

The Effect of Partial Replacement of Carbon Black by Carbon Nanotubes on the Properties of Natural Rubber/Butadiene Rubber Compound

Minna Poikelispää,¹ Amit Das,^{1,2} Wilma Dierkes,^{1,3} Jyrki Vuorinen¹

¹Department of Materials Science, Tampere University of Technology, Tampere, Finland

²Department of Elastomers, Leibniz Institute of Polymer Research Dresden, Dresden, Germany

³Department of Elastomer Technology and Engineering, University of Twente, Enschede, The Netherlands

Correspondence to: M. Poikelispää (E-mail: minna.poikelispaa@tut.fi)

ABSTRACT: The basic objective of this study is to investigate the mechanical properties of tyre tread compounds by gradual replacement of carbon black by multiwalled carbon nanotubes (MWCNTs) in a natural rubber–butadiene rubber-based system. A rapid change in the mechanical properties is noticed even at very low concentrations of nanotubes though the total concentration of the filler is kept constant at 25 phr (parts per hundred rubber). The correlation of the bound rubber content with MWCNT loading directly supports the conclusion that MWCNTs increase the occluded rubber fraction. Transmission electron microscopy reveals a good dispersion of the MWCNT up to a certain concentration. In the presence of MWCNT, a prominent negative shift of the glass transition temperature of the compound is found. Thermal degradation behavior, aging, and swelling experiments were also carried out to understand the resulting effect of the incorporation of MWCNT in the rubber matrix. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Carbon black (CB) is the mostly used filler in rubber compounds owing to its outstanding reinforcing properties based on the structure and physical bonding with the polymer. However, it has also drawbacks as, for example, in dynamic properties, which determine the key properties of many products such as tyres. Traditionally, silica is used to improve the dynamic properties of rubbers. The use of silica instead of CB improves friction properties of the rubber. Thus, silica-filled rubber is suitable for tyre applications as it causes lower rolling resistance when the material is used in tyre treads compared to CB-filled rubber. However, the use of silica has its drawbacks, too: The adhesion and interaction between the nonpolar rubber and the polar filler is poor. Therefore, surface modification is required to achieve the full advantages of silica. In addition, a good dispersion of silica particles into rubber matrix requires multiple mixing stages, which prolongs processing times and increases processing costs.¹

The drawbacks of CB and silica might be prevented with new filler systems, guaranteeing a good dispersion and a good polymer–filler interaction. Since Toyota presented the nanoclay-filled

polyamides in 1991, polymer research has been concentrating on nanocomposites. New types of nanofillers have been studied in rubber technology, too. Nanofillers, such as carbon nanotubes (CNTs) and layered silicates, are found to carry many benefits compared to conventional rubber fillers, CB, and silica. They have been reported to, for example, increase tensile strength, hardness, modulus, abrasion resistance, electrical conductivity, and chemical resistance.^{2–4}

CNTs are widely investigated nanofillers in rubbers. Owing to its tubular form, multiwalled carbon nanotubes (MWCNTs) have a high aspect ratio and therefore good reinforcing effect. Thus, it has a good potential to work as reinforcing filler in rubber. However, MWCNTs tend to form agglomerates and entanglements owing to the specific structure and the high surface area of particles and therefore they have high filler–filler interaction. A successful application of nanofillers depends mainly on a good dispersion, but achieving a good dispersion of MWCNTs during melt mixing is extremely difficult. Most of the recently published studies have been done with solution mixing owing to better dispersion.^{2,5–8} In addition, pretreatment of CNTs has proven to improve dispersion.^{9,10}

Table I. Formulation of the NR/BR Compounds and Mixing Procedure

Ingredients	Type/producer	Amount (phr)
NR	SMR10	20
BR	Buna-cis-132/Dow Chemical	80
MWCNT	Baytubes C 150 P/Bayer	x
CB	N-234/Evonik	25 - x
6PPD	Lanxess	2.0
TMQ	Lanxess	1.0
ZnO	Grillo Zinkoxid GmbH	5.0
TDAE-oil	Vivatic 500/ Hansen & Rosenthal GmbH	8.0
Stearic acid	Oleon N.V	2.0
Ceresine wax	Statoil Wax GmbH	1.5
CBS	Lanxess	1.5
Sulfur	Solvay Barium Strontium GmbH	1.5

Abbreviations: 6PPD: *N*-(1,3-dimethylbutyl)-*N'*-phenyl-1,4-benzenediamine, TMQ: 2,2,4-trimethyl-1,2-dihydroquinoline, TDAE-oil: treated distillate aromatic extract oil, CBS: *N*-cyclohexyl-2-benzothiazolesulfenamide, x: 0.5, 1, 2, 2.5, 5, 7.5, 10, and 12.5 phr.

Some of the recent researches have combined CNTs with other fillers. It was found that the combination of graphene and CNTs improves the dispersion of CNTs as well as mechanical properties in silicone rubber.¹¹ Bokobza et al.² used the blend of CB and MWCNTs in styrene-butadiene rubber (SBR), and they achieved improvements in the stress-strain properties owing to improved polymer-filler interaction compared to the CB-filled compounds. Verge et al.¹² showed that good dispersion can be achieved with nitrile butadiene rubber (BR) even by melt mixing as acrylonitrile units form free radicals during the mixing process which are able to react and graft onto the CNT surface.¹² The synergistic effect of expanded graphite and MWCNTs in the formation of a filler network and improved mechanical properties of solution SBR (S-SBR) mixed in an internal mixer was observed by Das et al.¹³

In this study, CB was partially replaced by CNTs. The effect of MWCNT loading on properties of a natural rubber (NR)-BR composite, prepared by melt mixing, was investigated.

EXPERIMENTAL

Materials

The CNTs were Baytubes C 150 P, delivered by Bayer. The diameter of the multiwall nanotubes was 13–16 nm and the length varied between 1 and 10 μm . The other materials used in the compound and formulation are summarized in Table I.

Preparation of Nanocomposites

NR, BR, nanofillers, and other ingredients excluding curatives were mixed in a Krupp Elastomertechnik GK 1.5 E intermeshing mixer (50°C, 90 rpm) for 5 min. The curatives were added on an open two-roll mill. In the reference compound, only CB

was used as filler in a concentration of 25 phr. In the MWCNT-containing compounds, a part of the CB (0.5, 1, 2, 2.5, 5, 7.5, 10, and 12.5 phr) was replaced by the same amount of MWCNTs.

Characterisations

The Mooney viscosity of the compounded material was measured in a MV 2000 Mooney Viscometer from Alpha Technologies. The measurement was carried out at 100°C including 1-min heating time and 4-min measuring time.

Curing studies and Payne effects were measured using an Advanced Polymer Analyzer 2000 from Alpha Technologies. Curing studies were carried out at 150°C for 25 min, and the optimum curing time was determined (t_{90} , time taking to reach 90% of the ultimate rheometric torque). The compounds were then vulcanized at their t_{90} value (Table II). The Payne effect was studied in a strain sweep from 0.28 to 100% at 100°C which is the commonly used temperature for these measurements.

Tensile tests of the samples were carried out with a Messphysik Midi 10–20 universal tester according to ISO 37. Dynamic properties were studied with a Pyris Diamond DMA from PerkinElmer Instruments, operating in tension mode. The measurements were done from -80 to +80°C at a heating rate of 10°C min^{-1} and a frequency of 10 Hz.

The volume resistivity was measured according to standard ISO 1853. The sample was rectangular with dimensions of approximately 140 \times 50 \times 2 mm (length \times width \times thickness). The resistances were measured with a Sefelec teraohmmeter MP1500P. The voltage used in the measurements was 10 V.

The volume fraction of the rubber was determined by swelling studies. Specimens with diameter of 12 mm and a thickness 0.2 mm were kept in toluene for equilibrium swelling. The sample was weighted before and after immersion as well as after drying. The volume fraction (V_r) of the rubber was calculated by

$$V_r = \frac{(D - FI) \rho_r^{-1}}{(D - FI) \rho_r^{-1} + A_0 \rho_s^{-1}} \quad (1)$$

where D is the weight of the dried sample, F is the weight fraction of insoluble components, I is the initial weight of the sample, ρ_r is the density of rubber, ρ_s is the density of solvent, and A_0 is the weight of absorbed solvent.¹⁴

The polymer-filler interaction was studied using a Kraus plot

$$\frac{V_{r0}}{V_{rf}} = 1 - m \left(\frac{\phi}{1 - \phi} \right) \quad (2)$$

with

$$m = 3C \left(1 - V_{r0}^{\frac{1}{3}} \right) + V_{r0} - 1 \quad (3)$$

where V_{r0} is the volume fraction of the polymer in the solvent-swollen gum, V_{rf} is the volume fraction of polymer in the swollen-filled rubber, C is a characteristic constant of the filler, and θ is the volume fraction of filler in the rubber. The m -value describes the reinforcing ability of filler. It is negative for reinforcing fillers: the higher m , the better the polymer-filler interaction.^{14,15}

Table II. Curing and Mechanical Properties of the CB/MWCNT-Filled Rubber

MWCNT/CB	Curing characteristics			Tensile characteristics			
	Scorch time ts2 (min)	Curing time t90 (min)	Torque S _{max} (dNm)	Tensile strength (MPa)	Elongation at break (%)	Modulus 100% (MPa)	Viscosity, ML (1 + 4)100°C
0/25	7.0	9.7	5.0	22.8 ± 2.6	593 ± 35	1.3 ± 0.05	43.6 ± 0.3
0.5/24.5	6.9	9.6	5.1	24.0 ± 2.9	622 ± 33	1.3 ± 0.05	45.2 ± 0.2
1.0/24.0	6.9	9.6	5.4	23.0 ± 1.0	622 ± 10	1.3 ± 0.05	46.2 ± 0.2
2.0/23.0	6.8	9.4	5.9	23.7 ± 2.9	584 ± 27	1.5 ± 0.05	50.8 ± 0.3
2.5/22.5	6.8	9.5	5.7	21.4 ± 1.9	599 ± 22	1.4 ± 0.04	47.7 ± 0.2
5.0/20.0	6.6	9.4	6.6	22.6 ± 1.7	577 ± 30	1.8 ± 0.03	51.6 ± 0.2
7.5/18.5	6.3	9.2	7.5	22.0 ± 1.4	560 ± 22	2.1 ± 0.04	56.2 ± 0.1
10.0/15.0	6.1	9.0	7.6	19.9 ± 1.3	540 ± 18	2.1 ± 0.06	59.6 ± 0.2
12.5/12.5	5.6	8.5	8.5	16.4 ± 0.5	467 ± 16	2.5 ± 0.12	61.9 ± 0.4

The state of dispersion of the CB and MWCNT particles in the NR/BR nanocomposites was investigated by transmission electron microscopy (TEM) using a JEM 2010 model. Ultra-thin sections were cut from the samples by an ultramicrotome (Leica Ultracut UCT) at -100° with a thickness of approximately 80–100 nm.

The thermal degradation kinetics of the compounds were measured by a Perkin-Elmer STA 6000 TGA in nitrogen atmosphere. The heating temperature was varied from 25 to 995°C and three different heating rates: 5, 10, and 15°C/min were used. The activation energy (E_a) was determined according to the Flynn–Wall–Ozawa method, which is based on the following equation:

$$\log \beta = -\frac{0.457E_a}{RT} + \log \left(\frac{AE_a}{Rg(a)} \right) - 2.315 \quad (4)$$

where β is the heating rate, E_a is the activation energy, R is the gas constant, T is the temperature in which the conversion is reached, α is the conversion degree, A is the exponential factor and $g(a) = \int_0^a \frac{da}{f(a)}$ is the integral conversion function. E_a is the slope of the line of $\log \beta$ versus $1/T$.^{16,17}

For ageing tests, compounds were kept in an oven at 70°C for 2, 7, 14, and 21 days. The elongation at break and stress at 100% strain (100% modulus, M_{100}) were measured on aged samples (three parallel measurements) according to ISO 37. The results were evaluated according to the Ahagon plot, which is used to describe the type of ageing using the 100% modulus and extension ratio at break (λ_b):

$$\lambda_b = AM_{100}^{-0.75} \quad (5)$$

where A is a constant characterizing the base formulation.^{18,19}

RESULTS AND DISCUSSION

Raw CNTs exist in agglomerated form and are heavily entangled like felted threads. Therefore, dispersion of the tubes into single particles is very difficult to achieve. To control the dispersion, the rubber vulcanizates containing 5 and 10 phr were selected for TEM experiments. Figure 1 shows the morphology of the matrix. The coexistence of CB aggregates and the thread-like

structures of the MWCNTs can easily be seen in all figures. The large areas of aggregated and agglomerated MWCNT were not observed in the compound filled with 5 phr MWCNT and 20 phr CB. Relatively large clusters of agglomerated MWCNT were detected in the compounds filled with 10 phr MWCNT and 15 phr CB, clearer in the smaller scale image in Figure 1(d). An explanation for this effect is that the dispersion is getting worse beyond a certain loading as the distance between nanofiller particles decreases and their tendency to form agglomerates increases. Thus, it can be concluded that the inclusion of at least up to 5 phr MWCNT could be done with the existing mixing and processing technology of rubber. MWCNTs are dispersed around CB particles. Thus, CB acts as a separator between MWCNT which facilitates dispersion. Mooney viscosities of the compounds are listed in Table II. The viscosity of the compounds increased proportionally with MWCNT concentration. The surface area of MWCNTs is higher than that of CB, which enables improved interaction with the rubber chains, resulting into a higher reinforcement effect. This fact corroborates the data obtained from bound rubber measurements. Bound rubber is the amount of rubber which is not extractable from an uncured rubber compound. The higher the bound rubber content, the higher the occluded rubber fraction. This is the rubber portion which suffers less from external stress. As shown in Figure 2, the bound rubber increases slightly up to a certain loading of MWCNT; beyond that the values remain almost stable. As shown in Figure 1, the MWCNTs are well dispersed up to a certain concentration, exposing their complete surface area to the rubber chains. After passing a particular concentration, the tubes are no more well dispersed, resulting in a lower degree of filler–polymer interaction and therefore the bound rubber remains unaltered at higher MWCNT concentrations. Figure 2 also shows the difficulties encountered in the BR measurements, especially for lower concentrations of nanotubes: the variation between single measurements is rather large.

The results of the curing studies are summarized in Table II. Scorch time decreases when CB is replaced by MWCNTs. Generally, addition of CB to rubber increases the rate of the curing reaction²⁰; however, an explanation for this effect is not given so far. In the present case, one of the reasons for the shorter

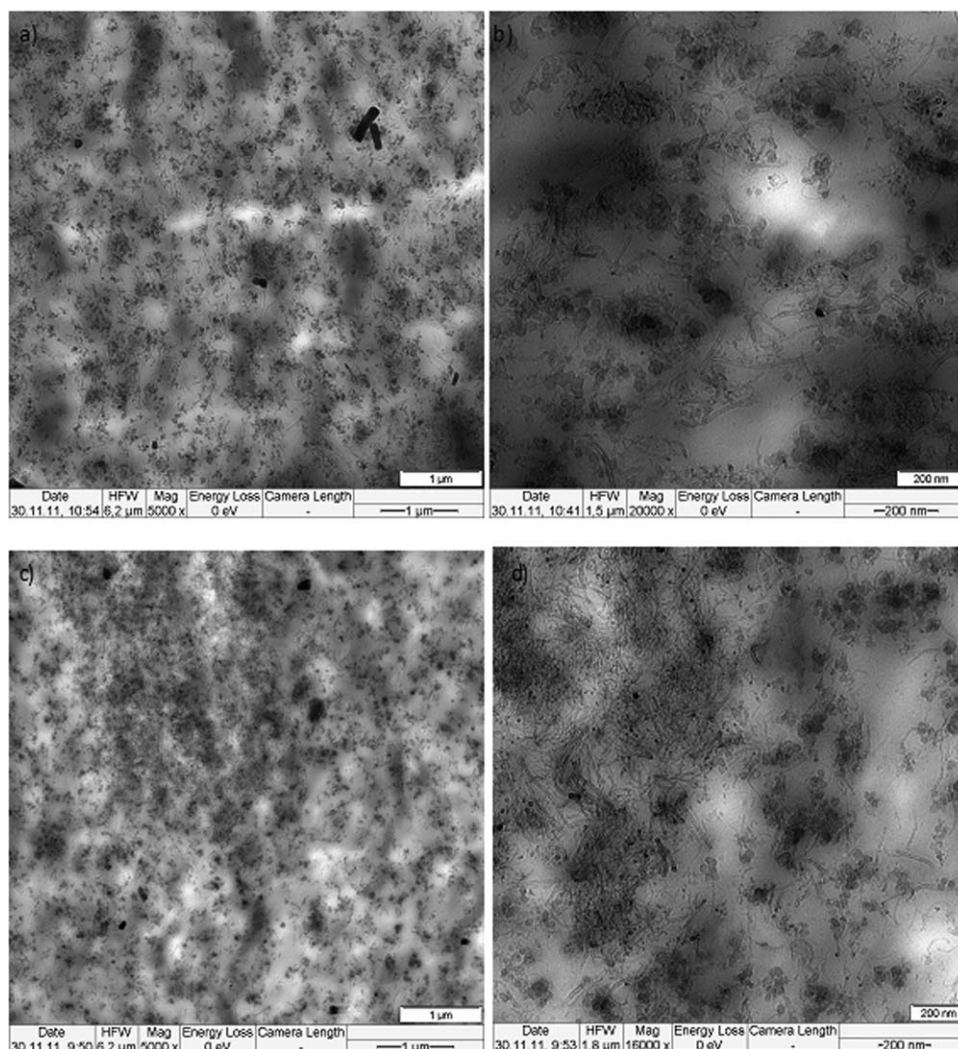


Figure 1. TEM images of the composites containing 5 phr MWCNT (a, b) and containing 10 phr MWCNT (c, d).

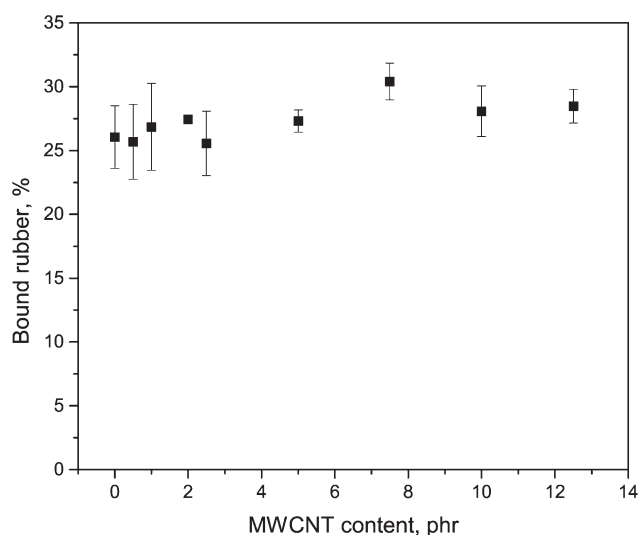


Figure 2. Variation of the bound rubber content with the increase of MWCNT concentration in the CB-filled NR/BR compound. The total amount of fillers was kept constant at 25 phr.

scorch time might be impurities in the MWCNTs: they contain about 10% of metallic impurities from the synthesis by vapour growth deposition. These metals in the tips of MWCNTs could participate in the sulfur vulcanization reaction and enhance the crosslinking reaction rate.²¹ Another explanation is the exceptional high value of thermal conductivity of MWCNTs: the nanotubes can more efficiently transport thermal energy through the matrix, resulting in a faster temperature increase of the material and thus shorter scorch time. A decrease in curing time is also observed, but the change is mainly owing to the reduction in scorch time; the curing rate is not influenced by the presence of MWCNTs. The maximum torque values increase when the amount of MWCNTs is increased, indicating a higher reinforcement effect of MWCNTs compared to CB.

Gradual replacement of CB by the same weight percentage of MWCNTs practically increases the total volume fraction of the fillers, which directly affects the moduli values. This is reflected in the properties of the vulcanizates with higher MWCNT loading: Modulus at 100% elongation starts to increase after incorporation of 2 phr MWCNTs, and a nearly twofold increase in 100% modulus is found at 12.5 phr MWCNTs as compared to

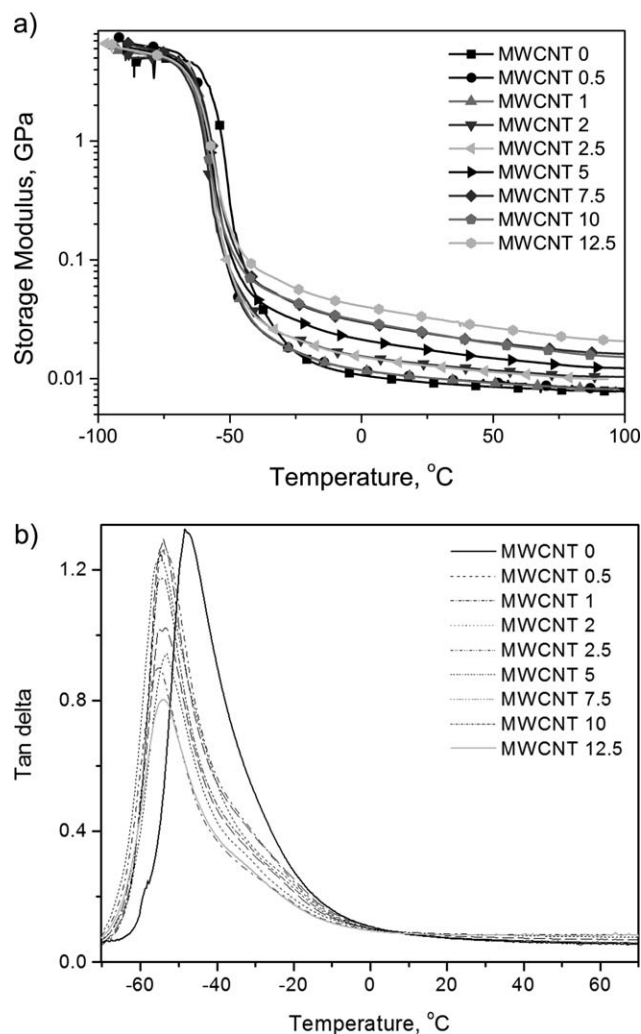


Figure 3. Temperature dependence of the (a) storage modulus and (b) loss tangent of the CB and MWCNT-filled compounds.

the composite containing only CB. The higher surface area of the MWCNTs and thus the increased interaction with the polymer also results in an increase of 100% modulus, tensile strength, and elongation at break when compared to the compound filled only with CB and as long as the MWCNT are well dispersed (Table II). When the amount of MWCNTs exceeded 5 phr, tensile strength as well as elongation at break starts to decrease again owing to insufficient dispersion of MWCNTs.

Analysis of the dynamic mechanical spectra can also help to understand the reinforcement effect of elastomeric materials. Figure 3 shows the storage modulus (E') and $\tan \delta$ values of the compounds as a function of temperature. It is observed that within the rubbery plateau area, MWCNTs increase the E' values of the compounds and make the material stiffer. At the same time, a prominent reduction of the $\tan \delta$ peak is also observed at higher MWCNT loadings, explaining the restricted motion of the rubber chains adhering to the MWCNT surface. A strong rubber–filler interaction is the reason for this behavior, which was also seen in the bound rubber experiments. It is also noticed that MWCNTs decreased the glass transition temperature (T_g) from -48 to -53°C in this study. In most of the

literature, it is claimed that the T_g increases when fillers, which interact with the polymer chains very firmly, are added. However, plenty of reports can be found describing a negative shift of the T_g of the polymer filled with different types of nanosized fillers. Allaoui and El Bounia²² showed that the T_g of CNT-filled epoxy is lower than that of unfilled epoxy in many studies. The decrease in T_g was explained with lower curing degree. They analyzed, published elsewhere, T_g values of CNT/epoxy composites and stated that especially single-wall CNTs decrease T_g of epoxy; for MWCNTs a clear trend was not found. However, in rubber the analogy with epoxy cannot be drawn. On the contrary to the existence of a glassy-like polymer, the existence of a very thin liquid-like polymer film near to surface of MWCNT can also be envisaged to give a possible explanation for negative shift of T_g .²³ The graphitic surface of the MWCNT which energetically is not favorable to adsorb the macromolecular chains could be the reason behind it.

The dependence of certain dynamic properties on the strain amplitude at low deformation range can help to understand the dispersion state of the fillers in a soft rubber matrix. It describes the filler–filler interactions between the filler particles: the higher the filler–filler interaction, the higher the modulus. But as these interactions are effective only on short distances, the modulus quickly decreases with increasing strain. This is called the Payne effect. This dependency is very strong when the fillers form a three-dimensional network within the rubber matrix. Reasonably, well-dispersed filler particles do not contribute as much as poorly dispersed fillers to the network, thus to the modulus. This effect is generally quantified by measuring a storage modulus as a function of strain. Figure 4(a) shows the strain dependency of the storage modulus of the MWCNT/CB-filled NR/BR matrix measured at 100°C , and Figure 4(b) shows storage modulus values at low strain (0.56%), illustrating the differences in Payne effect. It is evident from the figures that filler–filler interaction increases when the concentration of MWCNTs increases. The storage modulus at low strain is gradually increasing, illustrating strong network formation by the MWCNTs as CB is successively replaced. In general, a rubber matrix filled with a particular volume fraction of fillers shows a lower Payne effect when the fillers are better dispersed. An example for this effect is the addition of a silane coupling agent to a silica-filled system, leading to a decrease of the Payne effect as the rubber–filler interaction develops at the expense of the filler–filler interaction.²⁴ But in the case of MWCNTs with extremely high anisotropic character, the filler–filler interaction increases when the agglomerates are dispersed into individual tubes, as these latter form an interconnecting network throughout the matrix. Subramaniam et al.²⁵ proposed this mechanism and they observed that the well-dispersed tubes could show a strong Payne effect and badly dispersed tubes yield little effect in the strain dependence of the modulus values.

MWCNTs are known to increase electrical conductivity of polymers. It is obvious that higher amounts of MWCNTs decrease the resistivity of the composites. Figure 5 shows the dependence of DC electrical resistivity on MWCNT content. As the sample without MWCNT contained 25 phr CB, a percolated network of CB particles was already established, and thus the addition of

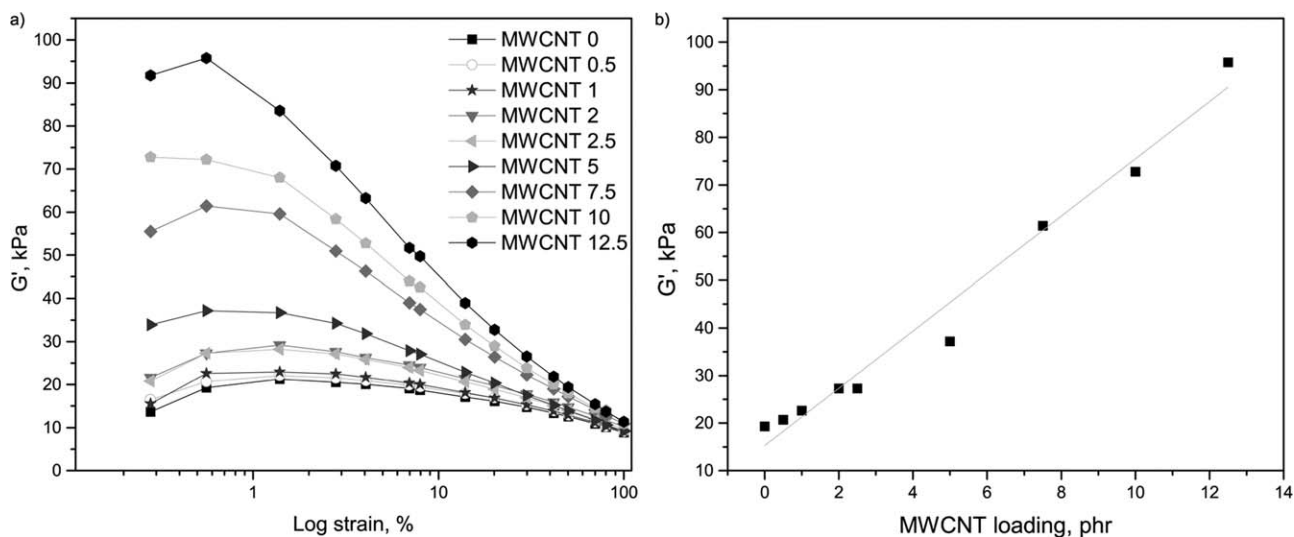


Figure 4. (a) Storage modulus of the compounds as a function of strain at 100°C and (b) storage modulus of the compounds at 0.56% strain with various concentrations of MWCNTs.

MWCNTs was not reflected by showing a rapid decrease of the resistivity. Nevertheless, after partial replacement of CB by MWCNTs, the composites show a decrease in resistivity, indicating the earlier discussed filler–filler network.

The volume fraction of the polymers can be calculated from swelling studies, and it is related to crosslink density. The volume fractions of the polymer in the MWCNT/CB-filled NR/BR compounds are listed in Table III, and it is obvious that the volume fraction of the compounds containing MWCNTs is higher than the fraction of the compound containing only CB. In these compounds, CB was partially replaced by MWCNTs. As MWCNTs have lower density than CB, the volume fraction of fillers increased with the addition of MWCNTs, even if the total amount of fillers was kept constant. The lower degree of swelling indicates higher crosslink density and higher reinforcement. However, it is observed that after addition of 7.5 phr of MWCNT, the degree of swelling does not change anymore with

the increase in MWCNT content, indicating decreased in crosslink density. This can also be seen in Figure 6(a), where the Kraus plots of the CB/MWCNT-filled NR/BR compounds are presented. The slope of the curves represents the polymer–filler interaction parameter. According to these results, with increasing MWCNT content the slope becomes steeper up to 10 phr, indicating higher rubber–filler interaction. With 12.5 phr MWCNT loading, the slope decreases substantially owing to an increased amount of agglomerates. It needs to be mentioned here that a higher amount of MWCNT not only increases the reinforcement of the rubber matrix owing to the higher volume fraction of the MWCNTs, but it simultaneously suffers from poor dispersion of the tubes as observed from TEM images. It would be very difficult to draw a clear conclusion from the swelling data alone, but together with the results mentioned above, the increase in higher reinforcement effect can be easily seen.

The activation energies of the thermal degradation of the compounds were calculated according to the Flynn–Wall–Ozawa method. Figure 6(b) shows the degradation kinetics and the

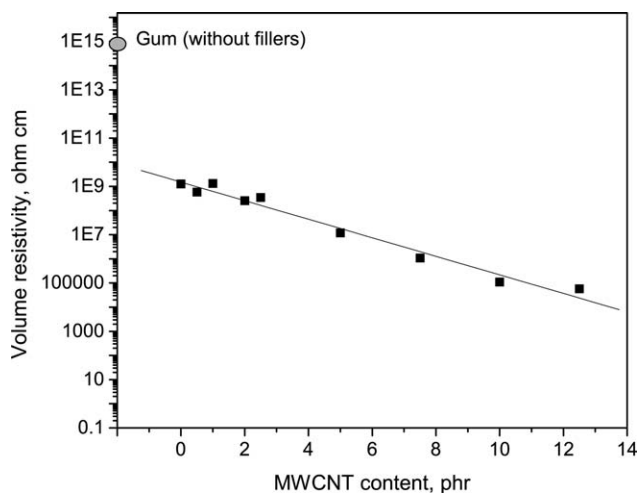


Figure 5. Volume resistivity of MWCNT/CB-filled NR/BR compounds.

Table III. Volume Fractions of the Rubber in a Swollen Network

MWCNT/CB concentration	Volume fraction (–)
0/25	0.173
0.5/24.5	0.185
1/24	0.198
2/23	0.185
2.5/22.5	0.190
5/20	0.204
7.5/17.5	0.210
10/15	0.197
12.5/12.5	0.202

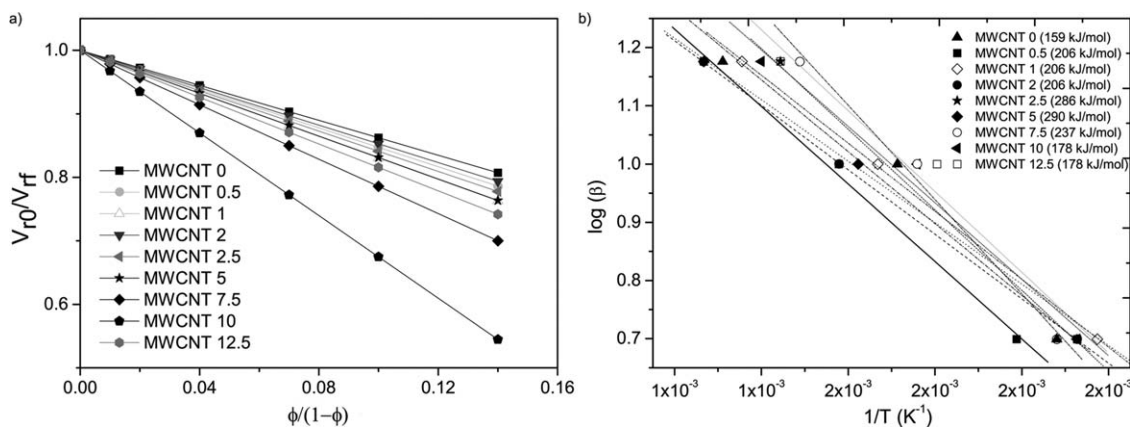


Figure 6. (a) Kraus plot and (b) Flynn-Wall-Ozawa plots of MWCNT and CB-filled NR/BR compounds.

activation energies at 40% conversion level of the MWCNT/CB-filled compounds. The activation energy varied from 159 to 286 kJ/mol with different MWCNT loadings. The activation energy increased gradually up to a 5-phr MWCNT loading. At higher MWCNT loadings, it decreased again most probably owing to the increasing amount of agglomerates which gives a more heterogeneous character to the rubber matrix. This prevents interaction with the rubber chains and makes the matrix degrade easily. Ageing of rubbers changes mechanical properties of rubber. Typical changes are an increase in modulus and decrease in elongation at break (ϵ), which is also valid with these compounds as summarized in Table IV. In many applications, it is important to be able to foresee the period that a rubber can be used under service conditions. Ahagon et al.¹⁸ observed that the modulus at 100% strain and elongation at break can be utilized

in the prediction of the life cycle of a tyre. If ageing is owing to further crosslinking, the slope of the plot of the logarithm of the extension ratio (λ_b) versus the logarithm of the modulus at 100% strain (M_{100}) should be about -0.75 . In Figure 7, the corresponding plots are shown. As shown in Figure 7, it is observed that the slopes are not exactly matching with each other and that they slightly deviate from the value -0.75 . The slopes lie in the range from -0.58 to -1.20 . No regular trend was found when CB is replaced by MWCNTs, and the presence of MWCNT does not seem to influence the aging behavior. The average value of the slope is found to be approximately 0.84. From this result, it can be concluded that ageing of MWCNT/CB-filled NR/BR compounds at 70°C is dominated by the formation of crosslinks and not by destructive degradation of the bonds.

Table IV. Elongation at Break and 100% Modulus Values of the Compounds After Ageing

MWCNT/CB content		Ageing 0 Days	Ageing 2 Days	Ageing 7 Days	Ageing 14 Days	Ageing 21 Days
0/25	ϵ (%)	616 ± 40	599 ± 22	514 ± 5	511 ± 50	495 ± 11
	M_{100} (MPa)	1.28 ± 0.06	1.50 ± 0.03	1.51 ± 0.04	1.56 ± 0.01	1.77 ± 0.06
0.5/24.5	ϵ (%)	618 ± 28	627 ± 5	510 ± 2	502 ± 12	531 ± 1
	M_{100} (MPa)	1.36 ± 0.06	1.38 ± 0.12	1.58 ± 0.18	1.7 ± 0.08	1.8 ± 0.08
1.0/24.0	ϵ (%)	634 ± 17	567 ± 22	512 ± 2	502 ± 10	510 ± 10
	M_{100} (MPa)	1.43 ± 0.01	1.48 ± 0.04	1.83 ± 0.02	1.85 ± 0.08	1.83 ± 0.02
2.0/23.0	ϵ (%)	561 ± 2	562 ± 17	446 ± 61	503 ± 14	502 ± 25
	M_{100} (MPa)	1.67 ± 0.04	1.73 ± 0.02	1.97 ± 0.02	2.15 ± 0.07	2.10 ± 0.04
2.5/22.5	ϵ (%)	599 ± 50	520 ± 41	528 ± 51	530 ± 32	505 ± 14
	M_{100} (MPa)	1.53 ± 0.01	1.63 ± 0.02	1.84 ± 0.06	1.97 ± 0.07	2.05 ± 0.02
5.0/20.0	ϵ (%)	601 ± 22	566 ± 46	522 ± 38	482 ± 52	428 ± 40
	M_{100} (MPa)	1.86 ± 0.09	1.94 ± 0.30	2.19 ± 0.01	2.32 ± 0.08	2.48 ± 0.01
7.5/18.5	ϵ (%)	622 ± 13	576 ± 54	504 ± 26	400 ± 13	461 ± 11
	M_{100} (MPa)	2.26 ± 0.03	2.37 ± 0.13	2.91 ± 0.01	3.15 ± 0.04	3.06 ± 0.18
10.0/15.0	ϵ (%)	512 ± 4	512 ± 33	460 ± 28	349 ± 42	391 ± 49
	M_{100} (MPa)	2.21 ± 0.05	2.35 ± 0.08	2.76 ± 0.02	2.87 ± 0.08	2.95 ± 0.10
12.5/12.5	ϵ (%)	439 ± 24	381 ± 18	371 ± 35	306 ± 37	299 ± 18
	M_{100} (MPa)	2.66 ± 0.04	2.84 ± 0.14	3.06 ± 0.03	3.48 ± 0.10	3.2 ± 0.19

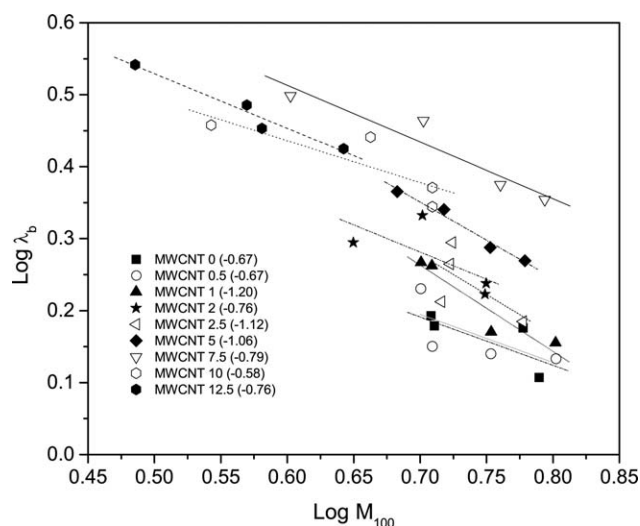


Figure 7. Ahagon plot of the aged samples.

CONCLUSIONS

Replacement of a small amount of CB by MWCNTs enhanced the mechanical properties of the model tread compound significantly. Up to 5 phr MWCNT loading, the dispersion of the tubes was found to be very good. The presence of CB facilitated the dispersion of the tubes in the soft rubber matrix. As the rubber was already filled with CB, the filler concentration was above the percolation threshold though a strong filler–filler network was formed after addition of MWCNT as indicated by strain sweep analysis. As a consequence, the addition of MWCNTs increased the electrical conductivity. The partial replacement of CB by MWCNT enhanced the rubber–filler interaction up to a certain concentration, which was very easily reflected in a Kraus plot analysis. Aging studies indicated a regular formation of new crosslinks which was shown by Ahagon plots.

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