

Curing enhancement and network effects in multi-walled carbon nanotube-filled vulcanized natural rubber: evidence for solvent sensing

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Abstract

Electrically and thermally conductive polymer composites offer great possibilities in various electronic fields because of their low weight and ease of processing. This paper addresses the curing behaviour and network properties of conducting multi-walled carbon nanotube (MWCNT)-reinforced natural rubber (NR) nanocomposites, emphasizing the sensing and diffusion performances. NR/MWCNT composites were prepared following a special master batch technique which allows the appropriate distribution of nanotubes within the elastomer. The sensing responses of the composites towards solvents were observed as variations in electrical resistance. Thermal resistance and glass transition behaviour were examined and correlated with the swelling measurements as evidence for solvent sensing. An optimum level of 3 phr of MWCNTs is understood to lead to the best properties for the NR/MWCNT composites. Finally, the structural morphology and interfacial interactions were found to have correlations with cure reactions, glass transition temperatures and sensing responses of all compositions.

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Supporting information may be found in the online version of this article.

Keywords: rubber; solvent sensing; curing; nanotubes; filler networks

INTRODUCTION

Rubber composites exhibit combined properties of the soft, elastic rubber matrix and the stiff, strong filler particles. Fillers of various dimensions are used to fabricate such composites of which carbon-based nanofillers are of the utmost importance.¹ This is because of the superior electrical, thermal and dielectric properties imparted to rubbers by these fillers and their very high mechanical strength.² Electrically conducting rubber composites find applications in electrostatic charge dissipation, touch control switches, electromagnetic induction shielding and surface heaters.³ Among the rubbers, natural rubber (NR) is the one most studied due to its ease of availability and processability. Though NR possesses very high and reversible deformability, its poor gum strength and modulus call for extra reinforcement.^{4,5}

The structural characteristics of carbon nanotubes (CNT) include large specific surface area, superior mechanical properties and very high thermal conductivity.^{6,7} CNTs are often incorporated into hierarchical structures to achieve many outstanding breakthroughs in technology ranging from consumer products like textiles to engineering designs like space elevators. CNTs belong to two classes: single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). Generally, MWCNTs are largely used in fabricating rubber composites due to their larger property variation when compared to SWCNTs.⁷ In addition, MWCNTs are good for dispersing in non-polar rubber media. The electrical properties, mechanical

strength and dielectric and sensing behaviour for NR/MWCNT composites are well established.⁸

When MWCNTs are dispersed uniformly in a polymer matrix, interconnecting filler networks are formed, trapping the elastomer molecules within. This happens at very low filler concentrations for MWCNTs and is marked by a sudden drop in electrical resistivity.^{9–11} Apart from achieving superior electrical conductivity, the MWCNTs (when properly aligned) enable the NR to show better thermal conductivity as well.¹² Multifunctional composite materials made by dispersing MWCNTs in NR using anionic surfactant were fabricated by Matos *et al.* They used a specific family of MWCNTs, the cavities of which were filled with nanowires of magnetic iron species and thereby developing magnetic, electrical and mechanical properties altogether in the same material.¹³

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Table 1. Composition of NR nanocomposites

Sample code	NR (phr)		MWCNT (phr)	ZnO (phr)	Stearic acid (phr)	MBTS (phr)	Sulfur (phr)
	From Master-batch	Added neat rubber					
NR	–	100	–	5	2	1.2	2.5
NR-1MC	10	90	1	5	2	1.2	2.5
NR-2MC	20	80	2	5	2	1.2	2.5
NR-3MC	30	70	3	5	2	1.2	2.5
NR-5MC	50	50	5	5	2	1.2	2.5

Here, latex stage mixing was done since the rubber was in the latex form. We have earlier reported the successful dispersion of nanotubes within a latex medium with the help of various surfactants and their influence on the filler network formation.⁴ Other than the latex stage mixing, rubber/CNT composites are prepared by other methods like solution mixing, melt blending, mill mixing, etc. In the matter of achieving intimate dispersion, solution mixing surpasses other methods; however, the use of organic solvents is not so preferred. Le *et al.* reported good level of interfacial interaction between the MWCNTs and the rubber chains by fabricating composites of MWCNTs with NR, deproteinized NR and a synthetic isoprene rubber using melt mixing.¹⁴ They demonstrated the role of non-rubber components like phospholipids in filler network formation and filler–polymer interfacial interactions.

In our previous work, we developed a specific master-batch technique which allowed the maximum distribution of MWCNTs within high-molecular-weight NR chains.¹⁵ It was found that the positron lifetime of such composites was significantly reduced in correlation with the decrease in number of voids due to good filler network formation. In addition, the mechanical and dielectric properties were also significantly enhanced. In the work presented here, NR/MWCNT composites were fabricated following the previously reported preparation method;¹⁵ however, the curing mechanism and thermal properties of the composites were investigated in detail. The present paper fully reports on the thermal characteristics of the rubber nanocomposites and correlates thermal behaviour with solvent swelling in terms of crosslink density. Swelling behaviour explains the swelling and network forming mechanism. The influence of temperature on the network formation is discussed with respect to the results of glass transition temperatures of the composites and swelling behaviour. Moreover, the application of the formulated composites for specific detection of organic solvents is demonstrated and discussed.

EXPERIMENTAL

Materials

Solid NR was procured from Rubber Board, Kottayam, India and MWCNTs from Nanoshel, Panchkula, India. Curing ingredients used for NR vulcanization were obtained from M/s Appollo Tyres while other additives used were purchased from M/s Sigma Aldrich.

Preparation of nanocomposites

The NR/MWCNT composites containing 1, 2, 3 and 5 phr of MWCNTs were prepared using a reported procedure.¹⁵ For this, about 110 g of neat NR was masticated in an open two-roll mill for 2 min, and then 11 g of MWCNTs was added into it and again mill-mixed for another 20 min. Afterwards, this master-batch was divided

in to five parts according to the ratio 1:2:3:5, and to each set was added neat NR to make the corresponding concentration of MWCNTs in the final composite as 1–5 phr. Each mixture was again mill-mixed for 16 min and curing agents such as zinc oxide (5 phr), stearic acid (2 phr), MBTS (1.2 phr) and sulfur (2.5 phr) were added during mixing. All composites were kept for 24 h to attain thermal stability (temperature equilibration) and then the curing tests were conducted. Table 1 summarizes the compositions of the prepared NR nanocomposites. The NR/MWCNT composites are indicated by NR-yMC, where y represents the corresponding filler concentration.

Characterization methods

Cure characteristics of the NR/MWCNT samples were investigated using a Monsanto R-100 moving die rheometer at a rotational frequency of 100 cycles min⁻¹. The curing was done at 160 °C in a hydraulic press according to the respective cure times of the samples obtained from the rheometer. The thermal properties of the composites were studied using TGA with a PerkinElmer Pyris 6 and DSC with a PerkinElmer DSC 8500. Swelling studies were conducted by keeping circular vulcanized nanocomposite samples of 1.8 cm in diameter in toluene at room temperature for 72 h (after 72 h, the swelling reached a saturation level). The weights were measured at regular intervals of time and the swelling ratio and diffusion coefficients were calculated. Sensing experiments were carried out at room temperature in a closed home-made chamber by measuring the electrical resistance values of samples in response to various solvents (introduced to the samples coated on interdigitated electrodes in <1 μL) using a Keithley 2400 series multimeter. Samples for analysing the morphology were prepared by sputter coating cryocut portions of the NR/MWCNT composite and images of the samples were obtained using SEM (JEOL JSM-6460LV).

RESULTS AND DISCUSSION

Cure kinetics

The cure kinetics and the processability of the NR/MWCNT composites were studied using rheographs.¹⁶ Vulcanization characteristics (minimum torque, maximum torque, scorch time and optimum vulcanization time) were determined on the basis of the vulcanization isotherms obtained using an oscillating disc rheometer. The maximum torque value indicates the extent of crosslinking and thus the stiffness of the composites. The maximum torque decreases initially (corresponding to the matrix rubber softening), then increases (corresponds to crosslinking) and thereafter becomes constant (cure reaction stops). This general trend is observed in this case as well.

Representative cure curves for the NR/MWCNT composites with variable MWCNT loading shown in Fig. 1 indicate the acceleration of NR vulcanization by the MWCNTs. This is observed from

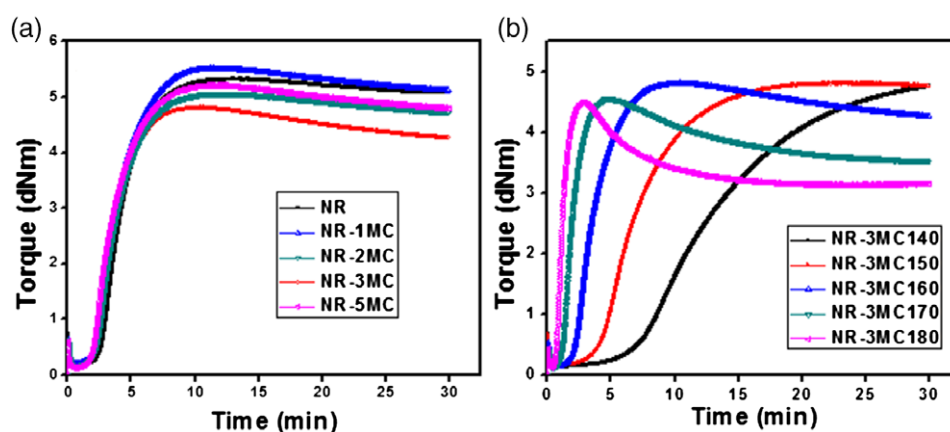


Figure 1. Rheographs of (a) NR/MWCNT composites at 160 °C and (b) NR-3MC at various temperatures from 140 to 180 °C.

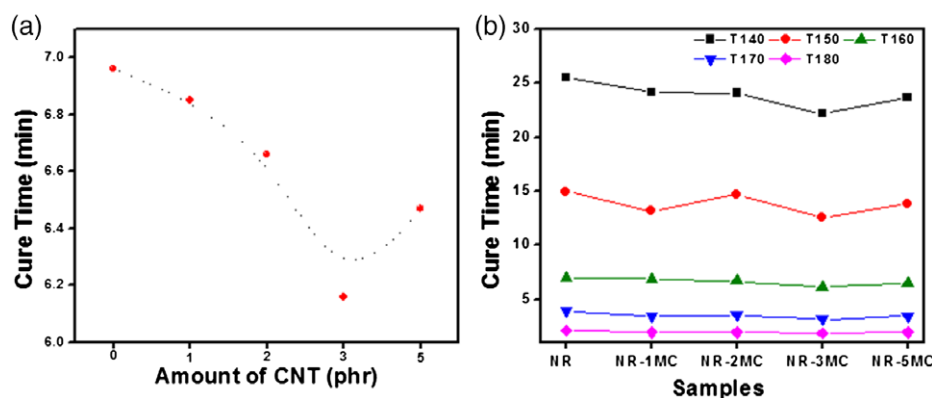


Figure 2. Variation of cure time with (a) MWCNT concentration and (b) temperature from 140 to 180 °C.

the curve shift towards shorter time with increasing filler concentration. Both the minimum and maximum torque values are also affected by the MWCNT concentration. For more clarity, all the vulcanization parameters, including the difference between minimum and maximum torque values, scorch time (T_{S2}), optimum cure time (T_{90}) and cure rate index, were determined (supporting information, Table S1).

It is interesting to note that the difference between maximum (T_H) and minimum (T_L) torque ($\Delta S = T_H - T_L$) increases immediately after the addition of 1 phr MWCNTs and decreases for further concentrations. The higher ΔS for NR-1MC compared to NR may be due to the resistance of the nanotubes towards polymer chain mobility.¹⁷ Or in other words, MWCNTs start making crosslinks within the rubber chains and thus torque becomes enhanced. However the behaviour at higher filler percentages is somewhat different from that of the usually expected polymer composite curing. In the case of NR-2MC and NR-3MC, the concentration of CNTs is becoming rather high to cause good plasticization effect. But at higher energy conditions, NR can also undergo chain scission, thus causing both the viscosity and torque to decrease. The lowest ΔS is observed for NR-3MC and this can be due to the good level of dispersion and better interfacial compatibility at this filler concentration in addition to the chain scission of NR. At 5 phr MWCNTs, the nanotubes start to aggregate and again resist NR chain mobility and increase the torque.

The scorch time (T_{S2}) is a measure of premature vulcanization and here its value is lower for the nanocomposites compared to neat NR. This is due to the participation of MWCNTs in the network

formation within the NR molecular chains and thus increasing the vulcanization rate.¹⁸ Or in other words, the MWCNTs behave like vulcanizing accelerators for NR. Among the nanocomposites, this increases with filler concentration, due to the higher filler contents (cure reaction can also happen within the filler networks), and at 5 phr MWCNTs the scorch time is the lowest because of the large amount of filler aggregates.

The optimum cure time (T_{90}) decreases with concentration of MWCNTs at 160 °C (supporting information, Table S1). This also points towards the acceleration of curing by the nanotubes. The lowest cure time is observed for the NR-3MC composite and again an increase in concentration delays the curing. For better understanding, the cure times for the samples are shown in Fig. 2.

Various parameters can be calculated from the torque–time curves and from the curing data. The cure rate index is calculated from the optimum cure time and scorch time, as per the following equation:

$$\text{Cure rate index} = \frac{100}{T_{90} - T_{S2}} \quad (1)$$

The cure rate index increases from 30.30 min^{-1} (neat NR) to 33.44 min^{-1} (NR-3MC) whereas it decreases to 28.82 min^{-1} for NR-5MC at 160 °C. The increased cure rate index for the NR-3MC composite is attributed to the increase in chemical crosslinks due to the interaction of MWCNTs with the NR matrix. This crosslinking during vulcanization can only happen at a higher temperature, whereas at room temperature or at lower temperatures MWCNTs act as reinforcing agents and cause comparatively higher viscosity and torque values.

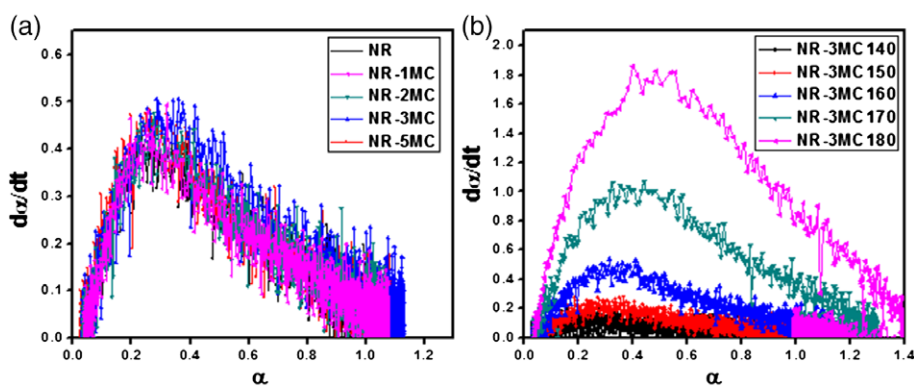


Figure 3. Vulcanization rate, $d\alpha/dt$, versus α curves of (a) NR and NR/MWCNT composites and (b) NR-3MC composite at various temperatures.

The cure characteristics of all composites were also studied at various temperatures. The influence of temperature on the torque of the composites is illustrated in Fig. 2(b). The rheographic profile of NR/MWCNT at a specific concentration of 3 phr and at different temperatures shows the variation in the onset of vulcanization. At lower temperatures, the vulcanization starts after a long time, and with increasing temperature the onset of vulcanization happens in a short time. Based on this, the optimum temperature was selected as 160 °C for curing and the samples were cured at this particular temperature for analysis of thermal properties and diffusion. The cure parameters at various temperatures are also included in the supporting information (Table S1). It is found that the trend in ΔS , T_{90} and T_{52} is almost the same for all the NR/MWCNT composites. However, with temperature, the parameters widely vary due to the change in the viscoelasticity of the medium. As the temperature increases, the molecules get enough kinetic energy and the chain structure loosens and torque value decreases. At higher temperatures, the sulfur atoms can also get inside the polymer chains and can make better networks. This is why the scorch time and cure time are found to be very low and the cure rate index high.

Since the cure reaction happens through multiple steps like onset of curing, curing and over-curing, the kinetic aspects of the cure reaction will be very useful for deriving the mechanism of curing in more detail. Based on the experimental results, the kinetic parameters of the composite systems were evaluated using a theoretical model.¹⁷

The degree of curing (α) at a time t is defined as¹⁹

$$\alpha = \frac{S_t - S_0}{S_h - S_0} \quad (2)$$

where S_0 , S_t and S_h are the torque values at zero time, at a specific time and at the end of curing reaction. This equation is based on the fact that the crosslinking density is proportional to the stiffness of the rubber composite.

Following the work of Shanmugaraj *et al.*,¹⁷ the autocatalytic kinetics model²⁰ is used here to study the isothermal vulcanization kinetics. This particular model as represented by Eqn 3, assuming the maximum reaction rate occurring at any point of time other than zero:

$$\frac{d\epsilon}{dt} = k(T) \alpha^m (1 - \alpha)^n \quad (3)$$

where k is the specific rate constant and m and n are, respectively, the reaction orders of autocatalytic and non-autocatalytic reactions. All parameters depend on temperature.

Figure 3 shows the variation of $d\alpha/dt$ against the degree of conversion for neat NR and NR/MWCNT nanocomposites. Figure 3(a) compares the $d\alpha/dt$ values among the NR composites. It is found that all the composites follow the same behaviour of curing with the maximum conversion α_{max} between 0.3 and 0.4. However, the maximum value is observed to be 0.35 for the NR-3MC composite. The experimental results were fitted with theoretical calculations as well. Close fitting with correlation coefficient almost equal to the numerical value is observed for the composites.

Figure 3(b) exhibits the variation in $d\alpha/dt$ with α for the NR-3MC composite at various temperatures. At any temperature, the reaction rate increases with the degree of conversion and reaches a maximum at conversions between 0.3 and 0.5. This is an indication of the autocatalytic characteristics of the curing reaction. Since the conversion rate depends on both unreacted and reacted materials, maximum reaction can occur at any time, after the commencement of the reaction. It is also clear from Fig. 3(b) that the cure rate *versus* conversion curves very much depend on temperature. With increasing temperature, the peak height increases, reaching a maximum of 0.45 at 180 °C. This influence of temperature on the vulcanization process is due to the lower viscosity (due to NR chain scission) at higher temperature which allows the formation of crosslinks between adjacent polymer chains.²¹

Temperature dependence of curing can be further explained by Arrhenius equations, which relate the rate constant (K) with temperature and are expressed as follows:

$$K = Ae^{-E_a/RT} \quad (4)$$

$$\ln K = \ln A - \frac{E_a}{RT} \quad (5)$$

where A is the pre-exponential factor. The Arrhenius plots of $\log K$ *versus* $1/T$ shown in Fig. 4 can be used to calculate the activation energy (E_a) which is a measure of the ease of crosslinking. From the slope of the curves, it is found that the activation energy of neat NR decreases with MWCNT loading. The lowest value of activation energy for NR-3MC is attributed to the maximum crosslinking occurring in this particular system.

All the cure kinetic parameters show a gradual increase in reaction rate constants and reaction orders of all composites with temperature. It is established that the MWCNTs can absorb some basic accelerator species during rubber vulcanization and its high surface-to-volume ratio imparts better physical interactions with NR and thus restricts the movement of rubber molecular chains.²² This is the reason for the higher activation energy and curing

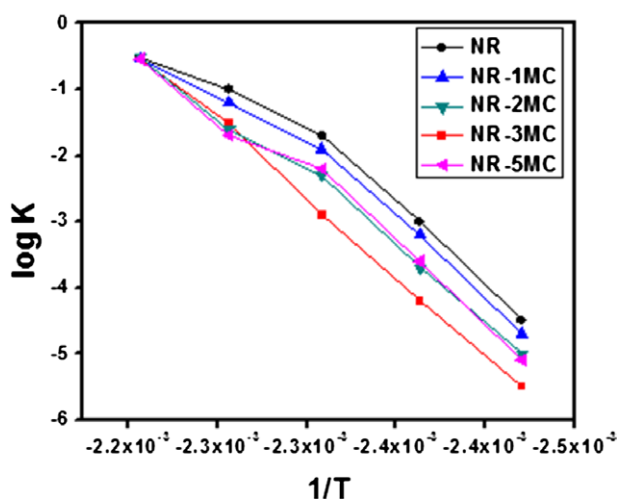


Figure 4. Plots of $\log K$ versus $1/T$ of neat NR and NR/MWCNT nanocomposites.

reaction for the MWCNT composites. Higher curing of NR-3MC is attributed to the uniform dispersion of MWCNTs within the matrix which provides good networking.

Thermal properties of NR and NR/MWCNT nanocomposites

CNTs are well established for their excellent thermal properties and for imparting good thermal stabilities to various polymers.²³ Here the thermal stability and the influence of MWCNTs on glass transition of the NR/MWCNT composites were investigated using TGA and DSC, respectively.

Figure 5(a) shows the TGA curves for neat NR and its MWCNT composites. All the composites show similar behaviour with a final degradation at about 450 °C. The mass loss and corresponding

Table 2. Mass loss, degradation temperature and glass transition temperature for NR and its NR/MWCNT composites

Sample	Degradation temperature (°C)	Glass transition temperature, T_g (°C)
NR	350.1	-56.5
NR-1MC	349.8	-56.9
NR-2MC	349.7	-57.0
NR-3MC	349.5	-57.5
NR-5MC	349.8	-57.9

temperature are presented in Table 2. Here the degradation temperature is given based on the initial step of mass loss. There is only a slight change in the temperature confirming the similar loss in mass for all samples due to NR chain scission. After this degradation, about 50% of the samples were gone. It can also be seen that the addition of MWCNTs does not improve the thermal stability of NR to a great extent.²⁴ However, at lower MWCNT concentrations, the composites are more similar to neat NR in the final degradation products. This is related to the concentration of MWCNTs in the NR composites. In order to get a clear picture about the thermal degradation, derivative thermogravimetry curves were obtained and are shown in Fig. 5(b). At a certain temperature the weight loss for the NR/MWCNT composites is smaller than that of neat NR, which can be attributed to the mobility of rubber molecular chains being restricted by MWCNTs. In addition, the MWCNTs conduct heat homogeneously and avoid concentration of heat. A shoulder observed near 450 °C for all samples can be attributed to the decomposition of NR hydrocarbon chains.

DSC was carried out based on the fact that the heat of a reaction is due to crosslinking within the system and is proportional to the extent of the reaction. The DSC curves obtained for the various MWCNT composites are shown in Fig. 5(c). Though the

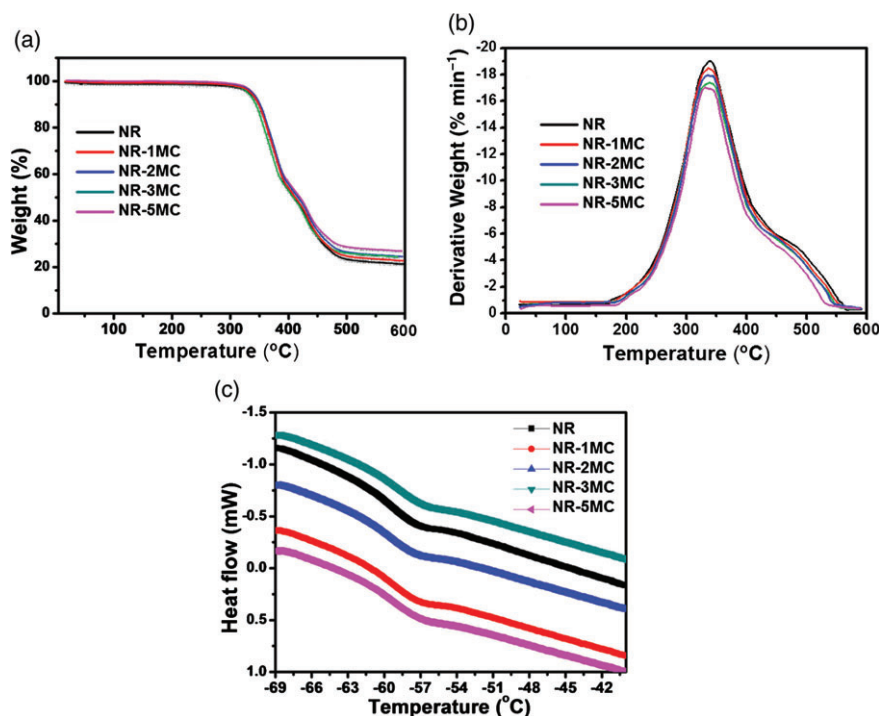


Figure 5. (a) TGA, (b) derivative thermogravimetry and (c) DSC curves of NR and NR/MWCNT composites.

composites appear to have similar glass transition behaviour, there is a slight variation in the glass transition temperature (Table 2). Neat NR and NR-1MC appear to have the same behaviour, as the lower percentage of MWCNTs is not enough for making good networks within NR. For the NR-3MC composite, the glass transition is higher than that for NR which is attributed to the enhanced crosslinks coming from the good dispersion of MWCNTs in NR. The agglomeration occurring in NR-5MC again restricts the cooperative motion of polymer chain segments and this is the reason why there is a regular increasing trend for the glass transition temperature values.

Solvent sensing characteristics

Sensing performance of samples was investigated in terms of electrical resistance variation before and after the introduction of solvent. Quantitative estimation of the sensing response is realized using the following equation:

$$A_R = \frac{R - R_0}{R_0} \quad (6)$$

where A_R is the relative resistance change, R is the electrical resistance of the sample in the presence of the solvent and R_0 is the initial sample resistance.

Experiments were conducted by clamping the sample (dried on an interdigitated electrode containing two terminal wires on both sides connected to a Keithley multimeter) in a closed chamber maintained at room temperature. A drop of solvent is introduced on the top of the sample through a micro-syringe placed at the top side of the chamber. Three organic solvents – benzene, toluene and *p*-xylene – were selected for analysis.

In order to exhibit a sensing response through resistance change, the sample should possess a minimum electrical conductivity. This is established in terms of the concentration of conducting filler particles in the matrix and mentioned as percolation threshold. For this reason, the sample containing 3 phr of MWCNTs was selected for the sensing experiments, the variation in electrical resistance of which is presented in Fig. 6. Benzene gives the maximum change in relative resistance due to its easy penetrating capability (low molecular weight) into the NR matrix. In contrast, xylene possesses comparatively higher molecular weight and thus exhibits less penetrating efficiency.⁸ In addition, the two -CH_3 groups in xylene cause steric hindrance and it has higher dipole moment when compared to benzene. The decrease in relative resistance seen in the case of toluene can be attributed to its faster rate of interaction with NR (toluene is a good solvent for NR). The mechanism of sensing is further substantiated with swelling performance.

Swelling and diffusion of NR/MWCNT composites

Swelling studies of the NR/MWCNT composites using toluene as solvent give information on the filler–polymer interfacial interactions, degree of filler dispersion and filler alignment in the matrix. The swelling index is a measure of swelling and is calculated using

$$\text{Swelling index (\%)} = \frac{m_s - m}{m} \times 100 \quad (7)$$

where m and m_s are, respectively, the weights of rubber composite sample before and after swelling.

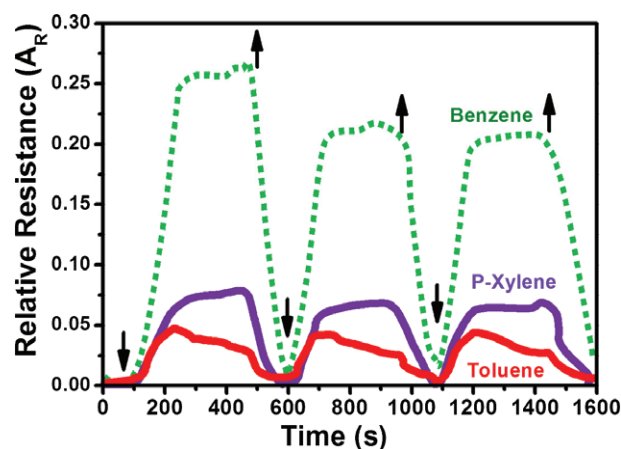


Figure 6. Variation in relative resistance of NR-3MC in presence of benzene, toluene and *p*-xylene. The downward and upward arrows, respectively, represent the application of solvent and its removal by heating.

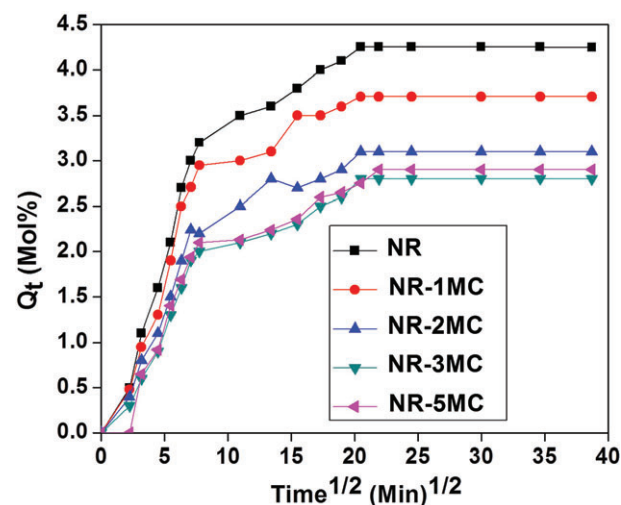


Figure 7. Variation of uptake of toluene with MWCNT loading for NR and NR/MWCNT composites.

Another parameter called the solvent uptake was also calculated using the following equation:

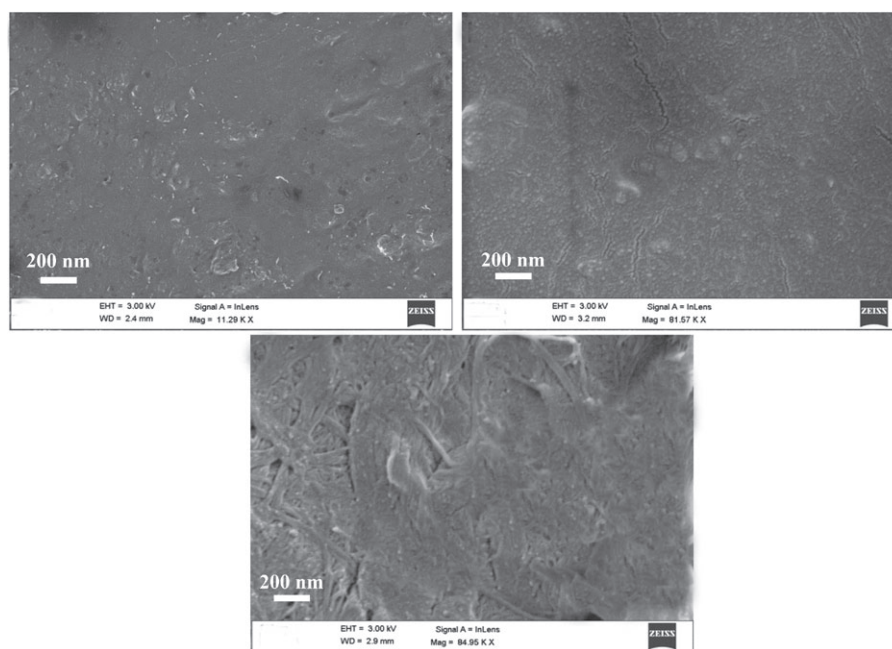
$$Q_t (\%) = \frac{(\text{mass of solvent sorbed}) / M_w}{m} \times 100 \quad (8)$$

where M_w is the molecular weight of the solvent and m the mass of the polymer (neat NR). All samples were analysed for sorption properties at various time intervals.²⁵ A plot of the solvent uptake Q_t versus square root of time ($t^{1/2}$) for NR and NR/MWCNT composites is illustrated in Fig. 7.

The plots of Fig. 7 contain two parts: one having high rate of solvent uptake due to the large concentration gradient of the solvent in the composite and the second with decreased solvent uptake due to the reduced concentration gradient.^{26,27} A non-polar solvent like toluene has low cohesive energy density and easily penetrates the polymer.²⁵ It is observed that the solvent uptake for the NR/MWCNT composites is lower than that of the neat polymer which is attributed to the longer tortuous path for the solvent offered by the nanofiller networks. Among the nanocomposites, the swelling rate constantly decreases up to 3 phr of the filler

Table 3. Swelling parameters for NR and its NR/MWCNT composites

Sample	Q	Q/Q ₀	Swelling index	D (×10 ⁻⁵ cm ² s ⁻¹)	Sorption coefficient S = M _α /M ₀	P = DS (×10 ⁻⁵ cm ² s ⁻¹)
NR	4.25	1	391.59	1.92	3.92	7.52
NR-1MC	3.71	0.87	341.84	1.99	3.42	6.82
NR-2MC	3.1	0.73	285.63	1.83	2.86	5.23
NR-3MC	2.8	0.66	185.99	1.63	2.58	4.21
NR-5MC	2.9	0.68	190.21	1.64	2.67	4.37

**Figure 8.** SEM images of (a) NR, (b) NR-3MC and (c) NR-5MC.

due to the good level of nanotube dispersion in NR. However, for NR-5MC the swelling rate is found to be little higher than the NR-3MC case because of the agglomeration from the higher filler concentration. The decrease in solvent uptake for the NR/MWCNT composites can also be due to enhanced polymer–filler interaction and the reduced transport area in polymer membrane in the presence of MWCNTs. The NR chains can also get trapped within the filler networks thus hindering the penetration of solvent.

The diffusion coefficient (D) defines the rate at which diffusion takes place and depends on the polymer segmental mobility. This kinetic parameter is defined by

$$D = \left(\frac{h\theta}{4Q_{\infty}} \right)^2 \quad (9)$$

where h is the sample thickness and θ is the slope of the initial portion of the Q_t versus $t^{1/2}$ curve. The values of diffusion coefficient along with other calculated swelling parameters are given in Table 3. The addition of MWCNTs decreases the diffusivity of NR as explained; however, similar D value is found in the case of the NR-1MC composite. This may be because of the low concentration of MWCNTs, not able to provide enough support to the polymer chains and thus making available spaces for the solvent molecules to accommodate.

Another parameter, Q , given in Table 3 also has significance for swelling behaviour. The reduction in Q is a measure of the degree

of polymer filler adhesion and it usually decreases for adsorbing filler surfaces.²⁶ Q/Q_0 gives the ratio of the equilibrium swelling of the sample to that of the neat rubber and it decreases with filler loading suggesting stronger filler–polymer interaction. It can also be explained in that when the MWCNTs interact strongly with NR, single polymer chains can cover many active sites on the filler surface and thus only smaller number of chains may get entrapped within the filler networks. It is the remaining unanchored polymer chains that contribute towards swelling. This is consistent with the non-polar interactions occurring in NR/MWCNT composites¹⁵ and change in free volume within the polymer.

In addition to diffusivity, the solvent penetration depends on the sorption behaviour of the material, and this is defined by the sorption coefficient $S = M_{\alpha}/M_0$, where M_{α} is the mass of the solvent taken up at equilibrium swelling and M_0 is the initial mass of the composite sample.^{28,29} The local mobility of the polymer after vulcanization gets restricted by reinforcement of nanoscale MWCNTs due to strong filler–polymer interactions and thus the solvent transport in such crosslinked systems becomes tortuous and this leads to poorer sorption behaviour.^{28–31} The permeation coefficient $P = DS$ gives the amount of solvent permeated through unit area of the sample per second. This also shows a decrease for the composites with the least value for NR-3MC. In short, all the swelling parameters in Table 3 show maximum swelling, diffusion and permeability for neat rubber and minimum for the NR-3MC composite.

The cure kinetics and swelling data confirm the formation of filler networks within the composites, especially at a loading of 3 phr MWCNTs. This substantiates the observed sensing performance of the samples. Overall, the molecular level orientation of fillers and the filler–rubber interfacial interactions contribute towards the thermal and electrical characteristics of the composites as evident from the thermal properties and relative resistance change.

Morphology of composites

Scanning electron micrographs of neat NR, NR-3MC and NR-5MC are shown in Fig. 8. Neat NR shows a smooth surface whereas in the composites the MWCNT fillers are clearly seen. The MWCNTs are uniformly distributed within the matrix in the case of NR-3MC, as a result of the master-batch mixing method. But for NR-5MC, aggregated MWCNT clusters are present. This substantiates the better dispersion of the nanotubes in the case of the NR-3MC composite and confirms the superior property of the composite with this particular composition.¹⁵ The morphology confirms the results obtained from cure kinetics, thermal data and the swelling behaviour.

CONCLUSIONS

Effective solvent sensing and the mechanism involved in it are well demonstrated in terms of molecular-level interactions occurring in the NR composites. The efficiency of two-roll mill mixing and master-batch method was utilized to derive the physical and chemical properties of NR/MWCNT composites. The cure kinetics data confirm the dependence of torque, scorch and cure time on temperature and rate of dispersion of MWCNTs in NR. The glass transition temperature obtained from DSC and the swelling parameters determined also show the maximum level of filler–rubber interaction in the NR-3MC composition. Crosslink density found from the swelling studies and cure kinetics match well and as a result a good correlation is observed between the swelling, cure reaction and thermal characteristics. Moreover uniform dispersion of nanotubes for this particular composite is evidenced from the SEM images. Finally, the MWCNTs form a large number of networks within the rubber matrix at specific concentrations which can be identified through thermal behaviour, swelling, relative resistance variation and cure kinetics, in addition to establishing a useful application of a solvent sensor in flexible electronics.

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SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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