Effect of Phenol Functionalization of Carbon Nanotubes on Properties of Natural Rubber Nanocomposites

P. Selvin Thomas,[1] Adedigba A. Abdullateef,[1] Mamdouh A. Al-Harthi,[1,2]
A. A. Basfar,[3] Sri Bandyopadhyay,[4] Muataz A. Atieh,[1,2] S. K. De[1]

[1]Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, 31261 Dhahran, Kingdom of Saudi Arabia
[2]Center of Research Excellence in Nanotechnology (CENT), King Fahd University of Petroleum and Minerals, 31261 Dhahran, Kingdom of Saudi Arabia
[3]Atomic Energy Research Institute, King Abdulaziz City for Science and Technology P.O Box 6086, Riyadh-11442, Kingdom of Saudi Arabia
[4]School of Materials Science and Engineering, University of New South Wales, Sydney-2052, Australia

ABSTRACT: This paper reports the results of studies on the effect of phenol functionalization of carbon nanotubes (CNTs) on the mechanical and dynamic mechanical properties of natural rubber (NR) composites. Fourier transform infrared spectrometry (FTIR) indicates characteristic peaks for ether and aromatic rings in the case of phenol functionalized CNT. Although differential scanning calorimetric (DSC) studies show no changes in the glass-rubber transition temperature (T_g) of NR in the nanocomposites due to surface modification of CNT, dynamic mechanical studies show marginal shifting of T_g to higher temperature, the effect being pronounced in the case of functionalized CNT. Stress-strain plots suggest an optimum loading of 5 phr CNT in NR formulations and the phenolic functionalization of CNT does not affect significantly the stress-strain properties of the NR nanocomposites. The storage moduli register an increase in the presence of CNT and this increase is greater in the case of functionalized CNT. Loss tangent showed a decrease in the presence of CNT, and the effect is more pronounced in the case of phenol functionalized CNT. Transmission electron microscopy (TEM) reveals that phenol functionalization causes improvement in dispersion of CNT in NR matrix. This is corroborated by the increase in electrical resistivity in the case of phenol functionalized CNT/NR composites. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2370–2376, 2012

Key words: natural rubber; carbon nanotubes; functionalization; dynamic mechanical properties

INTRODUCTION

Natural rubber (NR) exhibits outstanding properties such as green strength and tensile strength because it can crystallize spontaneously when it is strained. Rubbers are of great industrial importance due to the high and reversible deformability. However, the modulus and durability of raw rubber is low, and compounding it with reinforcing agents followed by crosslinking is essential for making it suitable for practical applications. Rubbers are usually reinforced with high amounts of carbon black and amorphous silica.[1–4] It is anticipated that the mechanical and physical properties of a rubber may be improved by addition of much less amount of fillers, if microscale fillers are replaced by nanoscale fillers. For example, incorporation of 10 wt % layered silicates in natural rubber resulted in significant increase in modulus.[5]

Although CNT has evoked much interest as a reinforcing filler in rubbers due to their outstanding physical and mechanical characteristics, its dispersion in rubbers is poor due to the high aspect ratio and agglomeration characteristics of CNT.[6–10] Methods to achieve improvement in the dispersion of CNT in the polymer matrix include use of dispersion aids or surface active agents and chemical functionalization of the CNT surface.[11–13]

Sui et al. fabricated CNT/NR nanocomposites through solvent mixing followed by a two-roll mill compounding and observed an increase in mechanical properties of the CNT/NR nanocomposites as compared to the neat NR.[14] Tonpheng et al. recently reported that liquid polyisoprene (PI) and its carbon nanotube (CNT) composites (1–20 wt %) can be crosslinked into network polymers by high pressure treatment and observed that the tensile strength and Young's modulus of PI increased with increasing pressure for the crosslink process, with a simultaneous
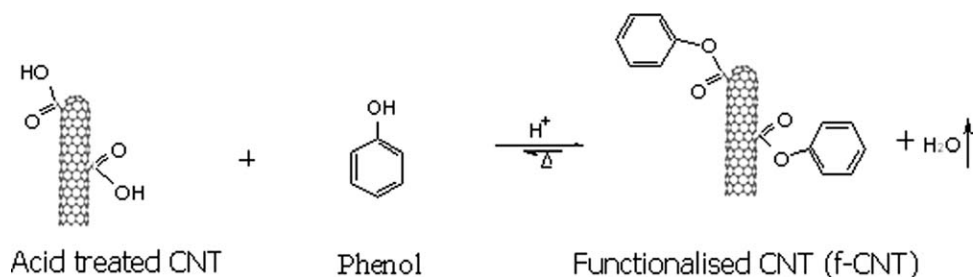
Scheme 1 Modification on CNT surface with phenol.

change in the composite behavior from elastomeric to brittle behavior.[15] Peng et al. adopted a self-assembly process combining latex compounding technique to develop NR/CNT composites and observed an increase in tensile strength and modulus in the presence of CNT.[16]

Polymer properties can be improved when CNT surface is modified by acid treatment and the carboxylic functionalized CNT can be further modified by reacting with thionyl chloride, followed by treatment with amines.[17–20] A recent publication reports the results of studies on carboxylic functionalization of CNT on the mechanical, dynamic mechanical, and electrical properties of CNT/NR composites.[21] The present article reports the results of studies on the effect of phenol functionalization of CNT on the mechanical and dynamic mechanical properties of NR nanocomposites and dispersion of CNT in NR matrix.

EXPERIMENTAL

Materials

Natural rubber used in this experiment is ribbed smoked sheet grade (RSS1) obtained from Amiantit Rubber Industries Ltd., Saudi Arabia, and CNT was purchased from Nanostructured and Amorphous Materials, Inc. USA. The purity of CNT is >95% and its outside and inside diameters are 10–20 nm and 5–10 nm, respectively, while its length is 10–30 μm. Toluene (98% purity), phenol (97% purity), nitric acid (69–71% purity), and sulfuric acid (98% purity) were of analytical grade and purchased from Sigma Aldrich.

Functionalization of CNT

CNT surface was functionalised in two steps. The first step was to incorporate —COOH functional groups onto the CNT to enhance its reactivity[11,12]; 1 g of CNT was treated with 10 mL of concentrated nitric acid at a temperature of 120°C for 48 h under continuous stirring by a magnetic stirrer. It was then washed with deionized water to remove excess nitric acid. In the second step, the acid-treated CNT was

reacted with phenol. This involves heating of phenol to its melting point in a reaction flask. Next CNT was added into the reaction flask using CNT–phenol ratio of 1 : 10 in parts by weight. The mixture was stirred for a few minutes and a few drops of sulfuric acid were added. The reaction was allowed to continue for 6 h. Then the resulting functionalised CNT was washed with toluene several times to remove any unreacted phenol, followed by washing with deionized water to remove any acid traces. The resulting CNT is designated as f-CNT and its characterization is discussed below. The schematic representation of the surface modification of CNT is given in Scheme 1.

Composite preparation

The composites were prepared by dissolving 25 g of natural rubber in 1000 mL of toluene. CNT in toluene was sonicated for 30 min to reduce the agglomeration of the nanotubes and was added to the dissolved rubber in concentrations of 1, 5, 10 g per 100 g of rubber. The NR/CNT mixture was mechanically stirred for 20 min for obtaining uniform dispersion and then dried in open air at room temperature. To study the effect of crosslinking, NR/CNT compositions as prepared above, were compounded using the vulcanization recipe as given in Table I. The compounding was done at 80°C for 15 min in a two-roll mill. Crosslinking (or curing) of the compounded samples was carried out in a hot press at 150°C for 30 min. NR compounds containing 1, 5, and 10% of CNT and f-CNT were molded on a hot press under a pressure of 350 kPa at a temperature of 150°C for 15 min to make flat sheets of 2-mm thickness. Five specimens each 35 mm in length and 2 mm in thickness were prepared from each batch and tested.

Characterization

CNT and f-CNT were characterized by using Fourier Transform infrared spectroscopy (PERKIN ELMER 16F PC FT-IR) instrument. FTIR samples were prepared by grinding dried CNT together with

TABLE I
Vulcanization Recipe for NR Composites

Component	Composition (phr)[a]
NR	100
CNT	0,1,5,10
Sundex oil[b]	10
ZnO[c]	4.8
Stearic acid	2.0
IPPD[d]	1.0
TMQ[e]	2.0
Wax	1.0
TMTD[f]	1.5
MBT[g]	0.5
Sulfur	0.4

[a] phr stands for parts per hundred parts rubber by weight.
[b] Processing oil.
[c] Zinc oxide (activator).
[d] N-isopropyl-N′-phenyl-paraphenylenediamine (antioxidant).
[e] 2,2,4-Trimethyl-1,2-dihydroquinoline (antioxidant).
[f] Tetramethyl thiuram disulfide (accelerator).
[g] 2-Mercaptobenzothiazole (accelerator).

potassium bromide (KBr) to make a pellet. The thermal properties of the composites were measured by using differential scanning calorimetry TA instruments (DSC-Q1000). Samples weighing about 7–9 mg were sealed in aluminum nonhermetic pans for the DSC measurements. The measurements were done in the temperature range of −80 to 100°C at a heating rate of 10°C/min under nitrogen environment with a flow rate of 50 mL/min. The obtained data was analyzed using the universal analysis 2000 software from TA instruments. Tensile tests were carried out on the cured samples using Zwick tensile testing machine with a specimen grip of 50 mm and testing speed of 500 mm/min following ASTM D412. Dynamic mechanical tests were conducted in tension mode using DMA Q800 (TA instruments) in the temperature range from −120 to 100°C at a frequency of 1 Hz and an amplitude of 10 μm.

To study dispersion of CNT in the NR matrix, Philips CM200 TEM was used with a field emission gun (FEG), which provides very high resolution for the TEM measurements under high vacuum. The samples were prepared using a Leica FC6 Cryo-ultramicrotome. A small piece of the sample was mounted in cellulose and was cut into slices of 60-nm thickness by a diamond knife. The DC volume resistivity of the composite materials having a wide range of resistivity were measured using instruments Agilent 4339B (high resistance meter attached with Agilent 16008B resistivity cell) for measurement range covering from 10^{16} to 10^6 ohm and GOM-802 (GW Instek DC milli Ohm Meter) attached with a home-made electrode in a measurement range from 10^6 to 10^{-3} ohm.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of CNT and f-CNT. The IR spectrum of CNT shows absorption band at 2920 cm^{-1} which is attributed to asymmetric and symmetric CH$_2$ stretching, 1698 cm^{-1} assigned to carboxylic C=O stretching and 1097 cm^{-1} corresponding to C—O stretching in alcohols. The presence of these functional groups on the surface of CNT indicates their introduction during removal of metal catalysts in the purification processes of CNT.[22,23] Carboxylic C=O stretching peak observed at 1693 cm^{-1} can be attributed to acid treatment of CNT. Further treatment of CNT with phenol gives peaks at 3493, 1646, 1452, 1229, 831, 812, 748, and 692 cm^{-1}. The peak at 3493 cm^{-1} corresponds to the —OH groups present on the CNT surface. The doublet peak at 1646 cm^{-1} corresponds to the phenol groups and a quartet around 830–690 cm^{-1} corresponds to the aromatic ring generated from the surface modification. The ether groups generated from the reaction between the phenol and —COOH groups in the CNT (Scheme 1) is represented by the peaks around 1230 and 690 cm^{-1}.[24–26]
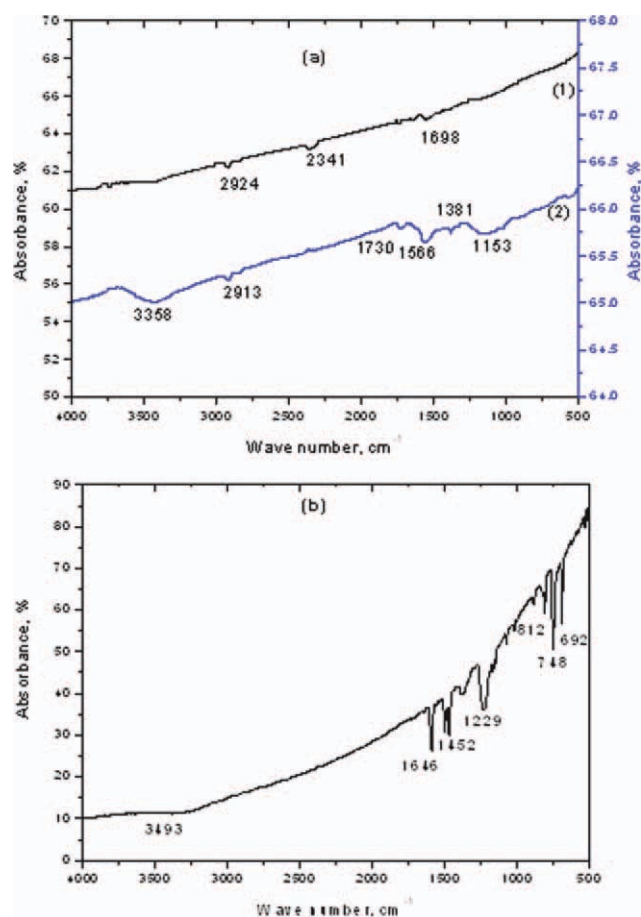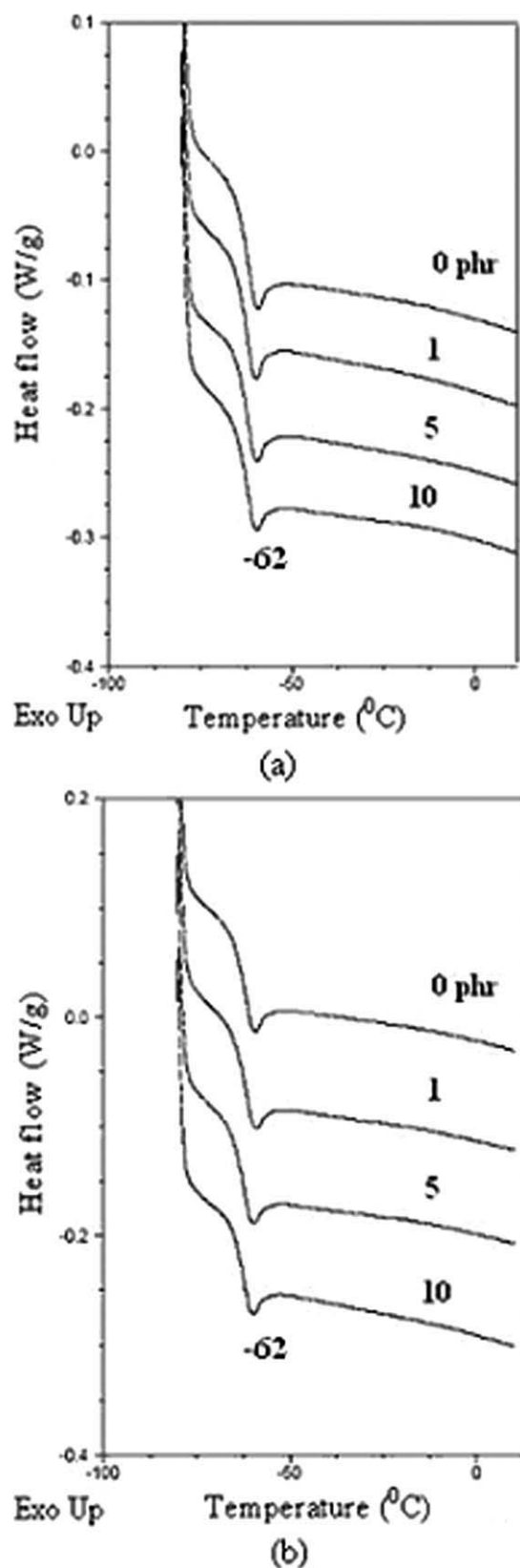

Figure 1 FT-IR spectra of (a) CNT (1) and acid modified CNT (2) and (b) phenol funtionalized CNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2 DSC thermograms of NR composites with (a) CNT and (b) phenol functionalized CNT.

Figure 2 shows the DSC heating curves of the composites with CNT as well as f-CNT. It is to be noted that the T_g of NR occurring at $-62°C$ remains unaltered in the presence of both CNT and phenol functionalised CNT. Presence of fillers such as carbon black has been reported to have no effect on T_g determined by the static method.[27] CNTs are found to behave similar to carbon blacks in this regard.

Stress–strain curves of the NR composites are given in Figure 3 and the results are summarized in Table II. The tensile strength of the composites shows an increase on incorporation of 1 phr of CNT, while higher loading of CNT causes a decrease in tensile strength. Incorporation of CNT causes an increase in Young's modulus of the composites at all loadings, while the elongation at break decreases at higher filler loadings. Phenol modification of CNT causes an increase in modulus at all loadings of CNT. But tensile strength shows a maximum at a loading of 5 phr beyond which it decreases, while the elongation at break shows a gradual decrease
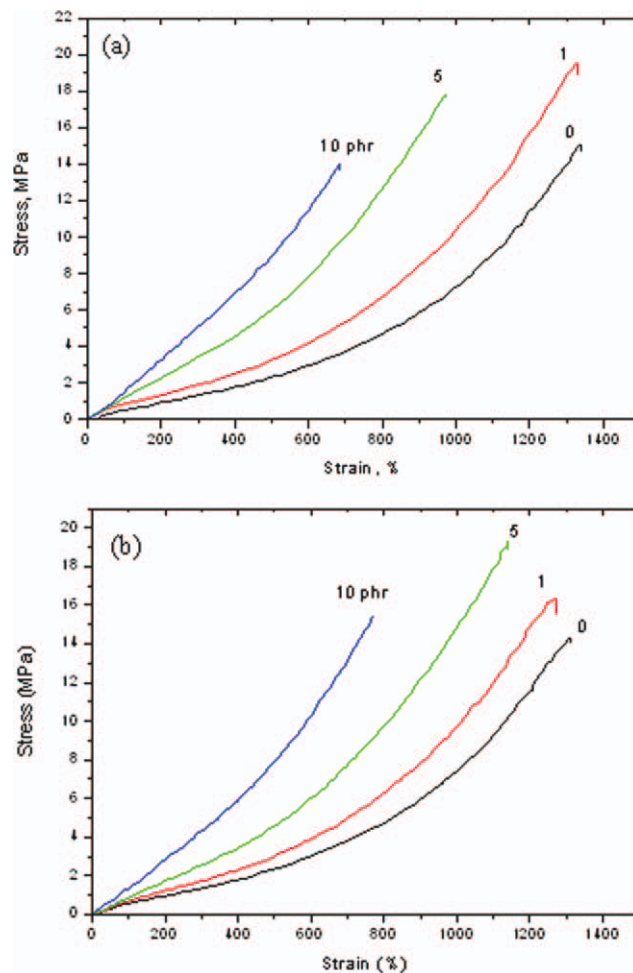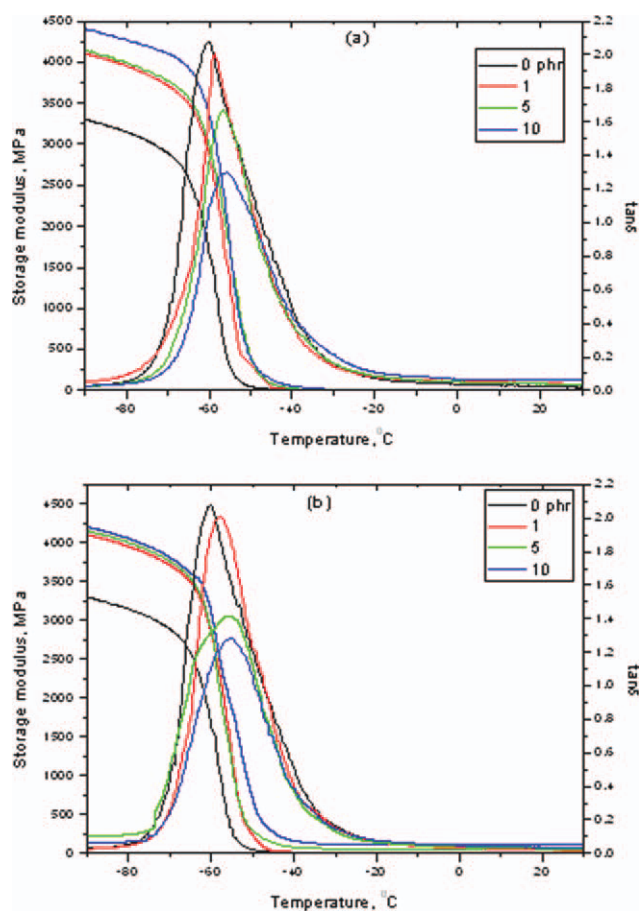

Figure 3 Stress-strain curves of NR composites with (a) CNT and (b) phenol functionalized CNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CNT loading (phr)	Tensile strength (MPa)	Modulus at 100% elongation (MPa)	Elongation at break (%)
0	14.9	0.5	1332
1	19.4 (16.3)	0.7 (0.7)	1271 (1278)
5	18.0 (19.2)	1.0 (1.2)	978 (1140)
10	15.4 (15.6)	1.1 (1.5)	727 (773)

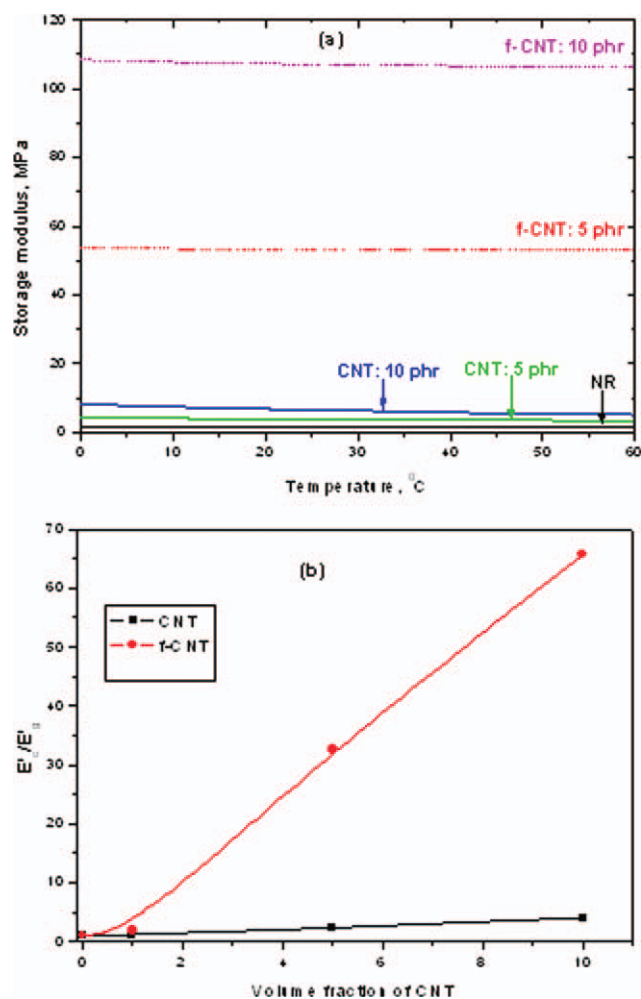[a] The values in parentheses correspond to the composites with phenol functionalised CNT

with increase in CNT loading. Sui et al. reported an increase in tensile strength in the case of CNT-reinforced NR.[14] Conventional reinforcing fillers in rubbers such as carbon blacks are known to cause increase in modulus with consequent decrease in elongation at break. In the case of natural rubber, tensile strength does not change significantly in the presence of reinforcing fillers, contrary to observations made with noncrystallizing rubbers such as styrene-butadiene rubber.[2] It is found that CNTs behave similar to carbon blacks in natural rubber

with regard to stress–strain properties, but the changes in the properties occur at much lower loadings than the carbon blacks.

Dynamic mechanical properties of the composites were measured to study the effect of CNT on the storage modulus and tan δ of NR. Figure 4(a,b) show the effect of surface modification of CNT on storage modulus and tan δ of the composites at different temperatures. Figure 5(a) displays the effect of phenol-functionalization of CNT on the variation of storage modulus in the temperature range of 0° to 60°C. Storage modulus values at room temperature are summarized in Table III. It is evident that the storage modulus increases in the presence of CNT and the effect is more pronounced in the case of phenol functionalized CNT. Figure 5(b) shows the variation of the ratio of E_c/E_o against filler loading at 25°C, where E_c is the storage modulus of the composite and E_o is the storage modulus of unfilled NR

Figure 4 Storage modulus and tan δ plots of NR composites with (a) CNT and (b) phenol functionalized CNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 Effect of phenol functionalization of CNT on variation of (a) storage modulus from 0° to 60°C and (b) E'_c/E'_o with filler loading at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Effect of CNT and Functionalized CNT on Storage
Modulus and Loss Tangent of NR Composites[a]

Loading of CNT (phr)	Storage modulus at 25°C (MPa)	$(Tan \delta)_{max}$	Temperature at $(tan \delta)_{max}$, °C[b]
0	1.6	2.1	−60
1	1.9 (2.0)	2.0 (2.0)	−58 (−57)
5	3.8 (53.2)	1.6 (1.4)	−57 (−56)
10	6.5 (107.1)	1.3 (1.2)	−55 (−54)

[a] The values in parentheses correspond to the composites with phenol functionalised CNT.
[b] Corresponds to glass–rubber transition determined by loss tangent measurements.

(that is, in the absence of carbon nanotubes). It is evident that with increase in filler loading the ratio increases slowly in the case of CNT, but the increase is sharp in the case of phenol functionalized CNT, indicating improved adhesion between NR and CNT in the case of phenol functionalized CNT. It is also evident from Figure 4 that tan δ decreases in the presence of CNT, but the decrease is more pronounced in the case of phenol functionalized CNT, particularly at high loadings (Table III), indicating pronounced filler-matrix adhesion.[28,29] It was found that the glass-rubber transition shifts marginally to higher temperature in the case of phenol functionalized CNT (Table III), which is indicative of improved filler-matrix adhesion although the phenomenon was not displayed in DSC studies.[30,31] Figure 6 depicts the values of the ratio of $(tan \delta)_c/(tan \delta)_o$ at different filler loadings, where $(tan \delta)_c$ is the $(tan \delta)_{max}$ for the composite and $(tan \delta)_o$ is the same for the unfilled NR. The lower ratio $(tan \delta)_c/(tan \delta)_o$ in the case of phenol functionalized composites in all loadings is indicative of improved filler-rubber bonding.[32,33]
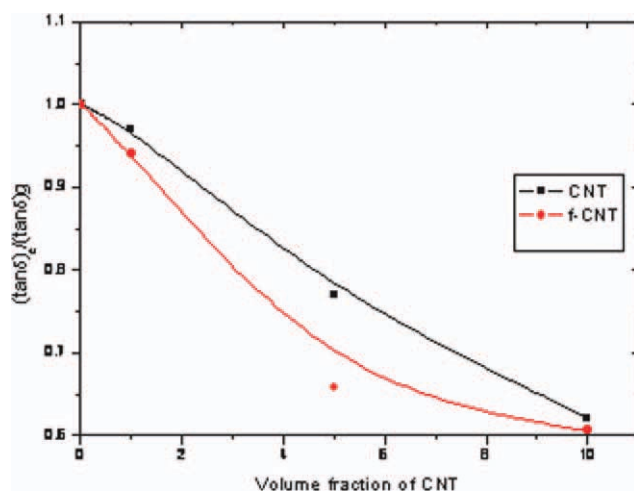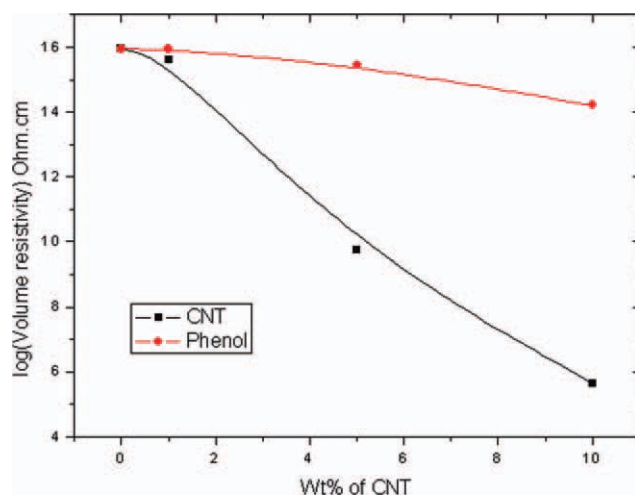

Figure 6 Effect of phenol functionalization of CNT on variation of $(tan \delta)_c/(tan \delta)_o$ with filler loading at T_g. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TEM images of representative composites are given in Figure 7. It is found that the dispersion CNT shows improvement in the case of phenol modified CNT, as compared to unmodified CNT. This is further corroborated by the results of the electrical resistivity measurements. Figure 8 shows that volume resistivity decreases on incorporation of CNT. Electrical resistivity is dependent on the degree of dispersion of electrically conductive fillers such as carbon black.[34] Higher is the degree of dispersion of the fillers; lower is the resistivity of the corresponding rubber composites, since the filler-filler contacts are broken down with increase in the
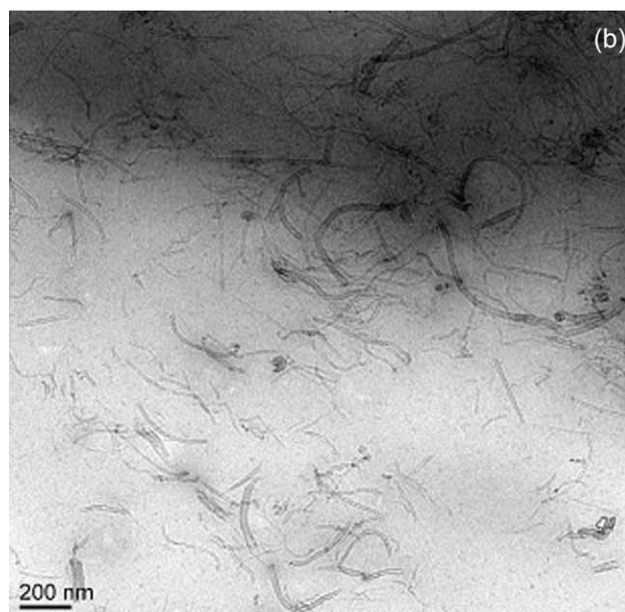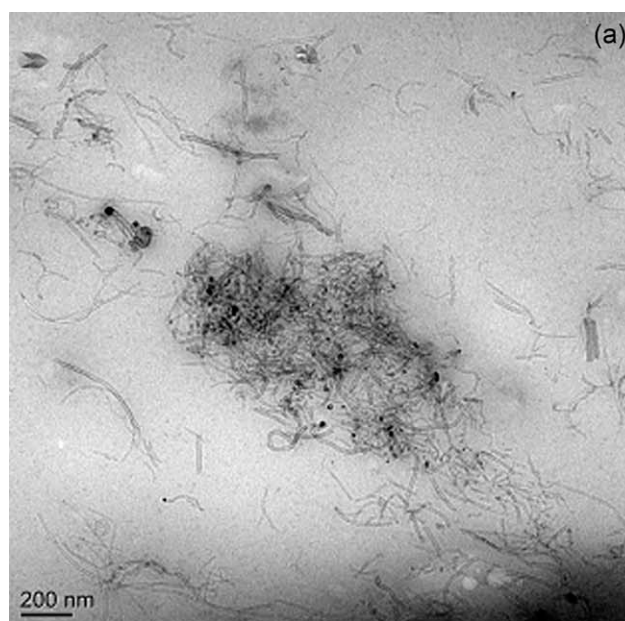
Figure 7 TEM images of CNT/NR composites containing 1 wt % filler (a) CNT and (b) phenol functionalized CNT.

Figure 8 Plots of volume resistivity of CNT/NR and phenol functionalized CNT/NR composites at 25°C versus filler loading [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degree of dispersion.[2,35,36] It has been reported earlier by Sui et al. that bonding between the CNT and the NR matrix is of physical nature.[14] Rajeev and De reported that the breakdown of filler-filler networks results in filler-matrix adhesion efficiency.[29]

CONCLUSIONS

To weaken the filler-filler agglomeration in CNT, the CNT surface was phenol functionalized. The CNT-NR nanocomposites were prepared by solvent mixing followed by two-roll compounding. Incorporation of CNT in NR matrix causes an increase in static modulus with consequent decrease in elongation at break. But the tensile strength reaches a maximum at a loading of 5 phr, beyond which the strength decreases. The dynamic modulus of the nanocomposites increases with increase in CNT loading and the effect is more pronounced in the case of functionalized CNT. Functionalization of CNT causes manifold increase in the ratio of storage modulus of the CNT/NR composite at room temperature to that of neat NR at all CNT loadings, indicating improved filler-matrix adhesion. This is corroborated by the drop in the ratio of the tangent loss at T_g of the CNT/NR composite to that of the neat NR at all CNT loadings. TEM and electrical resistivity measurements indicate improved dispersion of CNT in NR matrix upon phenol functionalization.

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