

# Effects of the Vulcanizing Reagent Addition on the Properties of CNTs/SBR Powder Composites

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**ABSTRACT:** Vulcanizing reagent (VR) suspensions with different sulfur additions were mixed with CNTs suspensions and SBR latex, and then powder CNTs/SBR (PSBR) composites were prepared by spray-drying process. Investigations showed that VR additions have significant influences on the properties of CNTs/PSBR composites. With the increment of VR additions, glass transition temperature ( $T_g$ ) of the composites increased gradually, and reached the maximum when the sulfur addition was 4.0 phr, and then it would decrease if the sulfur addition continued to rise. The elongation at break of the vulcanizates decreased linearly. The tensile strength and hardness reached the maximum when the sulfur addition was 4.0 phr, and almost kept constant when the addition continued to rise. Yet the tear strength reached the maximum when the addition was of

2.5 phr, and then decreased slightly when the addition exceeded 4.0 phr, which was corresponding to the structure designability of the composites affected by the sulfur aggregates in the matrix. Under different temperatures, when the vulcanizing temperature was 150°C, the vulcanizing speed was proper, vulcanizing time was prolonged, and the vulcanizing security was intensified. Compared with the vulcanization of carbon black/PSBR composites, more sulfur additions are needed in the vulcanization of CNTs/PSBR composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1836–1841, 2007

**Key words:** carbon nanotubes; styrene–butadiene rubber latex; spray drying; rubber nanocomposites; mechanical property

## INTRODUCTION

Recently, nanocomposites have attracted considerable attentions of researchers because of their unique physical and mechanical properties. There are several types of nanocomposites based on rubbers reported in the literatures, which were prepared with rubbers such as natural rubber (NR),<sup>1</sup> epoxidized NR,<sup>1</sup> styrene–butadiene rubber (SBR),<sup>2,3</sup> butadiene rubber,<sup>4</sup> acrylonitrile–butadiene rubber,<sup>2,4</sup> and so on.

The concept of reinforcement for rubbers is complex to define, but may be considered as the enhancement of the modulus, failure properties (tensile and tear strength), and abrasion resistance of the vulcanized rubbers. There are several fillers added into rubber composites to impart various properties to them in actual applications. Among these fillers, carbon black (CB) is the most important reinforcing reagent used in rubber industry. Because of its own organic features, CB is compatible with the elastomer matrix. It is well known<sup>5–7</sup> that the particle size, structure, and surface characteristics of the fillers are the main factors con-

trolling their reinforcement abilities. In particular, the filler particle size must be less than about a micrometer to produce significant reinforcement, and the strength of particles filled vulcanizates generally increases as the specific surface area of the fillers increases (i.e., particle size decreases).<sup>8</sup> In this sense, carbon nanotubes (CNTs) can be considered as the most effective reinforcement material in rubber composites because of their high aspect ratio (up to  $10^3$ ), elastic modulus (0.3–1.0 TPa) close to that of diamond, tensile strength of about 50 GPa, and light weight (density of about 1.3 g/cm<sup>3</sup>).<sup>9–13</sup> The authors have prepared CNTs/NR composite powders by spray-drying process, and the mechanical properties of the composites were much improved due to the modification effects of CNTs in rubber.<sup>14</sup>

In practice, preparation of high-strength nanocomposites has yet to overcome several obstacles. First, homogeneous dispersion and controllable alignment of CNTs in composites are desirable to achieve improvement of the mechanical properties. In addition, interface region properties are known to be necessary for load sharing between the matrix and the reinforcement material.<sup>15–17</sup> Second, the vulcanization of rubber composites is crucial to improve the physical and mechanical properties of the composites. Linear rubber macromolecules are needed to crosslink by ways of chemistry or other methods so as to form a stable space-network structure. This process is vital to the

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industrialization applications of rubbers. We have done some researches on the vulcanization of CNTs/NR composites.<sup>18</sup> It indicated that, in the vulcanization of CNTs/NR composites, more sulfur additions were required. With the addition of acid-treated CNTs, the vulcanization speed of the CNTs/NR composites decreased. And these phenomena did not occur in the CB-filled NR composites. However, there has yet been little knowledge of the vulcanization of CNTs/rubber composites. The main goal of this article is to make a comparison among the physical and mechanical properties of CNTs/PSBR composites with different amount of sulfur addition. The thermal and structural characters, and the vulcanizing and mechanical properties will be characterized.

### EXPERIMENTAL

The SBR latex SBR-50 is produced by Shandong Xiangfa industry and business Co., (Zibo City, ShanDong Province, China), with a solid content of 44.90%. CNTs are prepared by chemical vapor deposition process, i.e., the deposition of propane at 600–650°C with the catalyst of Nickel<sup>19</sup> and purified with HF and HNO<sub>3</sub>, and then cleaned and dried. CB (N326) is produced by Shandong Huadong Rubber Materials (Jinan City, ShanDong Province, China). Sodium dodecyl benzene sulfonate (SDBS) used as the dispersant is of analytical pure grade. The vulcanizing reagent (VR), sulfuric acid, nitric acid, and so on are of industrial pure grade.

CNTs and nitric–sulfuric acid (volume H<sub>2</sub>SO<sub>4</sub>: HNO<sub>3</sub> = 3 : 1), whose ratio<sup>20</sup> was 1 g CNTs with 10 mL mixed acid, were boiled and refluxed for 30 min, and centrifugally cleaned to neutral with deionized water. The acid-treated CNTs were mixed with 10 wt % of SDBS, and then were added into deionized water in a mass ratio of 1 : 10 between the CNTs and water. A suspension of CNTs in deionized water was obtained after supersonic stirring dispersion.

The conventional VR recipe for SBR was as follows (with 100 phr of the solid content of the added latex): Stearic acid (SA) 1.5 phr; Zinc oxide (ZnO) 5.0 phr; accelerant dibenzothiazole disulfide (DM) 3.0 phr. It is mentioned that the sulfur addition was adjusted in the range of 2.0–6.0 phr, as the CNTs could adsorb some additional sulfur. The VR was added into the surfactant and dispersant solution by stirring, and then the suspension containing the VR was obtained after ball-milling for several hours. The formulation of the compounds was as follows: SBR 100 phr, ZnO 5.0 phr, SA 1.5 phr, and DM 3.0 phr. The sulfur additions were 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, and 6.0 phr, respectively.

The recipe portion was as follows: SBR 100 phr (latex mass multiplied by the solid content), VR 1 phr, CNTs 50 phr (the mass of the CNTs suspension multiplied by the solid content). The CNTs suspension and VR suspension were added into SBR latex and stirred

homogeneously, and thus the mixed latex suspension with a total solid content of about 15% was obtained. With the B290 spraying dryer manufactured by Büchi (Switzerland), the mixture was sprayed and dried under conditions as follows:<sup>21</sup> air inlet temperature 160°C, suspensions feeding rate 240 mL/h, aspirator 35.2 m<sup>3</sup>/h, and air flow rate 667 L/h. Finally CNTs/PSBR composite-contained VR was obtained.

The morphologies of the fractures of the CNTs/PSBR composites were investigated by means of S-3500N scanning electronical microscopy (SEM) produced by Hitachi, Japan. The vulcanization properties were determined by a nonmotor rheometer MM4130C2 produced by the Beijing Huanfeng Mechanical Factory (Beijing City, China). The thermophysical properties of the composites were tested on DSC 2910 differential scanning calorimeter produced by TA (USA). The measure was performed when the temperature varied from –100 to 200°C at a heating rate of 10°C/min. The compounds were vulcanized at 150°C with a proper pressure.

The gel fractions of the vulcanizates were measured by solvent extraction method. This parameter would characterize the crosslinking degrees of the vulcanizates. Certain amount of vulcanizates was put in Sorbitic extractor, and then extracted with the toluene solvent for 24 h, and later dried to constant weight in an oven. The gel fraction was calculated according to the following equation:

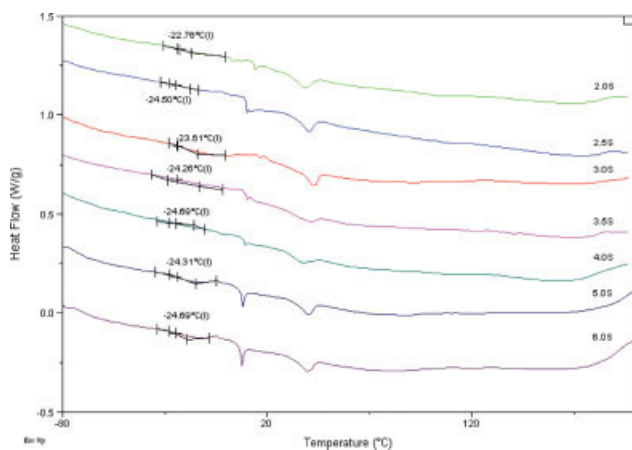
$$\alpha = \frac{W_2}{W_1} \times 100 \quad (1)$$

where  $\alpha$  is the gel fraction and  $W_1$  and  $W_2$  are the weights of the testing specimen before and after extraction, respectively. The results reported here were the averages of three measurements.

The tensile strengths of CNTs/PSBR vulcanizates were determined using a WDW-50 Electronical Versatile Tester according to GB/T 528-1998 (ASTM D 412-98a (2002) e1, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension), using dumbbell-shaped specimens. The hardness of the composites was measured using a Durometer, Shore A, according to ASTM D 2240-04, Standard Test Method for Rubber Property-Durometer Hardness, Shore A hardness. The tear strengths of the vulcanizates were performed according to GB/T 529-1999 (ASTM D 624-00 e1, Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers). Three samples were measured for every case, and the average of the values was taken.

### RESULTS AND DISCUSSION

The DSC curves of CNTs/PSBR composites with different VR additions were shown in Figure 1. The



**Figure 1** The DSC curves of CNTs/PSBR composites with different VR additions.

glass transition temperatures ( $T_g$ ) of CNTs/PSBR composites with different VR additions were acquired according to the DSC results and shown in Table I.

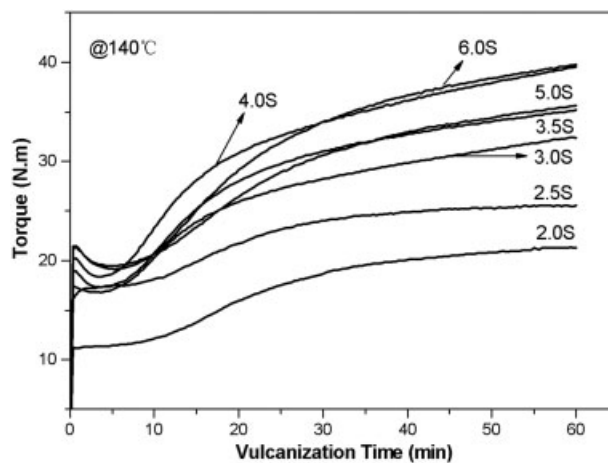
It can be seen from Figure 1 and Table I that  $T_g$  increases with the increasing VR addition up to 4.0 phr, and then decreases somewhat as the VR addition increased further to 6.0 phr.  $T_g$  reaches the maximum of  $-17.08^\circ\text{C}$  at the VR addition of 4.0 phr. This is because more S—S bonds were obtained in the vulcanization process with the addition of VR that made the free movement between the rubber macromolecules more difficult, and on the other hand, the excess VR added might result in local agglomerations of sulfur and then deteriorated the designability of the rubber matrix. The heat-absorption peaks at about  $7^\circ\text{C}$  were possibly owing to the additions of CNTs and the functional groups on the surfaces of the acid-treated CNTs, because the peaks only existed in the CNTs-filled PSBR composites compared with CB-filled PSBR composites and pure PSBR composites in our later work. And the peaks at around  $30^\circ\text{C}$  resulted from the gradual melting and amalgamation of the rubber structures in the composites.

As shown in Figure 2, the vulcanizing torques of the composites with VR additions of 4.0 phr and 6.0 phr were almost the maximum at all of the testing temperatures. Figure 2(a) showed that, with a sulfur addition

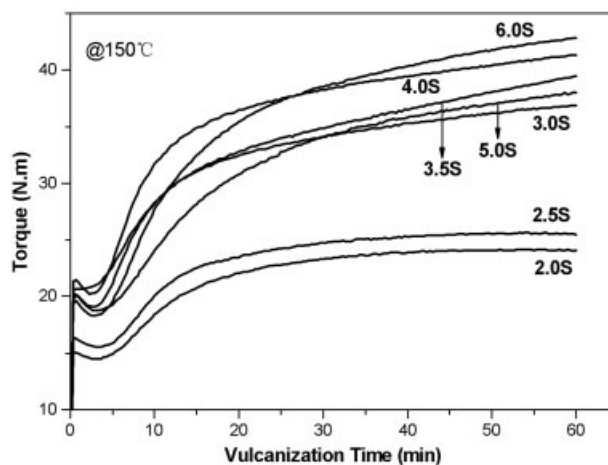
**TABLE I**  
 $T_g$  of CNTs/PSBR Composites with Different Vulcanizing Reagent Additions

S additions (phr)	$T_g$ ( $^\circ\text{C}$ )
2	-25.97
2.5	-24.5
3	-20.87
3.5	-19.57
4	-17.08
5	-20.54
6	-21.72

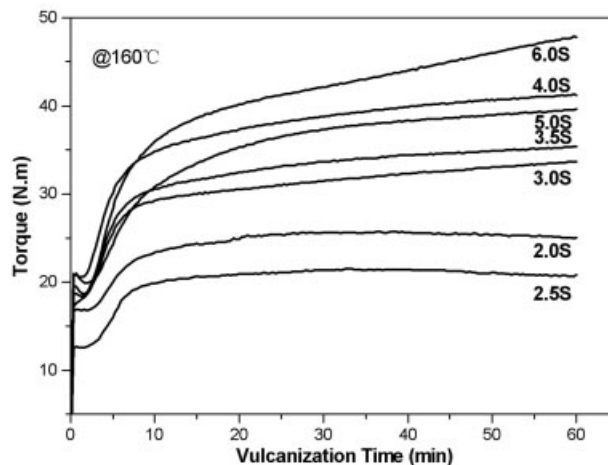
of 4.0 phr, the vulcanizing time was short and the vulcanizing efficiency was high at  $140^\circ\text{C}$ . Figure 2(b) revealed that the starting vulcanizing times were close



(a)

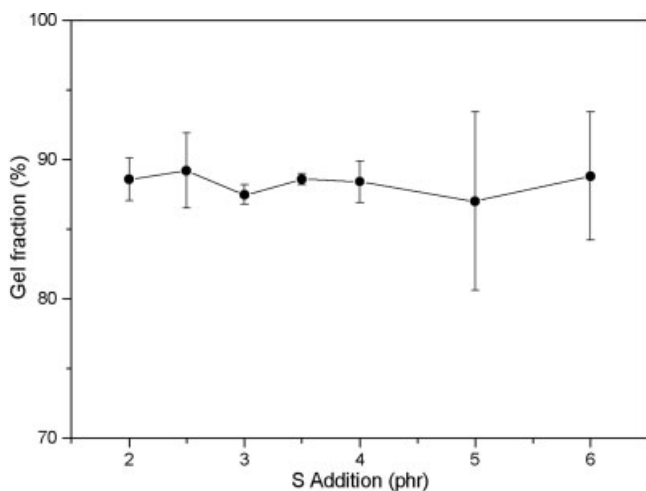


(b)



(c)

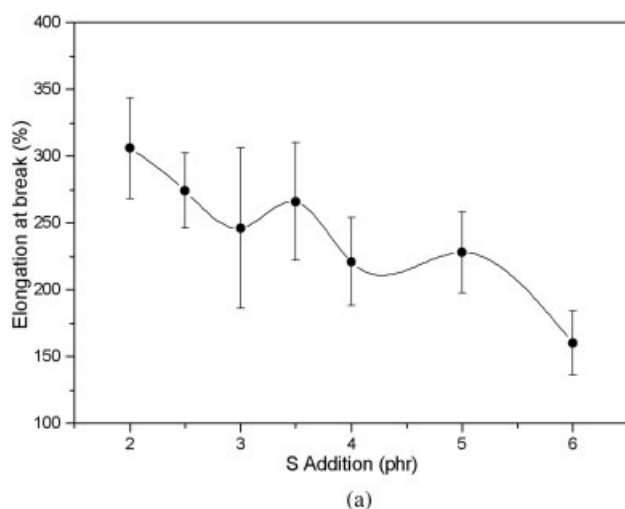
**Figure 2** Vulcanizing curves of the CNTs/PSBR composites with different additions of the VR at different temperatures. (a) Vulcanizing curves at  $140^\circ\text{C}$ . (b) Vulcanizing curves at  $150^\circ\text{C}$ . (c) Vulcanizing curves at  $160^\circ\text{C}$ .



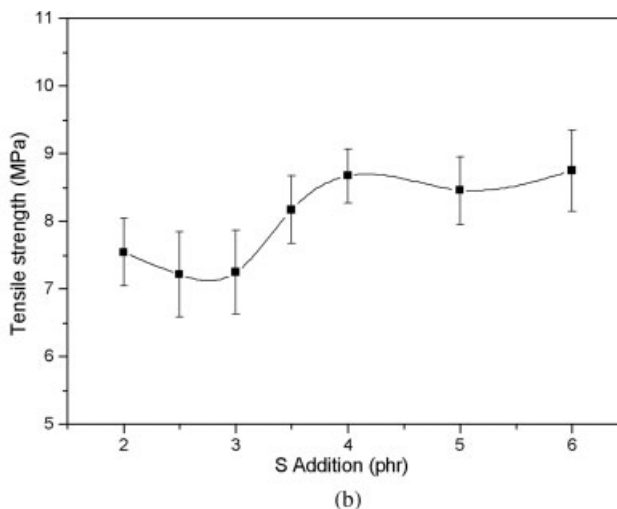
**Figure 3** Degrees of crosslinking of the vulcanized CNTs/PSBR composites.

to one another when the sulfur addition exceeded 3.0 phr, and the vulcanizing efficiencies were also high with different sulfur additions at 150°C. At 160°C, the starting vulcanizing times with different sulfur additions were even and short [Fig. 2(c)], which would improve the possibility of scorching and decrease the security of the vulcanization. Considering the vulcanizing efficiency and security, the vulcanizing effect of the composites with different VR additions would be best at a vulcanizing temperature of 150°C. Compared with the common vulcanization of CB/SBR composites, more sulfur was needed in the vulcanization of CNTs/PSBR composites.

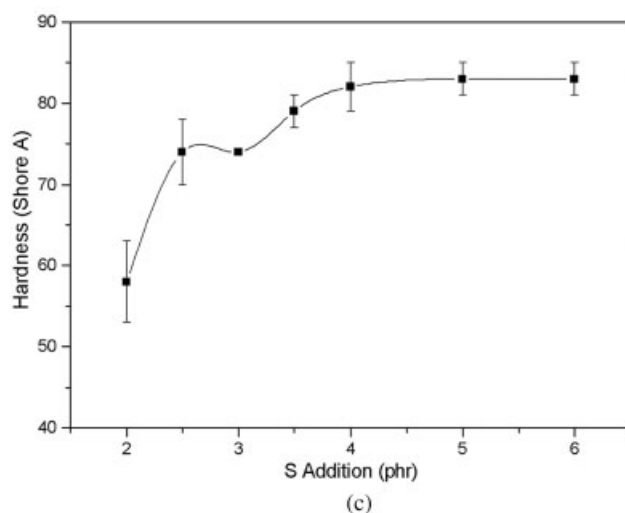
The crosslinking degrees of the CNTs/PSBR composites with different sulfur additions were shown in Figure 3. It can be seen that the crosslinking degrees of the vulcanizates differed slightly with the augment of the sulfur additions, and moreover, the error bars



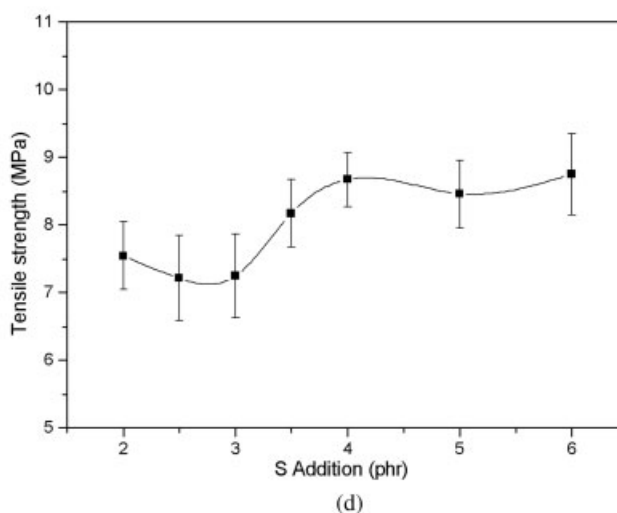
(a)



(b)



(c)



(d)

**Figure 4** Mechanical properties of the vulcanizates with different sulfur additions. (a) Elongation at break. (b) Tensile strength. (c) Hardness. (d) Tear strength.



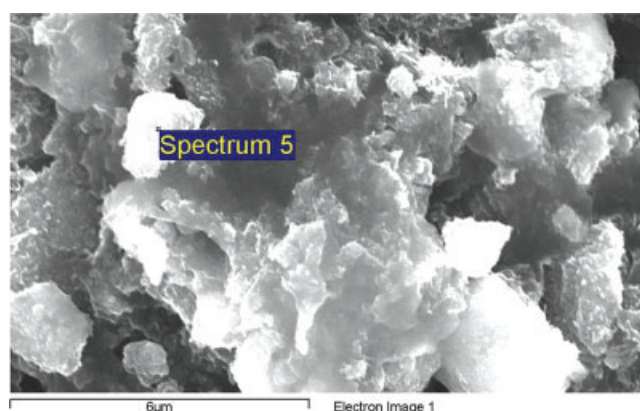
of the crosslinking degrees with the increasing sulfur addition tended to elongate, evidently after the sulfur addition exceeded 4.0 phr. It might be mainly due to the inhomogeneous dispersion of the additional sulfur in the vulcanizates.

The results of the mechanical properties testing were displayed in Figure 4. From Figure 4 it can be seen that with the increment of sulfur addition, the elongation at break decreased linearly, and the hardness and tensile strength increased gradually, and basically kept constant after the sulfur addition exceeded 4.0 phr. Yet the tear strength increased first and reached the maximum when the sulfur addition was of 2.5 phr, and thus decreased with more sulfur additions, and after the sulfur additions exceeded 4.0 phr, the tear strength decreased slightly, and ultimately kept constant. It should be mentioned that the tensile strength differed more slightly than other mechanical characteristics, with changes of the sulfur addition. With the increment of sulfur addition, there would be more S—S cross bonds in the rubber composites, and crosslinking would be enhanced to confine the movement of the rubber macromolecules that resulted in the decreased elongation at break and increased the hardness and tensile strength. However, when the sulfur addition exceeded 4.0 phr, the crosslinking of the rubber molecules would be closed to the saturated extent, and the increasing rate of hardness would decrease although the hardness continued to increase slightly. Meanwhile, the increasing rate of the tensile strength decreased, and the tensile strength even began to reduce. There would exist some free sulfur not crosslinked in the vulcanizates with an excess sulfur addition (e.g., 4.0 phr or more) that would behave as some impurities and affect the structure designability of the composites, and so resulted in some decreases of the mechanical properties. As described earlier, when the sulfur addition was about 4.0 phr, that was twice higher than that of sulfur addition in conventional vulcanized SBR filled with CB, it was the most beneficial for the strength and hardness of the vulcanizates filled with CNTs. This result was consistent with that of our previous work in NR filled with CNTs.<sup>14</sup>

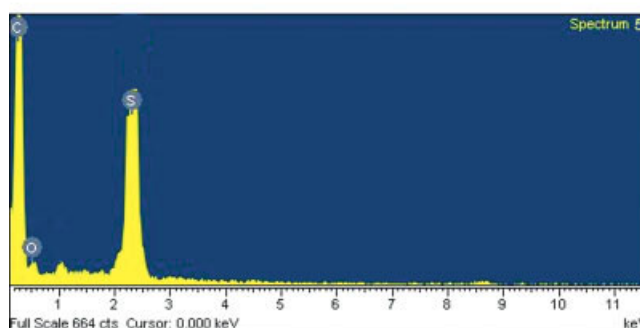
The fracture of the vulcanizate was shown in Figure 5. It can be seen that there were some sulfur aggregates in the marked region of the fracture of the sample with the sulfur addition of 6.0 phr. And also in the marked region, the content of sulfur is much higher than that in other regions from the Figure 5(b). This should be the attribution resulting in the decrease of the mechanical properties of the composites with more sulfur additions.

## CONCLUSIONS

1. With the augment of the sulfur addition, the glass transition temperature of the CNTs/PSBR



(a)



(b)

**Figure 5** The fracture and energy spectrum analyzed result of the vulcanizate with the sulfur addition of 6.0 phr. (a) The fracture of the composites, SEM. (b) Local compositions of the marked region in (a).

composites increased gradually, and reached the maximum when the sulfur addition was 4.0 phr, and it would decrease slightly when the sulfur addition continued to rise.

2. Under different temperatures, the vulcanizing torque of the rubber composites was almost the highest when the sulfur addition was 6.0 phr and 4.0 phr. When the vulcanizing temperature was 150°C, the vulcanizing speed was proper, vulcanizing time was prolonged, and the vulcanizing security was intensified. More sulfur addition was needed in the vulcanization of CNTs/PSBR composites than that in common CB/SBR composites.
3. With the increment of sulfur addition, the crosslinking degrees of the vulcanized rubber composites differed slightly, and yet the error bar of the crosslinking degree was elongated evidently after the sulfur addition exceeded 4.0 phr.
4. With the increment of sulfur addition, the elongation at break of the vulcanized rubber composites decreased linearly, and the hardness and tensile strength increased gradually. Yet the tear strength reached the maximum when the sulfur addition was of 2.5 phr, and then decreased

slightly when the sulfur addition exceeded 4.0 phr, which was corresponding to the structure designability of the composites that was affected by the sulfur aggregates in the rubber matrix. The tensile strength and hardness reached the maximum when the sulfur addition was 4.0 phr, and then almost kept constant when the sulfur addition continued to rise. As described earlier, when the sulfur addition was about 4.0 phr, which was twice higher than that of sulfur addition in the conventional vulcanized SBR filled with CB, it was the most beneficial for the strength and hardness of the vulcanizates filled with CNTs. This result was consistent with that of our previous work in NR filled with CNTs.

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