

Modified and unmodified multiwalled carbon nanotubes in high performance solution-styrene-butadiene and butadiene rubber blends

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ABSTRACT

The outstanding properties of carbon nanotubes have generated scientific and technical interests in the development of nanotube-reinforced polymer composites. Therefore, we investigated a novel mixing approach for achieving a good dispersion of multiwalled carbon nanotubes (CNTs) in a rubber blend. In this approach the CNTs were incorporated into a 50:50 blend of solution-styrene-butadiene rubber and butadiene rubber. First, the CNTs were predispersed in ethanol and then this CNT-alcohol suspension was mixed with the rubber blend at elevated temperature. The rubber nanocomposites prepared by such method exhibit significantly enhanced physical properties already at very low nanotube concentrations. Additionally, we have analysed the dielectric and thermal properties of the compound. The high aspect ratio of the carbon nanotubes enabled the formation of a conductive percolating network in these composites at concentrations below 2 wt.%. In contrast to the electrical conduction behaviour, the thermal conductivity of the composites has not been influenced significantly by the presence of carbon nanotubes. Dynamic mechanical analysis indicates that the incorporation of CNTs affects the glass transition behaviour by reducing the height of the $\tan \delta$ peak considerably. Above the glass transition temperature the storage modulus has been increased after incorporation of a small amount of CNTs. Finally, the 'Payne effect', an indication of filler-filler interactions, was observed at very low concentrations of CNT in the rubber matrix.

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1. Introduction

The length of a carbon nanotube is from a few microns up to millimetres, with a diameter of the order of nanometers. A single nanotube is hundred times stronger and six times lighter than steel and exhibits good electrical and thermal conductivities. Hence, the future of carbon nanotubes application can be easily envisaged from electrical sensors to reinforcing fillers, especially in the vast world of high performance materials. Tremendous attention is now paid from all over the world to the use of carbon nanotubes as electrical conducting and reinforcing fillers for polymers [1,2]. However, it is very difficult to disperse CNTs in polymers because they produce highly entangled agglomerates like felted threads. Owing to the strong van der Waals interaction and the inert graphite-like surface carbon nanotubes are very prone to form strong agglomerates.

Comparing with the enormous number of studies on the application of CNTs in epoxides, thermoplastics and fibres, there are

rather few reports dealing with applications of CNTs in elastomers [3–8]. Till now, it is a challenging task to disperse carbon nanotubes properly, to realise the full potential of this filler in improvement of the mechanical properties of different elastomers. Considerable improvement of physical properties was reported when multiwalled carbon nanotubes (MWCNTs) were incorporated in styrene-butadiene rubber (SBR) [3,4]. In another work, the reinforcing effect of single walled carbon nanotubes (SWCNTs) in natural rubber was revealed by dynamic mechanical analysis and Raman spectroscopy [5]. Here, a noticeable decrease of the loss tangent ($\tan \delta$) peak height, as well as a marked shift of glass transition temperature (T_g) towards higher temperature was observed. Fakhru-Razi et al. [6] showed that the initial modulus of a natural rubber (NR) composite was increased up to 12 times in relation to pure NR. Kim et al. [7] evaluated the mechanical, thermal and electromagnetic shielding properties of ethylene propylene diene monomer rubber (EPDM)-MWCNT composites. They concluded that the alignment of tubes in a EPDM rubber matrix, arising from the mill processing, resulted in significant improvements in mechanical, electrical and thermal properties. Wagner et al. [8] reported the improvement of the mechanical properties of MWCNT filled silicone rubber. In their

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work it was reported that with the increase of the amount of carbon nanotubes a remarkable enhancement of the initial modulus (Young's modulus) was observed, accompanied by a reduction of the ultimate tensile strength. However, at higher strains ($\approx 20\%$) the modulus was found not to change upon further increase of CNT concentration. Hydrogenated nitrile rubber was also used to prepare nanocomposites with CNT [9]. The authors reported a serious breakage of the CNTs during the ultrasonic dispersion, which resulted in a poor electrical conductivity of such nanocomposites. In order to get thermoplastic elastomer–CNT composites for tribological applications EPDM of a high ethylene content was spray-coated with an aqueous dispersion of the CNTs, which was then dried and melt blended with the thermoplastic elastomer [10]. Synthetic polyisoprene–CNT composites were also prepared by a solution method and the effect of stretching on the electrical properties has been discussed [11].

Thermal conductivity is defined as the quantity of heat that passes through a plate of a particular area and thickness per unit time when its opposite faces differ in temperature by 1° . In metals, the thermal transport follows approximately the pathway of conduction as the electrical conductivity. In this case freely moving valence electrons transfer not only electric current but also heat energy. However, the mechanism of the heat conduction is not governed only by the valence electrons, but also by a phonon mechanism. A phonon is a quantized mode of vibration, occurring in a rigid crystal lattice, such as the atomic lattice of a solid. The thermal conductivity of a multiwalled carbon nanotube is about ten times higher than that of a common metal [12]. Therefore, one can expect that the incorporation of CNT can significantly enhance the thermal conductivity of a polymer composite. Many efforts have been done to see the effect of CNT on the thermal conductivity of a CNT filled polymer. It is reported that the thermal conductivity of CNT–epoxy resin composites increases up to 60–125% depending on the type of loading of CNT in the matrix [13,14]. Liu et al. [14] reported an enhancement of 65% in thermal conductivity with 4 wt.% CNT loading in a silicone elastomer. In order to understand the thermal behaviour of CNT–epoxy composites, Gojny et al. [15] measured the thermal conductivity of composites of various types of CNTs in an epoxy matrix. They claim that in contrast to the improvement of the mechanical properties of the epoxy resin by CNT, where the big surface area of the CNT and good interfacial adhesion is necessary, a contradictive requirement is essential for an enhancement of thermal properties. The occurrence of an electrical conductivity can be attributed to the formation of conductive pathways when the filler content exceeds a critical volume fraction. But the thermal conductivity on the base of phonon transport depends on different pathways from one carbon tube to another one.

CNTs have also a graphite-like inert surface. Therefore, several approaches [16–18] have been developed to generate some

chemical functional groups on the surface of the tubes in order to get more filler–polymer interactions in the polymer composites. Very recently it has also been demonstrated that carboxyl modification of CNTs offered a highly reinforced and conducting natural rubber compound made by a latex coagulation method [19].

The present study reports about the preparation of MWCNT containing rubber nanocomposites with a very low loading of carbon nanotubes by a novel technique. In this technique predispersed ethanol mixtures of carbon nanotubes were mixed with rubber blends at elevated temperature using a two-roll mixing mill. In the mixing mill the ethanol vaporises and, simultaneously, the CNTs can be impregnated into the rubber matrix. The rubber matrix, considered here, is a 50/50 blend of solution-styrene–butadiene rubber (S-SBR) and polybutadiene rubber (BR). Similar compositions of rubber blends are widely used in a tire industry for high performance silica filled tire treads for passenger car applications (so called 'green' tire concept). In addition, in our present study hydroxyl modified carbon nanotubes were used as a functional filler with hydroxyl groups on the tube surface. A standard type silane-coupling agent was used to ensure the chemical linkage between the rubber and the hydroxyl modified carbon nanotubes.

2. Experimental

Solution-styrene–butadiene rubber (S-SBR, CE 3418-01) and polybutadiene rubber (BR, high *cis* Nd BR, CB25), were obtained from, Lanxess, Germany. Zinc oxide, stearic acid, diphenyl-guanidine (DPG), *n*-cyclohexyl-2-benzothiazole-sulfenamide (CBS) and soluble sulphur employed in this study were of industrial grades. Hydroxyl modified multiwalled carbon nanotubes and unmodified tubes were purchased from Nanocyl S.A., Sambreville, Belgium. Details are given in Table 1. The solvent used for the predispersion of the tubes was dehydrated ethyl alcohol (VWR GmbH, Darmstadt, Germany). A non-ionic surfactant (Tween 20, Sigma–Aldrich, Steinheim, Germany) was used for stabilizing the nanotubes in the ethanolic medium. The silane-coupling agent TESPT [bis(triethoxysilylpropyl)tetrasulfane] was collected from Degussa, Germany. This compound has been used in two mixes where silica and OH-MWCNT have been used as the fillers and the dosage of the coupling agent was 2.5 phr where 'phr' stands for (weight) parts per hundred with respect to rubber.

The multiwalled carbon nanotubes as-purchased from the market were visualized by environmental scanning electron microscope (E-SEM) and the micrograph is shown in Fig. 1. It can be seen from this picture that the tubes are highly entangled like a felted mass of textile fibres.

The multiwalled carbon nanotubes were dispersed in ethanol in the ratio 1:10 by weight in the case of unmodified carbon nanotubes. For the hydroxyl modified carbon nanotubes the tube–alcohol ratio was chosen to be 1:30. In each case 2.5 phr of the

Table 1
Characterization of MWCNT and OH-modified MWCNT

Product name ^a	Property	Unit	Value	Method of measurements
Nanocyl [®] -7000	Average diameter	nanometers	9.5	TEM
	Average length	microns	1.5	TEM
	Carbon purity	%	90	TGA
	Metal oxide (impurity)	%	10	TGA
	Amorphous carbon and carbon shells (impurity)	%	Not detectable	HRTEM
	Surface area	m ² /g	250–300	BET
Nanocyl [®] -3153	Average diameter	nanometers	9.5	TEM
	Average length	microns	<1	TEM
	Carbon purity	%	>95	TGA
	Metal oxide (impurity)	%	<5	TGA
	Amorphous carbon and carbon shells (impurity)	%	Not detectable	HRTEM
	–OH	%	<6	XPS

^a The values are taken from the data sheets of the producer.

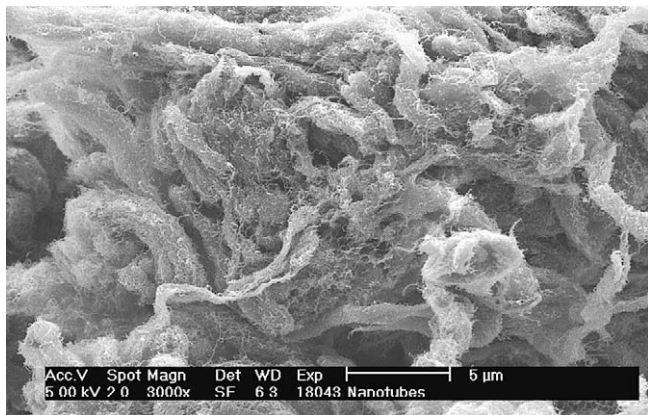


Fig. 1. SEM picture of carbon nanotubes.

non-ionic surfactant was added to the dispersed CNT [20–23]. This mixture was then treated gently by an ultrasonic bath ($200W_{\text{effective}}$; 25 kHz) for approximately 2 h. The mixture thus obtained mixed into the rubber. In the first step 50 g S-SBR and 50 g BR were mixed in an open two-roll mixing mill of laboratory size (Poly-mix 110L, size: 203×102 mm Servitech GmbH, Wustermark, Germany) during 5 min at 80°C . Then, the ethanolic CNT suspension was added to the mixture very slowly. The mixing time for the incorporation of the nanotubes was about 15 min. For comparison also rubber composites were produced where the carbon nanotubes were mixed directly (dry) into the rubber compound. Finally, the curing chemicals were incorporated into the composites at room temperature. The curing package was comprised with 1.4 phr sulphur, 2 phr DPG and 1.7 phr CBS. The total compounding cycle was finished within 25 min. The friction ratio of the rolling mill was 1:1.2 during the mixing tenure. After the mixing process the stocks were cured under pressure at 160°C to the optimum cure in respect to the t_{90} vulcanization time determined with a moving die rheometer (Scarabaeus V-50, Scarabaeus GmbH, Langgöns, Germany). Tensile tests have been done with a material testing machine (Zwick 1456, Z010, Ulm, Germany) with a crosshead speed of 200 mm min^{-1} (ISO 527).

Dynamic mechanical analysis was performed on an Eplexor 2000 N dynamic measurement system (Gabo Qualimeter, Ahlden, Germany) using a constant frequency of 10 Hz in a temperature range from -100 to $+80^\circ\text{C}$. The samples were analysed in the tension mode. For the measurement of the complex modulus E^* a static load of 1% pre-strain was applied, then the samples were oscillated to a dynamic load of 0.5% strain. The measurements were done with a heating rate of 2 K/min under liquid nitrogen flow. Strain sweep experiment was also carried out with the Eplexor. For this experiment tension mode was selected for the variation of the dynamic load from 0.01 to 40% at 10 Hz frequency. A pre-strain of magnitude 40% was chosen to hold the sample with the size of $10 \times 2 \times 35 \text{ mm}^3$. The dielectric properties were measured with a broadband dielectric spectrometer, BDS 40 system manufactured by Novocontrol GmbH, Germany. The investigations have been performed on disc shaped rubber samples with a thickness of 2 mm and a diameter of 20 mm. The samples were placed between two gold plated brass electrodes of 20 mm diameter. To provide a good contact between the sample and the gold electrodes thin gold layers have been sputtered onto the flat surface of the samples. In the frequency range between 0.1 Hz to 10 MHz real and imaginary parts of the conductivity and the permittivity were obtained.

DC conductivity measurements have been performed at room temperature with a high resistance meter (Keithley-6517A). The dimensions of the rubber samples for this experiment were 65 mm diameter and 2 mm thickness.

The thermal conductivity was measured by a laser-flash method. The rubber sample with 1 mm thickness was heated by short laser-flashes on one side and on the other side the increment of the temperature was detected by an infrared-sensitive detector. This experiment was done at ZAE Bayern, Würzburg, Germany. The thermal conductivity was then calculated according to the equation $\lambda = a \cdot C_p \cdot \rho$ where λ = thermal conductivity, a = thermal diffusivity, C_p = heat capacity, and ρ = density. The C_p value has been measured by a DSC instrument (DSC Q 1000, TA Instruments). The temperature scanning rate was 10 K/min and the C_p value was taken at room temperature.

For TEM experiments ultra-thin sections of the rubber composite were cut by ultra-microtome at the temperature of about -100°C and the images were taken by a Libra 120 transmission electron microscope (Zeiss, Oberkochen, Germany) with an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Morphology and physical properties

The structure of CNTs and the state of their dispersion in the S-SBR–BR blend (mixed in the wet method by ethanolic dispersion) were visualized using transmission electron microscopy. It can be observed from Fig. 2a and b that the diameter of the tube is varying from 6 to 27 nm; whereas the length of the tubes is varying from a few to several hundred nanometers. It is also revealed from Fig. 2a that the carbon nanotubes are forming percolating networks at 5 phr loading. However, with smaller magnification (Fig. 2b), it is obvious that the distribution of the CNTs is not homogeneous. Besides areas with agglomerated parts one can also observe finely distributed tubes.

The stress–strain diagrams obtained for all CNT-filled samples are shown in Fig. 3. It can be seen that with the incorporation of the CNTs the stress is increasing in all investigated composites with a sharp rise of the initial modulus. The vulcanizates obtained by dry mixing (classical method) show significant inferior properties compared to the ones mixed by an ethanolic dispersion with the same loading of tubes. The functionalized samples show similar properties compared to the wet mixed samples, only the elongation at break is slightly increasing. As well, the silanisation seems not to have a significant influence on the mechanical properties.

From this stress–strain experiment Young's modulus was evaluated and utilised to estimate roughly an apparent effective aspect ratio (length/width) of the tubes following the Guth–Gold–Smallwood equation [24–26].

$$E_f/E_u = 1 + 0.67v_f + 1.62f^2v_f^2, \quad (1)$$

where E_f is Young's modulus of the filled elastomer, E_u is the value for the unfilled rubber and v_f is the volume fraction of the filler. The shape factor (f) is defined as the aspect ratio of a non-spherical particle. The quadratic term of the above equation can be neglected at low filler concentrations and for low f values. The aspect ratios were calculated according to Eq. (1) and it was found that the f values are varying between 15–20 for the dry mixed compounds and 50–60 for the wet mixed compounds. The estimated values are far below the expected values for CNTs with an aspect ratio for a typical single stretched nanotube of nearly 1000. Agglomerates of bundled nanotubes, breakage of CNT during the ultra-sonification and processing are the main factors which are remaining on the opposition to utilize the high aspect ratio of the tubes for the reinforcement process. Recently, it has been reported that the Guth model and the Halpin–Tsai [3] model fit very well after considering the aspect ratio of 40–45 for multiwalled carbon nanotubes in styrene–butadiene rubber. The Halpin–Tsai model also describes

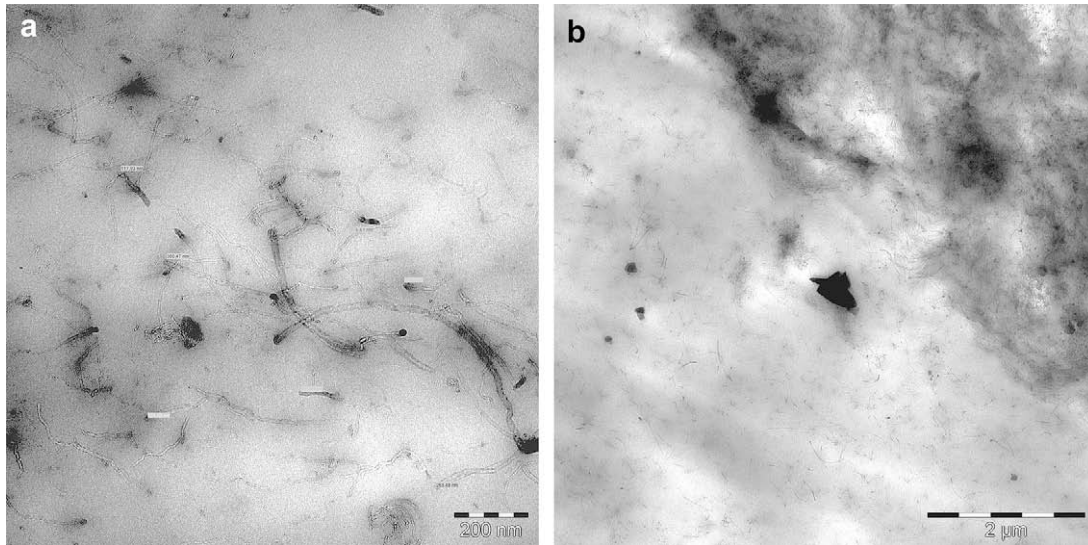


Fig. 2. TEM images of CNT filled (5 phr) SBR-BR blends produced by wet method.

the dependence of the aspect ratio of a fiber on the modulus of a reinforced polymer. It must be noted that originally Eq. (1) has been derived and validated for anisotropic fillers with relatively low aspect ratio. These fillers were assumed to behave totally rigid, i.e. like short fibres or anisotropic carbon blacks. For the CNTs the rigid condition is probably not fulfilled if the aspect ratio is large. Accordingly, the longer CNTs visible in the TEM micrographs of Fig. 2 will bend in the stress field of the rubber matrix and the strain amplification factor estimated with Eq. (1) can be considered only as an effective one. For that reason the fitted values for the aspect ratio f are expected to be smaller than the values obtained from morphological measurements. Nevertheless, we consider the presented procedure for a rough estimate of an apparent f value as useful, especially with respect to exploring different morphologies in dependence on the described mixing procedures (e.g., dry versus wet).

In our study, the wet mixed compounds show better results in terms of physical properties and electrical conductivity with a fixed loading of tubes as compared with the results described in Ref. [3]. The stress-strain study shows that a total separation or deagglomeration of the tubes cannot be achieved by the wet mixing method, but it offers a better dispersion of the tubes in the rubber matrix as compared with the conventional dry mixing. However, functionalised (OH-modified) CNTs do not show any significant difference with the unmodified one.

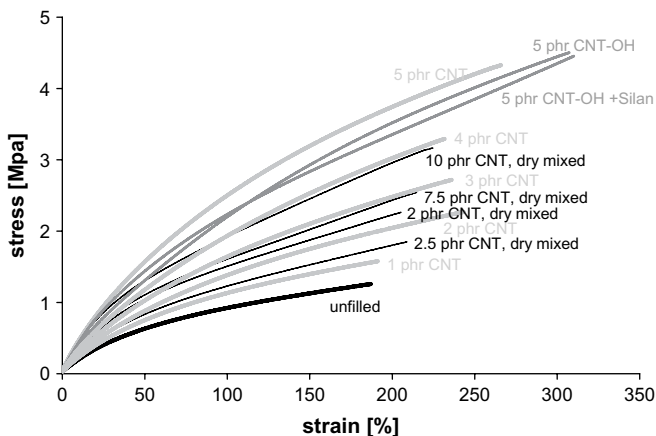


Fig. 3. Stress-strain diagram of CNT filled SBR-BR blend.

3.2. Dynamic mechanical measurements

The storage modulus of unfilled rubbers, E' , depends on frequency and temperature and is independent of the deformation amplitude. In contrast, E' for the filled rubber shows a significant dependency on the dynamic deformation [27,28], here the value considerably decreases with an increasing strain amplitude. This non-linear behaviour of filled rubbers is known as 'Payne effect' [27,28] and has been explained by the existence of a filler network in the rubber matrix above the percolation threshold. With increasing strain amplitude the filler network is breaking down which results in lowering of the E' value. Fig. 4 supplies an evidence of the existence of a carbon nanotube filler network in an S-SBR-BR blend prepared by the wet mixing method. For a pure rubber (not shown here) and at small CNT loading (up to 2 phr) no 'Payne effect' is observed. However, with the increase of the MWCNT content a gradual decrease in E' is observed in strain sweeps. So, even with 3 phr of MWCNT the tubes obviously form a continuous filler network in the rubber matrix. The OH-functionalised sample with 5 phr of CNT shows a significant lower E' value compared to the unfunctionalised one, with additional silane modification the value increases. This shows the opposite behaviour as known for silica filled samples, where silanisation reduces the Payne Effect to a certain amount. The concentration of hydroxyl groups, present on the surface of the nanotubes, is obviously not comparable to silica and does not allow the formation of hydrogen bonds between two adjacent modified tubes, hence the silanisation is not reducing the filler-filler interaction.

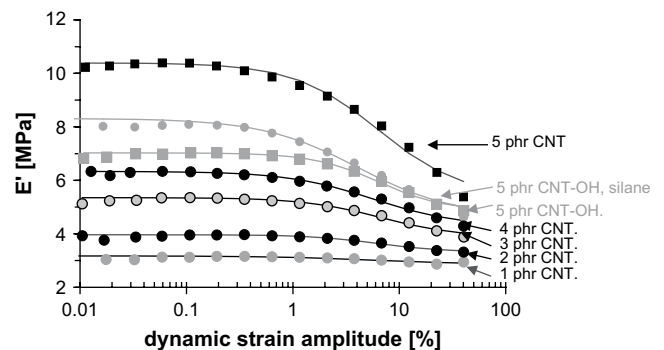


Fig. 4. Strain dependencies of dynamic properties for CNT filled S-SBR-BR blends.

The filler–filler network can be reformed again after a certain time interval. Payne revealed that the value of E' is largely recoverable upon return to smaller amplitudes in the linear regime. So, flexible rubber chains allow the filler particles to rearrange again to form a three-dimensional filler network in the rubber matrix [28]. In order to investigate the ability to recover the strain sweep experiments were also carried out in the reverse direction from higher to lower strain amplitudes for the samples with unmodified CNT dispersed by ethanolic suspension.

It is observed that the values do not reach its initial position within the relaxation time of the experiment, but a recovery of the E' values has been attained (Fig. 5). This behaviour of a rubber can be explained by the stress softening effect during the dynamic strain. Nevertheless, a high extent of recovery in the reverse amplitude sweep indicates that a good filler–filler network has been re-established at a low loading of tubes in the S-SBR–BR matrix. So, at least it can be said that rather than damage or permanent break of the tubes, the amplitude sweep disrupted the filler–filler network in the rubber matrix. It is noted that the absolute values of E' at small amplitudes are somewhat differed from each other as compared with the value obtained from the 5 phr CNT-filled compound (compare Fig. 4 with Fig. 5). The difference may be developed from ageing of the samples.

Figs. 6 and 7 show the temperature dependencies of the storage moduli, the loss moduli and the loss factors $\tan \delta$ of the CNT–rubber nanocomposites. Fig. 6 illustrates that with an increase in temperature the storage modulus of all samples decreases which is associated with the glass transition phenomenon of the elastomer chains. Above room temperature the value of E' increases as well with increasing filler loading. As seen in Fig. 7, the glass transition temperature at the maxima of the $\tan \delta$ plot does not change with the tube content in the rubber matrix. However, the peak height reduces considerably with higher CNT content. This behaviour also indicates the strong reinforcement efficiency with only low content of CNT.

3.3. Electrical conductivity

Above a critical volume fraction of carbon nanotubes, the percolation threshold, an interconnecting filler network is formed which results in a sharp drop of the electrical resistance of the nanocomposites.

The direct current (DC) electrical percolation behaviour of the nanocomposites is depicted in Fig. 8. It is evident from this figure that there is a sharp rise of conductivity when the filler concentration is increasing from 1 to 2 phr for the wet mixed samples. This sudden rise in conductivity is an effect of the formation of

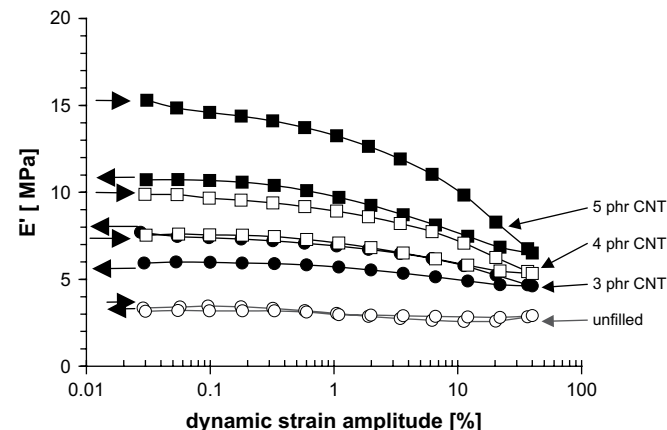


Fig. 5. Strain dependencies of dynamic properties for CNT filled S-SBR–BR blends.

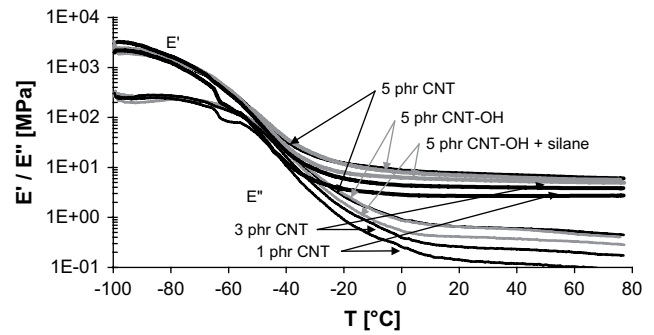


Fig. 6. Storage modulus E' and loss modulus E'' as a function of the temperature for a CNT filled SBR–BR blend.

a continuous network of the carbon nanotubes. The very high aspect ratio of the carbon nanotubes is mainly responsible for this percolation behaviour at very low loadings of CNT. In the case of dry mixed vulcanizates a steady increment of the conductivity can be observed starting at a CNT loading of 5 phr which is significantly later than in the wet mixed samples. Hence, the dispersion of CNT is considerably improved when the mixing is done by the ethanolic predispersion leading to the formation of the CNT network with a smaller amount of filler.

Additional frequency dependent measurements of the electrical properties are very useful for the investigation of the conduction mechanism between the nanotubes as well as the morphology of the CNT network. Fig. 9 shows the real part of the frequency dependent AC conductivity, σ' , at room temperature for the wet mixed CNT-filled rubber composites.

Again, the increase of conductivity at low frequencies with the incorporation of nanotubes is observable with a percolation threshold between 2 and 3 phr CNTs, which confirms the DC measurements. A cross-over from a plateau at low frequencies to a power-law behaviour at higher frequencies is observed for all samples, which is also a well-known characteristic for carbon black filled samples [29]. The characteristic cross-over frequency is shifted to higher values with increasing concentration of CNTs. For the unfilled and the low filled sample (1 phr) the slope m of the high frequency part above the cross-over frequency is nearly $m = 1.0$ indicating an isolator-like behaviour with an almost linear increase of the conductivity with frequency. For the filled samples with 2 phr CNT the slope is decreasing to a value around $m = 0.6$. This transition of the scaling behaviour results from the formation of a conducting CNT network on mesoscopic length scales. In the case

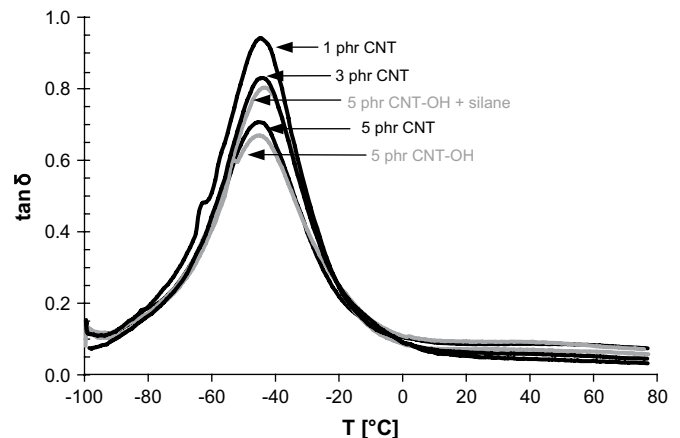


Fig. 7. Loss tangent ($\tan \delta$) as a function of the temperature for CNT filled SBR–BR blend.

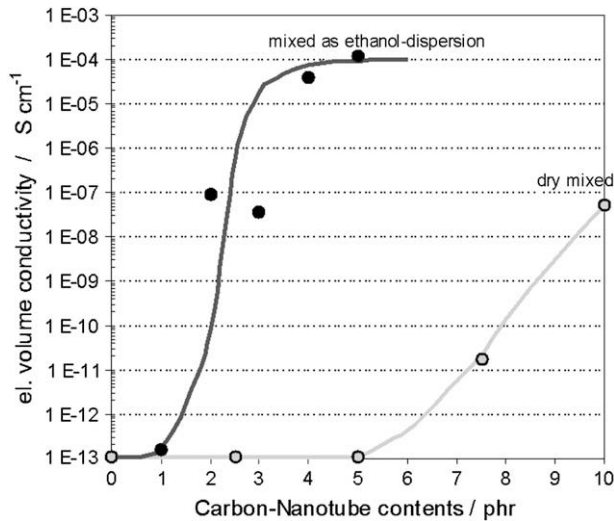


Fig. 8. Variations in DC electrical conductivity with the CNT content of S-SBR-BR blends. The square symbols represent the conductivity of the CNT filled vulcanizates mixed by wet mixing, the round symbols denote the conductivity of the dry mixed samples.

of carbon black composites a similar scaling behaviour with $m = 0.6$ has been observed and related to anomalous diffusion on a fractal percolation network [30].

The conducting nature of the composites becomes very pronounced above the percolation threshold of filler particles. Composites containing 3–5 phr of CNT are definitely above the percolation threshold as the power law regime is particularly shifted to higher frequencies and thus the material behaves as an Ohmic conductor with conductivity almost independent of frequency.

The frequency dependency of the real part of the permittivity of the wet mixed samples is shown in Fig. 10 and characterizes the polarisation of the sample in an alternating field. In the unfilled sample and the sample filled with 1 phr of CNT the permittivity has low values and behaves almost independent of frequency. With increasing incorporation of nanotubes this behaviour is changing. At low frequencies the permittivity is significantly increasing with the amount of filler but at a certain frequency a relaxation process takes place resulting in a drastical drop of the permittivity with increasing frequency. With increasing loading of CNT the relaxation transition is shifted towards higher frequency [30]. We point out that the behavior of the dielectric response functions shown in Figs. 9 and 10 is very similar to that of carbon black filled elastomers above the percolation threshold [29–31]. Accordingly, we can conclude that the very high values of $\epsilon' > 10^3$ at low frequencies for

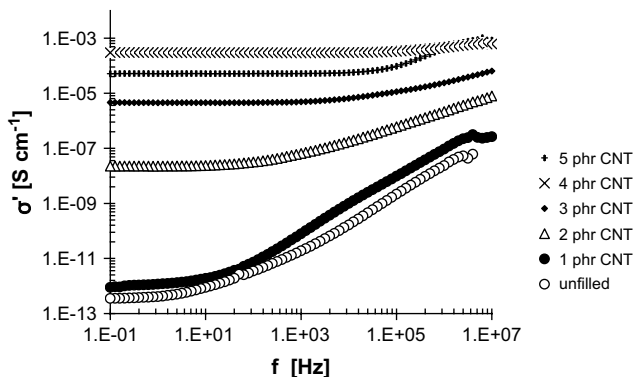


Fig. 9. Frequency dependence of the AC conductivity of SBR-BR blends (wet mixed).

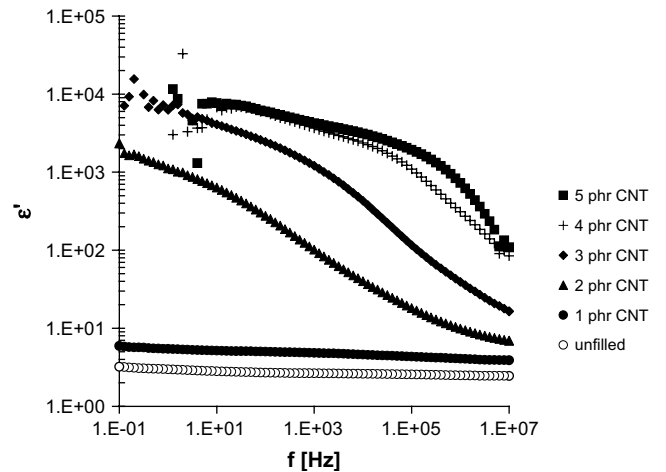


Fig. 10. Dependence of the dielectric constant (ϵ') of CNT filled SBR-BR blends (wet mixed).

the samples with more than 2 phr CNTs result from a combined effect of the disordered percolation structure and small gaps of the conducting CNT network, with various dead ends forming capacitances on different length scales. A detailed analysis of the data in Fig. 10 shows that the real part of the permittivity ϵ' for the systems above the percolation threshold exhibits a double-step behavior, indicating that two relaxation transitions take place at about 10^2 and 10^6 Hz, respectively. In previous studies on carbon black filled elastomers [31,32] the low frequency transitions have been related to the percolation structure of the filler network (cluster process) and the high frequency transition has been assigned to a gap process, referring to the tunneling or hopping of charge carriers over nanoscopic gaps between adjacent particles of the carbon black network. A similar interpretation can be assumed for the CNT network. Recent temperature dependent dielectric measurements at CNT-elastomer composites above the percolation threshold have shown that at moderate temperatures the conductivity is almost independent of temperature, indicating that quantum mechanical tunneling across the gaps takes place. However, at higher temperatures ($T > 40$ °C) the conductivity increases significantly with temperature, which can be related to a thermally activated hopping of the charge carriers over the gaps with activation energy of about 0.2 eV [33].

The advantage of the wet mixing process can also be justified by comparison with the AC conductivity measurements on the dry mixed samples (Fig. 11). In these dry mixed samples the power law with the exponent $m = 1$, indicating the isolator-like behaviour, is still operating up to 7.5 phr loading of the carbon nanotubes. The percolation threshold can be found in this case at around 10 phr CNT.

Fig. 12 displays the real part of the dielectric permittivity ϵ' of the dry mixed samples as a function of frequency in the range 10^{-1} – 10^7 Hz. For vulcanizates containing up to 7.5 phr of nanotubes, the permittivity values are very small and independent of the frequency. Only for the sample filled with 10 phr of CNT a high value of permittivity and the characteristic relaxation process are observed.

3.4. Thermal conductivity

Fig. 13 shows the thermal conductivity of the CNT/SBR-BR composites mixed with ethanol (wet mixing) in dependence of CNT concentration. It is observed that with an increase of the CNT content the thermal conductivity is only negligibly enhanced. Obviously, the effect of CNT on the thermal conductivity is small

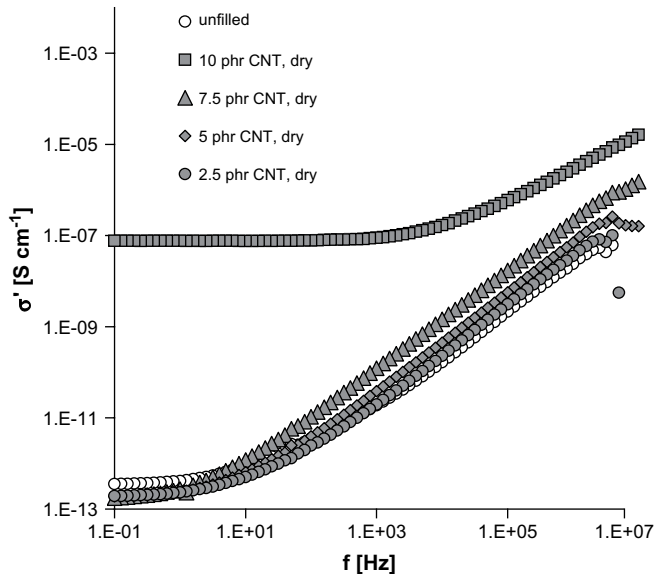


Fig. 11. Frequency dependence of the AC conductivity of SBR-BR blends (dry mixed).

and a percolation behaviour, as observed for the electrical conductivity (Fig. 8), is not found.

At present, a precise quantitative explanation cannot be offered. However, we want to give some possible qualitative explanations to encourage further discussions and experiments.

A possible conclusive explanation can be given by referring to the fact that also in the electrical measurements the expected maximum conductivity of the single tubes (about 10^4 S/cm) is by far not reached for the composites above the percolation threshold. Instead, the plateau value of about 10^{-4} S/cm for the percolated systems in Fig. 8 lies about eight orders of magnitudes below that of the single tubes. This demonstrates clearly that the charge transport through the tube network embedded in the polymer matrix is strongly hindered by hopping or quantum tunneling effects. This indicates that adjacent tubes do not touch but are separated by nanoscopic gaps. We point out that a similar effect was observed and well studied for carbon black filled elastomers [31]. Recently, the gap size of tunneling electrons in carbon black filled elastomers was estimated from dielectric relaxation data in the range 2–5 nm [32]. Accordingly, the presence of gaps in the CNT network is expected to limit the transport of charge carriers significantly

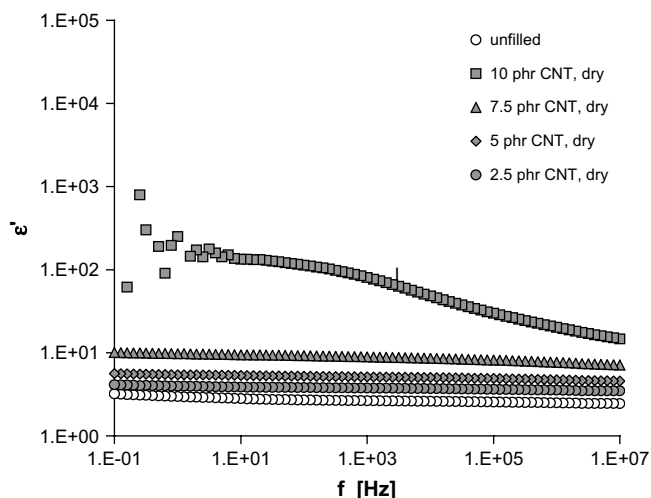


Fig. 12. Dependence of dielectric constant (ϵ') of CNT filled SBR-BR blends (dry mixed).

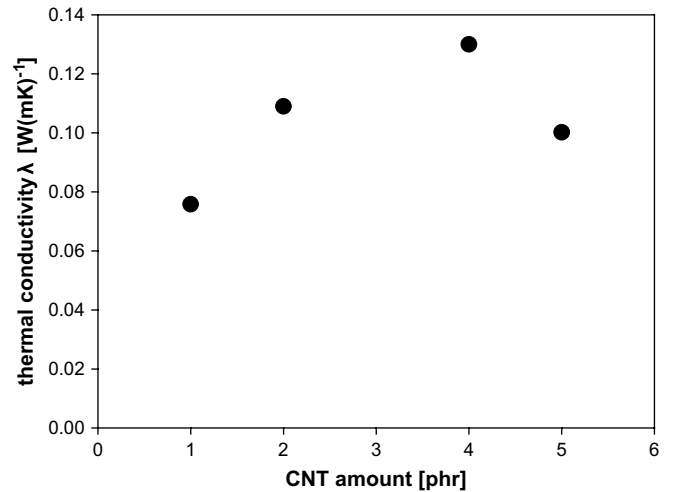


Fig. 13. Influence of CNT on the thermal conductivity of SBR-BR blends.

leading to a strong reduction of electrical and thermal conductivities induced by electron transport. However, the transport of heat in isolated MWCNTs is dominated by phonons showing a characteristic quadratic dependence on temperature in the range between 50 and 300 K, indicative of a two-dimensional nature of lattice vibrations in a MWCNT. The thermal conductivity exhibits a maximum at about 320 K of more than 3000 W/(m K) $^{-1}$, and for higher temperatures the thermal conductivity decreases due to phonon back-scattering effects. For MWCNTs dispersed in a polymer matrix, further scattering effects, e.g., interfacial boundary- and defect scattering, will appear leading to a drastic reduction of thermal transport properties [15]. In addition, the thermal transport through the MWCNT network by phonons will be strongly hindered by the gaps between adjacent tubes. From these arguments we conclude that the thermal conductivity of the CNT/rubber composites should lie several orders of magnitude below that of the isolated MWCNTs (up to 3000 W/(m K) $^{-1}$) [34,35] and also below that of the dry MWCNT network without polymers inside the gaps (about 50 W/(m K) $^{-1}$ measured, for example, for bundles or mats [34,36]). Accordingly, the thermal conductivity of the MWCNT network in rubber composites should be not much larger or even smaller than that of the pure polymer (about 0.1 W/(m K) $^{-1}$). This explains why the effect of CNT on the thermal conductivity depicted in Fig. 13 is small and a percolation behaviour is not found. In contrast, the typical percolation behaviour of the electrical conductivity seen in Fig. 8 results from the fact that the difference of electrical conductivity between the pure polymer ($<10^{-11}$ S/cm) and the tubes (about 10^4 S/cm) is about 15 orders of magnitude and, hence, much larger than that of the thermal conductivity with only 3–4 orders of magnitude.

We note that, principally, another explanation of the measured values of thermal conductivity is possible if orientation effects of CNTs – as a possible result of polymer processing – would come into play. The thermal conductivity of a two-phase system can be roughly estimated by considering the upper and lower bounds of the following inequality expression [37].

$$\sigma_{\text{lower}} \leq \sigma_e \leq \sigma_{\text{upper}} \quad (2)$$

where σ_e is an effective thermal conductivity. The upper bound, σ_{upper} , can be calculated as a simple arithmetic mean

$$\sigma_{\text{upper}} \equiv \langle \sigma \rangle = \sigma_{\text{polymer}}(1 - \phi_{\text{CNT}}) + \sigma_{\text{CNT}}\phi_{\text{CNT}} \quad (3)$$

where ϕ is the CNT volume fraction. σ_{polymer} is the thermal conductivity of polymer matrix and σ_{CNT} is the thermal conductivity of single CNT. The simple arithmetic mean represents an exact

solution in the case of macroscopically isotropic composites with non-zero phase conductivities in the limit of infinite space dimension [37]. The lower bound, σ_{lower} , can be calculated as the harmonic mean of thermal conductivities of the components:

$$\sigma_{\text{lower}} \equiv \langle \sigma^{-1} \rangle^{-1} = \left((1 - \phi_{\text{CNT}}) / \sigma_{\text{polymer}} + \phi_{\text{CNT}} / \sigma_{\text{CNT}} \right)^{-1} \quad (4)$$

It represents an exact solution in the case of simple laminate composites when the thermal conductivity is measured perpendicular to the conductive layers [37]. The upper limit of the thermal conductivity was estimated to be 68 W(mK)^{-1} and the lower limit to be 0.16 W(mK)^{-1} for our rubber sample filled with 5 phr CNT. The used values of thermal conductivity in Eqs. (3) and (4) are taken from the literature [1,38]: $\sigma_{\text{CNT}} \approx 1000 \text{ W(mK)}^{-1}$ and $\sigma_{\text{polymer}} \approx 0.1 \text{ W(mK)}^{-1}$. It can be deduced from Fig. 13 that the measured values of thermal conductivity for all investigated CNT concentrations lie in the range of the harmonic mean being even slightly lower than the predicted value of σ_{lower} . Thus, the data could be explained by orientation effects only if a perfect laminate-like orientation of the CNTs would be realized. However, this appears unlikely if the TEM micrographs shown in Fig. 2 are considered. For that reason, the first scenario should be preferred as a conclusive (qualitative) explanation of the thermal conductivity of CNT filled elastomers.

4. Conclusions

A huge progress in carbon nanotube applications based on polymer composites can only be realized when a proper dispersion of the entangled agglomerates of as-prepared CNT products will be achieved, without damaging their unique properties. The aim of this study was to obtain a good dispersion of CNTs by debundling or isolation of individual tubes from highly entangled primary agglomerates by a novel process of predispersing the nanotubes in a liquid medium. This method proved to be a promising and industrially viable one to produce rubber nanocomposites on a larger scale. It was observed that the mechanical properties of MWCNT filled S-SBR/BR blends are improved considerably compared to the unfilled rubber. The electrical conductivity experiments reveal the presence of a percolation network at low filler loadings, as low as 2 phr. In contrast, the percolation threshold for CNT–rubber composites obtained from classical dry mixing lies at 7.5 phr. The incorporation of CNT into the rubber compound results only in a slight enhancement of the thermal conductivity compared to that of the unfilled rubber. The theoretically predicted thermal conductivities of isolated tubes cannot be transferred into rubber-based composites in practice. Obviously, the large surface area of the carbon nanotubes leads to a strong phonon boundary scattering, which results in a poor thermal conductivity. A modification of carbon nanotubes by hydroxyl groups does not improve the materials properties of the resultant nanocomposites in our

study. Presumably, a reason is the insufficient number of introduced chemical groups of such modified tubes.

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