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Fine tuning of the dynamic mechanical properties of natural rubber/carbon nanotube nanocomposites by organically modified montmorillonite: A first step in obtaining high-performance damping material suitable for seismic application

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ABSTRACT

Hybrid natural rubber (NR) nanocomposites, containing 2 phr multiwalled carbon nanotubes (MWCNT) and different quantities (from 0 to 20 phr) of expanded organically modified montmorillonite (EOMt), were prepared in order to produce a NR based material with superior mechanical properties as a first step in obtaining a high-performance damping material suitable for seismic application. Initially a master batch of NR/MWCNT was prepared and then a dilution technique was used for the preparation of NR/EOMt/MWCNT nanocomposites. Raman spectra showed a strong interaction between the rubber matrix and MWCNT and the existence of an only physical mixture of the MWCNT and EOMt. This was reflected on the mechanical properties (both quasi-static and dynamic) which were found to change in the desired way. A remarkable improvement of the lower tensile modulus, tensile strength and storage modulus was achieved with the addition of MWCNT and then a gradual but permanent improvement of the above mentioned properties including improved elasticity and elongation at break with the addition of EOMt. DMA strain sweep measurements showed a pronounced non-linear dependence and a significant increase of the loss factor tan δ (a measure of the dissipation energy) for the nanocomposites with filler concentrations above the mechanical percolation threshold (16 phr).

1. Introduction

When high damping rubber material is designed usually two different approaches are used, one by using a rubber with inherent high damping, and the other by adding high levels of conventional fillers and plasticizers to rubber which has low damping. Both approaches fail to provide the necessary combination of properties; rubbers which are highly damping also show a strong dependence of properties on temperature, whilst the use of high levels of filler and plasticizer leads to unsatisfactory physical properties. Among the elastomers with inherent low damping natural rubber (NR) is the most frequently recommended material for use in elastomeric bearings due to its superior mechanical properties (Fuller et al., 1991, 1997; Groves, 1998). Combination of nanofillers and conventional fillers as a way of obtaining a high performance NR damping material, convenient for base seismic isolation, to our knowledge, was not yet used.

Addition of nanofillers in polymer matrices has attracted a huge scientific interest especially because they allow designing materials with finely tuned properties. The extent and type of tuning depends on several parameters: size of the nanofiller particles, their aspect ratio, state of dispersion, strength of the interaction with the matrix, formation of filler–filler networks etc. (Bhattacharya et al., 2008; Cuppoletti, 2011; Koo, 2006). Understanding and controlling the influence of these parameters on the sought macroscopic properties of the nanocomposites, and further more combining different nanofillers in order to get the desired tailor made properties, are crucial in the application oriented design of materials.

Among the nanofillers used for enhancement of the properties of elastomer based nanocomposites, layered silicates (Das et al., 2011; Galimberti et al., 2010; Galimberti, 2011; Ivanoska-Dacikj et al., 2014a; López-Manchado et al., 2004; Magaraphan et al., 2003; Rooj et al., 2012a, 2012b, 2013, 2014; Usuki et al., 2002; Varghese and Karger-Kocsis, 2003) and carbon nanotubes (CNT) (Das et al., 2008; Hoikkanen et al., 2015; Ivanoska-Dacikj et al., 2014b; Le et al., 2014a, 2014b, 2014c; Mahmood et al., 2014) are the most investigated, thanks to their unique properties. Montmorillonite (Mt) is the commonly used

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layered silicate, due to its large availability, low cost, high surface area and high cation exchange capacity. Additionally, with only one dimension at the nanoscale, purified Mt, with less than 1% of crystalline silica, is considered safe and can be handled as a standard powder (Galimberti, 2011). One of the drawbacks is its hydrophilic nature; therefore organo modified montmorillonite (OMt) is produced generally by ion exchange of interlayer cations with alkyl ammonium cations (Galimberti et al., 2011). Incorporation of OMt gives rise to rubber nanocomposites with enhanced mechanical properties (Ivanoska-Dacikj et al., 2014a; López-Manchado et al., 2004; Magaraphan et al., 2003; Usuki et al., 2002; Varghese and Karger-Kocsis, 2003). Yet this organophilic modification is not a guarantee for a good dispersion or even intercalation/exfoliation of the clay minerals, especially in non-polar rubber, like natural rubber (NR). A simple pre-treatment of OMt by long alkyl chain organic fatty acids is an efficient way to generate a highly exfoliated morphology of the clay mineral particles in non-polar rubber matrices. This organic fatty acid treated OMt is termed as expanded organoclay (EOMt) (Das et al., 2011; Rooj et al., 2012a, 2012b, 2013). CNT, on their behalf, are known to possess exceptional combinations of physical attributes such as high aspect ratio, large flexibility, low density and superior electrical and thermal properties (Dai, 2002). Various theoretical and experimental studies have revealed that CNT are ideal nanoreinforcements that significantly improve the mechanical and functional characteristics of polymer composites (Ashok et al., 2013; Rafiee and Firouzbakht, 2014; Rahmanian et al., 2015; Tzounis et al., 2014). A drawback is their potential hazardous properties (Stepa and Kuhl, 2014), additionally their fluffy appearance makes it really hard to handle them and to successfully incorporate in the rubber matrix. Their strong interaction with the matrix gives rise to a remarkable strength of the nanocomposite material but to the detriment of the elasticity (Rooj et al., 2015) and elasticity is one of the main characteristics of the rubber and a desirable property regarding the application.

Recently an increasing interest is becoming evident for incorporation of hybrid systems based on different fillers in elastomeric matrices. Mainly nanofillers (clay minerals, CNT, nanographite) are used in combination with nanostructured conventional fillers, such as carbon black (CB) and silica (Chattopadhyay et al., 2011; Galimberti et al., 2014; Malas and Das, 2012). All these works show significant enhancement of dynamic-mechanical properties thanks to the use of the hybrid filler system. It was reported by Galimberti et al. (2012, 2014) that the initial modulus values obtained with the hybrid CB-OMt and CB-nanographite filler systems are much higher than those, calculated through the simple addition of the two initial moduli of the composites containing only conventional fillers or only nanofillers. However, in these studies, the quantity of the conventional filler was kept quite high (60 phr), so the benefits of the nanocomposites defined as low weight materials with superior properties cannot be fully utilized. Very recently Rooj et al. (2015) reported about the successful EOMt assisted dispersion of MWCNT in NR. They kept a fixed amount of EOMt (5 phr) and varied the amount of MWCNT (2.5, 5, 10, 20). The initial modulus (M200) was significantly improved with the addition of MWCNT but the ultimate strength and strain were highest for the composite containing only EOMt. This simultaneous improvement of the elongation and strength at break when organo montmorillonite is added was also reported in the work of Ivanoska-Dacikj et al. (2014a).

The present work is based on the idea to utilize the benefits of a hybrid system based on different fillers (nano- and conventional) in order to obtain a novel hybrid elastomeric material, convenient for base seismic isolation, with excellent strength and elasticity and controlled/tailored energy dissipating capacity. The first task should be accomplished by the addition of nanofillers, and then through incorporation of reinforcing and non-reinforcing conventional fillers the energy dissipating capacity of the material should be tuned to a level between 10% and 20% (at 0.5 Hz and 100% shear strain), which is a precondition for the material to be classified as high damping (Naeim and Kelly, 1999).

In this work the focus was on the first step, obtaining NR based nanocomposites with superior properties, enhanced strength and elasticity, using hybrid EOMt/MWCNT filler system. The idea was to use a low quantity of MWCNT to remarkably enhance the mechanical properties of the nanocomposites and then with the addition of different quantities of EOMt to finely tune them. The quantity of MWCNT was purposely kept low to simplify the process of nanocomposite preparation, for reasons previously mentioned, their fluffy appearance and tendency to agglomerate. To maximize their safe handling and improve their dispersion in NR matrix, a master-batch of NR/MWCNT was prepared and then a dilution technique was used for the preparation of NR/EOMt/MWCNT nanocomposites. The nanostructure of the obtained nanocomposites was characterized by both X-ray diffraction (XRD) and transmission electron microscopy (TEM). Raman spectroscopy was carried out to investigate the interaction between NR matrix, MWCNT and EOMt. Quasi-static and dynamic mechanical measurements were performed on crosslinked samples. The analysis of the dynamic mechanical properties was used to understand the reinforcing effect of the hybrid nano fillers on the elastomeric matrix. Strain sweep measurements, carried out by applying cyclic deformations in the tension mode, were used to determine E' (storage) and E'' (loss) moduli. The dependence of E', measured at low strain (so called Payne effect), on the hybrid filler content was studied to investigate the existence of a percolation threshold in the NR matrix.

2. Experimental

2.1. Materials

The rubber compounds were based on natural rubber, 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 average diameter of 9.5 nm and 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-benzothiazolesulphenamide (TBBS) and N-cyclohexyl-2-benzothiazolesulphenamide (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

2.2.1. Preparation of expanded organomontmorillonite (EOMt)

The commercial OMt was expanded by intercalation of stearic acid in the interlayer space (Das et al., 2011). The stearic acid and OMt were mixed at mass ratio of 1:1 in porcelain mortar by a pestle. The mixture was kept in an oven at 90 °C for 15 min, then removed and grinded. In order to get a more homogeneous mixture, this process was repeated 3 times.

2.2.2. Preparation of the hybrid rubber nanocomposites

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 2 phr MWCNT and was mixed together with the EOMt (content varied from 0 to 20 phr), ZnO, 6PPD and stearic