Cold-drawing Behavior of Naturally Aged poly(ethylene Terephthalate)

N. AVRAMOVA and S. FAKIROV, *University of Sofia, Laboratory on Structure and Properties of Polymers, 1126 Sofia, Bulgaria,* and J. M. SCHULTZ, *University of Delaware, Department of Chemical Engineering, Newark, Delaware, 19716*

Synopsis

The cold-drawing behavior of naturally aged poly(ethylene terephthalate) (PET) is investigated and an attempt is made to compare the mechanical behavior of unaged commercial PET and material which has been naturally aged for 11 years. Mechanical, viscometric, DSC and IR measurements are applied. The previously observed unusual ability of fresh PET bristles to be cold drawn up to 15:1 is not achieved for the naturally aged material. This fact is related to chemical cross-linking occurring on the surface of bristles after drawing and thermal treatment. The cross-linked skin is unsoluble, infusible, and uncrystallizable. The natural aging defeats the ability of PET to respond to external treatments which would otherwise change the internal structure. Such a "stabilization" of material properties is a result of the transformation, during natural aging, of the original physical network into a chemical network consisting of covalent bonds.

INTRODUCTION

The drawing behavior of poly(ethylene terephthalate) (PET) has been studied extensively over many years, especially the relationship between mechanical properties and the development of an oriented structure.[1-8]. The highest room temperature deformation ability is found for material which has been drawn (usually some 5 X) and subsequently annealed above 220°C.[3,6,7] This behavior originates mainly from the solid-state postcondensation and partially from partial melting phenomena taking place during annealing in vacuum.[7] It is to be noted, however, that different investigators have reported different maximum total draw ratios. Prevorsek and Sibilia[3] report a maximum draw ratio of 6.6, Slusallek and Zachmann[6] a maximum of approximately 15, and Fakirov and Stahl[7] also a maximum of 15.

It is well known that aging of any kind has a negative effect on polymer materials.[19] Of particular interest is the influence of natural aging. The best method for establishing the latter effect is the comparison of material properties before and after natural aging. Unfortunately, in most cases, this is not possible because of the necessity for long aging times. For this reason, accelerated aging conditions (artificial aging) have commonly been used for the same purpose.[10] In such cases, an approximation of the data received for the desired exploitation period is usually made, but is not always justified.[9]

To avoid this disadvantage to some degree in the present study, an attempt is made to compare the mechanical behavior of unaged and naturally aged (for 11 years) commercial poly(ethylene terephthalate). Among the me-

chanical properties of particular interest was the ability to attain an extremely highly drawn state at room temperature. Such behavior has already been found for the same material before aging.[7]

EXPERIMENTAL

The starting material for the present investigation originates from undrawn commercial PET bristles with a diameter of about 1 mm. They were amorphous according to X-ray examination.[7] The same bristles have been subjected to natural aging at room temperature without direct exposure to the sun for 11 years. The experiments described in Ref. 7 were performed in 1972 on the same lot of material, but during the year of its synthesis.

The aged bristles have a relative viscosity $\eta_{rel} = 1.4$ in a 0.5 % solution in phenol/tetrachloroethane (1:1) at 20°C. A portion of the bristles was drawn on an Instron machine at a rate of 0.05 cm/min at room temperature or at 65°C. The drawing proceeded until all material had passed through a neck (this corresponds to a draw ratio of about 4:1). The undrawn and drawn samples were isothermally annealed simultaneously, the undrawn ones with free ends, a part of the drawn ones with free ends, and another part with fixed ends. The annealing took place for 0.5, 3, 5, 6, and 24 h in a continuously pumped oven (oil pump) with residual pressure of nitrogen. The annealing temperatures T_a of 240, 250, 255, 260, 265, 270, 277, and 280°C were used in order to create conditions leading to an additional solid-state condensation.[7] Two types of heat treatment were applied: (i) by putting bristles into an oven previously heated to the desired temperature (fast heating) and (ii) starting with a cool oven and heating at 3°C/min (slow heating).

After the appropriate annealing duration some of the samples were air-quenched (fast cooling) and the others were cooled at 3°C/min (slow cooling).

The orientation and thermal treatment conditions for each set of samples are shown in Table I. Each sample has been subjected to a second-stage drawing at either room temperature or 70°C, with a rate of 0.05 cm/min, (i.e., the same as in the case of the first-stage drawing).

The following quantities have been evaluated after the second-stage drawing: the relative elongation at break (ϵ_b) and the stress at break (σ_b). For each sample set, at least 3 – 5 specimens have been tested. The value of ϵ_b and σ_b (as well as other measured quantities) are given in Table II.

For some of the samples (only those annealed for 24 h at 250, 260, and 270°C) the solubility in a mixture (1:1) of phenol and tetrachloroethane at room and elevated temperatures has been determined. These results are shown in Table II. The amount of polymer corresponds to a 0.5 % concentration. Given in Table II are the minimum temperature/time conditions necessary to effect dissolution. For the completely dissolved samples, the relative viscosity at 20°C has been measured. This quantity is also given in Table II. The solid residue of partially dissolved samples has been washed with the same solvent, followed by alcohol, dried and characterized by infrared (IR) spectroscopy and (DSC) differential scanning calorimetry measurements.

For all the samples used, the glass transition temperature (T_g), melting

TABLE I
Annealing Conditions of PET Bristles Drawn 4 X at 20° and 60°C and Their Redrawing Conditions

Sample no.	Annealing conditions					Redrawing		Notes
	T_a(°C)	t_a(h)	Heating	Cooling	With free or fixed ends	T(°C)	(%)	
1.	—	—	—	—	—	20	45	
2.	240	5	Slow	Fast		20	50	Treated accord.[12]
3.	260	6	Slow	Fast	Fixed	20	20	Treated accord.[11]
4.	250	24	Fast	Slow	Fixed	20	20	
5.	250	24	Fast	Slow	Free	20	20	
6.	260	24	Fast	Slow	Fixed	20	20	
7.	260	24	Fast	Slow	Fixed	70	20	
8.	260	24	Fast	Slow	Free	20	20	
9.	260	0.5	Slow	Fast	Free	20	50	First drawing at 60°C
10.	265	5	Slow	Fast	Fixed	20	20	
11.	265	6	Slow	Fast	Free	20	50	First drawing at 60°C
12.	250+260	2+1	Fast	Fast	Free	20	70	
13.	250+260	4+2	Slow	Fast	Free	20	100	All the samples
14.	250+260	4+2	Slow	Fast	Fixed	20	100	
15.	250+260	4+2	Slow	Fast	Fixed	70	100	
16.	255+265	4+2	Slow	Fast	Free	20	20	Redrawn
17.	255+265	4+2	Slow	Fast	Free	20	20	With 0.05 cm/min
18.	260+270	4+2	Slow	Fast	Fixed	20	20	
19.	260+270	4+2	Slow	Fast	Free	20	100	Exceptthe last one
20.	270	24	Fast	Slow	Fixed	20	20	
21.	270	24	Fast	Slow	Fixed	70	20	
22.	277	24	Fast	Fast	Fixed	20	20	(0.005 cm/min)
23.	277	24	Fast	Fast	Fixed	70	20	
24.	280	5	Slow	Fast	Free	20	20	
25.	260	6	Slow	Fast	Fixed	20	20	

TABLE II
Solubility, Mechanical, and Calorimetric Data of Naturally Aged Drawn and Undrawn Annealed PET Bristles

Sample no.	Annealed for 24 h at T_a(°C)	Soluble in Ph+TCE °C	min	Solid residue (%)	η_{rel}	[COOH][16]	Mechanical tests σ_B kg/cm²	ϵ_B (%)	T_g (°C)	T_m (°C)	w_c (%)	T_m of solid residue
Undrawn												
1.	Unannealed	80	30	—	1.40	$508 \cdot 10^{-6}$	—	300	82	256	0.28	—
2.	250	140	30	—	1.62	Gel	—	—	81	258	0.30	—
3.	260	140	60	—	1.63	Gel	510	—	82	264	0.32	—
4.	270	150	150	—	1.56	Gel	510	—	80	262	0.31	—
Drawn and annealed with free ends												
5.	Unannealed	80	30	—	1.40	$516 \cdot 10^{-6}$	2038	45	83	246	0.23	—
6.	250	150	180	0.4	—	Gel	2038	20	80	254	0.33	Unmelt.
7.	260	150	180	0.6	—	Gel	2038	20	80	261	0.31	Unmelt.
8.	270	150	180	0.8	—	Gel	2038	22	79	265	0.34	Unmelt.
Drawn and annealed with fixed ends												
9.	Unannealed	80	30	—	1.40	$516 \cdot 10^{-6}$	2038	45	83	246	0.23	—
10.	250	150	180	1.5	—	Gel	1987	17	80	255	0.35	Unmelt.
11.	260	150	180	4.0	—	Gel	1987	19	81	254	0.32	Unmelt.
12.	270	150	180	4.4	—	Gel	2293	21	80	252	0.28	Unmelt.

point (T_m), and heat of fusion ΔH_m have been determined by means of differential scanning calorimetry using a Perkin-Elmer DSC-2C. The heating rate was 20°C/min and the amounts used were about 5 mg. These results are also shown in Table II. On the basis of the ΔH_m data, the degree of crystallinity (w_c) was calculated, using $\Delta H_m^0 = 5.8$ kcal/mol.[11]

An attempt was made to determine the end carboxylic groups for each sample from Table II by means of the method proposed by Pohl.[12]

RESULTS

As mentioned above, the main purpose of this study is to determine to what extent natural aging affects the unusual ability of fresh PET bristles to cold draw up to 15:1 (in two stages with intermediate high temperature annealing in vacuum).[7] This high ratio could not be achieved by simply reproducing the techniques described by Fakirov and Stahl[7] and Slusallek and Zachmann[6] using bristles which were aged 11 years, therefore, different combinations of mechanical and thermal treatment have been used. These combinations, as well as the achieved relative elongation at break ϵ_b during the secondstage drawing (redrawing), are summarized in Table I. For the majority of samples the ϵ_b values are 20%, for some 50 and 70% (Samples 1, 2, 9, 11, 12) and for only 4 samples $\epsilon_b = 100$ % (Samples 13, 14, 15, and 19). The best results ($\epsilon_b = 100\%$) are obtained with a stepwise temperature increase (4 h at 250° or 260°C, followed by 2 h at 260° or 270°C, respectively, applying an initially fast temperature increase and rapid cooling after annealing. The positive effect on the ϵ_b value of the rapid cooling is reported by Slusallek and Zachmann for fresh PET films.[6] This cooling effect may be related to the retention of amorphous matter created by partial melting at temperatures close to the melting point.[13]

At the same time, it is well known that thermal treatment of linear polycondensates at elevated temperatures under vacuum promotes additional solid-state condensation, resulting in a molecular weight increase.[7,14] Such a change should contribute to the considerable increase of the relative elongation during the redrawing.[7] Although an increase of the molecular weight has been achieved (Table II), none of the aged samples reached the ϵ_b values of 200 % typical for the fresh PET bristles[7] or films.[6] Furthermore, while both starting materials—the fresh and the naturally aged (not subjected to mechanical or thermal treatments)—demonstrate almost the same relative elongation, the annealing of the aged bristles results in a decrease of redrawing ability, as shown in Figure 1. Obviously, this mechanical behavior of the aged material is due to the physical and chemical changes of the polymer taking place during the 11 years of aging.

In the case of fresh bristles, the elongation to fracture, ϵ_b, for bristles annealed with fixed ends was insensitive to annealing temperature up to an annealing temperature of 190°C. Beyond that temperature, ϵ_b increased steeply with annealing temperature, as shown by the triangle points in Figure 1. The strain to break of the unannealed but aged bristles lies near the same value as that of the unannealed fresh bristles. However, for the aged material, annealing at relatively high temperatures produces a decrease, rather than an increase, in ϵ_b (circles in Fig. 1).
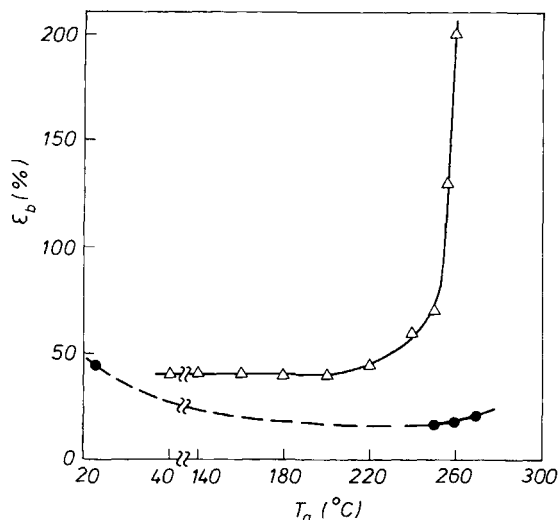
Fig. 1.   Dependence of the relative deformation at break (ϵ_b) on the annealing temperature for PET bristles: ($\triangle$) fresh one;[11] ($\bullet$) naturally aged during 11 years.

The behavior of the fracture stress for fresh and naturally aged material is also very different. Figure 2 shows the fracture stress, σ_b, for bristles annealed with fixed ends at various temperatures T_a. The temperature dependencies of the fresh (triangles) and the naturally aged (solid circles) materials are very different. One should especially note that in the temperature range over which the fresh material undergoes a large decrease in σ_b, the fracture stress of the aged bristles remains constant.

To test for cross-linking, or other chemical modification, the samples were tested for solubility in phenol/tetrachlorethane (1:1), for their solution viscosity, and for carboxylic groups. These results are shown in Table II.

As can be seen in Table II, annealing under vacuum at high temperatures leads to an increase in viscosity (i.e., an increase in molecular weight), reaching a maximum at $T_a = 260°C$ (Sample 3). At the highest T_a (270°) the η_{rel} value is lower, but still higher than that of the starting material (compare Sample 4 with Sample 1). At this extremely high annealing temperature a competitive chemical reactions appears (e.g., thermodestruction).

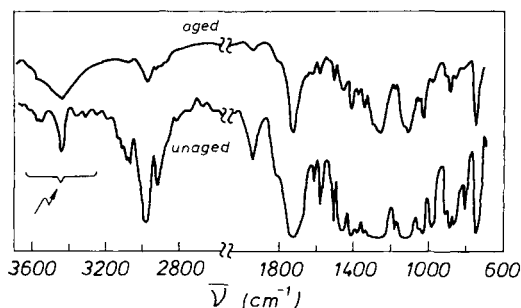For the undrawn samples an increase in the annealing temperature T_a

Fig. 2.   IR spectra for drawn fresh PET and for solid residue of a naturally aged PET, annealed at 270°C after drawing.

causes a decrease in solubility (Table II, Samples 1–4). A higher temperature and extended time were required even to dissolve the samples annealed at $T_a = 270°C$. During this dissolution some destruction may also occur and could contribute to the decrease of the measured η_{rel}, particularly since the dissolution at 150°C requires 150 min. It is *a priori* possible that the decreased solubility of the undrawn but annealed samples could be due to improved crystalline order (crystallite size and perfection) as a result of the thermal treatment. However, no remarkable change in the w_c values is observable and such an explanation is thereby unlikely. Thus, the limited solubility must originate from a molecular weight increase and/or from cross-linking.

Data for drawn samples is also shown in Table II. Basically the solubility depends on the annealing temperature and on whether the bristles were annealed with free or fixed ends. It should be noted that the orientation of the unannealed samples does not affect their solubility (Table II, Samples 1, 5, 9). All the drawn and annealed samples required a dissolution temperature of at least 150°C and a long dissolution time. The time required for dissolution increases with increasing T_a. It is worthwhile to note that in all these cases the dissolution process is incomplete. A solid residue remains even after 3 h heating at 150°C. The amount of residue is largest for the highest T_a values. Another peculiarity is that the amount of solid residue is larger for the drawn samples annealed with fixed ends than for those treated with free ends (Table II, compare Samples 6, 7, 8, and 10, 11, 12). The solid residues in these two cases differ even in their texture. The former are powderlike, while those from samples with fixed ends resemble thin (ca. 30 μm) films with almost the same length as that of the starting particles. Actually these filmlike solid residues represent the external shell of the bristles. After washing and drying they were examined by IR spectroscopy and DSC techniques (only for the drawn samples annealed at $T_a = 270°C$).

The IR spectra are shown in Figure 2. An increased hydroxyl group content in aged material, in comparison with the drawn unannealed fresh samples in the range 3650–3200 cm^{-1} can be established.

DSC curves for selected naturally aged specimens are shown in Figure 3. It is to be noted first that the undrawn samples display lower melting points than those drawn and annealed with fixed ends (Figs. 3 and 4; Table II). Fresh PET bristles, on the other hand, obey the general rule that annealed materials exhibit higher melting points than do unannealed,[15] due to the larger crystal thicknesses and increased perfection after annealing. In this context, the behavior of the aged material is highly unusual.

The difference of melting behavior between fresh and aged materials is further emphasized in Figure 4. Here, the melting points of bristles annealed with fixed ends are plotted against the annealing temperature, T_a. In the T_a range in which the melting point of the fresh material increases steeply, that of the aged material exhibits a small decrease. At 260°C the difference in melting points is 23°C. That the melting point of the aged material should be so relatively low is particularly surprising, since the fresh material was annealed only 6 h, as opposed to 24 h for the aged bristles.
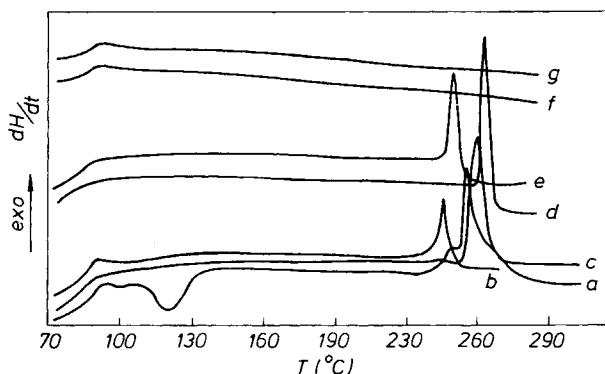
Fig. 3. DSC curves of naturally aged PET bristles: (a) undrawn, unannealed; (b) drawn, unannealed; (c) undrawn, $T_a = 270°C$; (d) drawn (free ends), $T_a = 270°C$; (e) drawn (fixed ends), $T_a = 270°C$; (f) solid residue of sample (e); (g) same sample after isothermal crystallization.

DSC curves for the undissolved residue are shown in Figure 3. Up to 300°C no melting peak can be observed for the unsoluble residue of aged material annealed with fixed ends at 270°C. A well-expressed glass transition appears, however, in this case, just as for all other samples studied. After the first heating in the DSC instrument, the same insoluble residue sample was cooled to 140°C and held at this temperature for 60 min in order to crystallize, and thereafter, cooled to room temperature. Subsequent DSC heating up to 300°C results in the same thermogram as obtained in the first heating (compare curves f and g). This result demonstrates that the solid residue of the drawn sample annealed with fixed ends at $T_a = 270°C$ (representing the external shell of the bristle) is amorphous and unable to crystallize, due probably to cross-linking.

As mentioned earlier, the measured heats of fusion were used to calculate degrees of crystallinity. The data is tabulated in Table II. A comparison between the crystallinities of fresh and aged materials which have been drawn and annealed with fixed ends is shown in Figure 5. It is seen that, for all annealing temperatures, the crystallinities of the aged specimens fall well below those of the fresh.
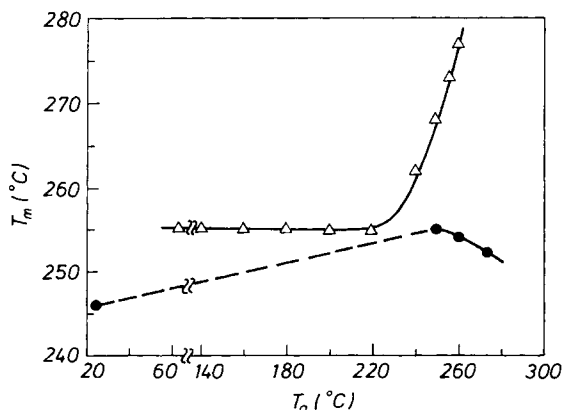

Fig. 4. Dependence of the melting point (T_m) on the annealing temperature (T_a) for PET bristles: (△) fresh;[11] (●) naturally aged during 11 years.

Discussion

The core of the interpretation of the results lies in the possibility that chemical cross-linking has taken place. In the fresh fibers, the mechanical properties are controlled by a time- and stress-dependent entanglement network. Cross-linking would shift that control toward a stable chemical network.

The existence of entanglements in PET has been investigated by several authors.[8, 16-18] Such physical entanglements have been used to explain the drawing behavior of this polymer in terms of the deformation of a molecular network. An entanglement network is described as follows. The macromolecules in the amorphous regions are linked to one another to form a network structure similar to that of a cross-linked rubber. However, the cross-links in the PET samples are physical in nature. They are comprised of chain entanglements within the amorphous regions, as well as intermolecular bonding forces at the amorphous-crystalline interface. That portion of the polymer chain between successive "crosslink points" is defined as a network chain. Each network chain is assumed to consist of several statistical links that can freely rotate about their main chain bonds. The statistical, randomly orienting link is comprised of several repeat units of the polymer.[19,20] It is found that the formation of a permanent physical network is very sensitive to the molecular weight.[21,22] It is reported also that the influence of the molecular weight on mechanical drawing can be due to either of two effects: (i) by an increase of the entanglement density with an increase in molecular weight and (ii) by a decrease of the chain slipping with increasing molecular weight.[23]

The results described above, as well as the fact that gel formation during determination of end carboxylic groups occurs (Table II), lead to the conclusion that the physical network of entanglements is at least partially transformed into a chemical network. The discovery of an insoluble skin is direct evidence for this conversion. The details of the conditions under which the insoluble residue forms are themselves interesting. Under identical thermal treatment conditions for drawn and undrawn material, only in the case of drawing and then annealing with fixed ends does one find an insoluble, noncrystallizable, infusible residue. The reason for this could be related to the fact that only when the ends are held fixed are the entanglement nodes stationary during annealing. For undrawn material or drawn bristles annealed with free ends, the molecules are able to slip through the entanglement nodes and relax.

There are at least four basic factors leading to chemical cross-linking in the present case: (i) long-term natural aging, (ii) thermal treatment at elevated temperatures and vacuum, (iii) orientation, and (iv) restriction of the relaxation processes during annealing due to fixed ends and the increasing of tension at the entanglement points. The importance of the last factor (iv) has been pointed out by Wunderlich,[24] who assumes that the chemical reactivity in the stressed entanglement points is considerably increased. Recently this statement has been supported by results on chemical healing (i.e., welding as result of chemical reactions at the contact surface of two polymer samples of linear polycondensates). This welding is

carried out for sheets under compressive stress (tension in the plane of the sheets), at temperatures below the onset of melting. It has been demonstrated[25] that solid-state transreactions between chains proceed rapidly and to a greater extent with partially (only in the amorphous regions) chemically cross-linked samples of nylons. This observation is explained by the restriction of chain mobility in amorphous regions due to the cross-linking. Thus a higher tension and a higher reactivity are achieved.

Both orientation and annealing with fixed ends improve the intermolecular contacts and, particularly in the entanglements points, the tension significantly favors the chemical reactions between contacting macromolecules. A reasonable question is why these effects are pronounced only with naturally aged material and not with fresh ones, where the same physical network exists. Probably additional chemical processes take place during the aging (e.g., formation of peroxide or hydroperoxide groups), which enhances the chemical cross-linking. In favor of this assumption is the observed increased hydroxyl group content in the insoluble residues (Fig. 2).

The mechanical behavior and the viscometric results also lead to the conclusion that chemical cross-linking has occurred. Viscometric results here as well as reported by other authors[14] show that annealing of undrawn PET at successively higher temperatures produces successively higher relative viscosity (i.e., higher molecular weight). Such a molecular weight increase should lead to higher levels of elongation at break (ϵ_b). On the other hand, it was found in the present case that annealing of drawn and aged material gave rise to a very large decrease in ductility, compared both with undrawn aged material and with drawn fresh material. At the same time the tensile strength of the aged material which has been drawn and annealed has maintained a constant level, even higher than that of the fresh bristles drawn and subsequently annealed above 250°C. This combination of results can be explained neither by a molecular weight increase via postcondensation nor by a molecular weight decrease via oxidative processes. The former would have produced greater ductility. The latter would lead to a marked decrease in the tensile strength, especially for the higher annealing temperatures.

A model which is consistent with mechanical behavior and the other results follows. The overall degree of cross-linking increases with increasing annealing temperature. The most extreme cross-linking occurs in a surface shell. The reason for the large cross-linking in the shell is likely the higher degree of orientation there, but could also be due to a requirement that reaction products diffuse out of the material. It is expected that cross-linking occurs in the core of the bristle, as well as the shell, as this material is also highly oriented. Fracture must begin with cracks in the shell and work across the bristle. The cracks in the shell may originate from thermal stresses during the cooling of the bristles from the melt or they may be created under the redrawing stress, the fixed, chemical crosslinks being points of relative weakness. In either case, the initial crack should go through the shell. There are now two quantities which increase with annealing temperature. One is the overall modulus E of the bristle (especially the core). This modulus must increase approximately linearly with the degree of cross-linking. The other quantity is the thickness of the stiff shell

and consequently of the initial crack length C. These should also increase approximately linearly with the degree of cross-linking. According to simple fracture theory, the fracture stress σ_b is proportional to $\sqrt{E/c}$. Since both E and c change in the same way with the degree of cross-linking (i.e., with $T_a - \sigma_b$) must remain constant, so long as this mechanism for fracture holds. On the other hand, the strain at failure ϵ_b is given approximately by σ_b/E and must decrease with annealing temperature, since E is increased.

Recall that an unusual melting point trend was observed. For the naturally aged material, the undrawn annealed samples display higher melting points than do those drawn and annealed with fixed ends. The fresh PET samples, on the other hand, exhibit the generally accepted situation–higher melting points for drawn material, due to the more favorable crystal growth and perfection conditions.[15]

The observed difference originates again from the chemical cross-linking of the aged samples, which are not able to reorganize at elevated temperatures during the temperature scanning in the calorimeter, in contrast to the undrawn ones, for which the network is not so effective. The chemical cross-linking restricts the crystallization processes during the annealing with fixed ends. It is to be noted also that there is a depression in the melting point of 11°C even for aged undrawn samples compared with fresh ones[19] (Table II). Since the undrawn aged material also forms a gel at elevated temperatures, this melting-point depression is reasonable. This interpretation of melting point effect is in line with the observation that degrees of crystallinity are always lower in aged annealed material than in fresh aged material.

Similar depression in T_m due to the chemical cross-linking has been observed on various nylons.[26-28] It has been demonstrated that partially cross-linked (only in the amorphous regions) nylons display a significantly lower melting point than the uncross-linked material because of the restricted motion of chain (i.e., suppressed recrystallization ability during scanning in the calorimeter).
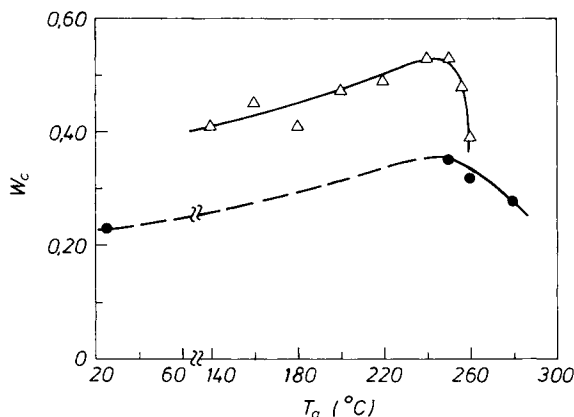

Fig. 5. Dependence of the degree of crystallinity (W_c) measured by DSC on PET bristles: (△) fresh ones;[11] (●) naturally aged during 11 years.
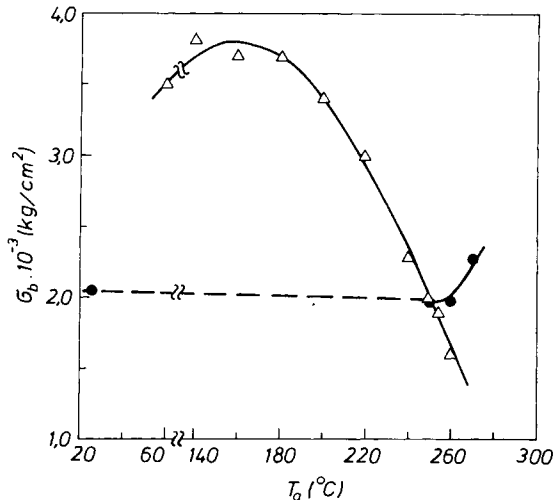
Fig. 6. Dependence of stress at break (σ_b) on the annealing temperature (T_a) for PET bristles: ($\triangle$) fresh;[11] ($\bullet$) naturally aged during 11 years.

During the discussion of the data in Table I, it was emphasized that the highest values of relative elongation are obtained after a stepwise T_a increase. The comparison of T_m and T_a (Table II) suggest a partial melting of material. This partial melting can be fixed only by quenching after annealing (Table I). The partial melting should act to increase ϵ_b. The experiments demonstrated that only after quenching of samples annealed at high temperatures could a relative elongation of 100% be achieved (Table I). Since the relative elongation is limited by the network (physical or chemical), the increased ϵ_b must originate from the additional amorphous material formed during partial melting. This result supports once again the statement that cross-linking takes place exclusively in the amorphous regions of PET.

Comparing all the data leads to an interesting conclusion. The aged material has quite a different response to external thermal or mechanical treatments in comparison to the fresh material (Figs. 1, 3–6). The aged material retains its properties regardless of the additional treatment. One can say that the aged material has lost its ability to respond to external treatments which could change its internal structure. Such a "stabilization" of material properties is a result of the transformation during the natural aging of the original physical network (originating mainly from entanglements) into a chemical network consisting of covalent bonds.

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