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New Fabrication and Mechanical Properties of Styrene-Butadiene Rubber/Carbon Nanotubes Nanocomposite

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A novel technology to prepare styrene-butadiene rubber (SBR)/carbon nanotubes (CNTs) composites was developed by combining a spray drying method and a subsequent mechanical mixing process. The cross-linking degrees of the vulcanized composites increased gradually with the additive CNTs contents. By comparing with those of the pure SBR composites, the mechanical properties such as tensile strength, tear strength and hardness of the composites filled with CNTs at certain contents were dramatically improved almost by 600%, 250% and 70%, respectively. The fabrication of the CNTs filled with SBR composites by combination of the spray drying method and subsequent mechanical mixing process was effective for enhancing the reinforcement effects of CNTs in rubbers. The novel technology can also open a new route for the modification and reinforcement on the nanocomposites with large amount of CNTs.

KEY WORDS: Carbon nanotubes; Styrene-butadiene rubber; Spray drying; Mechanical mixing; Nanocomposite; Mechanical property

1. Introduction

The concept of reinforcement for rubbers is complex to define, but may be considered as the enhancement of the modulus, failure resistance (tensile and tear strength) and other properties of the vulcanizates. Thus, the main target of filler addition is to improve certain properties and restrain some disadvantageous properties. It is well known that the structure and surface characteristics, especially the particle sizes of the fillers are the main factors controlling their reinforcing ability. In this sense, carbon nanotubes (CNTs) are believed to be one of the ultimate reinforcement materials for polymer matrix composites, because of their high aspect ratio (up to 10^4), specific surface area, Young's modulus (about 103 GPa) close to that of diamond^[1], tensile strength of about 50 GPa^[2], and light weight (density of about

1.3 g/cm^3)^[1–5].

However, in comparison with a great deal of studies on applications of CNTs in other polymers^[6–10], there are rather fewer reports dealing with applications of CNTs in rubbers for reinforcement. Preparation of high-strength rubber nanocomposites has yet to conquer several obstacles. Strong interaction and bonding are known to be desirable for load sharing between CNTs and the matrices to be reinforced. In addition, homogeneous dispersion and controllable alignment of CNTs in the matrices are crucial to achieve improvement of the mechanical properties. The authors have previously done some works on the reinforcement of CNTs in rubber matrices^[11–14]. Through conventional mixing method, CNTs could not be homogeneously and fully dispersed in the rubber matrix and there existed some CNTs conglomerations due to the high viscosity of the rubber^[15,16], and as a result, the reinforcement of CNTs in rubbers could not be effective. In this study, we selected commercial styrene-butadiene rubber (SBR), a typi-

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cal unsaturated polyolefin, as the matrix, which has been widely used in the fabrication of automotive tire sidewalls, cover strips, wires, cables, footwear, roofing barriers and sporting goods. At first, a suspension of CNTs in SBR latex was prepared to disperse CNTs in the liquid medium. Then the powder SBR composites filled with CNTs were prepared by using a spray drying process, which resulted in good dispersion of CNTs in the rubber matrix^[14]. Additionally, the obtained rubber composites were mechanically mixed with an open two-roll mixer in order to further improve the properties of the composites due to the further dispersion of CNTs in the composites and better interaction and bonding between CNTs and the rubber matrix.

2. Experimental

The SBR latex (SBR-50) with a solid content of 44.90% was supplied by Shandong Xiangfa Industry and Business Co., Ltd, China. High purity multi-walled carbon nanotubes (MWNTs) used in the experiments were prepared by chemical vapor deposition (CVD) method and treated subsequently by blended acid^[17]. Sodium dodecylbenzene sulfonate (SDS, analytical grade), $C_{18}H_{29}SO_3Na$, was used as the dispersant. All other curing reagents used here were of analytical grade purities.

The treated CNTs were mixed with 10 wt pct SDS, and then the mixture was added into deionized water in a mass ratio of 1:10 between the CNTs and water. After ball milling for several hours, the CNTs suspension with about 10 wt pct solid content was prepared. The vulcanizing reagent recipe we chose in this paper for SBR was as follows: benzothiazyl disulfide (DM) 3.0 phr (per hundred rubber: mass share for 100 mass unit of SBR), stearic acid (SA), 1.5 phr, zinc oxide (ZnO) 5.0 phr, sulfur 3.0 phr, where additive 1.0 phr of sulfur was used because rubber composites reinforced with CNTs needed more sulfur for vulcanization^[12,18]. The vulcanizing reagents were added into the dispersant solutions by stirring, and then the suspension containing the vulcanizing reagents was acquired after ball milling for several hours.

The formulations used here were as follows: SBR (the mass of SBR latex multiplied by the solid content) 100 phr, vulcanizing reagent 1 phr, and CNTs 0, 10, 20, 30, 40, 50, and 60 phr, respectively. The corresponding weight fractions of CNTs in the composites are 0, 8.2%, 15.1%, 21.1%, 26.2%, 30.8% and 34.8%, respectively. The CNTs and vulcanizing reagent suspensions were added into the SBR latex and stirred homogeneously, and then the mixed suspension with a total solid content of about 10% was obtained. The CNTs-SBR latex suspension prepared as described above was atomized and dried^[9], and then powders of SBR composites modified by CNTs were prepared. Then the powders of rubber composites were fully

mixed on an open two-roll mill at room temperature. The rotors operated at a speed ratio of 1:1.4. Finally SBR composites containing conventional vulcanizing reagents and different amount of CNTs were acquired.

The morphologies of CNTs, the SBR powders and the fractures of the vulcanized rubber composites were investigated by transmission electron microscopy (TEM, JEM-200cx), and scanning electron microscopy (SEM, S-3500N). The vulcanization properties were determined *via* a non-motor rheometer MM4130C2 produced by Beijing Huan-Feng Mechanical Factory, China. The compounds were vulcanized under an appropriate condition.

The cross-linking degrees of the vulcanizates were measured by solvent extraction method. Certain amount of vulcanizates was put in a Sorbitic extractor, and then extracted with toluene solvent for 24 h, later dried to constant weight in an oven. The cross-linking degrees were calculated according to Eq. (1):

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

where α is the cross-linking degrees, 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 vulcanizates with different CNTs loads were determined by means of a WDW-50 electronical versatile tester according to GB/T 528-1998 (Rubber, *i.e.*, vulcanized or thermoplastic-determination of tensile stress-strain properties), using dumbbell-shaped specimens. The hardness of the composites was measured with a durometer, Shore A according to ASTM D2240-2004 (the standard testing method of rubber characteristics, Shore A hardness). The tear strengths of the vulcanizates were tested according to GB/T 529-1999 (Rubber, *i.e.*, vulcanized or thermoplastic-determination of tear strength with trouser, angle and crescent test pieces). Three samples were measured for every case and the average of the values was taken.

3. Results and Discussion

Morphologies of the pristine and blended acid-treated CNTs are shown in Fig. 1, which shows that CNTs after acid treatment are of moderate lengths and less intertwined. It indicates that the acid-treated CNTs are more suitable for the reinforcement of rubbers. Additionally, according to the infrared spectroscopy analyzing results^[17,19–21], some functional groups such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (>C=O) were loaded on the CNTs surfaces after blend acid treatment. In the infrared spectroscopy, there evidently existed peaks of carbonyl and hydroxyl functional groups corresponding to wave number of 1750 and 3500 cm^{-1} , respectively. These

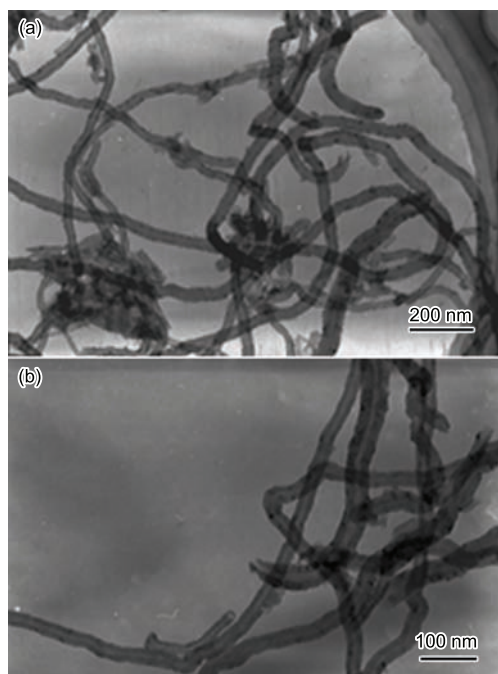


Fig. 1 TEM morphologies of the CNTs used in the experiments: (a) pristine, (b) acid-treated

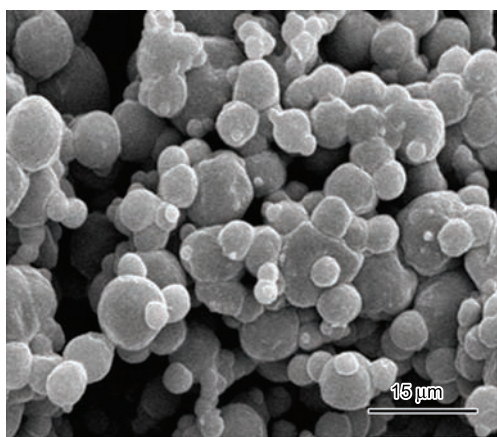


Fig. 2 SEM morphologies of the composites powders filled with 50 phr CNTs

functional groups improve the water-affinity of CNTs and thus are beneficial for the preparation of the suspension of CNTs in SBR latex. Moreover, the functional groups loaded on the surfaces of CNTs are favorable for improving the interfacial bonding between CNTs and the rubber matrix, and correspondingly, the improved bonding might enhance the mechanical capacities of the composites.

Morphologies of the powder SBR composites modified with CNTs are shown in Fig. 2. The powders are finely round with uniform diameters of no more than 10 μm . By this way, the dispersion of CNTs in the rubber matrix will be remarkably improved at least in the scale of the powder sizes, and then the rubber composites filled with CNTs will be reinforced effec-

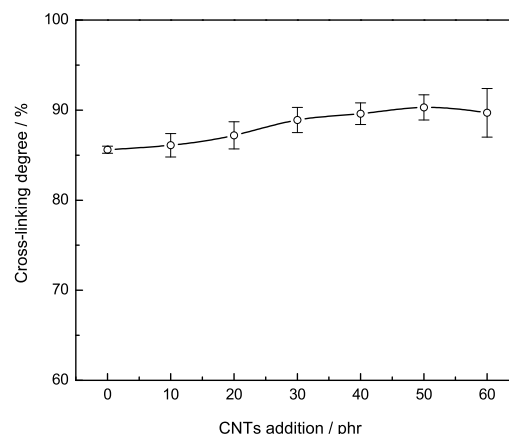


Fig. 3 Cross-linking degrees of the vulcanizates filled with different CNTs additions

tively.

The cross-linking degrees of the vulcanizates with different CNTs additions are shown in Fig. 3. It can be seen that the cross-linking degrees of the vulcanizates increase gradually with the increment of the CNTs additions and reach the maximum at 50 phr. With further additional CNTs, the cross-linking degrees of the composites do not increase any more due to the subsequently formed CNTs conglomerations, which can be proved by the greater scattering cross-linking degrees of the composites filled with 60 phr CNTs. The rubber matrix reinforced with the filled CNTs consists of two phases. One is the gel rubber phase formed by the combinative rubber molecules adsorbed on the CNTs surfaces, which cannot be dissolved by toluene. The other is the pure rubber phase consisting of the other free rubber molecules. In the gel rubber phase, the rubber macromolecules are in the restricted state, which makes them drop out of the vulcanizing action. On the other hand, because the vulcanizing reagents hardly dissolve in the gel rubber phase, the concentration of the vulcanizing reagents in the pure rubber phase increases with the increment of the gel rubber contents, which are dependent on the additive CNTs. Correspondingly the cross-linking degrees of the vulcanizates increase gradually with the CNTs additions.

The cause of the different concentration of vulcanizing reagents in the two phases of rubber reinforced with CNTs can be explained by the thermodynamics theory:

$$\Delta F = \Delta H - T\Delta S \quad (2)$$

where F is the free energy of a phase, H , T and S are the enthalpy, temperature and entropy of a phase, respectively. The rubber can be regarded as a special solution system in a broad sense. The rubber molecule chains are absorbed by the CNTs in the gel phase. In comparison with that in the pure rubber phase, the rubber molecules in the gel phase is more orderly and controlled. Therefore, ΔS of the vulcanizing reagent

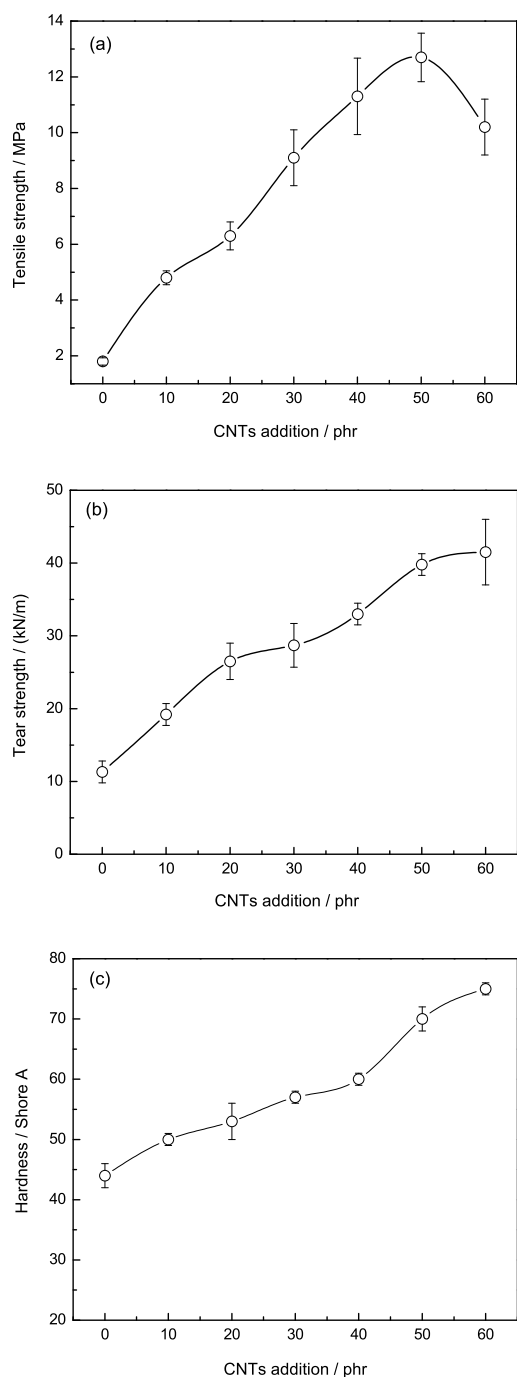


Fig. 4 Mechanical properties of the vulcanizates filled with different CNTs additions: (a) tensile strength, (b) tear strength, (c) hardness

dissolved in the pure rubber phase is greater than that of the vulcanizing reagent dissolved in the gel phase. Assuming that T and ΔH are constant, the reduction of free energy, that is ΔF in the gel phase is less than that in the pure rubber phase. The vulcanizing reagents will diffuse from the gel phase to the pure rubber phase and then make the concentration of vulcanizing reagent in the pure rubber phase increase. Hence, the cross-linking degrees of the vulcanizates increase with the augment of filled CNTs.

The mechanical properties of the vulcanizates are shown in Fig. 4. It can be seen that both of the strengths and deformation capabilities of the SBR vulcanizates increase evidently with increasing CNTs additions. The tear strengths and hardness of the composites increase linearly with increasing CNTs content up to 60 phr where the tear strength and hardness reach 41.5 kN/m and 75 Shore A, respectively, which are about three times and 65% higher than that of pristine SBR, respectively. The tensile strength increases firstly with increasing CNTs additions, and reaches its peak value of 12.7 MPa at 50 phr of CNTs, and then tends to decrease with further increment of CNTs content. The top tensile strength of the composites filled with CNTs is five times higher than that of pristine SBR. The hardness improvements can be attributed to the high strength and Young's modulus of the additive CNTs. The evident improvement of mechanical properties such as tensile and tear strengths of the composites can be explained as follows. The CNTs can be dispersed better in the rubber matrix through the novel spray drying process compared with the conventional mixing method. The further dispersion of CNTs and good interfacial bonding between the fillers and rubber matrix ascribe to the subsequent mechanical mixing process. During the mechanical mixing, the shear force can possibly make the CNTs align in a way. Also, the free group brought by the mechanical mixing can lead to the chemical action between the SBR and the active functional groups loaded on the surfaces of the acid-treated CNTs. However, when the CNTs addition exceeds certain content, it may result in some CNTs conglomerations in the rubber matrix, which will act as impurities and stress concentration spots during the tensile testing. As a result, the tensile strength decreases. The higher error bars of the tensile and tear strengths corresponding to the composites filled with more CNTs (see Fig. 4(a) and (b)) indicate the existing of CNTs conglomerations in the matrix.

In previous works reported on the composites modified with CNTs^[22–26], only small amount of CNTs no more than 10 wt pct were added into the composites for modification and reinforcement, and the properties of the composites showed insignificant improvements. When more CNTs were added into the composites for further improvement in some properties of the composites, the results always went contrary to our wishes. The critical factor was the homogeneous and sufficient dispersion of CNTs in the matrix. In this work, with the novel technology of spray drying and subsequent mechanical mixing^[27], 50 phr (33.3 wt pct) of CNTs was added in the rubber matrix for reinforcement and the mechanical properties of the composites were enhanced remarkably.

The fractures of the rubber specimens are shown in Fig. 5. It is noted that the CNTs are finely dispersed in the rubber matrix and then the reinforcement of

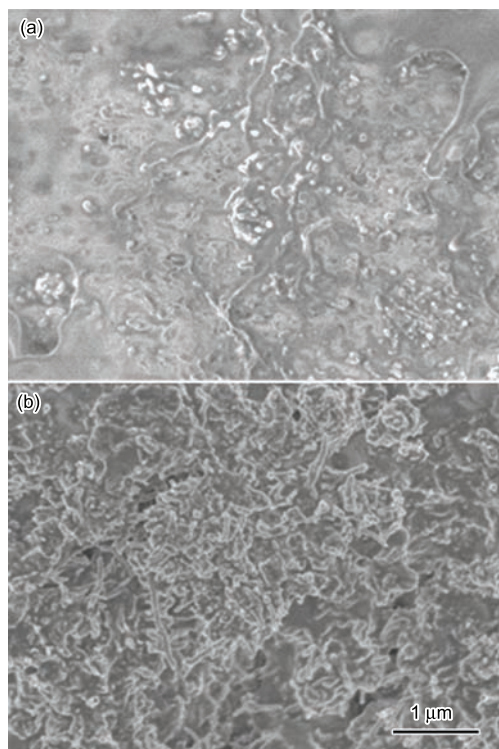


Fig. 5 Fracture SEM morphologies of the composites filled with different additions of CNTs: (a) 40 phr CNTs, (b) 60 phr CNTs

CNTs in SBR is brought into effect. There are many outcrops on the fractures of SBR vulcanizates (see Fig. 5(a)), which indicates that CNTs in the rubber matrix suffered effectively the mechanical load during the mechanical testing processes. The cross-linking structures, where CNTs acted as crunodes, would increase and the cross-linking density of the rubber matrix would increase as well with increasing CNTs content in SBR composites. Therefore, the loads would be transferred to CNTs linked with molecule chain sections of the rubber matrix. The load transformation effectively retards development of rubber silver veins and micro-cracks, which resulted from the stress concentration in the rubber matrix, and then the mechanical properties of the composites increase. However, the tendency of CNTs to accumulate in the rubber matrix will gradually increase with increasing CNTs content due to their nanometer scales and high aspect ratios. Once the CNTs content in the rubber matrix exceeds certain degrees, it will be propitious for CNTs to accumulate in the rubber matrix as shown in Fig. 5(b). Mechanical properties of composites may correspondingly decrease.

4. Conclusion

By means of novel spray drying process, the suspension of CNTs in SBR latex was applied to prepare SBR powders modified with CNTs with uniform diameters of about 5–10 μm . CNTs are well dispersed

in the rubber powders. CNTs are further dispersed in the matrix with subsequent mechanical mixing. Under the strong shear force during the mixing period, the CNTs are re-aligned and oriented. Simultaneously, the interfacial bonding between the CNTs and the rubber matrix are also improved. The cross-linking degrees of the composites vulcanized increases gradually with the augment of CNTs additions due to the good interaction between the CNTs and the matrix. These advantages bring the reinforcement of CNTs into effect. Compared with those of pure SBR composite, the hardness and tear strength of the composites filled with 60 phr of CNTs enhance by almost 70% and 250%, respectively, and tensile strength of the composites filled with 50 phr of CNTs improves remarkably by 600%. When the CNTs addition exceeds 50 phr, some CNTs conglomerations will form and then result in deteriorated dispersions of CNTs in the rubber matrix. It can be proved by the deduction of tensile strength and more scattered tear strength of the composites filled with 60 phr of CNTs. Through this work, a new route can be developed for the modification and reinforcements on the polymers with large amount of CNTs in good dispersion.

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