Structure Development in Poly(ethylene Terephthalate) quenched from the Melt at High Cooling Rates: X-ray Scattering and Microhardness Study

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Abstract

The structure and microhardness of poly(ethylene terephthalate) (PET) cooled from the melt, using a wide range of cooling rates, was studied. PET thin films rapidly cooled from the melt (cooling rates larger than 5°C/s) show a continuous variation of structure and properties depending on cooling rate. Results highlight differences in the micro-mechanical properties of the glass suggesting the occurrence of amorphous structures with different degree of internal chain ordering. The comparative X-ray scattering study of two glassy PET samples (7500°C/s and 17°C/s) reveals the occurrence of frozen-in electron density states giving rise to an excess of scattering for the amorphous sample solidified at a lower cooling rate. The initial glassy structure and its evolution during isothermal cold crystallization at 117°C of these two samples can be interpreted by assuming an improvement in the state of internal order. The differences in the incipient molecular ordering, which are detected by SAXS but not by WAXS, could be responsible for the hardening observed in the glassy PET samples.

Key Words. Poly(ethylene terephthalate), Solidification under fast cooling, Glassy states, Microhardness, SAXS and WAXS.

Paper submitted to: *Polymer*

August 1999

INTRODUCTION

The study of the crystallization of polymers under fast cooling (at times of the order of tenths of a second) has emerged as a new method of great technological interest [1]. This is so because it allows the control of thermal history and the analysis of crystallization kinetics at high cooling rates [1-5]. A continuous variation of morphology and crystal structure has been shown to be present when varying the cooling rate [3]. In polyolefins, i-polypropylene for instance, at high cooling rates (above 20°C/s) mesomorphic and crystalline phases may coexist with spherulitic morphology surrounded by a weakly birefringent medium. At lower cooling rates only the crystalline monoclinic phase is formed. This competition has been recognized and used to model the crystallization kinetics at high cooling rates by an extension of a non isothermal formulation of the Kolmogoroff-Avrami-Evans (KAE) approach [4,5].

In recent years the investigation of the microhardness (H) has appeared as a physical method which can provide a quantitative information on changes in the morphology of polymers [6,7]. Specifically the isothermal crystallization of PET from the glass at different annealing times and temperatures has been followed by microhardness [8]. Microhardness measurements could accurately detect the gradual transition between structures in which spherulitic growth is incomplete and structures in which a growth is completed. In the former materials H was shown to be an increasing linear function of the volume fraction of the spherulites. For the latter materials, H is nearly constant with annealing temperature [8] but depends on aging conditions [9]. The kinetics of crystallization for PET was also investigated in real time by measuring the variation of microhardness "in situ", as a function of time, at different crystallization temperatures [10]. The changes in microhardness of injection molded PET using a range of mold temperatures have also been discussed in the light of the volume fraction of spherulites filling the molds [11].

The aim of the present study is to extend the above investigations to analyze the structure development of thin amorphous PET films quenched at high cooling rates from the melt. Particularly, we will show that for the higher cooling rates used, glassy PET exhibits an amorphous structure which is characterized by relatively high hardness values and by a con-

current excess of X-ray scattering intensity at small angles, as compared with conventional amorphous PET.

EXPERIMENTAL

Materials

The material used for this investigation is a standard DMT based PET with an intrinsic viscosity of 0.62 dl/g kindly supplied by SINCO Eng. Italy. Before melting the material was dried at 150°C under vacuum for 12 h. Thin films of the material were molten at 280°C for 10 min and then quenched while the cooling history was recorded using a procedure recently described [1-3]. Different cooling conditions can be spanned in this way giving rise to a continuous variation of structure features: from highly crystalline samples to completely amorphous ones (see Table 1). In the case of PET the temperature window determining its solidification has been identified in the vicinity of 170°C, where the maximum of the kinetic constant vs. temperature dependence is found by modeling the crystallization kinetics with the mentioned KAF approach [12].

Therefore, the cooling rates measured at this temperature (Table 1) are those used throughout the paper in relation to the developed structure. In order to minimize the aging of the materials after their preparation, the samples were stored in a closed vessel with silica gel (dry atmosphere) inside a freezer.

Techniques

The density ρ of the samples was measured in a density gradient column containing a mixture of hexane and tetrachloroethane. From the density we have calculated the volume degree of crystallinity α by using the equation $\alpha = \rho_c(\rho - \rho_a)/\rho(\rho_c - \rho_a)$, where the density of the amorphous regions ρ_a was assumed to be 1.3349 g/cm³ [13] and the density of the crystals ρ_c was taken as 1.4895 g/cm³ [14].

Microhardness H was measured at room temperature using a Leitz "Durimet" tester with

Fig. 1 illustrates the changes occurring in the X-ray diffraction pattern of PET quenched from the melt at different cooling rates. With decreasing cooling rate one sees a gradual transformation from the original amorphous halo to the incipient appearance of the crystalline reflections, at about 1.5°C/s . In addition, one observes a continuous increase in the perfection of the crystals as revealed by the sharpening of the X-ray scattering peaks associated to the triclinic crystal phase [14]. The results of Fig. 1 also indicate that glassy PET samples are obtained for cooling rates larger than 5°C/s .

RESULTS AND DISCUSSION

The samples were characterized by X-ray diffraction performed at room temperature. A Seifert XRD 3000 θ/θ diffractometer using Ni-filtered Cu K α radiation and a scanning speed of about 1° (2 θ)/min were used. In addition, time resolved measurements of simultaneous, small and wide-angle X-ray scattering (SAXS and WAXS) during isothermal crystallization of two glassy PET samples with different cooling rates were performed at HASYLAB (Hamburg). Synchrotron X-ray radiation, with a wavelength $\lambda=0.150$ nm, at the polymer beam-line A2 was used. The accumulation time for each X-ray pattern was 30 seconds and the elapsed time between consecutive spectra was 60 seconds.

a Vickers square pyramidal diamond indenter. The H value (in MPa) was derived from the residual projected impression using the equation: $H = Kp/d^2$, where d is the mean diagonal length of the indentation in meters, p the applied force in Newtons, and K a geometrical factor equal to 1.854 [15]. Loads of 0.10, 0.15, 0.25 N to correct for instant elastic recovery were used. A loading cycle of 0.1 min to minimize creep of the material under the indenter

Chain Ordering of the Glassy State

of internal order which may become precursors of final crystalline states. Hence, it appears that different high cooling rates may give rise to glassy PET with H-values which could be connected to embryonic regions of higher density which, however, do not give rise to any WAXS signal. Embryonic chain ordering prior to isothermal crystallization from the glass has been reported for glassy PET [17] and poly(ether-ketone-ketone) [18] samples in which the SAXS maximum develops, during isothermal treatment, before the appearance of the WAXS crystalline peaks. Pseudonucleation density fluctuations have been proposed to be responsible for the ordering phenomena during the induction period, before cold crystallization in PET [17], as well as, prior to melt crystallization in poly(butylene terephthalate) [19] and isotactic polypropylene [20].

In order to verify the occurrence of possible 'frozen-in' electron density fluctuations, induced at different cooling rates, we have recorded the SAXS patterns, using synchrotron radiation, for the amorphous samples 1 and 7. Figure 5 illustrates the SAXS patterns of these two glassy samples, recorded at room temperature and normalized to the intensity maximum. The intensity difference curve (dotted line and insert of Figure 5) between the SAXS profiles of samples 7 and 1 is also shown. Although one sees the continuous character of the intensity curve of the individual SAXS profiles, the striking intensity maximum arising from the intensity difference between samples (insert) could be associated to the 'frozen-in' electron density fluctuations from sample 7 with reference to sample 1.

Taking into account that sample preparation was performed by cooling from the melt, it seems plausible to think that the different glassy structures obtained (samples 1 to 7 of Table 1) should arise because of differences in the heat exchange from PET samples. This idea aimed us to carry out additional experiments to induce embryonic precystallization states by annealing glassy PET at different times. Indeed, recent results confirm that the time scale for electron density fluctuations during cold crystallization depends on the level of "chain ordering" of the glassy state [21].

Fig. 3 illustrates the variation of H for the aged PET samples (see Table 1) as a function of macroscopic density. One clearly distinguishes between two regions of behavior: a) a fast linear increase of H vs. ρ for the amorphous (glassy) samples up to densities of 1.343 g/cm^3 and b) a second slower linear increase of H vs. ρ for the semicrystalline materials up to $\rho = 1.4 \text{ g/cm}^3$. In order to discuss the results we have represented in Fig. 4 the variation of H as a function of the degree of crystallinity, α , derived from density. For the semicrystalline samples ($dT/dt \leq 2.3^\circ\text{C/s}$) we confirm the linear variation of H as a function of α , which for $\alpha = 0$, extrapolates to $H = 152 \text{ MPa}$. However, for the samples crystallized at higher cooling rates with volume degree of crystallinity smaller than 5%, the X-ray diffraction pattern does not show any crystalline peaks (see Fig. 1). What could, then, be the reason for such a steep variation of H (from 129 up to 145 MPa) in these samples which do not exhibit any X-ray crystallinity? One possible explanation for the relatively high H values of the glassy samples could be given in the light of emerging local regions with different degrees of internal order

Structure-microhardness correlation

the melt at different cooling rates. different structures in the amorphous samples induced during the quenching process from samples still exhibit a large H -variation ($112\text{--}133 \text{ MPa}$) which suggests the occurrence of T_g which results in a hardening of the polymer. It is noteworthy that the amorphous fresh segmental mobility. Physical aging can be visualized as a densification mechanism [16] below that these changes may involve ordering of benzene rings within PET molecules reducing local molecular motions (conformational changes). In preceding studies we suggested [10] higher H -values than the freshly prepared ones. Physical aging below T_g is connected to samples) confirm this assumption [16]. The aged glassy samples show, indeed, distinct symbols) for the same samples measured after 2 min of thermal treatment at 95°C (fresh study can be attributed to physical aging of the samples. The lower H values obtained (open reported for glassy PET [8]. The high H -values detected for amorphous PET in the present observed for the higher cooling rates (amorphous PET) are larger than those previously

Development of microstructure during cold crystallization

To examine the influence of the initial glassy structure on the cold crystallization of PET, as revealed by microhardness, samples 1 and 7 were again selected. Fig. 6 shows the variation of H , measured at room temperature, as a function of crystallization time at $T_c=117^\circ\text{C}$ for these two samples. In both cases a gradual H increase with t_c leading to a final levelling-off after $t_c = 20\text{--}25$ min gives rise to final H -values of about 200 MPa. The results agree well with earlier data for PET samples crystallized at the same temperature [8]. There is, however, a notable H -time dependence on the cooling rate. While sample 1 shows an induction period ($t_{ind} \sim 6$ min) before H increases, sample 7 having higher initial H -values, shows an immediate H -increase. Beyond t_{ind} both samples present a similar H -increase with t_c . Sample 7, showing higher H values and larger SAXS intensity (see Fig. 5) than sample 1, probably entails "ordered embryonic states" (seeds) which are capable to crystallize more readily as a function of time. On the other hand, sample 1 requires an induction period of a few minutes before the first nuclei appear and develop into crystalline regions responsible for the H -increase observed. We suggest that the larger induction period detected for sample 1 should be related to the smaller low angle scattering intensity and the smaller H -values in relation to sample 7. This induction time difference cannot be explained by differences in equilibrium recovery by the glassy material which should be much faster at ca 40°C above the glass transition.

It is to be noted that after annealing at 117°C for $t_c \approx 20$ min the primary crystallization process ends up and the H -values level-off. However, for $t_c > 20$ min (secondary crystallization region), while H remains constant the crystallinity shows a further slight increase with t_c (see Fig. 7). One may ask, what is the origin for the different behaviour between H and α in the region of secondary crystallization? An explanation to account for this discrepancy could be due to the occurrence of a rigid amorphous phase within and in between the spherulites after the second crystallization regime has started. Hence, during primary crystallization the interspherulitic amorphous regions show a hardness value, H_a , which is smaller than the hardness of the crystals, H_c . However, after primary crystallization is completed, the

constant H -value attained, with a further increase in crystallinity due to secondary crystallization, suggests that H_c should be approximately equal to H_c . Consequently, from the two-phase model ($H = \alpha H_c + (1 - \alpha)(H_c)$, $H = H_c = H_c = H_c = 200$ MPa. If we use the equation for the crystalline hardness [6]:

$$H_c = \frac{H_c}{1 + \frac{l_c}{b}} \quad (1)$$

assuming a value for $H_c = 400$ MPa [20] it turns out that $b = l_c$. In previous studies, crystal thickness, l_c values of about 30 Å for PET samples annealed (crystallized) at 117 °C have been reported [20]. This should give b -values of about 30 Å, in good agreement with data of highly crystalline PET previously reported.

The cold crystallization of the samples 1 and 7 at 117°C has also been investigated, in real time, by simultaneous WAXS and SAXS experiments using synchrotron radiation at HASYLAB. The variation of the long period L with the crystallization time has been represented in Fig 8. For the shorter t_c values sample 1 clearly shows larger L values than sample 7. It seems that during primary crystallization (for $t_c \leq 25$ min) L is larger for sample 1 than for sample 7 while for $t_c > 25$ min (secondary crystallization) the L values are indistinguishable from each other.

The data concerning the initial development of L values (Fig. 8) seem to be in agreement with the initial H -values observed for samples 1 and 7 (Figs. 2-3). Indeed, a large long period represents a higher average length between regions of high electron density, i.e. a larger distance between the above mentioned 'embryonic states'. Consequently, sample 1 with a larger long period than sample 7 should show a smaller volume density of "ordered chain segments" thus giving rise to a smaller hardness value in relation to sample 7.

CONCLUSIONS

1. The properties and internal structure of glassy PET can be modulated by controlling the cooling rate of molten thin films. Amorphous PET samples were obtained for cooling rates larger than 4–5°C/s.

2. Amorphous PET reveals a distinct rise in hardness with decreasing cooling rate which is accompanied by small increasing variations in density as well as in the SAXS intensity. The varying hardness values for the glassy material can be associated to the presence of 'embryonic precrystallization states' which are revealed as an excess of SAXS intensity. The latter is larger the lower the cooling rate.

4. When glassy PET is annealed ($T_c=117^\circ\text{C}$) the samples having the larger induction period prior to crystallization are the ones with the lower initial hardness and scattering intensity values.

ACKNOWLEDGMENTS

Grateful acknowledgment is due to the International Joint Research Grant NEDO, Japan and to the DGICYT, Spain (Grant PB94-0049) for the support of this investigation. Resolved measurements of simultaneous SAXS and WAXS during isothermal crystallization of PET at the polymer beam-line A2 were funded by the Program Human Capital and Mobility, Access to Large Installations EC (TMR-Contract ERBFMGECT950059). Financial support to one of us (SP) is acknowledged from the Italian Ministry of Universities (ex 40% quota).

References

- [1] Brucato, V.; Crippa, G.; Piccarolo, S.; Titomanlio, G. *Polym. Eng. and Sci.*, 1991, **31**, 1411.
- [2] Piccarolo, S.; Saiu, M.; Brucato, V.; Titomanlio, G. *J. App. Polym. Sci.*, 1992, **46**, 625.
- [3] Piccarolo, S. *J. Macromol. Sci.-Phys., B*, 1992, **31**(4), 501.
- [4] Brucato, V.; Piccarolo, S.; Titomanlio, G. *Macromol. Symposia*, 1993, **68**, 245.
- [5] Brucato, V.; Piccarolo, S.; Titomanlio, G. *Int. J. of Forming Processes*, 1998, **1**, 35.
- [6] Baltà Calleja, F.J. *Trends in Polym. Sci.*, 1994, **2**(12), 419.
- [7] Baltà Calleja, F.J.; Fakirov, S. *Trends in Polym. Sci.*, 1997, **5**, 246.
- [8] Santa Cruz, C.; Baltà Calleja F.J.; Zachmann, H.G.; Striebeck, N.; Asano, T. *J. Polym. Sci., Polym. Phys., B*, 1991, **29**, 819.
- [9] Ania, F.; Martínez-Salazar, J.; Baltà Calleja, F.J. *J. Mater. Sci.*, 1989, **24**, 2934.
- [10] Baltà Calleja, F.J.; Santa Cruz, C.; Asano, T. *J. Polym. Sci., Polym. Phys.*, 1993, **31**, 557.
- [11] Baltà Calleja, F.J.; Baranowska, J.; Rueda, D.R.; Bayer, R.K. *J. Mater. Sci.*, 1993, **28**, 6074.
- [12] Brucato, V.; Piccarolo, S.; Titomanlio, G. "Analysis of Non-Isothermal Crystallization Kinetics of PET", European PPS Meeting, p. 5.30, 1995, Stuttgart, Sep. 26.
- [13] Fakirov, S.; Fischer, E.W.; Schmidt, R. *Macromol. Chem.*, 1975, **176**, 2459.
- [14] Gehrke, R.; Zachmann, H.G.; *Macromol. Chem.*, 1981, **182**, 627.

- [15] Baltá Calleja, F.J.; Martínez Salazar, J.; Rueda, D.R. *Encycl. Polym. Sci. Eng., Wiley-Interscience*, 1986, **6**, 614.
- [16] Struik, L.C.E.; "Physical Aging in Amorphous Polymers and other Materials" Elsevier, Amsterdam, 1978.
- [17] Imai, M.; Mori, K.; Mizukami, T.; Kajii, K.; Kanaya, T.; *Polymer*, 1992, **33**, 4451.
- [18] Ezquerro, T.A.; López Cabarcos, E.; Hsiao, B.S.; Baltá Calleja, F.J.; *Phys. Rev. E*, 1996, **54**, 989.
- [19] Hsiao, B.S.; Wang, Z.; Yeh, F.; Gao, Y.; Sheth, K.C. *Polymer*, 1998 **40**, 3515.
- [20] Terri, N.J.; Fairclough, P.A.; Towns-Andrews, E.; Komanschek, B.U.; Young, R.J.; Ryan, A.J. *Polym. Comm.*, 1998, **39**, 2381.
- [21] García, M.C.; Rueda, D.R.; Baltá Calleja, F.J.; *Polymer Journal*, in press.
- [22] Baltá Calleja, F.J.; Öhm, O.; Bayer, R.K. *Polymer*, 1994, **35**, 4775.

CAPTIONS TO FIGURES

Fig. 1 X-ray diffractograms of thin PET samples cooled from the melt at different cooling rates, dT/dt .

Fig. 2 Plot of microhardness, measured at room temperature, vs. the logarithm of cooling rate for PET samples: (●) 40 days after their preparation, (○) the same glassy PET samples treated at 95°C for 2 min.

Fig. 3 Plot of H as a function of the macroscopic density of the PET cooled from the melt.

Fig. 4 Microhardness dependence on degree of crystallinity, α calculated from density.

Fig. 5 SAXS intensity profiles, obtained at room temperature, for samples cooled at 17°C/s (7) and 7500°C/s (1). The intensity difference between the SAXS profiles 7 and 1 (dotted curve and insert) is also shown.

Fig. 6 Variation of H , measured at room temperature, for samples 1 (open circles) and 7 (filled circles) as a function of cold crystallization at 117°C for different cumulative times, t_c .

Fig. 7 Variation of degree of crystallinity, α (derived from density) of sample 7 upon isothermal cold crystallization at 117°C for different times.

Fig. 8 Variation of the long period measured during isothermal crystallization at 117°C for samples 1 (open circles) and 7 (filled circles).

Table 1. Density, Microhardness and Degree of Crystallinity of PET solidified from the melt at different Cooling rates

Sample	°C/s	ρ (g/cm ³)	H (MPa)	α (%)
1	7500	1.3392	129	3.09
2	700	1.3389	132	2.88
3	178	1.3394	136	3.24
4	88.5	1.3406	140	4.09
5	76.3	1.3408	143	4.24
6	18.7	1.3416	149	4.81
7	17.0	1.3410	143	4.38
8	4.70	1.3439	154	5.73
9	2.30	1.3590	157	17.08
10	1.70	1.3585	157	16.74
11	1.50	1.3610	159	18.48
12	0.60	1.3788	170	30.67
13	0.09	1.4006	174	45.19
14	0.04	1.3953	173	41.71

Fig 1

Fig 5

984

t_c

5.8