The Effect of In-Situ Functionalization of Carbon Nanotubes on Thermal Conductivities of Natural Rubber- Carbon Nanotubes Composites

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Abstract. Multiwalled carbon nanotubes (CNT) were used as filler in natural rubber (NR) and epoxydized natural rubber (ENR) composites with the aim to improve thermal as well as electrical conductivity of the composites. In previous studies it was examined how the in-situ functionalization of the CNTs with bis(triethoxysilylpropyl) tetrasulfide (TESPT) and aminopropyltriethoxy silane (APTES) during the mixing process of the rubber compound changes the mechanical and electrical properties as well as the vulcanization behavior [1, 2]. The present paper focuses on the thermal conductivity of rubber-CNT composites. It will be shown that the increase of thermal conductivities of NR and ENR composites with unfunctionalized CNT can be well described by a model developed by Nan [3]. The main parameters are the interfacial thermal resistance and the apparent aspect ratio of the CNTs in the composite. The in-situ functionalization of CNTs with TESPT or APTES reduces the thermal conductivities of the composites in comparison to the values obtained for composites with raw CNTs.

Introduction

Carbon nanotubes (CNT) exhibit a great potential as filler in nanocomposites due to their exceptional properties. Especially their extremely high mechanical strength, their high aspect ratio and their exceptional electrical and thermal conductivity resulted in numerous studies on polymer nanocomposites with improved mechanical, electrical and thermal properties. However, CNTs tend to agglomerate due to the strong Van der Waals interactions between the tubes and this prevents a perfect dispersion of the CNTs in the polymer matrix. It was found that especially for NR-CNT nanocomposites the interactions between the CNTs and the rubber matrix are week and can be improved by surface modification of CNTs with silanes [4]. The chemical surface modification of the CNTs resulted in a significantly lower electrical percolation threshold of the NR-CNT composites. Thermal conductivity values of 3000 W/mK have been published for individual multiwalled CNT [5] and it was therefore assumed that CNTs are also perfect filler to improve the thermal conductivity of polymers. However, the experimental results do not meet the expectations. Furthermore, there are only few studies on thermal conductivity changes of CNT composites due to surface modification of CNTs. Chemical surface modification of CNTs and chemical bonding between CNT and matrix can improve the dispersion and may also improve the phonon transfer at the interface and thus reduce the interfacial thermal resistance [6]. On the other hand, chemical surface modification is interrupting the π-electron system of CNT since sp^2-hybridized carbon atoms are converted into sp^3- hybridized carbon atoms. Furthermore, drastic conditions during chemical surface modification can truncate the CNT and reduce the aspect ratio. The published data

are contradictory. Increased thermal conductivity due to chemical surface modification was reported [7] as well as decreasing [8]. The aim of the present study was to prepare natural rubber composites with improved thermal conductivity. The effect of in-situ silanization reaction with APTES and TESPT on the thermal conductivities of ENR-CNT and NR-CNT composites was examined. In this study, a DSC based method proposed recently by Raimo [9] is used to determine the thermal conductivity changes resulting from chemical modification of the CNTs.

Experimental
Materials. ENR with a degree of epoxidation of 25 mol% and NR, air dried sheets, were used as rubber components. Composite composition, curing system and other additives are published in [1, 2]. The CNTs, NC7000 (Nanocyl, Belgium), have a purity of 90%, average diameter and length of the tubes are 9.5 nm and 1.5 μm, respectively. APTES and TESPT were used as coupling agents between CNT and the rubbers. The silane concentrations were varied and are given in the paper in milliliter of silane per gram CNT.
Sample preparation. The rubber-CNT composites were prepared by melt blending in an internal mixer (Brabender® GmbH & Co. KG, Duisburg, Germany). The silane coupling agents were added directly into the internal mixer. The details of the in-situ silanization procedure are describes in [1, 2]. The vulcanization was carried out at 160 °C. A heated press (Polystat 200T, Schwabenthan) was used for vulcanization to obtain slaps of 115x115x2 mm^3. Thin samples of 0.48 mm thickness for thermal conductivity measurements were vulcanized in a film maker (Specac equipped with an Atlas film press tool, LOT Oriel).
Methods. Thermal conductivity was measured on films of 0.48 mm thickness. Disc-shaped samples with a diameter of 2 mm were punched out of these films. For the DSC measurements, the samples were placed in the center of the crucible with an Indium disc of 1.4 mm diameter on their top. The samples were heated in the DSC (DSC823^e by Mettler Toledo) from 130°C to 190°C with a heating rate of 10 K/min under a nitrogen gas flow of 10 ml/min. The thermal conductivities were determined at the melting temperature of Indium (156,6°C) according to the method described in [9]. Electrical conductivities were calculated from volume resistivity measurements on slaps of 2mm thickness.

Results and discussion
The electrical conductivities of rubber-CNT composites with and without CNT modification are depicted in Fig.1. The addition of larger amounts of APTES shifts the percolation threshold of ENR-CNT composites to higher CNT concentrations (Fig.1a). This indicates that the dispersion of CNTs in the rubber matrix deteriorated due to the addition of APTES. Generally a higher electrical percolation threshold is found for NR-CNT composites compared with ENR-CNT composites (Fig.1b). The CNT surface modification with TESPT contributes to improved physical and chemical interactions at the interphase between CNT and matrix and promotes a better dispersion of the CNTs in NR and consequently leads to a decreasing electrical percolation threshold (Fig. 1b). Both silanes are able to react with existing hydroxyl groups on the CNT surface during the first mixing step of the in-situ silanization process. The sulfur containing TESPT can further react with the rubber's double bonds during the vulcanization process to form additional sulfur linkages between the rubber molecules and CNTs. The amine groups of APTES react with the epoxy rings of ENR during the first mixing step. This leads to a pre-crosslinking of ENR during the mixing process. The pre-crosslinking prevents a sufficient dispersion of the CNTs in the ENR matrix and therefore the electrical percolation threshold shifts to higher CNT concentrations (Fig. 1a).
Table 1 shows selected values of thermal conductivities of the vulcanized rubbers and CNT composites. It can be seen that the pristine rubbers exhibit equivalent thermal conductivities of 0.33 W/mK. The addition of 5 phr raw CNT leads to an increase of thermal conductivities (see also Fig. 2a for ENR-CNT composites). The in-situ silanization of the CNT with APTES in ENR-CNT composites results in a drastic reduction of thermal conductivity to almost half of the value observed for the comparable composite without APTES.
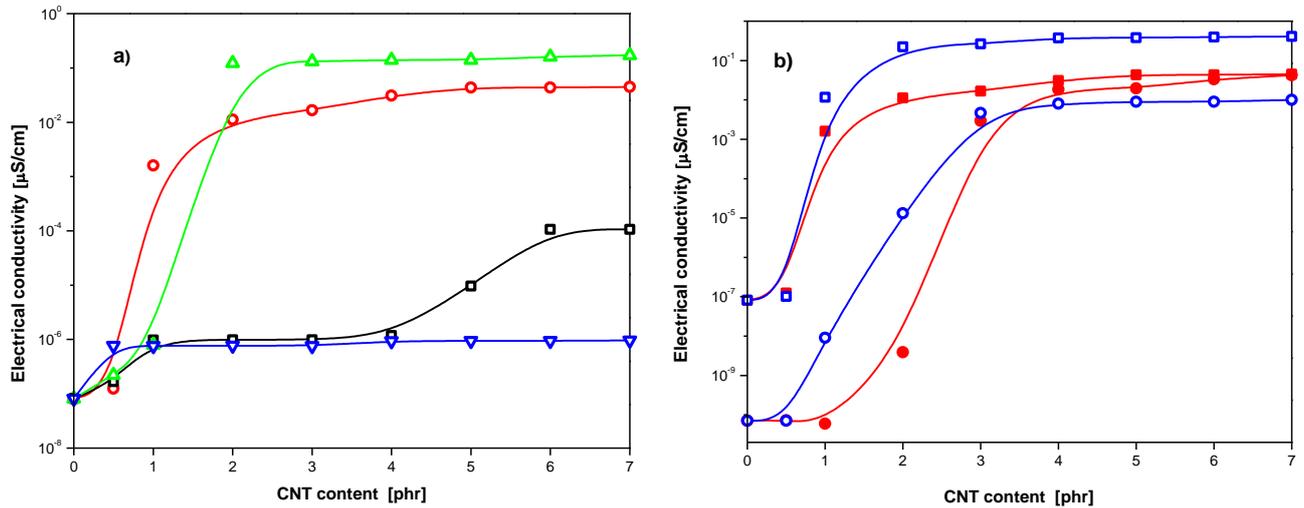
Fig. 1: Electrical conductivities of composites as function of CNT content, CNTs were modified with different amounts of silanes given in ml/g CNT: a) ENR-CNT, APTES amount: ○ − 0.00, Δ − 0.01, □ − 0.03, ∇ − 0.06. b) NR-CNT (circles) and ENR-CNT (squares), TESPT amount: ■, ● − 0.00, □, ○ − 0.06.

This value of 0.23 W/mK is even 30% lower than that of pristine ENR. Also the use of TESPT as coupling agent leads to a reduction of thermal conductivity compared with the composites without silane. The conductivity level of the pristine rubbers is reached in this case. **Fehler! Verweisquelle konnte nicht gefunden werden.**summarizes thermal conductivities of ENR-CNT composites with and without APTES. It turns out that the addition of APTES to the ENR-CNT composites reduces the thermal conductivity compared with the composites without APTES. At a constant CNT content, a decreasing trend of the thermal conductivity with increasing concentration of the silane can be observed.
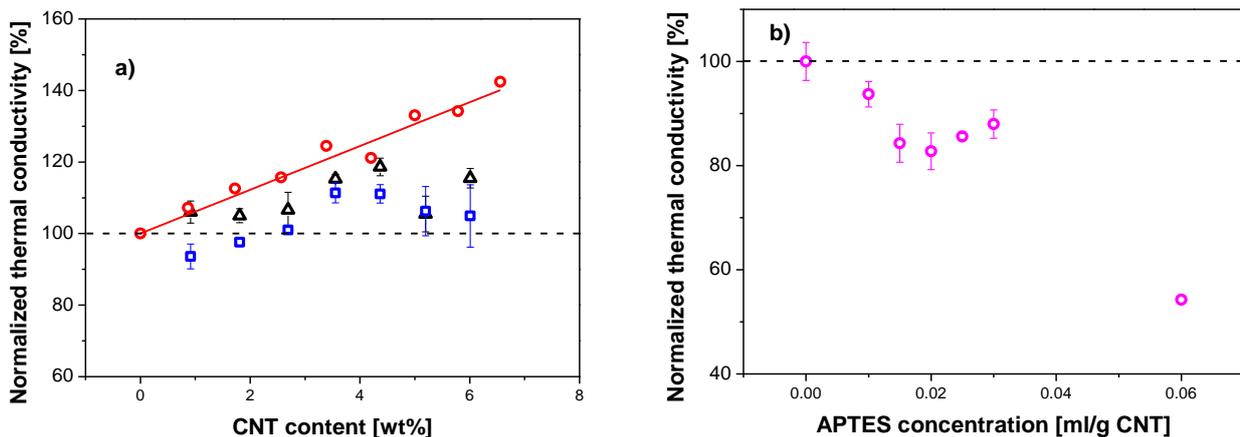
Fig. 2: Normalized thermal conductivity of ENR-CNT composites, CNTs were modified with different amounts of APTES given in ml/g CNT: a) as function of CNT content, APTES amount: ○ − 0.00, Δ − 0.01, □ − 0.03. The solid line was calculated using the model of Nan [3]. b) as function of APTES concentration at a constant CNT content of 5phr.

The thermal conductivity of the composites generally depends on some intrinsic structural parameters of the CNTs such as diameter and length of the tubes, the number of structural defects (sp^3) as well as the presence of impurities. We assume that the in-situ silanization has no impact on the intrinsic CNT properties since only the already existing functional groups have been used for the modification and the CNTs have not been treated with strong acids and truncated. The thermal conductivity of the composites depends additionally on the apparent aspect ratio of the CNTs which is related to the degree of dispersion and on the thermal resistance at the interface between tubes

and matrix. For NR-CNT composites one can assume that TESPT contributes to a better dispersion, i.e. higher apparent aspect ratio, and that the decreasing thermal conductivity can only be explained by the increase of the thermal resistance at the interface due to the created silane layer. In the case of ENR-CNT composites modified with APTES one has additionally to consider the decreasing degree of dispersion and probably also structural changes of the ENR matrix due to the pre-crosslinking during the mixing procedure.

Table 1: Thermal conductivities of selected samples

Sample	*Thermal conductivity [W/mK]*
ENR	0.33 ± 0.01
ENR-5phr CNT	0.42 ± 0.04
ENR-5phr CNT- APTES (0.06 ml /g CNT)	0.23 ± 0.01
ENR-5phr CNT- TESPT (0.06 ml /g CNT)	0.33 ± 0.03
NR	0.33 ± 0.02
NR-5phr CNT	0.44 ± 0.05
NR-5phr CNT- TESPT (0.06 ml /g CNT)	0.36 ± 0.02

Conclusions

In-situ silanization of the CNT surface decreases the thermal conductivity of rubber-CNT composites in comparison to composites with unfunctionalized CNT. This can be explained by the increase of the thermal resistance at the CNT- rubber interface (for TESPT modification) as well as by poor dispersion of CNTs due to pre-crosslinking in ENR-CNT modifies with APTES.

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