Structure and Mechanical Properties of Nanodispersed Fibrous Silicate-Reinforced Ethylene–Propylene–Diene Monomer Nanocomposites

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ABSTRACT: In this study, ethylene–propylene–diene monomer (EPDM)/fibrillar silicate (FS) nanocomposites were successfully prepared by mechanically blending EPDM with FS, which was modified by silane coupling agent KH570 containing methacryloxy group. The effects of silane content and modified FS on the dispersion of FS and mechanical properties of the composites were investigated. The impact of water in FS on mechanical properties of the composites was also evaluated. The results showed that modified FS could be dissociated into nanofibers dispersing evenly in the EPDM matrix by increasing substantially the loading of silane through the mechanical blending. The optimum loading level of silane coupling agent was up to 24 phr/100 phr FS. Silane KH570 could improve the dispersion of FS and strengthen nanofibers–rubber interfacial adhesion even at the loading of as high as 50 phr FS, making FS to exhibit excellent reinforcement to EPDM. Too much FS could not be completely dissoci- ated into nanofibers, slowing down further improvement. The EPDM/FS composites exhibited the similar stress–strain behavior and obvious mechanical anisotropy with short microfiber-reinforced rubber composites. With the increase in silane coupling agent and modified FS, the number of nanofibers increased because of the exfoliation of FS microparticles; thus, the mechanical behaviors would become more obvious. It was suggested that the free water in FS should be removed before mechanically blending EPDM with FS because it obviously affected the tensile properties of the composites. Regardless of whether FS was dried or modified, the EPDM/FS composites changed little in tensile strength after soaked in hot water. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1926–1933, 2011

Key words: fibrillar silicate; ethylene–propylene–diene monomer; nanocomposites; silane coupling agent; mechanical properties

INTRODUCTION

Short fiber-reinforced rubber composites (SFRC), which are prepared by dispersing short fibers into rubber matrix, can be made into reinforced composites like polymer blends.[1] The combination of the flexibility of rubber and the rigidity of fibers makes it maintain the unique high elasticity of rubber and the characteristic of the high modulus with low elongation.[1,2] SFRC exhibit a high transverse rigidity and longitudinal flexibility (that is, mechanical anisotropy); thus, they are suitable for being used as the base rubber of synchro-drive belt, for the composites can remarkably improve the transfer efficiency, bend-resistance, and fatigue-resistance properties of the synchro-drive belt,[3–5] the same as the polyester and nylon SFRC, which are widely used. However, for that the diameters of these short fibers are usually about tens of micrometers, to get desirable reinforcement effect, the fibers are needed to have a high aspect ratio (ratio of the length and the diameter); thus, the lengths of these fibers need to reach hundreds of micrometers, even some millimeters. Such length will make it difficult for fibers to be finely dispersed in rubber matrix, and then there may be stress concentrations inside the composites leading to fracture at low stress. Besides, such length will make the composites appearance rough and affect the resistance to abrasion, which might reduce the lifetime of synchro-drive belt.

Fibrillar silicate (FS) is one type of hydrated magnesium aluminum silicate clay composed of many fibrillar nano-single crystals, which are the smallest structure units with a length of 500–2000 nm and

10–30 nm in diameter.[6,7] The dominant of FS is attapulgite or palygorskite. There are large reserves of FS in South China (Jiang Su, Zhe Jiang, and An Hui provinces) and in the United States (Florida). We found that the interaction between FS single crystals was extremely weak, and the surface of FS was full of Si-OH. As a result, rubber/FS nanocomposites, such as styrene–butadiene rubber/FS, chloroprene rubber/FS, butyronitrile rubber (NBR)/FS, etc., were successfully prepared by the polymer emulsion co-coagulation method or the polymer melt blend method, which blended directly FS *in situ* modified by silane coupling agent in rubber matrix. The mechanism of dispersion and reinforcement of FS in different rubber matrix were explored. The improvement of FS–rubber interface, and the structures and the properties of composites were also studied. We found that rubber–FS composites possessed the similar stress–strain characteristics of SFRC and exhibited obvious anisotropy of mechanical properties.[6,8,9] Different from traditional microfibers, such as polyester and nylon, FS nanofibers are inorganic; thus, rubber–FS composites possess better heat resistance, processing flow properties, better appearance of products, and economic efficiency than those of rubber/microfiber composites.[10–14]

Ethylene–propylene–diene monomer (EPDM), which possesses excellent heat resistance and anti-aging properties, is applied to synchro-drive belt instead of natural rubber, styrene–butadiene rubber, and chloroprene rubber, to meet the higher heat-resistance requirement. In previous studies, we found that modified FS could be dissociated into nanofibers easily under mechanical shear in polar rubber, such as NBR and HNBR; however, it is undesirable that the dispersion of the nanofillers in nonpolar EPDM are always bad because of their incompatibility and lower surface tension.[15] We also found that the impact of silane coupling agent-modified FS on EPDM was more obvious than that on NBR and HNBR.[6,16] It is forever issue for EPDM how to improve the dispersion of nanofillers used to reinforce. Generally, the loading of the silane coupling agent is less than 5%.[8] Could the dispersion and the reinforcing effect of FS in EPDM be improved further when increasing the amount of silane coupling agent? FS is easy to absorb water. But it remains unclear whether the water in FS would influence the mechanical properties of the composites at both room and high temperature. In this study, we expected that the dispersion of FS in EPDM matrix could be improved by substantially increasing the amount of silane coupling agent, which was used to modify FS. The amounts of silane coupling agent and modified FS were discussed in detail how to affect the dispersion of FS, tensile stress–strain characteristics, compression stress–strain characteristics,

TABLE I
The Compositions of Materials

Ethylene propylene diene monomer (phr)	100
Dicumyl peroxide (phr)	4
FS (or modified FS) (phr)	Varied

mechanical anisotropy, heat resistance, and water resistance properties of the composites, to guide the application of EPDM/FS composites on synchro-drive belt.

EXPERIMENTAL

Materials

Ethylene–propylene ethylidene norbornene terpolymer (EPDM dual-edge J-4045) consisting of 53.0–59.0 wt % ethylene, with the iodine value of 19 ∼ 25, was produced by China Jilin Petrochemical Industrial Co. Ltd (Jilin Province, China); it has the third monomer of Ethylidene Norbornene (ENB). FS (1250 mesh) was obtained from Dalian Global Mineral Company (Liaoning Province, China). γ-(Methacryloxy)proxyltrimethoxy silane [KH570, $CH_2C(CH_3)COOCH_2CH_2CH_2Si(OCH_3)_3$] was bought from Nanjing Crompton Shuguang Organosilicon Specialties Co., Ltd (Jiangsu Province, China). Dicumyl peroxide and other chemical agents were purchased from chemical store.

Preparation of EPDM/FS composites

Two rolls of a hot two-roll mill (the diameter of roller is 160 mm and the length of roller working surface is 320 mm) were adjusted to the smallest distance at which rubber became fluidic, and then active agents and antioxidants were added in turn. FS or drying FS (dried in a blast oven at 120°C for 2 hr) and silane KH570 were added into EPDM step by step at 140 ∼ 150°C[2] to ensure a good dispersion. Vulcanizing agent was then added after the above masterbatch was cooled to room temperature (as shown in Table I). Finally, the compound sheets for vulcanization were obtained through the smallest two-roll distance to make nanofibril oriented. Cure time was determined with an oscillating disc rheometer, and the compound was vulcanized on a platen presser with 25-ton pressure. The 2-mm-thick tensile test pieces and 28 mm × 12.5 mm cylindrical compression test specimens were gauged through a die. The vulcanization temperature of EPDM was 160°C.

Characterization and test

Tensile, tear, and compression properties were measured using a universal material testing machine (LR30K PLUS), which was produced by British Lloyd Co. Tensile test, tear test, and hardness of the

composites were carried out according to ASTM D412-2006ae2, ASTM D624-2000(2007), and ASTM D2240-2005(2010), respectively. During tensile test and tear test, five specimens were required to give the average value. Tensile tests were carried out at 23°C and 120°C, individually. During the hardness test, three different spots were measured to give the average hardness value.

Compression test was carried out according to ISO7743-2008, and three cylindrical compression specimens were required to give the average value. The compression modulus at small strain ($\varepsilon < 6\%$) could be obtained from the compression stress–strain curves by the linear fitting method.

Tensile test specimens were soaked in water for 3 days at 80°C, then taken out, and dried at room temperature. The weight change was obtained by measuring the weight of specimens before and after soaking in water, and tensile test was carried out according to ASTM D412-2006ae2.

A CAMBRIDGE S-250MK3 scanning electron microscope was used to observe tensile fracture surface morphology of the composites. A Hitachi H-800-1 transmission electron microscope was used to observe the orientation of nanofibrils in the composites cut by microtome at −100°C along the direction parallel to the fibers.

RESULTS AND DISCUSSION

Amount of silane coupling agent

In previous work, for peroxide cured rubber matrix, we compared the reinforcing effects of modified FS with different types of silane coupling agents, finding that the reinforcing effect of modified FS with silane KH570, which contains allyl double bond-based silane, was the best.[8] Although the co-coagulation of rubber latex and FS aqueous solution was a preferred method to improve the dispersion of FS,[6] the polymer emulsion of EPDM did not exist. Thus, in our study, FS and silane KH570 were mixed into EPDM matrix step by step at 140 ~ 150°C by mechanical mixing. The mechanical shear force could transfer to FS because of the high viscosity of rubber, and then FS was modified and dispersed simultaneously. It was the *in situ* modification–dispersion method.[2] From Figure 1(a,b), regardless of the amount of FS was 30 or 50 phr, without silane KH570, the tensile stress–strain curves of EPDM/FS composites were the flattest. With the increase in silane KH570, the tensile stress–strain curves went up more sharply, the tensile stress at small strain increased, and the elongation at break decreased. It showed the typical stress–strain characteristics of SFRC, suggesting that the reinforcing effect of modified FS was better. When the loading of FS was 30
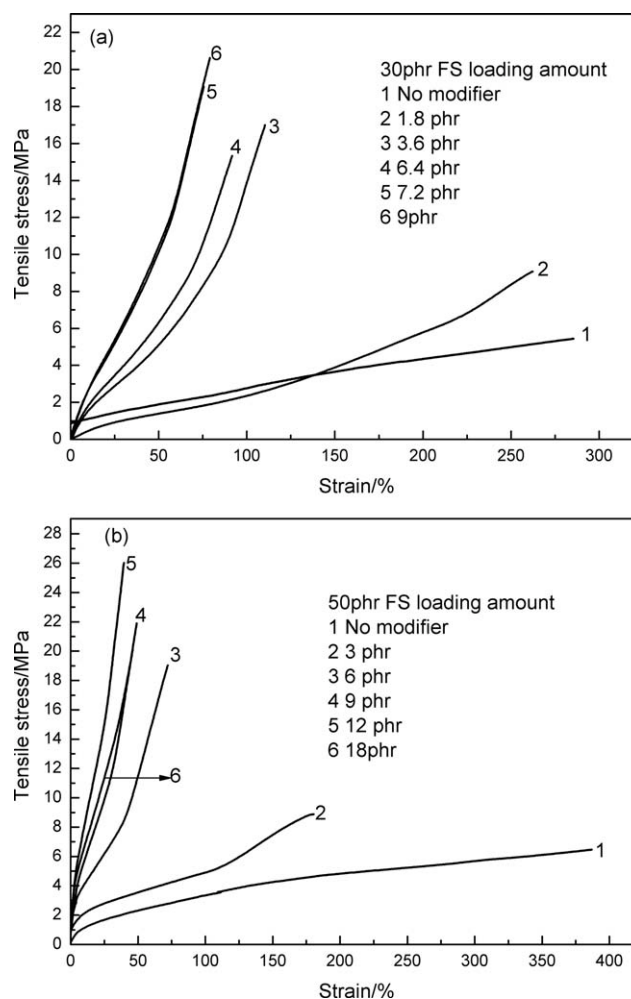

Figure 1 Tensile stress and strain relation of EPDM/FS composites individually filled with 30 phr (a) and 50 phr (b) modified FS with various silane KH570 amounts.

phr, the optimum amount of silane KH570 was 7.2 phr. Similarly, when the loading of FS was 50 phr, the optimum amount of silane KH570 was 12 phr. This meant that the optimum amount of silane KH570 was 24 phr/100 phr FS, much higher than the commonly used amount of silane coupling agent used to modify inorganic fillers (0.5–5%).[8] By further increasing the amount of KH570, the reinforcing effect of modified FS changed little, and even the tensile strength exhibited a slight decrease because of the plasticization effect of silane coupling agent. Excessive amount of silane KH570 might also consume vulcanizing agent (dicumyl peroxide) and affect the efficiency of the cross-linking.[16]

Seen from Figure 2(a), when FS was not be modified, most FS was dissociated into crystal bundles (unexfoliated agglomerates of nanofibers stacked in parallel as shown in transmission electron microscopy [TEM] micrograph) and some larger granular agglomerates (formed by crystal bundles as shown in scanning electron microscopy micrograph) were
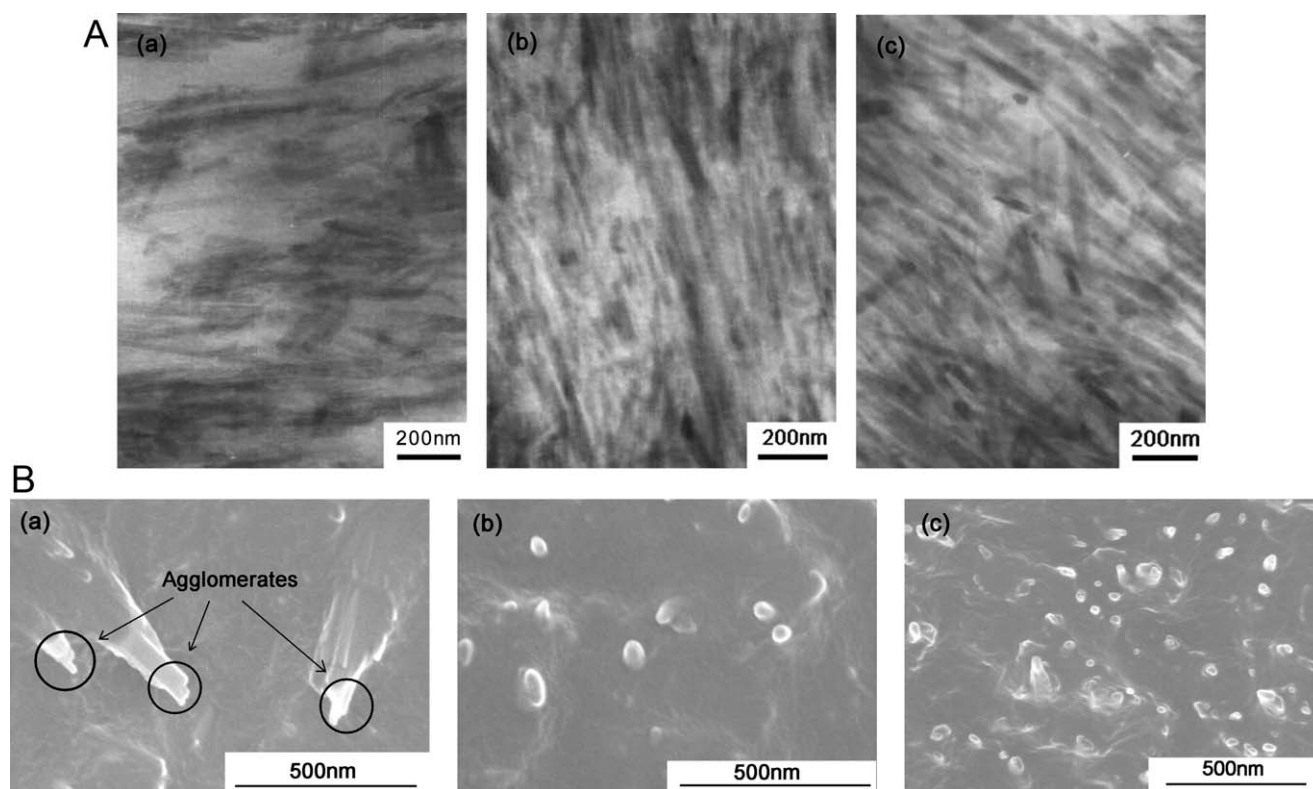
Figure 2 (A) TEM and (B) scanning electron microscopy micrographs of EPDM/FS composites filled with 50 phr FS with various silane KH570 amounts. (a) No modifier, (b) 6 phr KH570, and (c) 12 phr KH570.

dispersing in EPDM, the sizes of which were much smaller than the original value (2 ∼ 5 μm) of FS.[2] Only a little FS was exfoliated into nanofibers; thus, the fiber ends were few (white small points) as shown in scanning electron microscopy micrograph. The existence of these FS agglomerates indicated that there were a lot of nanofibers unreleased. On the other hand, these agglomerates were so loose that they were easy to pull out from the rubber matrix leaving cavities, which was an indication of poor interfacial adhesion. Thus, the stress–strain curve was very flat, similar to microparticles-reinforced rubber. With the increase in silane KH570, as seen from Figure 2(b,c), a growing number of FS were dissociated into nanofibers dispersing in EPDM matrix; thus, the number of FS agglomerates was less and less, and the number of fiber ends on the tensile fracture surface was more and more. The nanofibers also had a strong interfacial adhesion with rubber; thus, the composites exhibited the typical stress–strain behavior of SFRC. When silane KH570 was 12 phr, almost all the FS was dissociated into nanofibers dispersing in EPDM, and the number of fiber ends increased significantly, as shown in Figure 2(c); thus, the reinforcing effect of modified FS was the best. At the same time, FS nanofibers showed obvious orientation under the mechanical stress.

The surface modification of FS with silane not only substantially improved the exfoliation of FS, but also strengthened fiber–rubber adhesion, as discussed in detail in another publication.[8]

Amount of modified FS

EPDM was reinforced by the different amounts of FS, which was modified with KH570 at the best loading level of 24 phr/100 phr FS. Compared with unfilled pure EPDM rubber, from Figure 3(a), with the increase in modified FS, the tensile stress–strain curves went up more sharply, the tensile strength increased obviously, and the elongation at break decreased. From Figure 3(b), the tear strength and hardness of the composites also increased significantly. Because of silane KH570, FS nanofibers had a good interfacial bonding with the EPDM rubber.[8] As a result, the stress of rubber could be transferred effectively to the fibers because of the good interfacial adhesion, and then the fibers stood the stress until specimens fractured. The nanofibers could also prevent the microcracks from extending further and forming destructive large cracks; thus, tensile strength and tear strength of the composites were improved. When the amount of modified FS reached 70 or 90 phr, the tensile stress and tensile strength increased slowly down.
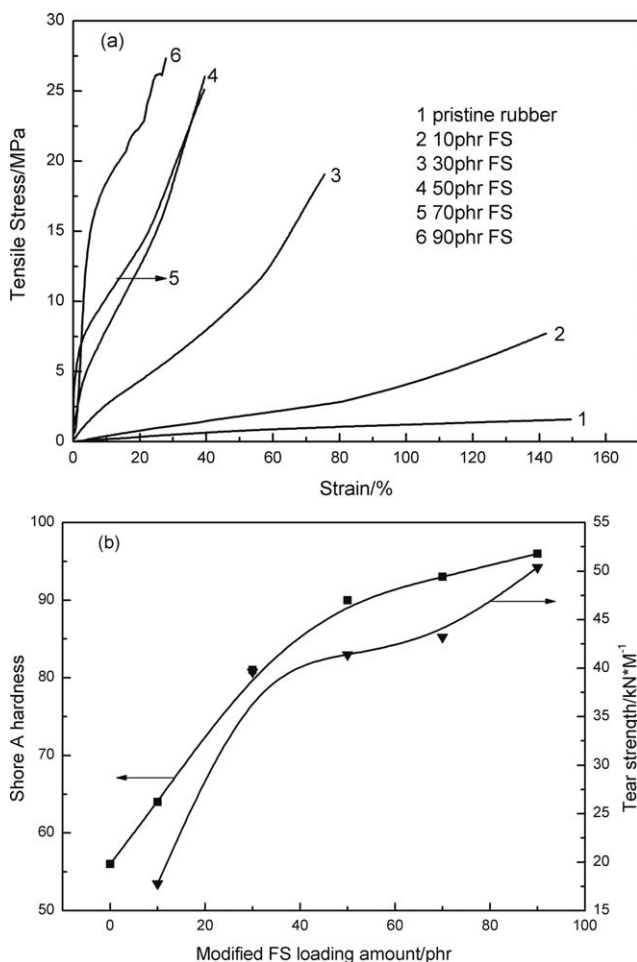
Figure 3 Tensile stress–strain curves (a) and shore A hardness and tear strength (b) of EPDM/FS composites filled with various modified FS amounts.

As seen from Figure 4, the percolation phenomenon in the rubber nano-reinforcement was revealed. That was, as the loading of modified FS increased, the tensile stress at 25% and 40% strain of composites first increased slowly and then increased rapidly, finally reached the balance. The percolation phenomena were related to the nano-reinforcing mechanism. The rubber reinforcement through modified FS was corresponding to the formation of the stretched chains between the neighbor FS particles during stretching; thus, the space between the neighbor FS particles must be close enough to make sure that the rubber's molecular chains can overlap at least two FS particle surfaces. The space was firstly determined by the amount of modified FS.[17]

As seen from Figure 5(a), when the amount of modified FS was 10 phr, almost all the FS were dissociated into nanofibers dispersing in EPDM. Because of the small amount of FS, the fiber ends on tensile fracture surface were few. Seen from the TEM micrograph, the nanofibers were distributed disorderly, because the oriented nanofibers under shear force on two-roll mill

might restore easily to original disorder state because of the good elasticity of EPDM filled with so little FS amount. As the amount of FS increased, the elasticity of EPDM became poor, which may be conducive to the orientation of the nanofibers. It was also observed from Figure 5(b) that a great amount of FS had been dissociated into nanofibers, when the loading of modified FS was 70 phr. Still, some very small FS agglomerates and bundles were found on the tensile fracture surface, which was consistent with the observation from TEM micrograph. As discussed above, when the amount of FS was 50 phr, the dispersion of FS was rather better. And too much FS could not be completely dissociated into nanofibers, and may be there were more unexfoliated agglomerates; thus, the tensile strength and tensile stress increased a little slowly.

The anisotropism of EPDM/FS composites

Fiber orientation makes SFRC exhibit the mechanical anisotropy, which is different from granular filler (such as carbon black) reinforced rubber. The short fibers in SFRC will be orientated along the shear direction using extrusion or calendar techniques; thus, SFRC exhibit mechanical anisotropy. There are two methods to characterize the fiber orientation: One is to observe directly the dispersion and orientation of the short fibers using TEM and various microscopy techniques. However, rubber has a very low glass-transition temperature as well as the excellent elasticity; thus, it is difficult to make the ultrathin slices fully parallel to the direction of fiber orientation. The other is the indirect characterization of the mechanical anisotropy (the performance differences between the parallel direction (L) and vertical direction (T) to fiber orientation), such as tensile modulus, flexural modulus, swelling property, thermal expansion property, and so on.
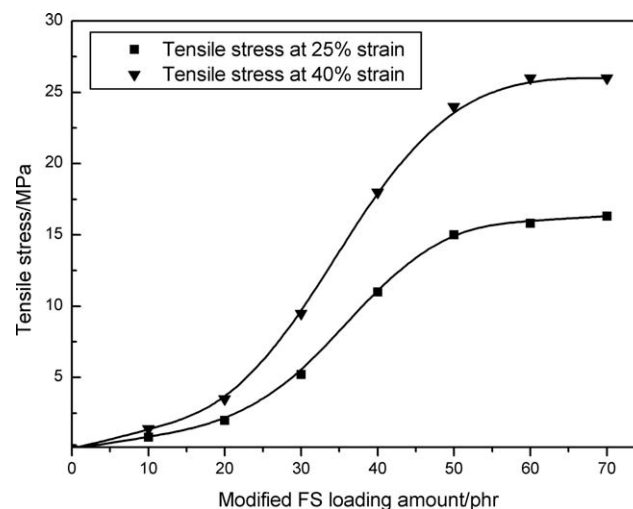

Figure 4 Tensile stress at 25% and 40% strain of EPDM/FS composites filled with various modified FS amounts.

TABLE II
The Anisotropy in Tensile Properties of EPDM/FS Composites Filled with Various Modified FS Amounts

Modified FS content	Fibers' direction	Tensile stress at 25% strain (MPa)	Tensile stress at 50% strain (MPa)	Tensile strength (MPa)	Elongation at break (%)
10 phr	L	1.0	1.6	7.7	153
	D	0.8	1.5	7.2	164
	T	0.7	1.3	6.9	180
30 phr	L	5.2	10.1	18.2	80
	D	2.1	3.4	10.8	136
	T	1.7	2.7	10.9	154
50 phr	L	15.0	–	25.3	40
	D	4.9	7.2	15.6	113
	T	3.8	5.5	13.1	117
70 phr	L	16.3	–	25.1	40
	D	8.8	12.0	16.5	77
	T	3.9	5.2	11.0	128

L, parallel to fiber; T, perpendicular to fiber; D, disordered fiber.

It can be seen from Table II that, with the same amount of modified FS, the tensile stress at 25% strain, tensile stress at 50% strain, and tensile strength of the composites at L direction were the highest, whereas those of the composites at T direction were the lowest, and those of nonoriented composites (disordered) were middle. But the law of elongation at break was just opposite. That is, elongations at break of the composites at L direction were the lowest and those of the composites at T direction were the highest. These are consistent with the results of traditional SFRC. The difference (anisotropy) of the tensile properties of EPDM/FS composites between L and T direction would be more obvious with the increase in FS. Figure 6 showed that the laws of the anisotropy of compression modulus were the same, when
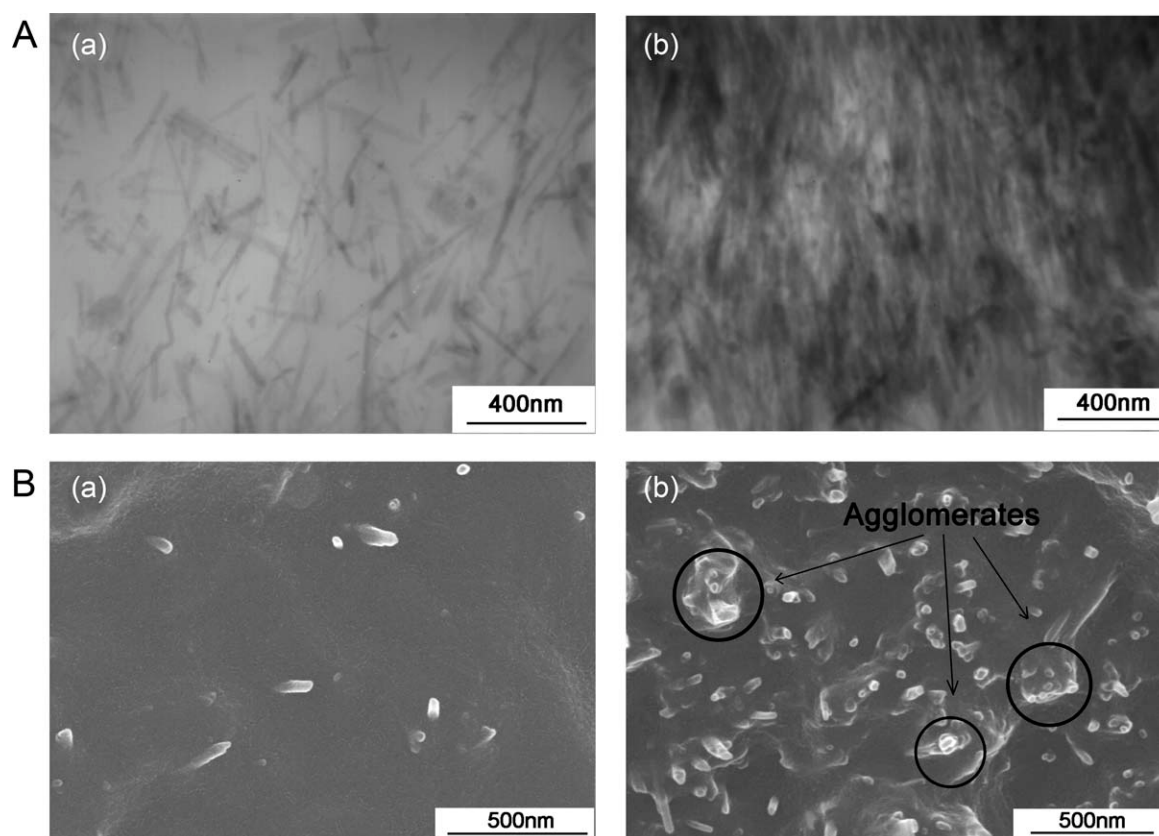

Figure 5 (A) TEM and (B) scanning electron microscopy micrographs of EPDM/FS composites filled with various modified FS amounts. (a) 10 phr FS and (b) 70 phr FS.
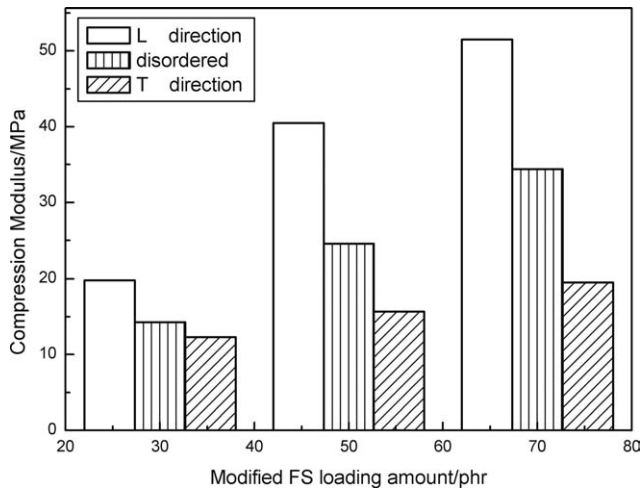
Figure 6 The anisotropy in compression modulus of the composites filled with various modified FS amounts.

adding different amounts of modified FS to reinforce EPDM composites.

According to stress transfer theory,[18] when an applied stress was given to the composites, the stress was produced in the rubber matrix, and then was transferred to fibers by fiber–matrix interface. When the fibers were orientated, the stress of composites could be transferred to fibers more effectively along the direction of fiber orientation. As a result, the fibers stood the stress until specimens fractured. Thus, the composites exhibited the maximum tensile stress and the minimum elongation in L direction and *vice versa* in T direction. This was mechanical anisotropy of SFRC. The anisotropy of SFRC was determined by the loading amount of fibers, fiber aspect ratio (length/diameter ratio), fiber orientation, fiber–rubber matrix adhesion, and the matrix itself.[19–22]

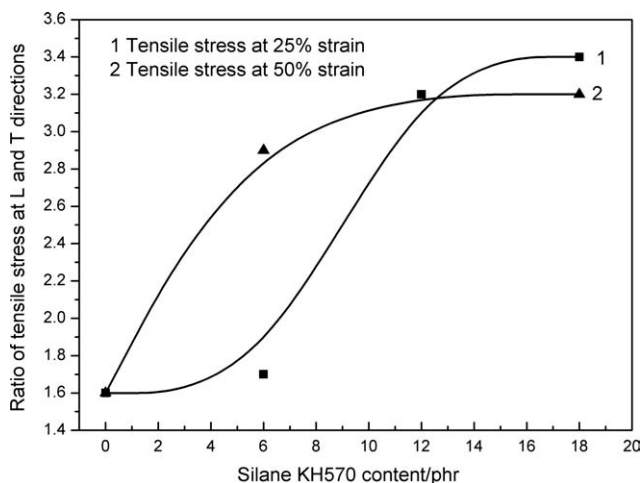Seen from Figure 7, when 50 phr FS without modification was used to reinforce EPDM, the difference

Figure 7 The mechanical anisotropy of the composites filled with 50 phr FS with various silane KH570 amounts.
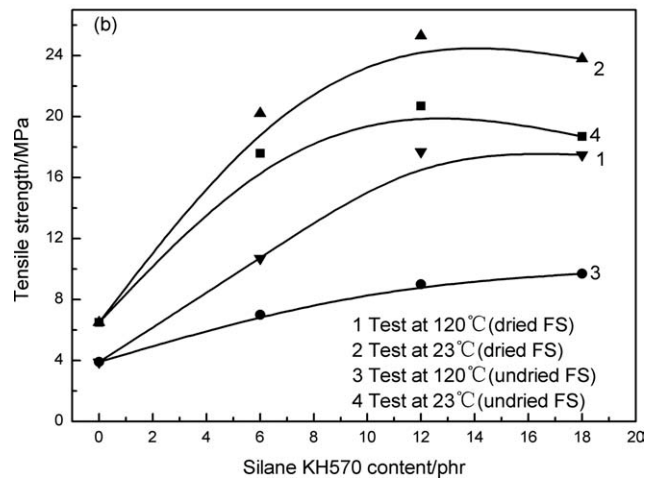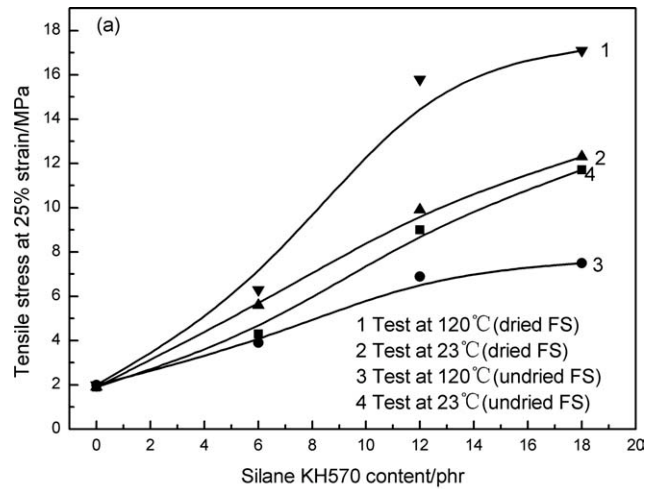
Figure 8 Tensile stress at 25% strain (a) and tensile strength (b) of EPDM composites filled with dried FS and undired FS individually with different silane KH570 amounts (FS loading: 50 phr).

of tensile stress at 25% strain and at 50% strain between L and T directions was slight. The difference became more and more obvious with the increase in silane KH570 at the same FS loading level. When the amount of silane KH570 was over 12 phr/50 phr FS, the difference in mechanical properties changed little. As discussed before, the modification with silane KH570 improved the exfoliation of FS, producing a large number of nanofibers; thus, the mechanical anisotropy was very obvious. When the amount of silane KH570 was 12 phr/50 phr FS, almost all the FS were dissociated into nanofibers; thus, the number of nanofibers no longer increased with the increase in silane. Thus, the amount of silane had a significant impact on the mechanical anisotropy of the composites.

Effect of water in FS

FS contains adsorbed water, zeolite water, crystal water, and structural water.[18] Adsorbed water and
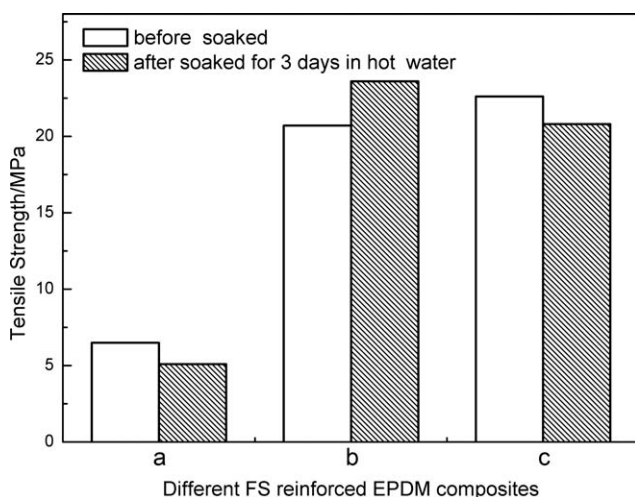
Figure 9 Tensile strength of the composites filled with various FS amounts before and after soaked in hot water. (a), Neither dried nor modified FS; (b), modified undried FS; and (c), modified dried FS. FS loading: 50 phr.

zeolite water belongs to free water, which may affect the modification with silane coupling agent and even the reinforcement of FS. Thus, it had a great impact on the composite properties that whether FS was dried or not. The content of free water in FS was measured to be 14%, and the water could be eliminated by drying the FS in a blast oven at 120°C for 2 hr. Seen from Figure 8(a), the drying had little effect on the tensile stress at 25% strain of the composites at room temperature, but obviously improved the tensile stress at 25% strain at 120°C(test temperature). It is puzzling that the tensile stress at 25% strain of the dried FS-reinforced EPDM composites at 120°C not fell but rose, compared with that at room temperature. From Figure 8(b), if the dried FS were used, the tensile strengths of composites at both room temperature and 120°C were significantly higher than those of nondrying FS-reinforced composites. This again proved the unique modification effect of silane to FS.

As can be seen from Figure 9, regardless of whether FS was dried or modified, the tensile strengths of EPDM/FS composites changed little after soaked in water at 80°C for 3 days when the loading of FS was 50 phr. There was no visible weight change in tested samples although FS is hydrophilic. It was probably due to the nonpolarity and hydrophobic property of EPDM. It was possible to be used under the moist condition.

CONCLUSIONS

EPDM emulsion was difficult to obtain; thus, the dispersion of FS in EPDM could not be carried out by the polymer emulsion co-coagulation method. By increasing the silane coupling agent substantially, modified FS could be fully dissociated into nanofibers dispersing uniformly in EPDM by the polymer melt blend method. The optimum loading amount of silane KH570 should be up to 24 phr/100 phr FS. The EPDM/FS composites exhibited the typical stress–strain characteristics of SFRC and the mechanical anisotropy, which would become more obvious with the increase in the modified FS and silane KH570, because it led to the increase in nanofibers. The free water in FS should be removed before using because it had a great impact on the tensile properties of the composites at both room temperature and high temperature. Regardless of whether FS was dried or modified, the tensile strength of EPDM/FS composites changed little after soaked in hot water for a long time.

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