Application of High-Tension Annealing to Nylon 46 Fibers

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ABSTRACT: To improve the tensile properties of nylon 46 fibers, high-tension annealing (HTA) was applied to nylon 46 fibers previously treated with high-temperature zone-drawing. Fibers produced by the high-temperature zone-drawing treatment had a tensile modulus of 7.2 GPa and tensile strength of 1.0 GPa. Two HTA treatments were carried out; the first (HTA1) treatment at 100°C under an applied tension of 538.2 MPa, and the second (HTA2) treatment at 150°C under 568.0 MPa. The fibers obtained finally had a tensile modulus of 8.4 GPa, tensile strength of 1.2 GPa and a storage modulus of 11.2 GPa at 25°C.

KEY WORDS High-Temperature Zone-Drawing / High-Tension Annealing / Nylon 46 Fiber / High-Modulus /

The microstructure and mechanical properties of nylon 6 and nylon 66 fibers have been extensively investigated. In contrast, fewer studies^{1–7} have been made on the mechanical behavior of nylon 46 fiber, particularly improvements of mechanical properties.

To impart superior mechanical properties to nylon fibers, many techniques have been proposed.^{8–14} High-temperature zone-drawing^{15–18} (HT-ZD) also leads to high-modulus and high-strength fibers. In our previous paper,¹⁹ the HT-ZD method applied to nylon 46 fibers was introduced and proved itself capable of improving mechanical properties. The resulting HT-ZD nylon 46 fiber had a tensile modulus of 7.2 GPa and a tensile strength of 1.0 GPa. The modulus obtained is almost two times that of the commercial nylon 46 fiber.²⁰ HT-ZD treatment was found to be effective in producing high-modulus nylon 46 fibers. However, the modulus of the HT-ZD fiber corresponds only to 15% of the theoretical modulus²¹ ($E_1 = 48$ GPa at room temperature).

HT-ZD can easily highly orient the crystallites in the drawing direction, but is not enough to arrange the amorphous chains in drawing direction. To further improve the mechanical properties of fibers, it is necessary to arrange amorphous chains that play an important role in the determination of the mechanical properties in the drawing direction. However, it is more difficult to develop the orientation of the amorphous chains in an oriented fiber because the segmental mobility of the amorphous chains is severely constrained by crystallites and molecular entanglements that act as physical crosslinks and hydrogen bonds between the chains.²²

High-tension annealing (HTA) was proposed as a way to further improve the mechanical properties of the fibers highly oriented by zone-drawing and/or zone-annealing.^{23–26} HTA was carried out near an a relaxation temperature under extremely high tension to arrange the amorphous chains in the drawing direction. HTA has been so far applied to the fibers such as poly(ethylene terephthalate) (PET),²³ poly(vinyl alcohol) (PVA),²⁴ nylon 6,²⁵ and nylon 66²⁶ fibers, to improve mechanical properties. We reported that amorphous orientation factors of those fibers were found to reach high values

by HTA and mechanical properties were further improved. For example, the storage modulus at 25°C for each of the HTA PET fiber,²³ HTA PVA fiber,²⁴ HTA nylon 6,²⁵ and HTA nylon 66²⁶—all produced using the HTA treatments—was 30, 78, 21.1, and 21.7 GPa, respectively.

The objective of the present study is to further improve the mechanical properties of nylon 46 fibers using HTA. Microstructural changes occurring during the process have been monitored by wide-angle X-ray diffraction, birefringence, differential scanning calorimetry, shrinkage measurements, and specific gravity.

EXPERIMENTAL

Material

The original material used in the present study was as-spun nylon 46 monofilament supplied by UNITIKA Ltd. The original fiber had a diameter of about 0.327 mm and a degree of crystallinity of 34.8% and was isotropic and opaque because of a small amount of TiO₂.

High-Temperature Zone-Drawing and High-Tension Annealing Treatments

The monofilament of the original fiber was initially treated three times with HT-ZD before HTA. HT-ZD was carried out using the apparatus described previously.¹⁹

A schematic diagram of the apparatus used for HTA is given in Figure 1. It consists of a load cell connected to a recorder, electric furnace of a 20 mm long, and Linead motor (Oriental Motor Co., Ltd.) which consists

Figure 1. Apparatus for the high-tension annealing.

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of a rack-and-pinion unit and a speed controller. The rack-and-pinion unit converts rotational motion of the motor into linear motion. One end of a fiber was fixed at a jaw equipped with the load cell, and the other was run through a heater and fixed at a jaw equipped with the edge of the rack, and the fiber was drawn at constant speed. When the temperature of the electric furnace reached the desired treating temperature, the fiber was drawn at a speed of 10 mm min^{-1} . When the tension applied to the fiber reached a desired value which is in the range of 70 to 90% of the strength at the break (σ_b), the stretching was stopped, and then the fiber was kept at constant length for a given time. This desired value is called the initial applied tension and designated as σ_0 . σ_b was previously estimated from the stress-strain curve recorded at the same temperature as the desired treatment temperature.

Measurement

The draw ratio was determined in the usual way by measuring the displacement of ink marks placed 10 mm apart on the fiber before drawing. The density of the fiber was measured at 23°C by flotation using a mixture of toluene and carbon tetrachloride.

Differential scanning calorimetry (DSC) measurements were carried out using a Rigaku DSC 8230C calorimeter to determine the degree of crystallinity (X_c) and melting temperature of the fiber. DSC scanning was performed within the temperature range from 25 to 300°C , using a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen gas atmosphere. The degree of crystallinity (X_c) was calculated by the following equation:

$$X_c = (\Delta H_f / \Delta H_0) \times 100$$

where ΔH_f is the heat of fusion for sample, and ΔH_0 is the heat of fusion (ΔH_0) for completely crystalline nylon 46, $\Delta H_0 = 210 \text{ J g}^{-1}$.²⁷

Thermal shrinkage was measured with a Rigaku SS-TMA at a heating rate of 5°C min^{-1} . Samples with a 15 mm gauge length between two jaws were held at a tension of 5 g cm^{-2} , the minimum tension to stretch a fiber tightly.

The orientation factors of crystallites (f_c) were evaluated using the Wilchinsky²⁸ method from wide-angle X-ray diffraction patterns. f_c was estimated using a (100) plane.

Apparent crystallite size was estimated from the broadening of the diffraction peaks by applying Scherrer's equation:

$$D_{hkl} = 0.9\lambda / \beta \cos \theta_{hkl}$$

where D_{hkl} is crystallite width normal to (hkl) plane, λ is the X-ray wavelength ($1.542 \text{ \AA}$), θ_{hkl} is the Bragg angle of the (hkl) plane, and β is the observed half-width of the peaks corrected for a instrumental broadening.

Tensile properties were determined with a Tensilon tensile testing machine (Orientec Co., Ltd.). Tensile modulus, tensile strength, and elongation at the break were determined from the stress-strain curves obtained at 25°C , RH 65%. The measurements were carried out using a gauge length of 5.0 cm and a crosshead speed of 0.5 cm min^{-1} . The dynamic viscoelastic properties were measured at 3.5, 11, 35, and 110 Hz with a dynamic

Table I. Optimum conditions for HT-ZD treatments

Treatment	Treating temperature	Applied tension	Heater speed
	$^\circ\text{C}$	MPa	mm min^{-1}
HT-ZD1	200	27.0	30
HT-ZD2	225	117	30
HT-ZD3	230	245	30

Figure 2. Changes in the tensile modulus of fibers at various applied tensions with treating temperature: (○), $\sigma_0 = 0.7\sigma_b$; (●), $\sigma_0 = 0.8\sigma_b$; (□), $\sigma_0 = 0.9\sigma_b$.

viscoelastometer VIBRON DDV-II (Orientec Co., Ltd.). Measurements were carried out over a temperature range of 25 to about 250°C at an interval of 5°C , and the average heating rate was 2°C min^{-1} . A fiber was held at 20 mm gauge length between two jaws.

Activation energy (ΔH_a) was estimated using the following equation:

$$\frac{f_1}{f_2} = \frac{\Delta H_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where f is frequency, T is peak temperature of α dispersion in temperature dependence of loss modulus (E''), and R is the gas constant.

RESULTS AND DISCUSSION

Optimum Conditions of High-Tension Annealing

The original nylon 46 fiber was initially drawn with HT-ZD before HTA. HT-ZD was carried out in three steps under the same optimum conditions as in our previous paper,¹⁹ given in Table I. These treatments produced a fiber whose crystallinity was 55.6% and a tensile modulus, 7.2 GPa.

HTA was carried out in two steps. The optimum conditions for the first step (HTA1) were determined from the relation between treating temperature (T_{HTA}) and tensile modulus of the fibers treated under different initial applied tensions (σ_0)—70% ($=0.7\sigma_b$), 80% ($=0.8\sigma_b$), and 90% ($=0.9\sigma_b$) of strength at the break (σ_b)—as shown in Figure 2. The condition for giving the maximum modulus was chosen as an optimum one for HTA1. σ_b was previously estimated from the stress-strain curve recorded at the same temperature as the given T_{HTA} . When $T_{\text{HTA}} = 110^\circ\text{C}$ and $\sigma_0 = 0.8\sigma_b$ ($=538 \text{ MPa}$), the tensile modulus shows the maximum value.

The optimum conditions for the second step (HTA2) were determined in the same manner as above. The optimum conditions for each HTA treatment are given in Table II. The optimum treating time for each step was 30 min. Microstructure and mechanical properties of the fiber obtained under the respective optimum conditions are described below.

Microstructures of HT-ZD and HTA Fibers

Table III shows the draw ratio (λ), density (d), degree of crystallinity (X_c), crystallite orientation factor (f_c), and apparent crystallite size normal to the (100) and (010) planes (D_{100} and D_{010}) for each fiber. X_c increased from 34.8% for the original fiber to 55.8% for the HT-ZD3 fiber. Although T_{HTA} in HTA2 was 115°C lower than a crystallization temperature (T_c) of 265°C for nylon 46, X_c increased up to 58.8% in the course of HTA. Such increase shows that the highly oriented amorphous chains easily crystallized even at temperatures much lower than the T_c . Crystallization in an oriented material is very much faster than that in its isotropic one.²⁹⁻³¹ X_c of the HTA2 fiber is larger than that of the HTA nylon 6 fiber reported in the previous paper.²⁵ The difference in X_c between nylon 46 and nylon 6 originated from a highly symmetrical molecular structure and fairly high amide groups content per unit length of chain for nylon 46 compared with those for the nylon 6.³² Although X_c increased during treatment, crystallite sizes (D_{100} and D_{010}) held constant at about 28 Å throughout HT-ZD and subsequent HTA treatments. It can be, therefore, considered that the increase in the X_c shows the evolution of crystallization along the drawing direction although there are no data about crystallite size perpendicular to the c -axis, that is, drawing direction. In fact, Peszkin *et al.* reported that further development of crystallization occurred along the fiber axis of the already-oriented crystals.³³ f_c increased dramatically up to 0.949 during the HT-ZD1 treatment and slightly during subsequent treatment. In HT-ZD, the crystallite may be grown direction because the zone-heater moves

in the fiber direction. Murthy *et al.*³⁴ reported that the crystalline orientation increased rapidly at small draw ratio (<3) and reached a plateau at higher draw ratio.

Figure 3 shows the DSC curves for the original, HT-ZD, and HTA fibers. The original fiber has a double melting peak (270°C and 283°C). The peak at 270°C can be attributed to melting of crystals in the original fiber, and that at 283°C to melting of the recrystallized crystals with a higher perfection during DSC scanning.^{35,36} The HT-ZD1 fiber had an endotherm with a peak temperature of 277°C and a shoulder on the higher temperature side of the peak. The shoulder is observed at the same temperature as that at the higher melting peak of the original fiber. However, in the DSC curves for the HT-ZD2, HT-ZD3, and HTA fibers, no shoulders are observed other than a sharp single peak. The melting peak shifts toward a higher temperature and becomes sharper with processing. The melting peak of the HTA2 fiber is located at 285°C, which is 2°C higher than the high melting peak of the original fiber. The shift of the melting peak toward higher temperatures implies an increase in crystal size.³⁷

Figure 4 shows the TMA curves for the original, HT-ZD1, HT-ZD3, and HTA2 fibers. The original fiber expands as temperature rises, whereas the HT-ZD and

Figure 3. DSC curves for the original, HT-ZD, and HTA fibers.

Table II. Optimum conditions for HTA treatments

Treatment	Treating temperature	Applied tension	Treating time
	°C	MPa	min
HTA1	110	538 (=0.80 σ_b)	30
HTA2	150	568 (=0.80 σ_b)	30

Table III. Draw ratio (λ), density (d), crystallinity (X_c), crystallite orientation factor (f_c), and crystallite sizes (D_{hkl}) of (100) and (010) planes for the original, HT-ZD and HTA fibers

Fiber	λ	d	X_c	f_c	D_{100}	D_{010}
		g cm ⁻³	%		Å	
Original	—	1.173	34.8	—	—	—
HT-ZD1	3.9	1.176	44.2	0.949	28.8	26.1
HT-ZD2	4.4	1.176	48.8	0.951	28.9	28.9
HT-ZD3	5.6	1.178	55.6	0.961	28.8	29.9
HTA1	5.6	1.179	58.6	0.961	27.9	28.9
HTA2	5.7	1.179	58.8	0.959	26.9	27.9

Figure 4. Temperature dependence of shrinkage for the original, HT-ZD, and HTA fibers: (---), original; (····), HT-ZD1; (— · — ·), HT-ZD3; (—), HTA2.

Table IV. Thermal shrinkage (St) at 200°C for the original, HT-ZD, and HTA fibers

Fiber	St/%
Original	-1.8
HT-ZD1	8.5
HT-ZD2	7.2
HT-ZD3	6.9
HTA1	6.9
HTA2	6.6

HTA fibers shrink. Thermal shrinkage during heating is associated with the chain folding in the amorphous regions.³⁸ In spite of the temperature range below a glass transition temperature, the treated fibers shrink with increasing temperature. This indicates that there occurred small rubber-elastic contraction of tie molecules above the subglass transition temperature (β relaxation at -73°C). In β relaxation, the non-hydrogen bonded amide groups begin to move, but this is not sufficient to overwhelm the expansion of the adjacent amorphous components.³⁹ The thermal shrinkage at 200°C , as shown in Table IV, decreases from 8.5% for the HT-ZD1 fiber to 6.6% for the HTA2 fiber. This implies that amorphous chains are locked into crystallites and no refolding may occur. In other words, the decrease in shrinkage with processing is probably attributed to increase in the crosslink density of the network built-up by the crystallites.

Mechanical Properties of HT-ZD and HTA Fibers

Table V shows the tensile properties for the original, HT-ZD and HTA fibers obtained under optimum conditions. Tensile modulus and strength increase stepwise with processing. The HTA2 fiber finally obtained has a tensile modulus of 8.4 GPa and a tensile strength of 1.2 GPa. The tensile modulus of the HTA2 fiber is about twice that of the commercial nylon 46 fibers²⁰ (3.9 GPa). However, HTA for nylon 46 fibers was less effective in improving the mechanical properties compared to PET²³ and nylon 6²⁴ fibers. It seems reasonable to suppose

Table V. Tensile properties for the original, HT-ZD, and HTA fibers

Fiber	Young's modulus	Strength at break	Elongation at break
	GPa	GPa	%
Original	1.2	—	—
HT-ZD1	5.6	0.7	24.8
HT-ZD2	6.5	0.9	21.7
HT-ZD3	7.2	1.0	10.3
HTA1	7.7	1.2	14.2
HTA2	8.4	1.2	12.7

Figure 5. Storage modulus (E') as a function of temperature at 110 Hz for the original, HT-ZD, and HTA fibers: (Δ), original; ($\blacktriangle$), HT-ZD1; ($\square$), HT-ZD2; ($\blacksquare$), HT-ZD3; ($\circ$), HTA1; ($\bullet$), HTA2.

that the amorphous chains are restricted by numerous hydrogen bonds because of fairly high amide group content and could not highly orient, and consequently, HTA for nylon 46 fibers was less effective in improving mechanical properties.

Figures 5 and 6 show the storage modulus (E') and $\tan \delta$ as functions of temperature at 110 Hz for the original, HT-ZD, and HTA fibers. E' increased stepwise with processing over a wide temperature range. In the HTA2 fiber finally obtained, maximum value at 25°C was 11.2 GPa, which is higher than E' (about 4.5 GPa at room temperature) reported by Kudo *et al.*⁶ E' of all the fibers decreased gradually with increasing temperature, and E' of the HTA2 fiber was 4.5 GPa even at 200°C . In the $\tan \delta$ -temperature curve (Figure 6), loss peaks are observed from 75 to 120°C . The peaks are called α relaxation peaks and originate with rupture of interchain hydrogen bonding due to increase of motion of chain segments in the amorphous regions.^{40,41} The α relaxation peak of the nylon 46 is located at a 10 – 20°C higher temperature than those of other nylons.⁴² The α relaxation peak shifts to a higher temperature, decreases in height, and becomes much broader with processing. HTA2 fiber has a peak value of 0.041 at 120°C . Changes in position and profile of the loss peak point out that

Figure 6. $\tan \delta$ as a function of temperature at 110 Hz for the original, HT-ZD, and HTA fibers: (Δ), original; ($\blacktriangle$), HT-ZD1; ($\square$), HT-ZD2; ($\blacksquare$), HT-ZD3; ($\circ$), HTA1; ($\bullet$), HTA2.

Figure 7. $\log f$ vs. $1/T_p$ plot for the α dispersion: (Δ), original; ($\blacktriangle$), HT-ZD1; ($\square$), HT-ZD2; ($\blacksquare$), HT-ZD3; ($\circ$), HTA1; ($\bullet$), HTA2.

the thermal mobility of amorphous chains is gradually restricted by the surrounding crystallites grown with processing. To estimate the degree of crystallite constraint on amorphous regions, activation energy for the α dispersion was calculated, using the Arrhenius equation, from plots of $\log f$ vs. the reciprocal of peak temperature ($1/T_p$), where T_p is the E'' peak temperature of the α relaxation at frequency f , as shown in Figure 7. Activation energy for each fiber is given in Table VI; the value of HTA2 fiber increased to $91.9 \text{ kcal mol}^{-1}$. Such increase proves that mobility of amorphous chains is restricted by the surrounding crystallites.

CONCLUSIONS

Our experimental data show that the high-tension annealing treatment is effective for improving the mechanical properties of nylon 46 fibers, and the results are as follows.

Table VI. Activation energy (ΔH) for the original, HT-ZD, and HTA fibers

Fiber	$\Delta H/\text{kcal mol}^{-1}$
Original	57.9
HT-ZD1	63.7
HT-ZD2	69.0
HT-ZD3	78.1
HTA1	84.9
HTA2	91.9

1. The degree of crystallinity increased to 55.8% by three HT-ZD treatments and then to 58.8% by HTA3.
2. The orientation factor of crystallites rose remarkably up to 0.949 with only HT-ZD1.
3. HTA3 fibers showed a tensile modulus of 8.4 GPa and storage modulus of 11.2 GPa at 25°C. The α peak in the $\tan \delta$ -temperature curve shifted to a higher temperature, reducing its magnitude with processing.

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