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Some Properties of Poly-(hexamethylene adipamide) in View of Terminal Group Balance

Masahiro Tomokiyo^{*1}, *Hitoshi Yamazaki*^{*1}, *Fumiaki Ise*^{*1},
Michiya Ohtsuka^{*1}, *Toshinori Koizumi*^{*2}, and *Kunihiko Okajima*^{*2}

^{*1}Fiber R & D section, Leona Plant, Leona Business Division, Asahi Chemical Industries Co. Ltd., 4-3623 Nagahama, Nobeoka, Miyazaki, Japan

^{*2}Fundamental Research Laboratory of Natural & Synthetic Polymers, Asahi Chemical Industries Co. Ltd., 11-7 Hacchonawate, Takatsuki, Osaka, 569 Japan

Abstract : An attempt was made to elucidate the effect of the terminal group on physical, rheological and thermal properties of poly-(hexamethylene adipamide) (nylon 66). For this purpose, the experiments on melt-flow, water adsorption and thermal behavior for nylon 66 chips having different molar fractions of amino terminal group f_N were carried out as well as structural analysis on the as-extruded yarns. It was found that an increase in f_N resulted in 1) the lowering of water absorption rate, 2) the increasing in activation energy for the melt flow for the nylon 66 chips, and 3) the increase in $\tan \delta_{max}$ and the decrease in T_{max} for α relaxation of the as-extruded yarns at 300°C. Analysis based on the rubber elastic theory for the melt revealed that higher activation energy is required for nylon 66 with larger f_N but failed to detect the evidence for the presence of chemical or pseudo-cross-linking for nylon 66 with higher f_N . These results support the idea that nylon 66 with high f_N has inherently stronger molecular interaction in the amorphous region to hinder the structural formation induced by heat and humidity.

1. Introduction

Nylon 66 is an important industrial material for fiber and engineering plastics, produced by polycondensation reaction of hexamethylene diamine and adipic acid. Its polycondensation nature allows us to easily control the terminal group ratio, for example, the molar fraction of amino end group f_N ((number of amino end group) / (total number of amino end and carboxyl end groups)), by changing initial charge of monomers. This operation is generally carried out to control its dyeability so as to meet the user's demands in the textile field. On the one hand, f_N is utilized as one of measures for the process control of the yarn production as well as melt viscosity does. Besides the dyeability, the properties such as the high tenacity, the high-water resistance, the easiness of after-finishing

and so on have been required even for textile nylon 66 yarns. So far, many studies have been made to improve the mechanical properties of nylon 66 yarn by mainly the stretching method and heat treatment[1-3], to elucidate the fiber structure formation during high speed melt-spinning[4-7] and to give information on structural change induced by water[8,9]. However, these studies have not been made from the standpoint, for example, of f_N . Thus, nothing has been clarified regarding the influence of f_N on physical, rheological and thermal properties of nylon 66 or this view point seems to have been apparently ignored. In this regards, a paper by Sebenda and Kralicek[10] dealing with Huggins coefficient k of nylon 6 dissolved in phenols in view of the end group effect should be noted but they seemed to refrain from extending or applying the concept to other solid properties of nylon 6. Therefore,

Table 1 Physical parameters of original nylon 66 chips and as-extruded yarns

Chip Sample	f_N	Mn	Rw^{*1} /% (log min) ⁻¹	T_m^{*2} /°C	T_c^{*2} /°C	ΔH_c^{*2} /J·g ⁻¹	MP^{*3}		ΔE^{*4} kcal·mol ⁻¹
							T_{m1} /°C	T_{m2} /°C	
A	0.192	16200	0.481	260.5	219. ⁸	56.5	148	183	7.23
B	0.362	16200	0.453	260.5	217. ⁷	54.5	160	183	10.75
C	0.470	17000	0.435	260.1	217. ²	55.4	161	183	11.79
D	0.616	16300	0.391	259.3	217. ⁰	58.0	162	183	14.79

*¹for the as-extruded yarns extruded under 7780sec⁻¹ at given temperatures, *² T_m , T_c and ΔH_c are melting point, crystallization temperature and heat of fusion for the chips evaluated during crystallization experiment annealed at 295°C, *³ MP is the melting point in polymer/water (1/1, W/W) system, T_{m1} is the melt-starting temperature and T_{m2} the melting peak temperature, *⁴the activation energy for melt flow.

if the relationships between f_N and the fundamental properties of polymer are established, it would be very useful for its quality control as well as its production control.

In this paper some important role of f_N on several properties of nylon 66 will be reported from the above point of view.

2. Experimentals

2.1 Nylon 66 chips

Four kinds of chips differing in f_N but with almost same number-average molecular weight Mn were prepared by conventional polycondensation in an auto-clave and Mn and f_N are listed in Table 1. The size of chips was adjusted to 1.6mm ϕ $\times$ 3mm. All polymers include a constant amount of a polymerization stabilizer (below 40 ppm). Mn was calculated from the following equation: $Mn = 10^6 \times 2 / (C_c + C_N)$

Here, C_c and C_N are the concentration (meq / kg-dry polymer) of carboxyl and amino end groups, respectively. C_c and C_N were determine as follows:

C_c : The precisely weighed nylon 66 chip (B = about 4g) was dissolved in 150ml of benzyl alcohol at 170 °C and titrated by a 0.1N NaOH dissolved in ethylene glycol (A ml) under the existence of 0.3 ml of color indicator (5 g of phenolphthalein, 5 g of cupric acetate and 12 g of titanium dioxide dispersed in 1l of benzyl alcohol).

$C_c = 100A \times F/B$; F : a factor coefficient of aq. hydrochloric acid

C_N : The precisely weighed nylon 66 chip (B = about

6 g) dissolved in 50 ml of 90 wt % of aqueous (aq.) phenol was titrated by 0.05N aq. hydrochloric acid (A ml) until the system becomes pH=3.0.

$C_N = 50A \times F/B$; F : a factor coefficient of aq. hydrochloric acid

2.2 Water-adsorption phenomena of the chips

Four kinds of the nylon 66 chips were vacuum-dried at 80°C for 12 h, then placed in a room controlled at RH= 65% and 20°C. The water content of chips was measured as a function of lapsed times based on an electric titration method using an apparatus (Mitsubishi CA-05 model, Mitsubishi, Japan) with aid of a water-vaporization apparatus (VA-05 model, Mitsubishi, Japan) under the following conditions: sample amount; ca. 1 g, vaporization temperature; 208°C, flow rate of the carrier gas (nitrogen); 300 ml/min, measurement ending sensitivity; 0.5 mg/s, delay time; 5 min, background; less than 0.05 μ g/s.

2.3 Melt flow and viscoelastic behaviors

Each chip having a constant water content (1000ppm) was extruded at given temperatures (T_m = 280, 285, 290, 295, and 300°C) through the spinneret with an inner diameter of 0.25 mm and length of 0.375 mm under several shear rates and the generated pressure difference Δp was measured by Capilograph model 1B, PMd/C (Toyo Seiki Co. Ltd., Japan). The shear viscosity (η) was calculated by the following equation.

$$\eta = \frac{\Delta p \cdot \pi \cdot D^4}{64QL} \quad (1)$$

Here, D and L are the diameter and the length of the spinneret, respectively, and Q is the extruded volume

(cm³/min).

Further, the diameter of the melt stream D' at 1 mm below the exit of the spinneret was measured by a Lazer apparatus. Using the elongation ratio parallel to the polymer stream $\lambda = (D'/D)^2$ the extruded polymer melt was analyzed by the rubber elasticity theory[11,12] as follows:

$$\frac{\tau}{T_m} = v_e k \left(\lambda - \frac{1}{\lambda^2} \right) \quad (2)$$

$$v_e = \frac{\rho N_A}{Me} \left(1 - \frac{2Me}{Mn} \right) \quad (3)$$

τ : shear stress generated inside the capillary (dyn·cm⁻²), k : Boltzmann's constant (1.38×10^{-16} erg·K⁻¹), v_e : network segment number (cm⁻³), ρ : polymer density (g·cm⁻³), N_A : Avogadoros number (6.02×10^{23} mol⁻¹), T_m : melt temperature (or extruding temperature) (K), Me : average molecular weight of the network polymer chain, Mn : number-average molecular weight of polymer.

$\lambda \cdot 1/\lambda^2$ relates to the inner pressure of the elongated melt sometimes including the contribution due to relaxation phenomena of molecular orientation of the melt[13,14].

2.4 Thermal analysis of polymer chips

DSC measurements on the chips described in section 2.1 were carried out on a DSC-200 instrument (Seiko-Denshi Co. Ltd., Japan). The sample was heated at heating rate of 50°C/min until the desired holding temperatures and then kept (or annealed) at the holding temperature for 5 min, then cooled at the cooling rate of 10°C/min. Crystallization peak temperature T_c was analyzed as a measure of crystallization rate of the polymer. In the same manner, the melting phenomena of the chips under the existence of water (polymer/water = 1/1, w/w) were also examined at the heating rate of 10°C/min.

2.5 Dynamic relaxation analysis on the as-extruded yarns

The extruded polymer melts at the shear rate of 7780 s⁻¹ and at $T_m = 300^\circ\text{C}$ described in section 2.3 were wound at the winding speed of 150 m/min and then immediately stocked under nitrogen atmosphere. The stocked as-extruded yarns were subject to dynamic relaxation measurement (loss tangent $\tan \delta$, loss modulus E'' and strage modulus E' as a function of temperature T) within 5 h by Vibron FP-01 (Orientec Inc., Japan). The

operating conditions are follows: frequency; 110 Hz, heating rate; 5°C/min, yarn length; 2 cm, measuring deformation; 16 μm , initial charge to yarn; 0.024 g/d. α and β dispersions known for nylon 66[15,16] were analyzed as a function of f_N . Two α relaxation peaks reported for nylon 6 by Prevorsek et al.[17] were conveniently termed as α_a and α_b from higher temperature in this paper. The similar analysis was made on the sample yarns treated by boiling water for 40 min at 130°C after conditioning of the yarns described above at RH = 65% and 20°C for 5 days in order to clarify the structural change in the amorphous region by water in view of f_N of polymers. Changes in Mn and f_N of the as-extruded yarns were also measured as a function of extruding temperature and are listed in Table 2.

Table 2 Mn and f_N for as-extruded yarns.

Chip Sample	Mn^*		f_N^*	
	290°C	300°C	290°C	300°C
A	16180	15728	0.190	0.189
B	16412	16309	0.366	0.364
C	17532	17421	0.478	0.477
D	16942	16855	0.632	0.630

*for the as-extruded yarns extruded under 7780sec⁻¹ at given temperatures.

3. Results and Discussion

3.1 Water adsorption rate

Fig.1 shows the dependence of water up-take (expressed in ppm) as a function of logarithm of the lapsed time t (min) for the four kinds of the chips. All the plot shows fairly-well linearity in the log t less than 2.8. The water adsorption rate Rw (ppm(log t)⁻¹) estimated from the slope of the plot is collected in Table 1. Rw tends to lower as f_N increases, indicating that the chips with high amino end group fractions are relatively insensitive to water. Note that Mn of the chips (samples A, B and D) utilized in this experiment is all in the same level although Mn of Sample C is slightly larger than others. This excludes the possibility of Mn -dependence of Rw . Thus, the relatively low Rw for the chips with larger f_N can be explained by either higher degree of crystallization or higher molecular

Fig. 1 The water adsorption of nylon 66 chips with different amino end group fractions f_N as a function of time (expressed in logarithm). $\circ$: chip with $f_N = 0.19$, $\triangle$: $f_N = 0.36$, $\square$: $f_N = 0.52$, $\diamond$: $f_N = 0.62$.

Fig. 2 The holding temperature-dependence of crystallization temperature T_c (a) and the heat of fusion ΔH_c (b): Symbols are the same as those in Fig.1.

packing density in the so-called amorphous region of the chips. The former can be denied by Fig.2, where the heat of crystallization ΔH_c and crystalline temperature (T_c) are plotted vs. holding (or annealing) temperature for each f_N . The values of T_m , T_c and ΔH_c for the chips

evaluated by the crystallization experiment annealed at 295°C are collected in Table 1. ΔH_c proved to be almost constant for all f_N values. T_m and T_c seem to be exceptionally higher for the chip with lowest f_N , and slightly decreases with an increase in f_N in other f_N region. This means that the determinant of water adsorption rate of the chips is neither the degree of crystallization nor the crystallization rate anticipated from T_c . The latter aspect will be discussed later in more details. The highest T_c value for Sample C in Fig.2 at annealing temperature of 280°C might relate to the highest M_n of this sample. However, at other annealing temperature region (e.g., 290°C, 300°C) it is obvious that the above thermal properties are not necessarily simply dependent on M_n because the plots of the thermal parameters exhibited no linearity regarding M_n . The reason for the highest T_c value for the chips with lowest f_N (Sample A) might be in part attributed to the lowest M_n . The figure also shows that T_c steeply decreases from 280 to 290°C, denoting that all chips have similar thermal history (all chips were polymerized at around 290°C). Without overcoming this thermal history in general any nylon 66 chips may have the incompletely melted crystalline nuclei, as proved for nylon 6 melt [18].

The results of DSC analysis on the melting phenomena of the chips/water (w/w = 1/1) coexistence system are also shown in Table 1. The melt-peak temperature T_{m2} for all chips fall to the same value (183°C) but the melt-starting temperature T_{m1} tends to shift to the higher temperature side with an increase in f_N although a steep change takes place when f_N goes from 0.19 to 0.36, approaching an asymptotic value (ca.160°C). These results might indicate that nylon 66 with a higher amino end group fraction tends to give relatively dense molecular packing in the amorphous region so as to restrict the water penetration or that nylon 66 with a high carboxyl end group fraction has exceptionally loose molecular packing in amorphous region. Note that T_m estimated for dry chips falls all to the similar level.

3.2 The f_N -dependence of flow characteristics of nylon 66

As shown in Table 2, M_n of samples B - D increases by extruding at 290°C and very slightly decreases from these M_n values by extruding at 300°C, and M_n of

sample A (with lowest f_N) keeps almost constant value at 290°C but decreases to some extent (3% level) by extrusion at 300°C. The increase in M_n seems to be larger for the chips with larger f_N although the increase is only 5% level. This indicates in turn that hydrolysis of nylon 66 somewhat effectively works on the polymer with low f_N (that is, the carboxyl end group rich polymer) even at a water content level of 1000pm. The f_N value is almost constant for samples A and B, and increases to some extent for samples C and D mostly due to the decrease in absolute value of carboxyl content. Then, in the case where f_N is used for the analysis the original value will be employed in the proceeding discussion.

Fig.3 shows the $\ln \eta$ vs. $1/T$ plots for each nylon 66 chip with different f_N in the shear rate range of 3900~23350 s⁻¹. For all nylon 66 chips at any shear rate there seem to be two linear regions above and below 290°C (ca. 1.78×10^{-3} K⁻¹). The slope above 290°C is steeper than that below 290°C. The temperature 290°C corresponds to the lower limit of annealing temperature where crystallization temperature T_c goes into slowly changing stage, as shown in Fig.2. More detail inspection of the plots reveals that 1) for nylon

Fig. 3 Arrhenius plot for the shear viscosity of nylon 66 melts: a) nylon 66 chip with $f_N=0.19$, b) $f_N=0.36$, c) $f_N=0.52$, d) $f_N=0.62$. ○: shear rate = 3800 s⁻¹, △: 7800 s⁻¹, □: 15600 s⁻¹, ◇: 23400 s⁻¹.

66 with $f_N=0.19$ the plots changed abruptly from 295 to 300°C, 2) the plots for nylon 66 with $f_N=0.36$ seems to be almost linear at temperature more than 285°C although showing a very slight decrease at more than 295°C and 3) those for other chips exhibited a reflection point at 290°C.

The gradient of the line in Fig. 3 gives the activation energy ΔE^* for melt flow in the following manner,

$$\eta = \eta_0 \exp \left(- \frac{\Delta E^*}{RT} \right) \quad (4)$$

where, η_0 is a constant independent of temperature, R is the gas constant. The ΔE^* values in the measuring temperature range, where M_n keeps almost constant are plotted against the shear rate for each chip in Fig.4. Here, the temperature region used for evaluation of ΔE^* is 285~295°C for sample A, 285~300°C for sample B, and 290~300°C for samples C and D. ΔE^* of the chips except for sample D with highest f_N is almost a decreasing function of the shear rate, as expected. That of sample D is almost constant at any shear rates. This means that the entanglement of polymer chains in the melt of nylon 66 with highest f_N is more resistant to shear flow or the relaxation of molecular orientation of the melt differs from that of other chips. In addition, nylon 66 with higher f_N gives a larger value of ΔE^* although some contribution of M_n to the ΔE^* value can not be completely denied, suggesting that nylon 66 with larger f_N has stronger molecular interaction in itself.

Fig. 4 Dependence of the activation energy parameter ΔE^* of flow of nylon 66 melts on shear rate: Symbols are the same as those in Figure 1.

The ΔE^* values at a shear rate of 7780 s^{-1} are collected in Table 1. Inspection of the value of ΔE^* (ranging from 800 to $1600 \text{ kcal mol}^{-1}$) reveals that the ΔE^* of melt flow is naturally far larger than that of hydrogen bonding ($3 \sim 8 \text{ kcal mol}^{-1}$). The melting and extruding procedures might influence the chemical structures of nylon 66, in most cases, the branching (for example, 8)), or pseudo cross-linking (Some author has pointed out that nylon 66 with high f_N is apt to relatively easily become gelatinous by severe heating[19]). This aspect will be briefly described in later.

Application of the rubber elastic theory to the nylon 66 melts differing in f_N is illustrated in Fig.5, where τ/T_m is plotted against $\lambda \cdot \lambda^{-2}$. Obviously, the plots for the chips with $f_N = 0.19$ and 0.36 are almost linear in all temperature range. The plot begins to scatter considerably in the range $f_N \geq 0.47$, especially in the low temperature region (less than 290°C). This might be attributable to the fact that nylon 66 with higher f_N needs more energy to flow and the above temperature region lays in the range where the drastic T_c change takes place, as shown in Fig.2. Ishibasi[14] has reported for nylon 6 melt that the plot of τ/T_m vs. $\lambda^2 \cdot \lambda^{-1}$ was linear but the substitution of τ to τ_e (the effective stress corrected by introducing the end correction factor) did not give linear plot, speculating that melt orientation proceeds in the capillary and practically no stress relaxation takes place inside the capillary. Here, he assumed that melt stream with maximum die swell diameter of D' deforms to the stream with a diameter D at the capillary exit. The similar plots (τ/T_m vs. $\lambda \cdot \lambda^{-2}$ plots) in the present case give the linearity in the limited temperature range as well as the τ/T_m vs. $\lambda^2 \cdot \lambda^{-1}$ plots do. This means that nylon 66 melt behaves almost similarly like nylon 6 melt although there may

Fig. 5 The plots of τ/T_m vs. $\lambda \cdot \lambda^{-2}$: a) chip with $f_N = 0.19$, b) $f_N = 0.36$, c) $f_N = 0.52$, d) $f_N = 0.62$. $\circ$: 285°C , $\triangle$: 290°C , $\square$: 295°C , $\diamond$: 300°C

be the difference in the degree of stress relaxation between the two polymers when the melt is inside the capillary and departing the capillary exit. From the plots the v_e and Me can be estimated and are listed in Table 3. By considering the Mn drops and thermal history of the polymer these values were estimated only at 295 and 300°C . With an exception (nylon 66 with $f_N = 0.19$ at 300°C), v_e seems to be a very slight increasing function of f_N , indicating that the attempt to detect some chemical cross-linking or pseudo cross-linking in view of f_N is difficult. In other words, there is no experimental evidence affirming the cross-linking for nylon 66 with high f_N . The large v_e for the above exception might be influenced by the effect of the decrease in Mn during experiment for nylon with lowest f_N .

3.3 Structure of the as-extruded yarns

Fig.6 and 7 show the loss modulus E'' and the storage modulus E' as a function of temperature for the as-spun yarns obtained at 300°C where the stable melt extrusion is possible due to very low content of incompletely melted crystalline nuclei. Both figures contain the data

Table 3 Parameters estimated for the extruded nylon 66 melts by rubber elasticity theory

Extruded temp./ $^\circ\text{C}$	f_N of the extruded nylon 66 melt							
	0.19		0.36		0.47		0.62	
	v_e / 10^{20} cm^{-3}	Me	v_e / 10^{20} cm^{-3}	Me	v_e / 10^{20} cm^{-3}	Me	v_e / 10^{20} cm^{-3}	Me
295	1.49		1.56		1.55		1.70	
300	(1.73)	(2412)	1.47	2724	1.48	2768	1.50	2718

* Me at 300°C was calculated using the average Mn of those evaluated for as-extruded yarns obtained at 295°C and 300°C .

Fig. 6 The plots of the loss modulus E'' for the as-spun yarns with different f_N as a function of temperature before (a) and after (b) boil treatment: symbols are the same as those in Fig.1.

for the samples before and after boil treatment. Amorphous parameters determined from dynamic relaxation analysis are plotted against f_N in Fig.8. Before the boil treatment α_a relaxation temperature $T_{\max}(\alpha_a)$ seems to slightly shift to the lower temperature side accompanying the increase in its intensity of $\tan \delta_{\max}(\alpha_a)$ as f_N becomes larger. $\tan \delta_{\max}(\alpha_b)$ and $\tan \delta_{\max}(\beta)$ for the as-spun fibers with highest f_N are conspicuously higher than others. Although not shown in Fig.8, $T_{\max}(\alpha_b)$ is lowest for the as-extruded fiber with lowest f_N , abruptly shifts to a higher temperature at $f_N=0.36$, then shifting to the lower temperature in the range $f_N \geq 0.47$. $T_{\max}(\beta)$ tends to shift to higher temperature with an increase in f_N , approaching an asymptotic temperature. Note that the α relaxation is attributed to the micro Brownian motion of segments related to hydrogen bonding[20,21] and β is responsible for either segmental motion related to non-hydrogen bonded amide groups[16,17] or the segmental motion of water-bonded amide groups [22,23]. Two distinct α peaks have been reported for nylon 6, one being (α_b) attributed to the region

Fig. 7 The plots of the storage modulus E' for the as-spun yarns with different f_N as a function of temperature before (a) and after (b) boil treatment: symbols are the same as those in Fig.1.

containing water and the other (α_a) being attributed to the region not containing water[17]. The increase in water content in nylon 6 causes the peak temperature to shift to the lower side and the intensity to increase [17]. Kunugi et al.[24] systematically investigated for nylon 6 fibers the effect of draw ratio on the α , β and γ relaxation peaks, revealing that the E'' peak temperatures for the α and β relaxation peaks shift towards higher temperature side accompanying the increasing in their intensities and the intensity of E'' for γ is greatly enhanced with keeping its temperature almost constant as the draw ratio becomes larger. They also claimed that β relaxation takes place without existence of water in polymer. On the one hand, Kolarik and Janacek[25] showed for nylon 6 that the β relaxation temperature shifts to the lower side and its intensity increases with an increase in water content of polymer. In the present case, the water content of the as-spun fibers is expected to be the following order as function of f_N : $f_N=0.19 > f_N=0.36 > f_N=0.47 > f_N=0.62$. The results concerning the β relaxation for the as-spun fibers except that with highest f_N are reasonably

Fig. 8 The plots of the parameters, representing amorphous structure of the as-extruded nylon 66 yarns, against the fraction of amino end group f_N : solid line; for the as-extruded yarns, broken line; for the yarns with boil treatment.

correlated with the above phenomenological observation, shown by Kolarik and Janacek[25]. The exceptional nature for the as-spun fiber with largest f_N could be attributed to higher molecular orientation of this yarn due to the relatively stronger resistance of melt flow during extrusion or relatively lower molecular relaxation nature of the melt-extrudate, according to the stand point by Kunugi et al.[24]. In another light of view, the results for the β relaxation seems to be largely categorized by the ionic nature (acidic; $f_N=0.19$, almost neutral; $f_N=0.48$ (~ 0.36), alkaline; $f_N=0.62$) of water in nylon 66, as has been proved by the present authors[26]. The stronger hydrogen bonding favors nylon 66 with larger f_N (alkaline) and the weaker hydrogen bonding is anticipated for nylon 66 with low f_N (acidic). Thus, we

tentatively considers that the β relaxation reflects essentially the segmental motion related to amide groups influenced by the manner of hydrogen bonding, which is determined by the existing state of water in polymer. The appearance of the two α peaks seems to depend on the water content of the samples, as shown by Prevorsek et al.[17]. However, both the peak temperature and the intensity of α_b peaks for the as-spun nylon 66 with $f_N \geq 0.36$ gave the reversed results as observed in view of water content. If the peak temperature is related to the degree of molecular orientation, the present results indicate that the yarns with larger f_N has relatively lower molecular orientation, which is inconsistent with the result for β relaxation. This also means that especially the α_b relaxation is not simple functions of water content and molecular orientation but also function of the manner of hydrogen bonding depending on the state of water related to f_N .

The characteristic $E' - T$ curves are also seen for the as-spun fibers with lowest and highest f_N before boil-treatment. E' for the former in the temperature region of $\text{ca. } 0 \sim \text{ca. } 70^\circ\text{C}$ is lowest and that for the latter abruptly decrease up to $\text{ca. } 40^\circ\text{C}$ then increases slightly, followed by decreasing again. The reason for the latter behavior is not clear at present but might be related to the existence of at least two quite different molecular packing states and the weaker one might be reorganized during measurement. The lowest E' value of the yarn with $f_N=0.19$ despite of its low intensity of E'' , shown in the above $E' - T$ curves means that this yarn has the low molecular packing density or the low degree of molecular orientation. In turn this means that yarns with larger f_N have the higher molecular packing density or the higher degree of molecular orientation. However as discussed before, we consider that yarns with larger f_N exhibits inherently stronger molecular interaction, leading to higher molecular packing density not to molecular orientation.

It is obvious also from Fig.6 and 7 that the boil-treatment promotes the so-called water-induced crystallization for all polymers used and the strains originally existed are almost equally released although some slight difference is seen among the yarns.

3. Conclusion

In this paper, the fractional balance of the two terminal groups in nylon 66 has been proved to be one of the important factors which controls water-adsorption phenomena, rheological, thermal, crystallization and mechanical relaxation behaviors. Nylon 66 rich in amino end group was proved to have relatively higher resistance to melt-flow and to water-absorption, leading to an idea that nylon 66 with a high molar fraction of amino end group has inherently stronger molecular interaction in the amorphous region to hinder the structural formation induced by heat and humidity. In this connection, the possible chemical change for especially the above nylon 66 during the present experimental procedures was not deducted from rubber-elasticity theory. More detailed study in this line might be required and is open to future study.

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