EFFECTS OF THERMAL AGEING ON THE LARGE STRAIN VISCOELASTIC RESPONSE OF EPDM RUBBER: EXPERIMENTS AND CONSTITUTIVE MODELING

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Summary The present work deals with the thermal ageing of a carbon-black filled EPDM rubber. Experimental observations based on measurements by gravimetry, calorimetry, infrared spectroscopies and multi-step stress relaxation are reported to understand the physico-chemical modifications of network structure and the resulting mechanical response in relationship with both temperature and time. The network alteration kinetics is deduced and coupled to physically-based constitutive equations in order to tentatively predict the thermal ageing effects on the time-dependent mechanical response of the studied EPDM rubber.

INTRODUCTION

Rubbers are extensively used in industrial applications because of their ability to withstand very large strains without appreciable permanent deformation and to absorb energy. Rubber components are often exposed to aggressive environmental conditions (temperature, oxygen, water, gamma radiation, etc.) during the in-service phase which can potentially affect their mechanical integrity and reduce their lifetime. Thus, the development of heuristic models for predicting the changes in mechanical response is of major importance for both design and maintenance of rubber structures. In the meantime, the determination of physico-chemical processes that drive the ageing kinetics is an essential prerequisite to propose a reliable constitutive model coupling the mechanical loading and ageing effects. Among all types of ageing the thermal one gives rise to complex phenomena at the molecular scale which are not clearly understood and are still the object of a vivid scientific debate [1-3]. It is however well recognized that during its thermal ageing, rubber may undergo significant changes in the primary structure due to oxidative chain scissions and cross-linking [2-4], but also to ageing-induced crystallization phenomena with a complex coupling between the fillers and the rubber matrix. Following the degree of exposure and the type of rubber, the different mechanisms may occur simultaneously which greatly complicates the establishment of structure-property relationships.

The present work is dedicated to a microscopic and macroscopic description of the thermal ageing effects on the large strain mechanical behavior and the long-term relaxation of a carbon-black filled EPDM rubber. Based on identified ageing degradation processes, a network alteration kinetics is proposed and coupled to a macroscopic mechanical model including micro-structural parameters (cross-link density, average molecular mass of elastically active chains and viscosity factors). Several results obtained under different ageing conditions illustrate this new scientific approach.

EXPERIMENTS

The material considered in this work is a carbon-black filled EPDM (Ethylene-Propylene-Diene Monomer) rubber. Thin-films, obtained by compression molding of as-received EPDM pellets, were isothermally aged in air at different temperatures and times. An important part of the work was focused on the determination of thermal ageing processes. After ageing, gravimetric measurements were undertaken to examine the weight variations of EPDM rubber due to oxygen grafting and release of volatile compounds. Fourier Transform Infra-Red (FTIR) spectroscopy was used to examine changes in concentration of thermal degradation products. The residual concentration of stabilizers was determined by measurement of the Oxidation Induction Time (OIT) by Differential Scanning Calorimetry (DSC) at 200°C in pure oxygen. DSC was also used to detect ageing-induced crystallization phenomena. The variations in molecular mobility due to oxidative chain scissions and cross-linking were examined by Dynamic Mechanical Thermo-Analysis (DMTA) in a tensile mode. The values of

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storage modulus at glassy and rubbery plateau and glass transition temperature were used to access the numbers of chain scissions and cross-link events versus time.
To characterize the consequences of thermal ageing on the mechanical behavior, monotonic tensile and stress relaxation tests were carried out at different stages of ageing using a servo-hydraulic testing machine equipped with a non-contact optical extensometer. Stress relaxation tests consist in multi-step relaxations at different strain levels under a loading-unloading cycle. All mechanical tests were carried out at room temperature and at constant strain rate. The thermal ageing effects on ultimate properties, the equilibrium material response (i.e. the state that is approached in long-term stress relaxation), the non-equilibrium material response (i.e. the time-dependent deviation from the equilibrium state) and the amount of hysteresis were examined in detail.

CONSTITUTIVE MODELING

Due to the presence of high nonlinear deformability, time-dependent phenomena and strong hysteresis upon cyclic loading, the constitutive modeling needs to be founded on finite strain viscoelasticity theories in a thermodynamically consistence way. Following a Zener representation, the macroscopic mechanical model includes two parallel resistances to describe the deformation mechanisms: one (a nonlinear elastic spring) accounts for the nonlinear equilibrium response and the other (a nonlinear elastic spring in series with a viscous dashpot) deals with the time-dependent deviation from the equilibrium state. The mathematical modeling is based on the multiplicative decomposition of the deformation gradient tensor into elastic and viscous parts [5]. To reduce the complexity of the model formulation the material is assumed to be isotropic and incompressible [6]. In order to propose a pertinent way to predict the effect of microstructure changes due to thermal ageing on the EPDM rubber mechanical response, only statistical mechanics network models of rubber elasticity were selected to describe the nonlinear elastic spring of the constitutive model. A general but thermodynamically consistent form of the flow rule for the viscosity is used in both the loading and unloading paths. A kinetic for the physical material (network) parameters affected by the network alteration due to ageing is proposed and introduced into the constitutive equations. Other theories of network alteration were recently proposed to capture for example the Mullins effect [7] or the low-cycle fatigue response [8] of rubbers. Note that the network alteration kinetic proposed in the present work relies on experimentally-based interpretations of the ageing processes. Simulation results for multi-step stress relaxation tests under loading-unloading paths at different temperatures and ageing times using the proposed theory show an encouraging correlation with the experiments. The capabilities of different forms of network models are critically discussed by comparisons with the experiments.

CONCLUSIONS

The coupling between mechanical loading and thermal ageing effect in a carbon-black filled EPDM was investigated both experimentally and theoretically. The experimentally-based network alteration kinetic coupled to a macroscopic mechanical model (simple enough to be applicable for finite element structural computations) was validated on well-controlled tests and seems to be a promising tool to predict the material response under more complex conditions (in terms of thermal ageing cycles, environmental conditions, etc.). Although the present work was dedicated to an industrial EPDM formulation, the proposed methodology is conceptually applicable to other types of rubbers.

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