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Thermo-viscoplasticity of carbon black-reinforced thermoplastic elastomers

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ABSTRACT

Observations are reported on carbon black–filled thermoplastic elastomer (TPE) in uniaxial loading–unloading tensile tests with various strain rates (ranging from 7×10^{-4} to 1×10^{-1} s^{-1}) at temperatures in the interval from 25 to 90 °C. A constitutive model is derived for the viscoplastic response of a TPE composite at three-dimensional deformations with finite strains. The stress–strain relations involve six adjustable parameters that are found by fitting the experimental data. It is shown that the model correctly describes the observations, and its parameters are affected by temperature and strain rate in a physically plausible way.

1. Introduction

This paper is concerned with the experimental and theoretical analysis of the mechanical response of a carbon black-reinforced thermoplastic elastomer (TPE) at quasi-static deformations with finite strains.

Thermoplastic elastomers are an important class of polymers that combine mechanical properties of rubbers with high-speed processability and recyclability of thermoplastics (Holden et al., 2004; Grady and Cooper, 2005). The experimental investigation focuses on the viscoplastic behavior of Thermoplast K reinforced with a relatively large amount (about 60–70 wt.%) of carbon black particles. The polymeric matrix of this composite consists of a hydrogenated styrene block copolymer (HSBC)-based thermoplastic elastomer with addition of polypropylene segments. A rather complicated chemical structure of the TPE composite and high concentration of filler ensures its strong thermal and chemical resistance. Due to these properties, Thermoplast K may be employed as a sealing material for low-temperature proton exchange membrane fuel cells (PEM FC) with operating temperatures up to 100 °C. From the standpoint of applications, the objectives of this work are (i) to study the mechanical response of Thermoplast K at various temperatures, and (ii) to develop a simple constitutive model for its thermo-viscoplastic response to be used in finite-element analysis of a fuel cell.

Mechanical properties of thermoplastic elastomers has attracted substantial attention in the past decade (Boyce et al., 2001a,b,c; Blundell et al., 2002, 2004; Le et al., 2003; Krijgsman and Gaymans, 2004; Baeurle et al., 2005; Indukuri and Lesser, 2005; Qi and Boyce, 2005; Drozdov, 2006, 2007; Drozdov and Christiansen, 2006, 2007; Laity et al., 2006; Long and Sotta, 2006; Yi et al., 2006; Roland et al., 2007; Sarva et al., 2007; Eceiza et al., 2008). Most of these studies, however, concentrated on the time- and rate-dependent behavior of unfilled TPEs at ambient temperature. Only a few works dealt with the viscoelastic and viscoplastic responses of thermoplastic elastomers reinforced with carbon black (Kurian et al., 1995; Datta et al., 1996; Katbab et al., 2000; Yamauchi et al., 2005), and none of them investigated mechanical properties at elevated temperatures. From the viewpoint of fundamental research, the objectives of the present study are (i) to report observations in uniaxial tensile tests with finite strains on a carbon black-reinforced TPE in a relatively large range of temperatures, and (ii) to analyze the effects of temperature and strain rate on adjustable parameters in the stress–strain relations.

Derivation of the constitutive model is based on a homogenization concept, according to which a complicated morphology of a TPE composite is replaced with a simple structure that captures essential features of its mechanical response. Following common practice (Tomita et al., 2007), a thermoplastic elastomer is thought of as a permanent non-affine network of chains bridged by junctions. The assumption that the network is permanent means that detachment of active chains from their junctions and merging of dangling chains with the network are neglected. With reference to Green and Tobolsky (1946) and Tanaka and Edwards (1992), the latter is tantamount to the neglect of viscoelasticity of the equivalent network. Non-affinity presumes that junctions slide with respect to their reference positions under deformation, which implies that the viscoplastic response is associated with sliding (plastic flow) of junctions. To simplify the analysis, it is postulated that plastic flow is volume-preserving, the strain energy of a chain is described by the neo-Hookean formula, and the energy of

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interaction between chains is accounted for by the incompressibility condition for the equivalent network.

The exposition is organized as follows. Observations in uniaxial tensile loading–unloading tests and relaxation tests at various temperatures are reported in Section 2. A constitutive model in finite viscoplasticity of TPE composites is developed in Section 3. In Section 4, the stress–strain relations are simplified for uniaxial tension of an incompressible medium. Adjustable parameters in the governing equations are found in Section 5 by fitting the experimental data. Results of numerical simulation for simple shear of a TPE composite are reported in Section 6. Some concluding remarks are formulated in Section 7.

2. Experimental results

Carbon black-reinforced thermoplastic elastomer Thermoplast K TV5LVZ [density 1.05 g/cm^3, melt flow index 12 g/10 min at 230 °C, elongation at break 520%, hardness (shore A) 50] was purchased from Kraiburg TPE GmgH (Germany). Dumbbell specimens for uniaxial tensile tests (ASTM standard D638) with cross-sectional area 10.2 mm × 3.4 mm were molded by using injection-molding machine Arburg 320C.

Mechanical tests were conducted with the help of universal testing machine Instron-5569 equipped with a thermal chamber and an electro-mechanical sensor for control of longitudinal strains in the active zone of samples. The tensile force was measured by a standard load cell. The engineering stress σ was determined as the ratio of the axial force to the cross-sectional area of specimens in the stress-free state.

The experimental program involved two series of tests. The first consisted of tensile loading–unloading tests (1 cycle) with the maximum engineering strain $\epsilon_{max} = 0.9$ conducted at the temperatures T = 25, 50, 70, and 90 °C with cross-head speeds of 1, 5, 10, 20, 100, and 150 mm/min. These cross-head speeds corresponded to the strain rates of 6.7×10^{-4}, 3.3×10^{-3}, 6.7×10^{-3}, 1.3×10^{-2}, 6.7×10^{-2}, and 1.0×10^{-1} s^{-1}, respectively. In a test, a sample was stretched up to the maximum strain ϵ_{max} with a constant strain rate $\dot{\epsilon}$ and unloaded down to the zero stress with the strain rate $-\dot{\epsilon}$. Each test was performed on a new specimen. In all tests at elevated temperatures, samples were pre-heated in a thermal chamber at the required temperature for at least half an hour, and, afterwards, equilibrated in the testing machine for 10 min before deformation.

To assess repeatability of observations, several tests were carried out on three different specimens (appropriate data are not presented). The maximum difference between the engineering stresses measured on different samples did not exceed 4%. This distinguishes the mechanical response of carbon black-reinforced TPEs from that of filled rubbers, as cyclic preloading of specimens is necessary in the latter case to reach an acceptable level of repeatability of measurements (Haupt and Sedlan, 2001).

The range of temperatures was chosen to cover the entire interval of operating temperatures of a low-temperature PEM FC. The interval of strain rates was restricted by the requirement that the duration of a test did not exceed 40 min (from below) and by the maximal cross-head speed of the testing machine (from above). The maximum engineering strain in tensile tests ϵ_{max} was limited by the range of admissible strains for the extensometer (less than 100%).

Observations in cyclic tensile tests at various temperatures T are reported in Figs. 1–4, where the engineering tensile stress σ is plotted versus tensile strain ϵ. The following conclusions are drawn:

1. The stress–strain diagrams at loading are strongly affected by cross-head speed. The engineering tensile stress grows with strain rate $\dot{\epsilon}$. The maximum increase in stress is about 27% at room temperature, 35% at T = 50, 40% at T = 70, and 65% at T = 90 °C, which means that the effect of strain rate on σ becomes more pronounced at elevated temperatures.
2. At room temperature, the stress–strain diagrams at unloading are practically independent of cross-head speed. With the growth of temperature, the influence of strain rate on σ at retraction becomes stronger. At the maximum temperature T = 90 °C, the tensile stress at unloading noticeably increases with $\dot{\epsilon}$.
3. The residual engineering strain ϵ (the strain at which the tensile stress vanishes at unloading) is practically independent of strain rate and temperature. In all tests, this strain belongs to the interval between 10 and 15%.
4. Given a strain rate $\dot{\epsilon}$, the engineering tensile stress is strongly affected by temperature. At the highest strain rate of 0.1 s^{-1}, the maximum tensile stress (reached at the maximum strain

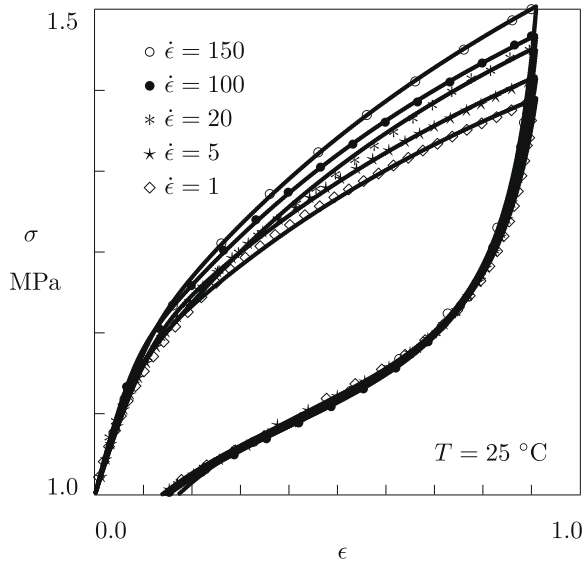

Fig. 1. Engineering stress σ versus tensile strain ϵ. Symbols: experimental data in loading–unloading tests with various cross-head speeds $\dot{\epsilon}$ mm/min at room temperature. Solid lines: results of numerical simulation.

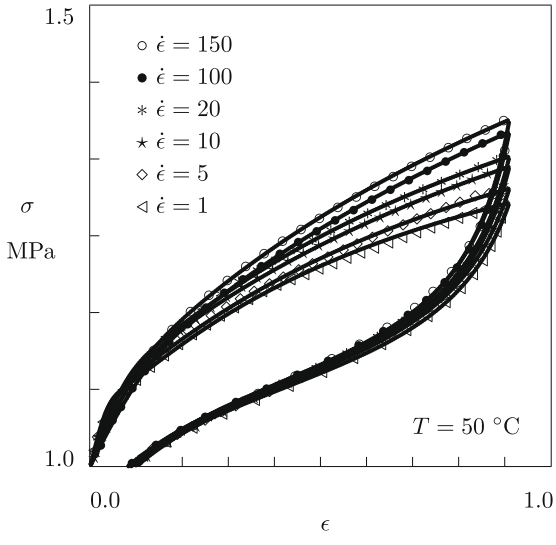

Fig. 2. Engineering stress σ versus tensile strain ϵ. Symbols: experimental data in tensile loading–unloading tests with various cross-head speeds $\dot{\epsilon}$ mm/min at T = 50 °C. Solid lines: results of numerical simulation.