Macromol. Symp. ***138**, 139–147 (1999)*

Influence of Water on the Physical Aging of Poly(ethylene terephtalate)

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SUMMARY : Physical aging in polyethylene terephtalate (PET) has been studied on samples well characterized in terms of aging history and their content of water. This allows us to better understand the role played by water in the complex phenomenology of the physical aging in a hygroscopic material as PET. No appreciable changes in the thermal behavior in the sample aged in water at room temperature for one month were noted, while substantial changes were observed in samples aged in more severe conditions like 50°C under vacuum and 50°C in water for one month. The results are consistent with the formation of small regions in which segments of chains are closely packed.

Introduction

When a polymeric material is cooled from the molten state to a temperature below its glass transition, T_g , the structural changes needed to maintain the thermodynamic equilibrium become slower and cannot occur in the time scale of the cooling. The amorphous phase is not in thermodynamic equilibrium and contains thermodynamic excesses of volume and enthalpy (1, 2). This produces appreciable changes in their physical properties. The changes of these properties, reported as "physical aging", are related to the conformational changes occurring to approach the thermodynamic equilibrium.

Physical aging can be detected with different techniques and among them differential scanning calorimetry (3, 5), creep measurements (1, 6, 7), tensile testing (5, 8, 9), dynamic mechanical measurements (5) are largely used.

While the phenomenology of physical aging is well known, the details of the molecular mechanisms are still matter of discussion.

CCC 1022-1360/99/$ 17.50+.50/0

In this work, the attention is focused on the role played by water on the physical aging of a hygroscopic polymer like polyethylene terephtalate (PET). The physical aging was investigated with the DSC and FTIR. Moreover, sorption of methylene chloride was also determined.

Experimental

Sample Preparation

Pellets of PET of intrinsic viscosity of 0.84 dL/g were kindly supplied by Montefibre s.p.a. (Italy). The pellets were dried at 50°C for two weeks with the nitrogen draft. Amorphous films were prepared by meltpressing the pellets at 290°C into a film shape of 100 μm and rapidly quenched into an ice-water bath at 0°C (sample Q0). The aged samples were prepared from Q0. The sample V50 was obtained by keeping the sample Q0 at 50°C under vacuum for one month, the samples W20 and W50 were obtained by keeping the samples Q0 respectively at 20 and 50°C in water for one month. All the samples were dried under continuous vacuum for 24 hours before testing.

GPC

The distribution of molecular masses in all the samples was determined by gel permeation chromatography (GPC). The analysis was carried out with a Varian model 2510 GPC equipped with UV/visible detector Varian model 2550. The samples were dissolved in a 98:2 by volume mixture of chloroform and hexafluoroisopropanol and passed through PL gel columns, heated at 40°C with a flow rate of 0.4 mL/min.

TGA

The thermogravimetric analysis was carried out using the system Mettler TG50-M3 in the range 25°C to 250°C, with a scan rate of 10°C/min.

DSC

Differential scanning calorimetry was carried out on samples of about 12 mg over the temperature range 0°C to 300°C, using a Mettler TA 3000 DSC, purged with nitrogen and chilled with liquid nitrogen. Runs were conducted at the heating rate of 20°C/min.

Optical Microscopy

A Zeiss polarizing microscope equipped with an exposure meter with which we are able to quantitatively determine the brightness of the viewing field and a hot stage. This apparatus was used for the determination of the kinetics of crystallization on all the samples. The formation of crystals in the interval 100 -180°C was followed by measuring the intensity of the transmitted light from samples placed in the hot stage between crossed polarizers (depolarized light intensity). The heating rate in the hot stage was 10°C/min. The data were reported as (I_t-I_o) / (I_∞ -I_o), where I_t, I_o and I_∞ are transmitted intensities recorded at a given temperature, at the beginning and at the end of the experiment, respectively. This ratio is reported versus the temperature and all the curves are typically S-shaped (10, 11).

FTIR

Infrared measurements were detected using a Perkin Elmer FTIR Paragon 500 spectrophotometer with a resolution of 4 cm^{-1} (30 scans collected).

Sorption Measurements

The sorption was measured by a microgravimetric method, using a quartz spring balance having an extension of 15 mm/mg. The penetrant used was CH_2Cl_2 and the experiments were conducted at 25°C. Sorption was measured at the vapor activity $a = p/p_o = 0.2$ where p is the actual pressure to which the sample was exposed and p_o is the saturation pressure at the temperature of the experiment.

Results and Discussion

PET is a hygroscopic thermoplastic polymer. It is well known that the presence of water in PET alters its physical properties and among them the glass transition temperature and the crystallization temperature (12, 14). For this reason we decided to put our samples under vacuum for 24 hours prior to testing. The thermogravimetric method was used to determine the residual water in our samples after this treatment. The results are in Table 1. From Table 1 we realize that, in spite of the treatment under vacuum, our samples still contain small amounts of water. Obviously, the samples aged in water contain more water than the reference sample Q0 and sample V50. In this study, it is very important to know the quantity of water contained in the samples in order to better understand the contribution given by the water and the contribution given by the physical aging on the variation of some properties. The presence of water can also degrade the polymer via hydrolysis but the analysis with the GPC did not reveal any variation in terms of molecular mass distribution.

The four samples were also characterized with the DSC. In the glassy PET three transitions are detectable with the DSC. The first is the glass transition occurring at about 80°C, the second is the crystallization with the peak centered at about 160°C, and the third is the melting with the peak at about 270°C. In Fig. 1, the DSC traces of the four samples are reported. In the figure, we report only the interval of temperatures in which the glass transition and the crystallization occur. The range of temperatures in which the melting of crystals occurs is not reported since the melting temperature and the enthalpy of fusion perfectly coincide in the four samples. In Fig.1, we notice that the reference sample Q0 and the sample W20 have the same profile. It means that, at least with this technique, the annealing at 20°C in water does not produce any effect. Conversely, on increasing the severity of the aging treatment (V50 and W50), the endotherm at the T_g appears and the crystallization occurs at lower temperatures. The appearance of the endotherm at the T_g is part of the phenomenology of the physical aging and it is explained as the recovery of the enthalpy lost during the annealing below T_g. The shift of the crystallization process must be related to the structural changes in the amorphous phase due to the physical aging. This point will be discussed in more details later.

Tab. 1 Residual water

Sample	Water
QO	0.11
W20	0.31
V50	0.09
W50	0.32

Crystallizable glassy polymers crystallize at temperatures above T_g. The progress of the thermal crystallization can be followed simply by reporting the ΔH of the exothermal transition versus the time the samples remain at the crystallization temperature. In Fig. 2, the

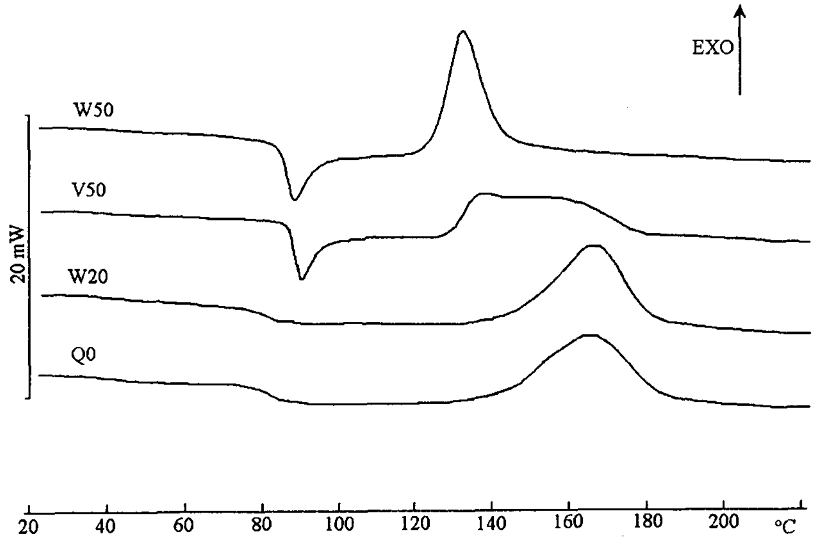

Fig.1: DSC traces

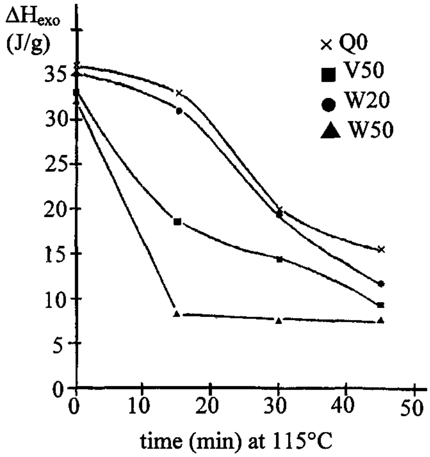

Fig.2: Enthalpy of crystallization as a function of the time of annealing at 115°C

enthalpy of crystallization is reported versus the time the samples are kept at 115°C. Also, in terms of thermal crystallization, the samples Q0 and W20 behave in the same way. Different behavior is exhibited by samples V50 and W50 and in particular the sample aged in the most severe conditions, W50, reaches the plateau value after 15 minutes at 115°C.

The thermal crystallization can also be followed with the polarizing optical microscope, putting the sample of PET in a hot stage at 115°C between crossed polaroids and detecting the transmitted intensity of the polarized light. When the crystallization occurs, the sample increases its birefringence because of the formation of crystallites. In fig. 3, the ratio $(I_t - I_o) / (I_\infty - I_o)$, that is proportional to the intensity of the transmitted light, is reported versus the temperature. At beginning of the experiment, the viewing field is dark and the ratio has the value zero, while, when the crystallization is completed, the viewing field is bright and the ratio is one. All the curves are typically S-shaped, but the samples aged in more severe conditions crystallize faster.

PET crystallizes with a triclinic cell and the moiety $O\text{-}CH_2\text{-}CH_2\text{-}O$ in the trans conformation. The kinetics of crystallization can also be followed with the IR analysis. The band 973 cm^{-1} is associated with the trans conformation of the ethylene glycol units (15, 16). The band 1578 cm^{-1}, insensitive to the conformational changes and to the development of crystallinity, was used as internal reference.

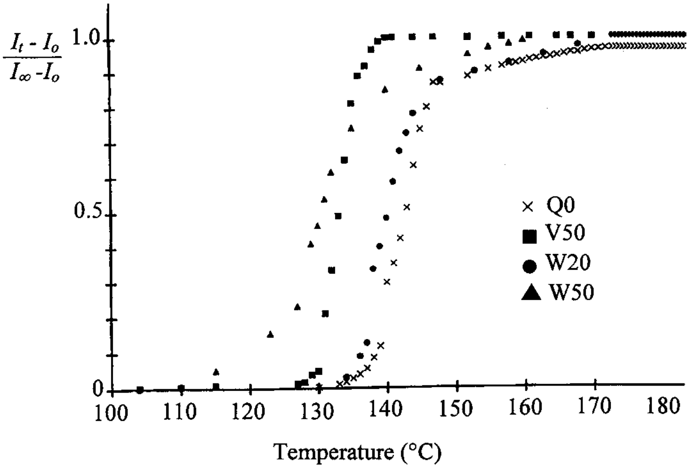

Fig.3: Reduced transmitted intensity as a function of the temperature

In Fig. 4, the ratio A_{973}/A_{1578} is reported versus the time the samples were kept at 115°C. The increase of trans conformations is faster in samples V50 and W50. Because of the increased sensitivity of the IR spectroscopy, with respect to the DSC, the curves correspondent to the samples Q0 and W20 are better separated.

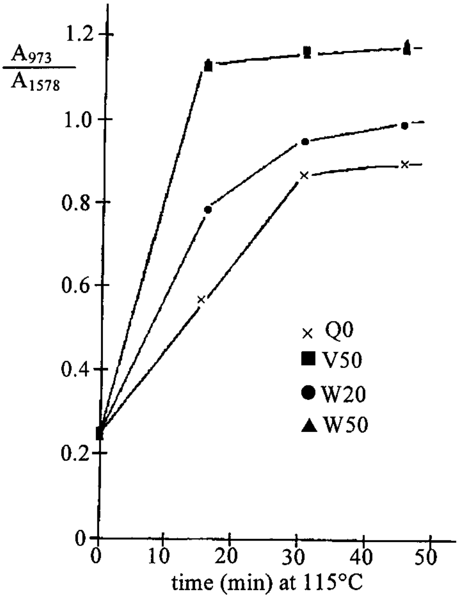

Fig.4: The absorbance ratio A_{973}/A_{1578} as a function of the time of annealing at 115°C

The data collected so far, with different techniques, are in good agreement. We notice that the aging at 20°C in water does not produce any effect. Conversely, the aging at 50°C under vacuum produces appreciable changes in the DSC traces and in the thermal crystallization detected with different techniques. Even more is caused by the presence of water at 50°C.

From these data we can state that the presence of water at 20°C does not produce any effect, at least in the time of our aging (one month). On the other hand, the presence of water is effective if the aging is carried out at 50°C. The phenomenology of the physical aging can be interpreted in terms of reduction of free volume, but also in terms of formation of ordered regions in the glassy state. Many authors are postulating the formation of regions in the glassy state in which interchain packing occurs. Recently, Qian (17-20) has proposed the concept of interchain cohesional entanglements of neighbouring chain segments in the glassy state. Cohesional entanglements can be considered as a sort of local nematic interaction between chain segments. Their presence in samples aged below the T_g is able to account for our experimental data. The appearance of the endotherm at T_g can be explained as the variation in the cohesional entanglement spacing. The endothermic process to disengage the cohesional entanglements accounts for the endothermic peak in the DSC curve. The increased rate of thermal crystallization in aged samples, can also be related to the presence of cohesional entanglements. At the glass transition the interchain packing relaxes by increasing the spacing between chain segments, but the structural organization of these tiny domains does not completely destroy acting as nuclei for the crystallization.

Tab. 2. Sorption of CH_2Cl_2 at a=0.2

Sample	Sorption (%)
QO	3.41
W20	3.40
V50	2.80
W50	2.42

The samples were also characterized in terms of sorption of methylene chloride at activity 0.2. Sorption measurements are useful for the determination of the permeable phase in a polymeric material (21, 22). In Table 2 the sorption in the four samples is reported.

From Table 2, we see that on increasing the severity of the physical aging the impermeable fraction increases. These data are in perfect agreement with the presence of cohesional entanglements that are impermeable to methylene chloride at the activity 0.2.

Conclusions

- The presence of water during the aging at temperatures below T_g does not produce appreciable changes in the sample aged at 20°C. Conversely, the presence of water at 50°C produces some detectable effects. This means that, although water generally acts as plasticizer in PET samples, with the consequent increase in the molecular mobility, the temperature of 20°C is still too low to promote the increase of mobility and therefore detectable effects on the properties in one month.
- The physical aging favors the thermal crystallization either in terms of crystallized material, or in terms of kinetics of crystallization.
- On increasing the severity of the physical aging, the fraction of the impermeable phase increases.
- The data are consistent with the formation of cohesional entanglements that account for the decrease of sorption and the increased rate of crystallization in the well aged samples.

This work was supported by "Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate II".

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