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The influence of cyclic loading conditions on the viscoelastic properties of filled rubber

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ABSTRACT

This study deals with the effect of cyclic loading on the viscoelastic properties of filled nitrile rubbers. Classic strain amplitude sweeps were first carried out at two different temperatures (ambient and 80 °C) on both filled and unfilled nitrile rubber specimens in order to observe the influence of the fillers, temperature and loading conditions on the Payne effect. Some specimens were then subjected to a high number of cycles to study the variations in the viscoelastic properties and the sensitivity of the Payne effect to cyclic loading tests at several given strain amplitudes. It appears that the viscoelastic properties of rubber significantly evolve during the cyclic tests, which raises the question of the concept of cyclic stabilized behaviour.

1. Introduction

Rubber components are widely used in various fields of engineering, such as the automotive industry and aeronautics, due to their high elasticity and high damping properties. The optimal design of such components must take into account the mechanical properties of rubber (see for instance Bergström and Boyce, 2000; Le Cam and Toussaint, 2009; Palmieri et al., 2009; Machado et al., 2010; Diani et al., 2004), including viscoelasticity. Classically, the viscoelastic properties of filled rubber are studied using dynamic mechanical analysis (DMA) or dynamic mechanical and thermal analysis (DMTA). This type of analysis provides the storage modulus E', the viscous modulus E'', and the loss factor $\tan\delta$ for a given double strain amplitude (DSA, defined as the strain range). In filled rubber materials, a decrease in the storage modulus is generally observed if the amplitude of the cyclic strain increases. This phenomenon, called the Payne effect (Payne, 1962) or the Fletcher–Gent effect (Fletcher and Gent, 1953), is not observed in unfilled rubber. Several studies have investigated the effect of degradation processes, such as irradiation or temperature (Celina et al., 1998; Delor-Jestina et al., 2000), on the mechanical properties of rubbers. Nevertheless, the effect of cyclic loading on viscoelastic properties has not been studied in the Payne effect strain domain. This lack of information is quite surprising, since rubber parts are subjected to such mechanical cyclic loading in many industrial applications.

This paper aims to investigate variations in the viscoelastic properties of filled nitrile rubber under cyclic loading, typically up to 10^6 cycles. These mechanical cycles were applied under compression. This distinguishes all the more singularly the present study, given that the viscoelastic properties of rubber are classically defined under tensile loading. Firstly, material behaviour was characterized using classic DMTA. Secondly, several DSAs were applied in order to observe and discuss the variations in material behaviour with respect to the number of cycles. Once the mechanical behaviour had been characterized at various DSAs, it became possible to discuss the evolution of the Payne effect at a given number of cycles. The effect

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of temperature was also investigated by performing the experiments at ambient temperature and 80 °C. A state of the art appraisal of the effect of fillers on the viscoelastic properties of rubber is presented initially. The material, the specimen geometry and the loading conditions are then detailed, and the results obtained are discussed. Finally, some perspectives are given for future work.

2. State of the art appraisal

Many theories have been proposed in the literature to discuss the viscoelastic response of rubber, but the physical mechanisms involved are still not clearly established. Nevertheless, several phenomena induced by the matrix and the fillers, as well as their interactions, are classically considered:

1. the formation of a filler network comprising filler-filler and filler-matrix interactions (Wang, 1999);
2. the existence of occluded polymer located within and between the filler aggregates, which increases the effective filler concentration (Morozov et al., 2010);
3. the formation of a layer of bound polymer around the filler particle surface (Morozov et al., 2010);
4. the interactions between fillers and matrix along the interface, which leads to adsorption and desorption of polymer chains at several mobility levels (Maier and Goritz, 1996);
5. the hydrodynamic effect (Einstein, 1906).

The first phenomenon quoted is activated when the filler fraction is sufficient to form a network, composed of agglomerates, i.e. clusters of aggregates, which are bound to each other by physical linkages (Wang, 1999; Medalia, 1978). During cyclic loading, this network successively disrupts and reforms. Thus, the evolution of the competition between the disruptions and reformations of this filler network drives the variations in the viscoelastic properties, more precisely the decrease in the storage modulus with an increasing DSA, which is called the Payne effect (Payne, 1962; Wang, 1999; Voet, 1975). Wang claims that this competition is the main, or even the sole cause of the Payne effect (Wang, 1999). Concerning the network of carbon black filler itself, Morozov et al. (2010) have shown that the filler network exists in four states, which depend on filler concentration:

- separates aggregates;
- individual clusters;
- cluster network with dense regions of cluster cores and aggregate branches linking neighbouring secondary structures;
- continuous filler structure.

It should be noted that the strength of the filler network also depends on the type of filler (Wang, 1999), more precisely on the filler surface characteristics (Wang et al., 1991a,b).

Some morphological features, like bound and occluded polymer volume fractions, depend on the state of the filler network. As mentioned above, disruption and reformation occur during mechanical cycles. If the filler network does not have enough time to recover its original structure during one cycle, E' begins to decrease. This phenomenon occurs once the DSA is sufficient to disturb the balance between disruption and reformation, and therefore ends once the filler network is completely disrupted. Consequently, the evolution of the filler network structure can be partly responsible for the variations in material behaviour for the intermediate strain amplitude values. The breakdown of the filler network allows the release of occluded rubber, which was originally trapped within the filler aggregates and contributed as a filler to the mechanical behaviour of the rubber. Occluded rubber may be a factor in the high initial level of E' and its release plays a role in the decrease in E'. Another reason for the difference in E' level between filled and unfilled rubbers resides in the polymer layer that surrounds the filler particles (Litvinov and Steeman, 1999). This layer contains:

- polymer chains in the glassy state;
- polymer chains with more mobility near the external borders.

This locally causes the density of the matrix cross-linkage to increase. Thus, the disentanglement of the polymer chains, which is initiated by straining, contributes to the increase in E' for small DSA ranges. Despite the numerous studies reported in the literature dealing with the Payne effect, the influence of the evolution of the matrix itself, as well as that of the fillers, on the viscoelastic properties of rubber when it is subjected to a high number of cycles (10^6 cycles) has never been investigated till now. This type of variation in the rubber microstructure is more commonly studied by chemists, who, using DMA or DMTA, tend to characterize the evolution of the microstructure when the material is subjected to photo-oxidation (Feller, 1994) or thermo-oxidation (Kumar et al., 2004) for instance. Even though these studies have improved knowledge of the mechanisms involved, none of them investigates the effect of the mechanical cycles on the microstructure itself and therefore on the evolution of the viscoelastic properties of rubber. This is the aim of the research described here.

3. Experimental setup

3.1. Materials and specimen geometry

The materials tested in this study are nitrile rubbers, respectively unfilled and filled with 35 phr[1] of carbon black and of a small amount of mineral fillers. They were vulcanized with sulphur. The following procedure was used to prepare the specimens: (i) a block was first obtained by compression moulding; (ii) which was then cut with a water jet cutting device to obtain specimens of 5×5 mm^2 square cross-section and 10 mm height; (iii) the resulting low aspect ratio was chosen in such a way that buckling, which might have occurred during the compressive tests, was

[1] Parts per hundred parts of rubber in weight.