Notes

Orientation of Amorphous Chains in Polyamide-6 Fibers through ^{2}H-NMR

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Received March 21, 1996

Revised Manuscript Received July 30, 1996

Introduction

Generally, in fiber technology, fibers are drawn after having been spun near the melting temperature. The draw ratio $\lambda = S_0/S$ is then deduced from sections S_0 and S of the materials before and after drawing.[1] For semicrystalline (PE, PP) or amorphous (PS, PMMA) high molecular weight polymers, the deformations at low and high temperatures are affine. In the molten state the deformations are also affine if the time of measurement is shorter than the reptation time. In such bulk or fiber oriented polymers the draw ratio can be easily measured by dimensional relaxation in the melt state. From the shrinkage Sh the draw ratio, λ, of the starting material is obtained from the following relation:

$$\mathrm{Sh} = \frac{l - l_0}{l} = 1 - 1/\lambda \qquad (1)$$

l and l_0 being, respectively, the length of the draw and relaxed samples.

This relation is true only if the polymer does not flow during the annealing process. For polyolefin, the melting point, T_m, is about 200 degabove the glass temperature T_g. Above T_m, the reptation time is greater than the time of annealing, typically a few seconds, though only for high molecular weights, i.e., $M_w > 10^5$. The reptation time follows the relationship $t \sim M^{3.4}$ and because polyamide (PA) typically has a molecular weight of 2×10^4 to 4×10^4, this characteristic time is 2×10^{-3} times lower than that of polyolefin. It is for this reason that at the melting temperatures, a drawn PA material does not relax to its original dimension. Flow occurs during annealing and melting, and eq1 is no longer valid to measure λ by a simple shrinkage experiment.

Thus there is no direct method for determining the true draw ratio of a PA stretched material. The aim of this paper is to show that quadrupolar NMR gives accurate measurement of orientation and draw ratio for polymer chains in the amorphous phase of the semicrystalline state.

NMR Method

Several authors[2−14] have described the measurement of the orientation of deuterated chains (free or cross-linked) and deuterated molecules of a solvent in elastomers and in block copolymers by quadrupolar NMR. In liquid systems the deuterated probe experiences fast reorientation movements; the quadrupolar splitting of the NMR line is

$$\Delta\nu \cong \nu_q \left\langle \frac{3\cos^2\Omega - 1}{2} \right\rangle \left\langle \overline{\frac{3\cos^2\theta(t) - 1}{2}} \right\rangle \qquad (2a)$$

where ν_q is the quadrupolar frequency (2×10^5 s^{-1}); Ω is the angle between the magnetic field and the drawing direction; and $\theta(t)$ is the angle between the major axis of the deuterium nucleus (i.e. the OD bond when deuterated water is used) and the drawing direction. The brackets represent the space average and the overbar denotes the time average for all the orientations of movement faster than $t_q \sim \nu_q^{-1}$. With angle Ω fixed, the splitting is therefore proportional to the strain function of the rubber elasticity theory, $\langle 3\cos^2\theta - 1\rangle \approx \lambda^2 - \lambda^{-1}$.

In PDMS rubbers it was shown by Sotta et al.[9−11] that the chains and the solvent have a similar orientation and the same variation with the elasticity term $\lambda^2 - 1/\lambda$:

$$\Delta\nu = k\nu_q(\lambda^2 - 1/\lambda) \qquad (2b)$$

where k is a constant. Nonetheless, when the concentration of deuterated solvent ($CDCl_3$) exceeds 30%, deviation occurs and the solvent becomes less oriented than the cross-linked polymer chains. Then the measurement of orientational order of the solvent molecules in concentrations of about 20% or less provides measurement of the chain orientation order in the polymer liquid phase (elastomer or semicrystalline material having an elastomeric phase).

Here we have applied this method for the study of polyamide-6 (PA6) materials, bulk and fibers, swollen with an aqueous solution containing 20% formic acid. The swelling ratio is 20% and independent of the draw ratio.

Characterization of the Materials

Vidahim firm (Bulgaria) supplied multifilament yarn of spun PA6. The cross-section is 2.7×10^{-6} m^2, and each filament has a tex value of 140. The draw ratio deduced from the section of the isotropic and oriented filament is $\lambda = 5$.

These materials were annealed for 10 min at several temperatures, $T < T_m$ ($T_m = 220$ °C) without stress. The shrinkage Sh was then measured at room temperature.

NMR measurements were performed with an AM250 spectrometer (^{2}H frequency: 38.40 MHz). The fibers

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S0024-9297(96)00436-6 CCC: $12.00

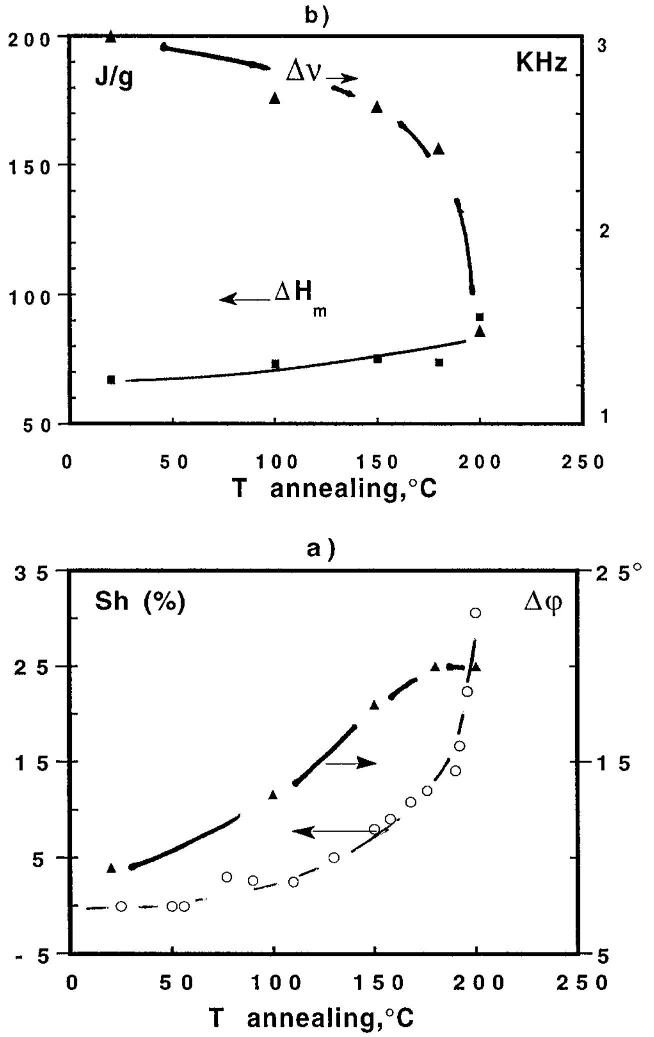

Figure 1. Characteristics of the dry and swollen fibers PA6 as a function of annealing temperature. Solid lines drawn through data as guidelines. (a) Shrinkage Sh and width $\Delta\varphi$ of the azimuthal scan of the crystalline (200) reflection of the dry fiber. (b) Melting enthalpy ΔH_m of the dry fibers and quadrupolar splitting $\Delta\nu$ of the fibers swollen at equilibrium in a solution of heavy water and formic acid (20%).

were parallel to the magnetic field ($\Omega = 0°$), and the spectra were recorded at 20 °C. The temperature was 70 deg above T_g, and the hypothesis of the fast movement regime is satisfied.

Figure 1a represents the variation of shrinkage Sh and the width at half-height $\Delta\varphi$ of the azimuthal scan of the WAXS (200) reflection as a function of the annealing temperature. $\Delta\varphi$ is a measure of the crystalline disorientation, while Sh measures the amorphous disorientation.[1]

DSC of annealed fibers shows that the melting temperature begins near 200 °C and the maximum of the melting peak occurs at 220 °C when the heating rate is 5 °C/min. The temperature $T_{\alpha c}$ of PA6 is located near 160 °C,[15,16] $T_{\alpha c}$ is the temperature of appearance of mobility of the chains in crystallites. For all the polymers, $T_{\alpha c}$ corresponds to the annealing temperature above which thickening of the lamellar crystals occurs.[17,18] This temperature depends on the thickness of the crystallites and is thus strongly related to the temperature of crystallization. In PP it has been shown that above the $T_{\alpha c}$ temperature, creeps become important. In PA6, the temperature where thickening of the crystallites appears is about 180−190 °C[16,17] which coincides with the $T_{\alpha c}$ temperature. Shrinkage of PA6 fibers becomes an important phenomenon above 170−180 °C because it correponds to the temperature where the crystalline chains have a certain mobility by allowing the relaxation process of the amorphous chains.

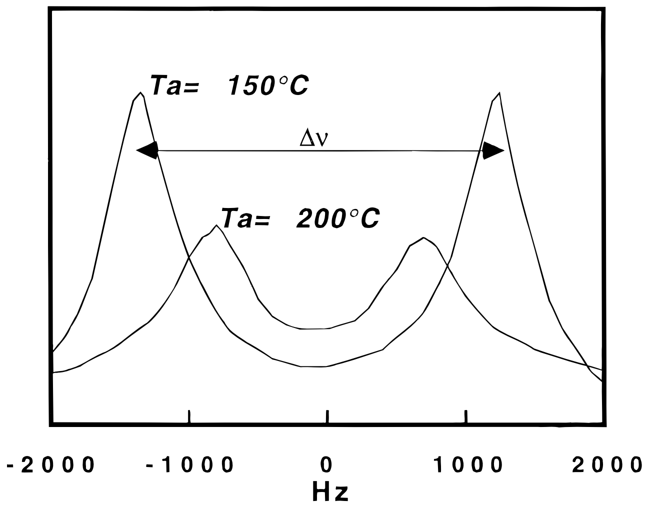

Figure 2. Typical NMR quadrupolar spectra observed on relaxed dry fibers and subsequently swollen at equilibrium in a solution of heavy water and 20% formic acid. The fibers relaxed at $T = 150$ °C (1) and $T = 200$ °C present different splittings $\Delta\nu$ and therefore different amorphous chain orientations.

It is important to remark that during this relaxation process, there is no conspicuous change in the crystallinity between 20 and 190 °C (Figure 1b). However, when the fibers are swollen at equilibrium in a heavy water−formic acid (20%) solution, little change in dimension along the fiber axis is measured.[19,20] Swelling is anisotropic, as noted by various authors, even if the small shrinkage observed along the fiber direction during swelling is negligible compared to the former thermal shrinkage (of the dry fiber before swelling).

As reported by Baldrian,[21] the profile of the WAXS reflexions (200) and (002, 202) does not change during swelling, which indicates that the characteristic dimensions and the total amount of crystallites does not change during the swelling. This demonstrates that D_2O−formic acid (20%) solution does not significantly change the structure of the material or the draw ratio of the amorphous chains. Finally, at room temperature and at the formic acid concentration we used, no changes in dimension, WAXS reflection, or NMR spectra were measured after 1 month of aging, thereby proving that no appreciable hydrolysis of the PA chains occurs.

Figure 2 presents the ^2H NMR spectra of PA6 fibers swollen with acidic deuterated aqueous solutions. The dry fibers were annealed respectively at 150 and 200 °C before swelling. Each spectra is a doublet with two lines separated by the quadrupolar splitting, $\Delta\nu$. Such figures are characteristic of solvent molecules probing an anisotropic amorphous polymer above T_g. The splitting, $\Delta\nu$, is rather large compared to the values measured in poly(ethyleneoxide) polyamide-6 block copolymers of similar draw ratios ($\Delta\nu \sim 100$ Hz).[14] If such a large value ($\Delta\nu = 1500$ Hz) is measured for the fibers annealed at 200 °C, this indicates that the complete relaxation of the fibers cannot be obtained, except by melting the material.

The swelling ratio is around 20% for the different materials, and in this range, deuterated species can be considered as probing the orientation of the amorphous

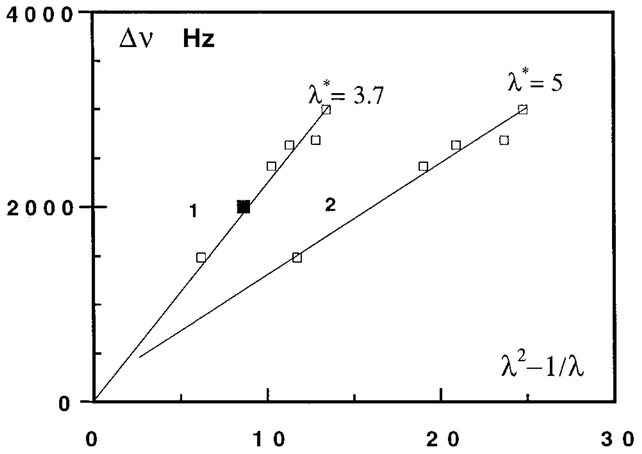

Figure 3. Variation of the quadrupolar splitting $\Delta\nu$ as function of the elasticity term $\lambda^2 - 1/\lambda$. The local draw ratio after partial shinkage is dependent on the true draw ratio of the initial fiber λ^* via relation 3. If one assumes that during fiber processing the deformation is affine $\lambda^* = 5$, then the line 2, $\Delta\nu = k(\lambda^2 - 1/\lambda)$, does not pass by the calibration point (plain symbol PA6 cold drawn at $\lambda = 3$). The best linear fit of all the points (line 1) gives the true draw ratio $\lambda^* = 3.7$. The slope k obtained is the same as that for PEBA in similar conditions.[14]

polymeric chains.[9−11] Because of the chemical exchange, the solution to be considered is a mixture of D_2O, HOD, and HCOOD with the $\cdots N-D$ coming from the exchanged amide group of the polymer in this acid solution. However, the spectra were deconvoluted and each peak fits a perfect Lorentzian shape, this proving that the exchange time between the different deuterated species is fast with regard to the inverse of the quadrupolar frequency ($\nu_q \sim 10^5\ s^{-1}$). Then, the solution can be considered as a pure averaged solvent for fixed temperatures and concentrations of the experiments. The interest in this solution (heavy water−formic acid) is its low cost and its low glass temperature (high mobility range for NMR studies).

Figure 1b reports the variation of $\Delta\nu$ with the annealing temperature of the dry fiber. As expected, $\Delta\nu$ decreases when the shrinkage increases, that is to say, when the amorphous chains become less oriented. Figure 3 presents the quadrupolar splitting as a function of the total extension factor $\lambda^2 - 1/\lambda$. The true draw ratio λ of the relaxed fiber is related to the true draw ratio of the original (nonannealed) fiber, λ^*, through the following relation:

$$\lambda = (1 - \mathrm{Sh})\lambda^* \qquad (3)$$

λ^* is determined by comparing the $\Delta\nu$ values of the relaxed fibers with the bulk PA6 materials drawn at ambient temperature (70 deg below T_g) and swollen with the same conditions. Yielding by cold-working of bulk PA produces a natural draw ratio of $\lambda = 3$ and does not involve a flow of the chains but only a deformation which is frozen. This material is used as a calibration sample. Comparing the fibers and the bulk calibration PA6, the best fit is obtained for $\lambda^* = 3.7$. Then, the PA6 fibers drawn at $\lambda = 5$ at high temperature have in fact a true draw ratio of 3.7.

It is of great interest to note that when the true draw ratio is used in relation to 2bis, the slopes $\Delta\nu/(\lambda^2 - 1/\lambda)$ for PA6 and PEBA block copolymers[14] are of the same order of magnitude (200 Hz).

In conclusion, quadrupolar NMR is a tremendous method to determine the local chain orientation of unknown PA6 fibers. As reported in semicrystalline elastomer polyamide−polyether, drawing at high temperatures is not affine. In a further publication, we will discuss in detail the mobility of water in such hydrophilic polymers.

References and Notes

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MA960436S