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Study of the reinforcing mechanism and strain sensing in a carbon black filled elastomer

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ABSTRACT

The mechanical and electrical properties of a styrene-butadiene rubber (SBR) matrix reinforced with carbon black, at various weight fractions were experimentally studied. The electroconductive composites were used for strain sensing, under tension, by measuring together strain and electrical resistance. The storage and loss modulus decrement with strain were also investigated, on the basis of Payne effect, while a micromechanical model developed elsewhere was employed for the interpretation of the reinforcing mechanism of the composites examined.

1. Introduction

The reinforcing mechanism of polymeric structure due to the presence of nanofillers, in spite of a large number of research works, is still a matter of great interest, especially at temperatures above glass transition temperature Tg, where melts and elastomers are also involved [1,2]. The effect of nanofillers on the mechanical performance as well as on the nonlinear viscoelastic response represents an issue of great importance, that needs to be further explored. A detailed presentation of theories attributing the nonlinear viscoelastic behaviour on filler agglomeration and network formation has been reported by Heinrich et al. [3]. According to these theories, the mechanical enhancement is due to the formation of filler structures, while the reinforcement decrement with increasing strain is assigned to the damage of these structures. Moreover, the effect of strain amplitude on the dynamic viscoelastic properties of carbon black filled elastomers, has been known for many decades, but it was distinguished by the work of Payne [4] and therefore this effect has been referred to as the Payne effect. In particular, the nonlinearity, with varying strain, of the dynamic mechanical properties elastomers filled with carbon black, has been the subject of previous works [5–9]. The Payne effect is of particular importance for a variety of applications, especially in tire industry, because the nonlinearity it refers to is in the strain range applicable in tire operations. Payne [9] has concluded that the nonlinear behaviour of filled vulcanized elastomers is rooted in the breakdown of carbon black network structure, and the energy involved in this breakdown comes from the van der Waals forces between the carbon black particles. Similar ideas have been proposed in previous works [5,7]. Later this interpretation however, has been questioned by several researchers [10,11], given that Payne effect is also observed at low filler loadings, where the inter-aggregate distances are beyond the range of van der Waals forces. Moreover, the viscoelastic nature of Payne effect could not be described by the proposed mechanism. In view of this, Sternstein and Zhu [1] introduced a new theory to account for the Payne effect. According to their analysis, temporary bonding of molecular chains to the filler surface result in trapped entanglements, affecting the mobility and conformational freedom of both near- and far-field matrix chains. In other words, the presence of entanglements, due to the long polymer chains, existing above Tg, has a strong effect on the material's viscoelastic behaviour. Among the large number of works discussing the Payne effect, physical models providing a quantitative description were

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presented by Kraus [12], Heinrich-Klüppel [13], Huber and Vilgis [14], while pure empirical mathematical models are presented in work of Dean et al. [15]. The mechanical enhancement of polymers, polymer melts and elastomers emerges from a variety of fillers and nanofillers, such as carbon black, carbon nanotubes, and graphene. Apart from the reinforcing effect, a common characteristic of the above-mentioned fillers is that when they have been implanted into an insulating polymer matrix, an electrically conductive polymer composite is obtained. Therefore, the intrinsic conductivity of these fillers makes them multifunctional and suitable for a wide variety of applications such as their usage as sensors for strain sensing for structural health monitoring [16]. The main concept is using the structural material itself as the sensor. This concept is also referred to as self-sensing and has the advantages of being low-cost, it can be applied to a large volume of the structural material and there is an absence of mechanical property loss. The concept is based on the monitoring of the changes in electrical conductivity in order to detect the onset, nature and evolution of dangerous deformation levels in advanced polymer-based composites. A lot of research on such nanocomposites under mechanical loading has been done concerning electrical measurements such as resistivity or capacitance to examine their potential use in deformation or pressure sensors [17–19]. The relationship between conductivity and stress-strain curve has been studied for two different matrices, thermoplastic and elastomeric, reinforced with carbon black [19], however, little attention has been paid to the mechanical enhancement of these materials and the related mechanisms.

The aim of the present work is twofold; first to study the reinforcing mechanism of carbon black filler in SBR elastomer, and the dynamic modulus decrement with strain amplitude within the context of hydrodynamic and micro-mechanics models, and second to examine the effect of the filler content on the electrical properties of SBR/nanocomposite, and its performance for strain sensing. Regarding reinforcing effect, the Young's modulus of the SBR nanocomposites has been described by well known equations, while the storage modulus decrement with strain has been elaborated on the basis of the existence of a filler network. It was found that the network junction model [11] describes better the reinforcing effect of the SBR/nanocomposite. Therefore, this model has been employed for the additional interpretation of the Payne effect. An additional interesting point is that the mode of deformation applied in our dynamic mechanical testing is the tensile one, unlike shear strain used in the majority of previous relevant works. The present work gives a further insight into the relationship between the filler structures, as well as the polymer dynamics in the interfacial region (between carbon black and elastomer), contributing this way to the interpretation of the reinforcing mechanism of the elastomeric matrix. Hereafter, the sensing behaviour of the SBR/nanocomposites has been thoroughly examined, in relation to the carbon black content.

2. Experimental part

2.1. Materials

The elastomeric material employed as a matrix was poly(styrene-co-butadiene) rubber (SBR, Unipetrol Group, Kralupy nad Vltavou, Czech Republic), which was produced by cold emulsion polymerization, and had a styrene content of 22.5–24.5 wt%, an antioxidant content of 1–1.75 wt%, an organic acid content of 5.0–6.5 wt%, and a Mooney viscosity (1 + 40 at 100 °C) of 47–56. SBR matrix was reinforced by carbon black (CB) of type Chezacarb A (Unipetrol RPA, Litvinov, Czech Republic), as a superconductive carbon black. The matrix was reinforced with 2, 5 10, 15 and 20 wt% of carbon black.

2.2. In situ electrical measurements upon tensile loading

The samples were subjected to tensile loading using an Instron 1121 tester. For each filler content at least three samples were measured. The specimen's gauge length was 20 mm, while the cross-section area was 1–2 mm in thickness and 4 mm wide. The crosshead speed was 10 mm/min. A scheme of the experimental setup is depicted in Fig. 1. A non-contact experimental method, based on a laser extensometer was employed for detailed strain measurement [20]. The maximum value of strain applied during the tensile experiments was 60% for materials. Higher strain values attained by the elastomeric material was not possible to be tested by this method.

During each experiment the electrical resistance along the gauge length of each specimen was monitored to observe the electrical behaviour of the material under mechanical deformation. For that reason, the tensile stress, the longitudinal strain and the electrical resistance as a function of time were measured simultaneously.

For the electrical measurements a Keithley Source-Meter 2400 was used. At each measurement a fixed direct current (DC) was applied to the two electrical contacts while the voltage drop between them was measured. For that reason, golden stripes had been sputtered on the surface of each sample, as shown in Fig. 1a, where copper cables were glued using electrically conductive glue. Then the relative change of the resistance ($\Delta R/R_0$) as a function of time was calculated, where R_0 is the resistance at the beginning of the measurement. Finally, the stress and the $\Delta R/R_0$ were plotted against strain. Electrical conductivity and percolation threshold was studied by dielectric relaxation spectroscopy (DRS) measurements in the frequency range 10^{-1}–10^{6} Hz at room temperature using an Alpha analyzer (Novocontrol). Golden electrodes were sputtered on both sides of round sample to assure good electrical contact between these and the gold-plated capacitor plates. Further details about the method can be found in our previous publications (e.g. Ref. [21]).

2.3. Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) experiments were performed using the TA Instruments DMA Q800 instrument. The mode of deformation applied was tension, and the mean dimensions of

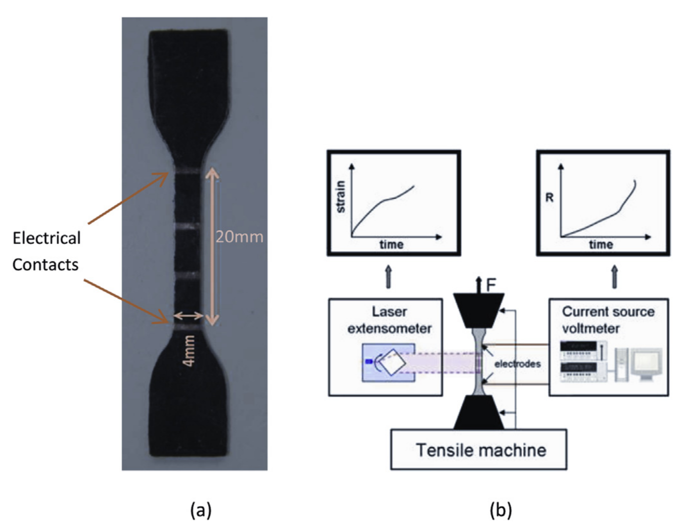

Fig. 1. (a) Picture of the sample with the golden stripes, (b) Experimental setup. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)