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Time and strain rate dependent mechanical behavior of individual polymeric nanofibers

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ABSTRACT

In this work, the small and large strain mechanical behavior of nanofibers electrospun from glassy polymers was shown to be diameter and time-dependent. Specifically, the creep compliance of as-elecrospun polyacrylonitrile (PAN) nanofibers increased with increasing diameter, while the tangent modulus, yield stress and tensile strength followed decreasing trends, which were attributed to increased molecular orientation with reduced nanofiber diameter. Furthermore, the nanofiber capacity for energy dissipation increased dramatically with the applied strain rate, as the yield and ultimate tensile strengths increased steadily with increasing strain rate. The effect of strain rate was less significant on the ductility of PAN nanofibers, and insignificant on the ductility of polystyrene (PS) nanofibers. This outstanding mechanical response was demonstrated by homogeneously deforming PAN nanofibers at strain rates as high as 200 s^{-1} and by PS nanofibers exhibiting necking at local plastic strain rates as high as 27,000 s^{-1}. The small strain time-dependent response of PAN nanofibers was modeled with a linear viscoelasticity model with diameter dependent constants, which provided a good description of the creep and strain rate behavior. The large deformation behavior was modeled via a modified rubber elasticity model which predicted quite well the overall mechanical response of PAN nanofibers.

1. Introduction

Time and length scales affect the mechanical response of soft nanoscale structures as a result of the material hierarchy that couples various length scales with different time constants. In the case of polymeric nanostructures, specimen size effects are closely related to the macromolecular structure and the increased degrees of freedom of surface vs. core (interior) molecules. For instance, polymer films with thicknesses below 50–100 nm have reduced glass transition temperature (T_g) (Ellison et al., 2005; Keddie et al., 1994; Priestley et al., 2005; Roth et al., 2007) which also determines their small strain mechanics. Similarly, polymer nanofibers with diameters less than 500 nm that are produced by electrospinning have demonstrated increased ductility and strength as a result of molecular orientation (Naraghi et al., 2011), which, in turn, is influenced by the details of the fabrication method and the increased role of surface molecules compared to the core molecules. Concomitant to size effects are temporal effects on the mechanical behavior of submicron scale polymeric structures (Naraghi et al., 2007a), wherein some bulk scale relaxation modes could be suppressed at the nanoscale (O'Connell and McKenna, 2005). Contrary to specimen size effects, time and strain rate effects remain vastly unexplored to date mainly due to the difficulty in obtaining temporally resolved mechanical properties of structures with dimensions of, or

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below, the order of the wavelength of visible light. While mechanical characterization tools are available for the study of nanostructures inside electron microscopes, the latter offer no temporal resolution. A prior study by this group has shown a close relationship between material heterogeneity and mechanical behavior at various strain rates (Naraghi et al., 2007a), via time resolved mechanical measurements on as-electrospun polyacrylonitrile (PAN) nanofibers. Temporal effects are pronounced not only on the small strain mechanical behavior, but also on the large deformation response of ultra-small polymer volumes due to multiple relaxation mechanisms, such as chain unfolding, molecular disentanglement, side group rotation, etc. This tight coupling of length and time scales has been advocated in a recent study on the thermoviscoelastic behavior of polystyrene (PS) thin films (O'Connell et al., 2008) where the applicability of a time–specimen size superposition principle was demonstrated, in an analogy to the time–temperature superposition principle. Compared to the bulk scale, more pronounced strain rate sensitivity is expected for polymeric nanostructures due to the increased contribution of free surface molecules that are subjected to reduced confinement compared to core molecules as well as the reduced coherency of the molecular chain entanglement network (Michler et al., 2006).

These nanostructural effects can be elucidated by properly combined specimen size and strain rate experiments, which are aided by creep or stress relaxation measurements. Such experiments with individual electrospun PAN and PS nanofibers have been realized in this work, by using a versatile microelectromechanical systems (MEMS) platform for nanomechanical testing (Naraghi et al., 2007a, 2007b; Naraghi and Chasiotis, 2009). This experimental study investigated the effect of strain rate on the small and large deformation properties of PAN and PS nanofibers subjected to nominally elastic strains and necking, respectively, and the creep response of PAN nanofibers subjected to nominally elastic strains While the majority of prior time dependent mechanical behavior studies with nanostructures have employed thin films, nanofibers are preferable because they offer larger surface-to-volume ratio for the same characteristic length scale (film thickness vs. fiber diameter), and therefore are more suitable to study the contribution of surface molecules to the nanoscale mechanical behavior, without reducing the fiber diameter to sub-hundred nanometer dimensions. Furthermore, ultra-thin films are not an appropriate type of specimen to study large deformations due to film wrinkling. The experimental results were rationalized with the aid of a viscoelastic and a viscoplastic model at small and large strains, respectively.

2. Experimental methods and materials

PAN and PS nanofibers were fabricated by the method of electrospinning using a home built apparatus. PAN nanofibers with molecular weight (MW) of 150,000 g/mol were fabricated using the conditions described in Naraghi et al. (2011) to obtain uniform cross-sectional density and homogeneous deformation during mechanical testing. Similarly, PS nanofibers with MW=2,000,000 g/mol were fabricated from monodisperse PS powders and were thermally annealed above the T_g of bulk PS (100 °C) for 100 min followed by slow cooling to room temperature at the rate of 0.25 °C/min, to obtain uniform fiber cross-sections and smooth fiber surfaces.

Two types of experiments were conducted in this study: (a) uniaxial tension experiments spanning six decades of cross-head strain rate between $2.5\times10^{-4}\,s^{-1}$ and $200\,s^{-1}$, for both PAN and PS nanofibers, and (b) creep experiments with PAN nanofibers at stresses below the fiber yield strength. Individual nanofibers with diameters of 200–700 nm and 25–35 μm length were tested using a MEMS based platform designed for soft nanofiber experiments in ambient conditions. In this experimental method, actuation with practically unlimited stroke is accomplished by an off-chip actuator, while the fiber strain and the applied force are directly computed by the application of Digital Image Correlation (DIC) on high magnification (500 ×) optical images (Naraghi et al., 2007b). The use of off-chip actuation allows for large fiber extensions and a broad spectrum of applied strain rates that are only limited by the camera frame rate. It is important to note that this experimental method provides independent measurements of force and fiber extension, which are naturally synchronized independently of the applied strain rate because they are computed from the same optical image. The reader is prompted to Naraghi et al. (2007b) for further details of this method and a short review of other experimental methods for nanofiber mechanical testing.

2.1. Mechanical testing of individual polymer nanofibers

For completeness, a brief description of the nanofiber testing methodology following the work in Naraghi et al. (2007a, 2007b) is provided. Fig. 1 shows two snapshots of the MEMS based nanomechanical testing platform during a uniaxial tension test of an electrospun PS nanofiber with 250 nm diameter. Fig. 1(a) shows the MEMS device before the nanofiber is loaded. The functional components of the MEMS device are labeled as 1, 2 and 3 in Fig. 1(b). Component 1 is connected to an actuator through the underlying silicon wafer, while components 2 and 3 are freestanding and are connected to each other through a pair of compliant beams whose stiffness is obtained by a calibration as described by Naraghi and Chasiotis (2009). During an experiment, component 3 is held stationary by an external probe, while component 1 is actuated to the left by an external piezoelectric actuator. The rigid body displacements in the direction of the fiber, u^1_{xx}, u^2_{xx} and u^3_{xx}, are obtained for components 1, 2 and 3, respectively, as shown in Fig. 1(b) by applying DIC to a series of images recorded during the test by a CCD camera. The displacement measurements u^1_{xx}, u^2_{xx} and u^3_{xx} allow for the independent calculation of the engineering stress as $\sigma_x=4k(u^2_x-u^3_x)/(\pi d^2)$, and engineering strain as $\varepsilon_x=(u^1_x-u^2_x)/L_0$, where L_0 is the initial length of the fiber in the undeformed state, k is the stiffness of the compliant beams connecting components 2 and 3, and d is the undeformed fiber diameter. Experiments at cross-head strain rates $2.5\times10^{-2}\,s^{-1}$ and $2.5\times10^{-4}\,s^{-1}$ were carried out by using a CCD camera with capability of up to 15 fps, while experiments at strain rates $2.5\,s^{-1}$ and $200\,s^{-1}$ were conducted with a CCD camera