



A master curve for the size and strain rate dependent large deformation behavior of PS nanofibers at room temperature

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ABSTRACT

Unlike the nominally brittle behavior of bulk polystyrene (PS), PS nanofibers with particular combinations of molecular weight (MW) and submicron scale diameters exhibit stable necking followed by pronounced strain-hardening, resulting in simultaneous increase in strength and ductility. The ratio, D_{norm} , of the fiber diameter, D , to the intrinsic macromolecular length scale described by the root-mean-square end-to-end chain distance, $R_{\text{ee}} \sim \text{MW}$, has been shown to be an effective scaling parameter to determine the initiation and evolution of necking and strain hardening in submicron scale unoriented PS fibers. In this study, the room temperature large deformation response of individual PS nanofibers is quantified for the first time over a broad range of strain rates between 10^{-4} – 10^2 s^{-1} . It is shown that for all combinations of MW in the range 123,000–2,000,000 g/mol and D in the range 200–750 nm that satisfy $D_{\text{norm}} < 10$, an increasing strain rate results in monotonic increase of the stress amplitude without any reduction in the nanofiber stretch ratio to failure. Furthermore, the experimental stress vs. stretch ratio curves for $D_{\text{norm}} < 10$ obeyed a multiplicative decomposition of stress into a shape and a rate component. This decomposition permits the construction of a normalized stress vs. strain master curve that captures well both the size effects, originating in the relative molecular and specimen length scales, and the strain rate effects on the mechanical behavior of PS nanofibers at room temperature.

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1. Introduction

While amorphous polymers are intrinsically tough under compressive loading, they display one of two distinct types of deformation when subjected to tension at the glassy state: (i) immediate failure after yielding due to severe localization of plastic deformation, e.g. polystyrene (PS) or polymethyl methacrylate (PMMA), or (ii) sustained large deformation after stabilization of strain localization, e.g. polycarbonate (PC) [1]. Harnessing the intrinsic ductility of the former class of polymers under tensile loading has been a topic of extensive research. To this goal, the composition of glassy polymers has been modified, e.g., by the addition of a rubbery second phase such as polybutadiene [2–5] or cavitating rubber particles, by the reduction of intrinsic softening via mechanical rejuvenation [6], or by orientation of polymer molecules via melt stretching [7]. Most of these methods have produced a modest increase in ductility (<50%) but often compromised the strength and stiffness of the neat polymer.

Recent room temperature (RT) uniaxial tension experiments with individual PS nanofibers have shown that the synergistic coupling between the intrinsic molecular length scale, as described by the root-mean-square end-to-end distance of an unperturbed polymer chain (R_{ee}), and the specimen structural length scale, as described by the fiber diameter (D), could be exploited to enable a brittle-to-ductile transition in PS nanofibers [8], when the ratio of D to R_{ee} (D_{norm}) falls below ~ 18 . This transition results in simultaneously increased tensile strength (by as much as $\sim 350\%$) and ductility (by as much as 4000%) compared to bulk-scale PS specimens subjected to tension. This radical modification of the tensile behavior of submicron PS fibers was controlled by adjusting D_{norm} without altering the polymer composition or structure. D_{norm} expresses the nanofiber diameter as a multiple of the molecular length scale (R_{ee}): a decreasing value of D_{norm} represents the influence of the increasing fraction of free-surface polymer chain segments which have reduced molecular constraints, on the effective mechanical behavior of a nanofiber.

This study focuses on the unexplored and intriguing viscous nature of the large plastic deformation of PS nanofibers as a function of D_{norm} , with particular emphasis on the relationship between

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the applied strain rate and the range of D_{norm} , which results in complete necking and subsequent strain hardening. Amorphous polymers exhibit time and temperature dependent mechanical behavior due to the contribution of different relaxation mechanisms taking place at various time and length scales, ranging from fast segmental scale motions such as side-group rotation, to relatively slower and larger scale cooperative molecular motions [9,10]. For instance, yielding of glassy polymers can be understood as the result of the competition between material softening and hardening, each having a different strain rate dependence according to the contribution of α - and β -relaxations [11,12]. Although numerous experimental and modeling studies have focused on elucidating the viscous character of elasto-plastic deformation processes and failure mechanisms in bulk amorphous polymers [11–17], very few studies have explored the rate dependent mechanical behavior of submicron scale specimens [18–20] despite overwhelming evidence indicating that amorphous polymeric nanostructures have different relaxation spectra compared to bulk, such as broadening and/or shift of the α -regime [21–28]. Experiments on the thermo-viscoelastic behavior of freestanding ultra-thin films of amorphous PS and poly(vinyl acetate) (PVAc) [18,29] alluded that, contrary to expectations about an increased mobility of polymer chain segments at the film's free surface, many relaxation modes (especially the slower relaxation modes) are likely to be suppressed at the film's free surface. Similarly, it has been shown that the slowest characteristic relaxation times of as-spun polyacrylonitrile (PAN) nanofibers display further retardation with decreasing fiber diameter, which originates in the increased fraction of surface chain segments in smaller diameter fibers [30].

This study focuses on elucidating the viscoplastic response of individual PS nanofibers at room temperature as a function of molecular and specimen dimensions and the rate of loading. Specifically, the effects of strain rate on the stability of post-yield necking, the stretch ratio due to necking, and the subsequent strain hardening response are studied as a function of D_{norm} . For the range of strain rates explored in this study, the strain rate sensitivity of yielding and post-yielding is evaluated as a function of D_{norm} , demonstrating that large deformation driven by stable necking occurs for $D_{\text{norm}} < 10$. Finally, a master curve that simultaneously captures the effects of molecular length scale, specimen size, and strain rate on the tensile stress vs. strain response of individual PS nanofibers is presented.

2. Materials and methods

2.1. Synthesis of polystyrene (PS) nanofibers

The extent of spatial confinement of macromolecules in sub-micron scale fibers is governed by the competition between two length scales: the fiber diameter, D , and the molecular length scale which is related to molecular weight, MW . To this effect, the

molecular length scale can be described by R_{ee} which is a function of MW [8]. In order to study the relative role of these length scales, PS fibers were synthesized by electrospinning solutions of mono-disperse linear atactic PS powders (Pressure Chemicals Inc.) in N,N -dimethylformamide (DMF) according to the conditions described in Table 1. All fibers were electrospun at 1 kV/cm average electric field (25 kV bias between the source and the collector that were separated by 25 cm) in room temperature conditions (22 ± 3 °C and $19 \pm 2\%$ relative humidity). The as-spun PS fibers were annealed in their freestanding configuration at 10–25 °C above their bulk T_g , and for durations that were longer than the reptation times of bulk-scale specimens, to devoid them of molecular orientation and the undesirable axially corrugated surface morphology arising from electrospinning [8]. Prior work by this group has shown that the geometry of the fiber cross-section and the fiber surface morphology define the evolution of the mechanical deformation [31]. The annealing times for different molecular weights are presented in Table 1 as multiples of the reptation times of the corresponding bulk scale samples ($\tau_{\text{d-bulk}}$). Naturally, these times are overestimates of the annealing times required for freestanding nanofibers which allow for faster relaxations compared to bulk PS. While the diameters of all PS fibers tested in this work were in the approximate range of 200–750 nm, the electrospinning community typically refers to them as nanofibers, which term is also used henceforth in this paper.

2.2. Mechanical experiments with individual PS nanofibers at different strain rates

The tensile behavior of individual, annealed, PS nanofibers was experimentally determined following a microelectromechanical systems (MEMS)-based mechanical testing methodology developed by this group before, which provides high resolution measurements of the applied force (engineering stress) and elongation (nanofiber stretch ratio) [32,33] at ambient conditions. The surface micromachined MEMS devices used in this method are comprised of the three main components shown in Fig. 1. A nanofiber is mounted across components (1) and (2), with component (1) fixed to the substrate carrier of the MEMS device and component (2) being freestanding. The freestanding components (2) and (3) are connected to each other through a set of parallel beams (only partially visible in Fig. 1) that act as an integrated force sensor whose stiffness is calibrated as described in Ref. [34]. In an experiment, the MEMS substrate carrier and therefore, the device components numbered (1), are translated to the left by a PZT actuator in nanometer-level displacement increments, while component (3) is held stationary with the aid of an external probe (not visible in Fig. 1). In the present study, actuation speeds in the range 15 nm/s – 6 mm/s were imposed with an external PZT actuator. These microscale tension experiments were performed under an optical microscope in ambient conditions (23 °C and 20–30% relative

Table 1

Electrospinning and annealing parameters used in the preparation of PS nanofibers. The polydispersity index (PDI) indicates the extent of dispersion in macromolecular chain lengths; a value of unity indicates no dispersion of the macromolecular length scale.

Molecular weight (g/mol)	PDI	Solution concentration (weight %)	Annealing conditions		Nanofiber diameter (nm)
			Temperature (°C)	Time ($\times \tau_{\text{d-bulk}}$)	
123,000	1.06	30 ^a	110	6.3	200–500
		30	110	6.3	700–900
400,000	1.06	15	120	8.3	150–250
		20	120	8.3	300–600
2,000,000	1.30	2.0	125	0.2	150–250
		4.5	125	0.2	300–800

^a Solution contained 1 wt% tetrabutyl ammonium chloride (TBAC) to reduce the nanofiber diameter.

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