Effects of Curing Systems and Polysulfonamide Pulp on the Curing Characteristics, Mechanical Properties, and Swelling Behavior of Ethylene–Propylene–Diene Elastomer Composites

Xiaolong Jia,[1,2] Yunhua Yu,[1] Gang Li,[1] Gang Sui,[1] Peng Li,[1] Xiaoping Yang[1]

[1]*Key Laboratory of Beijing City for the Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[2]*Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213*

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ABSTRACT: The effects of three curing systems and polysulfonamide (PSA) pulp on the curing characteristics, mechanical properties, and swelling behavior of ethylene–propylene–diene elastomer (EPDM) composites were investigated. The maximum torque value and the optimum curing time were highest for EPDM composites cured with a peroxide system, and they were closely followed by those cured with a sulfur system. In comparison with those cured with peroxide and phenolic resin systems, EPDM composites cured with the sulfur system showed higher mechanical properties and dimensional stability. With increasing PSA pulp content, the maximum torque value of the EPDM composites increased, whereas the optimum curing time of the composites decreased. The orientation percentage of the PSA pulp in the EPDM composites was maximum at 30 phr pulp, as determined from green strength measurements. In the longitudinal direction along which the pulp was oriented, the EPDM composites showed higher tensile strength as well as lower elongation and swelling ratios. Also, with increasing PSA pulp content, the tensile strength of the EPDM composites decreased up to 10 phr pulp and subsequently increased, whereas the elongation and swelling ratio of the EPDM composites decreased linearly. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1060–1067, 2010

Key words: composites; mechanical properties; swelling

INTRODUCTION

With their prominent mechanical properties, easy processing operations, and low cost, short-fiber-reinforced elastomer composites are of great importance for both industrial practice and academic innovation.[1–3] Extensive studies on the optimal designs of these reinforced composites have been undertaken.[4–6] Such reinforcement recipes combine the elasticity of elastomers with the strength and stiffness of short fibers to enhance the overall performance of composites. The properties and performance of short-fiber-reinforced elastomer composites are mainly affected by several factors, such as the nature of the fiber, the fiber dispersion, the fiber orientation, the contents of the fiber, and the interfacial bonding between the fiber and the matrix.[7–9] A variety of natural and synthetic short fibers, such as coir, cellulose, glass, nylon, and aramid short fibers, have been studied as reinforcements in both natural and synthetic elastomers by many researchers.[5,10–15] Among the various commonly used elastomers, ethylene–propylene–diene elastomer (EPDM) has been chosen in many fields because of its outstanding properties, such as high strength, good chemical resistance, and low specific gravity.[16–20] Recently, polysulfonamide (PSA) pulp, a similar product of aramid pulp and aramid short fibers, has emerged as a new reinforcing material in a wide range of product applications because of its high thermal stability, low cost, and rich resources.[21,22] The incorporation of PSA pulp can significantly improve the physical properties of EPDM composites. Our previous works[22,23] have initiated preliminary studies designed to detail the effects of PSA pulp on the ablation behavior and thermal properties of thermal-insulating EPDM composites. Besides these effects, the practical application of such composites in the field of thermal-insulating materials requires a complete understanding of their other physical properties,

Correspondence to: X. Yang (yangxp@mail.buct.edu.cn).
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especially with respect to the effects of curing systems and PSA pulp on the curing characteristics, mechanical properties, and swelling behavior of EPDM composites. However, such studies have not been reported up to now.

To bridge this gap, the curing characteristics, mechanical properties, and swelling behavior of EPDM composites reinforced with PSA pulp were investigated. To this end, (1) the effects of peroxide, phenolic resin, and sulfur curing systems on the curing characteristics, mechanical properties, and swelling behavior of EPDM composites were examined; (2) the variation of the curing characteristics of EPDM composites with the PSA pulp content was investigated, and the extent of pulp orientation was obtained from green strength measurements; and (3) the mechanical properties and swelling behavior of EPDM composites were analyzed to evaluate the effects of the pulp content and pulp orientation.

EXPERIMENTAL

Composite preparation

The materials used in this study were EPDM (iodine value of the diene monomer = 5), liquid EPDM, nanosilica, and additives with a weight ratio of 100 : 15 : 20 : 15 in accordance with our previous works.[22,23] The contents of the PSA pulp (0.5–3 mm long) were adjusted to 0, 10, 20, 30, 40, and 50 parts per hundred grams of EPDM (phr). The EPDM composites were cured with three curing systems: (1) a peroxide curing system based on 5 phr dicumyl peroxide and 3 phr triallyl isocyanurate; (2) a phenolic resin curing system based on 10 phr brominated phenolic resin; and (3) a sulfur curing system based on 2.5 phr sulfur, 4 phr zinc oxide, 2 phr stearic acid, 3.6 phr 2-sulfonyl dibenzo thiazole, and 1.5 phr diphenyl guanidine. All materials were mixed uniformly at 50°C with an internal mixer (Rheocord 90, Haake Mess-Technic GmbH, Goettfert, Germany) at a speed of 100 rpm for 10 min. Then, the mixture was passed through a two-roll mill (XK-560, Dalian Huari Machine Co., Dalian, China) along the milling direction with a nip gap of 0.8 mm and a speed ratio of 1 : 1.2. The passing process was repeated several times to maximize the pulp orientation along the milling direction.[1,8] The cured composite plaques were obtained via the molding of the mixture with iron frames 2 mm thick at 160°C under a pressure of 10 MPa for the optimum curing time. The optimum curing time, which was the time required to reach 90% of the maximum torque, was determined with a rheometer (P3555B2, Beijing Huanfeng Chemical Machine Co., Beijing, China) in advance.

Measurement of the curing characteristics

The curing characteristics of the EPDM composites were measured with a rheometer (P3555B2, Beijing Huanfeng Chemical Machine Co., Beijing, China) at 160°C at a rotational frequency of 100 cycles per minute. Samples of 8–10 g were used. The final values of the maximum torque and the optimum curing time were averages of five measurements.

Measurement of the mechanical properties

The cured and uncured composite plaques, 2 mm thick, were cut into dumbbell-shaped tensile specimens with a size of 115 × 6 mm^2 along the milling direction (longitudinal) and across the milling direction (transverse) in accordance with ASTM D 638. Mechanical properties were measured with a tensile testing machine (Instron 1121, Instron Co., Norwood, MA) at a crosshead speed of 500 mm/min with a 200-N load. The final values were averages of five measurements.

Swelling studies

The specimens of EPDM composites were immersed in *n*-heptane for 72 h at 30°C. The crosslink density of the EPDM composites was obtained with the following equation:[24]

$$\text{Crosslink density} = -\frac{\ln(1-\nu_r)+\nu_r+X\nu_r}{V_1\nu_r^{1/3}} \quad (1)$$

where X is the volume fraction of the elastomer in the swollen composite, V_1 is the molar volume of the solvent, and v_r is the Huggins elastomer–solvent interaction parameter. The final values of the crosslink density were averages of five measurements.

The swelling behavior of the EPDM composites was analyzed with the swelling ratio as calculated with the following equation:

$$\text{Swelling ratio (a)} = \frac{d_\infty}{d_0} \quad (2)$$

where d_∞ is the dimension of the specimen at equilibrium swelling and d_0 is the original dimension of the specimen before swelling. The cured composite plaques, 2 mm thick, were cut into rectangular specimens (25 × 10 mm^2) along the milling direction (longitudinal). The length (longitudinal), width (transverse), and thickness of the same specimens were accurately measured before and after 72 h of immersion in *n*-heptane at 30°C. The final values of the swelling ratio were averages of five measurements.

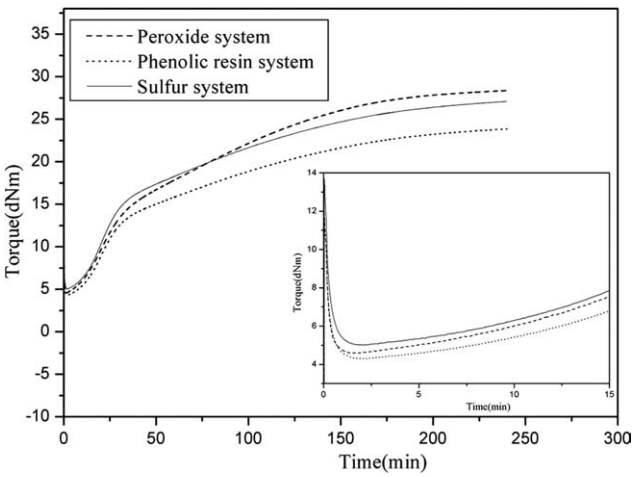

Figure 1 Curing curves of the EPDM composites with 10 phr PSA pulp that were cured with peroxide, phenolic resin, and sulfur systems. The inset shows the initial curing curves of these composites.

Morphology observation

Morphologies of fractured surfaces of EPDM composites were observed by scanning electron microscopy (S4700, Hitachi Co., Tokyo, Japan). The fractured surfaces of the composites were obtained by the breaking of the composites in liquid nitrogen. The composite specimens were coated with a thin layer of a gold alloy.

RESULTS AND DISCUSSION

Effect of the curing systems

Curing characteristics

Figure 1 shows the curing curves of EPDM composites with 10 phr PSA pulp that were cured with peroxide, phenolic resin, and sulfur systems. For all EPDM composites, as shown in Figure 1 and its inset, the torque values decreased initially, then increased linearly, and finally leveled off. The observed decrease in the torque values was due to the softening of the EPDM matrix, whereas the subsequent increase in the torque value was due to the crosslinking of the EPDM matrix. The final leveling-off meant the completion of the crosslinking. Table I shows the curing characteristics and crosslink density of the EPDM composites. As shown in Figure 1 and Table I, EPDM composites cured with the peroxide system showed the highest maximum torque value and optimum curing time, and they were closely followed by those cured with the sulfur system. These results conformed to those of similar studies performed with other polymer systems.[9,25] The observed difference in the torque values and curing time was ascribed to the different crosslinks existing in the microstructure of the EPDM composites cured with various systems, which affected the flexibility of the macromolecular networks and the stiffness of the EPDM matrix. Figure 2 shows structural features of EPDM composites cured with the peroxide, phenolic resin, and sulfur systems. As shown in Figure 2, rigid C—C bonds were generated by the peroxide and phenolic resin systems, whereas flexible mono-, di-, and polysulfidic bonds were formed by the sulfur system.[26,27] Because of the rigid nature of C—C bonds, the restriction of the deformation of molecular chains in the EPDM composites cured with the peroxide system was stronger, whereas there was less restriction for the deformation occurring in the EPDM composites cured with the sulfur system because of the presence of flexible polysulfidic bonds. However, despite the existence of the rigid C—C bonds, the maximum torque value and optimum curing time of the EPDM composites cured with the phenolic resin system were even lower than those of the EPDM composites cured with the sulfur system, and this could be attributed to the lower crosslink density of the EPDM matrix produced by the phenolic resin system, as shown in Table I. Additionally, it should be noted that the curing of all EPDM composites took a relatively long time. The reason is that the iodine value of the diene monomer and the contents of the curing systems in our study were relatively low, and this was very beneficial for avoiding the premature vulcanization (scorch) of the rubber composites.[27]

Mechanical properties

Figures 3 and 4 show the mechanical properties and stress–strain curves of EPDM composites with 10 phr

TABLE I
Curing Characteristics and Crosslink Density of the EPDM Composites

	Peroxide system	Phenolic resin system	Sulfur system					
Pulp content (phr)	10	10	0	10	20	30	40	50
Maximum torque (dN m)	28.4 ± 0.3	23.9 ± 0.2	22.7 ± 0.2	27.1 ± 0.2	27.7 ± 0.2	28.5 ± 0.2	28.9 ± 0.3	29.7 ± 0.3
Curing time (min)	121 ± 1	113 ± 1	127 ± 1	118 ± 1	115 ± 1	110 ± 1	108 ± 1	104 ± 1
Crosslink density $\times 10^3$ (mol/m^3)	2.2 ± 0.1	1.2 ± 0.1		1.9 ± 0.1				

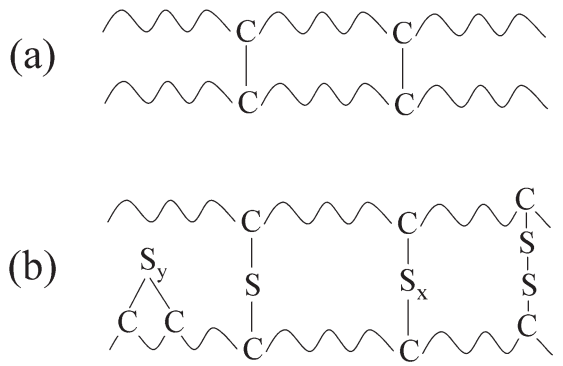

Figure 2 Structural features of the EPDM composites cured with (a) peroxide and phenolic resin and (b) sulfur systems.

PSA pulp that were cured with peroxide, phenolic resin, and sulfur systems. Although the flexible polysulfidic bonds were weaker and more readily broken than rigid C—C bonds, EPDM composites cured with the sulfur system exhibited higher tensile strength and break elongation than those cured with the peroxide and phenolic resin systems. The result was consistent with those obtained for other polymer composites by Huang and Liu.[28,29] According to Zhao et al.[30] and Thomas,[31] high stresses in the molecular network were relieved by the fracture of at least some of the polysulfidic bonds before backbone chains were broken. They stated that the broken polysulfidic bonds could reform again under a load to support stress and generate more energy dissipation because of the chain slippage, and this improved the mechanical properties of the elastomers cured with the sulfur system. Besides, in comparison with those cured with the phenolic resin system, the EPDM composites cured with the peroxide system showed more brittle-type behavior, as shown in Figure 4. This behavior resulted from the higher crosslink density of the EPDM matrix produced by the peroxide system during curing, as also evidenced by the higher maximum torque value shown in Figure 1 and Table I.

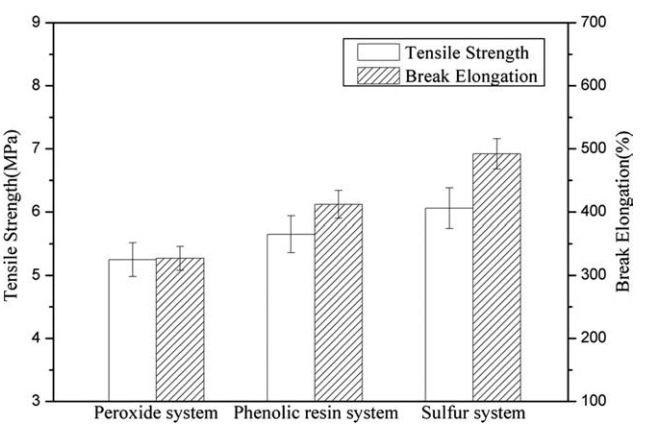

Figure 3 Mechanical properties of the EPDM composites with 10 phr PSA pulp that were cured with peroxide, phenolic resin, and sulfur systems.

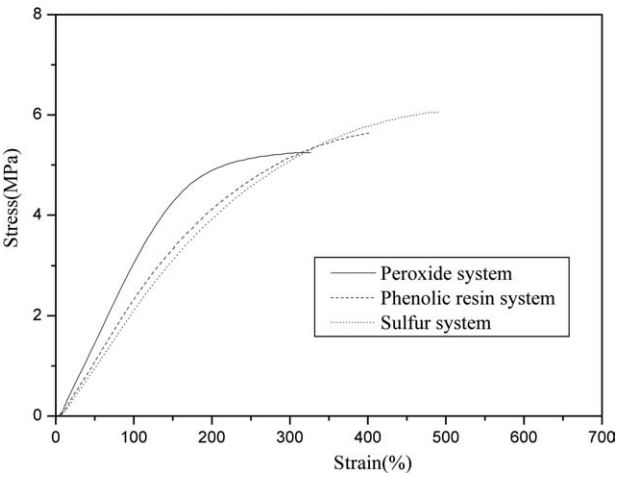

Figure 4 Stress–strain curves of the EPDM composites with 10 phr PSA pulp that were cured with peroxide, phenolic resin, and sulfur systems.

Swelling behavior

Figure 5 shows the swelling ratios of the EPDM composites with 10 phr PSA pulp that were cured with the peroxide, phenolic resin, and sulfur systems. For all EPDM composites, the swelling ratios in the longitudinal direction were minimum, whereas those in the thickness direction were maximum. This phenomenon was attributed to PSA pulp orientation along the longitudinal direction, and the pulp orientation is discussed in detail later in this study. Moreover, EPDM composites cured with the sulfur system exhibited less noticeable swelling behavior than those cured with the peroxide and phenolic resin systems. This result revealed that the sulfur system was the most efficient in restricting

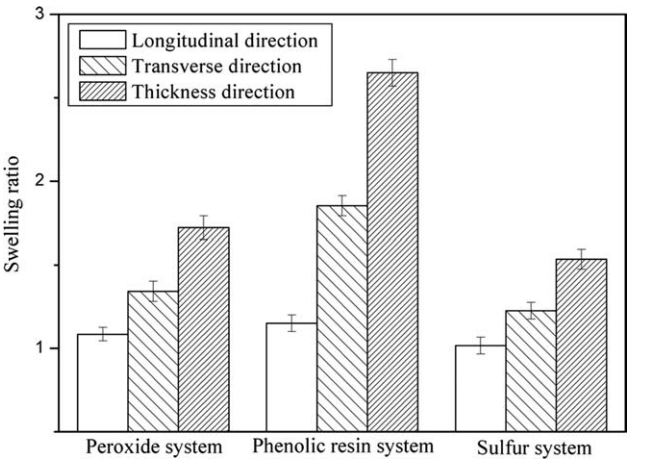

Figure 5 Swelling ratios of the EPDM composites with 10 phr PSA pulp that were cured with peroxide, phenolic resin, and sulfur systems.

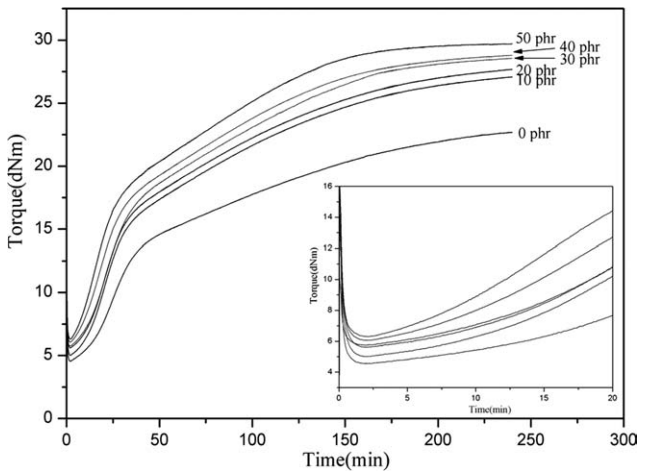

Figure 6 Curing curves of the EPDM composites with various PSA pulp contents. The inset shows the initial curing curves of these composites.

the transport of the solvent into the EPDM composites. Thus, the EPDM composites cured with the sulfur system showed higher stability in dimensions as well as higher mechanical properties, as mentioned previously. Therefore, the sulfur system was chosen to be curative in the next parts of this study.

Effect of the PSA pulp

Curing characteristics

Figure 6 shows the curing curves of the EPDM composites with various PSA pulp contents. As previously shown in Figure 1, the torque values of all EPDM composites with PSA pulp decreased initially, then increased quickly, and finally leveled off. In contrast to the EPDM composites without the pulp, the incorporation of the pulp enhanced the stiffness of the EPDM composites, and this showed the reinforcing effect of the pulp on the EPDM matrix. The maximum torque value increased with the PSA pulp content, and this indicated that the PSA pulp was an effective reinforcing agent for the EPDM matrix. However, with increasing PSA pulp content, the optimum curing time decreased, as shown in Table I, and this suggested that the PSA pulp effectively accelerated the curing reaction of the EPDM matrix. Manchado et al.[15] obtained similar results when they studied the processing behavior of EPDM composites reinforced with aramid short fibers, a similar product of PSA pulp. They concluded that aramid fibers could improve the curing efficiency of EPDM by increasing the degree of organization of the polymer molecules.

Extent of the PSA pulp orientation from green strength measurements

The anisotropy of the mechanical properties of short-fiber-reinforced composites has been reported elsewhere,[1,6,8] and it is due to the orientation of the majority of short fibers along the milling direction during the processing of the composites on a two-roll mill. The effects of processing parameters, such as the passing times, nip gap, and speed ratio, on the short-fiber orientation in elastomer composites was studied by Moghe.[32] He pointed out that the nip gap is the key factor and considerably affects the short-fiber orientation and that the orientation of the majority of short fibers is achieved during the first pass through the mill. The mechanical properties of short-fiber-reinforced composites mainly rely on the angle between the directions of the short-fiber orientation and the applied force. The short fibers can bear maximum loads when the alignment of short fibers is parallel to the direction of the applied force. Thus, in our present study, we aimed to orient the majority of the PSA pulp along the milling direction (longitudinal) to meet the expected loads on the prepared EPDM composites.

The extent of PSA pulp orientation in this study was obtained from measurements of the green strength of the composites on the basis of the following equation:[33]

$$\text{Pulp orientation}(\%) = \frac{S_L/S_{G,L}}{S_L/S_{G,L} + S_T/S_{G,T}} \qquad (3)$$

where S is the green strength and subscripts G, L, and T represent gum, longitudinal, and transverse, respectively.

Figure 7 shows the effect of the PSA pulp content on the orientation percentage of the pulp in the EPDM matrix. With low contents of the PSA pulp, the orientation percentage was low because random movement of the PSA pulp was allowed by more free space in the EPDM matrix, which increased the chaoticity of the pulp distribution and decreased the

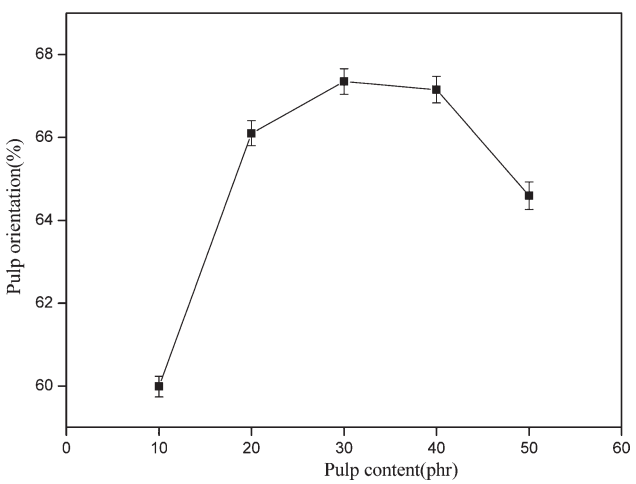

Figure 7 Effect of the PSA pulp content on the orientation percentage of the pulp in the EPDM matrix.

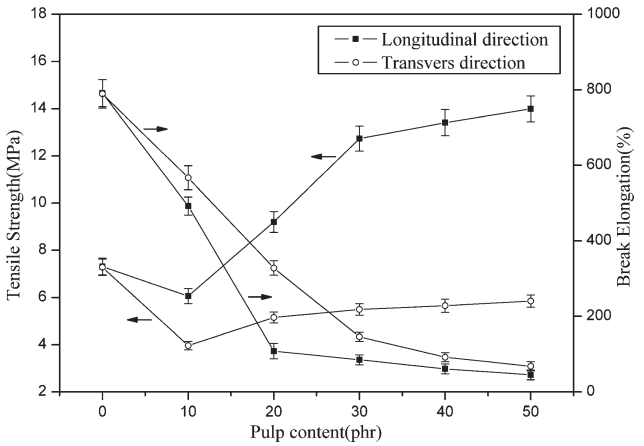

Figure 8 Effects of the orientation and content of the PSA pulp on the mechanical properties of the EPDM composites.

extent of the pulp orientation. With increasing PSA pulp content, the orientation percentage increased obviously. However, when the PSA pulp content was more than 20 phr, the increasing trend slowed. The orientation percentage even decreased slightly after 30 phr and decreased significantly after 40 phr; this indicated that the PSA pulp could not orient itself under the entanglement caused by the overpopulation of the PSA pulp in the matrix.

Effect of the PSA pulp orientation and content on the mechanical properties

Figure 8 shows the effects of the orientation and content of the PSA pulp on the mechanical properties of the EPDM composites, and Figure 9 shows the fractured surfaces of the EPDM composites with 20 phr PSA pulp. As shown in Figure 8, the tensile strength values in the longitudinal direction were higher than those in the transverse direction, whereas the elongation values in this direction were lower than those in the transverse direction. This phenomenon resulted from the PSA pulp orientation along the longitudinal direction, as can be clearly observed from the SEM photographs in Figure 9. The crack propagation and elastic deformation in the direction perpendicular to the pulp alignment were significantly inhibited by the PSA pulp, whereas those in the direction parallel to the pulp alignment came across less obstruction from the PSA pulp. The composites failure occurred primarily because of the breakage and pullout of the pulp when the pulp was oriented along the longitudinal direction. Hence, the composites exhibited higher tensile strength and lower elongation in the longitudinal direction.

Moreover, with increasing PSA pulp content, the tensile strength of the EPDM composites was minimum with 10 phr pulp and then increased; this showed the reinforcing effect of the pulp. Similar results were obtained by Jin et al.[20] The initial decrease in the tensile strength was due to a great stress concentration that resulted from the low pulp content and the more deformable matrix. The ability of the PSA pulp at low contents to inhibit crack propagation in the matrix was poor, and the pulp could not bear enough load when a large shear force was exerted on the interface between the pulp and EPDM matrix. However, the pulp at high contents could bear enough stress and formed strong frameworks that remarkably inhibited crack propagation in the matrix. Apparently, the pulp at higher contents restrained the elastic deformation of the matrix more obviously, so the elongation of the EPDM

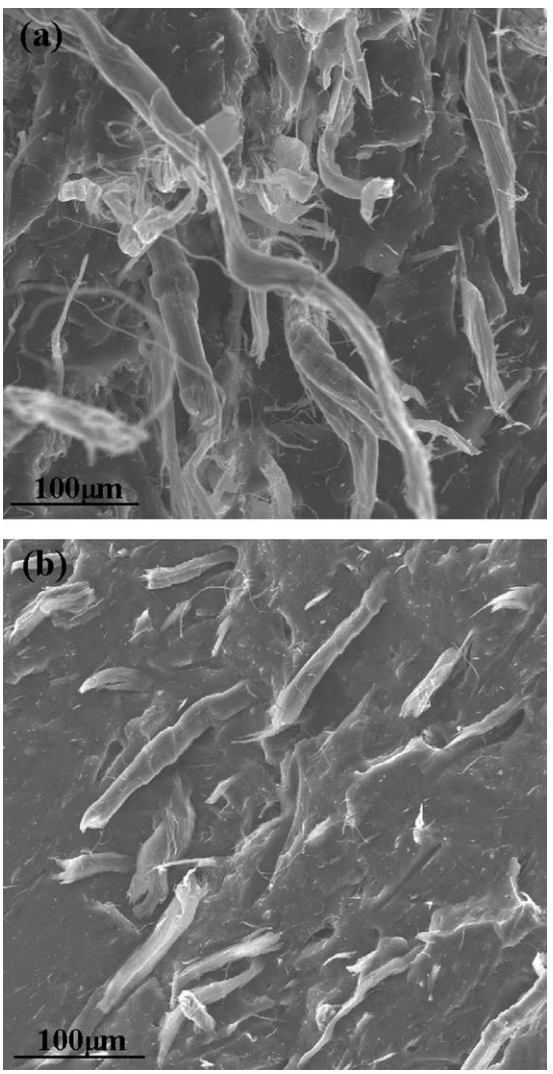

Figure 9 Fractured surfaces of the EPDM composites with 20 phr PSA pulp. The tested specimens were broken (a) perpendicularly and (b) parallelly to the milling direction. (a) The PSA pulp was pulled out from the fractured surface, and (b) the PSA pulp was lying parallel to the fractured surface. This indicated that the preferential orientation of the pulp was along the longitudinal direction.

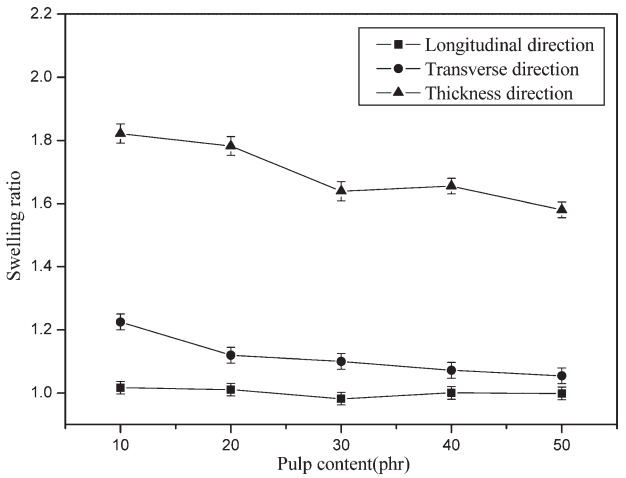

Figure 10 Effects of the content and orientation of the PSA pulp on the swelling ratios of the EPDM composites.

composites at failure decreased with increasing pulp content, as shown in Figure 8.

If we take into account the orientation percentage of the PSA pulp from the green strength measurements, with increasing PSA pulp content, the tensile strength of the EPDM composites should have increased to the maximum value with a pulp content of 30 phr and then dropped. However, this was not true according to the aforementioned results of this study. One hundred percent short-fiber orientation along the milling direction in the short-fiber-reinforced elastomer composites was definitely impractical if the standard elastomer processing and fabrication techniques were exerted. The pulp orientation achieved in the uncured EPDM composites by two-roll mixing was not maintained in the cured EPDM composites, and this was due to the shear flow that existed during compression molding. Therefore, the effect of the extent of pulp orientation as obtained from green strength measurements was not wholly reflected in the strength characteristics of the cured EPDM composites. As analyzed previously in Figure 8, the tensile strength of the EPDM composites was also related to the reinforcing effect of the PSA pulp on the EPDM matrix.

Swelling behavior

Figure 10 shows the effects of the content and orientation of the PSA pulp on the swelling ratios of the EPDM composites. With increasing PSA pulp content, the swelling ratios in the transverse and thickness directions decreased linearly, and this was attributed to the reduction of the volume fraction of the EPDM matrix and the increasing restriction of the solvent transportation in the composites generated with higher pulp content. However, with increasing PSA pulp content, the swelling ratio in the longitudinal direction nearly remained constant and was obviously lower than those in the transverse and thickness directions. This was clearly because the PSA pulp orientation along the longitudinal direction strongly restricted the swelling deformation of the EPDM composites and thus yielded only slight swelling in this direction. In addition, because of the higher pulp distribution in the transverse direction, the value and decreasing slope of the swelling ratio in the transverse direction were lower in comparison with those in the thickness direction, as shown in Figure 10. Thus, the swelling of the EPDM composites reinforced with the PSA pulp mainly occurred in the thickness direction.

The swelling ratio in a direction forming angle θ with the pulp orientation (a_θ) could be calculated with the following equation:[34]

$$a_\theta^2 = (a_T^2 - a_L^2)\sin^2\theta + a_L^2 \quad (4)$$

where a_L and a_T are the dimensional swelling ratios in the longitudinal and transverse directions, respectively. Figure 11 shows the dimensional swelling variation of the EPDM composites with angle θ in accordance with the equation, and various values of θ were assumed. For all EPDM composites with various PSA pulp contents, the swelling increased with θ increasing and reached the maximum when θ was up to 90°; this verified that the longitudinal direction was the preferential direction of the pulp orientation, as mentioned previously. The line corresponding to the EPDM composites without the PSA pulp was positioned above those of the EPDM composites with various PSA pulp contents, and this indicated that the pulp efficiently restricted the transport of the solvent into the composites and improved the stability of the dimensions of the composites.

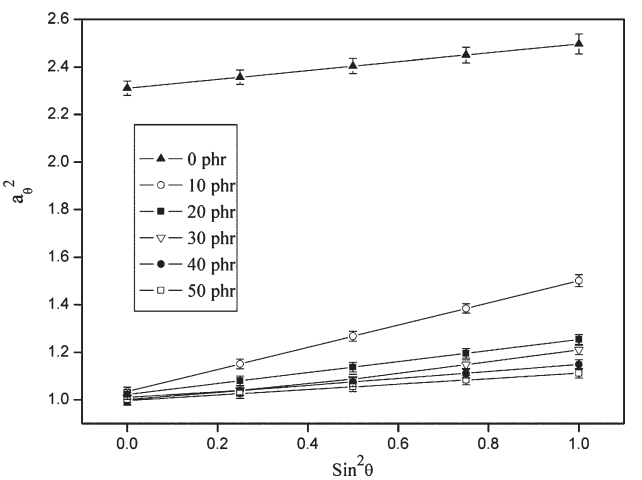

Figure 11 Dimensional swelling variation of the EPDM composites in various directions.

CONCLUSIONS

EPDM composites cured with the sulfur system exhibited higher mechanical properties and dimensional stability than those cured with the peroxide and phenolic resin systems. With increasing PSA pulp content in the EPDM composites, the maximum torque value increased, whereas the optimum curing time decreased; this showed the reinforcing and accelerating effects of the PSA pulp, respectively. The PSA pulp was oriented along the longitudinal direction, and this led to higher tensile strength as well as lower elongation and swelling ratios in this direction. Moreover, with increasing PSA pulp content, the tensile strength of the EPDM composites decreased initially and then increased, whereas the elongation and swelling ratio of the composites decreased linearly. However, the variation of the tensile strength of the EPDM composites with the PSA pulp content was not consistent with the extent of the PSA pulp orientation from the green strength measurements, and this was attributed to the partial change in the PSA pulp orientation during compression molding and the reinforcing effect of the PSA pulp on the EPDM matrix.

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