

The Influence of Annealing on the Thermal Properties of Poly(ethylene Terephthalate) Fibers

II. The Thermal Volume Expansivity of Annealed Pet Fibers

G. W. URBANCZYK and G. MICHALAK, *Institute of Fiber Physics and Textile Finishing, Technical University, Lodz, Poland*

Synopsis

The influence of annealing of PET fibers on their thermal volume expansivity has been examined. The annealing has been performed in air in the loose state of the fibers within the temperature range 130–210°C for 2,5,10, and 30 min. The established volume expansivity coefficients α_{25} give rise to the conclusion that three temperature intervals of annealing may be distinguished. The ascertained variation in α_{25} has been discussed on the basis of established morphological and fine structure changes caused in the fibers by the applied annealing.

INTRODUCTION

Extending the investigations devoted to the problem of the influence of annealing on thermal properties reported in the previous paper¹ an attempt has been made to elucidate the influence of annealing on the thermal volume expansivity of poly(ethylene terephthalate) (PET) fibers within the temperature range 19–25°C.

EXPERIMENTAL

Preparation of Samples

The studied material comprises samples of continuous PET filaments of linear density 220/48 d_{tex} drawn to a 4.5 draw ratio. The following samples have been investigated: (a) fibers annealed isothermally in a loose state at temperatures of 130,140,150,160,170,180,190,200, and 210°C in air for 2,5,10, and 30 min, and (b) fibers in their initial (unannealed) state for comparison. The values of indices characterizing the morphological and fine structure of all considered samples are presented in Table I.

Measurements

In an attempt to characterize the morphological and fine structure of the studied material, the following fiber characteristics have been investigated: the taut tie molecules (ttm) fraction, the overall orientation, the molecular orientation of the amorphous component of the fiber, the crystallinity, and the intermolecular cohesion. Methods used to achieve indices of these characteristics are described in the previous paper.¹

TABLE I
Morphological and Fine Structure Parameters of Examined PET Fibers

Annealing temp. (°C)	Annealing time (min)	Birefringence (n)	n/d	Volume crystallinity <i>xd</i> (%)	t _{tm} Fraction	Crit. dissol. time (sec)	Amorph. orient. function (<i>f_a</i>)
Without	—	0.1286	0.1296	36.7	0.107	9	0.50
	2	0.1681	0.1209	45.6	0.048	19	0.50
130	5	0.1615	0.1165	45.8	0.047	25	0.50
	10	0.1614	0.1184	45.4	0.045	41	0.47
	30	0.1653	0.1189	49.2	0.036	55	0.46
	2	0.1645	0.1184	48.1	0.045	40	0.49
140	5	0.1607	0.1156	48.6	0.041	35	0.49
	10	0.1593	0.1146	49.0	0.043	55	0.46
	30	0.1670	0.1202	48.8	0.036	74	0.45
	2	0.1628	0.1169	50.3	0.043	103	0.47
160	5	0.1572	0.1129	50.8	0.041	108	0.44
	10	0.1628	0.1170	51.3	0.043	106	0.44
	30	0.1622	0.1163	52.8	0.034	156	0.44
	2	0.1592	0.1139	53.5	0.041	160	0.46
180	5	0.1610	0.1154	53.1	0.038	150	0.44
	10	0.1606	0.1150	54.3	0.040	222	0.44
	30	0.1650	0.1180	55.6	0.029	245	0.43
	2	0.1637	0.1171	55.5	0.038	240	0.45
200	5	0.1601	0.1145	55.4	0.038	245	0.44
	10	0.1634	0.1167	57.8	0.039	323	0.44
	30	0.1663	0.1187	57.9	0.029	383	0.43
	2	0.1623	0.1158	58.7	0.021	329	0.44
210	5	0.1611	0.1150	58.1	0.031	405	0.43
	10	0.1573	0.1122	59.5	0.018	703	0.43
	30	0.1692	0.1203	62.3	0.021	1417	0.42

The values of the thermal volume expansivity coefficient, α_{25} were calculated from hydrostatic weight measurements using *n*-heptan as liquid. The sought after α_{25} values have been calculated from Eq. (1):

$$\alpha_{25} = (O_o - O_t)/O_t(t - t_o) \quad (1)$$

where O_o and O_t refer to fiber density at temperatures $t_o = 19^\circ\text{C}$ and $t = 25^\circ\text{C}$, respectively.

RESULTS AND DISCUSSION

The established values of thermal volume expansivity coefficients are listed in Table II and presented graphically in Figure 1. The layout of obtained α_{25} values shows that the thermal volume expansivity of PET fibers undergoes an essential alteration as a result of annealing.

The change in α_{25} depends on the annealing temperature and duration of the heat treatment. The character of the alterations is attributed first of all to the level of annealing temperature. Annealing time modifies only the range of changes and the α_{25} value, but does not alter the character of the variation.

TABLE II
Values of Volume Thermal Expansivity $\alpha_{25}(10^{-4}.K^{-1})$

Annealing temp. (°C)	Time (min)			
	2	5	10	30
130	2.9	3.3	3.4	3.4
140	2.7	2.8	2.9	2.8
150	2.6	2.6	2.6	2.5
160	2.5	1.8	2.6	2.4
170	1.8	1.7	2.3	2.3
180	1.7	1.7	2.2	2.2
190	1.6	1.6	2.0	2.0
200	1.9	1.8	2.1	2.4
210	2.5	2.5	2.4	3.0
Without		2.4		

The obtained results allow us to draw a conclusion that there three temperature intervals of annealing may be distinguished in which α_{25} values attain different levels and undergo different alterations with increasing annealing temperature.

The first interval refers to the temperature zone 130–150/160°C. Within this zone, the α_{25} values are larger than for unannealed fibers. Increased annealing temperature involves a monotonic decline of α_{25} . The second temperature interval refers to the range 170–190°C. Within this range, α_{25} values are lower than for the unannealed fibers. With increasing annealing temperature α_{25} diminishes continuously, reaching a minimum value at 190°C. The third temperature interval pertains to the temperature range 200–210°C. Within this zone, α_{25} increases with annealing temperature, reaching a level equal or higher than for unannealed fibers.

Comparing the changes in structure indices with alteration in α_{25} values, it can be seen that the change in α_{25} does not correlate with the variation

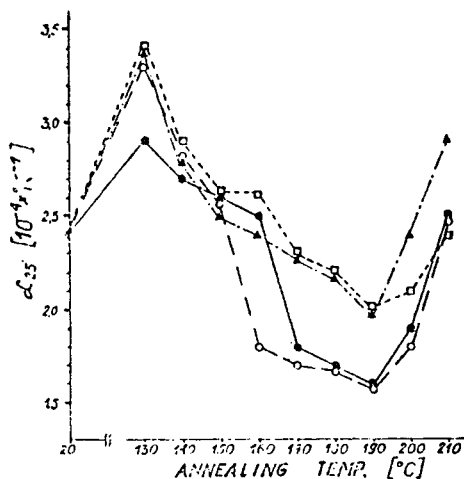


Fig. 1. Thermal volume expansivity coefficient α_{25} of annealed PET fibers (●—●) 2 min; (○—○) 5 min; (□—□) 10 min; (▲—▲).

in any particular structure parameter. This enables us to conclude that the ascertained alteration in α_{25} must be evoked by a complex change in different morphological and fine structure parameters of the fiber.

The explanation of the ascertained variation in α_{25} is complicated by the intricate essence of the volume expansivity of PET fibers. Similarly to other fibers, their thermal expansivity exhibits anisotropy and depends on the fiber crystallinity.

Neglecting the influence of orientation and considering a PET fiber simply as a system of anisotropic thermal expanding crystallites dispersed in isotropic thermal expanding amorphous matrix, the thermal volume expansivity of a fiber may be described by the expression

$$\alpha = x\alpha_{\parallel}^c + 2x\alpha_{\perp}^c + 3(1-x)\alpha^a \quad (2)$$

where x refers to the volume percent crystallinity, α_{\parallel}^c , α_{\perp}^c are the linear thermal expansivity coefficients, of the crystallites respectively, parallel and perpendicular to the direction of molecule axis, and α^a is the linear thermal expansivity coefficient of the amorphous regions. In attempting to elucidate the ascertained alternation in α_{25} resulting from annealing, we shall utilize the above equation. The observed increase in α_{25} within the first temperature interval explained in light of eq. (2) must be connected first of all with a strong enhancement of the component $x\alpha_{\parallel}^c$, to a minor extent, to an increase in the $2x\alpha_{\perp}^c$ component. The enhancing of the first term will be a result of increasing crystallinity x , and especially a very strong rise of α_{\parallel}^c . The last effect is, as has been discovered by Choy and co-workers,^{2,3} attributed to the reduction of ttm fraction. The increase in the second term will be in view of the independence of α_{\perp}^c from ttm fraction changes, only a consequence of increasing crystallinity. It may be assumed simultaneously that the change of the third term $3(1-x)\alpha^a$ will be of lesser importance. However, $(1-x)$ becomes smaller but α^a will still reveal large values because the intermolecular cohesion does not increase noticeably. As a result, the decrease of the third term is relatively small, but will prevail by the increasing of both the remaining terms of the sum.

The observed diminishing in α_{25} within the second temperature interval of annealing, compared to the first interval, may be attributed to the occurrence of a strong diminution of the component $3(1-x)\alpha^a$ and, to a lesser extent, to the reduction of the $2x\alpha_{\perp}^c$ term. The reason for the $3(1-x)\alpha^a$ decrease lies in a simultaneous decreasing of $(1-x)$ and α^a . The decrease in α^a will be a consequence of the strong growth of the intermolecular cohesion, which reduces the thermal expansivity of amorphous regions. The increase of intermolecular cohesion also can be recognized as the reason for α_{\perp}^c diminishing.

Analysis of the change of the last term $x\alpha_{\parallel}^c$ brings the conclusion that its growth will be relatively small (only a small further diminishing of ttm fraction). The influence of this growth will be outweighed by the diminishing of both remaining terms.

The explanation for the enhancement of α_{25} within the third annealing temperature interval, as compared to the second interval, needs to take into account additional new aspects of the fiber structure changes. As has

been stated by Fischer and Fakirov,^{4,5} in semicrystalline-oriented PET objects, a rebuilding of crystalline regions takes place as a result of annealing at temperatures $\geq 200^\circ\text{C}$. This rebuilding establishes the mosaic-block structure. In consequence, the density of crystalline regions decreases. The decrease in density must inevitably involve an essential growth in α_1^c . Taking this into account as the predominant reason of the observed α_{25} increase, the occurrence of the strong increase in $2x\alpha_1^c$ and the complementary simultaneously greater values of $x\alpha_{\parallel}^c$ should be recognized.

CONCLUSIONS

1. The performed investigations indicate that annealing of PET fibers in the loose state in air brings about an essential change of their thermal volume expansivity.

2. The alteration of thermal volume expansivity depends mainly on the annealing temperature, especially on the duration of the heat treatment. The influence of temperature manifests itself as three temperature intervals of annealing in which the thermal volume expansivity coefficient α_{25} attains different values. Within the temperature range $130\text{--}150/160^\circ\text{C}$, α_{25} values are greater than for the unannealed state and show a tendency to drop with increased annealing temperature. Within the temperature range $160\text{--}190^\circ\text{C}$ α_{25} values are smaller than for the initial state and become lower with increasing annealing temperature. Within the temperature interval $200\text{--}210^\circ\text{C}$, the α_{25} values, depending on duration of annealing, may be smaller or larger than for the initial state of the fiber. With increasing annealing temperature α_{25} increases.

3. The reason of such a specific layout of the relationship $\alpha_{25} = f/T_{\text{ann}}$ lies in the mutual competitive, counteracting effects of taut tie molecular fraction diminishing, crystallinity increasing, and intermolecular cohesion enhancement achieved by annealing. The alteration of morphological and fine structure resulting from annealing causes changes in α_{25} , which are in the course of things also a result of changed α_{\parallel}^c and α_1^c , of changed α^a .

References

1. Urbańczyk G. W., and G. Michalak, *J. Appl. Polym. Sci.*
2. Choy C. L., F. C. Chen, and E. L. Ong, *Polymer*, **20**, 1191 (1979).
3. Choy C. L., F. C. Chen, and K. Young, *J. Pol. Sci. Phys. Ed.*, **19**, 335 (1981).
4. Fischer E. W., S. Fakirov - *J. Mater. Sci.* **11**, 1041 1976.
5. Fakirov S., E. W. Fischer, R. Hoffman, and G. F. Schmidt, *Polymer*, **18**, 1121 (1977).

Received March 11, 1985

Accepted August 12, 1985