Experimental characterization and thermoviscoelastic modeling of strain and stress recoveries of an amorphous polymer network

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A B S T R A C T

An acrylate polymer network was submitted to thermomechanical shape memory cycles. The set of experiments characterized the material stress-free strain recovery and the strain-constrained stress recovery in uniaxial tension. Experimental parameters like temperature of strain fixation, amount of strain and heating rate, were varied in order to provide a relatively complete set of experimental data. A model combining the amorphous polymer viscoelasticity and its time–temperature superposition property was used to predict the shape memory behavior of the acrylate polymer network. All the model parameters were characterized using classical tests for mechanical characterization of polymers, which do not include shape memory tests. Model predictions obtained by finite element simulations compared very well to the experimental data and therefore the model relevance for computer assisted application design was assessed.

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1. Introduction

Shape memory polymers find applications in space systems, solar panels, textiles, and largely in medical devices. For computer assisted application design, it is critical for the engineer to have constitutive equations that represent well the material behavior with respect to time and temperature. Despite that fact, the number of papers dedicated to modeling shape memory polymers remains limited. We may divide the existing models into two categories: the models based on a bi-phasic representation of the material grounded on the rubbery/glassy state transition, first proposed by Liu et al. (2006) and adopted by Chen and Lagoudas (2008), Qi et al. (2008), Volk et al. (2010), Gilormini and Diani (2012), and the thermoviscoelastic approach early introduced by Tobushi et al. (1997) and improved by Diani et al. (2006), Nguyen et al. (2008), Castro et al. (2010),

Srivastava et al. (2010), Diani et al. (2012) and Yu et al. (2012).

Recently, Diani et al. (2012) showed that an epoxy network submitted to torsion shape recovery tests in large-deformation small-strain conditions, could be well predicted by simply introducing the material linear viscoelastic parameters into the large-deformation viscoelastic framework of Simo (1987) coupled with the material time–temperature superposition property. The model attributes the shape memory property of amorphous polymer networks to their viscoelasticity combined with time–temperature superposition. The model showed very good predictions of the kinetics of the shape recovery and presents the great interest to depend on parameters that can be determined by standard polymer characterization tests only. Nonetheless, the model had been only applied to small-strain shape recovery (strain <10%) and its ability to predict the stress history vs. time and temperature had not been tested yet. In this contribution, a complete set of strain and stress recoveries obtained during classical shape memory thermocycles is presented. For this

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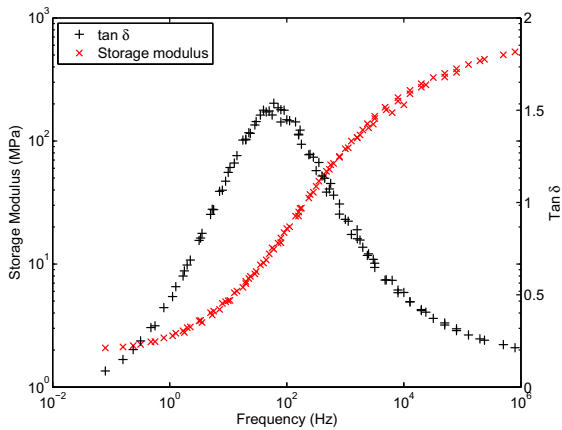*E-mail address:* juan-sebastian.arrieta-escobar@ensam.eu (S. Arrieta).

Fig. 1. Storage Young modulus and loss tangent angle master curves of the acrylate at the reference temperature $T_{ref} = 80\ °C$, obtained from the time–temperature superposition principle applied to the DMA tensile tests.

purpose, an acrylate polymer network was synthesized and submitted to thermomechanical cycles consisting in applying a uniaxial strain at high temperature, cooling down the material while maintaining the strain, releasing the stress and finally heating the sample stress-free or strain-constrained. Several experimental parameters were varied like the heating rate, the temperature of temporary strain fixation, and the amount of applied stain. The comparison between the model prediction and the experimental data assesses the model relevance for amorphous polymer networks shape memory application design.

2. Mechanics of the material

2.1. Material

The acrylate network composition was found in Safransky and Gall (2008). It was prepared by the copolymerization of benzyl methacrylate (BMA) with poly (ethylene glycol) dimethacrylate (PEGDMA) of molar weight 550 g/mol, which is used as crosslinking agent. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was added as

photoinitiator. Products were used as received from Sigma Aldrich. 90% molar mass of BMA was mixed at room temperature with 10% molar mass of PEGDMA and 0.5% of DMPA. The mix was cured in a UVP® ultraviolet chamber CL-1000 for 50 min. Final products are plates of 1.3 mm thickness from which dumbbell and rectangular samples are cut for thermomechanical tests and analysis.

2.2. Mechanical behavior characterization

The material viscoelasticity was characterized by tensile dynamic mechanical analysis (DMA) performed on a DMA Q800 from TA instruments. The material was submitted to isothermal frequency sweeps at 0.1% strain from 0.01 to 10 Hz, from 0 °C to 65 °C with 5 °C increments. The material viscoelasticity master curves shown in Fig. 1 were obtained from the DMA tests by applying the time–temperature superposition principle at the reference temperature of 80 °C. The horizontal shift factor a_T values used to build the master curves in Fig. 1 were found to satisfy the WLF equation of Williams et al. (1955):

$$\frac{1}{\log_{10}(a_T)} = \frac{-1}{C_1} - \frac{C_2}{C_1} \frac{1}{T - T_{ref}} \tag{1}$$

with $C_1 = 6.9$ and $C_2 = 87.9\ °C$ for $T_{ref} = 80\ °C$.

The material was also submitted to conventional uniaxial tension tests at various temperatures, using an Instron® 5881 testing machine equipped with a thermal chamber. Local strain measures were recorded by video extensometry. Tests were run at a constant crosshead speed of 10 mm/min. Fig. 2(a) presents the material stress–strain responses to monotonic loadings until break at a low temperature (25 °C) corresponding to the glassy state, at a high temperature (65 °C) corresponding to the rubbery state, and at an intermediate temperature (45 °C) at which the material is strongly viscoelastic. In the glassy state, the material presents a classic elasto-plastic behavior. In the rubbery state, it undergoes large strains and exhibits a hysteretic loop when submitted to a cyclic test (Fig. 2(b)). This phenomenon is enhanced in the viscoelastic transition (45 °C). At this temperature, the residual strain is completely recovered at zero stress within two hours but the
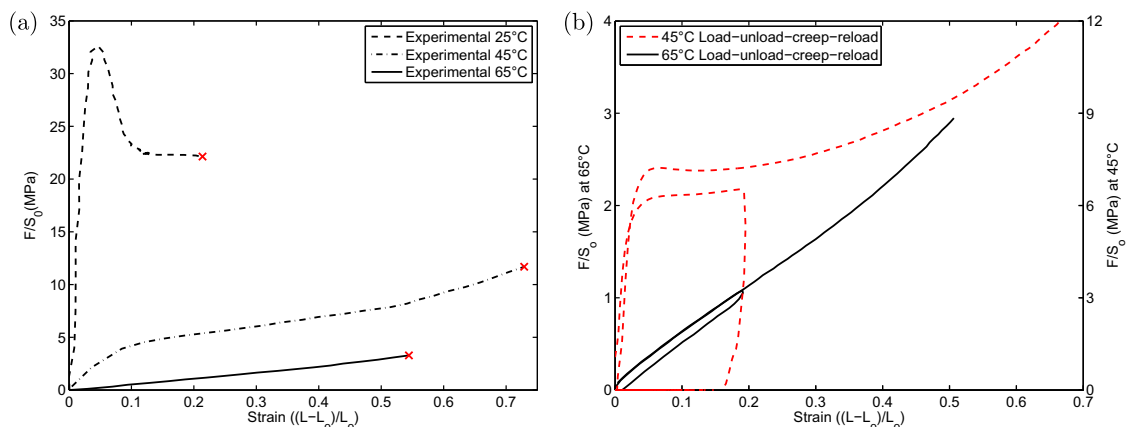

Fig. 2. Material uniaxial stress–strain responses for various temperatures during (a) monotonic tests and (b) cyclic tests defined by load, unload, residual strain recovery at zero stress and reload. Crosshead speed: 10 mm/min.