

The Influence of Annealing on the Thermal Properties of Poly(ethylene Terephthalate) Fibers I. The Heat Capacity of Annealed PET Fibers

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Synopsis

The influence of annealing of PET fibers on their specific heat capacity 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 obtained results give evidence that three temperature intervals of annealing may be distinguished. The ascertained variation of c_p has been discussed on the basis of established morphological and fine structure changes in the fibers caused by the applied annealing.

INTRODUCTION

Thermal treatment is one of the basic technological processes in the manufacturing and refinement of poly(ethylene terephthalate) (PET) fibers and finished products. Heat transfer causes an essential change in the morphological and fine structure of PET fibers. A direct consequence of these changes is an alteration of some physical and physicochemical properties of the PET fibers. Among the changes attributed to annealing are modification of the thermal properties, such as thermal resistivity, thermal conductivity, heat capacity, and thermal expansivity.

There is not yet adequate knowledge about the influence of annealing of PET fibers on their heat capacity, especially the recognition of the structural background of the variation of these thermal characteristics. In the present contribution an attempt has been made to extend the knowledge regarding the thermal property of PET fibers. The obtained results deliver not only some basic information about the influence of annealing upon the specific heat capacity, but also may be useful from the point of view of practical aspects of PET fibers processing.

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 the 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.

TABLE I
Morphological and Fine Structure Parameters of Examined PET Fibers

Annealing temp. (°C)	Annealing time (min)	Birefringence		Volume crystallinity xd (%)	ttm Fraction	Crit. dissol time (sec)	Amorph. orient. function (f_a)
		Δn	$\Delta n/d$				
Without	—	0.1286	0.1296	36.7	0.107	9	0.50
130	2	0.1681	0.1209	45.6	0.048	19	0.50
	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

Measurements

Assuming that the morphological structure of PET fibers is described by the widely accepted fibril-lamellar structure model introduced by Prevorsek,¹ the fraction of taut tie molecules (ttm) has been chosen as a parameter which decisively determines the morphological structure of the examined fibers. The ttm fraction of each sample has been estimated on the bases of measured fiber modulus E as a value resulting from the Takayanagi² model shown in Figure 1. Approximating the real morphological structure of a fiber by the Takayanagi model and assuming that taut tie molecules have the same modulus as the crystallites, the sought ttm fraction value b can be calculated from the relationship obtained by Mishra et al.³

$$b = \frac{V_a \cdot E(E_{\parallel}^c - E^a) - E^a(E_{\parallel}^c - E)}{V_a \cdot E_{\parallel}^c(E_{\parallel}^c - E^a) - E^a(E_{\parallel}^c - E)} \quad (1)$$

where E_{\parallel}^c is the crystalline modulus along the chain axis, E^a is the modulus of amorphous region, E is the measured fiber modulus along the fiber axis, V_a is the volume fraction of amorphous regions, $V_a = a(1-b)$.

The computation of ttm fraction in each sample has been performed by

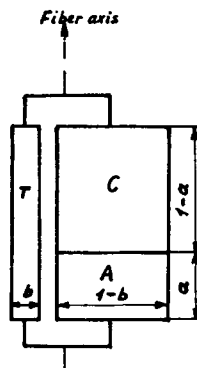


Fig. 1. Schematic representation of the Takayanagi model: C=crystalline block, A=amorphous region, T=taut tie molecules fraction.

following assumptions. As fiber modulus E has been taken as the tensile modulus calculated from the initial slope of the stress-strain curve ($\epsilon=2\%$) obtained in static mechanical measurements and carried out on an Instron strength tester. For E_{\parallel}^c the value reported by Sekurada and Kaji,⁴ $E_{\parallel}^c = 110$ GPa has been taken.

Regarding the dependence of E^a on the amorphous orientation function f_a , despite their relatively small alteration in our samples, differentiated values of E^a have been used in calculations. For the sample revealing the smallest f_a the value has been taken as $E^a = 2.1$ GPa, according the value reported by Choy et al.⁵ The E^a values for samples showing larger f_a have been established by multiplying the above value by a correcting factor. As the correcting factor has been applied, the quotient of f_a values refer, respectively, to the regarded sample and sample of smallest orientation, raised to a square. The V_a values have been calculated on the basis of measured volume percent crystallinity x_d as $V_a = 1 - x_d$.

As relevant fine structure characteristics of the examined samples, the overall orientation, the molecular orientation of the amorphous component of the fiber, the crystallinity, and the intermolecular cohesion have been chosen. The overall orientation has been evaluated on the basis of density-reduced birefringence, $\Delta n/d$. The molecular orientation of the amorphous component has been characterized by means of the orientation function f_a calculated from dichroic measurements of standard dyed fiber.⁶ Crystallinity has been evaluated on the basis of the volume percent crystallinity established by means of the flotation method in a mixture of *n*-heptane and carbon tetrachloride. Values of the critical dissolution time (CDT) in a mixture of phenol-tetrachlorethane 2:1 at 60°C have been used as a measure of intermolecular cohesion.⁷

The heat capacities of the examined samples were estimated at constant pressure from DSC diagrams using the relationship

$$c_p = H_s m_a c_{ap} / H_a m_s \quad (2)$$

where H_s and H_a refer to the amplitude of enthalpy change occurring as the temperature is increased from 20 to 25°C, respectively, for fiber sample

and reference substance (sapphire), m_s and m_a are weights of sample and reference substance, $c_{ap} = 775.4 \text{ J/kg.K}$ heat capacity of reference substance.

RESULTS AND DISCUSSION

The established c_p values for all examined samples are shown in Table II and demonstrated graphically in Figure 2. The obtained results give evidence that the heat capacity of PET fibers alters essentially as a result of applied heat treatment. The variation in c_p depends on both the annealing temperature and the time of heat treatment, their character is temperature dependent, as all thermal effects of annealing are strictly related to heat transfer from the surrounding fiber. The duration of annealing modifies only the relationship $c_p = f(T_{\text{ann}})$. It can be noted that, with increasing time, the effects of annealing become more strongly pronounced.

The obtained results allow us to conclude that three distinct temperature intervals of annealing of PET fibers exist, in which c_p attains a different level and undergoes different alterations with increasing temperatures of annealing.

The first interval corresponds to temperature zone 130–140°C. Within this zone, c_p after annealing is always larger than c_p of unannealed fibers and the increase in temperature is related to the increasing c_p . The second interval refers to temperature zone 150–170/190°C. Within this zone, c_p of annealed fibers is always larger than for the initial state, but the value of c_p diminishes with increasing temperature. The third interval pertains to temperature zone 170/190–210°C. Within this zone, c_p after annealing is always smaller than before and drops with increasing temperature to minimum, and then again reaches a higher level for the annealing temperature 210°C.

It may be noted that the duration of annealing does not influence the width of the first interval, whereas second and third intervals undergo alteration (i.e., the width of the second zone decreases and that of the third interval extends).

Comparing the changes in morphological and fine structure indices with

TABLE II
Values of Specific Heat Capacity c_p (cal/K⁻¹.g⁻¹)

Annealing temp. (°C)	Time (min)			
	2	5	10	30
130	0.412	0.363	0.396	0.376
140	0.421	0.453	0.429	0.441
150	0.405	0.442	0.452	0.433
160	0.398	0.428	0.474	0.344
170	0.332	0.415	0.380	0.340
180	0.323	0.241	0.346	0.227
190	0.305	0.192	0.254	0.194
200	0.151	0.167	0.226	0.090
210	0.140	0.163	0.216	0.097
Without		0.269		

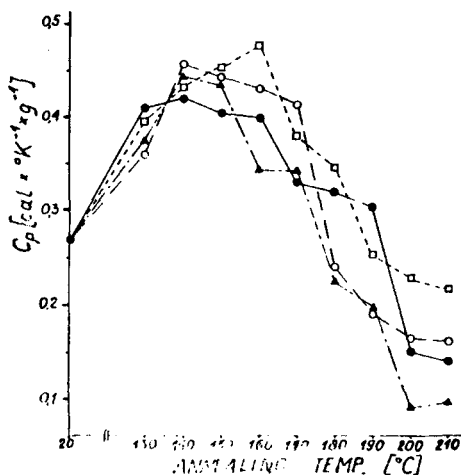


Fig. 2. Heat capacity c_p of annealed PET fibers., (●—●) 2 min; (○---○) 5 min; (□- - - -□) 10 min; (▲—▲) 30 min.

the alterations in c_p , it will be noticed that the change in c_p does not correlate with variation of any separate structure parameters. This leads to the conclusion that the ascertained alteration in c_p must be evoked by a complex change in different morphological and fine structure parameters.

A closer examination of the relations enables us to infer that the c_p values of annealed PET fibers are determined by a counteracting, mutually competitive influence of particular structure parameters. The level of c_p is always set by mutual opposite effects involved by the change of ttm fraction and overall orientation on one hand, and the change in crystallinity, on the other.

Heat treatment of fibers causes an increase in their internal energy. The increase in internal energy then demands a smaller amount of heat (i.e., will be characterized by smaller value of c_p), the lower the mobility of vibrating groups. This mobility will rise with decreasing ttm fraction, diminishing overall orientation, and will drop with increasing crystallinity.

The annealing within the first temperature interval (130-140 $^{\circ}$ C) leads to a relatively strong decrease in the ttm fraction compared to the increase in crystallinity and simultaneously to a drop of the overall orientation. Such changes must cause a noticeable increase in the internal freedom and through an elevated mobility of vibrating groups. Within the second temperature interval, the diminished ttm fraction resulting from annealing will be compensated for by the relatively strong increase in crystallinity. This and the drop in the overall orientation lead to a state of lower internal freedom and thus to lower mobility of the vibrating groups, which yields lower c_p values than for the first interval. Within the third temperature interval, the decrease in ttm fraction seems to be dominated by the very strong increase in crystallinity. This and the drop in the overall orientation must produce a strong reduction of internal freedom (reduction of vibrating groups mobility) which manifests itself by low c_p values.

The pronounced tendency to a renewed increase in c_p for annealing at 210 $^{\circ}$ C seems to be linked with the conversion of PET fine structure into the

so-called mosaic-block structure.^{8,9} It may be supposed that the level of internal freedom resulting from such rebuilding becomes higher; as a consequence, this leads to an increase in c_p .

CONCLUSIONS

1. The performed investigations indicate that annealing of PET fibers in the loose state in air brings about an essential change of their specific heat capacity.

2. The alternation of heat capacity depends mainly on the annealing temperature, and in the second range, on the duration of heat treatment. The influence of annealing temperature manifests itself as three temperature intervals, within which the heat capacity c_p attains different values and undergoes different alteration with increasing annealing temperatures. Within the temperature zone 130–140°C, the c_p values are greater than for the unannealed state and reveal a tendency to elevate with increased temperature. Within the 150–170/190°C zone, c_p values are also greater than for the initial state, but reveal a tendency to reduce with rising temperature. Within the 170/19–210°C range, the c_p values are smaller than for unannealed fibers and show a tendency to drop with increasing temperature.

3. The reasons of such specific layout of the relationship $c_p = f(T_{\text{ann}})$ lies in mutually competitive, counteracting effects of the diminishing ttm fraction and deterioration of the overall orientation on one hand and in the increasing of crystallinity on the other.

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