

Estimating Crystallinity in High Density Polyethylene Fibers using Online Raman Spectroscopy

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ABSTRACT: Online Raman spectra, obtained at different points along the spin line during pilot-scale nonisothermal melt spinning of high density polyethylene (HDPE) fibers, are presented for the first time. The fraction of the crystalline phase corresponding to each spectrum was determined from the normalized integrated intensity of the 1418 cm^{-1} Raman band. It is well established that this band represents the orthorhombic crystalline phase in polyethylene. The estimates of percent crystallinity obtained from decomposition of the Raman spectrum were compared with the percent

crystallinity from differential scanning calorimetry (DSC) measurements. It is concluded that online Raman spectroscopy can be successfully used to monitor the development of crystallinity in HDPE fibers as a function of distance from the spinneret. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 545–549, 2003

Key words: Raman spectroscopy; polyethylene; crystallization; fibers; processing

INTRODUCTION

A large fraction of synthetic polymeric fibers are manufactured by the melt spinning process. In this process, the polymer melt is converted into fibers by pumping it through a spinneret. The applied extensional force thins down the melt, which solidifies on cooling, resulting in the formation of fibers. It is well known that the macroscopic properties of these polymeric fibers are dictated by their morphology, which in turn depends on the spinning conditions used in their production. However, what is less well understood is how this morphology, and the associated fiber properties, actually develop in the spin line as a function of time. The spinning temperature, rate of cooling (of the melt), and the temperature and speed of the feed and draw rolls, together control the fiber morphology; that is, the degree of crystallinity and extent of molecular orientation achieved during fiber spinning.

High-density polyethylene (HDPE) is a commercially important, predominantly crystalline, linear form of polyethylene. Because of the importance of HDPE, the vibrational spectrum of polyethylene has been the subject of several investigations, and band assignments in its Raman spectrum are well established.^{1, 2} In the $1000\text{--}1500\text{ cm}^{-1}$ spectral region, the band at 1060 cm^{-1} is assigned to the C—C antisym-

metric stretch associated with the crystalline and amorphous regions of the polymer. The band at 1080 cm^{-1} is assigned to the *gauche* conformers present in the amorphous region and can be used to quantitate the amorphous content in the sample. Bands from 1400 to 1460 cm^{-1} correspond to methylene bending vibrations. In this region, the 1481 cm^{-1} Raman band has been unanimously assigned to the orthorhombic crystalline phase in polyethylene.^{1, 2} This band, which has previously been used to approximate the crystallinity of the sample,^{3–7} is a result of crystal field splitting of the two components of the methylene bending vibration when the unit cell is occupied by two structural units, as in the orthorhombic lattices.

It was first reported by Strobl and Hagedron that a simple two-phase model (amorphous + crystalline) was inadequate in describing all the features observed in the Raman spectrum of polyethylene.³ The presence of an additional disordered phase of anisotropic nature, where the chains are in *trans* conformation but have lost their lateral order, was postulated and has been confirmed by small angle X-ray⁸ and nuclear magnetic resonance (NMR) measurements.^{9, 10} This disordered phase is located at the interface between the crystalline and amorphous regions and has been associated with chain loops and entangled chain segments. In addition, these authors noted that in the case of polyethylene, the integrated area of the Raman twisting bands (i.e., bands in the $1295\text{--}1305\text{ cm}^{-1}$ region) remained the same for the melt as well as a fully crystallized sample. As a result, this area can be used as an internal standard to normalize all the band intensities in the Raman spectrum. Thus, the fractions of

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the crystalline (α_c), amorphous (α_a), and disordered (α_d) phases of semicrystalline polyethylene could be directly determined from the normalized integrated intensities of the appropriate bands in the Raman spectrum if the normalized intensity values for the limiting cases [i.e., a fully crystalline ($\alpha_c = 1$) and a totally amorphous ($\alpha_a = 1$) sample of polyethylene] are known. Although it is generally agreed that the fraction of the crystalline phase can be accurately determined from analysis of the Raman spectrum of polyethylene,^{3-6,11,12} conflicting points of view have been reported on the reliability of quantitative estimates of the disordered phase obtained from the decomposition of the Raman spectrum.^{11,12} As a result we have made no attempt to quantitate the disordered phase, although good correlations between drawability and the amount of disordered phase, determined using Raman, have recently been reported.⁷ These results indicate that a higher percentage of disordered phase restricts drawability due to chain entanglement in the interfacial region, which reduces deformability of the sample.⁷

A number of well-known methods are available for the determination of crystallinity in semicrystalline polymers. Crystallinity is commonly derived from heat of fusion, density, X-ray diffraction, and NMR measurements. However, most of these methods are not amenable for online monitoring. In an attempt to understand how the fiber morphology develops in the spin line, online X-ray patterns as a function of distance from the spinneret have been measured.^{13,14} However, online measurements using traditional X-ray equipment are tedious and require a rather elaborate and expensive experimental setup. In addition, X-ray measurements do not provide adequate information on the amorphous fraction of a semicrystalline polymer. Vibrational spectroscopic techniques, like Raman, offer an attractive alternative for online monitoring because they can provide detailed morphological information on both the amorphous and crystalline phases of a semicrystalline polymer, as long as the bands characteristic of each phase can be unambiguously identified. In addition, Raman spectra can be obtained from any sample with virtually no sample preparation and, because Raman spectroscopy typically involves the use of visible or near-infrared radiation, it is very amenable to fiber optic coupling using standard, low cost, silica fibers. It is thus possible to analyze normally inaccessible samples situated remotely from the spectrometer (e.g., at different points along a moving fiber spin line).¹⁵ Although the potential of a Raman-based technique to obtain spectra of polymers under processing conditions has long been recognized, online Raman data showing the development of crystallinity during actual fiber production has never been published in the open literature. The primary purpose of this paper is to demonstrate the

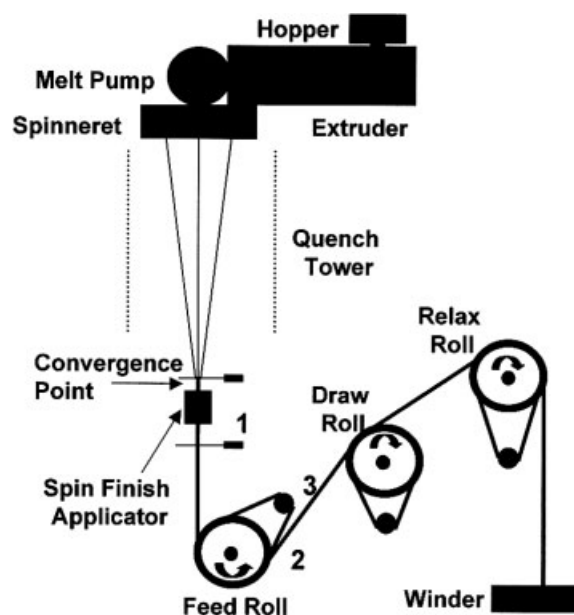


Figure 1 Schematic of the melt spinning line.

feasibility of using a Raman-based technique to monitor the development of crystallinity in melt spun polyethylene fibers.

EXPERIMENTAL

Melt spinning

Equistar, Inc. (Cincinnati, OH) donated the fiber-grade HDPE (Alathon R) chip used in this study. The HDPE was melt spun at 210°C on a pilot scale Hills, 1-in. diameter, single-screw extruder with an aspect (L/D) ratio of 30:1. Constant throughput was maintained at 3.97 g/min using a 1.168 cc/rev, Zenith (Sanford, NC) melt pump. A 3-hole, 1-mm capillary diameter spinneret was used in this work. The filaments were quenched using cooling air blown perpendicular to the direction of filament travel. The quench air temperature was $20 \pm 1^\circ\text{C}$ and the flow rate was maintained at 0.5 m/s. The filaments were passed around a constant speed feed roll, ~ 177 cm from the spinneret, maintained at a room temperature. The filaments were then passed around the draw and relax rolls and taken up on a bobbin, using a Barmag SW4 winder, for immediate crystallinity measurement by DSC. A schematic of the melt spinning line used in this work is shown in Figure 1. Threadline tension (spinning stress) was varied by employing selected take-up speeds (TUS). The draw and relax rolls were both held at the same speed and temperature as the feed roll to ensure that the fibers were not drawn before take-up.

Raman spectroscopy

Raman spectra were collected using a Renishaw System 100 Raman spectrometer coupled to a remote

Renishaw fiber optic probe head. The other components of the system included a 300 mW, 785 nm diode laser (Process Instruments, Salt Lake City, UT), a stigmatic single spectrograph, a two-dimensional, thermoelectrically cooled, deep depletion CCD camera, and a personal computer. The probe head was equipped with an Olympus LMPlanFI 20X (0.40 NA) ultra-long working distance (1.2 cm) objective. At the maximum setting on the laser, the probe typically delivered ~ 24 mW of depolarized laser radiation at the sample. Depolarized laser light was obtained by removing the polarizers from the probe head and wrapping a short length of the input multimode fiber optic cable, in small loops, around a 1/2-in. diameter electrical cable. It is believed that the resulting stress in the optical fiber will effectively scramble the laser polarization. The use of depolarized laser radiation is required for the estimation of crystallinity in the fibers because orientation-independent information is required in this case; that is, the orientation in the fiber should not affect the Raman band intensities and introduce error in the estimation of crystallinity.¹⁵

All the spectra shown here were acquired from a single fiber, with typical data acquisition times between 5 and 10 min. Because movement of the fiber in and out of the laser spot (~ 20 μm) was a problem, a small parallel ceramic guide was used to stabilize the fiber. Although this guide did not completely alleviate the problem of fiber movement, good Raman data were obtained, albeit at the expense of integration time. It is suggested that use of low friction grooved roller wheels may more effectively minimize the fiber movement. All data acquisition was performed using the Renishaw 'WiRE v1.3' software. Data were subsequently transferred into GRAMS/32 (Galactic Inc, Salem, NH) for processing and analysis. The raw Raman data were smoothed (binomial) and a linear baseline was subtracted from each spectrum. The areas under the peaks of interest were then estimated using the standard curve-fit routine in GRAMS/32. The peaks were fit multiple times to ensure reproducibility of the fit. A mixed Gaussian-Lorentzian function was used and the area of the Raman bands was used as the intensity value.

Measurement of crystallinity

Crystallinity of the HDPE fibers was estimated using a TA instruments (New Castle, DE) DSC 2920, differential scanning calorimeter. The instrument was calibrated using indium, and typically 3–5 mg of the fiber sample was used. The heating rate was 10°C/min. At least three replicate measurements were performed for each sample. The degree of crystallinity was calculated by dividing the experimentally determined heat of fusion for the sample by the heat of fusion

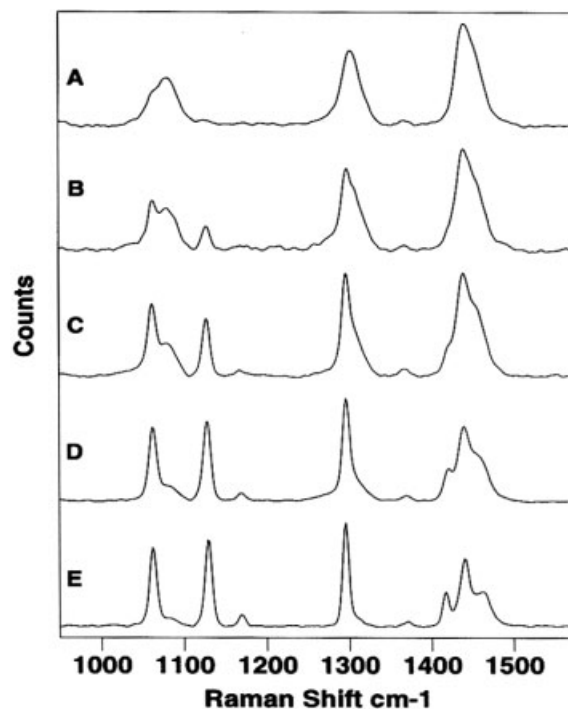


Figure 2 Online Raman spectra showing the evolution of crystallinity in HDPE fibers. Conditions: TUS, 200 m/min; no quench; distance below spinneret, (A) 45 cm, (B) 55 cm, (C) 65 cm, (D) 105 cm, and (E) 588 cm (between feed and draw roll).

corresponding to a perfect polyethylene crystal (290 J/g).¹⁶

RESULTS AND DISCUSSION

Typical online Raman spectra from a single HDPE fiber, obtained as a function of distance from the spinneret, are shown in Figure 2. The HDPE fiber spectrum obtained 45 cm below the spinneret is the HDPE melt spectrum with three broad bands centered at 1080, 1305, and 1440 cm^{-1} (Figure 2). As the fiber cools (crystallizes), the intensity of the broad amorphous band at 1080 cm^{-1} decreases, with a concomitant increase in intensity of the crystalline bands at 1060 and 1130 cm^{-1} . Similarly, the broad amorphous band centered near 1300 cm^{-1} is replaced by a narrow crystalline band at 1295 cm^{-1} and a broad amorphous band at 1305 cm^{-1} . Finally, the single amorphous band centered at 1440 cm^{-1} splits into three bands, of which the 1418 cm^{-1} band can be used to quantitate the sample crystallinity.

Online Raman spectra obtained at 45 cm below the spinneret, under different conditions of take-up speed and quench air, are shown in Figure 3 and can be used to qualitatively illustrate the effect of experimental variables on the online Raman spectra of HDPE fibers. These data suggest that at a fixed point along the spin line, the overall crystallinity developed in the fiber is a

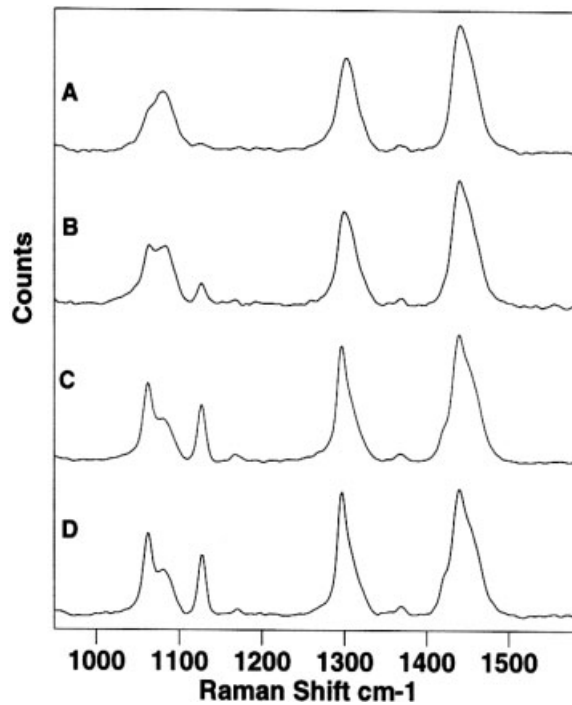


Figure 3 Effect of TUS and quench air on online Raman spectra of HDPE fibers: (A) 200 m/min and no quench; (B) 800 m/min and no quench; (C) 200 m/min, with quench; and (D) 800 m/min, with quench. All the spectra are normalized to unit area to allow direct visual comparison.

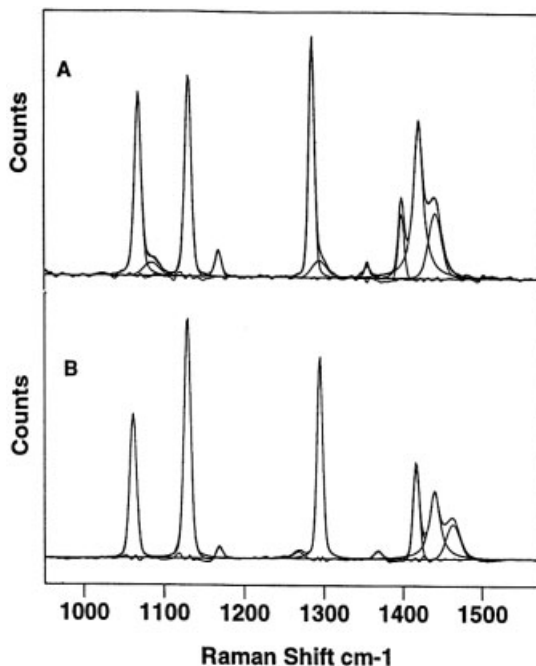


Figure 4 Raman spectra of polyethylene fiber with typical curve fitting results: (A) online spectrum of semicrystalline fiber measured 588 cm from the spinneret and (B) fully crystallized fiber from DSM Research measured offline using a remote fiber optic probe.

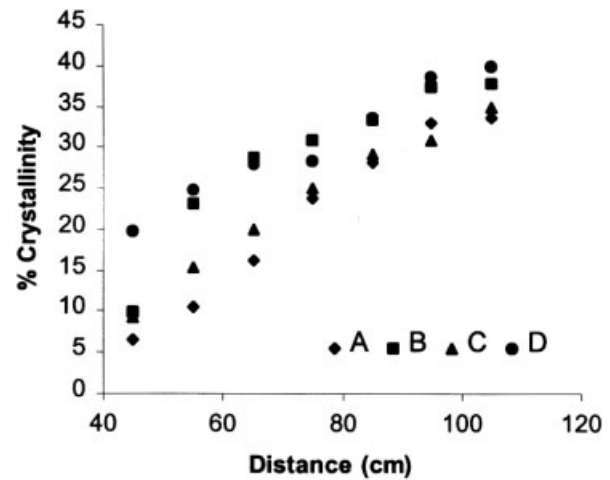


Figure 5 Plot of percent crystallinity as a function of distance from the spinneret, for HDPE fibers extruded at 3.97 g/min under different conditions of quench and take-up speed (TUS): (A) TUS of 200 m/min, with quench air turned off; (B) TUS of 200 m/min, with quench air turned on (0.5 m/s, 20°C); (C) TUS of 800 m/min, with quench air turned off; and (D) TUS of 800 m/min, with quench air turned on (0.5 m/s, 20°C).

function of the spin line stress and the cooling rate of the fiber. From a comparison of Figures 3C and 3D we conclude that, under identical conditions of quench, the amount of crystallinity developed in the filament increases with an increase in the TUS, as evidenced by the increased intensity of the shoulder at 1418 cm^{-1} . Increasing the TUS at constant mass flow rate decreases the fiber diameter, which in turn increases the cooling rate and stress (molecular orientation) in the filament, leading to an increase in the rate of crystallization.¹⁴ Similarly, increasing the cooling rate at a given TUS increases the acceleration and stress in the filament, thereby increasing the crystallization rates,¹⁴ as observed by comparing Figure 3A with 3C and 3B with 3D.

To estimate the crystallinity corresponding to each spectrum shown in Figure 1, we adopted the spectral decomposition procedure proposed earlier.³ The Raman spectra of a completely crystalline ($\alpha_c = 1$) and semicrystalline polyethylene fiber are shown in Figure 4 along with the typical results from the curve-fitting procedure used to estimate the areas of the Raman bands. The sample of fully crystallized polyethylene fiber (>99%), manufactured using a special proprietary process, was obtained from DSM Research. A single filament was carefully isolated and mounted across an aluminum washer under slight tension for Raman measurement using the remote fiber optic probe. As expected, the amorphous bands at 1080 and 1305 cm^{-1} are virtually nonexistent in the Raman spectrum of the fully crystalline fiber. In addition, the intensity of the 1418 cm^{-1} band is also significantly higher than that of a semicrystalline fiber sample. The

TABLE I
Final Crystallinities for the HDPE Fibers as Determined by Raman Spectra and Thermal Analysis

Sample ^a	$(I_{1418})_{\text{norm}}$ ^b	% c (Raman)	% c (DSC)
A	0.23	52.27	60.30
B	0.25	56.82	62.98
C	0.24	54.55	61.75
D	0.28	63.64	64.58

^a Extrusion conditions as shown in Figure 5.

^b normalized intensity from Raman spectrum measured between the feed and draw roll, 588 cm from the spinneret

normalization constant used to estimate the crystallinity along the spin line was derived from the normalized (with respect to the integrated area of the twisting bands) area of the 1418 cm^{-1} band in the Raman spectrum of the fully crystalline fiber. A value of 0.44 was obtained, which is in very good agreement with the value of 0.46 reported earlier.³ Thus, the fraction of the crystalline phase, α_c , corresponding to each spectrum shown in Figure 2, can now be determined directly from the integrated intensity of the bending mode at 1418 cm^{-1} according to eq. 1:

$$\alpha_c = \left(\frac{I_{1418}}{I_T \times 0.44} \right) \quad (1)$$

where I_T is the total intensity of the twisting bands and 0.44 is the normalizing coefficient derived from the spectrum of a fully crystallized sample of polyethylene.

The normalization constant derived from the 1418 cm^{-1} Raman band of the fully crystallized sample of polyethylene fiber was used to estimate the crystallinity along the spin line. Plots of percent crystallinity as a function of distance from the spinneret, for different conditions of quench and take-up speed, are shown in Figure 5. Each data point shown in Figure 5 is an average of three replicate measurements, with an average error of $\pm 4\%$. As mentioned earlier, during the melt spinning of polymer fibers there are two effects that influence the development of crystallinity in the spin line: the stress in the fiber and the cooling rate of the fiber. The results shown in Figure 5 are consistent with earlier observations¹⁴ and indicate that the conditions that increase the spin line stress result in a quicker rise in crystallinity, whereas low spin line stress leads to a more gradual rise in crystallinity with distance from the spinneret.

The final crystallinity for the HDPE fibers measured by DSC are compared with those obtained from the Raman spectra in Table I. The slightly higher crystallinity values measure by DSC may be because polyethylene has a very low glass transition temperature (T_g). As a result, it is possible that the fibers continue to crystallize beyond the spinning process, prior to DSC measurements.

CONCLUSIONS

Online Raman spectra showing the evolution of crystallinity during pilot scale melt spinning of HDPE fibers were presented for the first time. The normalized intensity of the 1418 cm^{-1} Raman band was used to estimate the crystallinity in the HDPE fibers. Good quantitative agreement between the final fiber crystallinity as measured by Raman and DSC were obtained. The ability to obtain online Raman spectra during fiber processing can be used to optimize and eventually control the fiber spinning process. On a fundamental level, Raman spectroscopy can be used to monitor the development of polymer morphology as a function of processing parameters along the entire length of the spin line. These measurements can then be used to optimize current computer models of the melt spinning process. Alternatively, from a more practical standpoint, a Raman-based sensor can be designed and installed at a convenient point along the spin line to predict the fiber crystallinity in real time, thereby resulting in significant cost savings because of reduced analysis time and better control over the fiber spinning process.

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