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EFFET OF STRETCHING ON THE NETWORK STRUCTURE OF CARBON BLACK FILLED EPDM RUBBERS

Nicolas CANDAU, Jean-Luc BOUVARD, Edith PEUVREL-DISDIER, Rudy VALETTE, Noëlle BILLON

MINES ParisTech, PSL Research University, CEMEF - Centre de Mise en Forme des Matériaux, UMR CNRS 7635, CS 10207, 06904 Sophia-Antipolis, France

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Introduction

Carbon black filled ethylene-propylene-diene-monomer (EPDM) has been widely studied in the recent years. Thanks to its good electrical properties, high resistance to ageing and mechanical properties, it is one of the best candidates for the automotive industry. The improvement of its mechanical properties should be based on a good understanding of the microstructural changes induced by loading. The damage mechanisms, i.e. cavitation / decohesion, are usually studied in the literature by in-situ SAXS [1] or volume changes [2]. However, to the authors' knowledge, no study was devoted to microstructural characterization allowing taking into account the heterogeneity of the rubber network. Thus, the present work proposes an approach to identify the network structural evolution of EPDM rubbers induced by loading combining volume measurements, swelling and thermoporosimetry.

Materials and experiments

The materials of the study are an extended and a non-extended oil carbon black filled EPDM obtained by sulphur vulcanization of the gum. They contain 80phr of carbon black (80 g of fillers per 100 g of rubber). The extended rubber contains 65 phr of paraffin oil.

EPDM samples were stretched uniaxially at room temperature with the strain rate 10^{-1}s^{-1} up to various stretching ratios λ . Tests were performed on an INSTRON tensile test machine. Two camera pairs – allowing neglecting the out of plane displacements – were positioned to measure the strain displacement field on the front and side faces of the samples. A speckle pattern was put on the surface sample. Digital Image Correlation was then used to measure the evolution of the displacement field during the mechanical test, giving access to the relative volume variation during loading $\Delta V/V$. Tested samples were then stored at 21°C during one week to allow slow reversible reorganization of the polymer chains. The center of the sample was then cut and submitted to *post-mortem* characterization. The effective network chain density (ν) – containing filler/rubber bonds, trapped entanglements and chemical crosslinks – is estimated from swelling in cyclohexane, from the Flory-Rehner equation [3] and the Kraus formula [4]. Swollen samples were then put in a DSC to perform thermoporosimetry experiments [5] in order to have access to the pores size of solvent confined in the polymer network (cooling from 21°C to -50°C at 10°C/min, holding at -50°C during 2min and heating at 10°C.min⁻¹ up to 30°C). During heating, the first peaks that appear correspond to the melting of the cyclohexane entrapped in the network. The last peak corresponds to the melting point of free cyclohexane $T_s = 7^\circ\text{C}$ (i.e. in excess), corresponding to infinite crystal.

Results and discussion

EPDM rubbers were stretched at 10^{-1} s^{-1} and at 21°C up to $\lambda=4$. The loading is associated with an increase of volume ($\Delta V/V$) up to 2% and 3.5% for extended and non-extended rubbers respectively. The higher $\Delta V/V$ value for the non-extended rubber compared to extended one is likely due to the higher stress experienced during stretching (because of higher volume fraction of fillers) which thus eases cavitation/decohesion. As compared to virgin samples (not submitted to loading), the effective network density of tested materials (ν) is decreased of 7% and 8% for extended and non-extended EPDM respectively. These results confirm that irreversible modifications take place in the network structure during stretching. Besides, a slight increase of the sol fraction of the tested rubber samples compared to virgin ones suggests that part of the chains are excluded from the elastically active network chains.

To further analyze the microstructural changes, thermoporosimetry experiments were carried out on the oil extended EPDM. Virgin and tested samples exhibit two principal melting peaks T_1 and T_2 below the melting peak of free solvent T_s ; suggesting the existence of two chain length populations. T_1 and T_2 are found higher in tested samples compared to those of the virgin ones. Then, the higher is the melting temperature; the larger is the average chain length (i.e. the lower is the effective network density). As a result, damage during stretching is accompanied by an average increase of all chain length populations.

These changes should be significantly increased for samples stretched up to the rupture ($\lambda=8$). Indeed, in that case, the effective network density is decreased of more than 20%. These results as well as complementary loading conditions (stop at various λ , accumulation of cycles at given λ) will be presented during the conference.

Conclusion

This work presents a new experimental approach for the study of the damage mechanisms in rubbers. An experimental device based on two camera pair systems has been developed in order to accurately measure the volume change of rubber samples during stretching. *Post mortem* analysis of the microstructure, combining swelling and thermoporosimetry experiments, were carried out. A good agreement has been found between the volume change and the microstructural evolution. They show a progressive damage of the rubber during stretching. By analyzing more complex loading conditions, this methodology should be an interesting way to more precisely identify irreversible mechanisms induced by stretching.

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