Study on preparation and properties of carbon nanotubes/rubber composites

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Carbon nanotubes (CNTs) have attracted a great deal of interest since their discovery in 1991 [1]. CNTs are new-type carbon materials with excellent electrical properties [2], high strength [3–6], heat conductivity [7, 8], etc. Recent researches suggest that CNTs hold promise as a possible reinforcing phase in preparation of novel polymeric composites [9–12]. Furthermore, the CNTs/polymer composites may exploit many advantages possessed by CNTs, such as excellent thermal stability, thermal and electrical conductivity, etc. A few studies have described the fabrication and properties of CNTs/polymer nanocomposites [10–13]. All the present researches illustrated that the dispersion of CNTs in polymer matrix and the interfacial interaction between CNTs and polymer were two critical factors to effect the comprehensive performances of composites, which are two key problems to solve because of the extremely inactive surface, nano-scaled diameter and high aspect ratio of CNTs. Therefore, in order to exhibit their potentials, the resolution of these two problems is the requirement. Although preparations of CNTs/resin composites have been widely reported, study on CNTs/rubber composites is hardly reported. However, CNTs filled rubber composites with high elasticity of rubber should be able to find very extensive applications in many fields, just like what conductive rubber composites filled with carbon fiber and carbon black do [14–16]. In the work described in this paper, for the first time, CNTs/rubber composites were studied.

Two methods were used to prepare the nanocomposites of hydrogenated nitrile rubber (HNBR) matrix. Method 1: CNTs was mixed into HNBR directly on a two roll mill with curing agent at 50°C for 10 min, and then the corresponding compound was vulcanized at 170°C through hot pressing for T_{90} (the optimum curing time), which is the optimum time for curing of rubber and measured by a disc-rotor rheometer produced by Beijing Huanfeng Machinery Factory. Method 2: low molecule liquid HNBR (LHNBR) was firstly dissolved in acetone, subsequently, the surface modified CNTs were added into the solution, and then the ultrasonic dispersion was used on the mixture. Removing the acetone from the mixture by vacuum drying, a compound with CNTs pre-dispersed in LHNBR was obtained. When the content of CNTs in the mixture varied, the amount of LHNBR in mixture still kept constant. The CNTs/HNBR composite was prepared by mixing the compound with HNBR by two roll milling, further vulcanizing through hot press using the same processing parameters applied in method 1. The morphology of CNTs and their dispersivity in HNBR rubber was studied by transmission electron microscope H-800. The CNTs/silicone rubber composites were prepared by method 1 using basically the same processing parameters.

In order to study the effect of CNTs on the vulcanization of composites, two kinds of vulcanizing agents, dicumyl peroxide (DCP) and 2,5-dimethyl-2,5-ditbutyl peroxy hexane (Varox), were applied for curing of the composites based on HNBR and Silicone rubber. The basic recipes of the composites are listed in Tables I and II. The cross-linking processes and characteristics are depicted in Table III and Fig. 1, respectively. The reason why the authors designated CNTs/silicone rubber composites is help to identify the intrinsic effect of nano-tubes on the vulcanization.

Table III summarizes the main vulcanization parameters of the curing process of the CNTs/HNBR composites cross-linked by Varox and DCP, respectively. It was found that the loading of CNTs had a remarkable effect on the cross-linking of rubber with Varox as curing agent, while hardly influenced the cross-linking with DCP as curing agent. In order to find why, the effect of CNTs loading

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TABLE I Basic recipes of the CNTs/HNBR composites

Mixing method	Method 2						Method 1
Recipe no.	1	2	3	4	5	6	7
HNBR	100	100	100	100	100	100	100
DCP	6	6	6	6	6	/	6
Varox	/	/	/	/	/	6	/
CNTs	0	2	7	15	25	25	25
LHNBR	6	6	6	6	6	6	6
TAIC[a]	2	2	2	2	2	2	2
Antioxidization agent 1010[b]	1	1	1	1	1	1	1

[a]TAIC: triallyl iso cyanurate; [b]antioxidization agent 1010:

TABLE II Basic recipes of the CNTs/silicone rubber composites

Recipe no.	Silicone rubber	Varox	CNTs
1	100	3	0
2	100	3	2
3	100	3	10
4	100	3	15
5	100	3	30
6	100	3	40

TABLE III Vulcanization parameters of the CNTs/HNBR composites

Vulcanization system	Varox		DCP		
CNTs (phr)	0	25	0	25	40
M_L (dNm)	1.30	1.08	4.49	3.31	4.14
M_H (dNm)	18.20	2.74	26.76	28.18	31.63
T_{90} (min)	10:51	\	8:29	8:38	8:26
Phenomena	Cured	Uncured	Cured	Cured	Cured

Note: M_L: minimal torque of curing curve, M_H: maximal torque of curing curve.

on the cross-linking of CNTs/Silicone rubber composites was also explored.

Fig. 1 clearly shows that the vulcanization time of the composites filled with Varox greatly increases with the content of CNTs, and the modulus of the composites when curing reaches balance dramatically decreases with the content of CNTs after loading of CNTs exceeds 15 phr, which is in contrast to that of the traditional composites filled with most fillers. Combining the results of the two kinds of composites, the effect of CNTs on the vulcanization of rubber is attributed to the strong absorption effect of CNTs to the liquid vulcanizing agent, i.e. Varox, which originates from the special hollow structure and extremely high specific area. When the loading of nanotubes is higher than 30 phr, the composites with Varox cannot even be cross-linked and presents viscous state. Therefore, Varox is not a good vulcanizing agent for composites filled with CNTs. On the contrary, the cross-linking effect of DCP for rubber is not seriously influenced by the presence of CNTs probably because of the solid state and chemical structure of DCP.

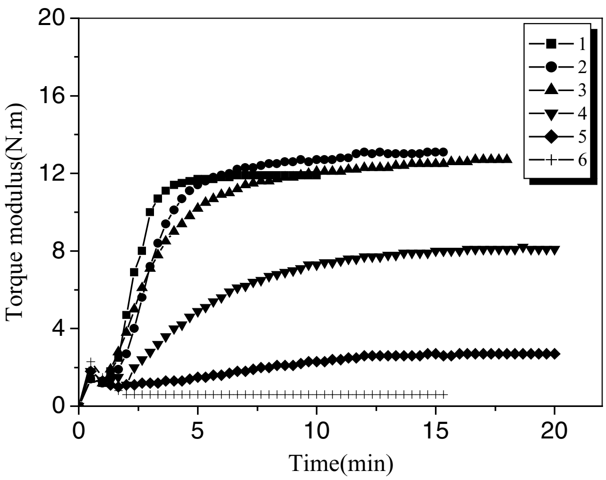
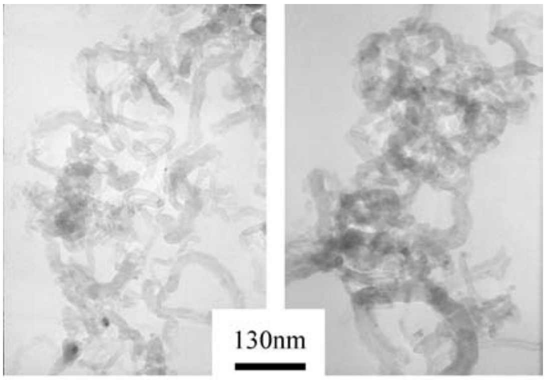
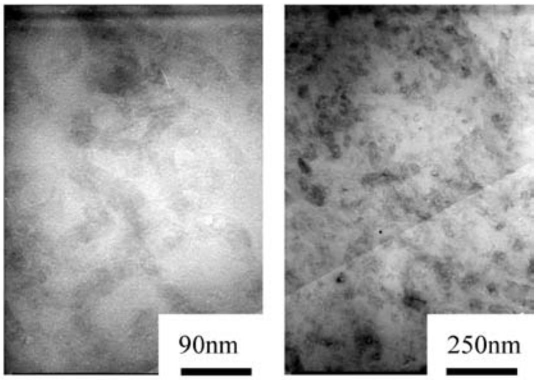


Figure 1 Vulcanization curve of the CNTs/silicone rubber.



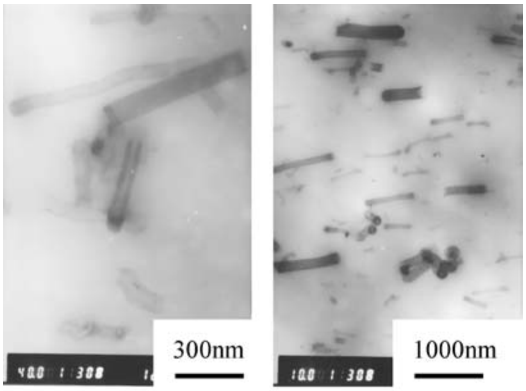
(1) Directly mixing method



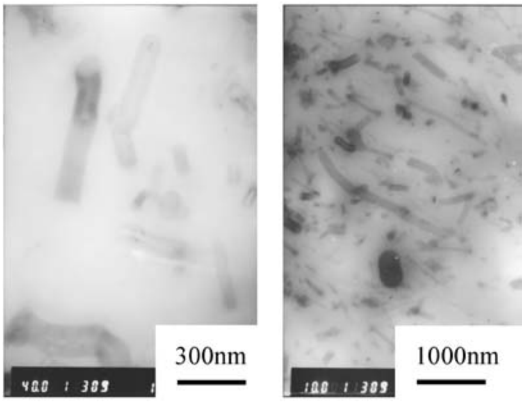
(2) Ultrasonic method

Figure 2 TEM micrographs of the CNTs/HNBR composites with 25 phr of CNTs prepared by the two dispersion methods.

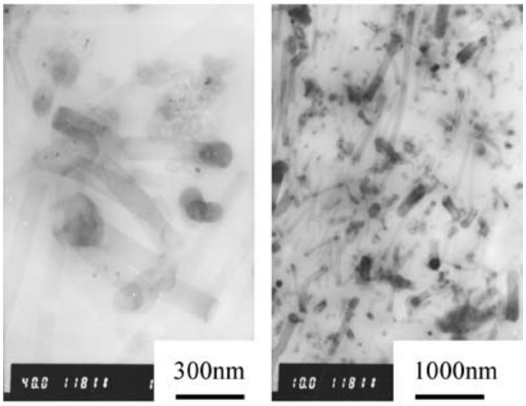
Two kinds of dispersing methods, directly mixing-dispersing and ultrasonic pre-dispersing technique, were utilized to prepare the CNTs/HNBR composites. The effects of the mixing methods and the content of CNTs on the dispersion morphology of CNTs in HNBR were characterized by TEM, shown in Figs 2 and 3. As can be clearly seen, the modified CNTs disperse very well in HNBR when the ultrasonic pre-dispersing technique is



(a) 7phr



(b) 15phr



(c) 25phr

Figure 3 TEM of the CNTs/HNBR composites with different contents of CNTs prepared by the ultrasonic method.

utilized to prepare the composites, and no apparent aggregations and entanglements of CNTs exist in HNBR, even at high CNTs loading. While using the directly mixing method, CNTs tend to entangle in HNBR. However, serious breakage of CNTs is also found, and is mainly caused by sequential mechanical processing, which exerts a strong shear stress on the dispersed CNTs with long aspect ratio. By this ultrasonic method, the nanocomposites of CNTs/HNBR was prepared.

The mechanical properties of the composites are listed in Table IV. Table IV shows that the tensile strength, stress at certain strain, hardness of the composites prepared by the ultrasonic method rise with increasing loading of CNTs. It can be concluded that CNTs have shown a great reinforcement effect to HNBR. Regulations of elongation at break and permanent set of composites with loading of CNTs better imply that the interfacial slippage between CNTs and rubber matrix takes place during the stretching of the composites due to the inert surface of CNTs, which results in the increase of permanent set and counteracts the macromolecules constraint caused by CNTs. Thus, developing advanced techniques to activate the surface of CNTs is a very important and challenging subject, especially in the view of reinforcement by means of CNTs.

TABLE IV Mechanical properties of the CNTs/HNBR[a] composites prepared by ultrasonic method

Loading of CNTs in HNBR (phr)	2	7	15	25
Hardness, Shore A	53	56	61	68
Tensile strength (MPa)	10.4	11.5	14.2	18.6
Elongation at break(%)	728	812	776	647
Stress at 100% strain, (MPa)	0.7	0.8	1.3	/
Stress at 300% strain (MPa)	0.8	1.5	4.1	7.0
Permanent set (%)	20	40	44	52

[a] Every composite contains 7 phr LHNBR.

CNTs can strongly absorb the liquid curing agent such as Varox, which subsequently caused a significant delaying of vulcanization of rubber, so the solid curing agent is more suitable for the CNTs/rubber composites, such as DCP. By using the ultrasonic technique to pre-disperse CNTs in LHNBR, the well-developed dispersion state of CNTs in HNBR was obtained, i.e., the CNTs/HNBR nanocomposites were successfully prepared. However, serious breakage of CNTs occurred during the mechanical mixing process. Fine dispersion and serious breakage of CNTs resulted in a general electrical conductivity of composite, which was not expected. Mechanical properties of composites cross-linked by DCP apparently increased with increasing of the content of CNTs.

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