Spectroscopic elucidation of structure-property relations in filaments melt-spun from amorphous polymers

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ABSTRACT

Melt spinning and drawing of amorphous cyclo-olefin and co-polyamide polymeric materials were performed to develop mono-component continuous filaments. Raman spectroscopy was employed to assess the effect of a static bending deformation on the microstructure of the filaments. Spectra stemming from the fiber regions under tensile and compressive loading do not show any appreciable shift of their vibrational bands as a function of applied strain. The bent filaments manage to redistribute strains without any stretching or buckling of polymer chains associated with peak shifting in the Raman spectrum. The influence of fiber draw ratio on the degree of molecular ordering was demonstrated by means of polarized Raman spectroscopy. An increase in draw ratio leads to a variation of the polarization ratio for spectroscopic bands located along the polymer backbone. We observed a correlation between the polarization ratio of these vibrational bands and the macroscopic tensile modulus of the material.

1. Introduction

High polymer solids are composed of regions with varying degrees of molecular order. The morphology of solid state polymers typically fluctuates continuously between ideal crystalline and fully amorphous states, where the term 'amorphous' is widely used in the field of polymer science to mean 'non-crystalline' [1]. The presence of an oriented amorphous (non-crystalline) phase plays a significant role in the microstructure of highly oriented semi-crystalline polymer fibers. This became apparent more than forty years ago, as Prevorsek and coworkers devised a set of experiments to elucidate which morphological characteristics of poly(ethylene terephthalate) (PET) fibers play a role in their thermal contraction [2]. In the performed experiments, they found a discrepancy between microfibril contraction and macroscopic fiber contraction which was explained in terms of the existence of two types of amorphous domains: those serving as intra-fibrillar tie molecules which connect the adjacent crystallites in a microfibril, and those acting as inter-fibrillar tie molecules which connect neighboring microfibrils, with the distinct characteristic that the inter-fibrillar amorphous domain is highly oriented [2]. The presence of three phases in PET consisting of crystalline, oriented amorphous and random amorphous phases was subsequently confirmed by other research groups, and methods for their quantification were proposed [3]. Years later, Bukosek and Prevorsek showed that although the three phase model can be used to describe the

microstructure of other fibers such as high tenacity polyamide 6 (PA6), it cannot be employed for instance to explain the morphology of textile PA6 which is produced by standard melt spinning [4]. In recent years, melt spinning and drawing of fully amorphous fibers has been performed in our research group, where the use of X-ray diffraction techniques has confirmed the presence of oriented amorphous domains in the melt-spun fully amorphous filaments, indicating that the degree of orientation is directly proportional to the draw ratio employed during fiber production [5,6].

A recurrent criticism in the fiber science literature is the lack of information regarding the structure of amorphous polymer fiber regions, which is mainly a result of the absence of long-range order which prevents the use of diffraction techniques for their analysis [7–9]. By means of molecular dynamics (MD) computer simulations, Brown and Clarke were able to model the amorphous region of an oriented semi-crystalline polymer fiber. They analyzed the influence of inter-chain forces during deformation, and found that under tension, inter-chain forces can have a significant effect by constraining the configurational rearrangements of individual chains within amorphous domains [7]. These results were confirmed experimentally by Hansen et al., who used nuclear magnetic resonance (NMR) spectroscopy to study phenylene group motions in polycarbonate (PC) as a function of tensile stress, showing that methyl group substitution at the *ortho* positions of the phenylene ring induces a significant restriction of motion due to steric hindrance coupled with Van der Waals interactions [10].

Along similar lines, the polymer science community has reiterated the lack of fundamental understanding on the molecular mechanisms associated with the plastic deformation of amorphous polymers [11–14]. Capaldi et al. have employed MD simulations of an amorphous polyethylene (PE) for the analysis of stress-induced mobility in the context of molecular level transitions between conformations [11]. Interestingly, it was found that the application of compressive stress does not induce a significant change in bond length or bond angle distribution; it merely promotes an increase in the dihedral angle transition rate (the rate at which a chemical bond changes its dihedral angle to accommodate the deformation) [11]. Analogously, Li et al. performed Monte Carlo simulations to investigate the tensile deformation of an amorphous polyolefin polymer [15]. Their analysis showed that during deformation, bond lengths remain relatively constant for strain values up to 60% [15]. MD simulations used by Hossain et al. to study the tensile deformation mechanisms of amorphous PE clearly suggest that the stress-strain curve has four distinct deformation regimes: elastic, yield point, softening and hardening [12]. Using model systems with varying chain lengths and number of chains, it was demonstrated that an amorphous PE with higher chain lengths has stiffer elastic regimes, higher yield stresses and a more pronounced softening regime. The simulations also show that fracture proceeds through chain disentanglement rather than a chain scission mechanism, where lower strain rates allow more time for chains to disentangle in order to better accommodate deformations [12].

Amorphous polymers offer significant advantages with respect to their semi-crystalline counterparts in terms of high light transmission, low birefringence, low water absorption, transparency and chemical resistance [16,17], which in turn provide a motivation to use such amorphous materials in the development of fibrous structures for novel applications. This is the case for cyclo-olefin polymers and copolymers, which are for instance being used increasingly to develop flexible, low field loss fibers which function as guiding elements for optical components used in the transmission of radiation in the terahertz frequency range [18–20]. Likewise, amorphous polyamides have the potential to be employed as fibers with outstanding second-order nonlinear optics properties which could be implemented as waveguides in optical systems [21–24].

In the present work, Raman spectroscopy was utilized to assess the effect of a static bending deformation on the microstructure of melt-spun amorphous filaments. An analysis of the Raman spectra allowed for the elucidation of the influence that fiber processing conditions (i.e. the draw ratio) have on the molecular ordering of the amorphous fibers. The ability of polarized Raman spectroscopy to accurately reflect the development of structural changes in amorphous polymers was demonstrated. A correlation between Raman polarization ratios and macroscopic tensile modulus was clearly observed.

2. Materials and methods

2.1. Materials

The cyclo-olefin polymer (COP) Zeonor® 1020R from Zeon Chemicals L.P. and the co-polyamide (CoPA) Grilamid® TR 90 from EMS-CHEMIE AG were used to produce melt-spun filaments. The chemical structures of these two polymers as reported in the literature are shown in Fig. 1 [25–27].
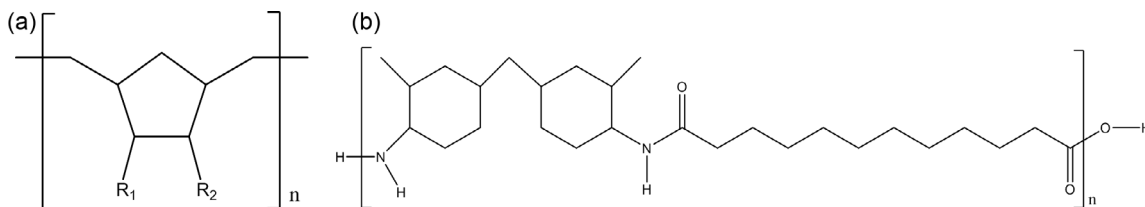

Fig. 1. Chemical structures of (a) COP and (b) CoPA [25–27].