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Effect of different ionic liquids on the dispersion and phase selective wetting of carbon nanotubes in rubber blends

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ABSTRACT

The aim of this work was to study the effect of the ionic liquids (ILs) with respect to their anion type and the length of alkyl chain as dispersing and coupling agent in carbon nanotube (CNT) filled styrene butadiene rubber (SBR)/natural rubber (NR) blends. We characterized the ILs by their surface tensions whereupon their different values explain the different compatibilities of ILs with the rubber components and the filler. The *wetting concept* was further developed in order to experimentally characterize the effect of the rubber-IL and CNT-IL compatibility on the selective wetting of CNTs in rubber blends. It was found that all the used ILs improved the dispersion of CNTs in rubber blends significantly. During the mixing process the IL layer pre-bound to the CNT surface was replaced mainly by the NR phase and, partly, by the SBR phase. Thus, ILs cannot be used as coupling agent in this rubber blend. For the ILs with surface tension similar to that of CNTs the filler was partly wetted by IL that imparts the mixture a high electrical conductivity directly after the mixing process. This high conductivity can be used for triggering the vulcanization of the blend by means of the Joule heating. The preferential localization of ILs in the rubber matrix - but not in rubber-filler interphase - considerably influences the cross-link behavior of the vulcanizates and thus their final mechanical properties significantly.

1. Introduction

Recently, nanofillers have been added into tire tread model compounds in order to impart them some functionalities like gas barrier, flammability resistance and electrical conductivity as well as polymer blend compatibility [1–6]. Although it is known today that the final application of rubber nanocomposites has not fulfilled all expectations from the past, carbon nanotubes (CNTs) are still of high interest in polymer respectively rubber-like materials, especially for tire applications [7]. For instance, the abrasion resistance of a tire tread composite based on styrene butadiene rubber (SBR)/natural rubber (NR) blends can be improved significantly by addition of CNTs together with carbon black (CB) [8,9]. It was also found that stiffness and damping characteristics as well as thermal stability of the hybrid filler composites are better than the CB filled blends. Although CNTs are an nanofiller with exceptional properties, the properties of CNT composites often lie under expectation so far, because CNTs are difficult to process due to their low dispersibility and their tendency to form aggregates [10,11]. From a thermodynamic point of view, a good dispersion of a filler in a rubber matrix can be adjusted by its solubility parameter [12], which can expresses the compatibility between materials. Several strategies have been proposed to improve the compatibility between polymer matrix and CNTs by surface modification of CNTs for example with carboxyl groups or silanes [13–20]. CNTs can be modified through *in-situ* polymerization of polyethylene (PE) or polypropylene (PP) on CNT surface with help of metallocene based complex [21–23]. Recently, Bergin et al. [24] demonstrated that the use of a suitable solvent can minimizes the Gibbs free energy of mixing, ΔG_{mix}, that leads to a good dispersion of CNTs and graphene from bundles or graphite to single layers or individuals. The

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concept is to choose a solvent that has a similar solubility parameter to that of the nanocarbon material. Using the same concept, Dooher et al. [25] and Ata et al. [26] could achieve lower percolation threshold of CNTs in rubber matrix and higher mechanical property by adjusting the solubility parameter. Recently, functionalization of CNTs with ionic liquids (ILs), a kind of molten salt with nearly zero vapour pressure and high thermal stability, is an interesting topic, because ionic liquids could provide a facile and promising method to control the surface properties of CNTs by means of cation–π interaction [27,28]. Through non-covalent functionalization of CNTs by IL an effective dispersion of CNTs can be achieved while still preserving their desired properties. Carrion et al. [29] produced different nanocomposites containing CNTs modified by IL [OMIM][BF4] and compared their tribological behavior with that of neat polymers and nanocomposites containing pristine CNTs. The best results were obtained with nanocomposites containing modified CNTs. This result was ascribed to a good dispersion of the CNTs in the polymer matrix, increasing their resistance to crack propagation and fracture, and also to the surface modification of the CNTs by the IL. Likozar [30] produced homogeneous hydrogenated nitrile elastomer/hydroxyl-functionalized multi-walled carbon nanotube solids with the aid of IL. Sekitani et al. [31] used an ionic liquid as a surfactant to mix long single-wall carbon nanotubes (SWCNT) into fluorinated rubber, and achieved 20 S/cm using a 10 wt% filler loading [32]. Ionic liquid was also used as dispersing agent for CNTs in thermoplastics like vinylidene fluoride-hexafluoropropylene copolymer (VDF-HFP) [32], polystyrene (PS) [33] and polymethyl methacrylate (PMMA) [34] as well as polyurethane (PU) [35]. Recently, we used a series of ionic liquids as surfactant for rubbers and rubber blends filled with CNTs in order to determine the coupling activity of ionic liquids between diene elastomers and CNTs [36–39]. We found that in contrast to the chemical modification the physical cation-π bondings between IL molecules and CNT surface can be dissolved and replaced by the rubber-CNT bondings under thermodynamic driving forces during the mixing process that leads to a completely different wetting behavior of the CNTs [40,41]. Thereby, the specific adjustment of the composite performance by controlling the rubber-filler interphase becomes difficult, in particular, in multiphase rubber blends. It lacks a consistent method for the quantitative characterization of the development of the structure and composition of the rubber-filler interphase during the mixing process of filled rubber blends so far. In this regard, the present work focuses on the characterization of the effectiveness of ILs with different molecular structure as dispersing and coupling agent for CNTs in rubber blends. The formation of the rubber-filler interphase, i.e. the selective wetting of the filler surface will be qualitatively and quantitatively characterized by taking into consideration the modified *wetting concept* and the *Z-model*, which were developed for filled rubber compounds in our previous works [40,41]. The elucidation of the relationship between the molecular structure of blend components, the selective CNT wetting, the filler dispersion and distribution, as well as the physical properties of filled rubber blends is the target of the work.

2. Materials and experimental

2.1. Materials and composite preparation

Solution styrene butadiene rubber (S-SBR) used was SPRINTAN™ SLR4602 (Styron Deutschland GmbH) with a styrene content of 21% and vinyl content of 63%. Mooney viscosity ML 1 + 4 (100 °C) is 65 MU. Natural rubber (NR) (Standard Malaysian Rubber (SMR 10), Weber & Schaer GmbH) was used as blend partner. NR was masticated in order to reach a Mooney viscosity similar to that of SBR. Multi-walled carbon nanotubes (CNTs) Nanocyl™ NC7000 (Nanocyl S.A., Belgium) were used as filler. Nanocyl possesses a broad length distribution with several nanotubes up to 10 μm. The amorphous carbon content of CNTs is about 3 wt% according to the thermogravimetric analysis made in the present work.

The imidazolium ionic liquids (ILs) used in our study were received from Sigma-Aldrich, Steinheim, Germany. Their chemical structure is given in Table 1. They differ from each other by cation length and the anion type. An IL/CNT/ethanol mixture with a mass ratio of 7/5/10 was prepared by grinding in a motar. Afterward, the IL/CNT/ethanol mixture was mixed into the SBR/NR 50/50 blend in an internal mixer (Rheocord 300p, ThermoHaake) by keeping the following mixing conditions: initial chamber temperature T_A of 80 °C, rotor speed of 75 rpm, fill factor of 0.78. The amount of the filler and additives used in the study was varied in parts per hundred rubber (phr). The curing package consists of 2.5 phr ZnO, 1 phr stearic acid, 1.4 phr sulfur, and 1.4 phr *n*-cyclohexyl-2-benzothiazole-sulfenamide (CBS).

2.2. Experimental

2.2.1. Optical microscopy

Optical microscopy was used to characterize the CNT macro-dispersion. The ratio of the surface of non-dispersed agglomerates to that of the image, A/A_0, is a measure for the filler macro-dispersion. The lower the value A/A_0 the better the dispersion of the filler.

2.2.2. Online measurement of the electrical conductance during mixing process

A conductivity sensor system was installed in the chamber of the internal mixer to measure the electrical signal of the conductive mixtures between the sensor and the chamber wall. The construction and position of the conductance sensors has been described in our previous works [42].

2.2.3. Measurement of the offline conductivity

Measurement of electrical conductivity of uncured and cured samples was carried out at room temperature by means of a multimeter 2750 (Keithley). The shape of the conductive test specimens was a rectangular strip, whose ends were coated by silver paste in order to receive a good contact with the electrodes.

2.2.4. Tensile test

Stress-strain measurements were performed according to ISO 37 using a tensile tester Zwick 1456, Z010 (Zwick GmbH, Ulm, Germany) with a cross-head speed of 200 mm min^{-1} at room temperature. The test specimens had a thickness of 2 mm and an initial length of 50 mm. All data presented are the average of five measured specimens for each sample.

2.2.5. Extraction experiment for determination of filler wetting in rubber blend

For the investigation of the rubber-filler gel of the compounds, 0.1 g of each raw mixture was stored for four days in 100 ml toluene at room temperature and then 40 ml ethanol was added to the solution. Upon seven days the rubber-filler gel was taken out and dried up to a constant mass. The rubber content in the gel L as a measure for the wetting behaviour of CNT surface by the rubber is determined according to Eq. (1) [43].

$$L^{B(SBR/NR)} = \frac{m_2 - m_1 \cdot c_{CNT}}{m_2} \tag{1}$$

The mass m_1 is corresponding to the rubber compound before