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Test Method

Optimization of the sealing performance in transient conditions of rubber based hybrid nanocomposites by carbon nanotubes, as assessed by a tailored recovery test

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ABSTRACT

A key property of rubbers for sealing applications is their ability to rapidly recover the deformation during a fast movement of the counterparts, occurring in a transient deformation phase. In this work, a simple experimental test method (recovery test) is put forward to mimic the transient phase and to get insight into the behavior of the material during such phase. The effect of the addition of small quantities of carbon nanotubes (CNT) to a carbon black filled nitrile butadiene rubber on the sealing ability of the material was studied. The recovery tests show that the overall recovery behavior is related mostly to the material stress relaxation behavior, while the recovery behavior at very short times, which is indicative of the performance during a transient deformation phase, is strongly influenced by the material elastic modulus and, therefore, it is improved by the presence of CNT in the elastomeric composite.

1. Introduction

Elastomers have unique properties compared to other classes of materials. They are virtually incompressible, highly deformable and have a very low elastic modulus and relatively low creep. Such properties make them the mostly used material for sealing applications. Among them, nitrile butadiene rubber (NBR) is one of the most used elastomers due to its low cost, excellent resistance to oil, fuels, alkalis and acids, low abrasion rate and good processability [1,2].

The target of a rubber seal is to guarantee no leakage of a fluid during service under several application conditions [1]. A key property for sealing applications is the rapid recovery of the seal deformation [3]. A leakage-free seal is able to deform following the movement of the counterparts during a transient deformation, such that the sealing force is maintained continuously at any time during the transient phase. The inability of material to readjust its shape in a very short time may be the cause of seal faults. Depending on the application, leakage of a seal may lead to catastrophic consequences (e.g.: the famous Challenger space shuttle explosion in 1986 [4]). The transient deformation phase may occur in dynamic sealing, where the counterparts have a relative motion between each other, but also in static sealing applications, where no relative motion is normally present between the counterparts, due to a joint loosening or due to a sudden load variation.

The relationship between the fundamental material properties and the seal behavior during the transient deformation phase is quite complex. To date, the commonly used properties to rank materials for sealant ability are compression set (the permanent deformation after a period under strain) and stress relaxation resistance. Compression set only relates to ability of rubber to retain the elastic properties when a strain is removed, whereas stress relaxation simulates the working condition of a static seal, because it describes the ability to maintain the force on the sealing surface [5]. However, the transient phase is similar to an unloading phase. Stress relaxation properties of the material affect this phase, but the relationship is not straightforward [6]. Moreover, good sealing ability does not only depend on the stress relaxation absolute value, but also depends on the relaxation strain rate values at very short times [5]. Finally, the level of deformation also has to be taken into account: seals operate under strain deformation in a range from 10% up to 30% in compression. The behavior of a seal is, therefore, complicated by the complexity of the material behavior and the operating conditions. In this work, a simple experimental test method is suggested to mimic the transient phase and to study

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the behavior of the material during the fast strain recovery phase.

Elastomeric materials are usually reinforced with different kinds of filler in order to tune their mechanical properties. Due to the increased need for more demanding and high performance elastomeric materials, more technological fillers, such as nanofillers, were developed. Nanofillers have primary particles that have at least one dimension in the nanoscale and, compared to traditional fillers (e.g. carbon black, CB, or silica) [7], they have higher specific surface area available to the contact with the polymer. Among them, carbon nanotubes (CNT) can be described as graphene layers rolled into cylinders, characterized by an outstanding elastic modulus, exceptional electrical and thermal conductivity, flexibility, bending strength, high aspect ratio and chemical inertness. As a consequence of their high aspect ratio and surface area [8,9], the addition of carbon nanotubes to an elastomeric matrix increases its elastic modulus, tensile strength and, in some systems, also elongation at break, more efficiently than common fillers such as carbon black [10,11].

Nanofillers are unlikely to replace traditional fillers in large scale applications, mostly due to their high cost. However, the use of hybrid fillers, combination of a traditional filler with small amounts of a nanofiller, can lead to a wider use of nanofillers in elastomer industrial applications and to remarkable properties improvement due to synergistic effects. One of the drawbacks of carbon nanotubes is the difficulty of distributing them in the matrix. The literature [12–14] shows that more uniform distribution and dispersion of CNT can be obtained in the presence of carbon black, and that a hybrid filler network is formed [14–19]. Addition of carbon nanotubes with carbon black, relative to the use of a single filler, is found to lower the percolation threshold, and improve many mechanical, electrical and thermal properties, at least within limited amounts of CNT and depending on filler dispersion [20].

In this paper, mechanical properties of NBR/hybrid fillers based composites for sealant applications, and particularly for the fast recovery behavior during a transient, high level deformation phase, were measured. An experimental test procedure (recovery test) was specifically developed to analyse the material sealing behavior during a transient deformation phase.

2. Experimental

2.1. Materials

A commercial grade of CB filled NBR with 33% nitrile content, a sulphur-based curing system and 30 wt% of carbon black was provided by Ligom srl (Grumello del Monte, Bergamo, Italy). The specific compound formulation and preparation was not disclosed for commercial reasons. The base material is designated as NBR60 (hardness of 60 Shore A).

Multiwall Carbon Nanotubes were Nanocyl NC7000 from Nanocyl, produced *via* the catalytic chemical vapour deposition process, with chemical purity of 90 wt%, average length of 1.5 μm, average diameter of 9.5 nm and surface area in the range of 250–300 m^2/g, as assessed by BET analysis.

2.2. Preparation of nanocomposites

Different weight percentages of CNT: 1, 2, and 4 wt% were added to the CB filled NBR. The corresponding parts in weight per hundred parts of rubber (phr) are reported in Table 1.

CNT were added to the base compound by an open mill. The compounds were passed 5 times through a two roll mill operating at 35–40 °C, rotation speed 26 rpm and 15 mm nip.

2 and 6 mm thick plates and cylinders (diameter: 30 mm, height: 13 mm) were compression molded with 150 bar pressure, at 170 °C for 20 min, according to the optimum cure time determined by rheometric curves. Samples were finally post cured in an oven at 130 °C for 2 h.

Table 1
CNT content in the CB/NBR based composites.

Material	CNT content [wt%]	CNT content [phr[a]]
NBR60	0	0
NBR60-1	1	1.4
NBR60-2	2	2.8
NBR60-4	4	5.7

[a] phr: parts in weight per hundred parts of rubber.

2.3. Characterization

TEM analysis was performed with a Zeiss EM 900 microscope applying an accelerating voltage of 80 kV. Ultrathin sections (about 50 nm thick) were obtained using a Leica EM FCS cryo-ultramicrotome equipped with a diamond knife. The sample was kept frozen at −130 °C during sectioning.

Shore A hardness measurements were performed on 6 mm thick plates (3 overlapping sheets of 2 mm thickness, according with ISO 7619-1:2010) [21]. Micro IRHD hardness measurements were performed on 2 mm thick plates according to ISO 48:2010 [22].

Compression set tests were performed on 13 mm diameter cylinders, cut from 6 mm thick vulcanized plates, according with ISO 815-2:2008 [23] standard. The specimens were compressed to 25% deformation, for 168 h at 150 °C, then were allowed to cool down at room temperature for 30 min before taking the measurement of the final height.

Tensile tests were performed in triplicate on dumbbell specimens (type 2 according to ISO 37:2005 [24]) cut from 2 mm thick plates, having a gauge length of 20 mm and a width of 4 mm. Tests were performed on a universal dynamometer Instron Series 3365, equipped with pneumatic grips, at a crosshead rate of 100 mm/min. Engineering stress and engineering strain were calculated as load divided by the unstrained specimen cross section area and as displacement over unstrained specimen gauge length, respectively.

Dynamic mechanical tests were performed on the cured specimens by a dynamic-mechanical analyzer Q800 (TA Instruments). Specimens having a nominal width of 5.5 mm were cut from the 2 mm thick plates and the gauge length was set at about 20 mm. The tests were carried out in tensile mode, at 1 Hz, at temperatures increasing from −100 °C to 150 °C at a rate of 1.5 °C/min. Oscillation amplitude ranged from 0.02% up to 0.07%.

Recovery tests were performed on 13 mm high cylinders, using the same dynamometer used for tensile tests, equipped with a load cell of 10 kN and compression plates. In order to reduce specimen adhesion to the plates, they were sprayed with talc powder. The recovery test consisted of the following phases: firstly, the upper plate was positioned in contact with the specimen, taking care to keep the contact load below 0.05 N (initial displacement). Then, the specimen was compressed up to a nominal strain deformation of either 10% or 30% (initial deformation), at a crosshead rate of 1 mm/min. The recovery phase followed: the upper compression plate was raised at a constant crosshead rate up to the initial displacement, and the compression force was recorded as a function of the compression displacement. The recovery velocities were 0.1, 1, 10, 100, 500 and 1000 mm/min (the maximum crosshead rate limit of the dynamometer is 1200 mm/min). For all the test conditions (combination of velocity and initial deformation), the recovery tests were performed both with and without a stress relaxation phase preceding the test. When the stress relaxation was performed, the specimen was kept compressed at room temperature at the