizates appeared to be very similar to those of the PSi-filled vulcanizates at silica contents of 0–30 phr. Above these concentrations, the properties of the PSi-filled vulcanizates improved, whereas those of the FASi-filled compounds remained the same. In the SBR sys-tem, the changing trends of all of the properties of the filled SBR vulcanizates were very similar to those of the filled NR vulcanizates, except for the tensile and tear strengths. For a given rubber matrix and silica content, the discrepancies in the results between PSi and FASi were associated with filler–filler interactions, filler particle size, and the amount of nonrubber in the vulcanizates. With the effect of the FASi particles on the mechanical properties of the NR and SBR vulcanizates considered, we recommend fly ash particles as a filler in NR at silica concentrations of 0–30 phr but not in SBR systems, except when improvement in the tensile and tear properties is required. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2119–2130, 2004

Key words: rubber; composites; mechanical properties; silicas; vulcanization

INTRODUCTION

The reinforcement of rubber by a filler is associated with chemical and physical interactions between the rubber and the filler that usually rely on the physicochemical character of the filler surface and the chemical nature of the rubber, although the precise mechanism of the reinforcement is not fully understood.[1] For most applications, a rubber compound must be reinforced mainly with carbon black and silica to improve the end-use performance. One of the general agreements on the use of rubber–filler reinforcements is based on the bound rubber theory, which can be considered in two different ways, once being adsorption effects in which van der Waals forces and chemical sorption play the main role and the other being the chemical reactions of the rubber molecules with active sites formed by the breakdown of the carbon black structure during compounding. In silica-filled rubber compounds, the reinforcement is related to adsorption effects. Apart from the bound rubber theory, additional crosslinking into the network structure due to the addition of fillers has been suggested to be responsible for the improvement of the elastic properties of filled rubber vulcanizates.[1] In general, the bound rubber content can be used to directly indicate the reinforcement level. Wolff[2] suggested that the bound rubber value of silica-filled rubber is much lower than that of carbon-black-reinforced rubber because the filler–filler interaction in silica-filled rubber is strong, but the filler–rubber interaction is relatively weak compared to carbon-black-filled rubbers. Therefore, little attention has been paid to studies of silica-filled rubber vulcanizates.

Despite the lower bound rubber and reinforcing levels, silica is still widely used as a potential reinforcing filler in rubber shoeing products and nonblack rubber products with lower prices. The interactions between the rubber and the silica can usually be enhanced with bifunctional organosilane coupling agents, which can establish molecular bridges as the

interface between the rubber molecules and the filler surface. There are a number of published articles that have reported various experimental techniques for investigating the effect of silica characteristics (type and grade, filler loading, surface treatment, filler dispersion, and particle size and structure) on the properties of both natural and synthetic rubber vulcanizates.[3–14]

Although silica is still widely accepted among rubber technologists, the use of some other fillers, such as clay,[15] lignin,[16] black rice husk ash (BRHA) and white rice husk ash (WRHA),[17–20] pulverized polyurethane (PU) foam particles,[21,22] and cellulose fiber,[23] has been attempted to replace silica in rubber compounds. Most articles have suggested that because WRHA and BRHA have a high silica content (ca. 90–95%), they could, in combination with a silane coupling agent, be used to replace the silica in rubber compounds because the curing rate and mechanical properties are improved because of additional crosslinking and better filler dispersion in the matrix phase.[17,19,20] Improved mechanical properties and rates of crosslinking were also observed with the addition of cellulose and glass fibers in natural rubber (NR), styrene–butadiene rubber (SBR), and ethylene–propylene diene monomers (EPDM) rubber vulcanizates.[23] Sims and Sombatsompop[21,22] used pulverized flexible PU foam particles (average particle size = 200 μm) as an alternative filler in conventional NR compounds. At the critical loading range of 20–30 phr for optimum mechanical properties, the mode action of the PU particles appeared to change from that of a suitable NR extender to that of an extending/reinforcing filler. The reinforcing mechanism of the PU filler in NR vulcanizates was attributed to chemical and physical adsorption between functional groups, including C=O and NH groups, on the filler surface and rubber molecules.

Ash residues are wastes of coal-fired power plants, and they are produced at the boiler outlet of plants; these include fly ash (FA) and bottom ash. It has been estimated that the total quantity of ash residue produced in Thailand in 2002 was 3 million tons, of which only 1.8 million tons were used for concrete construction applications.[24] In this study, we aimed to make use of FA as a potential filler in rubber materials because it contains nearly 50% silica by weight of the total FA and because the price is relatively low (ca. 50 times cheaper than any commercial silica on the basis of the purchase price in Thailand). In the existing literature, FA has been used as a filler mostly in thermosetting materials, such as unsaturated polyester.[25–29] Chand[25] found that increasing the volume fraction of FA reduced the tensile and impact strengths of polyester composites. The enhancement of these properties was obtained through the use of a silane coupling agent.[26–28] In fiber–epoxy composites, the addition of FA led to a reduction in the density and an increase in the modulus of the composites, with the latter effect caused by the better dispersion of the fiber in the polymer matrix.[29]

In the literature, experimental data and information on the use of FA particles as a filler in rubber materials are very rare. Only a few studies[30,31] have investigated the effects of FA particles on the properties of rubber vulcanizates. Garde et al.[30] indicated that the mechanical properties of polyisoprene rubber loaded with FA particles were inferior to those of polyisoprene filled with silica. Alkadasi et al.[31] found that the mechanical properties of FA-filled rubber vulcanizates improved to a certain FA loading with the incorporation of an appropriate amount of a silane coupling agent into the compounds. However, more conclusive evidence with sufficient experimental results on a wider range of properties and rubbers (natural and synthetic rubbers as well as unvulcanized and vulcanized rubbers) filled with FA particles are still needed. In this study, untreated FA particles were added as a filler into NR and SBR, and the cure characteristics and physical, mechanical, and morphological properties were studied in detail. We aimed to seek the optimum FA content to be added into the NR and SBR compounds to replace conventional silica filler without any filler surface treatment. Therefore, a wide range of properties of the FA-filled rubber compounds were studied, including cure time, compounding torques, bound rubber content, crosslink density, tensile modulus, tensile and tear strengths, hardness, abrasive resistance, elongation set, resilience, and loss tangent (tan δ). The results were compared to those of rubber compounds filled with conventional silica. Comments on the property differences between NR and SBR filled with FA particles at any given silica content are also given in this article.

EXPERIMENTAL

Raw materials

The rubbers used in this study were NR (STR20) supplied by Huay Chuan Co., Ltd. (Bangkok, Thailand), and SBR (SBR1712) supplied by BST Elastomers Co., Ltd. (Bangkok, Thailand). The SBR was comprised of 24.5% styrene, 28.8% oil, and 5.7% organic acid. Each rubber was mixed with different concentrations of precipitated silica (PSi) and FA particles as potential fillers in this study. The PSi was Hi-Sil 233-S supplied by PPG-Siam Silica Co., Ltd. (Bangkok, Thailand), and had a pH of 6.8, a bulk density of 0.235 g/cm^3, and a surface area of 128 m^2/g. The FA particles were supplied by Mae Moa Power Station of KNR Group Co., Ltd. (Lampang, Thailand). The chemical compositions of the FA particles used in this study were technically determined[24] and are listed in Table I. The average particle size of the FA used was 50–100 μm. In this study, we intended to examine the reinforcing effec-

TABLE I
Chemical Composition of the FA Particles

Chemical	Content (%)
Silica	46.25
Alumina	26.43
Iron oxide	10.71
Calcium oxide	7.61
Magnesium oxide	2.21
Sodium oxide	1.11
Potassium oxide	3.07
Sulfur dioxide	1.85

tiveness of the two fillers [PSi and fly ash silica (FASi)] in NR and SBR compounds with regard to various silica contents. Therefore, the required silica (FASi) content in the FA particles added to the rubber compounds had to be calculated with the information on the FA chemical compositions as given in Table I. Both of the fillers used in this study were untreated, and the silica contents of interest to this study ranged from 0 to 75 phr.

Rubber sample preparation

Rubber mastication and compounding

The formulation of the rubber (both NR and SBR) compounds was as follows: 100 phr rubber, 5.0 phr zinc oxide (ZnO), 2.0 phr stearic acid, 0.5 phr mercaptobenzthiazole (MBT), 0.2 phr diphenylguanidine (DPG), and 3.0 phr sulfur. The rubber products (samples) were made in two steps for property evaluations: mastication and compounding. In the mastication step, the rubber was masticated on a laboratory two-roll mill (Yong Fong Machinery Co., Ltd., Samutsakon, Thailand) for 5 min and was then mixed with a specific content of filler (PSi or FASi) for another 20 min. In the compounding step, the rubber and filler were compounded with prepared vulcanization chemicals on the two-roll mill for another 20 min, and the compounds were then kept at 25°C at 50% humidity before further use.

Rubber vulcanization

The resultant rubber compound was then compression-molded to a 90% cure with a hydraulic press (LAB TECH Co., Ltd., Bangkok, Thailand) at 170 kg/cm^2 with a 160°C cure temperature to produce vulcanized rubber. The cure time used for any individual compound was predetermined with a Monsanto moving die rheometer (MDR 2000, Eagle Polymer Equipment, Akron, OH) before the vulcanization process proceeded. The results of the cure time are discussed later.

Characterization

Cure time and compounding torques

The maximum torque, minimum torque, and cure time values of the rubber compounds were detected with the Monsanto moving die rheometer at a test temperature of 160°C.

Physical properties

Bound rubber content. A circular rubber specimen with a diameter of 12.7 mm and a thickness of 3 mm was used for the bound rubber analysis of the uncured rubber samples. Each specimen was weighed before immersion into 25 cm^3 of toluene. After 72 h of exposure to the solvent at 25°C, the sample was filtered and dried at room temperature to a constant weight. The bound rubber content is reported as the weight percentage of the insoluble polymer.[13]

Crosslink density. The determination of the crosslink density of the vulcanized rubber compounds was carried out with a swelling method.[32] The experimental procedure commenced when the vulcanized rubber samples were cut into small pieces and then weighed before they were immersed in toluene. The samples were kept in a dark place for 7 days. We removed the excess liquid on the surface of the specimens by blotting them with filter paper. The swollen samples were taken out and placed to dry at a controlled temperature of 21°C. The weight of the swollen samples was measured, and the crosslink density was calculated with the Flory–Rehner equation [eq. (1)]; the details of the calculations are found elsewhere:[33]

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = 2V_s \eta_{\text{swell}}\left(V_r^{1/3} - \frac{2V_r}{f}\right)$$

(1)

where V_r is the volume fraction of the rubber in the swollen gel, V_s is the molar volume of toluene (in this study, 106.2 cm^3/mol), χ is the rubber–solvent interaction parameter (in this case, 0.3795 for NR and 0.413 for SBR), η_{swell} is the crosslink density of the rubber (mol/cm^3), and f is the functionality of the crosslinks (4 for the sulfur curing system).

Mechanical properties

The tensile properties (modulus at 200% elongation, tensile strength, and elongation at break) of the rubber vulcanizates were tested according to ASTM D 412-92 (1998) with dumbbell-shaped samples; the tests were carried out with a universal testing machine (Autograph AG-I, Shimadzu, Tokyo, Japan). Tear strength was determined according to ASTM D 624-00 (2000) with angle-shaped samples and a Shimadzu tear

strength testing machine. Both the tensile and tear properties were tested at a speed of 500 mm/min. A hardness durometer (Shore A, model 475, PTC Instruments, Boylston, MA) was used for the hardness tests, with the test conditions in accordance with ASTM D 2240-97 (1997). Resilience tests were performed according to ASTM D 2632-01 (2001) on a Wallance Dunlop tripsometer (H. W. Wallance & Co., Ltd., Kingston, United Kingdom). The abrasive resistance was evaluated with a standard test according to DIN 53516 and performed on a DIN abrader (Hampden Test Equipment, Ltd., Northants, United Kingdom).

Traditional rubbers have the general capability of recovering rapidly to essentially their original dimensions after they are subjected to a strain of several hundred percent, whereas some newer elastomers retain a significant elongation set after the removal of the stretched force.[21] Consequently, we considered it appropriate to monitor the elongation set of the vulcanizates according to the following procedure. Rubber samples were strained to 150% and held in the strained state for 2 h. The length of a premarked section in the central portion of the specimen was measured after the removal of the stretched force. The constant length of the premarked section was then recorded to represent the value of the elongation set according to the following equation:

$$\text{Elongation set } (\%) = \frac{l_t - l_0}{l_0} \times 100 \qquad (2)$$

where l_0 is the length of the original premarked section and l_t is the length at a time after the removal of the stretched force.

Dynamic mechanical properties

The dynamic mechanical properties of the rubber vulcanizates were determined with a dynamic mechanical analyzer (model 2980, TA Instruments, Boston, MA). The shape of the test sample was rectangular, and it was 17.5 mm long, 15 mm wide, and 2 mm thick. The single-cantilever mode of deformation was used under a test temperature range of -80 to $10°C$ at a heating rate of $2°C/min$, a strain amplitude of 0.03%, and a frequency of 15 Hz. The cooling process was achieved through liquid nitrogen. The results were presented in terms of the loss tangent (tan δ_{max}). In this work, tan δ was the ratio of the loss modulus to the storage modulus.

Scanning electron microscopy (SEM) studies

Failure mechanisms were investigated with a Jeol JSM-6301F SEM machine at a 15-kV accelerating volt-
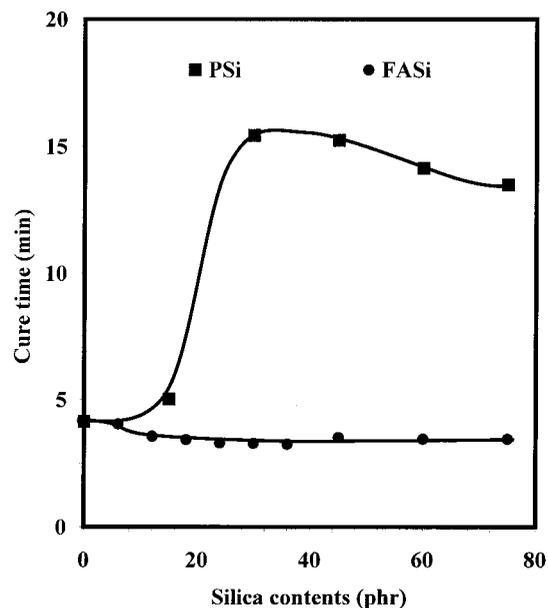

Figure 1 Relationship between the cure time and silica content for NR vulcanizates filled with PSi and FASi.

age. The composite fracture surfaces for examination were obtained from the tensile fracture surfaces.

RESULTS AND DISCUSSION

Figure 1 shows the effect of PSi and FASi loadings on the cure time in the NR compound. In general, PSi had an effect on the cure time change at silica loadings between 15 and 75 phr, whereas FASi had no effect for all of the loadings used. For the PSi filler, the cure time was independent of the PSi loadings up to 15 phr; then, the cure time sharply increased at further loadings. The cure time stabilization at the initial loadings (0–15 phr) was due to the fact that silica particles were separated from one another, forming a dispersed gel through the rubber matrix.[2] In this case, the crosslinking process had not yet been disturbed by the presence of silica particles. The sharp increase in the cure time at PSi loadings greater than 15 phr was caused by three possible reasons:

1. Filler–filler interactions: Because silica has a number of hydroxyl groups on its surface, which result in strong filler–filler interactions due to hydrogen bonding, the added silica particles became aggregated and formed a coherent gel in the rubber matrix.[2] This aggregation physically prevented the rubber from being readily vulcanized and, thus, increased the cure time.
2. Adsorption of acceleration on the silica surface: The cure accelerator used was adsorbed by hydrogen bonds on the silanol groups on the silica surface, and this led to the reduction in the cure
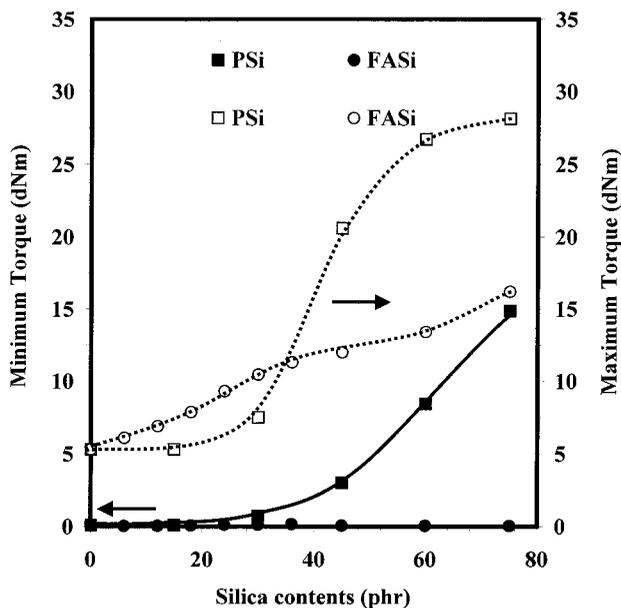
Figure 2 Variations in the minimum and maximum torques with silica content for NR vulcanizates filled with PSi and FASi particles.

time. This view is supported by the results of Choi et al.[14]

3. Reduction of zinc-complex formation: This involved the reactivity of the metal oxide (in this case, zinc oxide) for zinc-complex formation in the vulcanization process that was reduced by the presence of silica as a result of interaction between the silica and zinc oxide.[34,35] This delayed the vulcanization reaction.

From the previous explanations, if the addition of silica led to an increase in the cure time, one would, therefore, expect the cure time to increase with increasing FASi. However, as shown by the results in Figure 1, this was not the case; the cure time in the NR compound did not change with FASi loading. This was because the NR compound with FASi had excessive metal oxides (e.g., Al_2O_3, CaO, MgO) present in the FA particles, as listed in Table I, that probably acted as activators and accelerated the curing process. Interestingly, the rubber compounds with FASi needed less curing time to vulcanize than those with PSi, especially at high silica loadings. This would be a practical benefit for rubber manufacturers in terms of production time minimization.

Figure 2 shows the minimum and maximum torques of the rubber compounds filled with PSi and FASi fillers. The minimum torque for the PSi-filled rubber compound was stable at 0–30 phr PSi and then progressively increased at further PSi loadings. The unchanged minimum torque was related to the disperse gel, whereas the progressive increase in the min-

imum torque was due to the coherent gel (filler–filler interactions), as discussed earlier. However, the minimum torque for the FASi-filled rubber compound did not change with FASi content. Similar behavior was also observed for changes in maximum torque. The difference in the compound torque behavior between PSi and FASi fillers were associated with the silica formation network in the PSi and FASi fillers dispersed in the rubber matrix. The silica particles in the PSi fillers most likely interacted with one another, leading to silica aggregations and high filler–filler interactions as a result of the hydrogen bonds between the silanol groups on the silica surface,[2,14,33,34] whereas those in the FA particles were porous, and the silica atoms bonded with various metal oxides. Therefore, the aggregation of the silica particles in the FA filler was relatively less. As a consequence, the mixing or compounding torque for the FASi-filled rubber was lower. The silica aggregations in the PSi could be substantiated by consideration of the bound rubber results, which are shown in Figure 3. At silica contents between 30 and 75 phr, the level of the bound rubber content, trapped as a result of the filler–filler interactions, increased with silica content in the PSi filler. The increase in bound rubber content indicated some interaction between the rubber and the filler. For FASi, bound rubber did not occur and remained independent of the silica content, as observed during the experiment in that all of the rubber content in the NR/FASi compound was completely dissolved in the solvent.

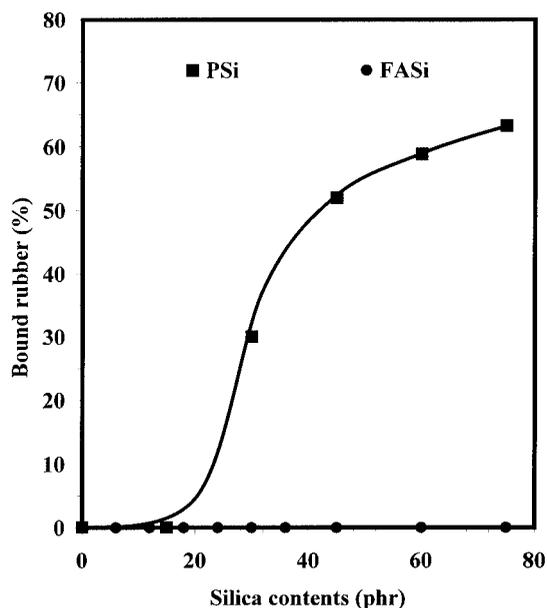Figure 4 shows the crosslink density of the NR vulcanizates added with different concentrations of

Figure 3 Effect of the silica content on the bound rubber level for PSi- and FASi-filled NR vulcanizates.
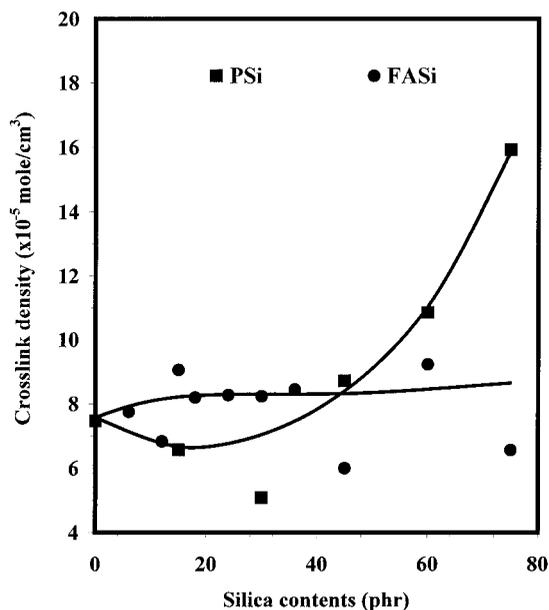
Figure 4 Effect of the silica content on the crosslink density for PSi- and FASi-filled NR vulcanizates.
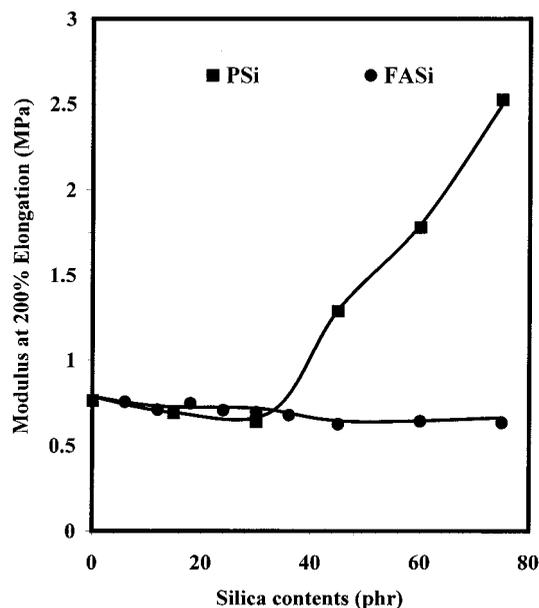

Figure 5 Variation in the modulus at 200% elongation with silica content for PSi- and FASi-filled NR vulcanizates.

PSi and FASi particles. The crosslink density results corresponded very well to the maximum torque results, as shown earlier. For the NR/PSi vulcanizate, the crosslink density with PSi was stable up to 30 phr and then progressively increased with further loadings. The change in the crosslink density for the NR/PSi vulcanizate reflected very well with that in the maximum torque shown in Figure 2. For NR/FASi vulcanizates, the crosslink density was again independent of the silica loading. There was no significant difference in the crosslink densities between the NR/PSi and NR/FASi vulcanizates at silica loadings of 0–30 phr. However, above these silica concentrations, the crosslink density of the NR/PSi vulcanizate was greater for any given silica content. The discrepancies in the crosslink densities between these two vulcanizates were related to two possible phenomena, the residual rubber content and the nonrubber content. With regard to the former, bound rubber may have still been present in the rubber compounds after the vulcanization process was complete. If so, the crosslink density measured was a combination of the true sulfur crosslinking and the residual bound rubber in the vulcanizates. This view was supported by Wang.[36] For the latter, for a given silica content, the amount of nonrubber content in the NR/FASi vulcanizate was greater than that in the NR/PSi vulcanizates because the FA particles used in this work contained approximately 43% nonsilica substances (see Table I); these substances diluted and replaced the rubber phase in the test specimen.

Figure 5 shows the tensile modulus at 200% elongation of the NR vulcanizates filled with the PSi and

FASi fillers at various silica concentrations. The changing trend of the modulus for both vulcanizates was similar to that of the crosslink density, as one would expect. Figure 6 shows the tensile strength and percentage elongation at break of the vulcanizates. As expected, the rubber vulcanizates filled with untreated silica showed a progressive decrease in tensile strength and elongation at break with increasing silica content. The decreased tensile and elongation proper-
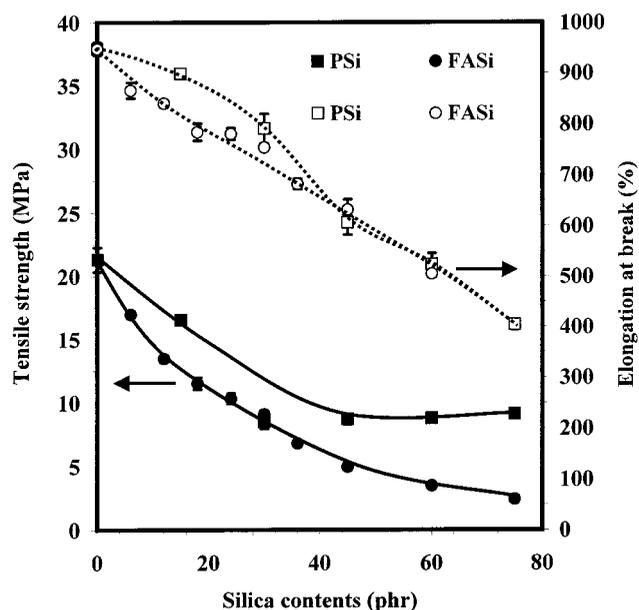

Figure 6 Variations in the tensile strength and elongation at break with various silica contents for PSi- and FASi-filled NR vulcanizates.

ties were due to low filler–rubber interactions, as also observed by Nasir.[37] However, at silica contents greater than 30 phr, the tensile strength of the PSi-filled vulcanizates stabilized, and the values were higher than those of the FASi-filled vulcanizates. The tensile strength stabilization resulted from an increase in the crosslink density of the vulcanizates at silica contents greater than 30 phr. The differences in the tensile strength results of the NR/PSi and NR/FASi vulcanizates can be explained with the SEM micrographs of the tensile-fractured surfaces of these two vulcanizates and also that of the unfilled sample, which are shown in Figure 7. The FASi/NR [Fig. 7(c)] phase interaction was poorer than the PSi/NR interaction [Fig. 7(b)], as indicated by some voids present between the FA particles and the rubber phase [Fig. 7(c)]. Also, because the FASi particles were porous, the rubber phase could have been trapped in the FA voids. This would have made the rubber phase less continuous and would thus have decreased the tensile properties. According to Figure 7(b,c), the particle size of the silica was much smaller than that of the FA, suggesting that the surface area for the silica to interact with the rubber molecules was greater. Another reason for the lower tensile strength of FASi/NR compared to PSi/NR was the greater amount of the non-rubber phase for a given test specimen.

The tear strength of the NR vulcanizates filled with PSi and FASi particles is illustrated in Figure 8. The tear strength of the FASi/NR vulcanizates monotonically decreased with silica content. This resulted from the low crosslink density and also from the poor interface (void defects) between the FA particles and the rubber phase. For the PSi/NR vulcanizate, the tear strength decreased up to a silica loading of 30 phr and then started to increase for further loadings. The increase in the tear strength of the vulcanizates at silica loadings greater than 30 phr linked well with the increase in the crosslink density, as discussed earlier. Figure 9 displays the hardness of the rubber vulcanizates influenced by silica content. The addition of both fillers resulted in a continuous increase in the hardness of the NR vulcanizates, but the rate of the increased hardness for the PSi/NR vulcanizates was greater, especially at high silica loadings. Figure 10 shows the effect of silica content on the abrasive resistance. The results are reported in terms of the volume loss of the vulcanizates; the greater the volume loss was, the lower the abrasive resistance was. It was clear that the abrasive resistance of the PSi/NR vulcanizate was much better than that of the FASi/NR vulcanizate, especially at silica loadings greater than 30 phr. This was expected because the crosslink density, hardness, and rubber content in the PSi/NR vulcanizates were greater.
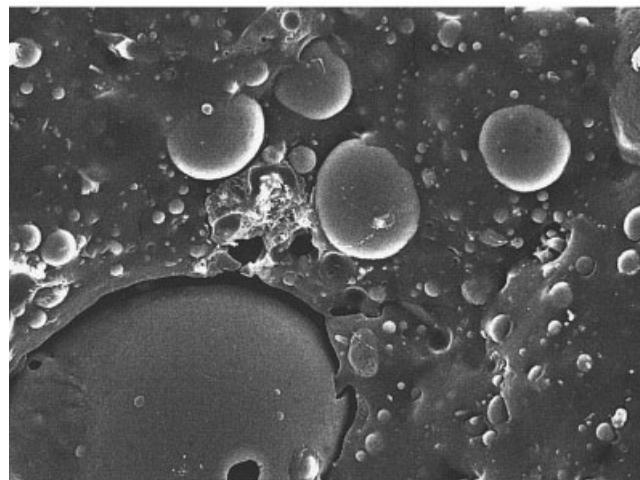
The ability of the rubber vulcanizates to recover after being mechanically loaded was evaluated
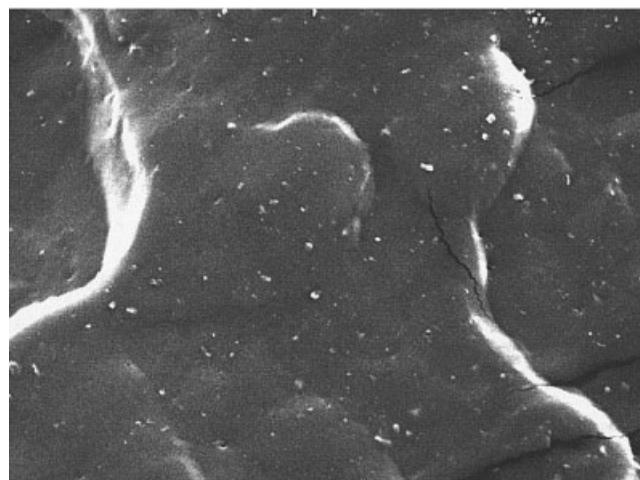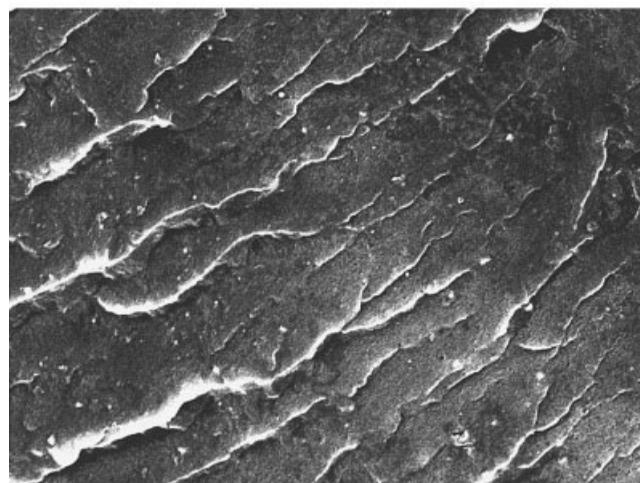
Figure 7 SEM micrographs of unfilled and silica-filled NR vulcanizates. (a) No filler; (b) 75% Psi-filled NR; (c) 75% FASi-filled NR.
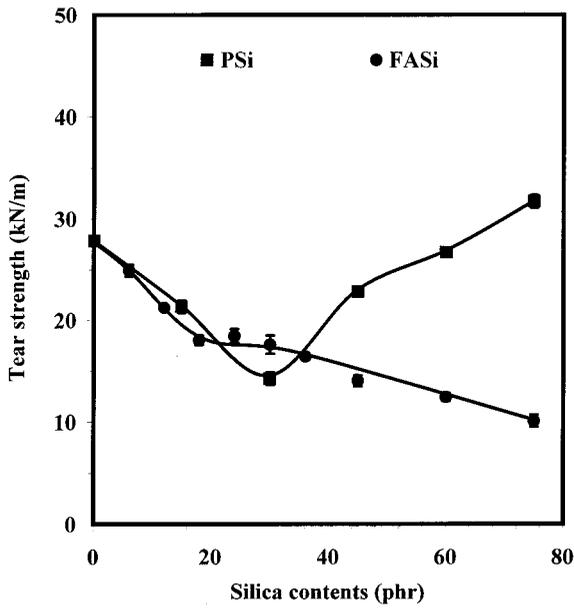
Figure 8 Tear strength of PSi- and FASi-filled vulcanizates at different silica contents.
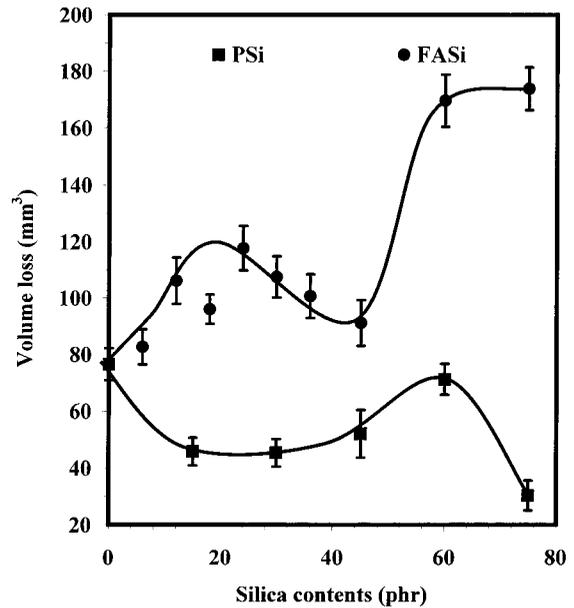

Figure 10 Abrasive resistance of NR vulcanizates filled with PSi and FASi particles.

through elongation set and percentage resilience tests, the results of which are shown in Figure 11. The results clearly suggest that the elasticity of the rubber vulcanizates decreased with the addition of silica. The use of FA as a filler gave rubber products with better elasticity than those of commercial silica, especially at silica contents greater than 30 phr. Figure 12 shows the changes in tan δ_{max} of the vulcanizates with various silica contents from the PSi and FASi particles. Tan δ_{max} decreased progressively with silica content. For

any given silica content, the value of tan δ_{max} for the PSi/NR vulcanizates was greater. The changes in tan δ_{max} were associated with filler–filler interactions that affected the mobility of the rubber molecules. We thought that the addition of silica into the NR compounds resulted in an increase in the filler network, which restricted the movement of the rubber molecules during dynamic deformation. This gave rise to a
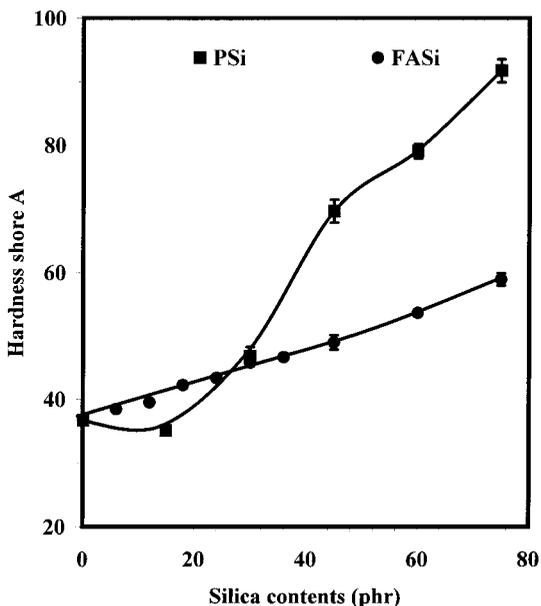

Figure 9 Hardness of PSi- and FASi-filled NR vulcanizates at different silica contents.
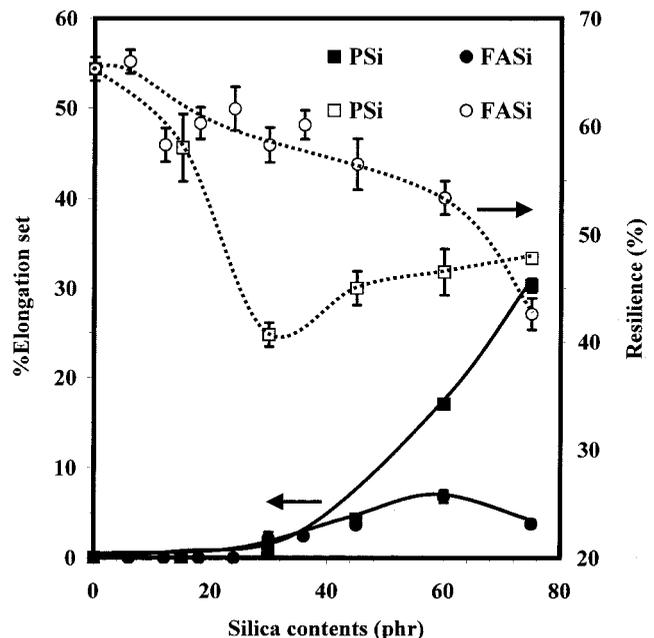

Figure 11 Elongation set and resilience properties of PSi- and FASi-filled NR vulcanizates at different silica contents.
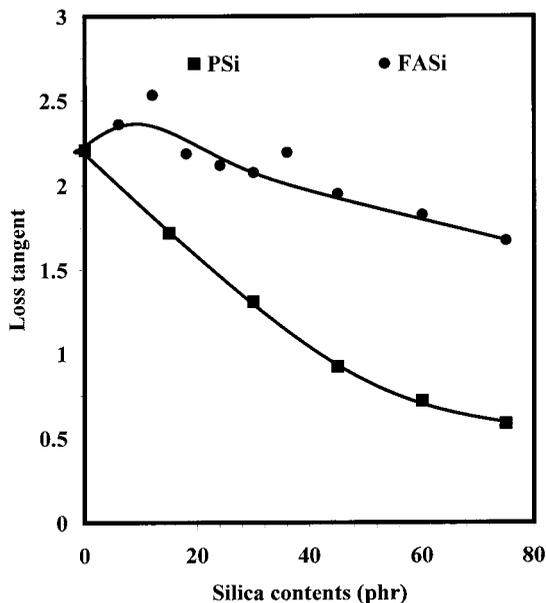
Figure 12 Effect of silica content on tan δ_{max} of NR vulcanizates filled with PSi and FASi particles.

higher elastic modulus and a lower tan δ_{max} compared to the unfilled NR vulcanizates. This view was in good agreement with Wang.[36]

SBR compound system and a comparison with the NR system

In this section of the study, the PSi and FASi particles were also used as fillers in SBR vulcanizates, and the properties of the filled SBR vulcanizates were evalu-
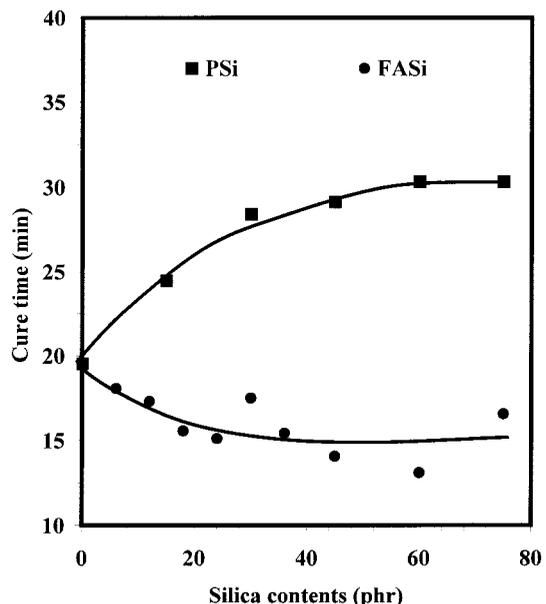

Figure 13 Relationship between the cure time and silica content for SBR vulcanizates filled with PSi and FASi.
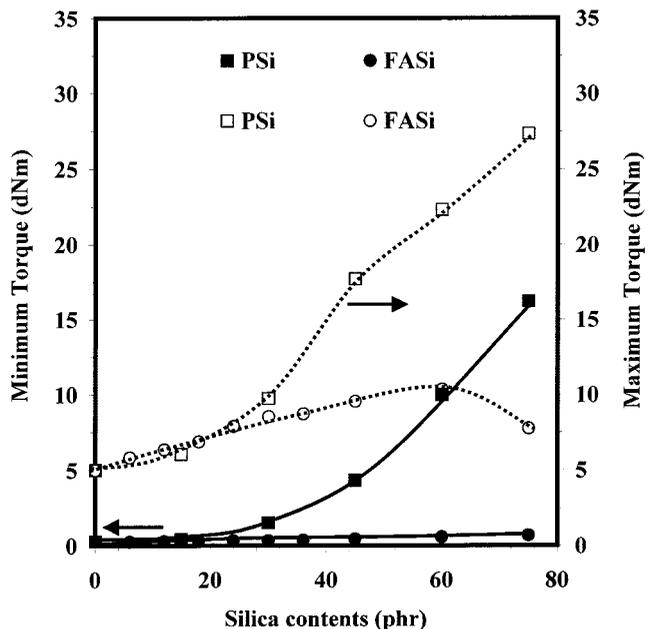

Figure 14 Variations in the minimum and maximum torques with silica content for SBR vulcanizates filled with PSi and FASi particles.

ated. The results were compared with those of the NR vulcanizates. Figure 13 shows the effect of PSi and FASi addition on the cure time of the SBR vulcanizates. The cure time of SBR increased up to 30 phr PSi before it leveled off at further PSi loadings. The increase in the cure time resulted from the coherent gel of the PSi throughout the rubber phase. For the FA particles, the cure time of the SBR vulcanizates did not change through the addition of FASi particles, which was very similar to the NR case. Again, the use of FA particles reduced the cure time considerably because of the presence of metal oxides in the FA particles, as already detailed. The cure time used for SBR was much greater than that for NR. This could be explained by a number of reasons as follows: (1) NR has more reactive sites to form crosslinking during vulcanization; (2) NR is more flexible than SBR, which makes the crosslinking process more feasible; and (3) SBR has a benzene group in the molecule, which could cause a stearic effect in the crosslinking reaction.

Figure 14 shows the effects of the addition of PSi and FASi to the SBR compounds on the minimum and maximum torques. The changing trends of the torques for the SBR vulcanizates were similar to those found in the NR vulcanizates, but the torque values for the SBR compounds for a given silica content were lower, which involved the initial molar masses of the rubbers used.[33]

Figures 15 and 16 show the modulus at 200% elongation and the tensile strength of SBR vulcanizates at various contents of the PSi and FASi fillers, respectively. Generally, the modulus and tensile strength of
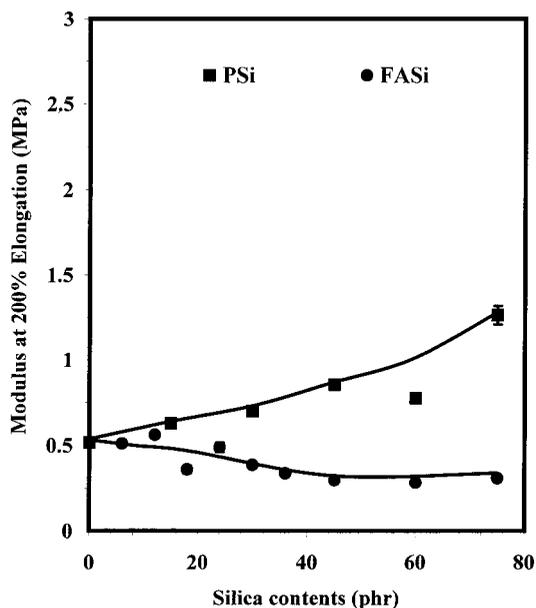
Figure 15 Variation in the modulus at 200% elongation with silica content for PSi- and FASi-filled SBR vulcanizates.

Figure 17 Effect of silica content on the crosslink density for PSi- and FASi-filled SBR vulcanizates.

SBR filled with PSi progressively increased to a maximum around 40 phr and then started to decrease at further loadings. The modulus and tensile strength for the FASi/SBR vulcanizates appeared to be independent of the silica content and were much lower than those of the PSi/SBR vulcanizates. This could be explained with the crosslink density results of the SBR filled with PSi and FASi, as shown in Figure 17, which suggests that for a given silica content, the crosslink density of the PSi/SBR compounds was much greater,
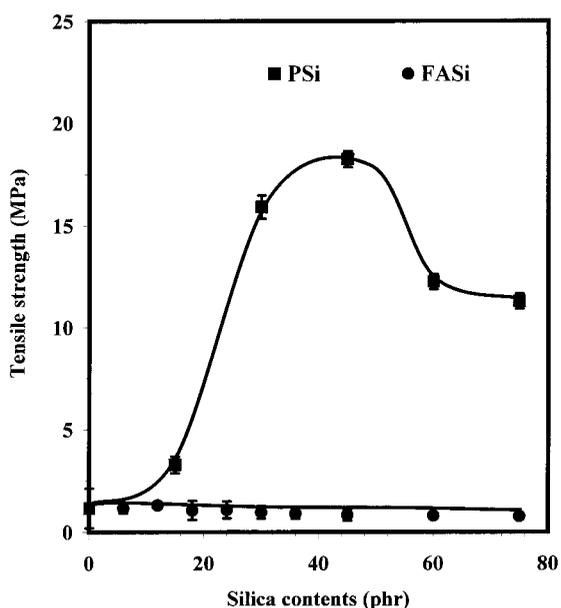

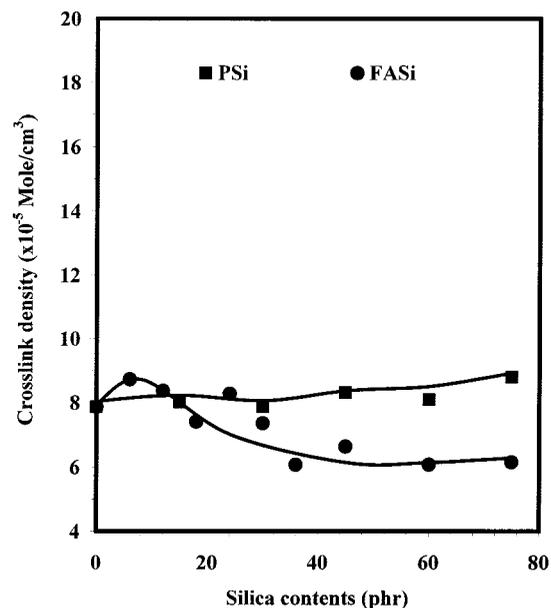**Figure 16** Tensile strength for PSi- and FASi-filled SBR vulcanizates at different silica contents.

especially at silica contents greater than 30 phr. The SEM micrographs of the PSi/SBR and FASi/SBR tensile-fractured surfaces given in Figure 18 could also be used to explain the differences in the tensile properties of these two vulcanizates. The homogeneity of the PSi/SBR sample was much better. When compared with the NR system, the modulus of the PSi/SBR vulcanizates was much lower, with the difference related to the molecular characteristics of the NR and SBR rubbers, as already discussed. However, the changing trend in the tensile strength for SBR was opposite that for the NR system. This finding was also observed by Nasir.[37] The tear strength of the SBR vulcanizates loaded with PSi and FASi particles is shown in Figure 19. The tear strength of the SBR vulcanizates progressively increased with the PSi content but was unaffected by the addition of FASi. With the effects of the FASi particles on the tensile and tear strength properties of the NR and SBR vulcanizates taken into consideration, it is obvious that FA particles can be recommended as a filler in NR compounds at silica concentrations of 0–30 phr but not in SBR compounds; the FA particles could be used only as an extender in SBR compounds.

CONCLUSIONS

Untreated PSi and FASi were loaded at different amounts into NR and SBR compounds, and the cure characteristics and final properties were monitored. The following findings were noted:

• For the NR system, the cure time and minimum and maximum torques of the NR compounds
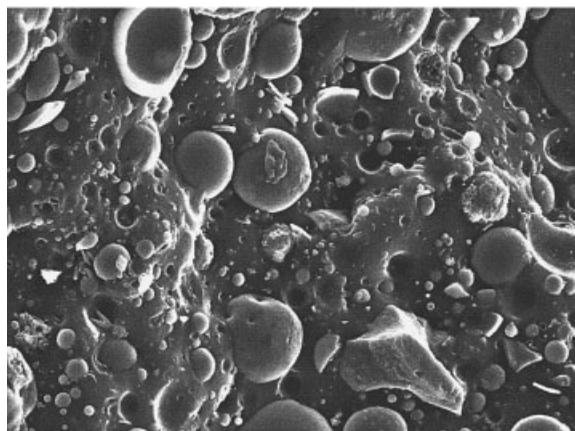
were unaffected by PSi loadings from 0 to 30 phr, and above these concentrations, the values progressively increased with PSi loading. The use of silica from FA particles resulted in a reduction in the cure time and low minimum and maximum torques, especially at high silica loadings; this was
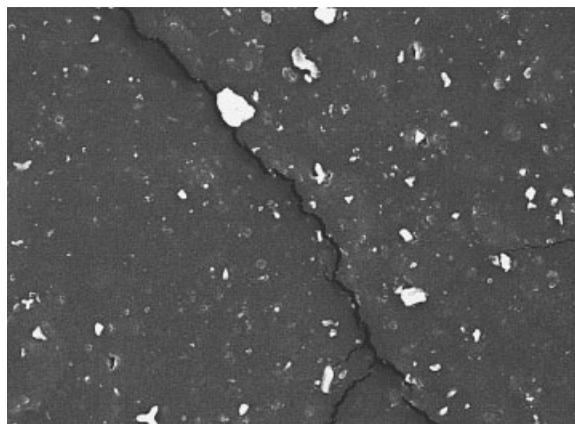
(a)
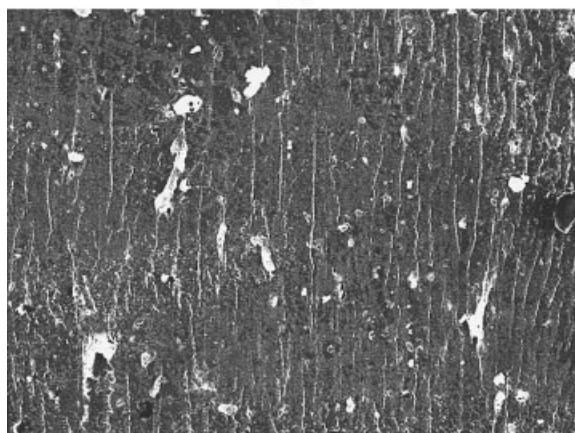
(b)

(c)

Figure 18 SEM micrographs of silica-filled SBR vulcanizates: (a) no filler, (b) 75% PSi-filled SBR, and (c) 75% FASi-filled SBR (570×).
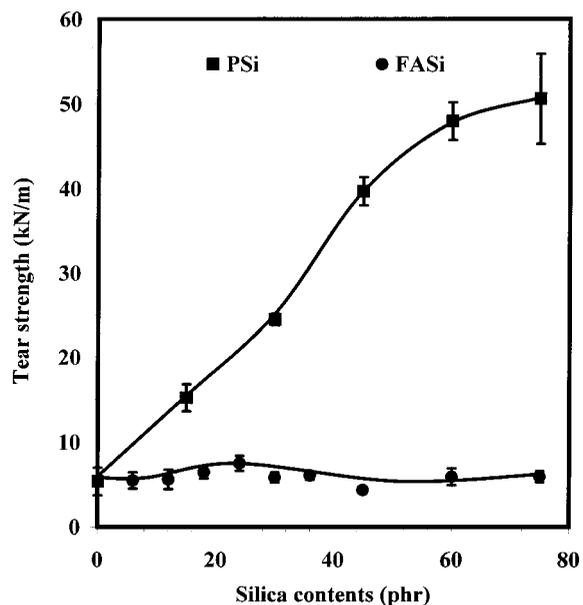

Figure 19 Tear strength of PSi- and FASi-filled SBR vulcanizates and different silica contents.

related to the silica structure within the filler. The vulcanizate properties of FASi-filled vulcanizates were similar to those of PSi-filled vulcanizates at silica contents of 0–30 phr. Above these concentrations, the properties of the PSi-filled vulcanizates improved, whereas those of the FASi-filled compounds remained the same.

- In the SBR system, the changing trends of all of the properties of the filled SBR vulcanizates were very similar to those of the filled NR vulcanizates. The overall properties of the filled SBR vulcanizates were lower than those of the filled NR vulcanizates except for the tensile and tear strengths. This indicated that silica and FA particles should be more recommended in NR rather than SBR systems.
- For a given rubber matrix and silica content, the discrepancies in the results between PSi and FASi were caused by differences in the filler–filler interactions, actual rubber content in the vulcanizates, and particle size of the fillers.
- FA particles can be recommended as a filler for NR compounds with silica contents of 0–30 phr but cannot be recommended for SBR compounds except when improvements in the tensile and tear strengths of the vulcanizates are required.

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