

Overall Properties of Fibrillar Silicate/Styrene–Butadiene Rubber Nanocomposites

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ABSTRACT: The mechanical properties, heat aging resistance, dynamic properties, and abrasion resistance of fibrillar silicate (FS)/styrene butadiene rubber (SBR) nanocomposites are discussed in detail. Compared with white carbon black (WCB)/SBR composites, FS/SBR composites exhibit higher tensile stress at definite strain, higher tear strength, and lower elongation at break but poor abrasion resistance and tensile strength. Surprisingly, FS/SBR compounds have better flow properties. This is because by rubber melt blending modified FS can be separated into numerous nanosized

fibrils under mechanical shear. Moreover, the composites show visible anisotropy due to the orientation of nanofibrils. There is potential for FS to be used to some extent as a reinforcing agent for rubber instead of short microfibers or white carbon black. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2725–2731, 2006

Key words: fibrillar silicate; styrene butadiene rubber; properties; anisotropy

INTRODUCTION

Fillers are playing increasingly important roles in the reinforcement of polymers and the reduction of their cost because of the limit of oil resources and the pressing need for environmental protection. For instance, the filler content in a rubber product is usually more than 40% in total weight. Fillers can be divided into granular, layered, and fibrillar shapes. Nanofillers not only remarkably improve the mechanical properties of polymers but also endow polymers with special properties such as electrical conductivity, flame resistance, and antibacterial effectiveness. Spherical fillers such as nano-silicon dioxide, nano-calcium carbonate, nano-titanium dioxide, and nanoalumina and layered nanofillers such as layered silicate (nano-single layer) and nano-molybdenum bisulfide were extensively used in the preparation of polymer-based nanocomposites^{1–7}; however, research on fibrillar nanofiller/polymer nanocomposites is rarely reported except for carbon nanotubes (CNTs). CNT/polymer composites prepared by in situ polymerization possess excellent mechanical, photoelectrical, and abrasion properties; still,

it is necessary for CNTs to have special surface modification because of the worse dispersion and poorer interphase bonding between CNTs and polymers.^{8–10} In addition, the expensive cost of CNTs is another obstacle to their application.

Fibrillar silicate (FS) is one type of hydrated magnesium aluminum silicate clay that is composed of many fibrillar nanosized single crystals. The dominant constituent of FS is attapulgite or palygorskite. FS has the structural formula $Mg_5[Al]Si_8O_{20}(HO)_2(OH)_4 \cdot H_2O$. The primary structural unit is the fibrillar nanosingle crystal, which is 100–3000 nm in length and 10–30 nm in diameter; single crystals compactly arrange in parallel to form into crystal bundles, and these crystal bundles then agglomerate into particles having diameters of 5–50 μm .^{11,12} FS/polyethylene and FS/polyamide 6 nanocomposites have been prepared by in situ polymerization with a good balance of strengthening and toughening.^{13,14} According to our research, modified FS using a silane coupling agent can also be directly separated into nanosized single crystals or crystal bundles (also called nanofibrils) in a rubber matrix under mechanical shear during direct blending. In this way, various kinds of FS/rubber nanocomposites with excellent performances were successfully achieved. The structural and mechanical properties of the composites were discussed as well as the surface modification and reinforcement mechanism of FS.^{12,15} It is very promising that the composites will be launched into future applications because of their cheap cost and simple preparation process.

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Therefore, the overall properties of the composites attract more attention. The overall properties of styrene butadiene rubber (SBR)/FS composites were investigated in detail in this article. We found that SBR/FS composites possessed characteristics similar to short microfiber reinforced rubber and obvious anisotropy but poor abrasion resistance. It was also expected that the corresponding compound would exhibit better flow properties as a result of the small dimensions of nanofibrils.

EXPERIMENTAL

Materials

SBR (SBR1502) was produced by Jihua Synthesis Rubber Factory. FS (>90% of particles are <25 μm) was obtained from Dalian Global Mineral Company. Nano-sized silicon dioxide (particle size = 30–40 nm) made by a precipitation reaction, also called white carbon black (WCB), was bought from Nanji Chemicals Factory. The silane coupling agent, bis(3-triethoxysilylpropyl) tetrasulfide [Si69, $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{S}_4\text{Si}(\text{CH}_2)_3(\text{OC}_2\text{H}_5)_3$], was procured from Shuguang Chemicals Company (Nanjing, China). Other chemical agents were purchased from a chemical supplier.

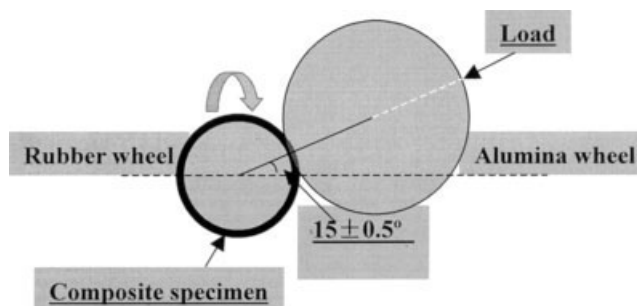
Surface modification of FS and preparation of composites

Surface modification of FS

A 20–50 wt % FS aqueous solution was put into a high-speed agitator and agitated at 800 rpm to separate FS into single crystals. Then, a mixture of Si69/alcohol (ratio of about 1:5) was added slowly and uniformly to the above solution, which was treated for 30 min at 60°C. The solvent was removed to attain dry solid particles, and then they were ground into powders. The amount of Si69 alcohol solution added was calculated according to a 2.4:100 weight ratio of Si69/FS.

Preparation of FS/SBR composites

Two rolls of a two-roll mill were adjusted to the smallest distance at which rubber becomes fluidic. Then, modified FS was added stepwise into the rubber to ensure good dispersion, vulcanizer and accelerator were added (Table I), and the compound was finally obtained. It was sliced into 1.5-mm pieces on the two-



Scheme 1 The Akron type test for rubber abrasion.

roll mill to prepare for vulcanization. Cure time was determined with an oscillating disk rheometer and the compound was vulcanized on a platen presser with 25-ton pressure. Test specimens were cut from vulcanized material (composite). The vulcanization temperature of SBR is 150°C.

WCB/SBR composites were also prepared using the same process as the FS/SBR composites, but WCB was added into the rubber instead of modified FS.

Tests and characterization

Tensile, tear, and hardness tests were carried out on the composites according to ASTM D 412, ASTM D 624, and ASTM D 2240, respectively. The heat aging resistance of the composites after 48-h aging at 100°C was determined according to ASTM D 573.

Abrasion properties

An Akron type abrasion tester was used to evaluate the abrasion properties of the composites, according to Chinese National Standard GB/T 1689-1998. The composite specimen was adhered to a rubber wheel, which rolls against an alumina one (Scheme 1), at a rotation speed of 76 ± 2 rpm for the rubber wheel, a constant load of 26.7 ± 0.2 N, and an angle of $15 \pm 0.5^\circ$ between the line connecting the centers of the two wheels and the horizontal line. The specimen wheel was prerotated for 10 min before testing. The weight loss of the specimen wheel was obtained after a rolling distance of 1610 m, and the abrasion volume (mL/1.61 km) was calculated by dividing the weight loss by the density of the composite specimen.

The Mooney viscosity of the compound was tested on a Monsanto Mooney viscosity tester. The Young's (tensile) modulus of the composites was measured according to Chinese Standard HG4-834-81. The sample size was $80 \times 10 \times 2$ mm and the gauge length was 50 mm. The sample was clamped vertically and the tensile load (final strain is <3%) retained for 15 min at a temperature of 23°C. The Young's modulus (E) was calculated according to eq. (1):

TABLE I
Compositions of Materials

Rubber (g)	100
Vulcanizer and accelerator (g)	10
Modified FS (g)	Variation

TABLE II
Mechanical Properties of Composites

	Amount of modified FS							
	30		40		50		60	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Hardness (Shore A)	69	78	73	80	75	83	79	85
Tensile stress at 100% strain (MPa)	7.3	8.4	7.6	10.4	7.8	12.2	10.2	13.7
Tensile strength (MPa)	14.1	14.3	14.7	16.0	14.4	17.5	18.8	20.5
Elongation at break (%)	350	260	344	238	336	233	309	233
Permanent set (%)	20	12	20	12	12	8	12	8
Tear strength (kN/m)	58.0		60.8		67.4		64.7	

$$E = \frac{PL_0}{b_0h_0(L - L_0)} \quad (1)$$

where P is the tensile load; L_0 is the length before loading; L is the length after loading for 15 min; and b_0 and h_0 are the width and thickness of the sample before loading, respectively.

A Cambridge S-250MK3 scanning electron microscope was used to observe the abrasion surface morphology of the composite. An H-800 transmission electron microscope was used to observe the dispersion of FS in the composite cut with a microtome at -100°C .

A PE7 dynamic mechanical thermal analyzer (PE Company) was used to evaluate the dynamic elastic

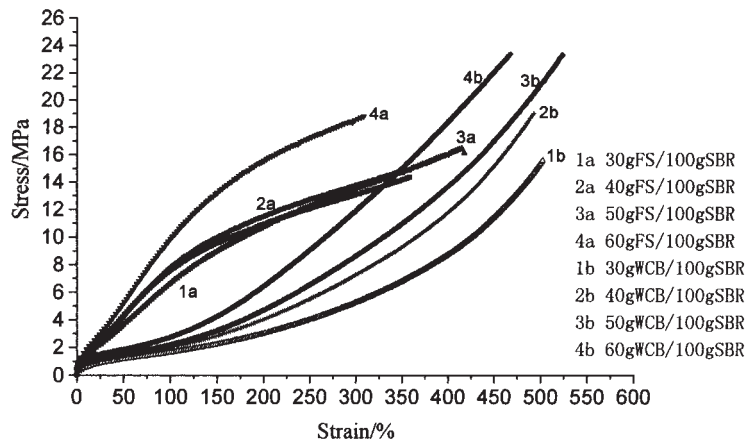


Figure 1 Stress and strain relations of FS/SBR and WCB/SBR composites.

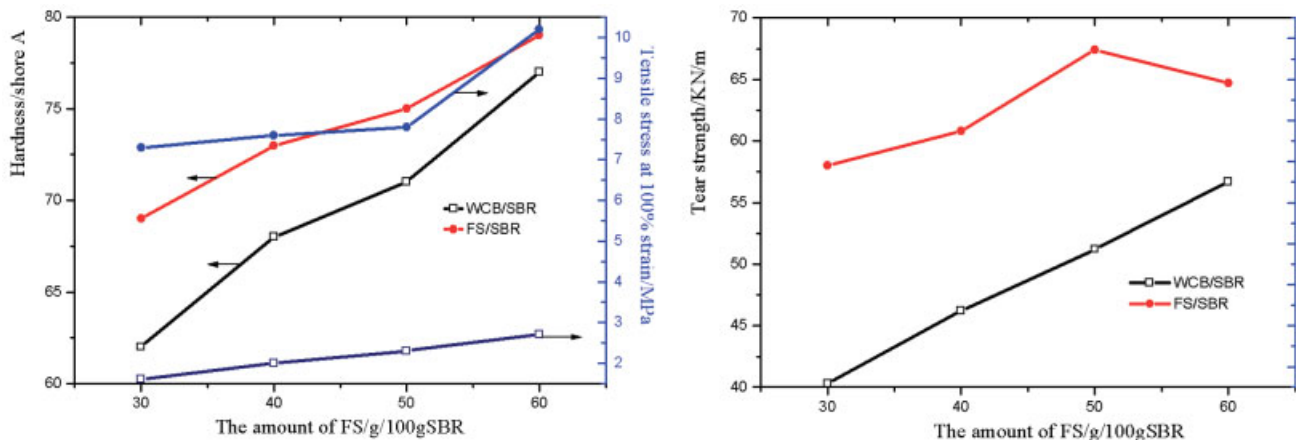


Figure 2 The tensile stress at 100% strain, hardness, and tear strength of FS/SBR and WCB/SBR composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

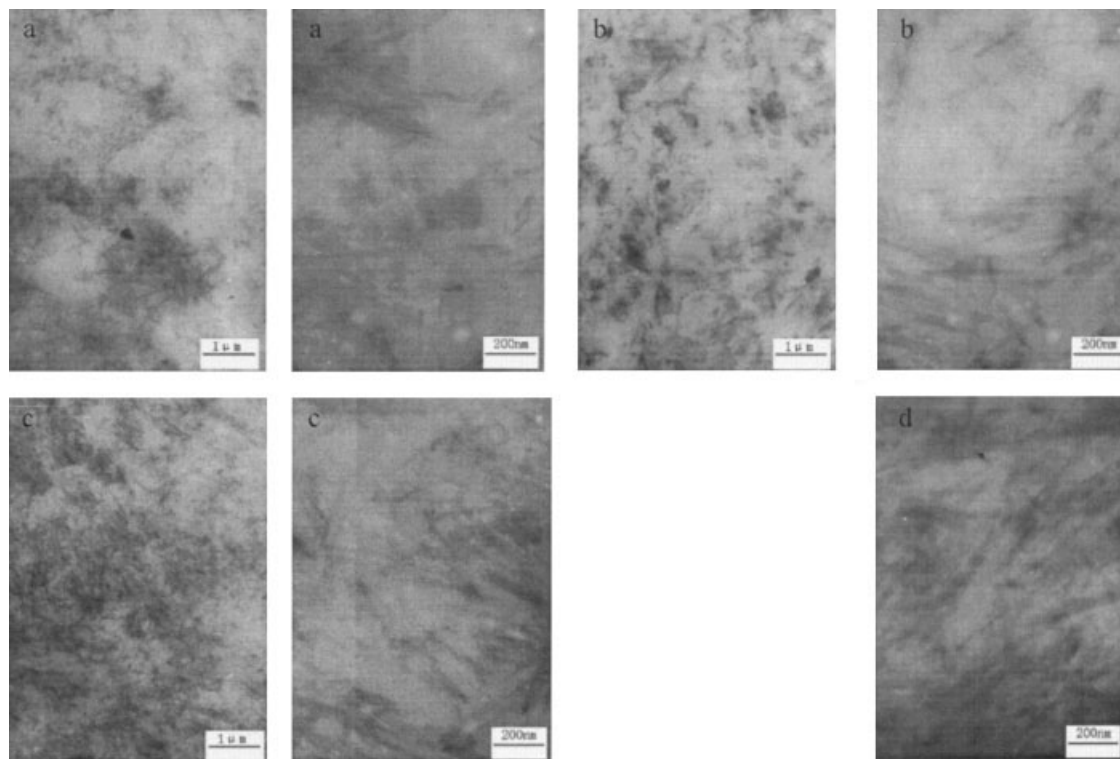


Figure 3 Transmission electron microscope observations of FS/SBR composites with (a) 30, (b) 40, (c) 50, and (d) 60 g FS/100 g SBR.

modulus (E') and loss tangent ($\tan \delta$) of the composites. The PE7 experimental setup was based on a single tensile mode. The frequency was 1 Hz and the strain was 0.5%. A temperature range from -100 to 50°C was used to obtain the glass-transition temperature.

RESULTS AND DISCUSSION

Mechanical properties of composites

The data in Table II show that FS/SBR composites prepared by direct blending possessed higher hard-

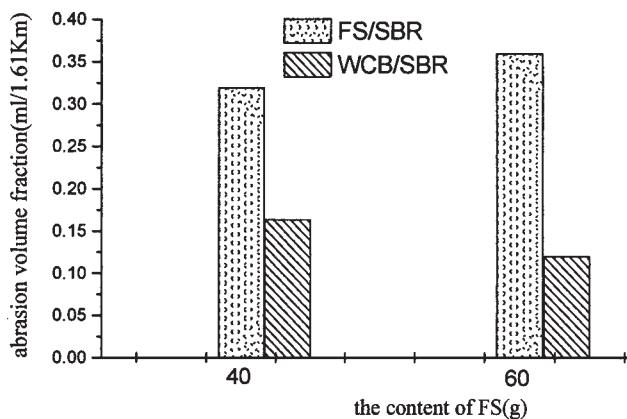


Figure 4 The abrasion resistance of FS/SBR and WCB/SBR composites.

ness, tensile stress at 100% strain, tensile strength, and very high tear strength, which demonstrated that modified FS showed excellent reinforcing effects. As the loading level of FS ascended, the composites had a distinct increase in hardness and tear strength but a decrease in elongation at break and permanent set. When the amount of FS was more than 60 g/100 g SBR, the tensile stress at 100% strain and tensile strength of the composites was again remarkably enhanced.

Because the heat aging resistance of rubber is concerned with its service life, the properties of FS/SBR composites after 48-h aging at 100°C were studied. As also shown in Table II, the composites had a visible increase in hardness, tensile stress, and tensile strength, but a small decrease in the elongation at break and permanent set, which indicated that the FS/SBR composites had very good heat aging resistance. Like unfilled SBR vulcanizate, the main reason is that the crosslinking density of SBR after aging increased when sulfur was chosen as the curing agent.

For a rubber matrix, spherical WCB is another conventional reinforcing filler, but not carbon black. As shown in Figure 1, the stress of FS/SBR and WCB/SBR composites increase with the increasing amount of reinforcing filler, but FS/SBR composites exhibited higher stress at $<300\%$ strain. Unfortunately, FS/SBR

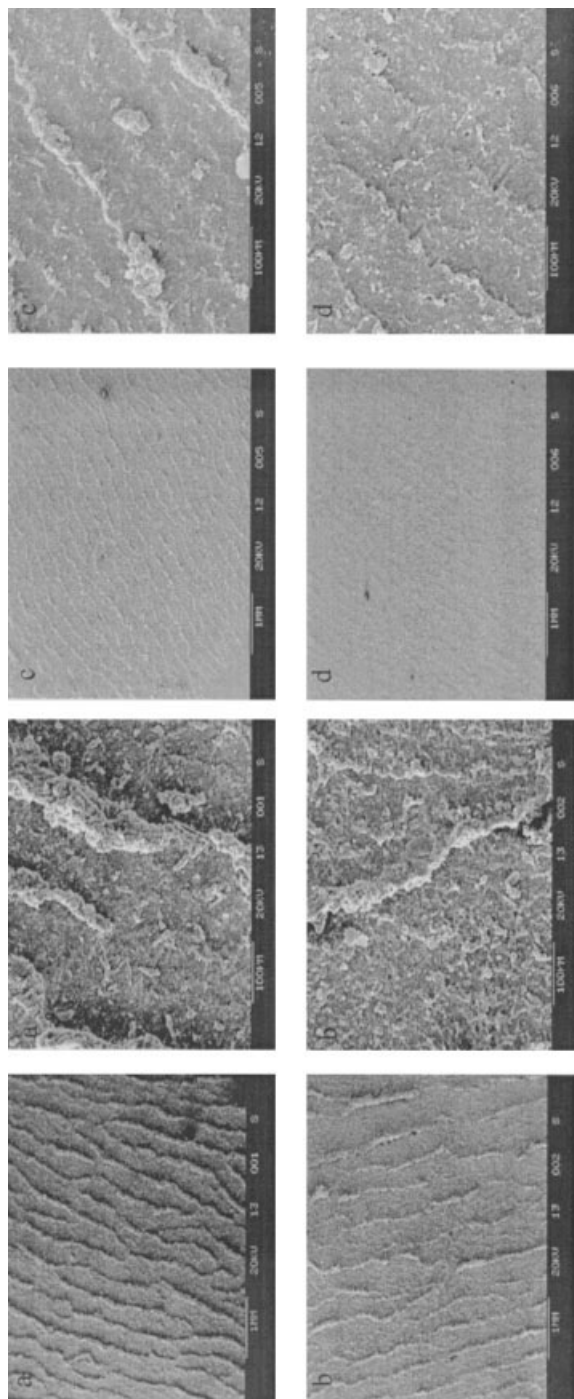


Figure 5 Scanning electron microscope observations of the abrasion surfaces of FS/SBR and WCB/SBR composites with (a) 40 g FS, (b) 60 g FS, (c) 40 g WCB, and (d) 60 g WCB.

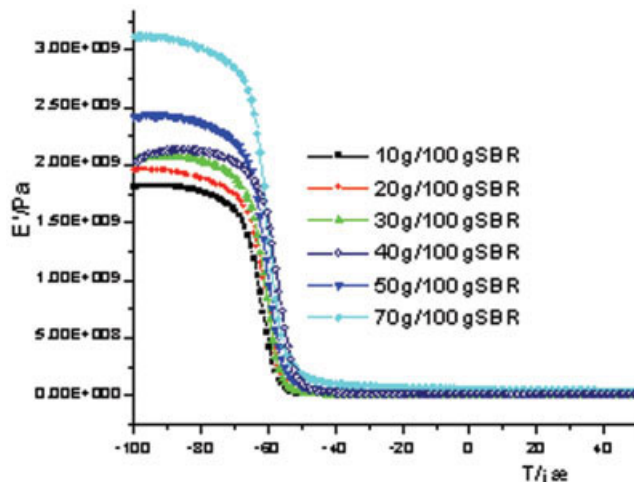


Figure 6 The relation of the dynamic elastic modulus of FS/SBR composites versus the temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composites possessed lower tensile strength. This was ascribed to the different shape of the filler. Figure 2 shows that FS/SBR composites exhibited much higher tensile stress at 100% strain and hardness than those of WCB/SBR composites with the same amount of reinforcing filler. It was noteworthy that FS/SBR composites had very high tear strength. In addition, FS/SBR composites showed characteristics similar to short microfiber reinforced rubber, for instance, high tensile stress at definite strain and tear strength, but low elongation at break. This would be very useful for

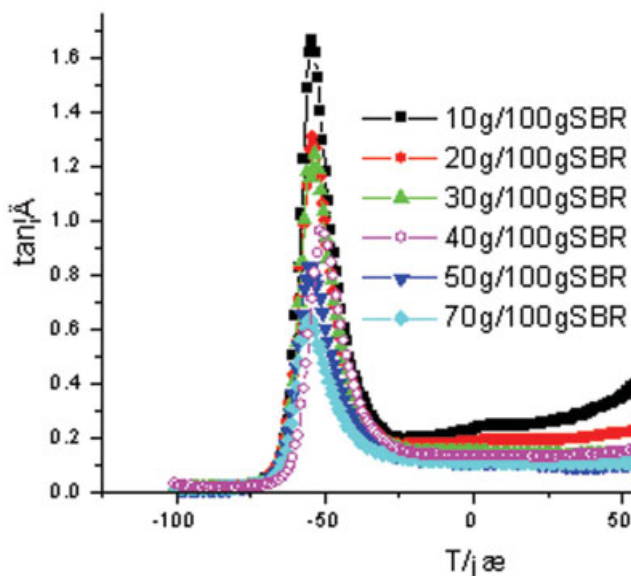


Figure 7 The relation of the loss tangent of FS/SBR composites versus the temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

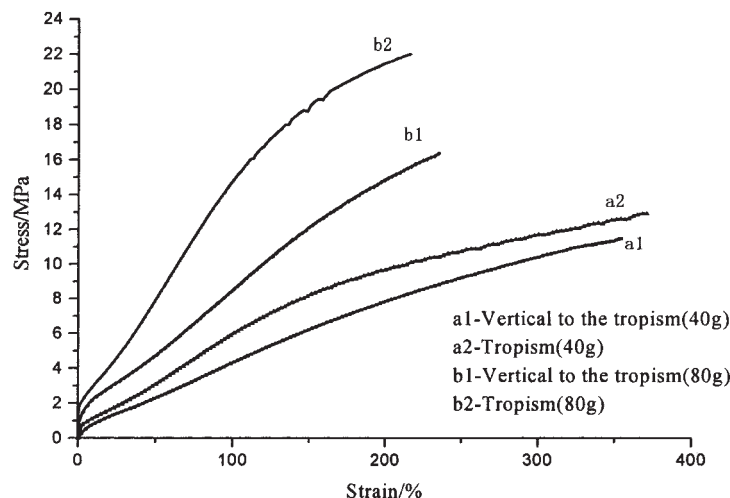


Figure 8 The stress and strain relation of FS/SBR composites in two directions.

special rubber products such as rubber V belts, synchrodrive belts, and so forth.

As can be seen from Figure 3, most of the modified FS could be separated into fibrils with diameters of <100 nm and dispersed in the SBR. Moreover, the more the amount of FS added, the higher the number of nanofibrils, which implied the separation of FS; and the dispersion of FS improved when the loading of FS was increased. As we observed, the uniformity of the FS dispersion was better when the loading level of FS was 50 or 60 g/100 g SBR. It was likely that the maximal shear force acted on the FS and increased with the increasing viscosity of the matrix, thus improving the separation and dispersion of FS.¹⁶ It is true that the viscosity of the matrix increased as the amount of FS increased.

Abrasion resistance of composites

According to the literature,¹⁷ the density of FS is very close to WCB (about 2.0 g/cm³); therefore, both have approximately the same volume fraction at the same weight fraction. Figure 4 shows that the amount of abrasion of FS/SBR composites was a little more than that of WCB/SBR composites. It was abnormal that the amount of abrasion of FS/SBR composites increased with increasing FS content.

Numerous deep and wide grooves appeared vertical to the abrasion direction in the FS/SBR composite and a coarse abrasion surface was formed, which are shown in Figure 5. Due to the stress effect on the end of the fibril, local stress concentration emerged in the composites so that the composites were worn and torn into many small particles, and some of these were pulled out. The effect became more marked as the content of FS increased. As a result, the abrasion coefficient increased and thus

the abrasion force rose greatly. Based on the analysis above, the composites were destroyed by compulsive tearing instead of expanding cracks.¹⁸ This was the reason that FS/SBR composites exhibited poor abrasion resistance, although their tear strengths were very high. Also seen in Figure 5 are numerous flat grooves on the abrasion surface of WCB/SBR composites, so flat that it was difficult to observe them, especially at a content of 60 g WCB/100 g SBR. Therefore, WCB/SBR composites exhibited excellent abrasion resistance.

Dynamic properties of composites

Figures 6 and 7 show that, as the amount of FS increased, the E' of the composites increased but the maximum of $\tan \delta$ ($\tan \delta_{\max}$) decreased. This agreed with spherical fillers such as WCB reinforced rubber. It was obvious that the rubber volume fraction decreased with the increasing amount of FS. The temperature corresponding to $\tan \delta_{\max}$ could be thought of as the glass-transition temperature (T_g) of SBR, which is about -50°C . We concluded that the content of FS had negligible effect on the T_g . When the tem-

TABLE III
Young's tensile Modulus of FS/SBR Composites

Content of FS (g/100 g SBR)	Young's tensile modulus (MPa)	
	Tropism	Vertical
30	7.51	6.19
40	10.80	10.65
50	13.71	12.32
60	22.40	13.58
70	23.16	14.80
80	26.88	16.81

perature is far less than the T_g , rubber molecules are glassy and cannot move; hence, the $\tan \delta$ is very low and the E' is very high. As the temperature rises but is less than the T_g , rubber molecules begin to move in limited volume, and the $\tan \delta$ gradually increases while the E' declines dramatically. When the temperature is more than the T_g , rubber molecules can move freely because of the rise in free volume of rubber, $\tan \delta$ begins to decline, whereas E' decreases to a minimum value and changes little. Therefore, the $\tan \delta$ of the composite appeared to be a maximal value.

Anisotropy of FS/SBR composites

To discuss the anisotropy of FS/SBR composites, during the preparation of the composites we adjusted the two rolls in the two-roll mill to the smallest interval in order to give the maximal shear to make nanofibrils oriented when the compound was sliced. As seen from Figure 8, FS/SBR composites exhibited higher stress in the tropism direction than that in the vertical to the tropism direction with the same amount of FS. It was obvious that the stress difference in the two directions became more distinct with the increasing FS content. As seen in Table III, it is also true for the Young's modulus of the composites. The difference in the Young's modulus in the two directions became more visible when the content of FS was more than 60 g/100 g SBR. Like short microfibers, nanofibrils could also be oriented along the shear direction. The more the amount of FS there was, the higher the number of nanofibrils and the more distinct the orientation of fibrils. As a result, the composites showed more evident anisotropy.

Flow properties of composites

It can be concluded from Figure 9 that the Mooney viscosity of FS/SBR and WCB/SBR compounds increased with an increasing amount of filler, but the increment of the former was more remarkable. It was very puzzling that the Mooney viscosity of the FS/SBR compound was the lower one at the same loading level of filler. In addition, it was very easy to mix FS with rubber and FS/SBR composites showed good appearance. As we knew, short microfiber reinforced rubber usually exhibits undesirable flow properties and appearance because of its large dimension. Therefore, it is possible that FS can be used to some extent in special rubber products instead of short microfibers.

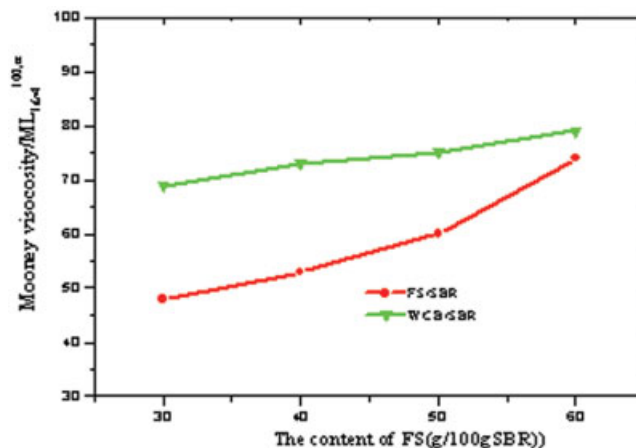


Figure 9 The Mooney viscosity of FS/SBR and WCB/SBR compounds. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

Cheap FS fibrils showed excellent reinforcing effects for SBR. FS/SBR composites exhibited characteristics similar to short microfiber reinforced rubber, for example, high stress at definite strain, high tear strength, and low elongation at break and anisotropy. In addition, the FS/SBR compound had good flow properties.

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