THE INFLUENCE OF DRAWING IN HOT WATER ON THE MORPHOLOGICAL PROPERTIES OF PET FILMS AS MEASURED BY DSC AND MODULATED DSC

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Abstract

PET films uniaxially drawn in hot water are studied by means of conventional DSC and modulated DSC (MDSC). Glass transition is studied by MDSC which allows to access the glass transition temperature T_g and the variations of $\Delta C_p = C_{p_l} - C_{p_g}$ (difference between thermal capacity in the liquid-like and glassy states at $T=T_g$). Variations of T_g with the water content (which act as plasticizer) and with the drawing (which rigidifies the amorphous phase) are discussed with regard to the structure engaged in these materials. The increments of ΔC_p at T_g are also interpreted using a three phases model and the 'strong-fragile' glass former liquid concept. We show that the 'fragility' of the medium increases due to the conjugated effects of deformation and water sorption as soon as a strain induced crystalline phase is obtained. Then, 'fragility' decreases drastically with the occurring rigid amorphous phase.

Introduction

Among semi-crystalline polymers, poly(ethylene terephthalate) (PET) is one of the most studied one because recrystallization could be obtained either by thermal treatment (isotropic structure) or by drawing (anisotropic structure). During its transformation from an initially wholly amorphous state (PET is widely used in fibres, films and bottles), a strain induced crystallized phase generally appears.

On the other hand, PET can be considered a hydrophobic polymer [1] with a rapid moisture sorption kinetics [2]. The effect of sorbed water molecules in PET (less than 1% in mass) is known to lead to classical plasticizer effects, evidenced ba-

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sically by a decrease of the glass transition temperature with increasing water content [3]. By drawing a dry PET film, depending on the draw ratio (λ) the initial amorphous phase is first oriented (up to $\lambda=2$) then a strain induced crystalline phase occurs ($\lambda>2$ [4]). In this work we propose to analyse both the drawing and plasticizer effects which can be realised on PET films by performing deformations in situ in hot water.

Differential scanning calorimetry is one of the most popular experimental methods used to characterise glass transition. If DSC leads to very good signals for amorphous PET (Fig. 1a), drawn and/or wet PET will show a glass transition accompanied by the occurrence of a succession of thermal phenomena (Fig. 1b). As a direct consequence, determination of T_g and furthermore of $\Delta C_p(T_g)$ are rather delicate.
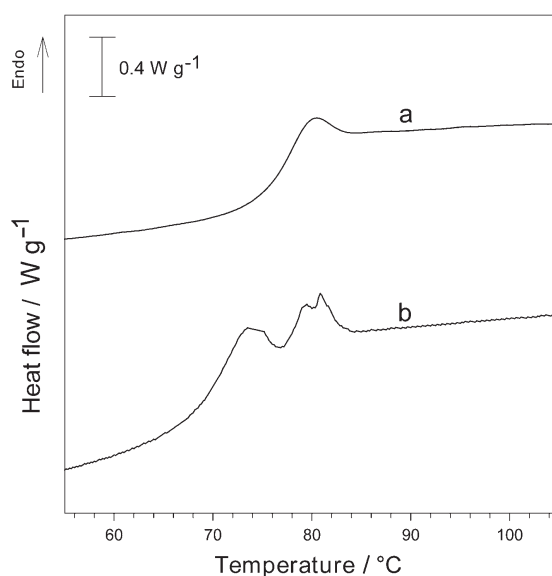

Fig. 1 Example of two DSC signals characterising the glass transition obtained on:
a – dry amorphous PET; b – PET drawn in hot water with $\lambda=2.3$

Recently an alternative experimental method based on calorimetric investigations has been proposed. It is a matter of the modulated differential scanning calorimeter (MDSC) method [5–9]. It subjects a sample to a linear heating ramp with superimposed low temperature oscillations (modulation). MDSC allows the knowledge of two time scales for the measurements concerning glass transition; a fast one fixed by the modulation time period and a slow one fixed by the average underlying heating or cooling rate [5]. Thus, this method is comparable to dynamic mechanical and dielectric measurements.

In this work we propose to analyse, by means of MDSC, the changes occurring during glass transition in hot water drawn PET samples.

Experimental

Drawn PET was prepared from 0.5 mm thick film of $\overline{Mn}$=31 000 g mol^{-1} and $\overline{Mw}$=62 000 g mol^{-1}. Measurements were first performed on the initial PET films. The films are isotropic and amorphous, judging from birefringence, density, and X-ray diffraction results. To obtain other samples, the initial film (8×5×0.05 cm^3) was immersed in hot water of 70°C for 1 h. Then, drawing was performed in situ at a strain rate of 0.14 s^{-1} using a tensile machine (Instron 4301). The draw ratio λ is defined as the ratio between the final length and the initial length. Finally, different samples were cut from drawn materials with λ ranging between 1 to 4.

Calorimetric investigations were performed using a Perkin Elmer DSC7 calorimeter for the conventional method and using a TA instrument DSC 2920 Modulated DSC. Temperature and energy calibrations of the conventional DSC were achieved at a heating rate of 10°C min^{-1} under nitrogen atmosphere using indium as standard. Flow rates of nitrogen are 25 and 50 mL min^{-1} for DSC7 and DSC 2920 respectively. Calibration of MDSC was performed with the same standard at a heating rate of 2°C min^{-1}. The modulation parameters were an alternative signal of 0.318°C magnitude and 60 s periodicity (heat only mode). The sample mass is close to 10 mg for DSC and MDSC. By DSC determined the crystallisation temperature T_c and the fusion temperature T_F determined by exothermic and endothermic peaks respectively. By MDSC, the reverse part of the signal was used to estimate the value of the glass transition temperature T_g taken as the onset of the transition. On the same curve, the value of $\Delta C_p = C_{p_1} - C_{p_g}$, where C_p is the specific heat (the indexes refer to the liquid and glassy states respectively) was determined at the mid-point of the glass transition T_g and was marked $\Delta C_p(T_{g_M})$. All the calorimetric curves presented in the following are normalised to 1 mg of matter.

Results and discussion

Figure 2 shows conventional DSC curves obtained for all the samples investigated in this work. On all the curves, we observe the glass transition, more or less well defined as a ΔC_p step or as a succession of small peaks in a temperature range close to 70°C. For draw ratio up to λ=2, a well-defined exothermic peak characterising the cold crystallisation is observed. This exothermic peak occurs for temperatures decreasing from 124 to 92°C as the draw ratio varies from 1 to 2. For λ>2, the exothermic transition seems more or less superimposed to the glass transition. Finally at high temperature (218 to 240°C), the endothermic peak of melting is observed. Table 1 reports the corresponding values.

Figure 3 shows four signals obtained by means of MDSC for PET at two different draw ratio λ=1 and λ=2.3 respectively. Curve a is the measured signal, d is the total heat flow, b is the reversed and c is the non-reversed part of the signals. As already mentioned, for λ=2.3 the total heat flow can lead to ambiguous determination of both the glass transition temperature and the value of $\Delta C_p(T_{g_M})$. Total MDSC heat flow and conventional DSC signals are exactly the same. As this work is focussed on the

glass transition, only the reverse signal is of interest and allows the estimation of the glass transition temperature T_g and the $\Delta C_p(T_{g_M})$ increment. The measured values for these two quantities are also shown in Table 1.

Table 1 Values of the different quantities determined from DSC and MDSC obtained for PET drawn in hot water for the different draw ratio

	Modulated DSC		Conventional DSC		
λ	$T_g/°C$	$\Delta C_p/J\ g^{-1}\ K^{-1}$	$\Delta H_c/W\ g^{-1}$	$T_f/°C$	$T_c/°C$
1.0	67	0.31	28.4	218	124
1.2	68		28.4	218	124
1.3	67	0.29	28.4	217	124
1.4			28.3	216	123
1.5	68		28.2	216	112
1.6	67		25.0	216	111
1.7	67	0.29	26.7	216	110
1.8	68	0.28	22.1	218	103
2.0	68	0.29	22.6	218	103
2.1	69		20.8	229	92
2.2	69	0.28	14.8	226	94
2.3	68	0.28	14.4	231	91
2.4	69	0.29	11.0	234	90
.2.5	70	0.28	11.1	233	89
2.6			12.6	235	89
2.7	71	0.28	8.1	237	90
2.8			9.8		
2.9	73	0.19	10.0		91
3.0			9.9		
3.1	73	0.19	8.3		
3.2			8.3	239	89
3.3	74	0.11	8.3	240	91
3.4	74	0.13	7.0	239	90
3.5	77	0.09	6.9	240	90
3.6	75	0.10	6.9	240	91
3.7	75	0.08	6.7	240	91
3.8	74	0.07	6.7	241	91

According to one of our previous works, the degree of crystallinity realised for a given draw ratio is determined by the values of the crystallisation enthalpy and of the melting enthalpy using the following relationship [10].

$$X_c = \frac{\Delta H_c^0 - \Delta H_c}{\Delta H_c^0} \frac{\Delta H_f}{\Delta H_f^0} \qquad (1)$$

where ΔH_f is the enthalpy of fusion of the sample, ΔH_f^0 is the calculated enthalpy of fusion of a wholly crystalline PET ($\Delta H_f^0 = 140$ J g^{-1}) [11], ΔH_c^0 is the enthalpy of crystallisation of an undrawn and initially wholly amorphous sample and ΔH_c is the enthalpy of crystallisation of the drawn sample.
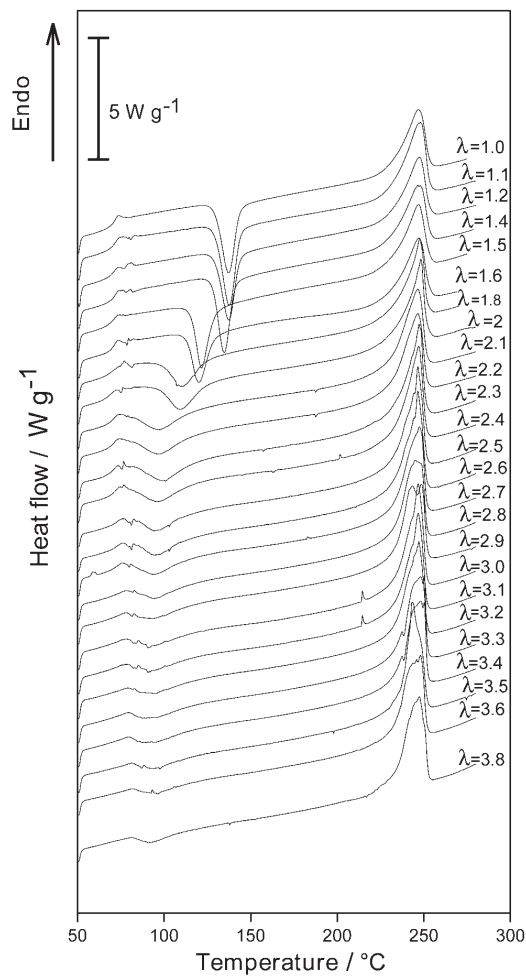

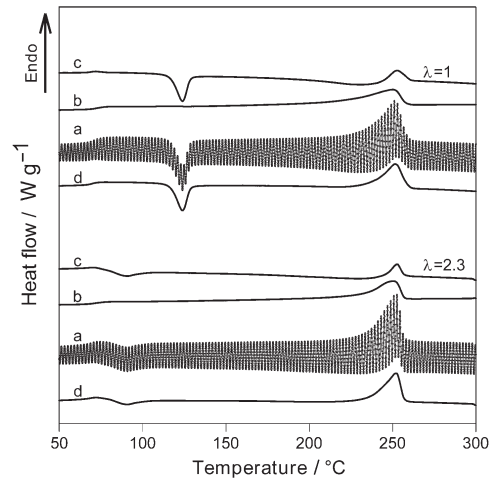**Fig. 2** DSC curves obtained on drawn PET showing the glass transition, the cold crystallisation and the melting

Fig. 3 MDSC curves obtained on a PET drawn in hot water with λ=1 and a PET with λ=2.3. The measured signal (curve a), the total heat flow (curve d), the reverse (curve b) and non-reverse (curve c) part of the signals are presented
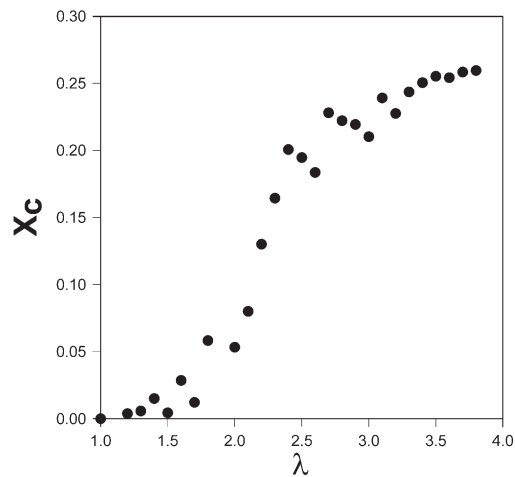

Fig. 4 Variations of the degree of crystallinity with the draw ratio, obtained for PET drawn in hot water

From our results, the obtained degree of crystallinity is nil for draw ratio up to λ=1.5 then increases linearly up to λ≈3 to reach a constant value X_c=0.27 for 3<λ<4 (Fig. 4).

Figure 5 shows the dependence of the glass transition temperature on the draw ratio. Up to λ≈2 the glass transition temperature remains constant (68±1°C). And increases for 2<λ<4 (T_g (onset) °C=4.07λ+60.15) to reach for λ=4 a value of 76±1°C. Classically, the increase of the rigidity in the amorphous phase can be associated to the decrease of free volume realised by the drawing. The lack of variation of the glass
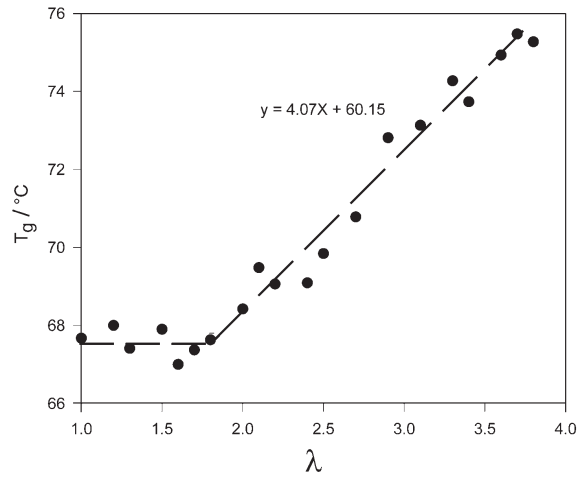
Fig. 5 Variations of the glass transition temperature (onset) with the draw ratio, obtained for PET drawn in hot water

transition temperature for draw ratio up to $\lambda=2$ also observed in experiments performed on dry samples [12], indicates that the magnitude of such deformation is not significant enough.

Figure 6 (curve a) does not show drastic changes of $\Delta C_p(T_{g_M})$ up to $\lambda=2.8$ while for greater deformations, this quantity decreases with λ. At this stage of discussion we have to take into account the fact that ΔC_p is given for unity of mass. So, when the sample contains a fraction of crystalline phase, the normalisation must not be made on the whole sample mass but only on the mass of the remaining amorphous phase.
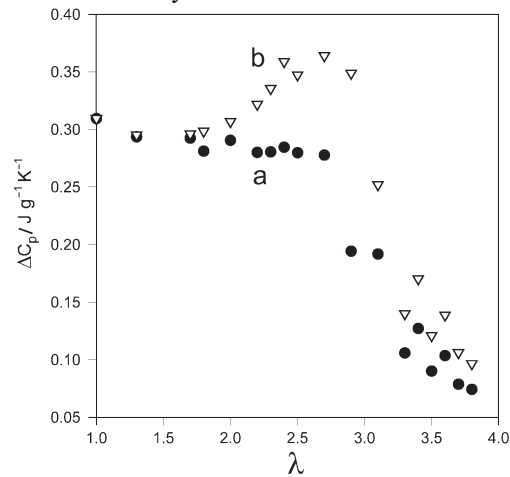

Fig. 6 Variations of ΔC_p at the glass transition with the draw ratio, obtained for PET drawn in hot water: a – as measured (•); b – values normalised to the real content of amorphous phase (∇)

The same remark can also be made for the existence of absorbed water molecules in the sample. However, because the water molecule mass fraction is very small (less than 1%), its influence on the determination of ΔC_p can be neglected. This is, however, not the case for the crystalline fraction. Now, using the crystallinity degree values previously determined, we have to recalculate the true ΔC_p values. This re-normalisation of ΔC_p to the real content of amorphous phase is shown in Fig. 6 curve b and leads to the following observations. Up to $\lambda \approx 2$, ΔC_p remains constant, which is normal because in this range of deformation no crystallisation occurs and deformations are not enough important (as observed for instance by birefringence measurements) [10] to modify drastically the amorphous phase. For $\approx 2 < \lambda < 2.8$, ΔC_p increases and is higher than the value expected for a classic amorphous PET. This behaviour is interesting. Indeed, the molecular re-organisation accompanying the crystallisation (for $\lambda \approx 1.5$ Fig. 4) is able to eject the water molecules in the remaining amorphous phase. A direct consequence is an increase of the water concentration in the amorphous phase. As the degree of deformation increases, the degree of crystallisation increases too, and formation of water clusters is possible. The second consequence is an increase of the free volume in the remaining amorphous phase (water plasticizer effect), which increases its 'fragility' as defined by Angell according to the strong-fragile glass former liquid concept [13]. Indeed, the rigidity of vitreous or liquid medium can be linked to the values of ΔC_p; a high ΔC_p value (for instance $\Delta C_p = 0.4$ J g^{-1} K^{-1}) characterises a 'fragile' glass forming liquid system while at the opposite a low ΔC_p value (for instance $\Delta C_p = 0.05$ J g^{-1} K^{-1}) characterises a strong glass forming liquid system. This can also be correlated to the number of energy minima available for the molecular segments during their cooperative relaxations: the greater the 'fragility', the greater the number of energy minima [14]. Thus in this range of deformation $\approx 2 < \lambda < 2.8$, the combination of orientation and plasticizer effects increases the 'fragility' of the amorphous phase. This behaviour remains the main one until the draw ratio is large enough ($\approx \lambda > 3$) to originate the formation in addition to the crystalline phase of a third phase, called rigid amorphous phase [10]. When this rigid amorphous phase occurs, the molecular mobility decreases drastically, the effects of the water molecules become negligible in comparison to the drawing effects. This important reduction of the molecular mobility can be associated to a decrease of polymer 'fragility'.

Conclusions

When glass transition phenomenon cannot be observed correctly by conventional DSC measurements, we have shown that the use of MDSC can be a powerful tool, which allows overcoming this difficult. In this work, we have determined, the different quantities characterising the glass transition temperature and the associated ΔC_p step of PET drawn in hot water with different draw ratio with this technique. We have shown that the conjugated effects of drawing and water sorption lead to increase the 'fragility' of the medium until the occurrence of the rigid amorphous phase is accom-

plished ($\approx 2 < \lambda < 2.8$), while the materials turn to a strong behaviour as soon as this rigid amorphous phase occurs.

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