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Influence of molecular weight on the microhardness of poly(ethylene terephthalate)

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Abstract Poly(ethylene terephthalate) (PET) was annealed in vacuum at different temperatures (190–260 °C) for different times (10 min–24 h) in order to examine the mechanical properties (microhardness) of PET samples with a wide range of molecular weights (10 000–120 000). Short annealing times result in a twofold decrease in mol. wt. due to hydrolytic decomposition. However, long annealing times give rise to a substantial molecular weight increase. It is found that microhardness (H) rises linearly with the degree of crystallinity obtained during up-grading of mol. wt. and its extrapolation leads to H-values of completely crystalline PET, $H_c^{PET} = 405$ MPa for samples with conventional mol. wt. and of 426 MPa for samples with mol. wt. higher than 30 000. It is shown that the increase of mol. wt. for each set of samples with a given range of degree of crystallinity also causes a slight increase of H. The influence of mol. wt. upon hardness is discussed in the light of the changes in the physical structure (crystallinity, crystal thickness) which is formed at given heat treatment conditions.

Key words Poly(ethylene terephthalate) – microhardness – crystallinity – high molecular weight

Introduction

Since its commercialization roughly 50 years ago poly(ethylene terephthalate) (PET) enjoyed manifold applications, ranging from clothing via capacitors and magnetic tapes to beverage bottles. Such a wide spectrum of uses implies widely different techniques and conditions of processing as well as various final polymer properties.

The three basic processing approaches, namely spinning, injection moulding and extrusion require different melt viscosities of the polymer. The common way for increasing of viscosity is the up-grading of the molecular weight. The fiber grade PET has typically a mol. wt. of about 20 000–22 000; for injection moulding and extrusion the mol. wt. should be around 26–28 000 and more [1].

It is well known that PET with higher mol. wt. cannot be obtained during its primary synthesis for a simple

reason – the increase of the melt viscosity hampers the stirring process. Decrease of viscosity by temperature increase is not the best solution because of occurrence of thermal decomposition. For this reason the synthesis of PET with mol. wt. higher than that of the fiber grade one is based on the inherent property of condensation polymers to undergo additional (post)condensation [2, 3]. Thermal treatment at temperatures close to but below T_m and eventual application of vacuum enhance the additional condensation. At the same time such a treatment results in a development of crystallinity which is undesired because it restricts or even eliminates the movement of chain ends necessary to come together in order to react for up-grading of the mol. wt. For this reason one needs hours in order to get molecular weights above 30 000. Temperatures below 180–190 °C are too low for occurrence of these reactions [3].

Another motivation for obtaining PET with higher mol. wt. was the attempt to apply the gel-spining technique to PET similarly to polyethylene where fibers with outstanding mechanical properties have been manufactured [4]. The materials studied in the present work were synthesized with this purpose in mind, following the reports on synthesis of PET with mol. wt. of a couple of hundreds by applying the solid-state postcondensation [5]. In addition, the PET samples with various mol. wt. (ranging from 10 000 up to 120 000) investigated in the present study offer the opportunity to examine the dependence of microhardness on mol. wt. similar to the case of other polymers [6, 7]. While in the case of polyethylene [6] very high molecular weights were covered, in a subsequent study on polyethylene oxide [7] the smallest mol. wt. were followed. In the second case a strong effect of mol. wt. on microhardness was registered and explained by the fact that the range of mol. wt. studied coincides with the transition from oligomers to polymers.

During the last two decades it was demonstrated [8–15], that microhardness technique as a nondestructive method, due to its simplicity and high sensitivity, makes it possible to derive relevant information about the structure of polymers. Relationships between microhardness and polymer crystallinity, crystal perfection, chain conformation and other structural parameters have been derived [8, 10, 15]. Hardness of polymers can also be correlated with many of their mechanical properties [8–11], which makes such measurements a fast and convenient method for material characterization. The microhardness technique has also been proved to detect polymorphic phase changes in polymers [12], and especially changes in polymer blends with composition [13, 14].

The purpose of the present work is to complement our previous studies on the effect of mol. wt. on the microhardness of polymers [6, 7] to the case of a range of intermediate molecular weights. For this purpose samples of PET with different mol. wt. (in the range 10 000 up to 120 000) were prepared by means of solid-state postcondensation [3]. The primary aim of the study was to distinguish between the contribution of the crystallinity and mol. wt. to the measured hardness value, as both quantities are developed simultaneously during the thermal treatment.

Experimental

Sample preparation

The starting PET was synthesized by applying a melt-condensation technique with Mn/Sb mixed catalyst. From this material (with $\bar{M}_v = 61\,300$) amorphous films were prepared by keeping samples for 4 min at 290 °C in a press followed by pressing the melt between two steel foils under 80 bar for 20 s under continuous pumping. Thereafter the material was quenched in ice water. From these amorphous films (samples S_1 and S_2, Table 1) PET with higher molecular weights were prepared by combination of appropriate annealing temperature and annealing time. The sample designation, treatment conditions as well as some characteristics of the samples obtained are summarized in Table 1.

The dried amorphous films (set S, Table 1) were treated at the respective annealing temperature (T_a), and time (t_a), (Table 1) under rotary pump vacuum using a frame of silicon rubber between the hot plates of the press. Finally, the films were quenched in ice water. The thickness of the obtained films was of 210 μm. Only sample D_1 was heated in an oven at a rate of 8 °C/min up to 260 °C, and after 6 h it was cooled down to room temperature in the oven. For the preparation of samples A_1–A_4 and B_4 the sample S_1 was used as a starting material. For the rest of samples (series B–D) samples S_2, characterized by a higher mol. wt., was employed as the starting polymer (Table 1).

Techniques

The degree of crystallinity (w_c) was calculated from the density (ρ) values. The latter was determined by means of gradient column using two intervals, from 1.33 up to 1.37 g/cm^3 and from 1.38 up to 1.43 g/cm^3 applying a mixture of tetrachloromethane and heptane. For the evaluation of w_c in wt% the following equation was used:

$$w_c = \frac{\rho_c}{\rho} \cdot \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)}, \quad (1)$$

Table 1 Sample designation, treatment temperature T_a and duration t_a, density ρ, the respective degree of crystallinity w_c, mol. wt. $\bar{M}_v$ and microhardness H of PET

Sample designation	Annealing		ρ [g/cm^3]	w_c [wt%]	$\bar{M}_v$ [g/mol]	H [MPa]
	T_a [°C]	t_a [min]				
Starting material, S	—	—	—	—	59 800	—
S_1	290	4	1.337	1.9	23 100	122
A_1	190	10	1.393	35.6	18 200	214
A_2	190	60	1.399	38.7	20 100	230
A_3	190	360	1.401	39.7	28 300	233
A_4	190	1440	1.401	40.1	25 900	234
S_2	290	4	1.336	1.8	34 000	143
B_1	230	10	1.409	44.6	23 200	243
B_2	230	60	1.403	41.3	45 500	240
B_3	230	360	1.405	42.5	97 800	259
B_4	230	1440	1.422	51.8	84 900	256
S_2	290	4	1.336	1.8	34 000	143
C_1	240	10	1.401	40.2	10 800	232
C_2	240	60	1.413	46.8	15 600	254
C_3	240	360	1.415	48.0	26 000	263
C_4	240	1440	1.402	40.6	121 300	246
D_1	260	360	1.4244	53.1	65 900	303

where ρ is the measured value of the density, ρ_a and ρ_c are the densities of the completely amorphous and fully crystalline PET, respectively. The following values were used, for $\rho_a = 1.334$ g/cm^3 and for $\rho_c = 1.515$ g/cm^3 [16].

For the evaluation of mol. wt. the viscosity of a solution of 0.2 g PET in 40 ml 1,1,1,3,3,3-hexafluorisopropanol (HFIP) was measured. The intrinsic viscosity was derived only from one measurement applying the equation [17, 18]:

$$[\eta] = \frac{1}{c}\left[\frac{\eta_{sp} - \ln \eta_{rel}}{\kappa' + \kappa''}\right]^{0.5} \quad (2)$$

where $[\eta]$, η_{sp} and η_{rel} are the intrinsic, specific and relative viscosities, respectively and c the polymer concentration. For κ' and κ'' the following values were used $\kappa' = 0.33$ and $\kappa'' = 0.132$. These values of κ' and κ'' were obtained by means of calibration measurements using PET samples with known mol. wt. [19]. The molecular weight was calculated from the Kuhn–Mark–Houwink equation:

$$[\eta] = \kappa M_v^{\alpha} . \quad (3)$$

The constants for PET dissolved in HFIP are $\alpha = 0.695$ and $\kappa = 5.2 \times 10^{-4}$ ml/g [20].

Microhardness (H) was measured at room temperature using a Leitz tester equipped with a square-based diamond indenter. The H-value was derived from the residual projected area of indentation according to the expression

$$H = k\frac{P}{d^2}\,(\text{Pa}) , \quad (4)$$

where d is the length of the impression diagonal in meters, P, the contact load applied in N and k is a geometrical factor equal to 1.864. A loading cycle of 0.1 min and loads of 0.5 and 1 N were used. Ten measurements for each point were averaged.

Results

The density, the degree of crystallinity, molecular weight and microhardness values for the different samples investigated are summarized in Table 1.

Let us highlight the effect of the very first heating (or melting of the starting material) on the mol. wt. One can see that, both, the melting at 290 °C only for 4 min and the shortest annealing used ($t_a = 10$ min) at the respective annealing temperature (190 °C, 230 °C and 240 °C, Table 1) result in a strong decrease of mol. wt. Melting leads to the decrease of mol. wt. by 50% (compare starting material with samples S_1 and S_2, respectively, Table 1).

The first annealing step induces a further decrease of mol. wt., particularly at 240 °C by more than another 50% (compare sample S_2 with sample C_1, Table 1). The observed changes in the mol. wt. after short thermal treatment (few minutes) are due to hydrolytic decomposition of PET caused by the residues of moisture in the samples because of incomplete drying [3]. Only after removal of these water traces the mol. wt. increases due to the dominant additional solid-state condensation, as can be

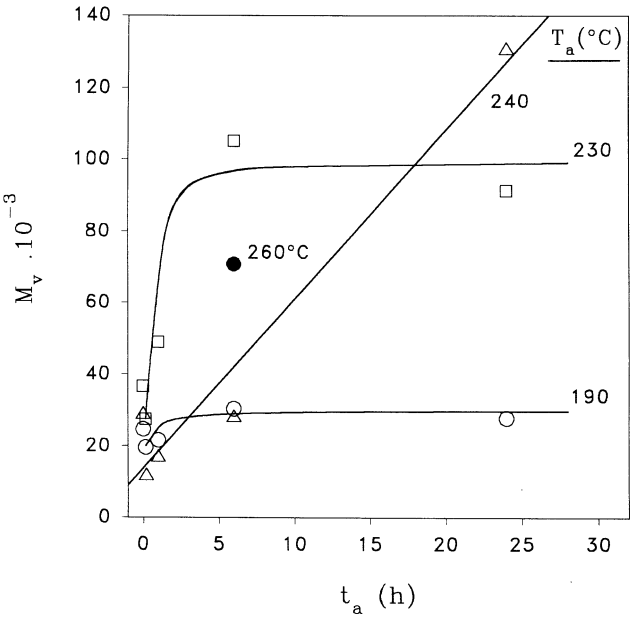

Fig. 1 Dependence of mol. wt. $\bar{M}_v$ for films of PET upon annealing time t_a for various annealing temperatures T_a (°C): (○) – 190, (□) – 230, (△) – 240, (●) – 260

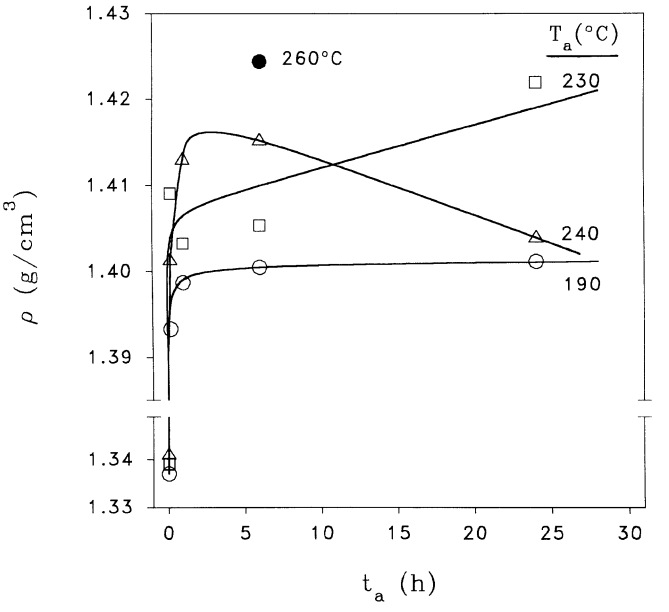

Fig. 2 Variation of density ρ of films of PET as a function of annealing time t_a for various temperatures T_a (°C): (○) – 190, (□) – 230, (△) – 240, (●) – 260

concluded from the data of Fig. 1. The variation of mol. wt. with annealing conditions is illustrated here. One can see that both factors, T_a and t_a, have a strong effect on mol. wt. Only, the annealing temperature of 190 °C is shown to be not sufficiently high for the occurrence of noticeable additional condensation. For this reason no increase in the mol. wt. can be observed at this temperature regardless of the annealing time. This result supports previous reports on the effect of T_a on mol. wt. [3]. When the temperature is closer to T_m, i.e. 230 °C and 240 °C an increase of mol. wt. can be observed within few to several hours (Fig. 1, 230 °C and 240 °C). The result that at $T_a = 230$ °C the increase of mol. wt. is faster than that at $T_a = 240$ °C is related to the above mentioned hydrolysis effect. Indeed, the starting annealing step (10 min) at 240 °C creates a stronger decrease of mol. wt. in comparison to the same 10 min step for 230 °C, i.e. a value of 11 600 in contrast to 25 000 (samples C_1 and B_1, respectively, Table 1). Therefore the slopes of the two lines are quite different. Regardless from the fact that for shorter annealing times (up to $t_a = 5$ h) a doubling of the mol. wt. occurs, the absolute values of molecular weight are still higher for the lower annealing temperature (230 °C, Table 1, Fig. 1).

From the data presented in Fig. 1 one can conclude that by an appropriate combination of annealing temperature and annealing time it is possible to obtain PET samples with rather different mol. wt. ranging from 10 000 up to 120 000 (Table 1). In addition, one sees that an increase in mol. wt. can only be expected after annealing times beyond 2–3 h. For shorter treatment times decomposition processes leading to a decrease of mol. wt. dominate (see Table 1).

It should be noted that the applied treatment conditions for up-grading of mol. wt. of PET and particularly the selected temperatures (190–240 °C) correspond to the most optimum crystallization temperatures of PET. For this reason, in addition to the observed chemical changes, parallel intensive physical processes are taking place as illustrated in Fig. 2. This figure depicts the change of the density ρ as a function of the annealing time t_a for different annealing temperatures T_a. One immediately sees the very strong effect of T_a on the ρ-values. On the other hand, prolonged annealing times t_a do not play an essential role because the rapid increase in ρ takes place practically within the very first hour of treatment (Fig. 1, Table 1). The obtained strong decrease in the ρ-value after a treatment time of $t_a = 24$ h for the 240 °C annealed sample can be associated to partial melting as reported earlier [21].

Table 1 also shows the parallel increase of microhardness with the degree of crystallinity. Figure 3 illustrates the linear increase of H as a function of degree of crystallinity for two groups of samples differing in molecular weight.

Discussion

The data presented in Table 1 and plotted in Figs. 1 and 2 show that by using different combinations of treatment

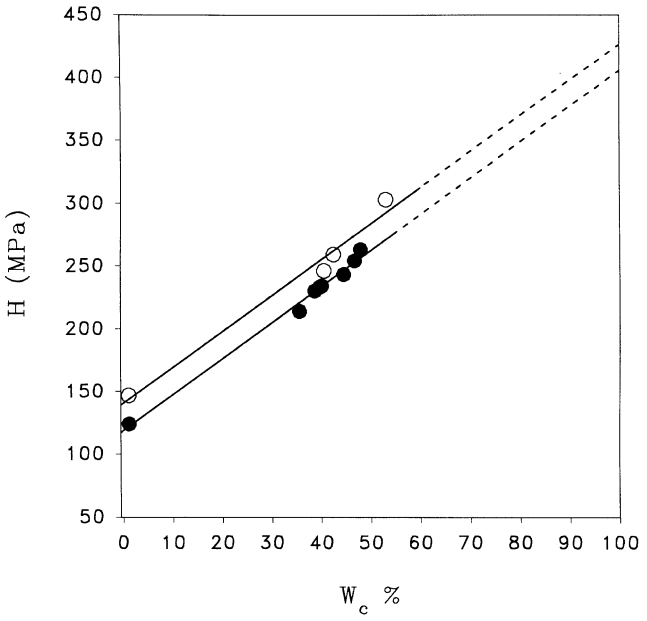

Fig. 3 Dependence of the microhardness H on the degree of crystallinity w_c for two sets of PET films differing in their mol. wt.: (●) – between 10 000 and 30 000, (○) – above 30 000

conditions it is possible to vary both the mol. wt. and the crystallinity of PET (Table 1). In order to examine only the effect of the crystallinity on microhardness, one has to select samples with approximately the same mol. wt. This is illustrated in Fig. 3 where the dependence of H on w_c is plotted for two sets of PET samples. The first set comprises samples with $M_w = 10\,000$–$30\,000$ and corresponds to PET conventionally used for various applications [1]. The second set refers to samples characterized by mol. wt.-values above 30 000 and higher.

From Fig. 3 we can write: $H = (H_c - H_a)w_c + H_a$ with a contribution of the amorphous and crystalline zones to the hardness H_a and H_c, respectively. The results suggest that the PET samples with lower molecular weight (10 000–30 000) show a lower H_a value than the higher molecular weight samples ($> 30\,000$).

First of all it should be noted that all the H and w_c measurements for the samples with lower mol. wt. correlate very well with each other lying perfectly on a straight line. These results (Fig. 3) demonstrate the most essential contribution of crystallinity, among other factors, to the microhardness value. Such a dependence of H on w_c makes it possible to obtain H-values for a fully crystalline PET (H_c^{PET}). The extrapolation of the experimental data leads to a value: $H_c^{PET} \simeq 405$ MPa.

Considering the dependence of H upon w_c the following observation should be noted. In contrast to previous measurements [22] on PET samples treated in a similar way, the present H-values are slightly higher. A possible explanation for the observed difference in the behavior of H could be the different extent of chemical interactions (additional condensation and transreactions) in both cases due to the different catalyst system used. In the former study [22] the annealing was carried out without any or in presence of Mn-catalyst and in the present work a mixed Mn/Sb catalyst is used. It has been demonstrated that the additional condensation and transreactions taking place in the crystalline phase result in perfectioning of crystallites [23]. The more intensive chemical reactions, as can be concluded from the increase of molecular weight (Table 1) admittedly lead, in the present case, to much more perfect crystallites with better mechanical properties, contributing in this way to the increased H of the treated samples (Fig. 3).

The obtained values are not far from the recently reported data for high-pressure crystallized PET with conventional mol. wt. [24].

The second set of samples, distinguished by much higher mol. wt., shows the same strong effect of w_c on H. The fact that both straight lines are nearly parallel to each other can be interpreted as an indication that the crystallinity contributes to the microhardness value in the same way regardless of mol. wt. values. The extrapolation to fully crystalline sample yields to $H_c^{PET} \simeq 426$ MPa.

Starting from the mutual position of the two straight lines, in Fig. 3 one can derive a preliminary conclusion concerning the effect of mol. wt. on microhardness – the samples with higher mol. wt. are characterized by slightly higher H-values.

This dependence is better illustrated in Fig. 4 where H is drawn as a function of mol. wt. Again two sets of samples, characterized by similar values of w_c, regardless of their treatment conditions, can be distinguished. The first set consists of samples having w_c-values of 39–42% and the second set refers to w_c-values above 45%. By taking into account the contribution of crystallinity to the microhardness one can conclude from the two straight lines (Fig. 4) that the increase of mol. wt. results in a slight but systematic increase of microhardness for the two sets of samples. Again the samples with higher mol. wt. display higher H-values as concluded from Fig. 3.

How can the observed relationship between mol. wt. and microhardness be explained? Obviously the effect of mol. wt. on microhardness is transferred via the physical structure (crystallinity and crystal thickness) arising during the respective treatment. By starting from the very general knowledge about the effect of mol. wt. on structure formation in polymers, one hardly can expect that species with highest mol. wt. are distinguished by the most perfect structure resulting in the highest H-values. This apparent contradiction is related to the peculiarity in the

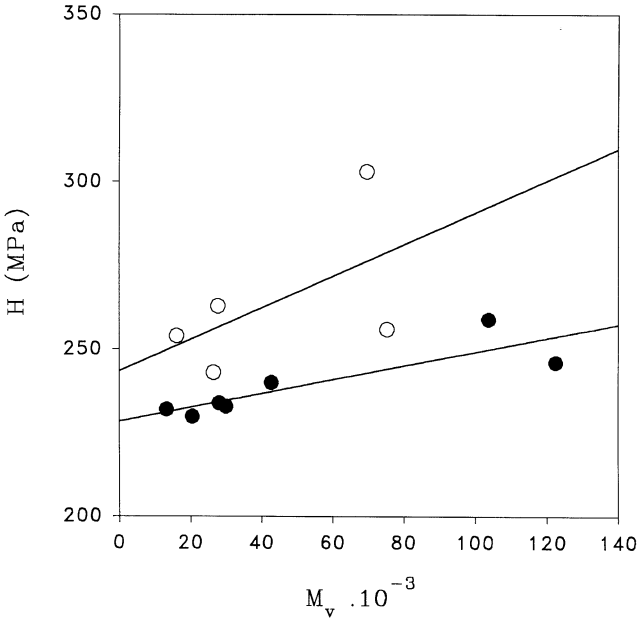

Fig. 4 Dependence of the microhardness H on the mol. wt. $\bar{M}_v$ of two sets of PET films differing in their degree of crystallinity w_c: (●) – w_c between 39% and 42%, (○) – w_c between 43% and 53%

preparation of PET samples with higher mol. wt. Since this is done by means of long annealing times at very high temperatures favoring the formation of a rather perfect structure, the samples with the highest mol. wt. values are expected to present also the most perfect structure. This suggestion is supported by the data displayed in Fig. 4. The PET samples characterized by the higher H-values have crystallinities around 50% while the set with lower H values has crystallinities of only nearly 40%. The dependence of H on mol. wt. might be related with changes in the lamellar thickness as shown in previous studies [22, 24].

Conclusions

In summarizing the results obtained, one may conclude that the influence of mol. wt. on hardness can be explained through the specific microstructure arising for a given set of treatment conditions. For a completely amorphous material having a preserved chemical composition there are no obvious reasons to expect a significant influence of mol. wt. on microhardness as demonstrated by the present measurements.

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