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Influence of ageing on the cold crystallization of glassy poly(ethyleneterephthalate)

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SUMMARY

The thermal crystallization from the glassy state of different samples of Poly(ethyleneterephthalate) (PET) was investigated with different techniques, such as infrared and x-ray analysis and polarized optical microscopy.

The different samples of PET were obtained by ageing the glassy PET films at room temperature and at 60°C; the behaviour of these films was compared with that of the fresh sample, put at the crystallization temperature as soon as prepared.

The temperature of crystallization was 120°C.

All the techniques, investigated to follow the crystallization phenomenon, show that the fresh sample crystallizes with longer times than the others.

This result was correlated with the initial structural organization of the glassy amorphous films.

Keywords: Poly(ethyleneterephthalate), Cold crystallization, Kinetics of crystallization.

INTRODUCTION

The thermal crystallization from the glassy state is important for theoretical, as well as for technological reasons (1-6). It can be an easier way for obtaining and studying polymeric materials that crystallize slowly and with difficulty from the melt; on the other hand the crystallization behaviour can help clarify many structural aspects of the starting amorphous films. In fact the kinetics of crystallization and the final structure of the material can be influenced by the initial organization of the amorphous polymer.

Poly(ethyleneterephthalate) (PET) is one of the most commercially important polyesters. Several authors have investigated its crystallization from the glassy state (7-13) but many aspects have not yet been fully clarified. PET, below its glass transition temperature, like other polymers, undergoes a phenomenon of physical ageing involving changes of its physical properties, and influencing its performance and lifetime (14-19).

Previous studies from our laboratory have shown the influence that cooling conditions and ageing temperatures and times have on the transport properties of dichloromethane vapours in several glassy polymers (20-24). We found that in glassy films of PET the physical ageing at different temperatures influenced either the diffusional behaviour, which is strictly correlated with the chain mobility, or the solvent-induced crystallization.

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Moreover, in the amorphous samples, the ageing at 60°C reduced the sorption of vapour at low activity; we interpreted this phenomenon as due to the presence of ordered domains impermeable to the penetrant. At higher activities they became permeable and, in fact, a transition in the sorption curve was observed (25).

In the present paper we analyse the thermal crystallization induced in amorphous glassy films of PET obtained in different ageing conditions, in order to investigate the effects of the initial structural organization on the kinetics of the process.

EXPERIMENTAL

Pellets of PET of intrinsic viscosity 0.84 dL/g were kindly supplied by Montefibre S.p.A. (Italy). Glassy amorphous films were obtained by moulding the pellets, in a hot press, at 290°C into a film shape 0.05 mm thick, and rapidly quenching to 0°C in ice water.

The crystallization phenomenon was followed at 120°C on the film as soon as obtained (sample Q_0), after 1 month at room temperature (sample Q_{25}), and after 1 month at 60°C (sample Q_{60}).

Infrared spectra were detected at room temperature by using a IFS66 FTIR spectrophotometer, collecting for each sample 32 scans. The resolution was 2 cm^{-1}.

Wide angle x-ray diffractograms (WAXD) were obtained by using a PW 1710 Philips powder diffractometer (Cu kα - Ni filtered radiation). The scan rate was $8°\theta min^{-1}$.

The three films were kept for successive periods of annealing times at 120°C; after each interval of time, the infrared spectrum and the x-ray diffraction pattern were obtained in order to follow the crystallization phenomenon.

Samples Q_0, Q_{25} and Q_{60}, all of thickness 50 μm, were put into a Jenapol polarizing microscope, equipped with a photomonitor that makes it possible to quantitatively determine the brightness of the viewing field. The temperature was adjusted at 120°C and the transmitted intensity was detected as a function of time. It was then reported as

$I_r = (I_t - I_o)/(I_f - I_o)$, where I_t , I_o and I_f are the intensities trasmitted at time t , at the beginning and at the end of the experiment respectively.

RESULTS AND DISCUSSION

Infrared analysis

The crystallization kinetics were studied annealing the quenched amorphous films for different times at a temperature of 120°C. The crystalline phase is characterized by chains in zig-zag planar conformation.

The infrared analysis is based on the presence in the spectra of many bands whose intensity increases on increasing the regular conformation of the chains. We followed, for the three samples, the increase of the conformational band at 973 cm^{-1} as function of annealing time.

This band, very sensitive to the development of order in the polymer, is associated with the trans conformation of the O-C-C-O group along the PET chain. Using the band at 1578 cm^{-1}, insensitive to the development of crystallinity, as an internal reference band, it was possible to define the crystallinity of PET from FTIR spectra (12). Since the 973 cm^{-1} band is related to the ordered conformation of the chains, we prefer to report the ratio $R = A_{973}/A_{1578}$, as an index of the order developed during the annealing.

In Fig.1 we report the R index as a function of annealing time at 120°C for the three samples.

We observe that there is a significant difference in the increase of R with the time, for the three samples: sample Q_0 shows the slower increase of the R parameter, reaching a plateau value after 20 min, whereas 10 min and 5 min are needed for sample Q_{60} and Q_{25} respectively. It is worth noting the particular behaviour of the curves in this first stage. In fact, a very rapid initial increase, from R=0.3 to R=0.53, completed in 1 minute, is observable for all the samples. Afterwards the primary stage starts preceded by a plateau of constant value of the R parameter, that, in the case of sample Q_0 shows the duration of 5 minutes. A possible explanation could be the formation of a local non crystalline molecular order, into the amorphous material obtained in the first minute. This hypothesis is in agreement with studies led through the "microhardness" technique in which liquid-liquid transitions dependent on time and temperature of ageing, are shown during the first stages of the thermal crystallization of PET (13).

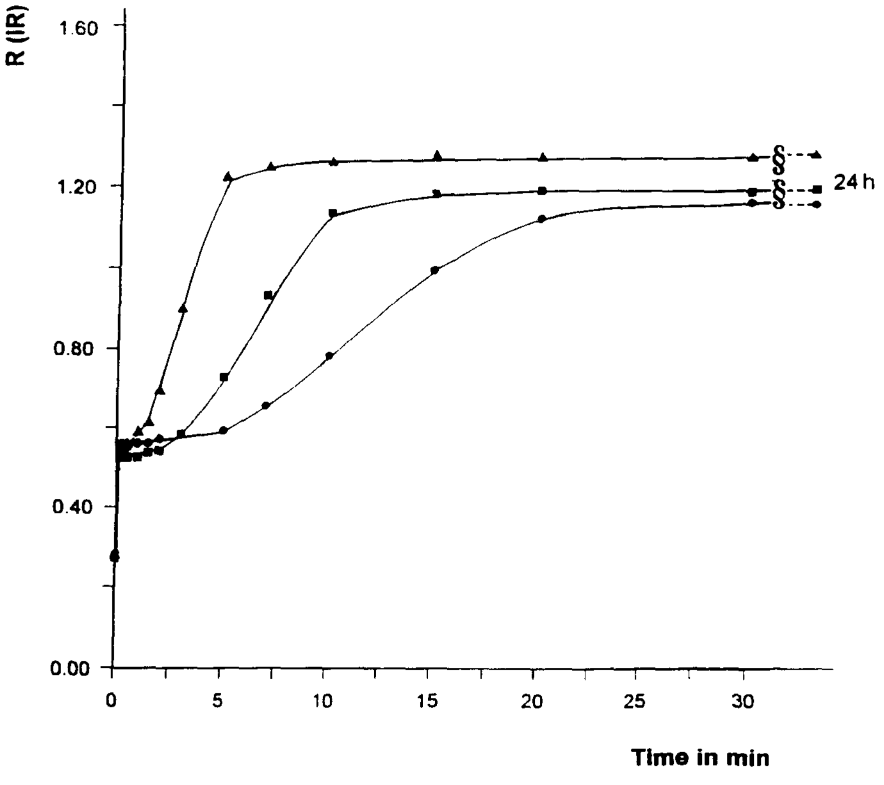

Fig. 1
The infrared parameter R (A973/A1578) as a function of the annealing time at 120°C
for the samples Q_0 (●), Q_{25} (▲) and Q_{60} (■).

X-ray analysis

The crystallization kinetics of samples Q_0, Q_{25} and Q_{60} were also analyzed through the x-ray technique.

From diffraction patterns (WAXD) of the PET films annealed at 120°C for different times, we can obtain the crystallinity as the ratio of the crystalline peaks area (subtracting the amorphous contribution) over the total diffraction area, according to a widely diffused method (26). In Fig.2 we report the increase of the crystalline order, X_c, as a function of annealing time. Up to 20 minutes it is possible to observe more clearly the different behaviour of the three samples.

In fact, whereas for sample Q_{25}, the process of crystallization starts at 90 seconds, we must wait until 3 min and 5 min, for obtaining an observable crystallinity in samples Q_{60} and Q_0 respectively.

Also this technique gives the information that the fresh sample Q_0 crystallizes much more slowly than the aged samples

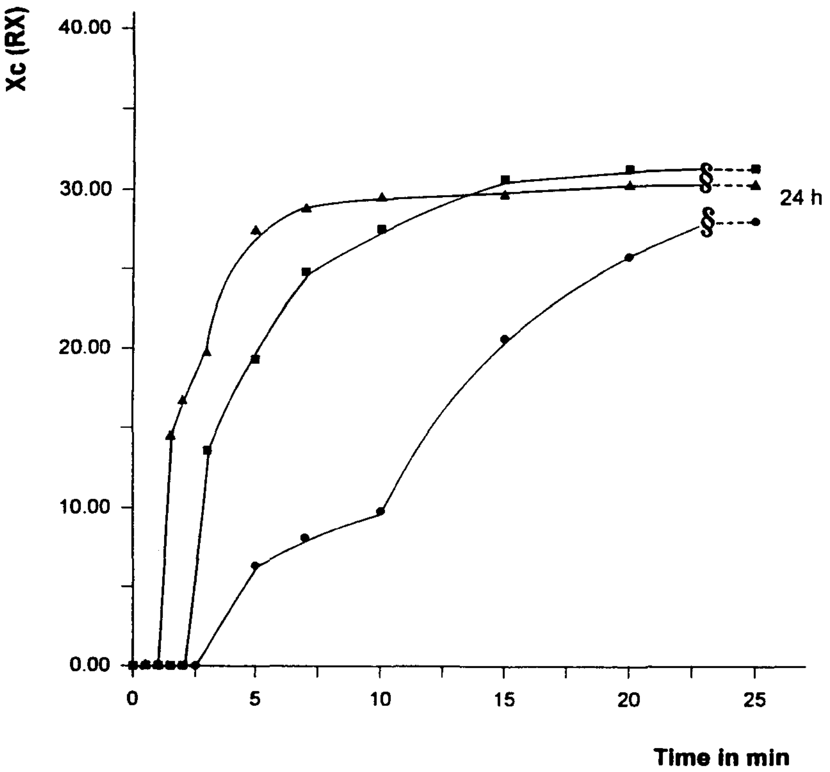

Fig. 2
The x-ray crystallinity X_c as a function
of the annealing time at 120°C
for the samples Q_0 (●), Q_{25} (▲) and Q_{60} (■)

Optical analysis

The crystallization process can be followed in the optical microscope, putting the samples of PET at 120°C and detecting the transmitted intensity of the polarized light through them.

At the beginning of the experiment, the amorphous samples are dark; when the crystallization starts the transmission of light is due to the formation of birefringent ordered zones, and therefore it can be correlated with the crystallization phenomenon.

In Fig.3 we report the reduced transmitted intensity, Ir, as a function of time. Also with this technique we observe different kinetics of crystallization for the three samples: the fastest for the sample Q_{25}, intermediate for the sample Q_{60}, and the slowest in the case of sample Q_0.

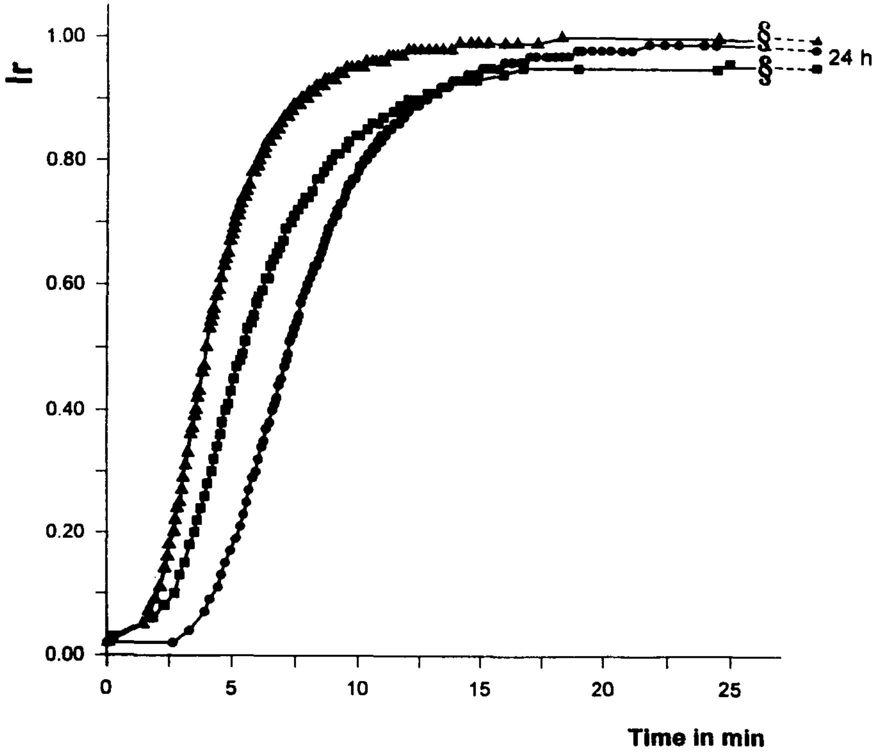

Fig. 3
The reduced transmitted intensity I_r as a function of the annealing timeat 120°C for the samples Q_0 (●), Q_{25} (▲) and Q_{60} (■).

It is possible to compare the influence of the structural organization of the three starting samples on the kinetics of crystallization, from Figs.1, 2 and 3. We observe that, with all the techniques, sample Q_{25}, aged at room temperature for 1 month, shows the fastest crystallization; instead, sample Q_0, put at crystallization temperature as soon as prepared, crystallizes more slowly. Intermediate behaviour, but nearer to sample Q_{25} is shown by sample Q_{60}, annealed at 60°C for 1 month.

On the basis of the transport properties, in the amorphous samples of PET annealed at 60°C, we hypothesized the presence of "ordered domains", of dimension such as to be impermeable to the penetrant vapour at low activity. Moreover the process of solvent induced crystallization was delayed in the fresh sample, therefore we concluded that the presence of these domains in the aged samples favoured the crystallization process (25).

The present results, regarding the effects of ageing in different conditions on the thermal crystallization rate, lead us to the conclusion that also in the thermal crystallization these domains, constitute possible nuclei of crystallization that favour the process.

The absence of these "more organized zones" delayes in the fresh sample the crystallization, as all the techniques clearly show.

CONCLUSIONS

We have investigated the crystallization process from the glassy state of three samples of Poly(ethyleneterephthalate), aged at different temperatures for different times.

According to previous results (25), the three samples analyzed have a different structural organization. The different structural organization is reflected in different crystallization kinetics at 120°C: the sample crystallized as soon as prepared shows the slowest kinetics, whereas the fastest is shown by the sample aged at 25°C. This result leads to the conclusion that the possible presence of "ordered domains" in the aged sample favours the crystallization at 120°C, because these domains constitute nuclei of crystallization.

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