

Effect of a Coupling Agent on the Properties of Hemp-Hurd-Powder-Filled Styrene–Butadiene Rubber

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ABSTRACT: Styrene–butadiene rubber (SBR) composites filled with hemp hurd powder (HP) were prepared with bis(3-triethoxysilylpropyl) tetrasulfide (Si69) as a coupling agent. The effects of the filler content and coupling agent on the curing characteristics and dynamic mechanical properties of the composites were studied. The results indicate that with increasing filler loading, the torque values increased and the curing time decreased. The mechanical properties improved with increasing filled HP content up to 60 phr. Usually, long fibers led to a sharp decrease in the toughness of the composites, whereas short fibers, such as HP, had a

positive effect on the elongation at break within the loading range studied. The extent of the filler–matrix interaction and the scanning electron micrographs of the fractured surfaces confirmed that the addition of Si69 improved the interfacial interaction between HP and the SBR matrix, which led to an increase in the maximum torque and the mechanical properties. Moreover, the coupling agent was helpful in dispersing the filler in the rubber matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 681–689, 2011

Key words: adhesion; composites; mechanical properties

INTRODUCTION

In recent years, wood-based fillers have been explored as reinforcing fillers in polymers.^{1–4} Compared with inorganic fillers, biodegradable lignocellulosic fillers possess several advantages, including a lower density, easy availability, renewable nature, the production of less environmental pollution, and lower abrasion with minimum harm to equipment.^{5,6} Thus, the introduction of wood-based fillers in polymers can result in new and recycled materials that can be used in civil products, buildings, and industrial areas.

Hemp cultivation has a long history in China because of the lower labor input and smaller pesticide dependence. With environmental deterioration and a lack of energy, natural hemp fiber has attracted industrial interest. Some studies on the use of hemp fibers in polymers have been reported. Pracella et al.⁷ investigated the effect of grafted polymer compatibilizers on the properties of hemp fiber/PP composites and verified that the compatibilizer improved the fiber dispersion in the polymer matrix and the interfacial adhesion. Mishra et al.⁸

reported that after esterification with maleic anhydride, composites filled with hemp fiber showed less adsorption of water than untreated fiber composites. However, a great amount of hemp hurds (accounting for 70–80% of the hemp stem) are disposed by combustion or landfilling every year; this results in resource waste and environmental pollution. Therefore, attempts to use hemp hurd powder (HP) as a filler in polymer composites not only contributes to solving the environmental problem, but it also has potential economic value.

However, the high content of hydroxyl and polar groups in cellulosic molecular chains impart natural fibers with strong hydrophilic characteristic, which is the main factor of incompatibility with hydrophobic polymer matrixes.⁹ As a result, natural-fiber-filled composites have weak interfacial adhesion and poor properties. Various attempts to improve the interfacial adhesion and mechanical properties of filled composites have been carried out, including chemical pretreatment,¹⁰ corona treatment,¹¹ grafting,¹² and the use of various coupling agents or bonding agents.^{7,13} Among these methods, coupling agent modification appears to be a quick and effective method of providing good interfacial adhesion. Ismail et al.¹³ observed that the addition of a phenol formaldehyde/hexamethylene tetramine bonding system improved the rubber–filler interaction and mechanical properties, whereas some other authors¹⁴

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Figure 1 SEM micrograph of a 400-mesh HP sample.

have reported that the incorporation of various coupling agents has also improved the properties of rubber composites filled with natural fibers.

Compared with wood-based fibers, agricultural crop fibers such as hemp have significant advantages, such as their shorter cultivation period and ecofriendly nature. To date, few studies have been concerned with the subject of HP utilization in polymeric materials. Thus, it was our aim to assess the potential utilization of a relatively new type of filler derived from waste hemp hurd. In this study, bis(3-triethoxysilylpropyl) tetrasulfide (Si69) was selected as an effective coupling agent, and the effects of the filler content and coupling agent on the curing characteristics, dynamic mechanical properties, mechanical properties, and rubber–filler interactions of HP-filled styrene–butadiene rubber (SBR) composites were investigated.

EXPERIMENTAL

Materials

SBR (SBR-1502) was provided by CNPC Jilin Chemical Co. (Jilin, China). Si69 was purchased from Nanjing Shuguang Chemical Group Co. (Jiangsu, China). Other chemicals, such as zinc oxide, stearic acid, sulfur, and accelerators, were commercial grade and were bought from Beijing Chemical Reagent Shop (Beijing, China). HP (400 mesh, humidity = 6%), with a length of 20–100 μm and a diameter of 2–40 μm , was provided by the Hemp Materials Research Center of China (Quartermaster Research Institute, General Department, People's Liberation Army, Beijing, China). The morphology of the HP used in this study is shown in Figure 1.

Sample preparation

The HP was dried at 80°C to remove the moisture. To uniformly coat the coupling agent on the HP sur-

face, we dissolved Si69 in ethanol at a weight ratio of 1 : 2. The pH of the solution was adjusted to 5 by the addition of acetic acid. The solution was then sprayed onto the HP surface (the weight ratio of Si69 to HP was 3 : 100) in a high-speed mixer, and the content was mixed for 5 min. To complete the reaction of HP with the coupling agent and to remove the remaining solvent and moisture, we moved the treated HP from the mixer to an oven at 80°C.

SBR, HP, the vulcanizing ingredients, and other additives were mixed into the compound in a 6-in. two-roll mill (Zhanjiang Rubber and Plastics Machine Factory, Guangdong, China), according to the formulation listed in Table I. The compound was then vulcanized in a standard mold with a pressure of 15 MPa at 150°C. The optimum curing time was determined with a disc oscillating rheometer (P355B2, Beijing Huafeng Chemical Industry Machine Plant, Beijing, China). The vulcanized samples were conditioned for 24 h before testing.

Characterization

The tensile and tear properties were measured with a CMT4104 electrical tensile tester (SANS, Shenzhen, China) at a crosshead speed of 500 mm/min, according to ASTM D 412 and ASTM D 624, respectively. An XY-1 rubber hardness apparatus (Shanghai No. 4 Chemical Industry Machine Factory) was used to measure the hardness of the vulcanizates according to ASTM D 2240.

Strain sweep experiments were performed with RPA 2000 rubber process analyzer (Alpha Technologies Co., Michigan, USA) at a fixed frequency and 60°C. The strain was varied from 1 to 42% at a frequency of 10 Hz for cured compounds and from 1 to 400% at 1 Hz for the uncured compounds.

The morphology of the composites was studied by scanning electron microscopy (SEM, S-4700, Hitachi Co., Tokyo, Japan) at an acceleration voltage of 20

TABLE I
Formulations of the SBR Composites

Material	phr
SBR-1502	100
Zinc oxide	5
Stearic acid	2
Diphenylguanidine (accelerator)	0.5
2,2'-Dibenzothiazole disulfide (accelerator)	0.5
Tetramethyl thiuram disulfide (accelerator)	0.2
Sulfur	2
Poly(1,2-dihydro-2,2,4-trimethylquinoline) (antioxidant)	1
HP	0,15,30,45,60,75
Si69	3 ^a

^a Parts per hundred parts of HP.

TABLE II
Curing Characteristics of the SBR Compounds Filled with HP

HP (phr/100 phr SBR)	M_{\max} (dNm)	M_{\min} (dNm)	ΔM (dNm)	t_{10} (min : s)	t_{90} (min : s)
SBR/HP					
0	52.94	9.71	43.23	6 : 30	13 : 55
15	56.17	10.42	45.75	6 : 25	12 : 54
30	62.31	11.98	50.33	6 : 22	12 : 39
45	64.27	13.44	50.83	5 : 40	12 : 06
60	66.79	15.02	51.77	5 : 23	11 : 53
75	68.15	16.18	51.97	5 : 16	11 : 45
SBR/Si69-HP					
15	57.11	10.25	46.86	6 : 07	12 : 43
30	62.05	11.07	50.98	5 : 26	12 : 28
45	65.88	12.86	53.02	4 : 59	12 : 01
60	69.75	13.29	56.55	4 : 27	11 : 49
75	72.14	15.08	57.06	4 : 09	11 : 37

kV. Before observation, the fractured surfaces of the samples were sputtered with a thin layer of gold to eliminate electrical charging during examination.

RESULTS AND DISCUSSION

Curing characteristics

Table II shows the effect of HP loading on the curing characteristics of the composites with and without the coupling agent treatment. Unlike the inorganic mineral fillers, which caused an increase in t_{90} [the time at which the torque reached the value of $M_{\min} + 90\% \Delta M$, where M_{\min} is the minimum torque and ΔM is the difference between the maximum torque (M_{\max}) and M_{\min}], the addition of HP reduced t_{90} . A similar observation was also reported by Jacob et al.¹⁵ and Geethamma et al.¹⁶ for natural-fiber-reinforced rubber composites. The decrease of the curing time was attributed to the higher energy input and greater heat buildup during mixing due to the higher viscosity (related to changes in the minimal torques) of the compounds filled with HP. The decrease in the scorch time (t_{10}) with increasing HP concentration that we observed was attributed to the presence of more crosslinked precursors in the rubber blend, according to earlier studies.¹⁷ The low surface reactivity of the fillers in general posed low restrictions to the macromolecular chain motions during the curing process. Thus, the low surface reactivity of HP was also responsible for enhancing the curing characteristics. At the same loading, the composites with Si69-pretreated HP (hereafter denoted as SBR/Si69-HP) had t_{90} and t_{10} values lower than those of the unmodified HP (hereafter denoted SBR/HP). Similar trends were also observed by Ishak and Bakar¹⁸ and Hashim et al.¹⁹ using different types of silane coupling agents. According to their studies, the curing enhancement could be partially attributed to the tetrasulfidic groups exerting their influence as sulfur donors in the vulcanizing process.

As expected, M_{\max} and ΔM increased with increasing HP loading and the addition of Si69. In general, M_{\max} gives an idea about the shear modulus of fully vulcanized compounds and mainly depends on the crosslink density and molecular chain entanglement; ΔM represents the extent of crosslinking at a given temperature. So the changes can be an indication of the existence of significant differences in the matrix-HP interfacial interaction. The coupling agent improves the polymer-filler interaction, which results in a higher crosslinked density of the vulcanizates. M_{\min} of SBR/Si69-HP compounds showed a lower value at the same HP loading compared with that of SBR/HP compounds. M_{\min} was an indirect measure of the viscosity of the uncured blends. Thus, the observation could be related to the improvement in the HP filler dispersion in the SBR phase. This was supported by the SEM micrographs of the filled vulcanizates, as shown in Figure 2(b,d). Further discussion of the micrographs is given in next section.

Fracture morphology

The tensile and cryofractured surfaces of the samples were observed by SEM. Figure 2 shows the SEM fractographs of the HP-filled SBR composites. At 15-phr filler loading, the composite without the addition of Si69 exhibited a rough fractured surface with many agglomerates (marked with the arrow) because of the filler-filler interaction [Fig. 2(a)]. The SBR/Si69-HP composite showed better filler dispersion with fewer undispersed agglomerates [Fig. 2(b)]. Moreover, there existed smaller gaps in the interfacial area for the 15-phr Si69-HP composites. This is an evidence that the introduction of Si69 improved interfacial bonding between HP and the SBR matrix.

To further confirm the effect of Si69 on the HP dispersion in the rubber, the cryogenically fractured surfaces of composites with a high level loading,

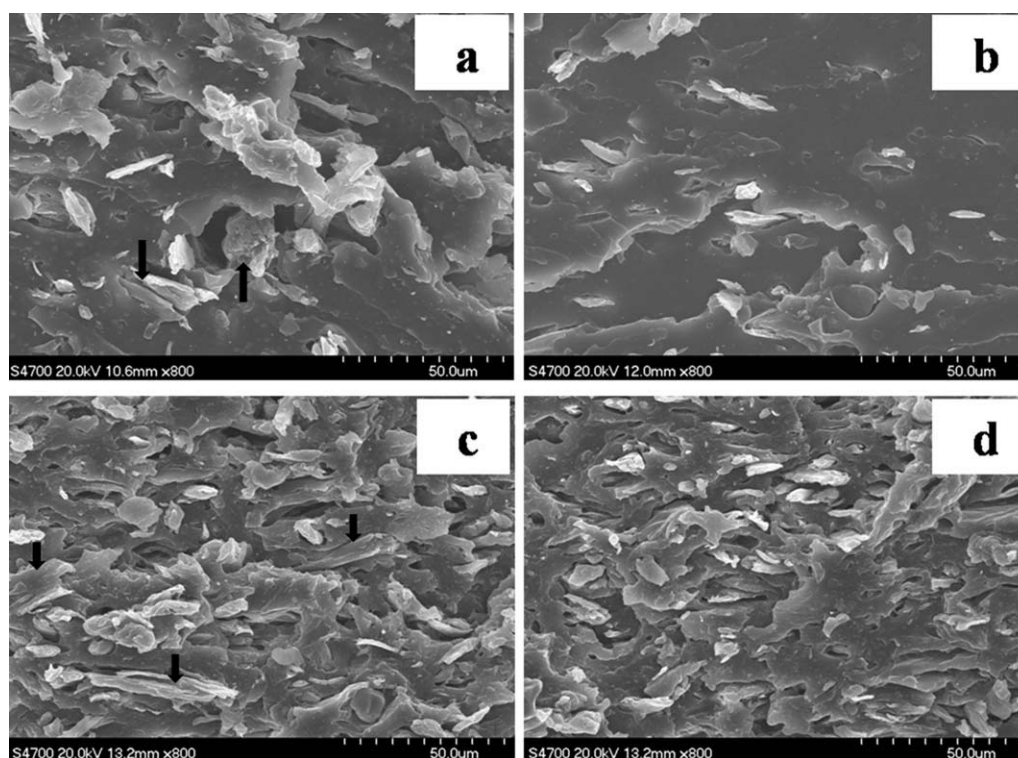


Figure 2 SEM images of fracture surfaces of SBR vulcanizates: (a) tensile fracture with 15 phr HP, (b) tensile fracture with 15 phr Si69-HP, (c) cryofracture with 45 phr HP, and (d) cryofracture with 45 phr Si69-HP.

45 phr [Fig. 2(c,d)], were observed. For similar composites but without the presence of Si69 [Fig. 2(c)], the aggregation of HP appeared more evident, and there were more agglomerates (marked with the arrow) on the fractured surface. On the contrary, HP with Si69 treatment was well dispersed and firmly embedded in the SBR matrix [Fig. 2(d)]. The observations highlighted the fact that at a high level of HP loading, the presence of Si69 played an important role in the improvement of both the filler dispersion in rubber phase and HP–matrix adhesion.

Stress–strain behavior

It is well known that the stress–strain curves of filled vulcanizates are affected by the size and the distribution status of fillers,²⁰ and the interfacial interaction between the matrix molecules and filler surface.²¹ For vulcanizates filled with fibers, the interaction has a vital effect on the stress–strain curves. Therefore, both the nature and content of fibers and the introduction of surface modifiers may change the stress–strain behaviors of the filled vulcanizates.

The stress–strain curves of the filled vulcanizates with different HP concentrations are shown in Figure 3(a). At 15-phr HP content, the stress–strain behavior was conventional and did not show the yield phenomenon similar to that shown by the vul-

canizates filled with carbon black or silica.^{20,22} With an increase in the HP loading from 30 to 75 phr, the strain–stress curves of the vulcanizates tended to produce an obvious yield point [marked with the arrow in Fig. 3(a)], which was the characteristic of rubber vulcanizates filled with short fibers. This phenomenon was an indication for the debonding of the fibrous filler–matrix interface. After the yield point, the reinforcing effect of HP basically disappeared with further deformation. In contrast to the case of the vulcanizates filled with long fibers,²² the tensile stress of the composites with HP did not further decrease with increasing strain until failure. Unlike synthetic fibers, the hemp hurd fiber had a lower strength and toughness. Thus, it was easy for the hemp fiber to break down because of the applied shear stress during deformation and to bear the stress transference from the matrix. As we observed, the occurrence of the yield behavior appeared to shift toward a lower strain with increasing HP content; this was attributed to poor filler dispersion in the rubber and numerous stress concentration sites resulting from the filler agglomerates. In all cases, the initial slope of the stress–strain curves took on a steep uprising trend and showed the ability of HP to significantly improve the stress of the composites at low strains.

The load–deformation curves for the SBR/Si69-HP are shown in Figure 3(b). The stress–strain behaviors

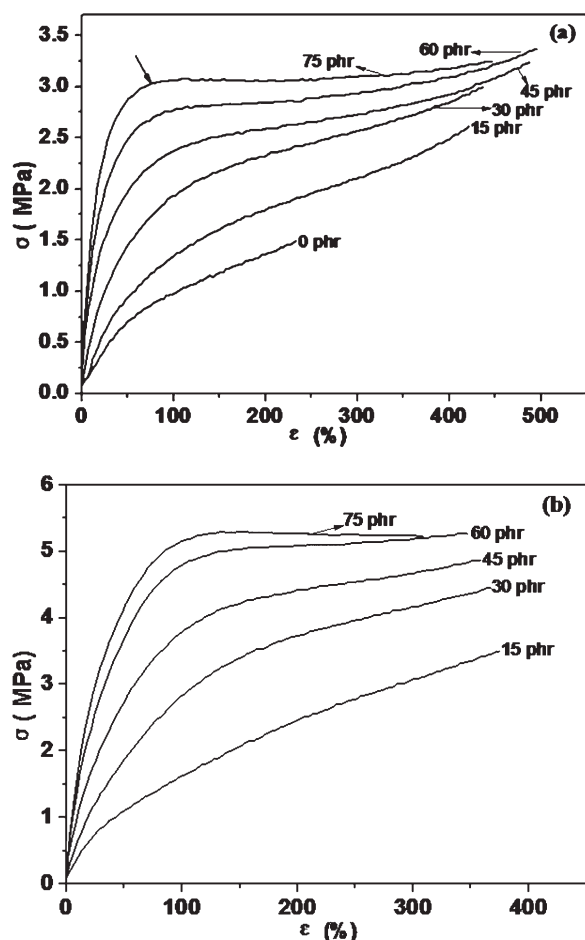


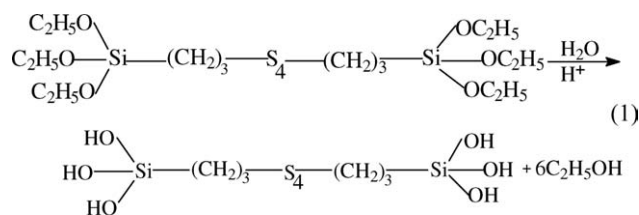
Figure 3 Stress–strain (σ – ϵ) curves of cured HP–SBR vulcanizates: (a) SBR/HP and (b) SBR/Si69-HP.

were similar to those of the previously discussed SBR/HP. However, compared with SBR/HP, the vulcanizates with Si69 had a larger strain value, after which the yield behavior was initiated. When the coupling agent was introduced onto the HP surface, the hydrophilic character of the HP particle was changed into a hydrophobic one; this resulted in the enhancement of the filler–rubber matrix interaction. Thus, the addition of the Si69 coupling agent reduced the agglomerate size of the fiber bundles in the rubber matrix and facilitated the reformation of the filler–matrix-related network during deformation, which consequently deferred the occurrence of debonding between the fiber and the matrix. In contrast to the composites filled with the inorganic fillers, the composites filled with Si69-HP did not show a Payne effect;²³ this led to a decrease in the tensile modulus at initial strains. The Si69 coupling agent, with a bifunctional group in one molecule, produced chemical bonding between HP and SBR, and the strong interaction offset the negative effect resulting from the decreasing filler size.

Mechanical properties

The mechanical properties of the filled rubber composites were closely linked to the filler-related network. When the filler was uniformly dispersed in the rubber matrix and there existed strong interfacial bonding between the filler and the matrix, the filler acted as a carrier of loading and support stresses effectively transferred from the matrix. The tensile and tear strengths of the SBR vulcanizates filled with unmodified and Si69 modified HP with respect to the increase in the filler loading are shown in Figure 4. Compared with the control gum, the addition of HP did not have a negative effect on the mechanical properties. The result was contrary to the those of previous reports on natural-fiber-filled natural rubbers;¹⁰ this was partially attributed to the inherent high strength of natural rubber resulting from strain-induced crystallization. For both SBR/HP and SBR/Si69-HP, the tensile strength increased with increasing HP content from 0 to 60 phr and then took on a slight change with increasing HP loading. At a higher HP concentration, the agglomerates of HP particles easily formed in the rubber matrix. The poor filler dispersion created more sites of stress concentration and, consequently, decreased the occurrence of stress transference. With increasing HP loading, elongation at break (E_B) of the SBR/HP increased [Fig. 4(a)]. When the loading of HP increased from 0 to 60 phr, E_B reached its maximum value. This was entirely different from the previous report,²⁴ in which the E_B of composites showed a drastic decrease with the addition of short fibers.

As shown in Figure 4, the Si69 coupling agent had a remarkable effect on the mechanical properties of the HP-filled vulcanizates. At the same filler content, the mechanical properties of SBR/Si69-HP were much better than those of SBR/HP. It was obvious that the addition of Si69 greatly increased the tensile strength, modulus, and tear strength of the composites (Fig. 4). As we all know, Si69 is a coupling agent that is commonly used in rubber products. In the presence of moisture, the silane can react with water to form silanol and alcohol. The reaction mechanisms are as follows:



Then, the silanol can react with the hydroxyl group attached to the cellulose molecules through an ether linkage with the removal of water:

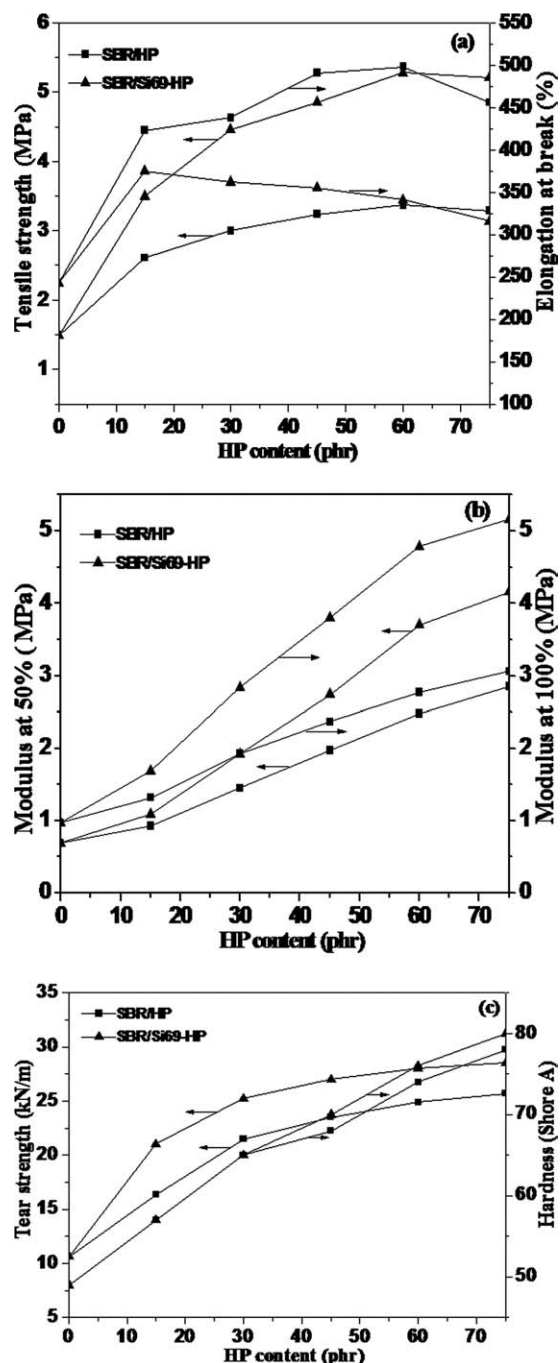
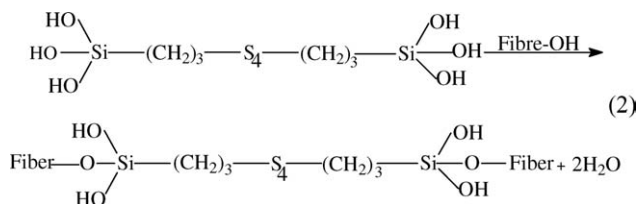


Figure 4 Effect of the HP content on the mechanical properties of SBR vulcanizates: (a) tensile strength and EB, (b) modulus at 50 and 100%, and (c) tear strength and Shore A hardness.



Finally, the rubber matrix can interact with the functional group of the silane coupling agent

through either a covalent bond or a hydrogen bond. Moreover, the polysulfide bond of the Si69 molecule can react with the diene unit of SBR,²⁵ this produces a strong chemical bonding between SBR and the hemp fiber. Thus, the stronger interfacial adhesion between HP and the matrix causes better stress transfer from the matrix to the fibers and leads to a higher tensile strength. At a filling content of 60 phr, the tensile strength value of SBR/Si69-HP was 56% higher than that of SBR/HP [Fig. 4(a)]. On the other hand, the incorporation of Si69 considerably reduced E_B because of a better filler dispersion and interfacial adhesion.

The modulus at 50% elongation and the modulus at 100% elongation substantially increased with increasing HP content and the introduction of Si69 [Fig. 4(b)]. This resulted from the fact that the addition of both rigid fiber fillers and Si69 improved the stiffness of the composites and, therefore, decreased the deformability at low strains. The tear strengths of SBR/HP and SBR/Si69-HP increased with increasing HP content and reached corresponding maximum values of 25.7 and 28.5 kN/m, respectively, when the HP content was 75 phr [Fig. 4(c)]. The change in the Shore A hardness demonstrated the fact that the introduction of HP in the rubber matrix improved the stiffness of the composites.

Polymer–filler interaction of the SBR vulcanizates

We studied the polymer–filler interaction by swelling the SBR vulcanizates in toluene. The specimens were swollen in toluene at room temperature for 72 h to achieve swelling equilibrium and were then vacuum-dried at 80°C to remove the absorbed solvent. The extent of interaction between the filler and rubber matrix could be assessed according to the Kraus equation:²⁶

$$\frac{V_{r0}}{V_{rf}} = 1 - m \left[\frac{\Phi}{1 - \Phi} \right] \quad (1)$$

where V_{r0} is the volume fraction of the gum vulcanizate, V_{rf} is the volume fraction of the elastomer in the solvent-swollen filled sample, Φ is the volume fraction of the filled HP, and m is the polymer–fiber interaction parameter obtained from the slope of the plot of V_{r0}/V_{rf} versus $\Phi/(1 - \Phi)$. Φ was calculated as follows:

$$\Phi = \frac{m_H/\rho_H}{m_H/\rho_H + m_r/\rho_r} \quad (2)$$

where m_H and m_r are the weights of the HP filler and rubber, respectively, and ρ_H (1.486 g/cm³) and ρ_r (0.998 g/cm³) are the densities of the HP filler and rubber, respectively, by experimental measurement.

TABLE III
Data Used in the Calculations of V_r and m

HP (phr/100 phr SBR)	V_r	A_s (g)	f	d (g)	w (g)	m
SBR/HP						
0	0.2152	1.5926	0	0.5027	0.5035	—
15	0.2166	1.3934	0.1304	0.5103	0.5124	0.065
30	0.2231	1.1787	0.2308	0.5074	0.5102	0.176
45	0.2251	1.0055	0.3103	0.4925	0.5037	0.146
60	0.2272	1.0166	0.3750	0.5608	0.5782	0.131
75	0.2270	0.8958	0.4286	0.5436	0.5604	0.103
SBR/Si69-HP						
15	0.2358	1.2054	0.1304	0.4925	0.4936	0.871
30	0.2460	1.0393	0.2308	0.5091	0.5113	0.622
45	0.2526	0.9722	0.3103	0.5514	0.5580	0.490
60	0.2564	0.8363	0.3750	0.5379	0.5492	0.399
75	0.2598	0.7766	0.4286	0.5601	0.5748	0.341

Both V_{r0} and V_{rf} were determined by the following equation:

$$V_r = \frac{(d - fw)/\rho_r}{(d - fw)/\rho_r + A_s/\rho_s} \quad (3)$$

where d is the deswollen weight of the vulcanizate, f is the mass fraction of the filler, w is the initial weight of the vulcanizate, ρ_r is the density of the rubber, ρ_s is the density of the solvent (0.867 g/cm³), and A_s is the amount of the solvent absorbed. All of the values used in these calculations are given in Table III.

The ratio V_{r0}/V_{rf} represents the extent of swelling of the rubber matrix in the presence of HP. When there was better adhesion between the filler and matrix, the stronger interface restricted the entry of the solvent, and thus, the filled vulcanizates showed lower V_{r0}/V_{rf} values. As shown in Figure 5, the V_{r0}/V_{rf} value decreased with increasing HP content and varied from 15 to 60 phr. This indicated that there was good bonding between the SBR matrix and HP. At the same HP concentration, the SBR/Si69-HP showed smaller V_{r0}/V_{rf} values; this was an indication that Si69 improved the interfacial interaction between HP and SBR. The changes in m , shown in Table III, also confirmed this fact. In Figure 5, the fitting curves further confirm the result. The improvement in the HP-matrix interaction with the addition of Si69 was consistent with the results from the curing characteristics and the mechanical properties, as discussed previously.

Dynamic mechanical properties

The effect of the amplitude dependence of the dynamic viscoelastic properties of the filled rubbers was investigated with the RPA 2000 rubber process analyzer, which could carry out strain scanning in a broad range and show information on the filler-related networks. Figure 6 presents the dependence

of the storage modulus (G') of the uncured compounds on the strain. The compounds showed the Payne effect. G' decreased sharply at low deformation and gradually converged to the same value with increasing strain amplitude. The Payne effect was especially pronounced for the SBR/HP compounds with high loading; they had poor filler distribution in the rubber matrix. The compounds without Si69 possessed much higher elastic modulus values than those with Si69 at initial strains, when the content of HP was beyond 45 phr [Fig. 6(a,b)]. In contrast to the compounds with high loading, those with low loading (from 15 to 45 phr) showed a slight change in G' with the addition of Si69; this was attributed to the co-effect of both the poor dispersion of the unmodified HP and the enhanced interaction between the modified filler and the matrix on G' . Moreover, we also found that G' of the compounds without Si69 decreased faster than that of the compounds with Si69 at a relatively low strain amplitude. The result further demonstrated that

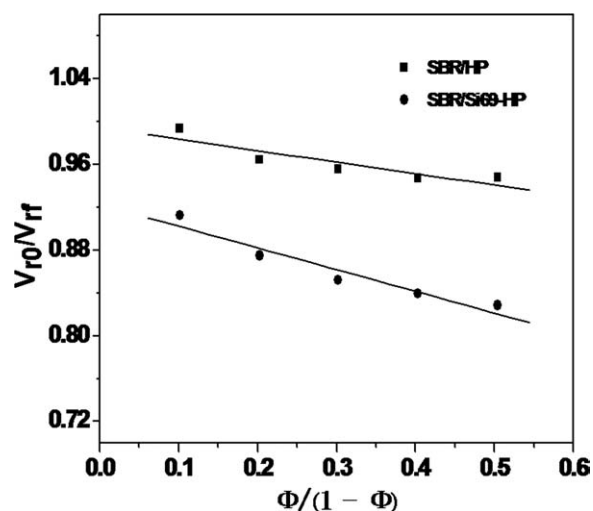


Figure 5 Variation of V_{r0}/V_{rf} with $\Phi/(1 - \Phi)$.

Si69 enhanced the filler–matrix compatibility; this, consequently, contributed to the reconstruction of networks during the deformation.

To further investigate the effect of the coupling agent on the dynamic properties of the HP/SBR composites, the dependency of the mechanical loss factor ($\tan \delta$) of the cured composites on the strain was studied. As shown in Figure 7, $\tan \delta$ increased nonlinearly with increasing HP loading. $\tan \delta$ was the ratio of the loss modulus to G' ; this indicated the high elasticity over the viscous responses. It was also greatly dependent on the breakdown and reformation of filler-related networks; this was primarily affected by the filler–matrix interaction. Usually, the enhanced adhesion between fillers and the matrix tends to increase G' of composites and decrease the hysteresis of vulcanizates; this leads to low $\tan \delta$ values. Therefore, the interaction is one of the factors that mostly affect the value of $\tan \delta$. The stronger the interfacial interaction is, the lower $\tan \delta$ is. This

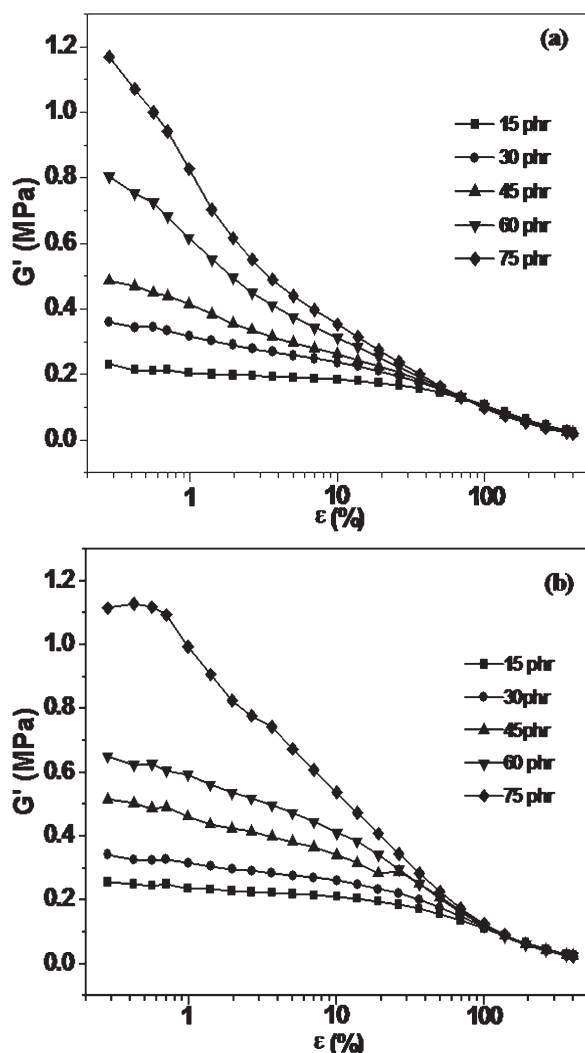


Figure 6 RPA 2000 analysis of uncured HP-SBR compounds: (a) SBR/HP and (b) SBR/Si69-HP (ϵ = strain).

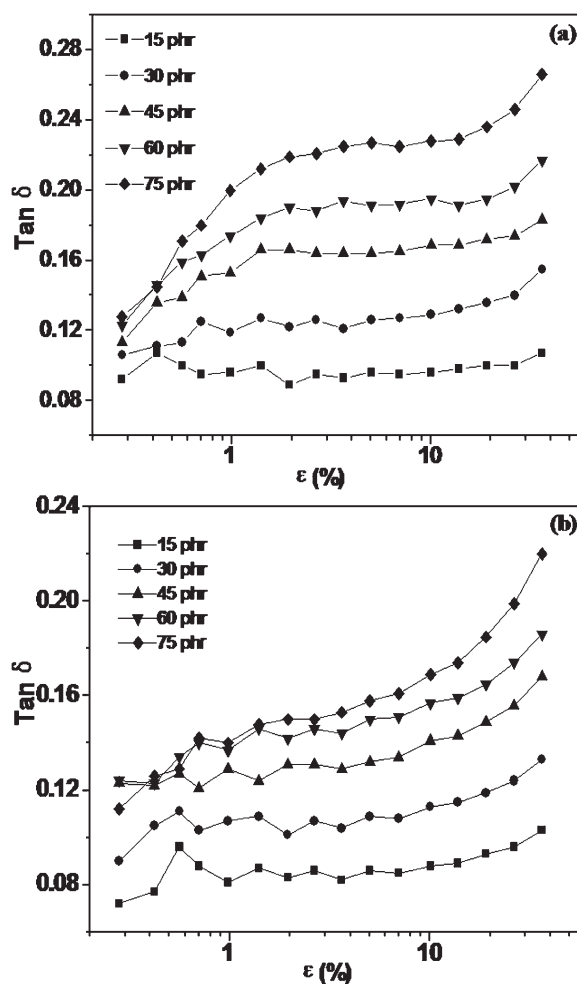


Figure 7 RPA 2000 analysis of cured HP-SBR vulcanizates: (a) SBR/HP and (b) SBR/Si69-HP (ϵ = strain).

was the reason why the addition of Si69 effectively reduced the $\tan \delta$ value during the deformation (Fig. 7). As indicated in the previously discussed mechanical data and SEM micrographs, the presence of Si69 achieved the better bonding between HP and the SBR matrix.

CONCLUSIONS

The addition of HP filler and Si69 facilitated the vulcanizing process of the filled SBR composites, however, and resulted in an increase in the M_{\max} values. The mechanical properties of the SBR/HP increased with HP filler loading from 0 to 60 phr. The Si69 coupling treatment significantly improved the tensile strength, tensile modulus at low strains, and tear strength of SBR/Si69-HP; it also had a slight effect on the hardness. The stress–strain curve, polymer–filler interaction, dynamic mechanical properties, and SEM micrographs showed that the introduction of Si69 enhanced the HP–matrix interfacial interaction and the filler dispersion in the SBR

matrix; these results agreed well with the mechanical properties. The Si69-modified HP had a good reinforcement effect as a filler for SBR and has promising prospects because of its low cost, low density, and ecofriendliness.

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