



Research paper

Benefits of hybrid nano-filler networking between organically modified Montmorillonite and carbon nanotubes in natural rubber: Experiments and theoretical interpretations

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ABSTRACT

In this paper some new aspects to the hybrid nano-filler networking in elastomer matrix under dynamic mechanical loading conditions and some new methods to reveal a hybrid nano-filler synergy are applied and discussed. Electron spin resonance (ESR) spectra of the multi-walled carbon nanotubes (MWCNT) present in the natural rubber (NR) based nanocomposites were investigated and the dependence of the double integral of resonance spectra on the amount of expanded organically modified montmorillonite (EOMt) present in the NR was established. Its decrease with an increasing amount of EOMt confirmed the synergy between these two nano-fillers. DMA temperature sweep measurements were performed and the cluster-cluster aggregation (CCA) model was used to assess the apparent filler networking energy. The obtained results suggest that the presence of the EOMt above a critical amount strengthens the hybrid-filler networking. In order to investigate how different ratios of these two nano-fillers influence the strain dependency of the storage modulus, strain sweep measurements were performed in tensile mode, and the CCA-model was used to describe the Payne effect.

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1. Introduction

The use of rubber in different fields of application implies the incorporation of fillers in an elastomer matrix. This is an unavoidable process of practical interest which aim is to achieve a significant reinforcement of the mechanical properties of these relatively soft networks, i.e. cross-linked elastomer chains. Active fillers like carbon black or silica are mainly used for this purpose, as they lead to a strong modification of the rubber properties. Besides reinforcement deriving from the presence of these rigid particles in the matrix and their interfacial interaction, there is an additional reinforcement essentially caused by the formation of a complex structure of the active fillers also known as filler networking. The role of this filler networking in rubber reinforcement has been investigated since >50 years by several authors (Payne, 1965; Kraus, 1965; Medalia, 1973) and later more sophisticated approaches have been developed (Heinrich and Klüppel, 2002; Klüppel, 2003; Heinrich and Vilgis, 2015). One of the fundamental micro-mechanical concepts of non-linear viscoelasticity of filled rubber, based

on fractal approaches of filler networking, is the cluster-cluster aggregation (CCA)-model (Klüppel, 2003). This model considers the filler network as a result of kinetical cluster-cluster-aggregation of filler particles in elastomers and is based upon the assumption that the particles are allowed to fluctuate around their mean position in a rubber matrix (Raos et al., 2000). The fluctuation is enabled by the polymeric structure of highly entangled rubbers and takes place around the particles mean position with a fluctuation length of the order of the entanglement length of the rubber (Heinrich et al., 1988; Klüppel and Heinrich, 1995; Klüppel et al., 1997). The strain in dynamic mechanical measurements introduces fluctuations in a filler network by forcing the system to take different configurations. Thus, filled rubbers with respect to strain will display many unusual phenomena that are usually observed in glass-forming materials, powders or flocculated colloids, but now demonstrated in filled rubbers (Raos et al., 2000). This has important implications with regard to our understanding of the strain amplitude dependency of the dynamic modulus of filled rubbers and the CCA-model offers a reasonable theoretical basis for understanding such behavior (Klüppel, 2003).

It is important to note that all these models are developed on rubber filled with carbon black as the most widely used filler in rubber

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products. It is interesting to see whether they could also be applied to describe the behavior of rubber nanocomposites since these last decades we witness a rapidly growing interest in replacement (partial or total) of conventional fillers by nano-fillers in polymer matrices when high performance low weight polymer products are demanded. Different nanofillers are successfully used to achieve high reinforcement. The most investigated, thanks to their unique properties and with demonstrated abilities to enhance the mechanical properties of elastomers, are layered silicates (López-Manchado et al., 2004; Das et al., 2011; Rooj et al., 2012a,b; Ivanoska-Dacicj et al., 2014) and carbon nanotubes (CNT) (Le et al., 2014a,b,c; Mahmood et al., 2014; Hoikkanen et al., 2015). Moreover, the combination of these two nanofillers engenders synergism which results in their better dispersion (Lan and Lin, 2009; Ivanoska-Dacicj et al., 2015a) and enhancement of the nanocomposites properties (Rooj et al., 2015; Ivanoska-Dacicj et al., 2015b).

The electron spin resonance (ESR) spectroscopy is a powerful technique for the investigation of carbon-based materials. Experiments have demonstrated that a lot of factors affect the appearance of the carbon nanotubes ESR spectra. Some authors reported (Bandow, 1996; Coleman et al., 2000) symmetric line shapes (mostly Lorentzian) while others reported asymmetric Dysonian line shapes (Petit et al., 1997). The resonance spectrum of isolated carbon nanotubes will represent a symmetrical Lorentzian or Gaussian shape. Agglomerated nanotubes are characterized by interconnected conducting domains of the order of 1 to 100 μm (Venema et al., 2000; Belin and Epron, 2005) and such structures are characterized by resonance spectra presenting a Dysonian like shape. In composite materials, if the dispersion of nanotubes is good, the resonance line will present a symmetrical shape below the electrical percolation threshold. Above the percolation threshold the composite becomes conducting and a Dysonian-like resonance shape is expected (Chipara et al., 2006). Typically, the ESR spectrum of carbon nanotubes contains several contributions (Poole and Farach, 1999; Bai and Allaoui, 2003); a very broad line characterized by a g -factor (Zeeman splitting factor) value >2.00 assigned to catalyst's impurities (magnetic nanoparticles) and a narrow line located near $g = 2.0023$ assigned to conducting electrons delocalized over carbon nanotubes (Chipara et al., 2009).

The present work is based on the idea to reveal the reasons of the already confirmed benefits arising from the incorporation of hybrid nanofiller systems (different by chemical composition, form and rigidity) in the elastomer matrix (Rooj et al., 2015; Ivanoska-Dacicj et al., 2015b) by applying and discussing some new aspects and methods. Series of NR based nanocomposites containing different ratios of organomontmorillonite (OMt) which layers were further expanded for better dispersion (EOMt) and multiwall carbon nanotubes (MWCNT) are prepared. The effect of the synergism between MWCNT and EOMt on the ESR lines is characterized by the dependence of the double integral of the resonance spectra on the amount of EOMt present in the NR matrix. DMA temperature sweep measurements are performed and the cluster-cluster aggregation (CCA) model is used to assess the apparent filler networking energy. In order to investigate how different ratios of these two nano-fillers influence the strain dependency of the storage modulus, strain sweep measurements are performed and the CCA-model was used to describe the Payne effect. Finally, tensile test measurements are performed to demonstrate the benefits from the incorporation of these significantly different two nanofillers on the mechanical properties of the hybrid nanocomposites.

2. Experimental

2.1. Materials

The NR-compounds were based on a Standard Malaysian Rubber (SMR 10). The organomontmorillonite (OMt) used was Nanofil 15 supplied from Süd-Chemie AG Moosburg, Germany. Distearyl dimethylammonium chloride (QUAT) was used as an organic

modifier. The specific gravity of this OMt was 1.8 g cm^{-3} with an average particle size of 25 μm . Carbon nanotubes, NC7000, a multiwall carbon nanotubes (MWCNT) produced by catalytic carbon vapor deposition (CCVD) process, were supplied by NANOCYL S. A. (Belgium). They were 90% pure containing 10% metal oxides and had an average diameter of 9.5 nm and an average length of 1.5 μm . The stearic acid was purchased from ACROS Organics, Geel, Belgium with 97% purity. The vulcanizing accelerators *N*-tert-Butyl-2-benzothiazolesulfenamide (TBBS) and *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS) were provided from Rhein Chemie Rheinau GmbH, Mannheim, Germany. Sulfur (S), *N*-(1, 3-Dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD) and zinc oxide (ZnO) used in this study were of industrial grade.

2.2. Preparation of the rubber nanocomposites

The preparation of EOMt is fully described in reference (Ivanoska-Dacicj et al., 2015b). The preparation of the hybrid rubber nanocomposites was performed in the following manner: The MWCNT were first dispersed in ethanol in a ratio 1:20 by weight. This pre-dispersion is required regarding the safe manipulation of the MWCNT, but it also enhances their dispersion in the rubber (Das et al., 2008). Then the batch composed of 100 phr NR and 10 phr MWCNT was mixed in an internal mixer (Haake Rheomix) at a fixed rotor speed of 60 rpm, at 90 °C for 20 min. Afterwards, this masterbatch was diluted with NR to a target of 6 phr MWCNT and was mixed together with the EOMt (content varied from 0 to 20 phr), ZnO, 6PPD and stearic acid in the internal mixer at 90 °C with 60 rpm rotor speed for 10 min. In the last step of the preparation of the hybrid nanocomposites, vulcanization accelerators TBBS and CBS together with the sulfur were added to the compound in an open two roll mill (Polymix 110L, size: 203 × 102 mm Servitec GmbH, Wustermark, Germany) at 90 °C. The milling was performed at 0.5 mm and later 0.3 mm nip gap for 5 min. The formulations of NR compounds expressed as parts per hundred of rubber (phr) are shown in Table 1.

The test samples were molded and cured to 2 mm plates by compression molding (150 kN) on an electrically heated hydraulic press at 150 °C. The rubber samples were vulcanized up to their respective optimum cure time (t_{90}), previously determined with a vulcameter (Scarabaeus, Langgöns, Germany), and then stored for 24 h before the tests were performed.

2.3. Characterization

Electron spin resonance (ESR) measurements were performed on a Varian E-109 spectrometer operating at 9.29 GHz, equipped with a Bruker ER 041 XG microwave bridge and a Bruker ER 4111 VT temperature unit. Spectroscopic parameters were: microwave power 10.0 mW, modulation amplitude 0.1 mT, scan range 10 mT and scan time 60 s. The measurements were performed at room temperature.

The state of the dispersion of the hybrid nanofillers in the rubber matrix was investigated using transmission electron microscopy (TEM) with the microscope JEM 2010 model (JEOL Ltd., Japan). The ultra-thin

Table 1
Formulation of different NR compounds.

Sample code	NR ^a	MWCNT	EOMt
NR-0	100	0	0
NR-C6M0	100	6	0
NR-C6M4	100	6	4
NR-C6M8	100	6	8
NR-C6M12	100	6	12
NR-C6M16	100	6	16
NR-C6M20	100	6	20

^a Mass of the ingredients was taken in parts per hundred of rubber (phr). The ingredients which amounts were kept constant in all compounds were ZnO 5 phr, stearic acid 2 phr, 6PPD 1 phr, CBS 1.5 phr, TBBS 0.2 phr and S 1.5 phr.

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