Effect of the Structure on Sorption and Diffusion Processes in Polyamide 6, Part 1: Activation Energy and Thermodynamic Parameters of Water Desorption in Oriented and Unoriented Polyamide 6

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ABSTRACT: Effect of the structure on desorption of water in polyamide 6 is studied by differential scanning calorimetry and thermogravimetry. Oriented and unoriented polyamide 6 fibers annealed in water at 100°C for different times (2 s up to 1 h) are characterized by their structure and transport properties. It is found that water treatment leads to substantial change in the polymer structure (including phase transition even at room temperature). Activation energy and enthalpy of water desorption are determined, and their high values ($E_a = 60-130 \text{ kJ/mol}$; $\Delta H_d = 950-1360 \text{ J/g}$) are attributed to the formation of strong sorbent–sorbat bonds. Both parameters are influ-

INTRODUCTION

The structure of semicrystalline polymers is still faced with several principal questions in spite of the great number of studies and proposed models.^{1–10} This is especially valid for oriented semicrystalline polymers, whose structure is more complicated if compared to unoriented ones. Most important questions are related to the structure of amorphous regions in oriented fibers and films.^{11,12} The concepts for three-phase model suggest the existence of one crystalline and two amorphous structures (rigid and liquid), and also suppose that amorphous structure along the fiber axes is different from that perpendicular to it.^{3,13–16}

Diffusion of low molecular compounds in semicrystalline polymers is strongly affected by polymer structure. On the other hand, application of diffusion analysis can highlight problems concerning specific incorporation and distribution of crystallites into amorphous matrix, providing information for the microstructure, which is not accessible to other meth-

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ensed substantially by the polymer structure (degree of crystallinity and orientation). Besides, it is found that the temperature of water desorption (T_d) is also very sensitive to the structure. The T_d -values increase sharply with rise of degree of crystallinity, being always considerably lower for oriented fibers. This quite unexpected result is also confirmed and further interpreted in the next parts of the article. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 122–129, 2007

Key words: desorption; water; polyamide 6; structure; activation energy; fibers; thermal analysis

ods. For this reason, we applied this sensitive to the structure method for characterization of polyamide 6.

Sorption of water plays a very important role, especially in properties of hydrophilic polymers as polyamides.^{17–22} Water sorption has been widely investigated during the last three decades. Relatively great numbers of studies are focused on the diffusion process,^{23–27} and especially on the influence of matrix molecular orientation.^{28–33} Nevertheless, the mechanism of incorporation of water molecules into the polymer substrate is still a matter of discussion.

The present article is first part of a series of articles presenting a systematic investigation on sorbent-sorbat relationships of low molecular compounds in polyamide 6 fibers. The goal was (1) to estimate how the fiber structure affects sorption and diffusion processes in polyamide 6, and (2) by investigation of sorption and transport phenomena to provide information about specific molecular structure and dynamics. Both equilibrium sorption and the rate of sorption (diffusion) and desorption of water and other low molecular compounds into oriented and unoriented polyamide 6 were studied. The aim of the present first part is to characterize the fiber structure and to investigate its effect on the kinetic and thermodynamic parameters of water desorption process in oriented and unoriented polyamide 6.

EXPERIMENTAL

Materials and methods

Commercial polyamide 6 fibers produced by Vidachim AD, Bulgaria, unoriented (6400 dtex, 140 f) and oriented by drawing (1350 dtex, 140 f), free of TiO₂, were investigated. Both oriented and unoriented fibers were subjected simultaneously to the following treatments:

- a. annealing in vacuum for 3 h at 200°C (oriented samples being with free or fixed ends);
- b. annealing in water medium at 100° C for different times (t_a): 2, 5, 10, 20, 30, 60, 180, 1800, and 3600 s (annealing with free ends). After the corresponding time, specimens were removed from bath, the excess of water was taken up by pressing between blotting paper, and samples were conditioned as mentioned later;
- c. conditioning for 1 week at room temperature and about 60% relative humidity. These are so called air-dry samples, being unannealed or annealed. They were kept in a dessicator until the measurements. To maintain a controlled relative humidity 60% over a long period of time, saturated salt solutions of NaBr and NaCl were used;
- d. wetting of unannealed oriented and unoriented fibers by immersing into water bath at 20°C for 3 h and removing the excess of water by pressing between blotting paper. The measurements of these wet samples were performed immediately after preparation.

The samples were characterized in respect of their structure by wide-angle X-ray scattering (WAXS) and thermal analysis (differential scanning calorimetry, DSC, and thermogravimetry, TG). The accuracy for the temperature is $\pm 1^{\circ}$ C, for the enthalpy is $\pm 5\%$, and for the weight measurements is $\pm 2.10^{-6}$ g. X-ray diffraction studies were performed applying a Siemens diffractometer with Ni-filtered Cu Kα radiation, 30 kV and 15 mA, with a scanning rate of 4°. A Mettler TA 3000 system was used for the thermal analyses employing different heating rates in the range of 0.5-50 K/min in the temperature interval between 10 and 300°C and a sample amount of \sim 10 mg. The relationship between structure and kinetic and thermodynamic parameters of water desorption process was studied.

Degree of crystallinity, w_c , of polyamide 6 fibers was estimated by two independent methods: WAXS and DSC. Experimental details are described in Ref. 34. Determination of w_c from WAXS data was based on the well-known method of Hermans and Weidinger.³⁵ For the separation of crystalline and amorphous diffraction, we applied our results on X-ray study of completely amorphous polyamide $6^{36,37}$ A value of 188 J/g³⁸ was used for the melting enthalpy of ideal crystal in calculations of w_c from calorimetric data. This value (188 J/g) was also obtained for the same type of polyamide 6 fibers by extrapolation of crystal size and density.³⁴ Application of higher value, for example reported in more resent work value 230 \pm 20 J/g,³⁹ leads to results for w_c , which are unrealistic and not consistent with the X-ray data.

In fact, there is a great discrepancy in the literature data for ideal melting enthalpy of polyamide 6 (values vary between 134 and 230 J/g). A compromise value of 230 J/g is assumed to differ from the real one by ± 30 J/g.³⁸ We assume that polymorphism of polyamide 6 is the main reason for such a discrepancy. The same problem exists with other thermodynamic parameters of polyamide 6, for instance, equilibrium melting temperature.⁴⁰

RESULTS AND DISCUSSION

Degree of crystallinity

Degree of crystallinity is an important characteristic of semicrystalline polymers for the sorption and diffusion of water molecules, since they permeate mainly in the amorphous regions. The time dependence of degree of crystallinity, w_c , of unoriented and oriented polyamide 6 fibers annealed in water at 100°C is presented in Table I.

It is seen from Table I that unannealed and annealed for a very short time (up to 10 s) fibers display higher values of w_c (DSC) than w_c (WAXS). Most likely, this is due to additional crystallization of polyamide 6 in the calorimeter during DSC experiments. However, aiming preserving of the amorphous phase, this effect could not be avoided, e.g. by selective crosslinking, applied in Ref. 40 for more correct determination of the equilibrium melting temperature of polyamide 6.⁴¹

The thermal treatment in water at 100°C leads to measurable increase of w_c even for very short times of annealing ($t_a = 5$ s), as seen from Table I, WAXS data. In comparison with annealing in vacuum,^{34,42} annealing in hot water is much more efficient for the increase of crystallinity. This result is very important taking into account that many processes (dyeing, etc.) and practical applications of polyamide 6 products are connected with hot water media treatment.

Crystallite sizes

In addition to degree of crystallinity, the sizes of crystallites are also important for the sorption and transport phenomena. The crystallite sizes, l_c , in polyamide 6 fibers were calculated from the WAXS dif-

TABLE IDSC and WAXS Data for the Degree of Crystallinity, w_{cr} of Drawn (or) and Undrawn (iso) Polyamide 6 FibersAnnealed in Water at 100°C for Different Times(2 up to 3600 s)

Annealing time (s)	w_c			
	DSC		X-ray	
	Oriented (%)	Isotropic (%)	Oriented (%)	Isotropic (%)
0	36	23	25	17
2	37	24	33	22
5	36	26	34	23
10	37	24	34	24
20	33	24	35	24
30	36	25	34	25
60	38	25	35	25
180	36	26	37	26
1800	39	28	39	27
3600	41	29	40	29

fraction maximums using the Sherrer's equation (constant K = 0.89)⁴³:

$$l_c = K\lambda/\beta_{1/2}\cos\Theta \tag{1}$$

Dependence of l_c on the annealing time t_a in water at 100°C of unoriented and oriented polyamide 6 fibers is presented in Figure 1. It is seen that the annealing leads to a significant increase of crystallite sizes for both unoriented and oriented samples. It should be pointed out that this effect is measurable even after a few seconds of treatment. The result is consistent with the earlier discussed increase of degree of crystallinity (Table I, w_c (WAXS)).

In our past systematic studies of processing–structure–properties relationship in polyamide 6, it was established that at isothermal secondary crystallization a bidimensional thickening perpendicular to the fiber axis of already existing crystals occurs.^{42,44–46} This finding is very important in respect of transport properties and will be discussed further again.

As illustrated by WAXS curves in Figure 2, even a few seconds experienced by polyamide 6 fibers into boiling water already have effect on the crystal phase. This is consistent with the results for w_c and once more confirms the higher efficiency of the thermal treatment in water compared to annealing in vacuum.^{34,42,44–46}

Specific characteristic of all polyamides is the presence of inter- and intramolecular hydrogen bonds in both crystalline and amorphous regions.^{47–49} These strong bonds increase the cohesive forces between macromolecules. The observed acceleration of crystallization process by annealing in water medium can be explained by the influence of water molecules on the macrochains mobility. Water molecules have plasticizing effect above T_{gr} and facilitate the chain

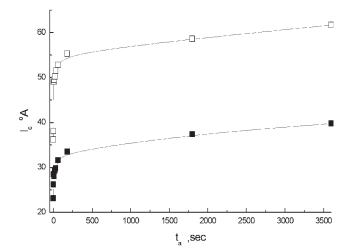


Figure 1 Dependence of crystallite sizes, l_c , of unoriented (\blacksquare) and oriented (\square) polyamide 6 fibers annealed in water at 100°C for different time, t_a .

mobility. Effectively, this is equivalent to an increase of the annealing temperature. In fact, at room temperature, amorphous part of air dry polyamide 6 is

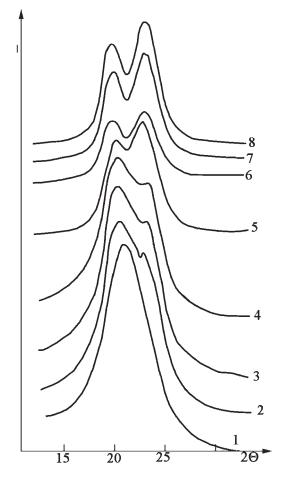


Figure 2 Diffractograms of polyamide 6 fibres annealed in water at 100°C for different times, t_a . Curves 1, 2, 3, 4 are for unoriented samples and $t_a = 0$, 2, 5, 180 s and curves 5, 6, 7, 8 are for oriented samples and $t_a = 0$, 2, 5, 180 s.

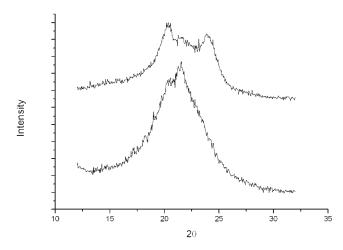


Figure 3 WAXS diffractograms of polyamide 6 unoriented fibres: bottom curve—air-dry sample, top curve after 24-h immersion in water at 20°C.

in glassy state, while in wet samples it is in rubbery state. Most likely, for this reason, we observed even at room temperature structural chances (including phase transition) in polyamide 6, which are typical for the annealed samples (Figs. 2 and 3).

Phase transition of γ -modification into α -modification

It is well known that $\gamma \rightarrow \alpha$ transition in the crystal phase of polyamide 6 occurs at drawing and at thermal treatment above 160°C.^{21,22,40,49–51} The present investigation indicates that the transformation of γ phase into α -phase takes place at lower temperature (100°C) and for a very short time of treatment (2–5 s) when compared to the conventional annealing in vacuum or inert atmosphere. This is seen from Figure 2, where the X-ray diffractograms of unoriented initial and annealed in water at 100°C polyamide 6 fibers are presented. Diffractograms of oriented samples are shown for the sake of comparison.

It is reported⁵² that water increases the α -crystalline fraction at the expense of both noncrystalline and γ -crystalline components of polyamide 6 films by 2 h boiling in water at 100°C. To the best of our knowledge, structural changes in immersed, only for a few seconds in boiling water polyamide 6, have not been reported before the present article.

Phase transition was observed even at room temperature. As seen from Figure 3, unoriented polyamide 6 fibers undergo $\gamma \rightarrow \alpha$ transformation after 24-h storage into water bath at 20°C. It is known⁵³ that aqueous solutions of iodine complex compounds cause structural changes ($\alpha \rightarrow \gamma$ transition) in polyamide 6 at room temperature. It has been also reported⁵² for moisture-induced slight $\gamma \rightarrow \alpha$ phase transformation at 22°C. A better expressed $\gamma \rightarrow \alpha$ transition at 23°C has been observed, but only after prolonged (192 h) storage in water of polyamide 6 filaments.⁵⁴

The earlier discussed acceleration of both $\gamma \rightarrow \alpha$ transition and crystallization of polyamide 6 is related at least to two factors. In the first place, this is the plasticizing effect of penetrated in polyamide water molecules, which enhance the segmental mobility. Second, we suppose that thermal treatment in water media is more effective in comparison to annealing in vacuum due to better heat conductivity. A conclusion can be drawn that these effects together facilitate structural reorganization and lead to increase of (i) overall degree of crystallinity; (ii) crystallite sizes; and (iii) density of crystal phase (density of monoclinic α -modification is 1.225 g/cm³ (Ref. 55), while for the γ -phase it is 1.16 g/cm³ (Ref. 56). Thus, a conclusion can be drawn that the hot water treatment of polyamide 6 facilitates such structure changes, which lead to a more compact ordering of macromolecules in crystal regions.

Activation energy and thermodynamic parameters of water desorption in polyamide 6

Usually, the activation energy for transport processes is determined from the temperature dependence of corresponding coefficients in Arrhenius plot.⁵⁷ In the present investigation the activation energy, E_a , for desorption of water in polyamide 6 was determined from calorimetric and thermogravimetric data. For this purpose we applied for the first time the method of Ozawa,⁵⁸ which has been developed for determination of activation energy of crystallization and chemical decomposition. This method is based on determination of corresponding thermal effects at different heating rates. The following equation is used:

$$d\ln q/d\ln \left(1/T'\right) = E_a/R \tag{2}$$

where *q* is the heating rate, T' is the temperature at which a certain degree of transition, *x*, is achieved, *R* is the gas constant, and E_a is the activation energy of the process.

Activation energy of water desorption was determined by means of eq. (2) for polyamide 6 fibers with different prehistory and structure: unoriented and oriented; unannealed and annealed in water at 100°C for 3600 s; annealed in vacuum for 3 h at 200°C. Each kind of samples was studied by DSC and TG at different heating rates q from 0.5 up to 50 K/min. The peak maximum T of water desorption process from DSC or TG data was taken as T'. It should be pointed out that T' is strongly affected by the heating rate, while the melting temperature, T_{m} , remains practically unchanged, as it is seen from Figure 4.

Figure 4 DSC curves of unoriented polyamide 6 fibres at heating rate 10° C/min (top curve) and 20° C/min (bottom curve).

150

T, C

200

300

250

100

The experimental data for oriented, unannealed polyamide 6 fibers in coordinates of Ozawa are plotted in Figure 5. Two straight lines with different slopes are obtained, whose intersection corresponds to a temperature about 90°C. Two values for the activation energy of water desorption process are evaluated from the slopes: 22 and 89 kJ/mol, respectively. Figure 6 shows the results for unoriented, unannealed samples, leading to one value for $E_a = 56$ kJ/mol.

In Figure 7 are presented the data for oriented fibers, annealed in water at 100°C for 3600 s. Again two straight lines are observed, giving two values for E_a : 30 and 91 kJ/mol. The slope here changes at about 70°C. For unoriented samples annealed under the same conditions, $E_a = 63$ kJ/mol is evaluated (Fig. 8).

Figure 5 Ozawa plot of the kinetic of water desorption for unannealed oriented polyamide 6 fibres (air-dry).

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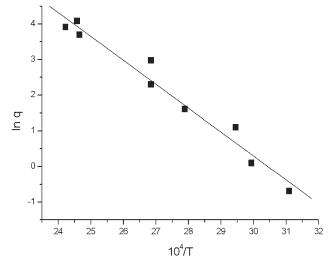


Figure 6 Ozawa plot of the kinetic of water desorption for unannealed unoriented polyamide 6 fibres (air-dry).

For unoriented fibers annealed in vacuum at 200°C for 3 h also, one value was evaluated, $E_a = 80$ kJ/mol (Fig. 9). Oriented fibers annealed with fixed ends at 200°C for 3 h are characterized by two different values of activation energy $-E_a = 55$ kJ/mol and $E_a = 130$ kJ/mol determined from the two straight lines whose intersection is in the vicinity of 35°C.

The results presented in Figures 5–9 are concerned for the air-dry samples with water content 3–4%. For the treated with water at 20°C, both oriented and unoriented wet fibers which contain about 10% water, $E_a = 66$ kJ/mol, was evaluated (Fig. 10).

The results for activation energy of water desorption of polyamide 6 fibers undergoing different treatments are summarized in Table II. In general, it was found that the annealing, i.e., the rise of overall

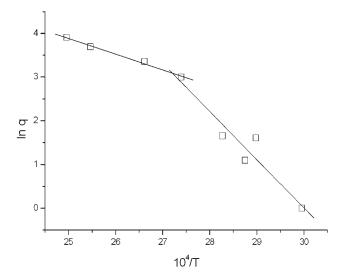


Figure 7 Ozawa plot of the kinetic of water desorption for oriented fibers annealed in water at 100°C for 3600 s (air-dry).

ပီ

0

50

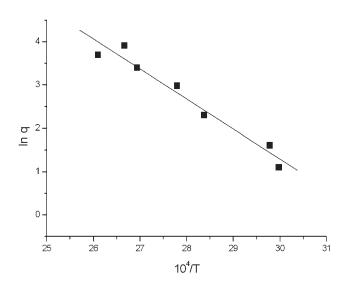


Figure 8 Ozawa plot of the kinetic of water desorption for unoriented polyamide 6 fibres annealed in water at 100°C for 3600 s (air-dry).

crystallinity, leads to some increase of E_a for all kinds of samples. However, the results for air-dry oriented fibers differentiate basically from that for unoriented ones. Presence of breaks on Arrhenius plots was established for all air-dry oriented samples, which demonstrates change in the mechanism of the process in the vicinities of 90, 70, and 35°C, depending on the previous thermal treatment. It should be pointed out also that evaluated values for activation energy of water desorption before the breaks are 2.5–4 times lower than after them.

Obviously, the process of water desorption in fibers is strongly affected by the matrix molecular orientation. Presumably, there is a specific peculiarity in oriented air-dry fibers, which is neglected by

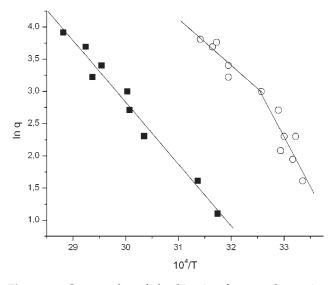


Figure 9 Ozawa plot of the kinetic of water desorption for unoriented (\blacksquare) and oriented (\bigcirc) polyamide 6 fibers annealed in vacuum at 200°C for 3 h (air-dry).

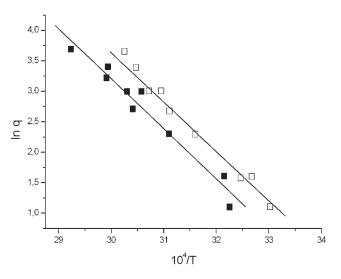


Figure 10 Ozawa plot of the kinetic of water desorption for unoriented (\blacksquare) and oriented (\square) polyamide 6 wetted fibers containing 10% water.

isotropisation and also by wetting. All unoriented and only wet oriented samples display absence of breaks on relevant Arrhenius plots. Surprisingly, the E_a -values for unoriented samples are equal to the average of corresponding two E_a -values for oriented fibers (Table II). Most likely, the appearance of two slopes in Arrhenius plots of oriented air-dry samples is related with relaxation processes taking place at heating. Oriented samples annealed at 200°C with free ends do not fit satisfactorily eq. (2) (data are not given). This fact also could be connected with relaxation and needs further study and explanation. The evaluated comparatively high values of activation energy are evidenced for strong sorbent-sorbat interactions. These findings are connected with the mechanism of water sorption in polyamides,^{28–33} which is still disputable^{15,21,28,29} They will be further discussed.

The earlier observations were also confirmed by the data for the enthalpy of desorption process, ΔH_d . This thermodynamic parameter was evaluated from the area under desorption peak and the weight loss under the same conditions. The average values of

 TABLE II

 Activation Energies E_a (in kJ/mol) of Water Desorption for Polyamide 6 Fibers After Different Treatments

Sample treatment	E_a (kJ/mol)
Oriented unannealed	22;89
Unoriented unannealed	56
Oriented annealed at 100°C in H ₂ O 3600 s	30;91
Unoriented annealed at 100°C in H ₂ O 3600 s	63
Oriented annealed at 200°C in vacuum 3 h	55; 130
Unoriented annealed at 200°C in vacuum 3 h	80
Unoriented unannealed moisted	66
Oriented unannealed moisted	66

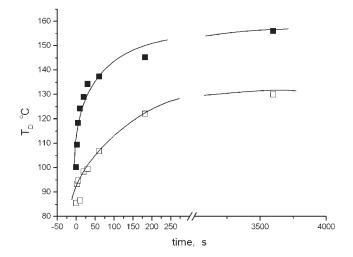


Figure 11 Dependence of the temperature of water desorption maximum, T_d , on the annealing time, t_a , for unoriented (\blacksquare) and oriented (\square) polyamide 6 fibers annealed in water at 100°C.

 ΔH_d were evaluated from about 300 DSC experiments. For the air-dry unoriented fibers the average enthalpy of water desorption is 1312 J/g, while for the air-dry oriented samples ΔH_d is 948 J/g (about 30% lower). For the wet samples containing 10% water, both oriented and unoriented, ΔH_d , is 1140 J/g. It is interesting to note that this value is the average of ΔH_d -values for air-dry unoriented and oriented fibers. Similar to activation energy, the enthalpy of water desorption is strongly influenced by the draw-induced matrix orientation. Once again it should be pointed out that such effect of orientation is observed (to our knowledge for the first time) only for the air-dry fibers, while for the moistened samples it disappears.

These results are also in accordance with the data obtained for the temperature of desorption maximum (T_d). In Figure 11 is shown the dependence of T_d on the annealing time t_a for both oriented and unoriented fibers annealed at 100°C in water. T_d sharply increases with annealing time up to about 250 s and then the effect levels on. It should be noticed that the temperature of desorption peak of oriented samples is always lower than T_d of unoriented ones. Since the rise of T_d with increase of annealing time is faster for unoriented fibers, the difference $\Delta T_d = T_d$ (unoriented) $- T_d$ (oriented) also increases.

Lower T_d -values for oriented fibers were observed always and for all kind of samples: air-dry, moistened, unannealed, or annealed. Similar data that clearly distinguish water sorption properties of unoriented and oriented fibers were not found in the literature. Depending on the water content and thermal treatment, the difference ΔT_d changes from 5 up to 35°C. The average value of difference ΔT_d was evaluated from about 300 DSC and 200 TG experiments. It is 24°C for the air-dry samples being much higher when compared to moistened fibers, where this difference is only 7°C. Obviously, the temperature of water desorption in polyamide 6 fibers is a parameter which is strongly structure-sensitive. T_d is especially sensitive to the existence of molecular orientation in polymer matrix. Once again, it should be pointed out that the effect is very strong for air-dry fibers and becomes smaller with increase in water content. This observation is consistent with the earlier discussed effect of the orientation on the other parameters (E_a and ΔH_d).

It is interesting also to estimate the influence of degree of crystallinity on desorption process. This can be clarified by comparison of Figures 1 and 11. The annealing results in rise of overall crystallinity (Fig. 1) and crystal sizes,⁴² both in unoriented and in oriented fibers. As a result, desorption process hinders and T_d increases (Fig. 11). At first glance, the relation is simple and obvious, but in fact, the role of fiber orientation is specific and not simple. Although the degree of crystallinity of oriented samples is higher when compared to unoriented ones (Fig. 1, Table I), desorption temperature is always lower for oriented fibers. This result is consistent with earlier discussed results for activation energy and enthalpy of desorption. Hence, a conclusion can be drawn that the fiber orientation favors desorption process. This quite unexpected result is in contradiction with the reported data for diffusion in oriented polymers.^{32,33}

It is generally accepted that oriented polymers have higher density and lower diffusion coefficients than unoriented ones. It has been shown that orientation strongly reduces diffusion, which leads to an increase of activation energy and decrease of diffusion coefficients of organic molecules in polyethylene.³³ There are some data for diffusion in polyamide 6¹⁹ but, unfortunately, authors compare samples with different degree of orientation and do not comment isotropic ones.

CONCLUSIONS

It was found that water accelerates considerably the structural changes in polyamide 6. Even at room temperature $\gamma \rightarrow \alpha$ transformation in the crystal phase is observed, which is typical for the annealed samples. Thermal treatment in water medium is much more efficient when compared to annealing in vacuum or inert atmosphere. Even very short annealing times (a few seconds) lead to such reorganizing of crystal regions, which increase their total amount, crystallite sizes, and density. Water molecules interact strongly with polyamide 6, which reflects high

values of activation energy and enthalpy of water desorption.

Desorption of water in polyamide 6 fibers is affected by many factors: degree of crystallinity, molecular orientation, and water content. The drawninduced orientation of polyamide 6 fibers plays a key role for the water desorption process. A sharp effect was found on activation energy, enthalpy of desorption, and temperature of water desorption. Contrary to the reported data for reduction of diffusion and decrease of diffusion coefficients of oriented polymers, we demonstrated that orientation enhances the water desorption.

The thermodynamic characterization of systems polymer–water is relatively poor in the literature. Therefore, a further discussion on the established results for thermodynamic and kinetic parameters of water desorption will be presented in the next articles from this series. Investigation on diffusion and sorption processes in polyamide 6 using different low molecular compounds is also in progress.

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