Polymer 63 (2015) 10–18

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Production and characterization of melt-spun Poly(Ether Ether Ketone) fibers for biomedical applications

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ARTICLE INFO

Article history:
Received 12 November 2014
Received in revised form
3 February 2015
Accepted 10 February 2015
Available online 28 February 2015

Keywords:
PEEK
Fiber
Structure-processing-property relationship

ABSTRACT

Melt-spun Poly (Ether Ether Ketone) (PEEK) fibers were produced on a custom built melt-spinning system. Fibers of two different grades were spun at two different draw-down ratios, with one of three possible post-spinning treatments: as-spun, annealed, or hot drawn. Fibers were characterized with SEM, DSC, WAXS, and tensile testing. Hot drawn fibers had the highest degree of crystalline orientation ($S = 0.81$). Modulus, strength, and yield stress, were found to be 1.7 GPa, 175 MPa, and 45 MPa, respectively for as-spun fibers. As-spun fibers had strains-to-failure as high as 215%, which decreased to about 25% after hot drawing. Annealed and drawn fibers had similar crystallinity and crystalline orientation, but drawn fibers had significantly higher moduli of 2.8 GPa and 5.2 GPa, and strength of 195 MPa and 480 MPa, respectively. Fiber properties were found to be tunable to a number of combinations, with potential for numerous applications as novel biomaterials.

1. Introduction

Poly(Ether Ether Ketone) (PEEK) is a high-performance semi-crystalline thermoplastic that was first synthesized in the late 1970s, and has become increasingly popular in the orthopedics communities due its biocompatibility, mechanical properties, and wear properties [1]. It has seen good success in aerospace and automotive industries, finding service in components that need to withstand high operating temperatures, or in applications demanding high strength-to-weight ratios [2,3]. More recently, it has become popular as a material for use in spinal orthopedics. The most common manifestation is in carbon fiber reinforced (CFR-PEEK) spinal fusion cages, originally termed the Brantigan cage [1]. Additional work has explored the use of CFR-PEEK as an injection molded total hip stem [4]. Early clinical trials have also seen rods of neat PEEK, such as the CD Horizon Legacy PEEK posterior rod implemented into rigid pedicle screw/rod constructs for spinal fixation with the aim of reduction of adjacent segment disease through more dynamic fixation [1,5–7].

PEEK has been the subject of much exploration for past several decades since its conception. Dawson and Blundell were among the first to report basic materials data for the polymer, reporting on unit cell parameters, its T_g of ~144 °C and T_m in the range of 334 °C [8]. Blundell and Osborn expounded on the morphology of PEEK and noted that it followed closely the behavior of PET, but for systematically higher temperatures [9]. Additionally, it was found that annealing significantly impacted the thermal behavior by affecting the crystalline morphology. Amorphous samples were found to exhibit structural changes in the way of a crystallization exotherm occurring just above the glass transition [9]. Many others have contributed to the fundamental knowledge of PEEK mechanical properties, rheology, degradation, and effects of crystallization and orientation of the polymer [10–15].

Melt-spun fibers offer potential enhancements in properties and structure for high-demand applications. The concept of this technology is not new; indeed highly oriented polymer fibers have been investigated for decades. Typically, high performance fibers are made of high molecular weight polymers, such as ultra-high molecular weight Poly(Ethylene) Spectra fibers. While PEEK is a relatively low molecular weight polymer by comparison, it nonetheless is enticing as a potential material for high performance fibers due to its high strength and modulus in the isotropic state. Until now, melt-spun PEEK fibers have not been extensively investigated for their potential in biomedical applications. Several studies discuss the structural changes and mechanical enhancements in PEEK fibers over typical bulk PEEK. Karacan characterized structural

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http://dx.doi.org/10.1016/j.polymer.2015.02.015
0032-3861/

properties of as-spun and drawn PEEK fibers using X-ray diffraction and optical microscopy techniques [16]. Song et al. correlated changes in birefringence, crystallinity and mechanical properties with draw ratio of PEEK fibers [17]. Everall et al. showed methods for calculating crystallinity in uniaxially oriented PEEK fibers using polarized Fourier transform Raman spectroscopy [18]. Often, the focus has been on the characterization of structural and mechanical properties for such end-applications as co-mingled PEEK/carbon fiber multifilaments for fabricating CFR-PEEK composite materials. Upon processing of reinforced composites wherein PEEK becomes the matrix phase of the material, the structural and mechanical enhancements gained in the spinning process are lost upon melting and re-crystallization of the polymer amongst its reinforcement. It is believed that melt-spun PEEK fibers could be candidates for numerous end applications. These may include exploitation of the PEEK fibers' enhanced mechanical properties and structure in self-reinforced composites for spinal fusion applications, and particularly as hot compacted thin films as a means of mitigating the effects of fretting corrosion in modular tapers of total hip replacement devices. Materials for these potential applications would differ from the traditional PEEK matrix-based composite materials because they are intended to be solely comprised of PEEK and utilize PEEK fiber as a reinforcing phase within a matrix of PEEK, thus allowing for enhanced mechanical properties while also taking advantage of its biocompatibility and familiarity as an approved biomaterial.

The goal of this work is to elucidate the mechanical, thermal, and structural properties of melt-spun PEEK fibers. Fibers were fabricated according to a range of spinning and post-processing conditions that were subsequently characterized. A number of techniques were employed including differential scanning calorimetry (DSC) to observe the effect of processing on T_g and T_m, Wide Angle X-ray Scattering (WAXS) to observe crystallinity, crystal size, and crystalline orientation, and tensile testing to determine how mechanical properties varied with respect to spinning and post-processing conditions. This study serves to demonstrate the potential of melt-spun PEEK fibers to be tuned to a range of structural and mechanical properties, such that they might find use in a wide range of biomedical and orthopedic applications upon further development.

2. Experimental

2.1. Sample preparation

In this work, two different grades of PEEK with differing melt flow properties and, thus, differing relative molecular weights, were melt-spun into fibers at one of two different draw-down ratios. These four groups of fibers were then subjected to either hot drawing or annealing, whereas a third set of samples were left in the as-spun state. PEEK fibers were prepared with a custom built piston driven melt extruder, shown schematically in Fig. 1. Evonik 4000G PEEK pellets (Evonik Degussa, Germany) and Victrex 150G PEEK pellets (Victrex, Conshohocken, PA) were chosen as the two grades to study, with $M_N \approx$ 115,000 g/mol and 83,000 g/mol, respectively [19]. It should be noted that these estimates are based off of available literature for Victrex PEEK, with the understanding that the Evonik 4000G is similar in properties, including molecular weight, to available Victrex grades. Although the molecular weights of these two grades are relatively low, molecular weight was chosen as a factor to study due to the differences in flow characteristics noted both in materials data sheets and through observation in preliminary melt spinning trials.

Evonik or Victrex granules were spun into fibers onto a take-up drum with a Newmark Systems motion control system controlling

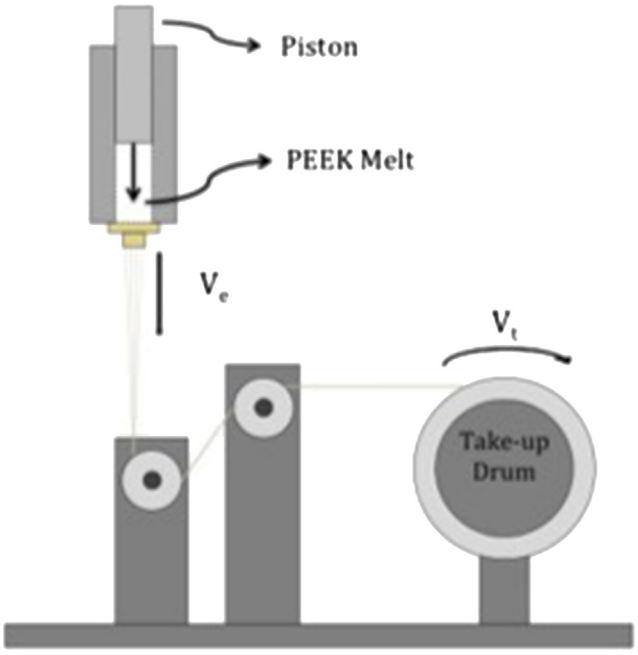

Fig. 1. Schematic of custom built melt-spinning setup.

the rotation and translation of the take-up, as well as the speed of the mechanical actuator mounted to force the piston head into the melt reservoir (Newmark Systems, CA, USA). Given that the melt range of both grades of PEEK were found to be between 335 °C and 345 °C, a barrel temperature of 395 °C was selected through several preliminary trials as giving rise to a stable spinning process with minimal fiber breakage and reasonable reproducibility. Fibers of either high or low viscosity grades were spun at a draw-down ratio (DDR) of either 100 or 200, where DDR is defined in Equation (1) as the ratio of linear take-up velocity to extrusion velocity for a single filament.

$$DDR = \frac{V_{take-up}}{V_{extrusion}} \tag{1}$$

Here, $V_{take\text{-}up}$ is considered as the linear velocity of the take-up drum, and $V_{extrusion}$ is considered as the velocity of a cylindrical column of molten PEEK exiting a single aperture of the spinneret per unit time. $V_{extrusion}$ was found by considering a constant volume problem wherein the velocity of the piston created a change in volume of the reservoir containing molten PEEK, which could then be correlated to a volume, and finally a length, of melt extruded from the spinneret area per unit time. Fibers were produced in 5 filaments bundles using a brass spinneret with 5 corresponding apertures of nominal diameter of 0.750 mm.

2.2. Post-spinning treatment

After fibers were initially spun, they were designated for one of three treatment groups. Each grade of PEEK and each DDR condition were subjected to this grouping of treatments. Specifically, one group of fibers would be left as they had been spun, in the “as-spun” group. Another would subjected to an annealing process, owing to the fact that exploratory work determined as-spun fibers tended to have low crystallinity as compared to bulk un-oriented PEEK. In the annealing process the fibers were lightly constrained and heat-treated in an isothermal oven at 280 °C for 90 min. Fibers treated this way were designated as the “annealed” group. Finally, a