

# Preparation and Mechanical Properties of Natural Rubber Powder Modified by Carbon Nanotubes

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**ABSTRACT:** A suspension of carbon nanotubes in natural latex was obtained by liquid mixing and then was used to prepare powder natural rubber composites modified with carbon nanotubes by means of spray drying process. The composite powders were round-like and fine, with an average diameter of less than about 5  $\mu\text{m}$ . The dispersion of carbon nanotubes in the rubber matrix was improved remarkably compared with that obtained by the mechanical mixing method. By means of vulcanization tests, it was found that the addition of vulcanizing agent necessary for the powder rubber containing carbon nanotubes should be evidently greater than that in rubber prepared by mechan-

ical mixing, there evidently existed vulcanization reversions for the natural rubber prepared by mechanical mixing, which disappeared in the powder rubber containing carbon nanotubes prepared by the spray drying process. The mechanical properties of the powder natural rubber containing carbon nanotubes were much improved because of the modification effect of carbon nanotubes in rubber. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4697–4702, 2006

**Key words:** carbon nanotubes; spray drying process; powder rubber; vulcanization; mechanical property

## INTRODUCTION

Rubbers produced by crosslinking amorphous, gum elastomers are soft and weak. Reinforcement with hard “domains” can increase stiffness and resistance to fracture. The stiffness increase is reasonably well understood. It involves a hydrodynamic effect, a shape factor, and sometimes occlusion of rubber within “void space” of filler aggregates. Rubber is generally reinforced when filled with some additions such as fiber, carbon black (CB), clay, and silicates. CB is the most widely used filler in rubber for reinforcement. To produce significant reinforcement, the filler particle size must be less than about a micrometer. As specific surface area increases (i.e., particle size decreases), the strength of particles filled vulcanizates generally increases.<sup>1–3</sup> However, if the domain size is greater than about 1  $\mu\text{m}$ , reinforcement is absent or minimal, regardless of the domain shape, and even if the bonding between the matrix and domains is quite

strong. Small hard domains (e.g.,  $<0.1 \mu\text{m}$ ) are necessary and sufficient for substantial reinforcement.

Jiang and Hamed<sup>4,5</sup> discovered recently that raw ethylene-propylene-diene monomer (EPDM) containing a small amount of buckminsterfullerene ( $\text{C}_{60}$ ) and exposed to ultraviolet light became strong and elastic. The strength was significantly higher than that achievable by simple free-radical crosslinking with peroxide. It was particularly noteworthy that the EPDM/ $\text{C}_{60}$  sample has high modulus and high tear strength. It appeared that the EPDM/ $\text{C}_{60}$  formed a nano-composite in which the  $\text{C}_{60}$  reinforced the rubber and acted as a multifunctional crosslinker. The demonstration of nano-scale reinforcement of rubber suggested that other approaches to achieve nano-sized reinforcement should be explored.

Since the innovative discovery of Iijima in 1991,<sup>6</sup> carbon nanotubes (CNTs) have interested scientists and engineers from all over the world. With the outstanding mechanical and physical properties and application prospects in engineering materials, CNTs were expected to be a good fillers in polymer materials for modifications.<sup>7,8</sup> However, comparing with the great deal of studies on applications of CNTs in other polymers,<sup>8</sup> there were rather fewer reports dealing with applications of CNTs in rubbers for reinforcement. López-Manchado et al.<sup>9</sup> characterized the effects of the incorporation of single-walled carbon nanotubes (SWNTs) on the physical and mechanical properties of natural rubber (NR) by means of dynamic

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mechanical analysis, differential scanning calorimetry, and Raman spectroscopy to obtain information about of the possible interactions between both materials as well as the dispersion of SWNTs on elastomer matrix. The dynamic mechanical analysis confirmed the reinforcing effects of the nanotubes on elastomer matrix. In fact, the incorporation of low concentrations of SWNTs gives rise to a more rigid material, which is reflected in a marked increase of the storage modulus. This effect is not noticeable with equal CB dispersion in the blend. We have made some efforts to apply CNTs in rubbers for reinforcement.<sup>10,11</sup> The rubber composites containing CNTs were made by means of mechanical mixing process, but the effect was not as good as that expected. The results showed that CNTs evidently reinforced the rubber composites with higher properties such as rebound resilience, compression fatigue, and aging resistances than those of the rubbers filled by CB. However, the tensile and tear strengths of the rubber composites containing CNTs were lower than those of the rubber filled with CB. Observation of the fractured surfaces under scanning electronic microscopy (SEM) has revealed that there existed more CNT agglomerates in the rubber matrix. According to the fundamentals of composite reinforcement,<sup>1</sup> the fillers must be fully dispersed in the matrix materials. However, the high viscosity of the elastomeric polymer matrix makes it difficult for the fillers to disperse within it. This might be one of the main effects deteriorating the properties of the rubber composites prepared by mechanical mixing processes.

Therefore, CNTs must be fully dispersed in the matrix materials to realize its reinforcement effect in elastomeric polymers. On the other hand, the preparation technologies of rubber powders with smaller sizes have developed much recently and have greater applications. In this paper, NR powders filled by CNTs with diameters of several micrometers were prepared by means of Büchi B-290 Mini Spray Dryer produced by Büchi Com., Switzerland. By this way, the dispersion of CNTs in the rubber matrix would be expected to remarkably improve at least in the scale of the powder sizes, and then the rubber composites filled with CNTs would be effectively reinforced. In addition, the rubber powders could be processed into rubber products with vulcanization. Moreover, the rubber powders containing dispersed CNTs could be added in other polymers for modification.

## EXPERIMENTAL

The CNTs used in this paper were prepared by chemical vapor depositing (CVD) method. The CNTs were treated in HF for 24 h, and then rinsed continuously to chemically neutralize with deionized water. CNTs with high purity were obtained after drying. The CNTs were treated in a blended acid solution with a

volume ratio 3:1 of vitriol to nitric acid, and the CNTs load was 1 g for 10 mL of blended acid solution. The solution was boiled for 30 min and then rinsed to become chemically neutral. The CNTs acid-treated were obtained after drying.

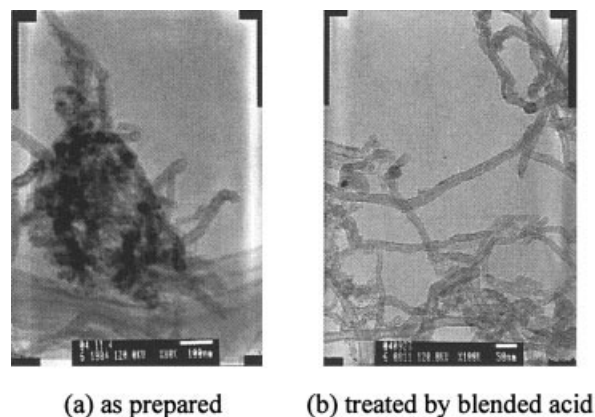
The NR latex used was produced by Beijing Rubber Latex Factory with a solid content of 60%. Sodium dodecylbenzene sulfonate (SDAS) was used as a dispersion reagent. The vulcanizator consisted of sulfur, 1.4 g; stearic acid SA, 3 g; ZnO, 4 g; accelerant DM, 0.1 g; and accelerant CZ, 1.3 g. The total was defined as one mass share (phr) of vulcanizator.

The CNTs treated by the blended acid were mixed with 10 wt % of SDAS, 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 suspension was then added into NR latex, and a suspension of CNTs in the NR latex was obtained by adding proper amount of deionized water and was stirred fully for more than 2 h. The ratio between the mass sum of CNTs and CB and the mass of the solid content in the NR latex was controlled to be 50%. Suitable amount of deionized water was added into the suspension of CNTs/CB in the NR latex by stirring it for more than 2 h, and then CNTs-NR latex suspension was obtained. After ball-milling and dilution with proper amount of deionized water, the vulcanizator dispersions were added into the CNTs-NR latex suspension. A CNTs-NR latex suspension containing vulcanizator with about 10% of total solid content was obtained after full stirring.

The CNTs-NR latex suspension prepared as described earlier was atomized and dried by means of Büchi B290 Mini Spray Dryer (Büchi Com., Switzerland), and then NR powders modified by CNTs were produced. The preparing process and the powder sizes were controlled by modification of the working conditions of the spray drying processes. The optimized parameters of the spray drying processes are as follows: the liquid entering temperature, 180°C; the liquid flowing rate, 15%; and the inspiriting rate, 100%. It is suggested that the liquid entering temperature should be 120°C if the rubber powders would be used to produce vulcanized rubber products.

The vulcanization processes of the NR powders with different fillers containing vulcanizators were measured by means of MM4130C2 Non-Rotor Vulcanizer produced by Beijing Huan-Feng Chemical Machinery Plant. The vulcanized NR powders were prepared into standard specimens and then the mechanical properties were measured by means of WDW-50 Electronical Versatile Tester.

The morphologies and fractures of the NR powders and CNTs were observed and investigated by means of JEM-200cx transmission electronical microscopy (TEM) produced by NEC, Japan, and S-3500N scan-



**Figure 1** Morphologies of CNTs under different conditions (TEM): (a) as prepared and (b) treated by blended acid.

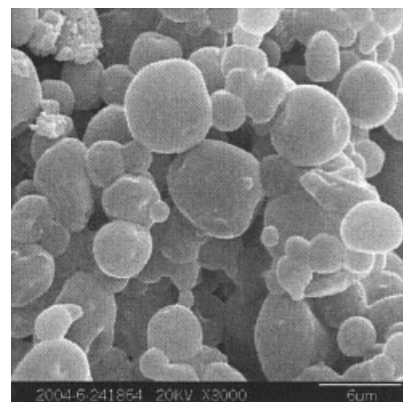
ning electronical microscopy (SEM) produced by Hitachi Com., Japan.

## RESULTS AND DISCUSSION

Figure 1 shows the morphologies of the CNTs under different conditions. CNTs were desired to be with moderate lengths and relatively lower entangled degrees taking its dispersion in the rubber matrix into account. Therefore, the CNTs after blended acid treatment were suitable for use in this study, based on the observation in Figure 1. In addition, according to the infrared spectroscopy analyzing results,<sup>12–14</sup> some functional groups such as hydroxyl ( $-\text{OH}$ ), carboxyl ( $-\text{COOH}$ ), and carbonyl ( $>\text{C}=\text{O}$ ) were loaded on the CNTs surfaces after blended acid treatment. In the infrared spectroscopy, there evidently existed peaks of carbonyl and hydroxyl functional groups corresponding to wave number  $1750$  and  $3500\text{ cm}^{-1}$ , respectively. These functional groups improved the water-affinity of CNTs and then were beneficial to preparation of the CNTs-NR latex suspension. Moreover, the functional groups loaded on the surfaces of CNTs were favorable to reinforce the interfacial action between CNTs and the rubber matrix and then to improve the mechanical capacities of the composites.

The dispersion reagent was added into CNTs which would be beneficial for CNTs to suspend in water and stimulate CNTs to disperse in the NR latex. However, overfull dispersion reagent added would weaken the interfacial coalescence between CNTs and the rubber matrix, and then deteriorate the properties of the composites. So, it was necessary to determine a suitable dosage of the dispersion reagent. By means of a sedimentation experiment the suitable dosage of the dispersion reagent was found to be about 10%.

During the mixing processes of CNTs-water suspension and NR latex, it was easy for the latex to coagulate because of the  $\zeta$  potential reduction of the

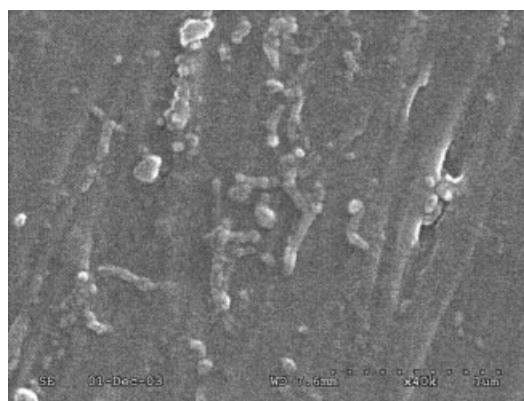


**Figure 2** Morphology of the CNT modified NR powders (SEM).

latex resulted from additions of CNTs. When the  $\zeta$  potential reduced to a certain critical value, the electrostatic repellant forces between the latex particles would not be enough to counteract the ubiquitous van der Waals forces between the suspended particles. So, the balances between the latex would be broken, and then the latex would coagulate by collisions between the latex particles due to their thermal movements. A rational preparing process was determined after a series of experiments, and then applied to prepare the CNTs-water-NR latex suspensions with good suspension capabilities.

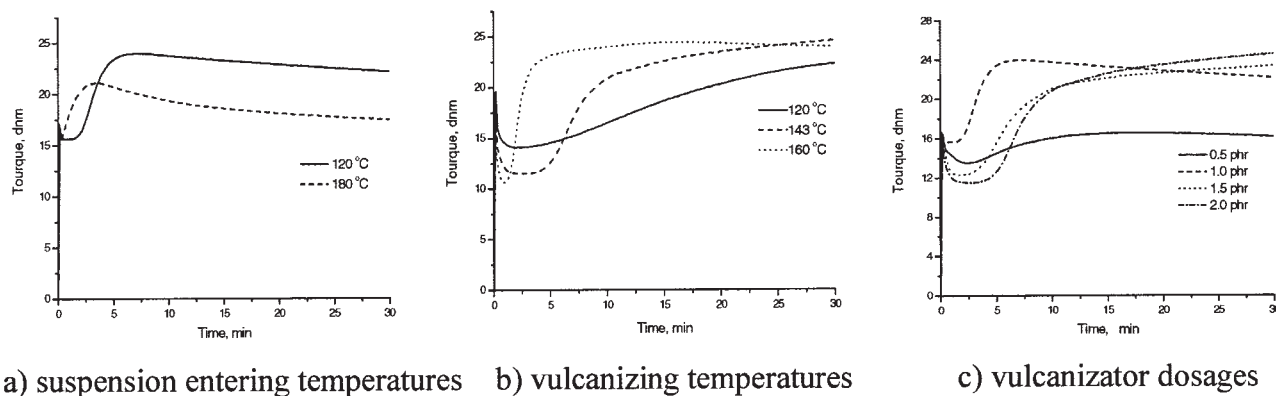
The morphology of the CNTs modified NR powders under SEM was shown in Figure 2. It was seen that the powders were finely spherical with uniform diameters of about  $2\text{--}5\ \mu\text{m}$ . Figure 3 shows the fracture surfaces of the tensile specimens prepared from the CNTs modified NR powders. It was noted that CNTs were fully dispersed in the NR matrix and had a good interfacial interaction with the rubber matrix.

The shear modulus of vulcanized rubbers should be proportional to the crosslinking density (i.e., network chain numbers in unit volume) of the vulcanized rub-



**Figure 3** Fracture of the tensile specimens prepared from the CNT (20 phr) modified NR powder (SEM).





**Figure 4** Effects of the spray drying processes and vulcanizing conditions on the vulcanizing capabilities of the NR powders: (a) suspension entering temperatures, (b) vulcanizing temperatures, and (c) vulcanizator dosages.

bers, that is  $G = \nu KT$ , here,  $G$  denotes shear modulus,  $\nu$  denotes the crosslinking density,  $K$  denotes Boltzmann constant, and  $T$  denotes temperature. In fact, the vulcanizing curves determined by means of vulcanizers reflected variations of the shear modulus of the vulcanized rubbers. Therefore, the capabilities of the vulcanized rubbers could be directly reflected by the vulcanizing curves. Moreover, the vulcanizing capabilities were closely related with the processing conditions and the vulcanizator dosages. In this paper, the effects of the spray drying processes and vulcanizing conditions on the vulcanizing capabilities of the NR powders were investigated. The results were shown in Figure 4.

Figure 4(a) showed the vulcanizing curves of the CNTs modified NR powders prepared at different suspension entering temperatures during the spray drying processes. It was shown that it was more beneficial for raising the shear modulus of the rubber powders to make the suspension enter the chamber at 120°C rather than at 140°C. Because the rubber molecules would not be crosslinked at relatively lower temperatures, and would fully be crosslinked after hot pressing in molds, and so it was propitious to obtain high mechanical properties. If the liquid entered the spray chamber at higher temperatures, crosslinking of the rubber molecules should have occurred partly before being crosslinked fully. It instead was harmful to the mechanical properties of the vulcanized rubbers.

In general, the suitable vulcanizing temperature of NR is 143°C, and the optimized vulcanizing temperature of NR latex is about 60°C. However, the optimized vulcanizing temperature for NR powders prepared by spray drying processes is uncertain up to now. It was seen from Figure 4(b) that, when the vulcanizing temperature was 120°C, there was a relatively longer time before sufficient vulcanization, and the peak torque after 30 min was the lowest among the three cases at different vulcanizing temperatures. The vulcanizing time was short corresponding to the vul-

canizing temperature of 160°C, the torque reached the peak value in 5 min, but on the other hand, with somewhat a vulcanizing reversion. The best vulcanizing property was corresponding to the curve taken from the vulcanizing process at 143°C, and it was noted that there existed not any reversion during the vulcanizing process. Therefore, when the NR powders modified by CNTs prepared by spray drying processes were applied to make rubber products, the vulcanizing temperature should be approximately same as that during the conventional methods for NR products.

The vulcanizator dosage used in conventional mechanical mixing processes for NR preparations was taken as 1 phr, the vulcanizing properties of the NR powders modified by CNTs with different dosages of vulcanizator were respectively investigated. The results are shown in Figure 4(c). Because CNTs were fully dispersed in the NR latex and the dispersion effects in liquid state were perfectly maintained during the spray drying processes, the CNTs dispersed finely in the NR matrix, that is the CNTs contacted fully with the NR molecules. Therefore, the dosage of vulcanizator desired for the NR powders to be fully vulcanized should be rationally bigger than that necessary during the conventional mechanical mixing processes. In addition, it was noted in Figure 4(c) that there existed evident vulcanizing reversion for 1 phr of the vulcanizator, and then the vulcanizing reversion disappeared when the dosage of vulcanizator increased to 1.5 phr or more.

The standard specimens for measurements of the mechanical properties were made from the prepared NR powders. The results are shown in Table I. It was seen that both strengths and deformation capabilities of the NR powders were related closely with CNT content in the NR powders. All mechanical properties such as tensile strength, elongation at break, and tear strength of the NR powders first increased evidently with the increasing CNT content, and reached their

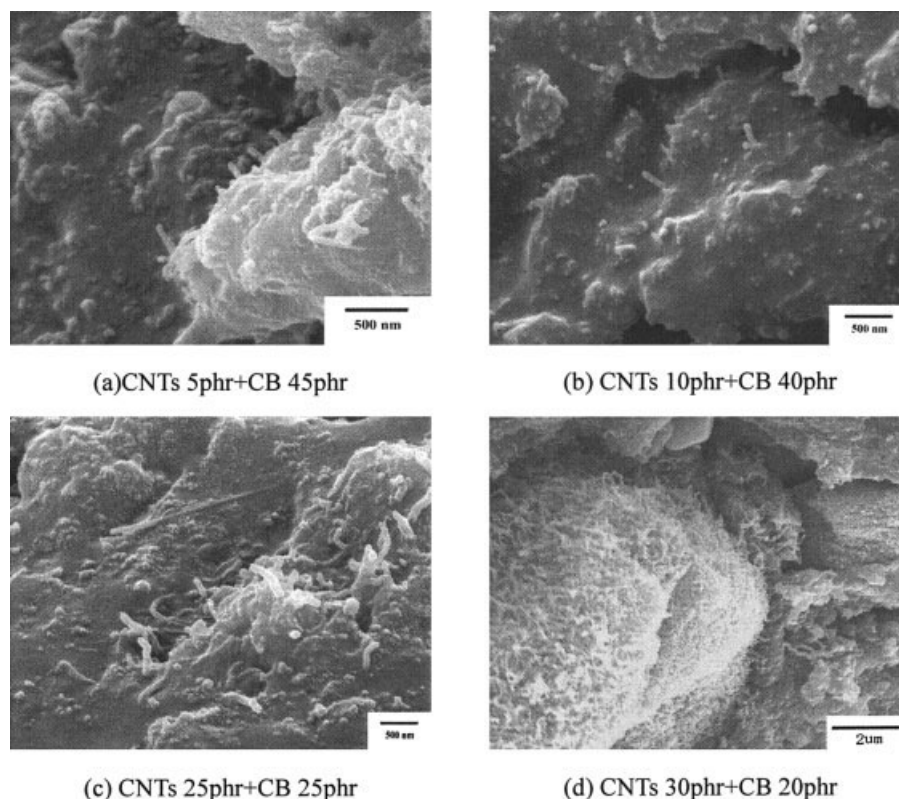
**TABLE I**  
**Mechanical Properties Measured with Specimens Made of NR Powders Modified by CNTs**

Fillers	Tensile strength (MPa)	Elongation at break (%)	Tear strength (KN/m)
CB 50 phr	15.42	576	53.9
CNTs 5 phr + CB 45 phr	13	437	63.04
CNTs 10 phr + CB 40 phr	20.8	650	60.9
CNTs 20 phr + CB 30 phr	17.4	1210	57.3
CNTs 25 phr + CB 25 phr	17.75	594	86.5
CNTs 30 phr + CB 20 phr	12.38	587	67.5
CNTs 50 phr	16.18	640	50

peak values at certain CNT contents, which were respectively, 20.8 MPa for tensile strength at 10 phr of CNTs, 1210% for elongation at break at 20 phr of CNTs, and 86.5 KN/m for tear strengths at 25 phr of CNTs. Then, all the mechanical capacities of the NR powders tend to decrease with further increase in CNT content up to 50 phr, at which CB was replaced completely by CNTs. These results could be attributed to two factors, as follows: first, a number of CNT conglomerations would be formed when CNT content reached certain amounts and then resulted in deteriorated dispersions of CNTs in rubber matrix; second, the reinforcing effects of CB in NR decreased with increasing CNT content (that was corresponding to

decreasing CB content) and were cleared away when CNT content reached to 50 phr (CB was correspondingly completely replaced by CNTs). In addition, CB acted as a good separator for preparation of NR powders. Complete absence of CB would result in disadvantageous effects to mechanical capabilities of NR powders. The results shown in Table I indicate that the general mechanical properties of the NR powders modified by CNTs were optimized with 10–25 phr of CNT contents.

The fractures of the rubber specimens are shown in Figure 5. It was noted that the dispersion of CNTs in the rubber matrix was evidently improved [see Figs. 3 and 5(a–c)], and then the reinforcements of CNTs in



**Figure 5** Fracture morphologies of NR powders with different fillers (SEM): (a) CNTs 5 phr + CB 45 phr, (b) CNTs 10 phr + CB 40 phr, (c) CNTs 25 phr + CB 25 phr, and (d) CNTs 30 phr + CB 20 phr.

NR were brought into effect. There were some outcrops of the broken CNTs on the fractures of NR specimens with different CNT contents. The outcrops indicated that CNTs in the rubber matrix suffered the mechanical loads effectively during the testing processes. When CNT contents were small, there were only few outcrops on the fracture [see Fig. 5(a)]. The outcrops increased with increasing CNT content in the NR powders. In addition, CNT accumulations appeared gradually with increasing CNT content and even more seriously when CNT content reached to 30 phr or more. The crosslinking structures in which CNTs acted as crunodes would increase and the crosslinking density of the rubber matrix would increase as well with increasing CNT content in NR powders. Therefore, the loads would be transferred to CNTs linked with molecule chain sections of the rubber matrix. The load transformation retarded the development of rubber silver veins effectively and microcracks resulted from the stress concentration in the rubber matrix, and then the mechanical properties of the rubber material increased. However, the tendency of CNTs to accumulate in the rubber matrix would increase gradually with increasing CNT content due to their nanometer scales and high aspect ratios. Once the CNT content in the rubber matrix exceeded certain amounts, it would be propitious for CNTs to accumulate in the rubber matrix, as shown in Figure 5(d). Mechanical properties of the rubber material would correspondingly decrease.

### CONCLUSIONS

1. After being treated in blended acid and loaded with functional groups, CNTs were endowed with high hydrophilic properties and were used to prepare suspension of CNTs in deionized water. The suspension was mixed with NR latex by stirring it completely, and then CNTs-NR latex suspension was prepared, in which CNTs were finely dispersed. In the suspension of CNTs in NR latex, the optimized content of surfactant SDAS was about 10%.
2. By means of spray drying process, the suspension of CNTs in NR latex was applied to prepare

NR powders modified by CNTs with uniform diameters of about 2–5  $\mu\text{m}$ . CNTs were fully dispersed in the NR powders and had a good interfacial interaction with the NR matrix.

3. When compared with NR materials prepared by the conventional mechanical mix processes, the NR powders modified by CNTs prepared by means of spray drying process desired more vulcanizater. The demand of the vulcanizater to fully vulcanizing the NR powders modified by CNTs was about 1.5 times or more as large as that for conventional NR mechanically mixed. Moreover, vulcanizing reversions did not exist in the fully vulcanized NR powders modified by CNTs.
4. CNTs were fully dispersed in NR powders prepared by spray drying process and effected for reinforcement. The mechanical properties of the NR powders were effectively improved under certain CNT contents. The peak values of tensile strength, elongation at break, and tear strength of the NR powders reached 20.8 MPa, 1210%, and 86.5 KN/m at 10, 20, and 25 phr of CNTs, respectively.

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