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

A. Andrés Leal^{a,*}, James P. Best^b, Daniel Rentsch^c, Johann Michler^b and Rudolf Hufenus^a

^aLaboratory for Advanced Fibers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland.

^bLaboratory for Mechanics of Materials and Nanostructures, Empa, Swiss Federal Laboratories for Materials Science and Technology, Feuerwerkerstrasse 39, 3602 Thun, Switzerland.

^cLaboratory for Functional Polymers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland.

*corresponding author

Email addresses: Andres.Leal@empa.ch (A.A. Leal), James.Best@empa.ch (J.P. Best), Daniel.Rentsch@empa.ch (D. Rentsch), Johann.Michler@empa.ch (J. Michler), Rudolf.Hufenus@empa.ch (R. Hufenus).

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.

Keywords

amorphous polymer; glassy polymer; melt spinning; polarized Raman spectroscopy; molecular orientation

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 Figure 1 [25-27].

2.2. Nuclear magnetic resonance (NMR) spectroscopy

As received COP was dissolved in tetra-deuterated 1,2-dichlorobenzene (99 at. % deuterated) from ARMAR Chemicals to prepare solutions with a concentration of 60 mg/cm³ for NMR analysis. Clear solutions were obtained after two hours of ultra-sonication. ¹H and ¹³C NMR spectra were obtained at 400.1 (100.6) MHz on a Bruker Avance III 400 NMR spectrometer. The NMR experiments were performed at 298 K using a 5 mm BBO CryoProbe™ Prodigy applying the Bruker standard pulse programs and parameter sets. The ¹H/¹³C chemical shifts were referenced internally using the resonance signals of 1,2-dichlorobenzene at 7.40/130.1 ppm. Generally, no resolved coupling pattern was observed in the ¹H NMR spectra. For ¹³C NMR data d = CH and t = CH₂ groups. The numbering of positions of the COP structure used for NMR chemical shift assignment is shown in Figure 2.

2.3. Fiber development

COP and CoPA were melt spun on Empa's pilot plant using a single screw extruder with screw diameter of 18 mm and a length-to-diameter (L/D) ratio of 25 [28]. The extruder was equipped with three independently controlled heating zones. The extruder supplies the polymer melt to a melt pump which in turn feeds the molten material to the spin pack. After exiting the spinneret, the extruded monofilaments were immediately subjected to a draw-off process by means of three heated godets. The draw ratios reported in Table 1 reflect the difference in speed between godets 1 and 3 (draw ratio = speed of godet 3 / speed of godet 1). As a final step, the drawn filament is immediately wound onto a bobbin which rotates at a speed equal to that of godet 3. Table 1 shows the winding speeds for the different specimens under analysis in the present study. It has been shown that the presence of bulky cycloaliphatic substituents attached to the polymer backbone prevents the melt spinning and drawing processes from inducing the molecular order required for the development of fibers having a semi-crystalline structure, and therefore both materials remain in an amorphous state, as indicated by dynamic scanning calorimetry and wide angle X-ray diffraction measurements [5].

2.4. Raman spectroscopy

Confocal Raman spectroscopy of amorphous fibers was performed with a 532 nm visible light source in a commercial system (ND-MDT, Russia). A 100X objective was utilized (NA 0.95, Olympus) with a laser power of 0.19 mW at the sample surface. It was observed that this power intensity did not cause damage to the fiber. A CCD detector was utilized with grating wavelength 580 nm, and optimized pin-hole diameter of 45 μm. The achieved spectral resolution was approximately 2.7 cm⁻¹ with a spot size of approximately 1 μm. Fibers were aligned parallel to the sample stage in an initial $\overline{RR}$ direction. A collection time of 100 s was used to collect enough spectral information from each sample. Measurements were made parallel to the beam $\overline{RR}$ regarding output and input light, and

completely perpendicular between in/out light and the sample orientation ($\overline{ZZ}$). Additionally either/or the in/out light was rotated 90° ($\overline{RZ}$ and $\overline{ZR}$). Collected spectra were baseline-subtracted and normalized using a high intensity peak for all light orientations (1445 cm⁻¹ COP, 1454 cm⁻¹ CoPA). As $\overline{RZ}$ and $\overline{ZR}$ measurements were found to be equivalent, only $\overline{RZ}$ spectra were utilized for analysis. For measurements on bent fibers, un-polarized incident light was utilized to investigate fibers deformed to a bending radius of approximately 2 mm.

2.5. Tensile properties

The tensile characteristics of the melt spun filaments were determined using a Statimat ME + from Textechno GmbH with a 10 N load cell. A series of 20 specimens were tested for each filament type using a gauge length of 200 mm and a cross head speed of 1000 mm/min. Young's modulus values were determined according to ASTM D2256 [29].

3. Results

3.1 NMR spectroscopy of the cyclo-olefin polymer

The generic chemical structure of the COPs from Zeon Chemicals is shown in Figure 1a as is typically described in the literature [27]. Yamazaki reported that the two substituents R₁ and R₂ attached to the cyclopentane are often connected to form an alicyclic compound [27]. Given that a precise description of the chemical structure of the COP used for melt spinning in the present work is imperative for an accurate interpretation of the Raman spectra discussed in the following section, 1D NMR experiments (detailed chemical shift assignments included in the experimental section; 2D NMR data annexed as supplemental online material) were performed to identify its chemical composition. Figure 2 shows the regions of interest of the 1D ¹H and ¹³C NMR spectra of the COP under analysis along with the corresponding assignments of NMR chemical shift to the structure.

3.2 Raman spectroscopy

Raman spectroscopy was used to examine bending deformations on the microstructure of the amorphous filaments, along with the influence that fiber processing conditions (i.e. the draw ratio) have on the molecular ordering of the resulting fully amorphous melt-spun material.

3.2.1 Spectral analysis

Figure 3 shows the Raman spectra of drawn COP and CoPA filaments collected in the 200 – 2000 wavenumber range, where expected vibrational modes have been assigned to various vibrational regions. From detailed studies on polyethylene and ROMP reactions [30-33] as well as on amorphous polyamides [34] and polyamide 12 [35], C-C bending (δ) and stretching (ν) vibrational modes were

assigned for both COP and CoPA to low wavenumbers ($500\text{-}1150\text{ cm}^{-1}$), with rocking (ρ), twisting (τ) and bending C-H bands at higher wavenumbers ($1150\text{-}1500\text{ cm}^{-1}$). Different authors have ascribed the vibrational bands at 1088 , 1167 , 1297 and 1449 cm^{-1} to the amorphous phase regions in polyethylenes and cycloolefins [30-32, 36]. In the spectrum of CoPA an additional broad peak is observed at 1646 cm^{-1} assigned to the keto-amide group, which is particularly sensitive to the state of hydrogen bonding in the polymer [34]; this feature is not present in the COP fiber.

3.2.2 Analysis of static bending deformation

The melt-spun amorphous filaments under analysis display a significantly better recovery from a bending deformation than various semi-crystalline melt-spun fibers commercially available, such as for polyester and polyamide [5]. This is likely possible as the amorphous fibers are able to redistribute applied compressive strains in a way which prevents them from reaching their yield strain criterion at radii of curvature where semi-crystalline materials already undergo plastic deformation [5]. It has been demonstrated by various authors that certain Raman vibrational bands of a polymer specimen will exhibit a shift in their peak position when the material is subjected to a mechanical deformation. The peak shift is the result of stretching or buckling of the polymer chains, and subsequent changes in the average bond length [37-39]. In an attempt to identify the effect that a bending deformation will have on the amorphous filaments at the molecular level, a series of Raman spectra were acquired across the equator of a bent filament. The filament was scanned from the inner (compressed) to the outer (tensed) surface. It can be observed in Figure 4 that the spectra stemming from the fiber regions under tension and compression do not show any appreciable shifts in the peak positions and widths of their vibrational bands for the two amorphous fibers under consideration. A lack of Raman band shift as a result of an applied force is typically associated with an alignment of the polymer chains without energy dissipation [40]. The fiber specimens under Raman analysis were deformed to a radius of curvature of approximately 2 mm, which corresponds to applied compressive (ϵ_c) and tensile (ϵ_t) strains at the periphery of the bent fiber in the order of 6% and 1%, respectively. It is known from previous work that $\epsilon_c = 6\%$ will already induce plastic deformation in the material [5]. Micro-Raman spectroscopy performed by Herrera Ramirez et al. [41] on polyamide 66 filaments under axial deformation has shown that the wavenumbers representative of the amorphous domains do not shift when the fiber is subjected to an external load for ϵ values of up to 12%, a value well beyond the yield point of the material. The lack of Raman shifts in the filaments under study in the present work confirms the ability of the amorphous phases to realign and shift their polymer chains in accordance to the applied deformations, giving a highly amorphous material an extremely good capacity to recover from a bending deformation [5]. This experimental result is in agreement with the theoretical considerations reported by various authors based on

molecular dynamics and Monte Carlo simulations, which indicate that no significant change in bond length distribution is to be expected during tensile and compressive deformation of amorphous polyethylene [11, 12, 15]. Additionally, the CoPA peak at ca. 520 cm^{-1} was found to be reproducibly suppressed in compression. This band is likely to be a rotation of bending motion against a relatively low potential, and it is reasonable to suggest that its suppression can be related to stress changes in the fiber, as has been reported for other materials [42].

3.2.3 Polarized Raman spectroscopy

The melt spinning and drawing processes induce a certain degree of molecular orientation on the amorphous filaments under study [5]. Therefore, the influence of the degree of molecular orientation on the Raman spectra of a fully amorphous filament was additionally analyzed. Polarized Raman spectroscopy provides a powerful tool in the assessment of molecular orientation. The orientation dependence of both light and chemical bonds is exploited to elucidate variations in the Raman spectra as a result of a change in the ordering of molecules within a structure [43]. Consequently, Raman spectra were acquired using polarized filters for both the incident laser light, and the scattered light. While keeping the orientation of the fiber constant, the laser light orientation could then be varied to excite bonds aligned along different directions. The measurement methodology and analysis was based on the work of Adar and Noether for their polarized Raman analysis on drawn poly(ethylene terephthalate) fibers [44]. Defining the system Z axis as being parallel to the fiber direction and R being a radial direction perpendicular to Z with the fiber lying flat on the stage of the microscope, spectra were collected at a polarization angle where the light intensity was maximized for both the sample input and output ($\overline{RR}$), where the first letter indicates the incident laser light polarization, and the second the scattered light polarization. Then the polarization of the output light was rotated 90° and spectra with $\overline{RZ}$ polarization were acquired. Finally, both laser and Raman polarization were rotated 90° from the original setup so that spectra with $\overline{ZZ}$ polarization could be recorded. Such measurements were performed for COP and CoPA fibers with different draw ratios applied during their fabrication and are shown in Figure 5, while Figure 6 illustrates the evolution of the $\overline{RR}:\overline{ZZ}$ ratio for dominant peaks in the Raman spectra as a function of the fiber draw ratios reported in Table 1. In the as-spun (undrawn) state, the filaments are in a highly un-oriented condition and this expected high degree of isotropy is confirmed in Figure 6 by the fact that the $\overline{RR}:\overline{ZZ}$ ratios are close to 1 for all vibration bands under consideration, where a value close to 1 implies that the intensities of the polarized Raman bands in the two directions are indistinguishable [44]. Further, Figure 6 shows that as the draw ratio increases, the polarization ratio for spectroscopic bands located along the polymer backbone such as for C-C stretching (ν_{C-C}) as well

as CH_2 rocking (ρ_{CH_2}) and twisting (τ_{CH_2}) decreases for both COP and CoPA, a trend clearly observed by other authors for highly oriented fibers and films [43-46]. In contrast, Figure 6b shows how the polarization ratio obtained from the secondary amide C=O stretching vibration band located at 1638 cm^{-1} is directly proportional to the degree of draw ratio imparted to the CoPA fiber. This behavior can be ascribed to the fact that as the degree of molecular orientation in the fiber increases, the possibility that the secondary amine engages in intermolecular hydrogen bonding with neighboring chains is enhanced considerably [47, 48], providing an energetic barrier for the ketone group to be realigned in the fiber direction, which in turn also promotes an $\overline{RR}:\overline{ZZ}$ ratio > 1 for this vibrational band.

It is a well-known fact that as the degree of anisotropy increases in an organic fiber, the tensile modulus of the material will be correspondingly enhanced as the polymer chains are progressively aligned in the fiber direction [49]. Therefore, the $\overline{RR}:\overline{ZZ}$ polarization ratio of a C-C stretching vibration located on the polymer chain axis can be expected to correlate with the tensile modulus for the filaments with varying degrees of drawing. Figure 7 presents the plots of intensity ratios versus tensile moduli for the different C-C stretching vibrations under analysis. The good correlation between intensity ratio and macroscopic stiffness confirms that the C-C stretching bands are located on the polymer backbone. Jee et al. have used poly(vinyl alcohol) (PVA) filled with carbon nanotubes in a wet-spinning process to demonstrate the effect of material orientation on the polarized Raman intensity ratios of stretching vibrations and the resulting tensile modulus [50]. By varying the shear stress induced by the spinneret during fiber spinning, they were able to control the degree of orientation of the nanotubes in the PVA. An increase of nanotube orientation in the fiber direction led to smaller intensity ratios of the graphitic C-C stretching vibration and higher tensile moduli values [50]. Similarly, an enhancement of molecular ordering in the non-crystalline COP and CoPA fibers leads to a significant reduction of the Raman intensity ratios. Ultimately, the accuracy of the spectroscopic characterization is confirmed by the measured elastic moduli.

4. Conclusions

This work has focused on further advancing the understanding of the structure-property relations encountered in amorphous polymers, as well as to illustrate the role played by the processing parameters on the resulting degree of ordering of melt-spun filaments. The analysis of amorphous materials is successfully performed by means of spectroscopic techniques, where the use of Raman measurements allows for the identification of the effect of a bending deformation on the molecular ordering of the material. Additionally, polarized Raman spectroscopy clearly illustrates how an undrawn amorphous filament is truly in an almost fully isotropic state, while the drawing process

induces a progressive degree of ordering, where the oriented amorphous material shows a continuous enhancement of its macroscopic tensile modulus. Further studies will focus on investigating the relation between degree of orientation in the amorphous fiber and thermal contraction in addition to the effect of polymer chain cyclic orientation and randomization on the mechanical properties of the amorphous filaments.

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Figure Captions

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

Figure 2. (a) ^1H and (b) ^{13}C NMR spectra with assigned resonances to the chemical structure of COP (Zeonor® 1020R). ^1H NMR ($\text{o-CD}_2\text{Cl}_4$, 400.1 MHz): δ/ppm 2.63 (2H, H-3); 1.97 (2H, H-4); 1.82 (2H, H-2a); 1.82 (1H, H-5a); 1.82 (1H, H-1a); 1.57 (2H, H-6); 1.42 (1H, H-1b); 1.36 (2H, H-2b); 1.00 (1H, H-5b). ^{13}C NMR ($\text{o-CD}_2\text{Cl}_4$, 100.6 MHz): δ/ppm 46.0 (d, C-3); 43.2 (d, C-4); 36.8 (t, C-5); 30.6 (t, C-6); 28.5 (t, C-2); 28.0 (t, C-1).

Figure 3. Collected confocal Raman spectra of COP (draw ratio 3.0) and CoPA (draw ratio 2.5) fibers. Expected vibrational mode ranges are also shown.

Figure 4. Raman spectra of COP (draw ratio 3.0) and CoPA (draw ratio 2.5) filaments during bending experiments with overlays of spectra for the compressed (inner) and tensed (outer) bent surfaces.

Figure 5. Polarized Raman spectra of (a) COP and (b) CoPA fibers with varying draw ratios. Asterisks indicate the spectral bands analyzed in Figure 6.

Figure 6. Evolution of the $\overline{RR}:\overline{ZZ}$ ratios against fiber draw ratios for (a) COP and (b) CoPA. Data points are fitted with a linear regression.

Figure 7. Correlation between the $\overline{RR}:\overline{ZZ}$ ratio of different C-C stretching bands and tensile modulus for (a) COP and (b) CoPA filaments with varying draw ratios.

Tables

Table 1. Melt spinning parameters of COP and CoPA filaments.

Polymer	Spinneret diameter (mm)	Draw ratio	Fiber diameter (μm)	Winding speed (m/s)	Linear density (g/km)	Tensile modulus (GPa)
COP	0.5	*	200	---	32	1.4
	0.4	1.5	145	5.00	14	2.5
	0.4	2.0	125	6.67	12	2.6
	0.4	2.5	115	8.33	9.4	3.4
	0.4	3.0	110	10.0	6.5	4.0
CoPA	0.5	*	705	---	372	1.3
	0.5	1.0	100	6.67	7.0	1.7
	0.5	2.0	90.0	13.3	5.9	3.2
	0.5	2.5	72.0	16.7	3.7	3.8

*Fibers collected right after the spinneret, before they reached the first godet.

Graphical abstract