Correlation between Local Mobility and Mechanical Properties of High-Speed Melt-Spun Nylon-6 Fibers

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ABSTRACT: This article establishes the processing–microstructure–motion–property relationship of high-speed melt-spun nylon-6 fibers. From solid-state $^1$H NMR relaxation studies, all nylon-6 fibers spun at 4500–6100 m/min showed three-component exponential decay with the time constants $T_{1r,1}$, $T_{1r,II}$, and $T_{1r,III}$, indicating that there existed three different motional phases. These phases were assigned to immobile crystalline, intermediate rigid amorphous, and mobile amorphous regions. The determination of the correlation time ($\tau_c$) of the respective phases provided information about the local molecular mobility of each phase with respect to the spinning speed. As the spinning speed increased, $\tau_c$ of the crystalline region increased (4500–5200 m/min) and then reached a plateau. However, $\tau_c$ for the rigid amorphous region increased from 5200 m/min onward, indicating that the rigid amorphous chains were more oriented and constrained in the spinning speed range of 5500–6100 m/min. The drastic increase of the maximum thermal stress for all fibers from 5500 to 6100 m/min was coincident with the $\tau_c$ characteristics of the rigid amorphous region. The significant increase in tenacity and Young’s modulus and the large decrease in elongation at break at 5500–6100 m/min were also in good agreement with the local molecular motion of the intermediate rigid amorphous phase in the nylon-6 fibers. © 2001 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 39: 993–1000, 2001

Keywords: high-speed melt-spun nylon-6 fiber; solid-state pulsed wide-line $^1$H NMR spectroscopy; spin–lattice relaxation time in the rotating frame ($T_{1r}$); correlation time ($\tau_c$); local molecular mobility; thermal stress; tensile property

INTRODUCTION

The macromolecular orientation and mechanical properties of synthetic fibers are highly dependent on the spinning conditions and processing history of the given polymer. High-speed melt spinning for nylon-6 fibers imparts stress and temperature conditions high enough to induce orientation and crystallization on the spin line, thereby requiring no additional drawing process. Thus, high-speed melt spinning results in improved productivity, raising both scientific interest and technical importance. The desire to increase spinning speed relates directly not only to the productivity but also to the physical and me-
channical properties of nylon-6 fibers. It is necessary to understand the relationship between the spinning speed and properties on the basis of details of the microscopic structure and molecular motion.

Many reports on the microstructure of nylon-6 fibers produced at variable spinning speeds describe a two-phase model: crystalline and amorphous phases. Recent studies, however, have revealed that there exist three different phases in nylon-6 fibers: crystalline, oriented amorphous, and amorphous regions. Murthy et al. analyzed structural developments of nylon-6 fibers that occurred during processing by employing X-ray diffraction and concluded that the microstructure consisted of crystalline, anisotropic amorphous, and isotropic amorphous components. Kwak et al. revealed that high-speed melt-spun nylon-6 fibers were composed of three different phases—immobile (crystalline), intermediate (rigid amorphous), and mobile (pure amorphous)—on the basis of relaxation and motion characterized by solid-state NMR spectroscopy. In this article, we use solid-state NMR spectroscopy to confirm the presence of three microphases in nylon-6 fibers produced at variable spinning speeds and determine the local molecular mobility of the respective phases.

The pulsed wide-line $^1$H NMR relaxation technique provides a convenient way to get information about the average local motion in an entire fiber system. Spin–lattice relaxation times in the rotating frame ($T_1^p$’s) are most sensitive to motions in the range of tens of kilohertz to a few hundred kilohertz. $T_1^p$’s obtained at various temperatures must be analyzed by Bloembergen–Purcell–Pound (BPP)/Kubo–Tomita (KT) theory to obtain the correlation time ($\tau_c$), which is a relative measure of local motion. With this study, we aimed to correlate $\tau_c$ with physical and mechanical properties such as thermal stress, tenacity, elongation at break, and Young’s modulus of the high-speed melt-spun nylon-6 fibers. The correlation of properties dependent on spinning speeds with molecular motion provides information about the processing–structure–motion–property relationships of high-speed melt-spun nylon-6 fibers.

THEORETICAL BACKGROUND

Spin–lattice relaxation measurements have been widely used to characterize chain dynamics in polymer solutions, and the same general approach can be extended to solid-state polymers. In the pure spin–lattice measurement, that is, in the laboratory frame, the frequencies observed are related to the Larmor frequencies of the nuclei involved. However, in $T_1^p$ measurements, the observed frequency is given by the magnitude of the spin-lock field, that is, in the frequency range of tens of kilohertz. The $T_1^p$ relaxation is important for solid polymers.

$^1$H $T_1^p$, as a function of temperature can be directly measured with the pulse sequence $^1$H spin–lock–$\tau$ pulse. When a $\pi/2$ pulse ($B_1$) is applied, the phase of the $B_1$ field is shifted by 90° so that it lies along the $y$ axis, and the protons are spin-locked along that direction. For the duration of the spin-locking pulse, protons are forced to precess about the $y$ axis, their rotating frame, with the frequency $\omega_1 = \gamma H_{1B}$. During spin locking, magnetization is brought back to the effective $B_1$ field direction ($y$ axis) and decays exponentially with $T_1^p$.

$$M(\tau) = M_0 \exp(-\pi T_1^p)$$ (1)

where $M_0$ is the intensity of the signal at $\tau \geq 5T_1^p$. Exponentially, $T_1^p$ is determined by the observation of the free induction decay with various spin-locking times ($\tau$). From the $T_1^p$ values, however, molecular mobility cannot be directly determined, and it is common to convert $T_1^p$’s to $\tau_c$’s. To relate $T_1^p$’s to molecular mobility, it is necessary to determine $\tau_c$, for which quantitative analyses by BPP/KT theory provide relationships between the relaxation rate, internuclear distance, resonance frequency, and spectral density function of molecular motion (i.e., a measure of the relative amount of motion). For protons, the principal mechanism of relaxation is through time-dependent dipolar interaction, and the relaxation rates are given by

$$\frac{1}{T_1^p} = \frac{3}{2} \gamma^2 \hbar^2 I(I + 1) \times \left[ \frac{1}{4} J(2\omega_1) + \frac{5}{2} J(\omega_b) + \frac{1}{4} J(2\omega_b) \right]$$ (2)

where $\gamma$ is the proton magnetogyric ratio, $\hbar$ is Planck’s constant divided by $2\pi$, $r$ is the distance between coupled spins, $I$ is the spin quantum number $(1/2)$, $J(\omega)$ is the spectral density function
at a particular frequency, $\omega_1$ is the spin-lock field frequency, and $\omega_0$ is the Larmor frequency, respectively. Because $J(\omega)$ is given by

$$J(2\omega_1) = \frac{24}{15r^6} \left( \frac{\tau_c}{(1 + 4\omega_1^2\tau_c^2)} \right)$$

$$J(\omega_0) = \frac{4}{15r^6} \left( \frac{\tau_c}{(1 + \omega_0^2\tau_c^2)} \right)$$

$$J(2\omega_0) = \frac{16}{15r^6} \left( \frac{\tau_c}{(1 + 4\omega_0^2\tau_c^2)} \right)$$

the relation between relaxation and molecular motion is established as

$$\frac{1}{T_{1p}} = \frac{3}{10r^6} \gamma^4 h^2 \left[ \frac{5/2\tau_c}{(1 + \omega_0^2\tau_c^2)} + \frac{\tau_c}{(1 + 4\omega_0^2\tau_c^2)} + \frac{3/2\tau_c}{(1 + 4\omega_1^2\tau_c^2)} \right]$$

(3)

With this relation, $\tau_c$ values can be extracted by nonlinear curve fitting of $T_{1p}$ data at the corresponding temperatures. $\tau_c$ is defined as the average time required for motional events and commonly expresses the local molecular mobility. According to BPP/KT theory, $\tau_c$ decreases as the motion gets faster, and so the mobility increases.

**EXPERIMENTAL**

**Preparation of High-Speed Melt-Spun Nylon-6 Fibers**

Nylon-6 fibers used in this study were supplied by Hyosung Co., Ltd. (Korea). The relative viscosity of the nylon-6 was 2.45, the amine end-group content was 0.052 mol/g, and the monomer content was 8.24 wt %. The polymer chips were dried in a vacuum oven at a temperature of 110 °C for 4 h, which gave a moisture content of less than 400 ppm. Fiber samples were prepared by melt spinning at spinning speeds of 4500–6100 m/min. The extrusion temperature of the polymer was 265 °C, the spinneret had 24 holes (whose diameters were 0.25 mm and whose lengths were 0.5 mm), the fibers were cooled by crossflow air at 18 °C, the fineness of the fibers was 70 den, and the filament contents were 24. The filament diameter was 19.29 μm at every spinning speed. The conditions for high-speed melt spinning are summarized in Table I.

### Variable-Temperature, Solid-State Pulsed Wide-Line $^1$H NMR Spectroscopy

Measurements of $^1$H $T_{1p}$, 140 to 360 K for the nylon-6 fibers were performed with a Bruker MSL-200 spectrometer (200.13 MHz for $^1$H). A $^1$H spin-lock–delay–τ-pulse sequence was employed with a $^1$H 90° pulse width of 4.5 μs and a repetition time of about 5$T_{1p}$ for the net magnetization to be completely relaxed. Typically, 35–40 different τ values were used, and the free induction decay signals accumulated over several hundred times were Fourier-transformed and then integrated to obtain the decay curve. The various temperatures were established by the regulation of the heat current in a steady dry-air flow over room temperature and in a steady cold-nitrogen-gas flow from the dewar below room temperature.

### Thermal Stress Analysis

Thermal stress measurements were performed with a Kanebo thermal stress tester. A loop of filaments was suspended by hooks under a constant pretension. The heating rate was 2.5 °C/s, and a shrinkage force generated on heating was recorded as a function of temperature from 30 to 220 °C.

### Tensile Test

The stress–strain curves were measured with an Instron tensile tester at room temperature. The conditions of high-speed melt spinning are summarized in Table I.

<table>
<thead>
<tr>
<th>Spinning Speed, $v_s$ (m/min)</th>
<th>4500</th>
<th>4900</th>
<th>5200</th>
<th>5500</th>
<th>5800</th>
<th>6100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion rate (g/min)</td>
<td>32.5</td>
<td>35.4</td>
<td>37.6</td>
<td>39.8</td>
<td>41.9</td>
<td>44.1</td>
</tr>
<tr>
<td>Fluid velocity, $v_d$ (m/min)</td>
<td>27.6</td>
<td>30.1</td>
<td>32</td>
<td>33.8</td>
<td>35.8</td>
<td>37.4</td>
</tr>
<tr>
<td>Melt draw ratio, $v_s/v_d$</td>
<td>163</td>
<td>163</td>
<td>163</td>
<td>163</td>
<td>163</td>
<td>163</td>
</tr>
</tbody>
</table>

**Table I. Conditions of High-Speed Melt Spinning**
gauge length was set to 20 cm, and the elongation rate was 20 cm/min.

RESULTS AND DISCUSSION

Figure 1 shows representative room-temperature $^1$H spin-lock relaxation decays for the samples prepared at various spinning speeds. All decays were fit to within 1% of the total signal by three exponential equations with $T_{1r}$'s differing by about an order of magnitude each, which correspond to the three different motional regions (i.e., I, II, and III):

$$M(t) = M_{0,1}e^{-\frac{t}{T_{1r,1}}} + M_{0,II}e^{-\frac{t}{T_{1r,II}}} + M_{0,III}e^{-\frac{t}{T_{1r,III}}} \quad (4)$$

Each magnetization intensity was also fit to double exponentials according to the conventional two-phase model. However, the standard errors of estimate for fitting to triple exponentials were much lower than those for double exponentials, and it was concluded that three phases were generated in high-spinning-speed melt-spun nylon-6 fibers. The three possible phases are assumed to be immobile (crystalline), intermediate (rigid amorphous), and mobile (pure amorphous) regions.

Figure 2 shows the temperature dependence of $T_{1r}$'s from 140 to 360 K for each phase of nylon-6 fibers spun at 4500 m/min. $T_{1r}$ plots versus reciprocal temperatures exhibit a minimum, which indicates the occurrence of the most efficient spin–lattice relaxation. $T_{1r}$'s of both II and III components tend toward equality at the observed minimum at about 240 K, and the minimum of
the I component was at about 260 K. The right side of the minimum is the slow-motional region, whereas the left the fast-motional region. With the BPP/KT relationships between $T_{I_p}$ and $\tau_c$ (eq 2), the quantitative determination of local molecular mobility and the assignment of each phase were performed. The $\tau_c$ values versus the inverse temperature for the spinning speed of 4500 m/min are shown in Figure 3. The $\tau_c$'s of each component decrease in the sequence I, II, and III; other samples in the spinning speed range of 5200–6100 m/min showed the same trend, although those data are not shown here.

In Figure 4, $\tau_c$'s of each region as a function of the spinning speed at room temperature are shown. As the spinning speed increased up to 5500 m/min, $\tau_c$'s of the crystalline region increased significantly, whereas those of the rigid amorphous region changed slightly. At a spinning speed of 5500 m/min, $\tau_c$ of the rigid amorphous region started increasing. These results indicate that crystallization in the early stage (4500–5200 m/min) is accompanied by molecular orientation and that the molecular packing induces the chains of the crystalline region to be constrained.

Figure 2. Temperature dependence of $T_{I_p}$ for (a) the I component (●), (b) the II component (□), and (c) the III component (▲).

Figure 3. $\tau_c$ versus inverse temperature for nylon-6 fiber with a spinning speed of 4500 m/min.

Figure 4. $\tau_c$ versus spinning speed of nylon-6 fibers.
However, in the later stage, 5500–6100 m/min, effective crystallization was induced in rigid amorphous regions rather than in crystalline regions. On the whole, $\tau_c$ of the mobile amorphous region was little affected by an increase in spinning speed.

Figure 5 shows thermal stress curves at various spinning speeds. For amorphous polymers, thermal stress has a maximum in the neighborhood of the glass-transition temperature due to the contraction of molecular chains in the amorphous region, whereas for well-oriented crystalline polymers, the maximum thermal stress comes out in the vicinity of the melting temperature caused by the contraction of oriented molecular chains in the crystalline region. For semicrystalline polymers such as nylon-6 fibers, however, mixed behavior of these two phenomena is seen. As shown in Figure 5, all the nylon-6 fibers exhibited a maximum in the region between glass-transition and melting temperatures.

Figure 6 shows the maximum thermal stresses and the maximum-thermal-stress temperatures as a function of spinning speed. The maximum-thermal-stress temperature of nylon-6 fibers had values between the glass-transition and melting temperatures, indicating that the maximum thermal stress is characteristic of the oriented amorphous region, that is, the rigid amorphous region. As the spinning speed increased, the maximum thermal stress increased slightly in the beginning but changed abruptly in the region 5500–6100 m/min. These results indicate that in this range of spinning speed, the increase of spinning speed induces the chains of the rigid amorphous region to be constrained rather than those of crystalline region, thereby causing a drastic increase in the maximum thermal stress. These results coincide well with the decrease of local molecular motion of the rigid amorphous region.

Figure 7 shows tenacity, elongation at break, and Young's modulus as a function of spinning speed. Tenacity and Young's modulus increased monotonously, whereas elongation at break decreased as spinning speed increased. Some previous studies\textsuperscript{7,18} attempted to explain the increase of tenacity and modulus with birefringence and crystallinity in conjunction with $\alpha$ and $\gamma$ crystals. In our previous study,\textsuperscript{10} the birefringence of the nylon-6 fibers produced at spinning speeds ranging from 4500 to 6100 m/min was measured with a polarizing microscope with a Berek compensa-
The crystallinity was determined by density measurement and NMR relaxation decay behavior. The birefringence and crystallinity of the nylon-6 fibers in our case reached a plateau in the spinning speed range of 5500–6100 m/min, which cannot successfully explain the increase of tenacity and modulus in that region. However, this increase can be explained on the basis of the molecular motion of the respective phases in the nylon-6 fibers. That is, in the region of 5500–6100 m/min, where the birefringence and crystallinity reach a limiting value, the large decrease in the molecular mobility, indicated by the large increase in $\tau_c$, of the rigid amorphous phase indicates a higher degree of molecular packing in this phase, which results in the higher tenacity and modulus value. Recognizing that the degree of elongation of the fibers is mainly ascribed to the amorphous region, we also know that the larger decrease of the elongation at break in the fibers spun at 5500–6100 m/min is related to the larger increase of $\tau_c$.

**CONCLUSIONS**

The correlation of the local molecular mobility and mechanical properties for high-speed melt-spun nylon-6 fibers, in conjunction with spinning speeds, was investigated. The local molecular mobility of the fibers was characterized by solid-state pulsed wide-line $^1$H NMR spectroscopy. The $T_{1p}$ results confirmed that there existed three different motional phases in all samples: the immobile crystalline, the intermediate rigid amorphous, and the mobile amorphous. From the variable-temperature $T_{1p}$ measurements, $\tau_c$ as a measure of molecular motion was calculated for the respective phase by BPP/KT theory. As the spinning speed increased, $\tau_c$ of the immobile crystalline region increased; thus, the molecular mobility decreased at spinning speeds between 4500 and 5200 m/min and then reached a plateau. In contrast, the molecular motion of the intermediate rigid amorphous region began to decrease at spinning speeds higher than 5200 m/min. By correlating the molecular motion with the physical/mechanical properties of the nylon-6 fibers, we could explain from the perspective of molecular motion the realization of the thermal stress, tenacity, elongation at break, and Young’s modulus, particularly at higher spinning speeds.

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**REFERENCES AND NOTES**