Preparation and properties of carbon-nanotube composites with natural rubber and epoxidized natural rubber

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Abstract: Composites of carbon-nanotubes (CNTs) and natural rubber (NR), as well as epoxidized natural rubber (ENR), were prepared by melt compounding in an internal mixer. The state of CNT dispersion was determined by examination of the electrical percolation threshold of the composites. The composites with the more polar ENR exhibit a lower percolation threshold than those with NR matrices. It was also shown that two-step processing using an internal mixer and two roll mill resulted in a better CNT dispersion and lower percolation threshold. The effect of CNTs on vulcanization and crosslinking were investigated by oscillating rheometer and DSC measurements. The crosslink densities of the composites were determined by equilibrium swelling measurements as well as hysteresis tensile tests. A significant increase in crosslink densities of the composites with increasing CNT content was detected. Increasing CNT content also resulted in accelerated crosslinking reaction. The thermal conductivity of the composites was tested by DSC measurements. A very large increase of thermal conductivity could be obtained with a low CNT content. However, it turned out that the increase of thermal conductivity is restricted by the thermal resistance at the interface between CNTs and the matrix.

Keywords: carbon-nanotube composites, natural rubber, percolation threshold, thermal conductivity.

Otrzymywanie i właściwości kompozytów kauczuku naturalnego i epoksydowanego kauczuku naturalnego napełnionych nanorurkami węglowymi

Streszczenie: Otrzymywano kompozyty kauczuku naturalnego (NR) i epoksydowanego kauczuku naturalnego (ENR) z nanorurkami węglowymi (CNT) w procesie bezpośredniego mieszania składników w stanie stopionym. Stabilność dyspersji CNT oceniano na podstawie wartości elektrycznego progu perkolacji wytworzonych kompozytów. Stwierdzono, że kompozyty na bazie bardziej polarnego epoksydowanego kauczuku naturalnego wykazują niższy elektryczny próg perkolacji niż kompozyty otrzymane z udziałem kauczuku naturalnego. Wykazano, że nanorurki węglowe są lepiej zdyspergowane w nanokompozytach wytworzonych w dwuetapowym procesie, obejmującym mieszanie i walcowanie. Wpływ dodatku nanorurek węglowych na czas wulkanizacji i czas sieciowania kompozytów na bazie kauczuków naturalnych wyznaczano za pomocą reometru oscylacyjnego oraz metodą różnicowej kalorymetrii skaningowej (DSC). Gęstość usieciowania kompozytów oceniano na podstawie pomiarów pęcznienia równowagowego, a także krzywych histerezy w teście rozciągania. Zaobserwowano istotny wzrost gęstości usieciowania kompozytów wraz ze wzrostem zawartości CNT. Metodą DSC oceniano też przewodność cieplną. Niewielki dodatek nanorurek węglowych do kauczuków powodował zauważalne zwiększenie przewodności cieplnej, limitowane jednak przez opór cieplny na granicy faz między nanorurkami węglowymi a matrycą kauczuku naturalnego.

Słowa kluczowe: kompozyty z udziałem nanorurek węglowych, kauczuk naturalny, próg perkolacji, przewodność cieplna.

Polymer composites with carbon-nanotubes (CNTs) as filler have achieved scientific and industrial interest due to the outstanding properties of the CNTs. A complete distribution of the CNTs in the polymer matrix is essential for the exploitation of the excellent properties of the CNTs in the composites. The uniform distribution of CNTs in the polymer matrix is prevented by the strong Van-der-Waals interactions between the nanotubes. The achievement of a very low percolation threshold is emi-

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nently important in the case of CNT-elastomer composites to maintain the elastomeric properties of the matrix. Due to their extremely high modulus and tensile strength and their large aspect ratio, CNTs are supposed to be perfect reinforcing fillers. Additionally, they offer the chance to obtain rubber composites with a certain electrical conductivity and improved thermal conductivity since CNTs themselves exhibit outstanding electrical and thermal conductivity [1, 2].

Several methods of dispersing CNTs in natural rubber (NR) have been examined, including mixing of CNTs and natural rubber (NR) latex [3—5] or distribution of CNTs and NR in toluene followed by evaporation of the solvent [6—9]. The aim of this study was to reach a sufficient dispersion of CNTs in NR and a low electrical percolation threshold by direct melt blending of all composite components. The measurement of the electrical percolation threshold is frequently used to rate the quality of CNT dispersion [10]. NR processing generally includes blending of the components in internal mixers and two roll mills. Those techniques have also been used to prepare NR-CNT composites. Composites with extremely high CNT content of 25 parts per hundred rubber (phr) were prepared [7, 11] using an internal mixer. Processing of composites by means of a two roll mill was applied to compare the resulting properties of NR-CNT composites and NR carbon black (CB) compounds [12—14]. It turned out that the mechanical properties of the NR-CNT composites were better than the properties of comparable NR-CB composites although the bound rubber content in NR-CNT composites was significantly lower than that of CB composites [13, 15]. The bound rubber content is an indication for the level of polymer-filler interactions. Therefore it was argued in [13, 15] that there are only weak interactions between CNTs and NR and that the reinforcing effect of CNTs is mainly due to their high aspect ratio and to physical entanglements with the rubber molecules.

Epoxidized natural rubber (ENR) is a modification of NR. Epoxy groups are randomly distributed along the NR chain and cause a more polar character of the polymer. This results in improved oil resistance, low gas permeability and good mechanical properties. Until now, only a few studies have been published about ENR-CNT composites [16]. The CNTs have been functionalized with an aminosilane. The paper contained evidence that the epoxy groups of ENR react during the processing with available carboxyl or hydroxyl groups on the surface of the CNTs, as well as with the amino group of the silane [16]. In this paper, ENR with a degree of epoxidation of 25 % was also applied as matrix polymer in direct comparison to NR. The aim was to study the effect of the polar epoxy groups on the composite properties. It is assumed that the epoxidation will improve the interactions between CNT and the rubber matrix and lead to better CNT dispersions.

It is expected that during the mixing of the rubber and the CNTs a thorough filler network will be formed at low CNT concentrations. During the vulcanization process the rubber network will be created. The question, whether the CNTs have any effect on vulcanization and crosslinking was discussed only in a few papers [12, 16, 17] and the results and interpretations are contradictory. An acceleration of the vulcanization reaction and a decreasing activation energy of vulcanization was found in [12] for a quite large CNT content of 10 phr. A deceleration of the NR vulcanization reaction was observed in the case of CNTs functionalized with aminosilane in NR [17]. Similar results were found for ENR and explained with the adsorption of accelerator of vulcanization on the CNT surface due to functional groups existing there.

This paper will therefore address the question whether the CNT network has any effect on the vulcanization process. Results of the examination of the vulcanization reaction as well as of crosslink density measurements will be presented.

Furthermore, the change of thermal conductivity of NR and ENR composites due to the action of CNTs was investigated. CNTs have unusually high thermal conductivities. Thermal conductivity values of 3000 W/mK have been published for single CNTs [18]. Therefore, the CNTs should be a suitable filler to improve the thermal conductivity of materials. However, only values of 153 W/mK were found for bulk CNT samples such as buckypaper produced from aligned CNTs and even lower values were detected for buckypaper with randomly oriented CNTs [18]. The improvement of thermal conductivity in the case of polymer composites is generally poor. Values in the order of 0.1—1.0 W/mK for CNT loadings between 1—10 wt % have been reported [19].

The interfacial thermal resistance, Kapitza resistance, may reduce the thermal conductivity. A model to estimate the thermal conductivity of CNT composites taking into account the Kapitza resistance at the interface of CNTs and matrix and the aspect ratio of the CNTs was developed by Nan [20, 21]. We have applied this model to evaluate the thermal conductivity of NR- and ENR-CNT composites.

EXPERIMENTAL PART

Materials

The rubbers used in this study were Natural Rubber (NR) (Standard Malaysian Rubber, SMR-L) and epoxidized NR with a degree of epoxidation of 25 % (ENR) supplied by the Prince of Songkla University, Thailand. Multi walled carbon-nanotubes (CNTs) type NC7000 (purity >90 %) were supplied by Nanocyl (Belgium) and used as received. The average length and diameter of the CNTs were 1.5 μm and 9.5 nm, respectively [22].

Sample preparation

The CNT composites were produced by direct melt blending of the CNTs and the elastomer in an internal mixer (Rheomix 600/Haake Polylab QS). An additional compounding step was carried out for one series of samples on a two roll mill. The compositions of the composites are summarized in Table 1. The vulcanization was carried out in a heated press (Polystat 200T, Schwabenthan) at 10 Pa and 170 °C. Slabs of 115 × 115 × 2 mm^3 were obtained.

Table 1. Materials and composition of samples given in parts per hundred rubber

Component	Content, phr
NR or ENR rubber	100
Stearic acid (Pristerene 4931, Croda GmbH)	2
Zinc oxide (Harzsiegel 1001, Norzinko GmbH)	4
Plasticizer (Shell Ondina 941, Shell Chemicals)	5
Preparation of soluble sulfur, sulfur content 83 % (Strukturol SU 120, Schill + Seilacher "Struktol" GmbH)	2
N-cyclohexyl-2-benzo-thiazolesulfenamid (CBS) (Vulcacit CZ / EG-C, Lanxess)	1
Multi walled carbon nanotubes (CNT)	0—8

Thin films of the composites (0.48 mm thickness) were vulcanized in a heatable press (Specac equipped with an Atlas film press tool, LOT Oriel) to obtain the samples for thermal conductivity measurements.

Methods of testing

Electrical conductivity — Slabs of 2 mm thickness were placed in a Faraday cage (Fetronik) and used to measure the volume resistivity using a tera ohm meter (Knick). A comparator resistor of 1 MΩ in serial connection was applied to measure resistivities lower than 10^6 Ω.

Mechanical properties — Tensile tests and hysteresis tensile tests were carried out with a Zwick 1465 universal testing machine. Samples according to DIN 53 504 were punched out of the vulcanized slabs. Hysteresis tensile tests were used to evaluate the crosslink densities according to the Mooney-Rivlin equation (see text). Since the Mooney-Rivlin Equation is only valid for unfilled elastomers, the method of Mullins [23] was applied to account for the CNT content. Therefore, ten hysteresis cycles to 70 % of the average elongation at break were carried out in hysteresis tensile tests. It was assumed that the polymer-filler and filler-filler interactions were completely broken after ten hysteresis cycles. DMA measurements were used to study the Payne-effect (DMA/SDTA 861e, Mettler-Toledo). Samples with 4.2 mm diameter and 2 mm thickness were placed between the shear clamps of the instrument and measured under shear deformation at room temperature. A test frequency of 1 Hz was applied.

Crosslink density — Two different methods were used to determine the crosslink density: equilibrium swelling using the Flory-Rehner approach [24] and hysteresis tensile testing and application of the Mooney-Rivlin equation [25].

Vulcanization — The crosslinking reaction was investigated with an oscillating rheometer (D-MDR 3000, MonTech) according to DIN 53529. The test temperatures were 160, 170 and 180 °C. Non-isothermal DSC measurements (DSC 823e/700, Mettler-Toledo) were carried out using heating rates between 5 and 30 K/min.

DSC measurements — The thermal conductivity was determined by DSC measurements (DSC 823e/700, Mettler-Toledo) according to a method described in ref. [26]. Disks of 1.7 mm diameter were punched out of the 0.48 mm thin films and placed with an indium disk of 1.5 mm diameter on their top in the centre of the DSC crucible. The melting endotherm of indium was measured with a heating rate of 10 deg/min. DSC measurements with different heating rates were carried out on unvulcanized composites to evaluate the activation energies of vulcanization.

RESULTS AND DISCUSSION

Percolation threshold

The challenge for the application of CNTs as fillers in rubber is to approach very low filler percolation thresholds in order to maintain the overall properties of the rubber. This requires an almost perfect distribution of single CNT molecules in the matrix, which is prevented by the strong Van-der Waals interactions between the CNTs that lead to agglomeration. The most common method to characterize the state of the dispersion is the determination of the percolation threshold. The percolation threshold describes the filler concentration necessary to create a thorough filler network. The percolation threshold can be determined either by rheological measurements, *i.e.* detection of a Payne effect, or by measurements of volume resistivity or electrical conductivity [10]. Figure 1 shows the results of resistivity measurements for NR and ENR composites, which were prepared by direct melt blending of all rubber components in an internal mixer. It can be seen that percolation occurs at quite high CNT concentrations compared to CNT composites with other elastomers [27]. The ENR composites exhibit a percolation threshold at *ca*. 4.5 wt % CNTs whereas about 6 wt % CNTs are necessary to reach percolation for NR composites. The ENR has a higher viscosity than those used for NR. This can be one explanation for a better dispersion of CNTs in the ENR matrix.

There are several studies on CNT composites with NR published in the literature [6, 13, 28, 29]. Composite preparation is often started with the dispersion of CNTs in a solvent or latex by ultrasonic treatment [28, 29]. Bokobza found an electrical percolation threshold between 2.9 and

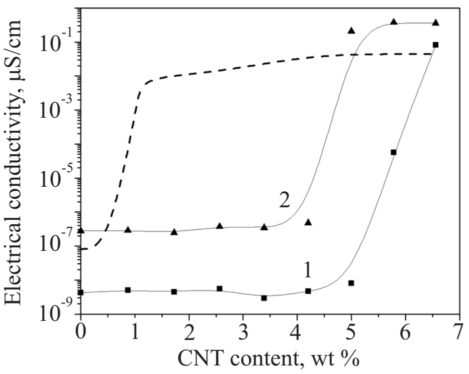

Fig. 1. Electrical conductivity of: NR — 1 and 2 — ENR CNT composites prepared by direct melt blending as a function of CNT content, the dashed line displays conductivities of ENR composites prepared by direct melt blending plus additional mixing on a two roll mill

3.8 wt % of CNTs for NR composites prepared from a dispersion of CNTs and rubber in toluene [6]. Generally, it is agreed that there are only weak interactions between NR and CNTs that leads to lower bound rubber contents of CNT composites compared to composites with carbon black [13, 15, 28]. It is assumed that the more polar ENR exhibit better interactions with the CNTs. This can be another explanation for the lower percolation threshold observed in this study.

It is also interesting to note in Fig. 1, that there are significant differences of the electrical conductivity of the unfilled rubbers due to their chemical structure and that those differences disappear above the percolation threshold. It is clear from this data that the CNT network now plays a dominant role for the charge transfer.

The dashed line in Fig. 1 shows data obtained for ENR-CNT composites that have been prepared by direct melt blending and additional mixing on a two roll mill. The percolation threshold can be significantly shifted to lower CNT concentrations by the additional mixing step.

Figure 2 shows example results of DMA measurements of NR composites. It can be seen that the storage modulus is independent of the strain amplitude as long as no continuous filler network exists. The storage modulus decreases with strain amplitude for samples with higher CNT concentrations due to the breakdown of the filler network. This is described as the Payne effect and confirms the formation of a CNT network. Figure 2 also shows that the storage modulus increases significantly even at small CNT concentrations. Thus, the CNTs exhibit a strong reinforcing effect.

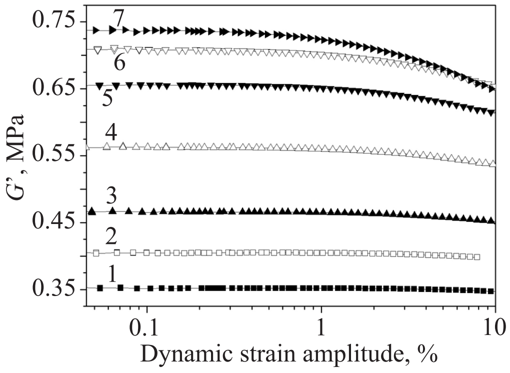

Fig. 2. Storage modulus (*G′*) of NR composites as a function of dynamic strain; amplitude and CNT content given in wt %: 1 — 0, 2 — 0.87, 3 — 1.72, 4 — 3.38, 5 — 4.20, 6 — 5.00, 7 — 6.56

Vulcanization and crosslink density

One aim of the project was to study the effects of the CNT filler network formed during the mixing process of the CNTs and the rubber components on the vulcanization behavior of the rubber. Therefore, vulcameter measurements were carried out. It was observed that the dynamic torque in all unvulcanized, as well as in vulcanized, composite samples increased with higher CNT contents due to the reinforcing effect of the CNTs.

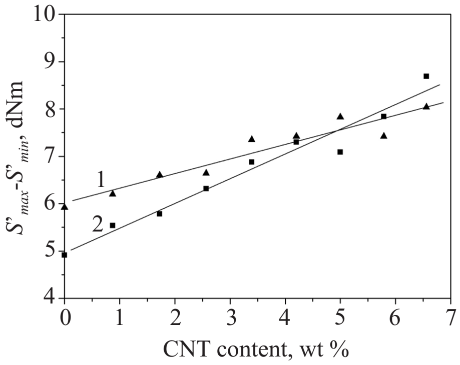

Fig. 3. Difference between maximal and minimal torque (S′) as a function of CNT content: 1 — ENR composites, 2 — NR composites

Figure 3 shows the difference between maximal and minimal torque $S'_{max} - S'_{min}$. The torque difference increases with higher CNT contents, which can be discussed as a consequence of an increasing network density. Therefore, the crosslink densities of the composites were determined. The reduced degree of swelling according to eq. (1), which takes the filler content into account, was obtained from equilibrium swelling measurements [30].

$$Q_r = \frac{(m_q - m_r)\cdot\rho_p}{m_r\cdot(1-\omega_f)\cdot\rho_s} \qquad (1)$$

where: m_q and m_r — the masses of swollen and re-dried samples, ρ_p and ρ_s — the densities of polymer and solvent, and ω_f — the weight fraction of the filler, respectively. The crosslink density ν was calculated using the Flory-Rehner eq. (2)

$$\nu = \frac{-\ln(1-\phi_P) + \phi_P + \chi\cdot\phi_P^2}{V_L\cdot\left(\phi_P^{\frac{1}{3}} - \frac{\phi_P}{2}\right)} \qquad (2)$$

where: V_L — molar volume of solvent, ϕ_p — volume fraction of polymer in the swollen sample and χ — Flory-Huggins interaction parameter.

The degree of swelling decreased with higher CNT contents. Similar results were also reported in [6, 31] and discussed as an effect of hindrance of swelling by the nanotubes due to interactions between polymer and filler. Since hindrance of swelling cannot be excluded, hysteresis tensile testing and the Mooney-Rivlin eq. (3) were also applied to determine the crosslink density.

$$\sigma = 2\cdot\left(C_1+\frac{C_2}{\lambda}\right)\cdot(\lambda-\lambda^{-2}) \text{ or } \frac{\sigma}{2\cdot(\lambda-\lambda^{-2})} = C_1+\frac{C_2}{\lambda} \quad (3)$$

C_1 and C_2 are the Mooney — Rivlin parameters, which can be determined by a plot of the reduced stress $\sigma / 2(\lambda - \lambda^{-2})$ as a function of the reciprocal extension ratio λ^{-1}. The crosslink density was calculated with eq. (4) in which *R* and *T* are the perfect gas constant and the thermodynamic temperature, respectively.

$$2C_1 = \nu RT \quad (4)$$

Since the Mooney-Rivlin equation is only valid for unfilled elastomers, the method of Mullins [23] was applied to account for the CNT content. A strong Mullins effect was observed for composites with higher CNT contents. It was assumed that a complete decomposition of filler-filler and filler-polymer interactions had been reached after 10 hysteresis cycles.

The calculated crosslink densities of NR and ENR composites are presented in Fig. 4. It can be seen that the crosslink density increased significantly with higher CNT contents and that a linear relation between CNT content and crosslink density exists. This can be concluded from the results of both methods. The straight lines for NR composites determined by the two different methods exhibit the same slope but the results obtained from the Flory-Rehner calculation are shifted to lower crosslink densities. A shift of crosslink density values can be explained by insufficient knowledge of the polymer-solvent-interaction parameter. Small changes of this temperature and the concentration dependent parameter of the Flory-Rehner Equation can result in a pronounced shift of the values along the ordinate. For pure ENR, one can observe that the crosslink densities determined by both methods are quite similar but that the values determined by the equilibrium swelling experiments increase significantly greater with CNT content than that of the hysteresis tensile tests. In this case, it can be assumed that stronger filler-polymer interactions, which are already dissolved during the hysteresis tensile tests, are the reason for hindrance of swelling of the ENR composites. Stronger filler-polymer interactions can also be a reason for the lower electrical percolation threshold of ENR composites as compared to the NR composites. Increasing crosslink densities were also found for other investigated composites [27].

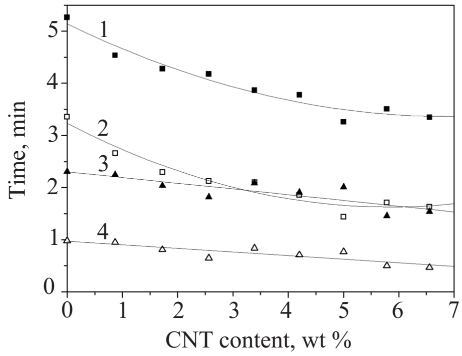

Fig. 5. Induction time (open symbols) and vulcanization time (solid symbols) for NR — 1, 2 and ENR — 3, 4 composites as a function of CNT content

The vulcameter measurements also revealed that the induction and vulcanization time decreased with increasing CNT content. This can be seen in Fig. 5. A linear decrease of the determined times with increasing CNT con-

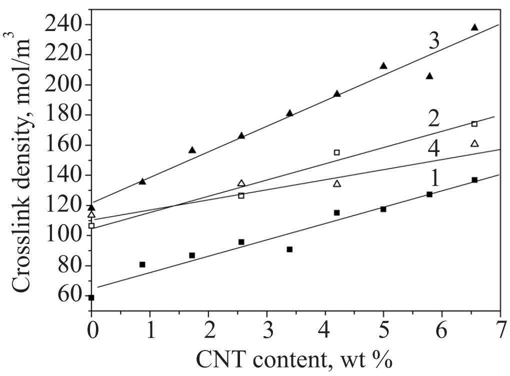

Fig. 4. Crosslink densities of NR — 1, 2, and ENR — 3, 4 composites as a function of CNT content calculated by Flory-Rehner eq. (solid symbols) and by Mooney-Rivlin eq. (open symbols)

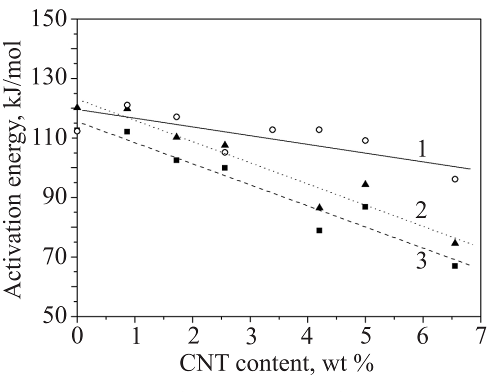

Fig. 6. Activation energy of vulcanization for ENR composites as a function of CNT content: results of isothermal vulcameter measurements and calculated with a 1st order kinetic model — 1 and results of non-isothermal DSC measurements calculated according Ozawa — 2 and Kissinger — 3

tent was found for ENR whereas the data of NR composites can be fitted with a polynomial of the 2nd order. This indicates that CNTs accelerate the vulcanization reaction.

Therefore, the vulcanization kinetics were investigated and results of ENR composites are shown in Fig. 6 as an example. Kinetic studies based on the vulcanization isotherms and using a 1st order kinetic model revealed that the activation energy of vulcanization E_A decreased with higher CNT contents. This was also found for other CNT composites [27]. Non-isothermal DSC measurements with different heating rates have been carried out to verify the trend. The data were evaluated according to Kissinger eq. (5), which is based on a 1st order kinetic model and according to the Ozawa eq. (6) which is based on a "model free" approach [32].

$$E_A = -R \cdot \frac{d\left\{\dfrac{\ln\beta}{T_p^2}\right\}}{d\left\{\dfrac{1}{T_p}\right\}} \tag{5}$$

$$E_A = -R \cdot \frac{d\ln\beta}{d\left\{\dfrac{1}{T_p}\right\}} \tag{6}$$

T_p and β of eqs. (5) and (6) are the peak temperature of the vulcanization reaction and the heating rate, respectively. Higher CNT contents resulted in decreased activation energies of vulcanization. There are still only a few studies reported in the literature dealing with the effect of nanotubes on the crosslinking kinetics of rubbers. The results and interpretations are contradictory. The adsorption of vulcanization accelerators or polymer chains on the CNT surface was discussed as one reason for a lower rate of vulcanization and increased activation energy in [7, 31, 33]. Other authors described an acceleration of the reaction [11, 12] and discussed that this is due to the increased thermal conductivity of the composites. Taking into consideration that often the examinations have been carried out of samples with very high CNT loadings of 10—25 phr [11, 12] and our studies use low CNT concentrations. Our results obtained so far suggest an acceleration of the vulcanization reaction. The effects are detectable at very low CNT concentrations.

Thermal conductivity

The thermal conductivity was determined by DSC measurements at the melting temperature of indium (156.6 °C) according to the method of Raimo [26] using eqs. (7)—(9). The quantity R_0 is the resistance at the contact area between sample crucible and DSC instrument platform and is considered as a source resistance of the DSC. R represents the thermal resistance of the sample. In a DSC experiment the heatflow difference W between sample crucible and reference crucible is measured as a function of time or temperature and the thermal conductivity of the sample κ can then be calculated from the determined slopes of the DSC reference peak of indium dW_{In}/dt and that of the indium melting peak in presence of the sample as indicated in Fig. 7.

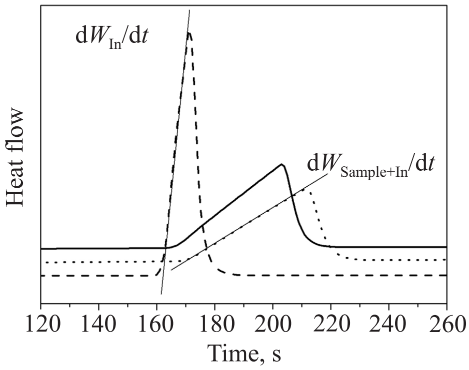

Fig. 7. DSC plots for measurements of thermal conductivity: indium reference measurement (dashed line), indium on NR with 0 phr CNTs (dotted line) and indium on NR with 8 phr CNTs (solid line); the curves are shifted along the heat flow axis for clarity

$$\frac{dW_{In}}{dt} = \frac{1}{R_0} \cdot \frac{dT}{dt} \tag{7}$$

$$\frac{dW_{Sample+In}}{dt} = \frac{1}{R_0 + R} \cdot \frac{dT}{dt} \tag{8}$$

$$\kappa = \frac{d}{R \cdot A} \tag{9}$$

$dT/dt = \beta$ is the heating rate of the DSC experiment, whereas d and A are the sample thickness and contact area between sample and indium, respectively. The measurements were carried out on thin, vulcanized films of 0.48 mm thickness. Figure 8 shows the results for NR and ENR composites. One can see that the thermal conductivities of NR and ENR are not significantly different. Regression with a 2nd order polynomial results in values of 0.281 W/mK and 0.266 W/mK for NR and ENR, respectively. A model for the prediction of the thermal conductivity of CNT composites κ_C was proposed by Nan [20, 21] and is given in eq. (10). The model takes the thermal conductivities of filler and matrix κ_F and κ_M, the aspect ratio of the filler $\alpha = l/d$, as well as the Kapitza resistance R_κ into

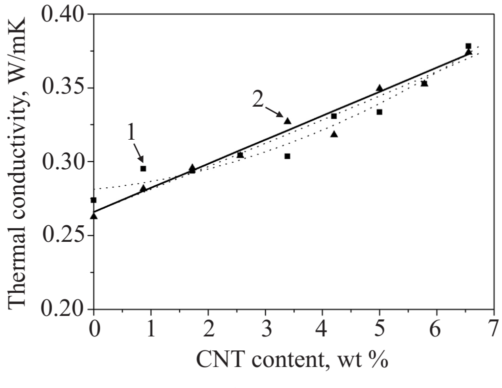

Fig. 8. Thermal conductivity of NR — 1 and ENR — 2 composites as function of CNT content; the dotted lines represent polynomial regression functions, the solid line was calculated according to the model of Nan [21]

account. The Kapitza resistance is the thermal resistance at the interface between filler and matrix and corresponds to the temperature drop at the interface divided by the heatflow density.

$$\kappa_C = \kappa_M + \frac{\phi_F \cdot \alpha}{3} \cdot \frac{1}{\frac{\alpha}{\kappa_F} + \frac{2R_\kappa}{d}} \qquad (10)$$

The solid line in Fig. 8 represents the calculated thermal conductivity of ENR composites. For the calculations of the thermal conductivities, the volume fraction of CNTs was calculated using a density value of 1.8 g/cm^3 [34], but for the sake of clarity, data in Fig. 8 are displayed as weight fractions. The parameters used for the calculation are: $\kappa_F = 2000$ W·m^{-1}·K^{-1} and $\kappa_M = 0.266$ W·m^{-1}·K^{-1}. The Kapitza resistance of $R_\kappa = 8.5 \cdot 10^{-8}$ m^2·K·W^{-1} was determined by regression of the experimental data. The value is in good agreement with published data [35].

It can be seen that the Nan model is in good agreement with our experimental data. The change of thermal conductivity of elastomer/CNT composites was not discussed in the literature so far [36]. For epoxy/single-walled carbon nanotube composites an increase of thermal conductivity to 125 % was found by addition of 1 wt % CNT [37] whereas a CNT loading of 50 % for cellulose acetate increased the thermal conductivity by just a factor of two [19]. It was also reported that the alignment of CNT could further increase thermal conductivity [38]. We can therefore conclude that our results are in general agreement with other data. Thus the high expectations to improve thermal conductivity by use of CNT as filler in elastomers cannot fully be met due to the thermal resistance at the CNT/elastomer interface.

CONCLUSIONS

Composites of CNT and natural rubber, as well as epoxidized natural rubber, have been prepared by direct melt compounding in an internal mixer. Our results indicated the degree of dispersion could be significantly improved by an additional mixing step on a two roll mill. It could also be shown that the more polar ENR exhibited a lower electrical percolation threshold, *i.e.* better CNT dispersion, than NR due to stronger polymer-filler interactions. The effect of the CNT on the vulcanization behavior and the resulting crosslink densities were evaluated. A significant increase of apparent crosslink density was found with higher CNT contents. Furthermore, it can be concluded that the CNT resulted in an acceleration of the crosslink reaction. A notable increase of thermal conductivity of the elastomers was reached at low filler loadings. It could be shown that thermal conductivity is restricted by the interfacial thermal resistance.

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