Dispersion and distribution of carbon nanotubes in ternary rubber blends

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ABSTRACT

Structure and morphology of carbon nanotubes (CNTs) filled ternary styrene butadiene rubber (SBR)/ nitrile butadiene rubber (NBR)/natural rubber (NR) blends were characterized quantitatively by means of the *wetting concept* und qualitatively supported by transmission electron microscopy (TEM) and atomic force microscopy (AFM). It was found that CNTs mainly reside in the polar NBR and non-polar NR but not in weak polar SBR. Such unusual localization of CNTs in ternary SBR/NBR/NR can be explained by taking into consideration the presence of phospholipids in NR. Phospholipid can act as coupling agent bonding the α-terminal of NR with the CNT surface through cation-π interactions, which make NR be competitive with NBR with respect to CNT hosting. Setting the equilibrium CNT loadings experimentally determined by the *wetting concept* into the *Z-model* recently developed in our previous work by keeping unchanged the surface tension values of SBR and NBR a corrected value of surface tension of NR was determined, which involves the effect of phospholipids.

1. Introduction

Carbon nanotubes (CNTs) have a wide range of potential applications in many industrial areas because of their outstanding electrical and mechanical properties. Recently, they have been used as filler in rubber and rubber blends to create new functionalities and/or to improve various properties of tire tread compounds [1–3]. Generally, it is well-known that a good dispersion and homogeneous phase selective distribution of filler in polymer blends are necessary for optimization of composite properties [4–11]. While the selective filler localization and its effect on mechanical and electrical properties of CNT filled thermoplastic/thermoplastic blends have been comprehensively characterized [4–7], it is still incomplete in the field of rubber/rubber blends so far [8–11]. Furthermore, polymer blends containing more than two rubber components have been prepared with filler in order to obtain synergistic properties of composites [12–15]. For instance, ternary blends on the basis of natural rubber (NR), butadiene rubber (BR)

and ethylene propylene diene rubber (EPDM) were used for tire sidewalls showing excellent ultimate properties, better ozone resistance and fatigue resistance under dynamic load [13]. The dispersion and phase specific distribution of CNTs in ternary blends have not been characterized so far because of the lack of suitable testing methods. In the present work we used the method of the online measured electrical conductance and *wetting concept* as well as *Z-model*, which were further developed for ternary blends [16,17] for characterization of the kinetics of CNT dispersion and distribution in ternary blends based on styrene butadiene (SBR), nitrile butadiene rubber (NBR) and NR.

2. Experimental

2.1. Materials and mixture preparation

Solution styrene butadiene rubber (S-SBR) used was SPRINTAN SLR-4601 (Styron Deutschland GmbH) with a styrene content of 21% and vinyl content of 63%. Nitrile butadiene rubber (NBR) Perbunan 3445F (Lanxess) with a nitrile content of 34% and natural rubber (NR) SMR10 (Standard Malaysian Rubber, Weber & Schaer GmbH) were also used. NR was masticated by means of two-roll

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mill before use in order to obtain a similar Mooney viscosity value as the other blend partners. Multi-walled carbon nanotubes (CNTs) (Nanocyl™ NC7000, Nanocyl S.A., Belgium) with an average diameter of 10 nm and a broad length distribution with several nanotubes up to 10 μm were used as filler. A peroxide (Peroxan DC, Pergan GmbH, Germany) was used as vulcanizing agent for all the mixtures.

For preparation of CNT filled compounds and blends an internal mixer (Rheocord 300p, ThermoHaake) was used by keeping the following mixing conditions: initial chamber temperature T_A of 50 °C, rotor speed of 75 rpm, fill factor of 0.68. A conductivity sensor system was installed in the chamber of the internal mixer to measure the electrical signal of the conductive mixtures [18]. CNT filled compounds were prepared by mixing 7 phr CNTs with different rubbers investigated. Ternary blend CNT–SBR/NBR/NR from *statistic mixing* was prepared by mixing 5 phr CNTs with 33/33/34 SBR/NBR/NR blend in one-step mixing process. For achieving ternary blends from *masterbatch mixing* different CNT masterbatches were prepared by pre-mixing CNTs in each rubber and then the masterbatch was mixed with two other fresh rubbers. The recipes were formulated in order to receive three blends (CNT–SBR)/NBR/NR, SBR/(CNT–NBR)/NR and SBR/NBR/(CNT–NR) with the composition corresponding to that of the statistic blend. For an effective dispersion of CNTs in rubber matrix an ethanol-assisted mixing process (*wet mixing*) according to Das et al. [19] was applied, however, no further non-ionic surfactant was used for stabilizing the nanotubes in the ethanolic medium. CNTs were first wetted with a certain amount ethanol to a paste. Then, it was added into the mixing chamber with rubber for preparation of the composites and masterbatches. Ethanol was entirely vaporized during the mixing process. A ratio ethanol/CNT of 3.7 was chosen for a good dispersion of CNTs. Samples were taken out during the mixing process at different times for further investigation. At a mixing time of 46 min 1.5 phr peroxide was added. Samples taken out at 50 min were compression-molded at 160 °C and 100 bar for t_{90} to obtain a sheet used for mechanical testing.

2.2. Determination of rubber layer L

An amount of 0.1 g of each uncured mixture was stored in 100 ml toluene at room temperature for 7 days. After 4 days the solvent was completely renewed. The solution was cast from the flask and the rubber–filler gel was taken out and dried up in an oven with a temperature of 70 °C for 3 h to a constant mass. At least two experiments were carried out for each sample. Rubber layer L was calculated using Eq. (1) [16,17].

$$L = \frac{m_2 - m_1 \cdot c_{CNT}}{m_2} \quad (1)$$

The mass m_1 is corresponding to the rubber compound before extracting. m_2 is the mass of the rubber–filler gel, which is the sum of the undissolvable rubber part and the mass of CNTs. c_{CNT} is the mass concentration of CNTs in the composite.

2.3. Experimental determination of filler distribution in blends by the wetting concept

Experimental determination of filler distribution by means of the *wetting concept* was carried out according to our procedure described in details in our previous work [16,17]. The filler amounts $S^{B(SBR)}(t)$, $S^{B(NBR)}(t)$ and $S^{B(NR)}(t)$ localized in the SBR, NBR and NR blend phase, respectively, in ternary SBR/NBR/NR blend can be calculated according to Eqs. (2)–(4).

$$\frac{S^{B(SBR)}(t)}{S^{B(NBR)}(t)} = \frac{L_P^{NBR}}{L_P^{SBR}} \cdot \frac{L^{B(SBR)}(t)}{L^{B(NBR)}(t)} \quad (2)$$

$$\frac{S^{B(NBR)}(t)}{S^{B(NR)}(t)} = \frac{L_P^{NR}}{L_P^{NBR}} \cdot \frac{L^{B(NBR)}(t)}{L^{B(NR)}(t)} \quad (3)$$

$$S^{B(SBR/NBR/NR)}(t) = S^{B(SBR)}(t) + S^{B(NBR)}(t) + S^{B(NR)}(t) \quad (4)$$

$S^{B(SBR/NBR/NR)}(t)$ is the total filler amount wetted by the blend at the mixing time t. The plateau values L_P^{SBR}, L_P^{NBR} and L_P^{NR} are the rubber layer at the end of the wetting process of SBR, BR and NR in single compounds determined from Fig. 3a. $L^{B(SBR)}(t)$, $L^{B(NBR)}(t)$ and $L^{B(NR)}(t)$ are the rubber layer of the blend component SBR, NBR and NR at mixing time t, respectively. Their sum is the rubber layer $L^{B(SBR/NBR/NR)}(t)$, which is experimentally determined by the extraction experiment of the blend. Using FTIR analysis of the rubber–filler gel the values of $L^{B(SBR)}(t)$, $L^{B(NBR)}(t)$ and $L^{B(NR)}(t)$ can be determined from $L^{B(SBR/NBR/NR)}(t)$ and the ratio of peak area A^{SBR}/A^{NBR} and A^{NBR}/A^{NR} according to Eqs. (5) and (6) as described in our previous works [16,17].

$$\frac{L^{B(SBR)}(t)}{L^{B(NBR)}(t)} = \frac{1}{f_{SBR/NBR}} \frac{A^{SBR}(t)}{A^{NBR}(t)} \quad (5)$$

$$\frac{L^{B(NBR)}(t)}{L^{B(NR)}(t)} = \frac{1}{f_{NBR/NR}} \frac{A^{NBR}(t)}{A^{NR}(t)} \quad (6)$$

The slope $f_{SBR/NBR}$ = 0.31 and $f_{NBR/NR}$ = 1.1 were determined using calibrations curves [16]. Setting $L^{B(SBR)}/L^{B(NBR)}$ and $L^{B(NBR)}/L^{B(NR)}$ into Eqs. (2)–(4) the phase specific distribution of CNTs in ternary rubber blend can be determined.

2.4. Structural and mechanical characterization

Optical microscopy – Optical microscopy was used to characterize the CNT macrodispersion. The ratio of the surface of non-dispersed agglomerates to that of the image A/A_0 is a measure for the filler macrodispersion.

Transmission electron microscopy (TEM) – Ultrathin sections with approximately 50 nm thickness cut from compression-molded plates with a diamond knife (35° cut angle, DIATOME, Switzerland) at −120 °C using a cryo-ultramicrotome RMC PowerTome PT–PC with CRX cryo-chamber (RMC, Tucson) were used for transmission electron microscopy (TEM). The sections were collected on carbon coated copper grids. The specimens were investigated by means of a LEO 912 Omega EFTEM at an accelerating voltage of 120 kV using the zero loss mode.

Atomic force microscopy – Investigations of filler distribution were carried out by an Atomic Force Microscope (AFM) Nanowizard®II (JPK-Instruments, Berlin) with a scan-head of $100 \times 100 \times 15$ μm³. For maximum resolution the z-scanner range was reduced to 1.5 μm. Super sharp silicon cantilever (SSS–NCHR, Nanosensors™, with tip diameter of approx. 4 nm was used only. The AFM was operated in intermittent mode with a constant lever amplitude to keep the interaction forces in a same level to achieve a comparable phase distribution for all samples. All samples were produced by cutting in a cryo-chamber CN 30 of a rotary microtom HM 360 (Microm) with a diamond knife at −120 °C.

FTIR spectroscopy analysis – The analysis of the rubber–filler gel was carried out by use of a FTIR spectrometer S2000 (Perkin Elmer) equipped with a diamond single Golden Gate ATR cell (Specac). The ATR cell was pressed on a shapeless piece of rubber–filler gel with a measuring area of 2 mm × 2 mm. Five spectra were recorded for each sample.

Pyrolysis gas chromatography/mass spectroscopy (Py–GC/MS) – Pyrolysis gas chromatography was performed using a Pyrola 2000 (Pyrol AB), which is coupled to a Trace GC (Thermo Scientific) and Trace DSQ MS (Thermo Scientific). Helium was used as carrier gas with a flow rate of 1.1 mL/min. Whole cell (0.5 mg) was