

Hybridized Reinforcement of Natural Rubber with Silane-Modified Short Cellulose Fibers and Silica

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ABSTRACT: Natural-rubber-based hybrid composites were prepared by the mixture of short cellulose fibers and silica of different relative contents with a 20-phr filler loading with a laboratory two-roll mill. The processability and tensile properties of the hybrid composites were analyzed. The tensile modulus improved, but the tensile strength and elongation at break decreased with increasing cellulose fiber content. The scorch safety improved with the addition of 5-phr cellulose fiber in the composites. The Mooney viscosity significantly decreased with increasing cellulose fiber content. To modify the surface properties of the cellulose fiber and silica fillers, a silane coupling agent [bis(triethoxysilylpropyl)tetrasulfide, or Si69] was used. The effects of Si69 treatment on the processing and tensile properties of the hybrid composites were assessed. We found that the silane treatment of both fillers had significant benefits on the processability but little benefit on the rubber reinforcement. The strength of

the treated hybrid composite was comparable to that of silica-reinforced natural rubber. Furthermore, to investigate the filler surface modification and to determine the mixing effects, infrared spectroscopic and various microscopic techniques, respectively, were used. From these results, we concluded that the fillers were better dispersed in the composites, and the compatibility of the fillers and natural rubber increased with silane treatment. In conclusion, the hybridized use of short cellulose fibers from a renewable resource and silica with Si69 presented in this article offers practical benefits for the production of rubber-based composites having greater processability and more environmental compatibility than conventional silica-filler-reinforced rubber. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3242–3254, 2011

Key words: biofibers; composites; fillers; morphology; rubber

INTRODUCTION

The majority of conventional fillers used in rubber industries are carbon black and silica because of their relatively high reinforcing efficiency. In general, a silica-reinforced rubber shows a comparable tensile strength to one reinforced with carbon black, but the modulus is relatively lower.¹ Because of the unpopularity of dirty work conditions, silica is always chosen for nonblack applications, where some functional properties, that is, high tear strength, good aging resistance, good abrasion resistance, and low heat buildup, are required. Unlike the compounding of carbon black, the incorporation of silica into natural rubber is rather difficult, as they are incompatible. The surface of silica is highly hydrophilic because of the presence of silanol ($-\text{SiOH}$).² These silanol

groups easily form hydrogen bonds with each other; this results in agglomerates and a higher compound viscosity. This makes processing more difficult. In addition, the presence of agglomerates adversely influences the properties of rubbers.³

Currently, the demand for reinforcing fillers from renewable resources, such as plant-based natural fibers, for the production of biosustainable composite materials is increasing in research areas and manufacturing because of their ease of processing, low cost, low density, biodegradability, and good mechanical properties. Natural-fiber-reinforced polymer composites are now used as alternative low-cost/sustainable materials for structural and nonstructural applications, such as building products, automotive applications, packaging, furniture, and consumer goods. In the past, a variety of short natural fibers were incorporated into natural rubber, and their reinforcement was discussed.^{4–10} It was reported that they did not provide the same level of reinforcement compared to carbon black and silica; that is, the tensile strength and elongation at break of natural-rubber-based composites substantially decreased

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with the addition of natural fibers. In many cases, the loading of fibers that gave optimal fiber orientation and acceptable mechanical properties was found to be 20–30 phr.^{5,7,8} Because of the high stiffness of natural fibers, however, the modulus of natural-rubber-based composites increases with fiber content. Moreover, natural fibers can be added to rubber to improve or modify certain properties, such as green strength, creep resistance, hardness, aging resistance, dynamic mechanical properties, dimensional stability during fabrication, and real-time service, and to reduce the cost of fabricated articles.

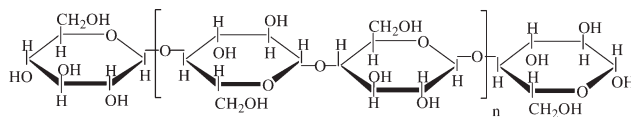
It is well established that blending of two or more fibers and/or fillers gives the potential for preparing new engineering materials with specific and improved properties.¹¹ In hybrid filler-reinforced composites, the properties are mainly dependent on the properties of the individual fiber/and or filler, composition, and surface treatment.^{7,11} Recently, studies of the synergetic effects of natural fibers and particulate fillers compounded with different polymeric matrices on the physicomechanical properties of hybrid composites have been reported.^{12,13} These studies showed encouraging results, in which the improvement of specific properties was observed together with additional environmental and cost benefits. Therefore, it is anticipated that the combined use of both short natural fibers and silica will enable one to merge the beneficial effects of individual reinforcement for the development of materials with desirable properties. In practical applications, such as for automobile tires, the combined use of natural fibers and silica has been applied widely to improve the processability, dimensional stability, and mechanical balance between the abrasion resistance and rolling characteristics.^{14,15} Tire-tread compounds containing short natural fibers together with precipitated silica are used to enhance ice traction for icy roads.¹⁶ However, no systematic study of composites made of natural rubber reinforced with hybrid fillers from natural fibers and silica particulates and the effects of the natural fiber/silica ratio on composite performance has been reported so far. In this study, the primary objective was to examine the effects of the ratio of short natural fibers to silica on the curing/rheological characteristics and tensile properties of natural rubber. To increase the surface affinity, the natural fiber and silica surfaces were also treated with a silane coupling agent. The changes in the chemical structure of the fillers after treatment were studied with Fourier transform infrared (FTIR) spectroscopy. The effects of silane-treated natural fibers and silica on the curing properties, Mooney viscosity, and tensile properties of the hybrid composites were examined. The morphology of the composite was also investigated with different microscopic techniques.

EXPERIMENTAL

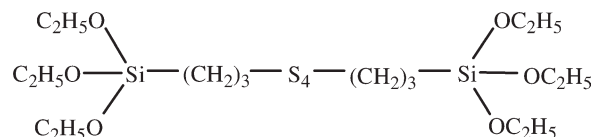
Materials

Chemicals

Natural rubber (STR 5L) was obtained from Thavorn Industry Co., Ltd. (Songkhla, Thailand). Cellulose fibers (ARBOCEL B00) with a fiber length of 120 μm and a fiber diameter of 20 μm were supplied in fibrous form (Fig. 1) by JRS Co., Ltd. (Rosenberg, Germany). These cellulose fibers were very short fibers, were produced from soft wood, and consisted exclusively of native cellulose, which is a hydrophilic glucan polymer consisting of a linear chain of 1,4-anhydroglucose units containing alcoholic hydroxyl groups ($-\text{OH}$), as shown in the following structure:



Precipitate silica (Ultrasil VN 3 GR) was manufactured by United Silica (Siam), Ltd. (Rayong, Thailand). The average particle size and specific surface area of the silica were 10–40 nm and 210 m^2/g , respectively. The silane coupling agent [JJ-Degussa (Thailand) Co., Ltd., (Bangkok, Thailand)] used was bis(triethoxysilylpropyl)tetrasulfide (Si69). The structure of the silane coupling agent was as follows:



The rubber compounding ingredients, including zinc oxide (ZnO; Global Chemical Co., Ltd., Samutprakarn, Thailand), stearic acid (Imperial Chemical Co., Ltd., Pathumthani, Thailand), sulfur (Ajax Chemical Co., Ltd., Samutprakarn, Thailand), *N*-tert-butyl-2-benzothiazyl sulfenamide (TBBS; Bayer Thai Co., Ltd., Bangkok, Thailand), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ; Flexsys, Antwerpen, Belgium) were commercial grade. Diethylene glycol (DEG) was supplied by Sigma-Aldrich Pte Ltd., Singapore. Acetone (Fisher Scientific UK, Ltd., Loughborough, United Kingdom) were analytical-reagent grade and were used as received.

Silane (Si69) treatment

Because silane concentrations of 0.225–1.15% of fiber weight and 2% of silica weight were reported to be optimum dosages for the pretreatment of henequén fibers and silica, respectively,^{17,18} in this study, the pretreatment with silane was carried out at a silane

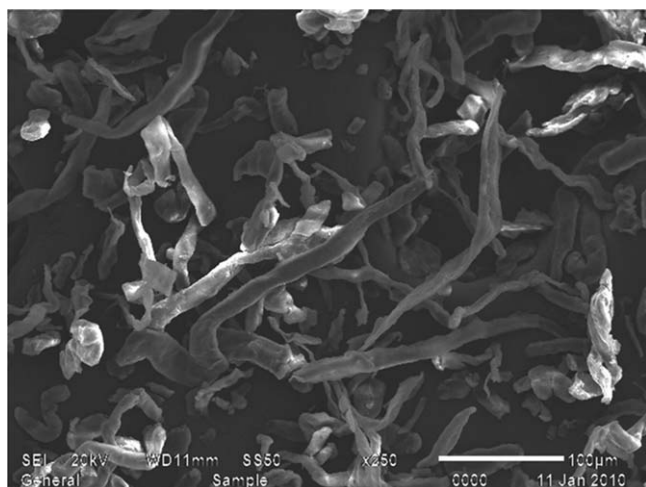


Figure 1 SEM photomicrograph of ARBOCEL B00 showing a fiberlike structure.

concentration of 2 wt % of filler content. Si69 (2 g) was diluted in acetone (500 mL). The Si69 solution was added with oven-dried cellulose fibers or silica (100 g). The mixture was stirred for 1 h at 30°C to ensure the uniform distribution of the silane coupling agent. The fillers were removed from the mixture, washed several times with acetone to remove the unreacted silane coupling agent, and dried at 100°C for 24 h in a hot-air oven and then at 100°C for 3 h in a vacuum oven.

Fabrication of the hybrid composites

The compounding of the natural rubber, silica, cellulose fiber, and rubber additives was carried out with a laboratory two-roll mill (150 × 300 mm²; Chaicharoen Karnchang Co., Bangkok, Thailand) at room temperature. The formulation of hybrid composites is given in Table I. The natural rubber was first masticated on the mill, and the compounding ingredients were added in the following order: stearic acid, ZnO, TMQ and TBBS (accelerator), fillers (cellulose fiber and silica), and sulfur. The cellulose fiber and silica were added with DEG before compounding. To study the hybrid effect on properties of the natural rubber composites, the total filler content was kept constant (20 phr), whereas the loading ratio of cellulose fiber to silica was varied. We sheeted out the compounds by passing them through a small nip of the rolls and kept them for 16 h before the oscillating disc rheometer (ODR) test. The sheeted compounds were placed in a mold and hot-pressed under hydraulic pressure at 150°C for the respective optimal cure time obtained from the ODR test.

ODR measurements

The cure characteristics of the rubber compounds were measured on an oscillating disc rheometer

(ODR 2000, Monsanto Co., Ltd., Ohio, USA). The measurement was performed at 1 arc degree and 150°C according to ASTM D 2084-81.

Mooney viscosity [ML(1+4), 100°C] measurements

The Mooney viscosity of the rubber compounds was measured after compounding with a Mooney viscometer (SPRI, Ltd., Sondes Places, United Kingdom) according to the testing procedure described in ASTM D 1646-94. The Mooney viscosity was recorded after the samples were preheated for 1 min with a total testing time of 4 min. The test temperature was set at 100°C.

Mechanical measurements

The tensile testing was performed on a Hounsfield tensometer (model H10KS, Hounsfield Test Equipment Ltd., Surrey, United Kingdom) according to ASTM D 412-98. The dumbbell-shaped test specimens were cut from vulcanized rubbers. The specimens were stretched at room temperature (25 ± 2°C) with an extension rate of 500 ± 50 mm/min. The average tensile properties for each cellulose fiber/silica-reinforced natural rubber hybrid composite were determined from five specimens.

FTIR spectroscopy

The FTIR spectra were recorded on a Bruker EQUINOX 55 (Bruker Optics GmbH, Ettlingen, Germany) in the range 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. The spectra were obtained with the KBr pellet technique. Before characterization, the fiber and silica were dried, and the samples (1.15 mg) were crushed into fine particles and mixed with KBr powder (3.45 mg). The mixtures (0.77 mg) were then pressed into thin discs.

Scanning electron microscopy (SEM)

JEOL JSM-6510 LA and JSM-5800 LV scanning electron microscopes (JEOL Ltd., Tokyo, Japan) were used to

TABLE I
Formulation of Short Cellulose Fiber/Silica Hybrid Filler Reinforced Natural Rubber Composites

Ingredient	Parts per hundred rubber (phr)
Natural rubber (STR 5L)	100
Stearic acid	1
ZnO	5
Polymerized TMQ	1
TBBS	0.7
DEG ^a	1.6
Sulfur	2.5
Cellulose fiber/silica	0/20, 5/15, 10/10, 15/5, and 20/0

^a The concentration of DEG used was 8 wt % of the filler.

TABLE II
Effect of Various Cellulose Fiber Contents on the Cure Characteristics and Mooney Viscosity of Untreated Cellulose Fiber/Untreated Silica Hybrid Filler Reinforced Natural Rubber Composites at a Total Filler Loading of 20 phr

Cellulose fiber content (phr)	M_L (dN m)	M_H (dN m)	T_{s1} (min)	T_{c90} (min)	ML(1+4), 100°C
0	5.70	26.30	3.80	10.80	42
5	5.60	25.00	5.00	11.50	33
10	5.70	23.80	5.50	12.50	25
15	5.20	26.90	5.30	10.20	18
20	4.80	27.30	5.50	10.50	15

examine the cellulose fiber and composite morphologies, respectively. The composite sample pieces were immersed in liquid nitrogen and cracked. The fiber and fracture surfaces were sputter-coated with a thin layer of gold to prevent electrical charging during the examination. SEM photomicrographs of the fracture surfaces were taken at magnifications of 400, 10,000, and 20,000 \times . The X-ray silicon mapping of the hybrid composite samples was examined with an Oxford energy-dispersive X-ray spectroscopy system attached to the SEM microscope.

RESULTS AND DISCUSSION

Effect of the loading of short cellulose fibers/silica without silane surface treatment

Processing properties

The cure characteristics and Mooney viscosity [ML(1+4), 100°C] of the hybrid composites were determined as a function of the cellulose fiber content, and the total hybrid filler content was kept constant at 20 phr. The results are given in Table II. Minimum torque (M_L) obtained from ODR testing is normally related to the viscosity of a rubber compound. The M_L value of single-fiber-filled compounds was lower than that of the unhybridized silica-filled compounds, and M_L seemed to be almost the same, regardless of the hybrid silica/fiber composition (Table II). The fiber-filled compound showed a lower viscosity, probably because of the larger size of the cellulose fibers and less interaction among the fibers compared with silica. The Mooney viscosity, taken as a measure of rubber compound viscosity, for the hybrid composites showed a decrease with increasing cellulose fiber. The compound viscosity decreased because the filler–filler interaction decreased as more fibers were added to the hybrid filler composition. Additionally, it was reported that the fibers could interact with silica particles, which thus reduced the reaggregation of silica during compounding.¹⁹ Because of the viscosity change, the energy required in processing would

have been considerably reduced with the addition of short cellulose fibers. The maximum torque (M_H) is considered as a measure of modulus for cured rubber composites.²⁰ M_H seemed to be independent of the cellulose fiber loading. The scorch time (T_{s1}) and optimum cure times (T_{c90} 's) were measures of the times corresponding to the onset of curing or the crosslinking reaction and to 90% of complete curing, respectively. The introduction of cellulose fibers at the small level of 5 phr into the composite led to an increase in T_{s1} , whereas there was no noticeable change with a greater fiber loading. A previous study conducted by Bai and Li¹⁹ showed that the partial replacement of silica with microcrystalline cellulose in styrene–butadiene rubber/polybutadiene blends decreased the mixing temperature measured during compounding. The temperature was used as an indicator of the heat generated during rubber compounding. They described that when the aggregations of fillers were broken down, friction occurred, and heat was generated. Because of less interaction between the cellulose fibers than with silica, the lower thermal history experienced in the hybridized composites when compared with the silica composites might have explained the increase in T_{s1} . The hybrid composites containing a 5-phr fiber loading also showed higher T_{c90} values than that of the single silica composites. A further increase in the fiber loading appeared to affect T_{c90} in the random behavior. The reason for the independence of T_{c90} on the amount of hybridized fiber at a higher level (5 phr) requires further study. According to Bai and Li,¹⁹ when the amount of silane-coated silica replaced with microcrystalline cellulose increased, T_{c90} did not change in the predicted manner. However, the observation in this study clearly indicates that the increase in T_{s1} and cure time was only attained at a low fiber level, and neither of the properties were differentially affected by increasing fiber content. The observed increase in T_{s1} in the natural rubber added with cellulose fiber suggested that the hybridized cellulose/silica filled natural rubber exhibited more scorch safety over the unhybridized-silica-reinforced natural rubber. This means that when the fibers were added in the rubber compositions, they helped delay the start of the curing process of the rubber during the filling of a mold cavity. Curing characteristics, such as scorch delay, would be advantageous in rubber processing, such as in injection-molding, extrusion, or transfer-molding operations.

Tensile properties

The tensile properties for the hybrid filler composites as a function of the cellulose fiber content are presented graphically in Figures 2–4. As shown in Figure 2, the tensile modulus at 100% elongation at break of the vulcanized natural rubber (0.88 MPa) improved after the incorporation of a single filler,

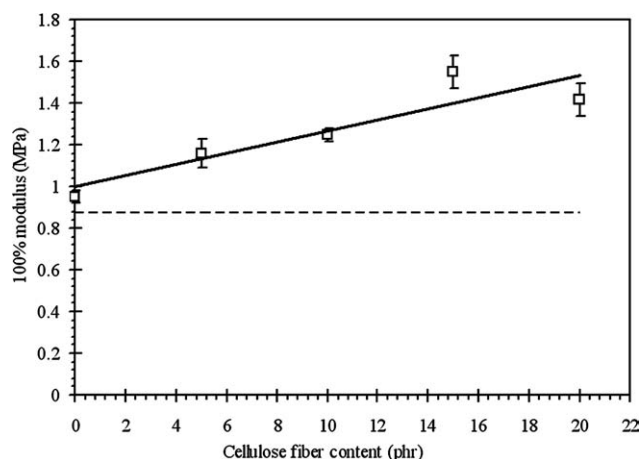


Figure 2 Effect of various cellulose fiber contents on the tensile modulus at 100% elongation of the untreated cellulose fiber/untreated silica hybrid filler reinforced natural rubber composites at a total filler loading of 20 phr. The 100% modulus of neat natural rubber is represented as a dashed line.

either silica or cellulose fiber. At a filler loading of 20 phr, the tensile modulus of the unhybridized cellulose fiber composite was higher than that of the silica composite by almost 1.5 times. This indicated that the cellulose fiber imparted much more material stiffness compared with silica. Increasing the fiber loading increased the rubber modulus because of the effect of fiber stiffness. The elongation at break of the different hybridized composites slowly decreased as more fibers were incorporated, but the observed values of elongation at break were found to be comparable with that of the cured natural rubber (700%) within experimental error, as shown in Figure 3. The tensile strength is shown in Figure 4.

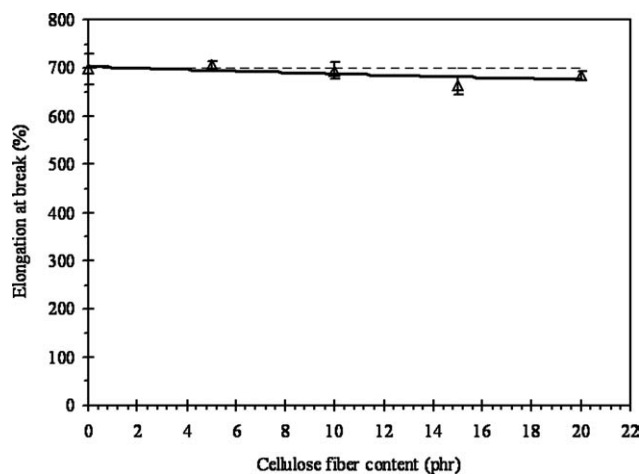


Figure 3 Effect of various cellulose fiber contents on the elongation at break of the untreated cellulose fiber/untreated silica hybrid filler reinforced natural rubber composites at a total filler loading of 20 phr. The elongation at break of the neat natural rubber is represented as a dashed line.

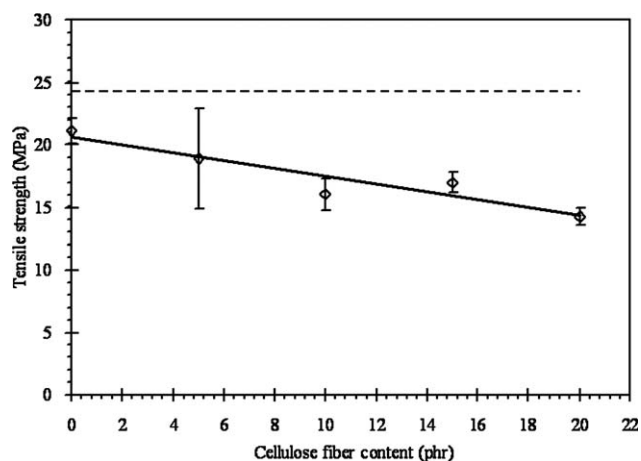


Figure 4 Effect of various cellulose fiber contents on the tensile strength of the untreated cellulose fiber/untreated silica hybrid filler reinforced natural rubber composites at a total filler loading of 20 phr. The tensile strength of the natural rubber is represented as a dashed line.

The tensile strength of both the unhybridized silica and short fiber composites were comparatively lower than that of the vulcanized natural rubber (24.33 MPa). Figure 5 shows the fracture surfaces of the natural-rubber-based single filler composites investigated by SEM. Generally, the cellulose fibers showed poor fiber dispersion over the rubber surface, as shown by the presence of fiber aggregates and holes left over the composite surface because of fiber pullout [Fig. 5(a)]. The fiber aggregation resulted in the reduction of the contact area between the fiber and rubber matrix; this increased the defect in the hybrid composites. This effectively reduced the stress transfer from the rubber matrix to the fiber; this lowered the tensile strength of the natural rubber. The silica-filled composite showed a rather smooth surface, as observed at the same magnification [400 \times , Fig. 5(b)]. At a higher magnification of 20,000 \times [Fig. 5(c)], it was evident that the primary silica particles aggregated into larger particles with an average size of about 0.1–0.5 μm , which caused a decrease in the degree of natural rubber reinforcement. For the composites containing the single filler, the reduction in tensile strength was more significant in the case of the cellulose-fiber composite. It is known that the tensile strength of a filled rubber basically depends on the filler size and surface area.²¹ Therefore, it seems to be reasonable that the difference in the tensile strength of the single cellulose fiber composite as compared with that of the single silica composite was accounted for by differences in the filler factors. The inferior reinforcement by the cellulose fiber was due to the larger size of the fibers compared to that of the silica fillers; hence, smaller effective surface areas were available for interaction with the rubber matrix. Thus, the tensile strength of

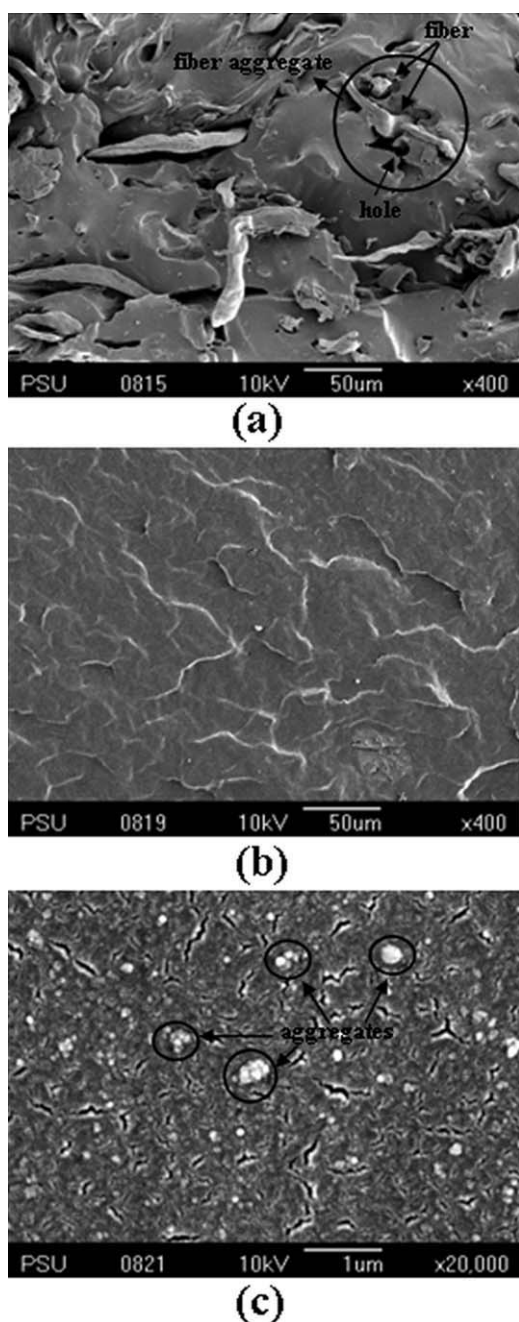


Figure 5 SEM photomicrographs of the natural rubber reinforced with (a) 20-phr untreated cellulose fiber at a magnification of 400 \times , (b) 20-phr untreated silica at a magnification of 400 \times , and (c) 20-phr untreated silica at a magnification of 20,000 \times .

the hybridized composites also decreased with fiber loading because of the decrease in the effective surface area with increasing fiber fraction.

Effect of the Si69 treatment

FTIR spectroscopic analysis

The FTIR technique was used to investigate the change in the surface chemistry of the cellulose fiber

and silica after silane treatment. Figure 6 shows the spectra of the two cellulose fibers, unmodified and Si69-modified fibers in the region from 4000 to 400 cm^{-1} . In addition, the spectrum of Si69 is shown for comparison [Fig. 6(a)]. In the spectrum of the untreated cellulose fiber [Fig. 6(b)], the broad and strong peaks at 3380 and 2885 cm^{-1} were due to hydrogen-bonded $-\text{OH}$ vibration and $\text{C}-\text{H}$ stretching from the $-\text{CH}_2$ group of the cellulose structure in the fiber, respectively. The peak at 1643 cm^{-1} is usually assigned to the stretching vibration of $\text{H}-\text{O}-\text{H}$ due to absorbed water,²² which was probably collected during sample preparation. The peaks at 1432 and 1373 cm^{-1} were ascribed to the bending vibration of $-\text{CH}_2$. The peak observed at 1050 cm^{-1} was due to the $\text{C}-\text{O}$ stretching of cellulose fiber. Upon treatment with the 2% Si69 solution, new absorption bands emerged at wave numbers of 2961, 1238, and 1065 cm^{-1} , as shown in Figure 6(c); this was clearly not seen in the spectra of the corresponding untreated fiber. The appearance of a small absorption peak at 2961 cm^{-1} was found in the same region of the stretching vibration of the $-\text{CH}_2$ and $-\text{CH}_3$ groups of Si69 at 2973, 2923, and 2887 cm^{-1} . It was reported that the IR absorption band around 1200 cm^{-1} was attributed to $\text{C}-\text{O}-\text{Si}$,²³ and this band was found to be present in pure silane (1246 cm^{-1}) and in the treated fiber (1238 cm^{-1}). To explain the existence of the band at 1065 cm^{-1} , the spectra of the two fibers in the 1400–600 cm^{-1} region were compared, and they are shown in Figure 7. It was clear that the band at 1050 cm^{-1} present in the untreated fiber was replaced by a broad band ranging from 1080 to 1050 cm^{-1} after the treatment. This indicated that the $\text{C}-\text{O}$ groups in the treated fiber had different local chemical environments. Also, Si69 showed a characteristic absorption peak due to the stretching of $\text{C}-\text{O}$ at 1098 cm^{-1} [Fig. 6(a)].

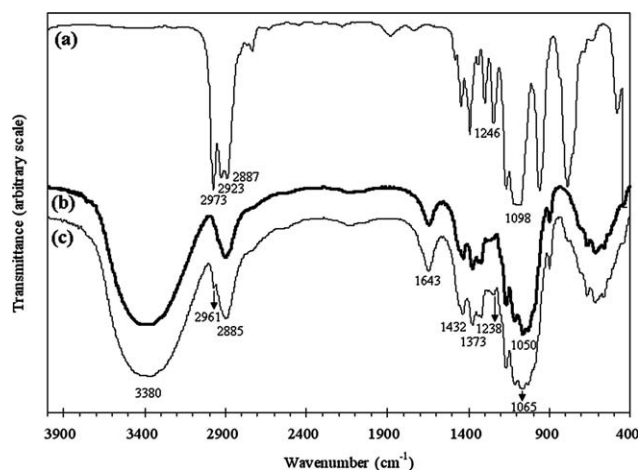


Figure 6 FTIR spectra of (a) Si69, (b) the untreated cellulose fiber, and (c) the Si69-treated cellulose fiber in the region 4000–400 cm^{-1} .

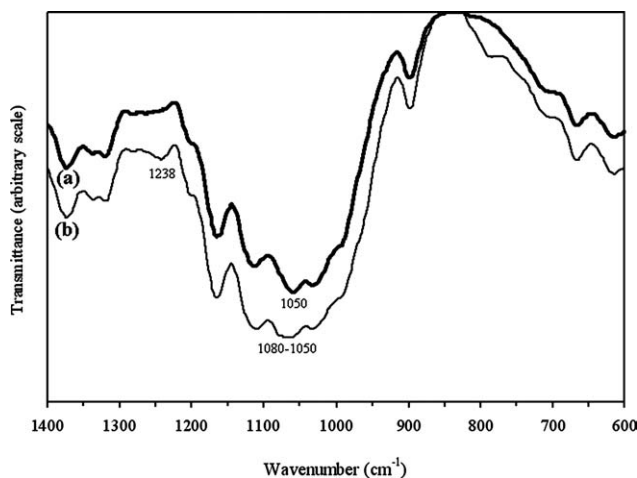


Figure 7 FTIR spectra of the (a) untreated cellulose fiber and (b) Si69-treated cellulose fiber in the region 1400–600 cm^{-1} .

Therefore, the characteristic band centered at 1065 cm^{-1} in the 1080–1050- cm^{-1} region was likely related to the $\text{CH}_3\text{CH}_2\text{—O}$ groups of silane. Conclusively, the presence of IR absorption bands in the ranges of 2961, 1238, and 1065 cm^{-1} for the Si69-treated cellulose fiber proved that the fiber surface was modified by the absorption of silane. Figure 8 shows the spectra of the untreated silica and Si69-treated silica. The IR spectrum of the untreated silica showed a peak at 3440 cm^{-1} due to the O—H stretching of the silanol group (Si—OH). The absorption band at 1632 cm^{-1} corresponded to the stretching vibration of the O—H bond. The strong and intense peak observed at 1094 cm^{-1} corresponded to the asymmetric stretching of the siloxane group (Si—O—Si) in the silica structure.²⁴ The peaks at 960 and 800 cm^{-1} were due to the stretching of Si—O in silanol and the deformation of Si—OH, respectively. The peak at 470 cm^{-1} was assigned to Si—O—Si symmetric stretching. The spectrum of the Si69-treated silica typically showed absorption bands due to the vibration of specific functional groups in the silica structure, as stated earlier, except for the small absorption peaks at 2977 and 2925 cm^{-1} . These two peaks were due to the stretching of the —CH_2 and CH_3 groups in Si69; these indicated the presence of Si69 on the silica. The absorption peak of the C—O

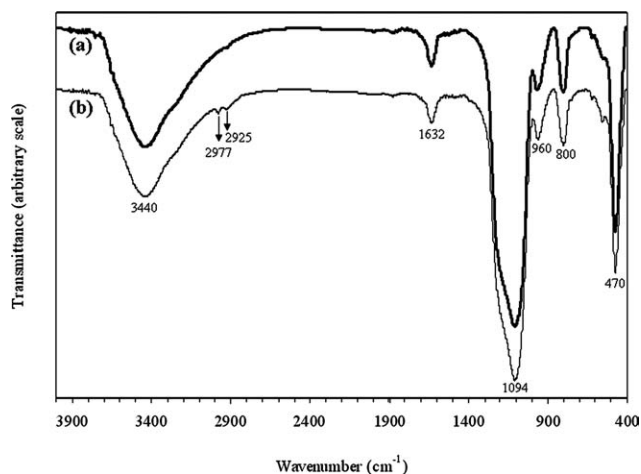


Figure 8 FTIR spectra of the (a) untreated silica and (b) Si69-treated silica in the region 4000–400 cm^{-1} .

bond at about 1098 cm^{-1} [Fig. 6(a)], due to the presence of silane, could not be identified because of interference with the stretching of the Si—O—Si bond in the silica structure. However, the symmetric stretching of the alkyl group in silane at 2977 and 2925 cm^{-1} seemed to suggest the deposition of Si69 on the silica surface.

Processing properties

The curing characteristics and viscosity of the Si69-treated 10/10 cellulose/silica composites and the corresponding untreated hybrid composites are compared in Table III. The M_L and Mooney viscosity values decreased after the surface modification with the silane solution; this indicated a reduction in the compound viscosity, which resulted in an improvement in the processability characteristics. The reduction in viscosity was explained by a decrease in filler–filler interaction due to the silane treatment. This explanation was supported by SEM observation, X-ray silicon mapping, and optical microscopic examination, as discussed later. M_H increased for the treated hybrid composite with respect to the corresponding untreated hybrid composite because of the increase in crosslink formation. The Si69 used in this study possessed tetrasulfane groups ($\text{—S}_4\text{—}$), which are rubber

TABLE III
Cure Properties and Mooney Viscosity of the Untreated and Si69-Treated Cellulose Fiber/Silica Hybrid Filler Reinforced Natural Rubber Composites

Type of hybrid composite	M_L (dN m)	M_H (dN m)	T_{s1} (min)	T_{c90} (min)	ML(1+4), 100°C
Untreated hybrid composite	5.70	23.80	5.50	12.50	25
Si69 treated hybrid composite	3.17	26.26	8.60	13.97	20

Relative loading of the cellulose fiber/silica = 10/10 phr/phr.

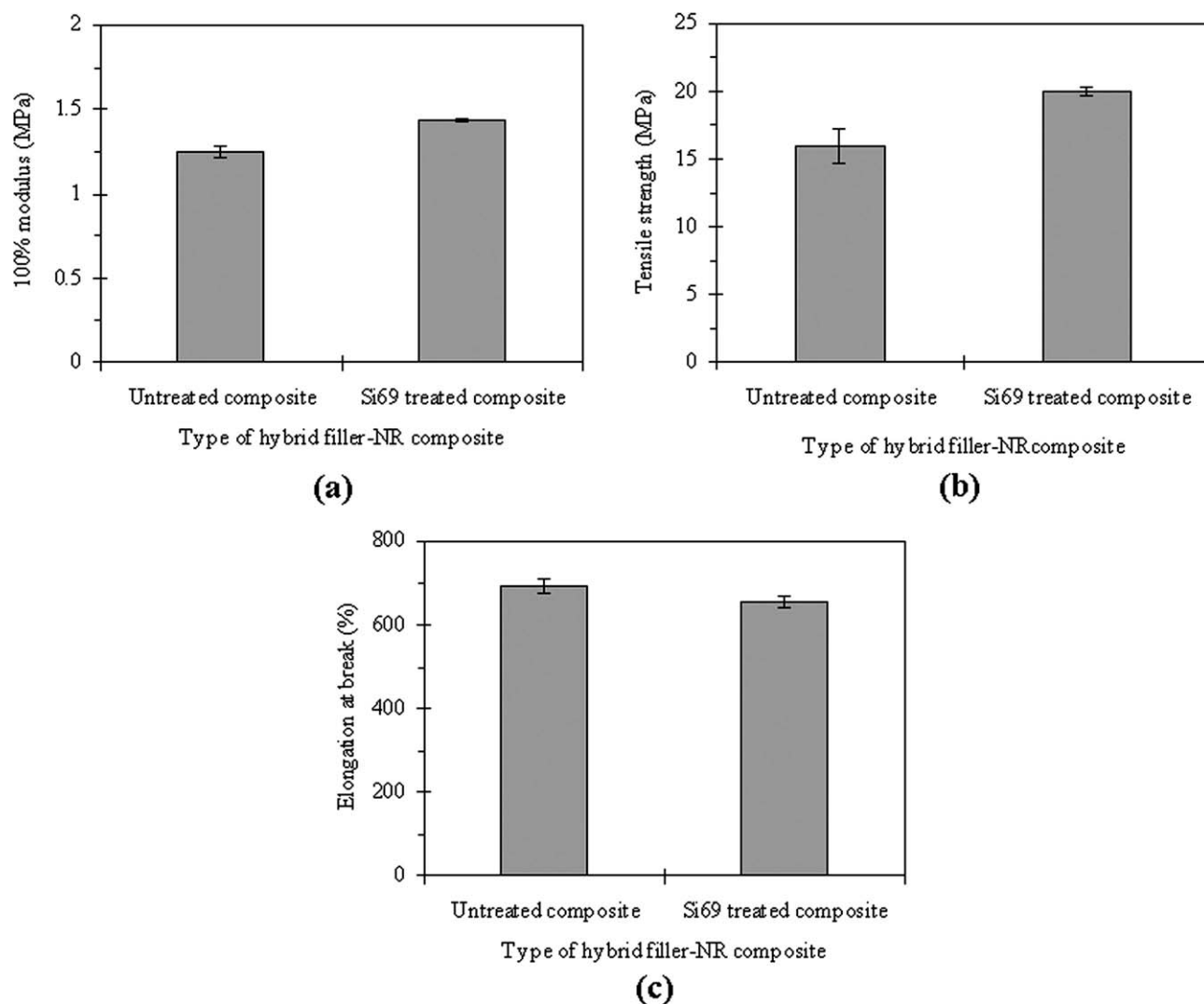


Figure 9 Comparison of the tensile properties: (a) 100% modulus, (b) tensile strength, and (c) elongation at break for the untreated and Si69-treated 10/10 cellulose fiber/silica hybrid filler reinforced natural rubber (NR) composites.

active.² When the treated hybrid fillers were used to reinforce rubber, they likely exposed the sulfur-functional surfaces for interaction with the rubber matrix. It was reported that the polysulfidic groups of the silanes on the treated fillers were highly unstable, and the dissociation of these sulfur groups resulted in active sulfur radicals.²⁵ The active sulfur radicals then reacted with the rubber to form crosslinks via sulfur bonding during fabrication. It was obvious that the addition of the treated fillers increased T_{s1} and the cure time. The reason for this increase was probably an improvement in the filler dispersion²⁶ and an increase in steric hindrance for crosslinking due to the presence of bulky groups (triethoxysilylpropyl groups) in the long-chain Si69.²⁷ The increments of T_{s1} and cure time with the incorporated Si69 was previously reported in the natural rubber reinforced with grass-fiber filler⁴ and a natural rubber/styrene butadiene rubber blend filled with precipitated silica.¹⁸

From these results, it was clear that the silane treatment of the fiber/silica hybrid filler provided extended scorch safety and improved processability.

Tensile properties

Figure 9 shows the tensile properties of the 10/10 unmodified and surface-modified cellulose fiber/silica hybrid filler reinforced natural rubber composites. It was clear that the modulus [Fig. 9(a)] and tensile strength [Fig. 9(b)] of the Si69-modified hybrid composites were higher than those of the corresponding unmodified hybrid composites. The improvement levels of the modulus and tensile strength were about 15 and 25%, respectively. The explanation for this improvement was that there was an increase in both interfacial bonding at fiber/silica-rubber interface and the dispersability of cellulose fiber/silica within the rubber matrix due to the

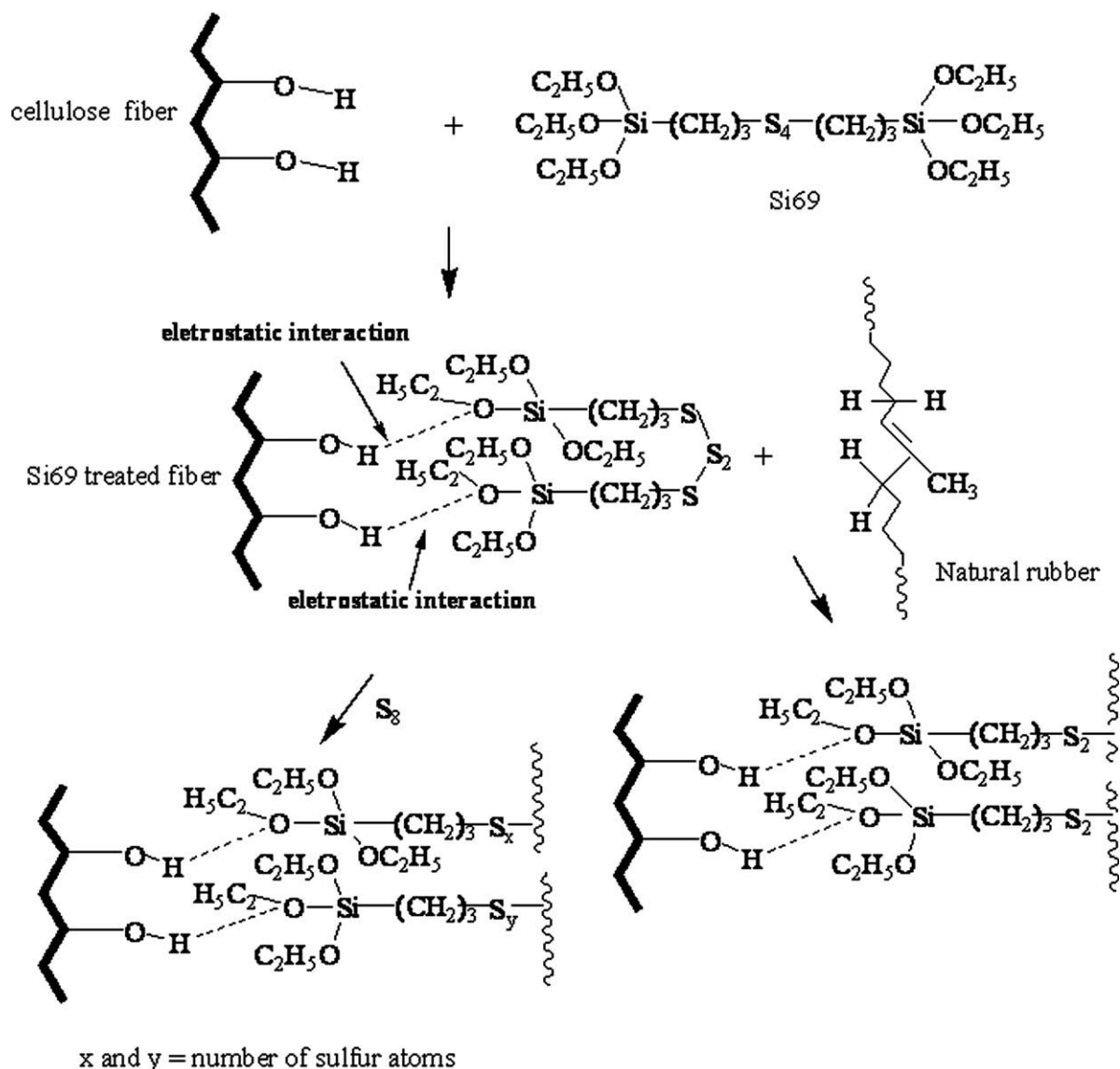


Figure 10 Schematic presentation proposed for the reaction between Si69 and the cellulose fiber.

increase in the surface affinity of the hybrid fillers to the rubber matrix by Si69 treatment. The natural rubber filled with the treated hybrid fillers had a lower elongation at break than that filled with the untreated hybrid filler [Fig. 9(c)]. This was because the natural rubber matrix grew stronger and stiffer with inclusion of the treated fillers; this resulted in a lower elongation. It is well accepted that natural rubber inherently shows a high tensile strength because of strain-induced crystallization. When the cellulose/silica fillers were added to the natural rubber, we found that the strain-induced crystallization was not visibly observed until the filled rubber samples were stretched to an elongation of more than 300%. To prevent any crystalline interference on the rubber reinforcement, it was suitable to define the stress at any load level less than 300% (e.g., 100% modulus of the hybrid composites) as a measure of

reinforcement level. For the composites combined with modified fiber/silica, although the use of the silane coupling agent increased the modulus at 100% elongation, this increase was not so significant. Also, among the characteristics of the filler, such as size, shape, and surface activities, a number of factors strongly affected the rubber reinforcement, which in turn, controlled the mechanical and physical properties of the rubber composites. They were the degree and type of adhesion between the filler and rubber matrix^{24,28} and filler dispersion.^{29,30} To take advantage of the reinforcing fillers, a strong adhesion at the fiber/silica–rubber matrix interface is needed for an effective stress transfer and load distribution throughout the interface. This situation, however, was not the case for the surface modification of the cellulose fiber/silica. The Si69 coupling agent used in this study may have reacted with the surface

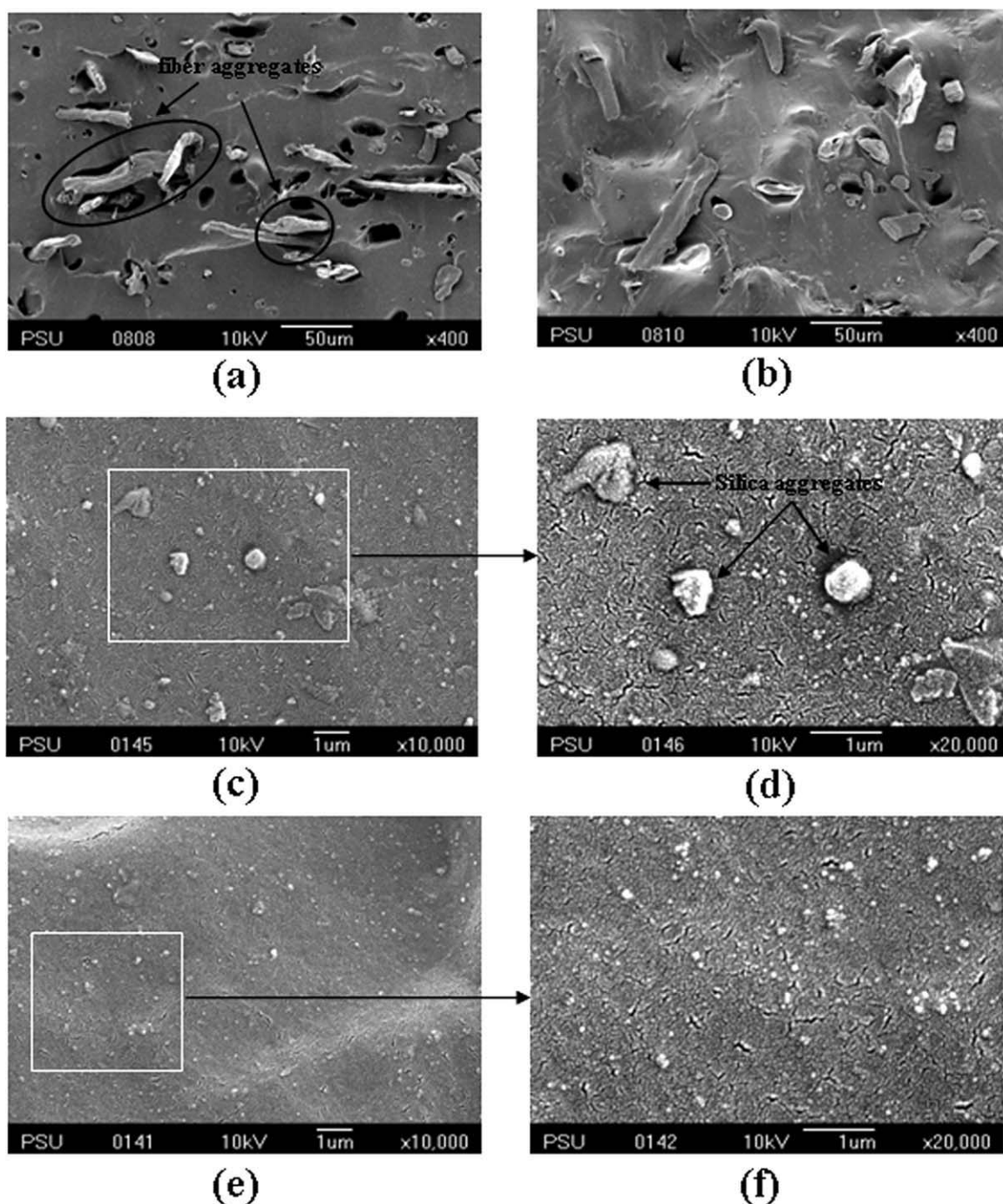


Figure 11 SEM photomicrographs of the surface fractures for the natural rubber composites reinforced with (a) 20-phr untreated cellulose fiber at a magnification of 400 \times , (b) 20-phr Si69-treated cellulose fiber at a magnification of 400 \times , (c,d) 20-phr untreated silica at low and high magnification (10,000 and 20,000 \times , respectively), and (e,f) 20-phr Si69-treated silica at low and high magnification (10,000 and 20,000 \times , respectively).

functionalities, that is, the hydroxyl groups of the cellulose fiber, as shown in Figure 10, and the silanol groups present on the silica surface, through relatively weak electrostatic interactions. The Si69-modified fiber/silica further reacted with the natural rubber by disproportionation of the sulfur groups in Si69 or in combination with the curing agent, such as sulfur, to form a chemical link between the coated

silane and natural rubber matrix during rubber vulcanization. This feature suggests weak interfacial bonding of the fiber/silica surfaces with rubber, which therefore, resulted in limited rubber reinforcement. Likewise, the good dispersion facilitated the various chemical and/or physical interactions to take place at the filler–matrix interface, and it prevented the formation of structural flaws, that is,

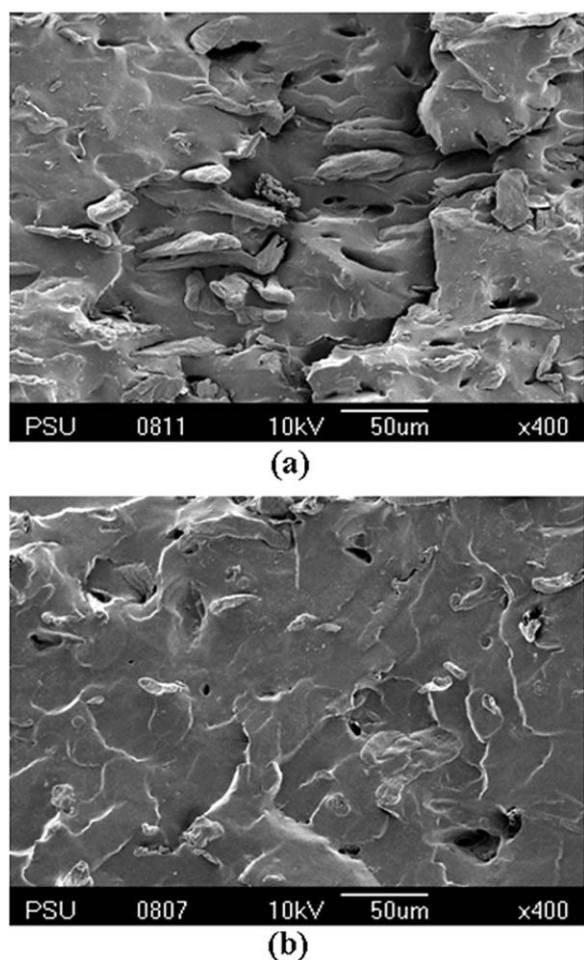


Figure 12 SEM photomicrographs of the surface fractures for the (a) 10/10 untreated cellulose fiber/silica hybrid filler and (b) 10/10 Si69-treated cellulose fiber/silica reinforced natural rubber composites at a magnification of 400 \times .

filler agglomerates, which weakened the rubber network.³¹ In this way, the dispersion of filler played an important role in the mechanical properties of the rubber composites. To qualitatively assess the effect of Si69 treatment on the filler dispersion, the fracture surfaces of different kinds of single-filler composites were observed with SEM images. The SEM images in case of the untreated and Si69-treated single filler-based composites were compared at three different magnifications, as shown in Figure 11. As illustrated in Figure 11, there was a dispersion improvement in the short cellulose fiber and silica in natural rubber matrix after silane treatment. This was because the silane treatment imparted a hydrophobic character to the fiber/silica surfaces, which resulted in a decreased aggregation of fiber/silica and, thus, better fiber/silica–rubber interaction, as shown in Figure 11(b,e,f). Figure 12 shows SEM photos of the rubber containing 10/10 cellulose fiber/silica hybrid filler. For the untreated hybrid composite [Fig.

12(a)], the image shows that fibers were not evenly dispersed and that the untreated cellulose fibers had a greater tendency toward fiber aggregation compared with the silane-treated fibers [Fig. 12(b)]. This suggests that the fiber dispersion was improved; this, thereby, improved the fiber–rubber interaction, as shown in Figure 12(b). However, because of the presence of a weak fiber–rubber interface, as discussed earlier, the reinforcing effect was not so clear, although the fiber dispersion was good. A similar observation was reported by other researchers.²⁸ Considering these SEM images, we found it difficult to draw any conclusion regarding the morphology of the hybridized silica filler. Therefore, characteristic X-ray (energy-dispersive X-ray spectroscopy) silicon mapping was performed to determine a concentration range of silicon to establish the distribution of the silica particles. Figure 13 shows the X-ray silicon mapping of the 10/10 hybrid composites as a function of the local distribution of silicon. The greater brightness indicates larger groups of the silicon element that were locally positioned in the hybrid composites. It was obvious that the images displayed the variation in brightness across the surface. Judging from the intense brightness of Figure 13(a), the local aggregation of silica was dense and unevenly distributed throughout the rubber surface in case of the untreated hybrid composites. On the other hand, the filler aggregates clearly became less dense and better distributed over the rubber surface modified with Si69-treated silica [Fig. 13(b)]. To elucidate the state of dispersion in more detail, the fracture cross sections of both the untreated and Si69-treated hybrid composites were treated in the manner of the Nissan-ARC (N-ARC) method developed by Nissan ARC Ltd. (Yokohama, Japan).³² The cross sections of these samples were at first ground with an abrasive paper disc (no. cc120 to 1000, San-kyo Rikagaku Co., Ltd., Okegawa, Japan) and were next polished with an Al₂O₃ (Showa Denko, Tokyo, Japan) powder to obtain the ultrafine polished surfaces. The Nissan-ARC treated surfaces were brought to examine under an optical microscope.³³ The optical micrographs are shown in Figure 14. As shown in Figure 14(a,b), the fracture surface of the untreated hybrid composite revealed thin, long-shaped structures that were part of fibers (original length of the fiber = 120 μ m) and small spherical-shaped particles (several micrometers in size) that were an agglomeration of primary silica particles; they were nonuniformly dispersed throughout the rubber matrix. In contrast, the photograph shown in Figure 14(c,d) indicates that the Si69-treated fiber/silica were more uniformly dispersed within the rubber matrix. Again, the quality of filler dispersion was improved with silane treatment. This improved morphology contributed to both better processability

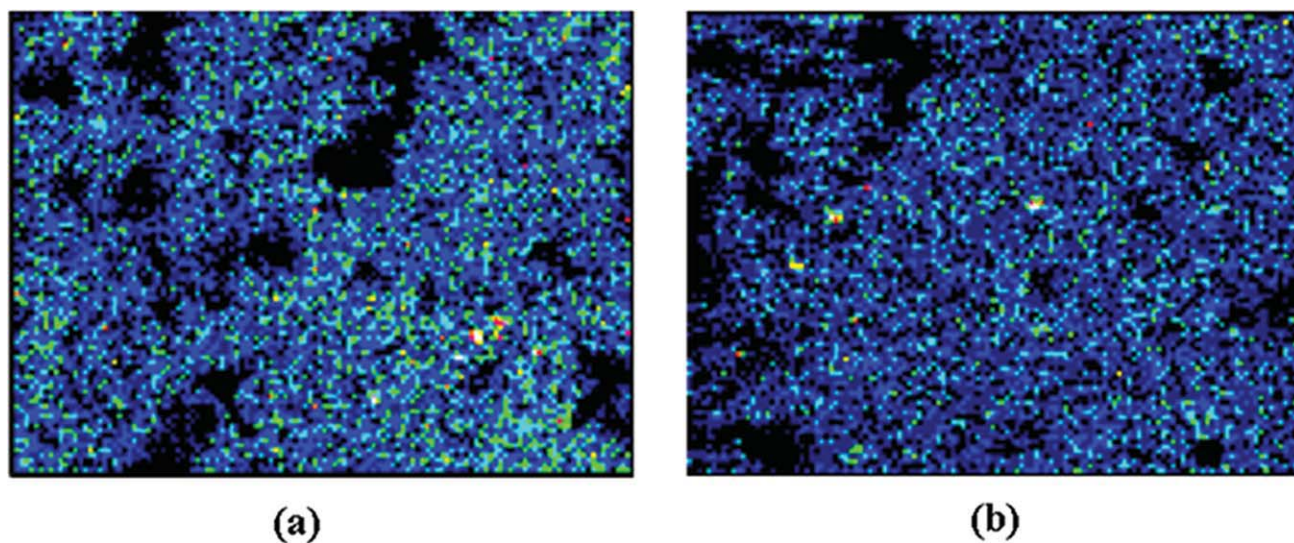


Figure 13 X-ray silicon mapping images of the (a) untreated 10/10 cellulose fiber/silica hybrid filler reinforced natural rubber and (b) 10/10 treated cellulose fiber/silica hybrid filler reinforced natural rubber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

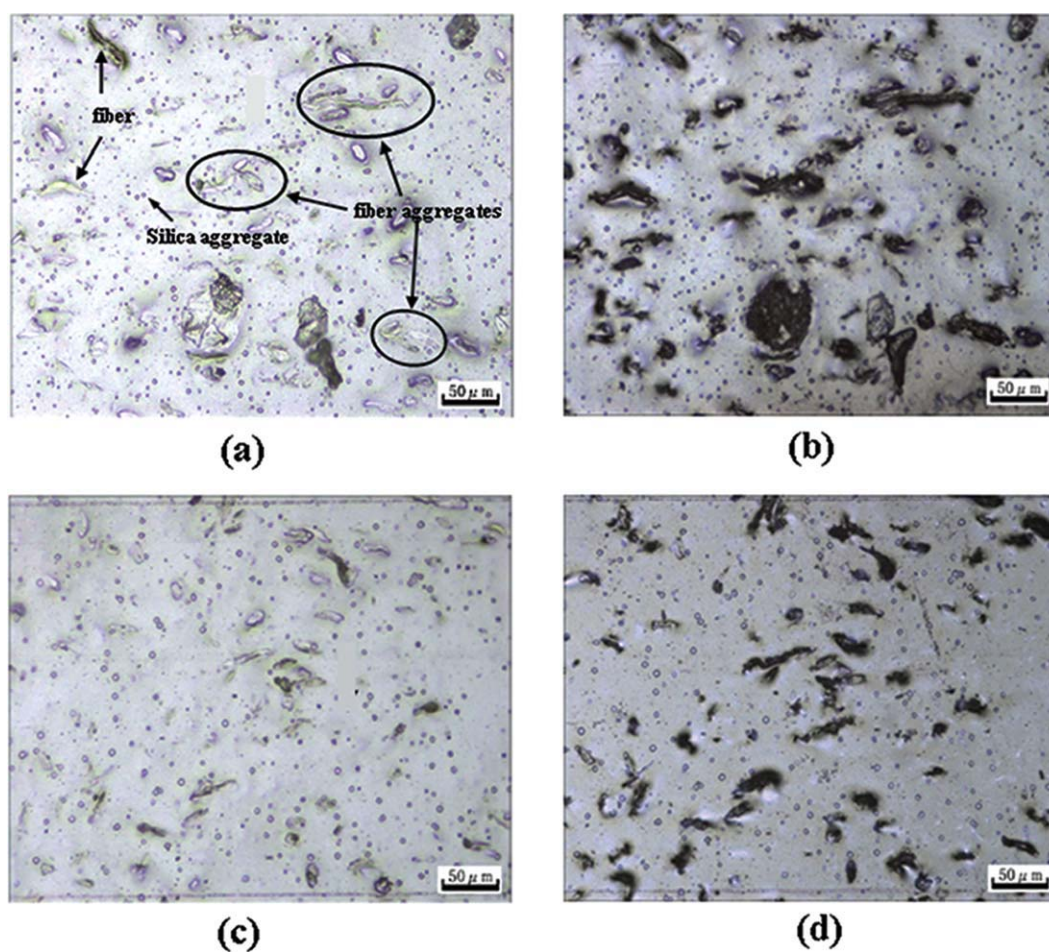


Figure 14 Fracture cross section of (a,b) untreated 10/10 cellulose fiber/silica hybrid natural rubber composites at low and high contrast adjustment, respectively, and (c,d) Si69-treated 10/10 cellulose fiber/silica hybrid natural rubber composites at low and high contrast adjustment, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the reduction of compound viscosity (Table III), as stated previously. It was also interesting to note that the strength of the treated hybrid composites (20 MPa) was in the same order with that of the silica–natural rubber composite (21 MPa), but it was not above that of the neat rubber matrix (24 MPa). Furthermore, the strength of the treated hybrid composite was not significantly improved over that of the untreated one, whereas these composites exhibited a great improvement in processability (Table III). The strength of the treated hybrid composites would have been much improved if chemical bonds were formed between the natural fiber/silica and silane and between silane and natural rubber. This observation supported the fact that the surfaces of the fiber and silica were modified mainly through the weakly bound silane coupling agent, which allowed greater surface affinity to the natural rubber matrix. As a result, the dispersion of the fibers and silica particulates progressed well when those of the untreated composites were compared, and a lower composite viscosity was obtained.

CONCLUSIONS

Hybridized reinforcing fillers, short cellulose fibers, and silica were used to prepare natural-rubber-based composites. The cure properties, viscosity, and tensile properties of the hybridized composites were determined with various relative concentrations of short cellulose fibers and silica at a fixed total hybrid filler loading. T_{s1} showed an increase when the amount of silica was replaced with 5-phr cellulose fiber. The Mooney viscosity dramatically decreased when the composites were combined with more cellulose fiber. The tensile modulus of the natural rubber incorporated with cellulose fiber was higher than that of natural rubber filled with silica by about 1.5 times. The introduction of more cellulose fiber also increased the tensile modulus but decreased the tensile strength and elongation at break. The surface modification of hybridized fillers by the Si69 coupling agent gave a significant improvement in the processing characteristics of the composites. However, the improvement level in the modulus and tensile strength was not so significant. This study clearly showed that the hybrid filler, short cellulose fibers, and silica, when combined with the Si69 silane coupling agent, could be used as substitutes for silica to improve the processability of the products with the environmental advantage and acceptable performance for rubber applications. More study is necessary to better understand how the cellulose

fiber affects the viscosity of the hybrid natural rubber composite. The use of silica combined with different fiber sizes or smaller fiber sizes to reinforce the hybrid composite will be the subject of a future publication.

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