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Effect of a Thermotropic Liquid Crystalline Polymer on the Physical Ageing of PET

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In this work the effect of the presence of a thermotropic liquid crystalline polymer (TLCP) on the physical ageing of poly(ethylene terephthalate) (PET) was investigated. Physical ageing of PET and its blends with a TLCP was carried out by annealing the samples at 60°C for several ageing times. Structural relaxation has been revealed by DSC through the analysis of position and magnitude of the endothermic peak superposed on the glass transition. It was found that the peak increases and shifts towards higher temperatures as the annealing time increases for all materials analysed. With respect to the PET matrix, blends submitted to physical ageing show an increase in the ageing rate by a percentage that increase with the amount of TLCP. Moreover, increasing the fraction of liquid crystalline component, a continuos decrease of the cold crystallisation temperature has been also observed.

Keywords: poly(ethylene terephthalate); physical ageing; enthalpy relaxation; differential scanning calorimetry; thermotropic liquid crystalline polymer; PET/TLCP blends

INTRODUCTION

Structural alterations and physical changes are known to result from ageing glassy polymers below their glass transition temperatures[1-6]. When samples are quenched from the melt in their glassy state, molecules are frozen into a non equilibrium state with higher energy and volume than would be present at their corresponding thermodynamic equilibrium state. Over time the glassy

structure is gradually reorganised towards an equilibrium state by eliminating some of the excess enthalpy, affecting in particular properties depending on molecular mobility. This process is called structure relaxation or generally physical ageing. The long-range chain conformational structure and interchain aggregation of an amorphous polymer will depend on the way the solid was prepared and on the thermal and mechanical history of the sample. Several papers[2, 7-11] report on the formation of ordered structures in amorphous polymers during physical ageing. In particular many studies on the effect of local chain organisation on the enthalpy relaxation of glassy polymers were done on poly(ethylene terephthalate). PET, in fact, can be obtained easily in different glassy states by selecting a suitable preparation conditions.

In recent years considerable attention has been focused on blends of thermoplastic polymers like PET and thermotropic polymers[12-14]. It is well known that TLCPs offer the potential of enhanced properties and improved processability owing to their highly anisotropic molecules which organise in ordered domains and orient easily during flow. These blends are essentially incompatible and the properties are significantly affected by degree of dispersion, shape, size and orientation of the TLCP, and by interfacial adhesion between the two phases.

In a previous work[15] the effect of physical ageing on blends composed of PET and a TLCP (Rodrun 3000) has been analysed by transport properties. The results have shown that shorter ageing times are required to increase the imper-meability of the blends respect to the pure PET. Following these results, the aim of this work is to better understand how the presence of TLCP influences the ageing phenomena of PET. Physical ageing was studied by measuring enthalpy changes by differential scanning calorimetry (DSC). Using this technique enthal-py relaxation for different ageing conditions can be determined from the shape and position of the endothermic peak that appears around T_g when the sample is aged at a temperature below T_g[16].

EXPERIMENTAL

The study was conducted on a commercial poly(ethylene terephthalate) (PET) with intrinsic viscosity 0.6 dL/g provided by Montefibre and on its blend with a thermotropic liquid crystalline polymer. The TLCP used was the Rodrun 3000, a copolyester composed of 60% mol *p*-hydroxybenzoic acid and 40% mol PET, produced by Unitika. A Gimac single screw extruder (L/D=24, D=12 mm, temperature profile: 270-275-280 °C), provided with an extrusion head of 200 mm x 0.5 mm, was used to make cast films from net PET and from three blends PET/TLCP containing 2, 10 and 30% w/w of Rodrun 3000. In order to suppress the effect of the previous thermomechanical history, samples for testing were prepared moulding the cast films at T=280 °C and P=4 bar for 2 min using an hydraulic press and quenching them in an ice water bath. The sheets obtained were about 50 μm thick. The annealing of the samples has been performed in a vacuum oven at T_a=60 °C for different times (from 6 to 1440 h). The unaged and aged samples were amorphous as revealed by X-ray diffraction analysis.

Calorimetric measurements were performed with a Mettler Differential Scanning Calorimeter mod. DSC30 calibrated for temperature and enthalpy with metallic standards (indium and zinc). In order to minimise thermo-oxidative degradation phenomena all scans were run under a nitrogen gas purge. DSC thermograms were obtained from 9-10 mg samples at various ageing times, sealed in standard aluminium pans, heated from 30 to 300 °C at a heat-ing rate of 10 °C/min. Enthalpy relaxation developed during the physical ageing was calculated integrating the endothermic peak area at T_g of the aged specimens.

RESULTS AND DISCUSSION

In order to characterise the evolution of ageing in the materials, amorphous samples were prepared for DSC measurements by melting the films of the net

materials and blends at 2, 10, and 30% w/w of Rodrun 3000 in PET and quenching them in ice water. DSC thermograms for amorphous PET annealed at T= 60°C for different times are shown in Fig. 1. As expected the curves show an endothermic peak at T_g as a result of the structural relaxation process that the material undergoes. Increasing ageing times the endothermic peak moves towards higher temperatures, increasing its amplitude. These behaviours are established features of physical ageing for glassy polymers, as reported by other authors[1, 5, 16].

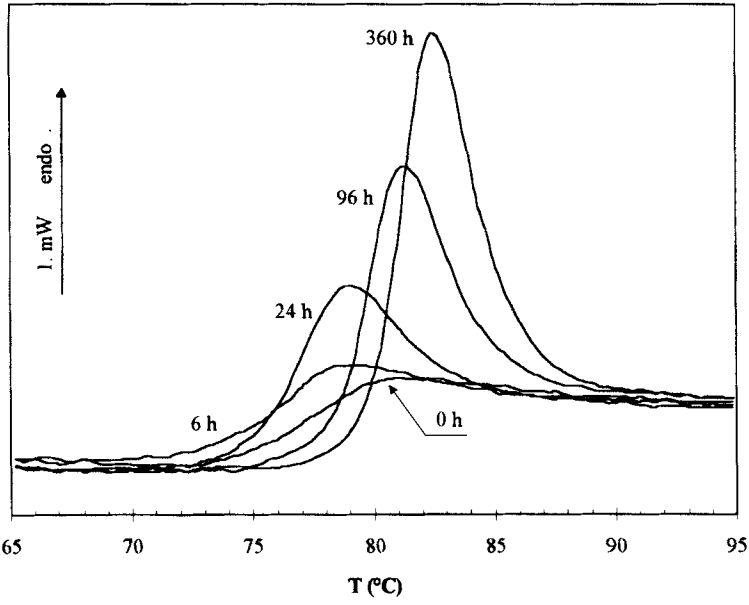

FIGURE 1 DSC thermograms for amorphous PET annealed at T= 60°C for different times.

Samples of pure TLCP were prepared and annealed in the same conditions used for PET to investigate if also this polymer undergoes ageing phenomena. In Fig. 2 DSC curves are reported. As it can be observed also the Rodrun 3000 undergoes a structural relaxation, however the temperature range

do not overlap with that of PET.

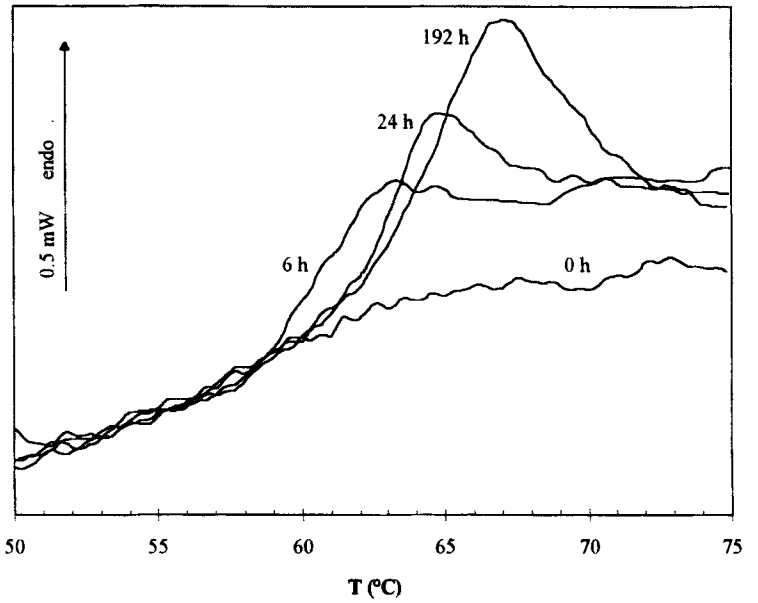

FIGURE 2 DSC thermograms for Rodrun 3000 annealed at T= 60°C for different times.

In Fig. 3 the dependence of enthalpy relaxation ΔH on the ageing time is shown for both materials. The slope of this curve is a measure of the relaxation rate, which is high at the beginning either for PET and Rodrun 3000. Increasing ageing time it falls due to the decrease of the free volume of the system, and therefore in the molecular mobility. It appears that the Rodrun 3000 approaches a metastable equilibrium earlier than PET.

Blends at different ratios (2, 10, 30% w/w) of TLCP in PET have been prepared in order to evaluate the effect of the mesophase on the enthalpy relaxation of PET. The thermal behaviour of this system was analysed in a

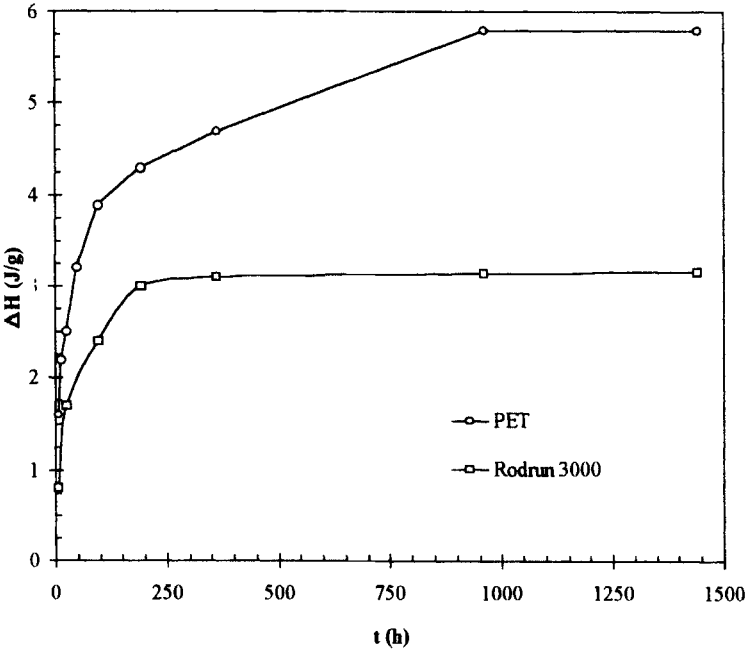

FIGURE 3 Enthalpy relaxation in function of the ageing time for PET and Rodrun 3000 samples.

previous work[17] and the results have shown that the system is essentially incompatible. Samples of each blend were annealed at T_a=60 °C at the same ageing times used for PET and DSC measurements were carried out.

All DSC curves of the blends show an endothermic peak around T_g of PET. In particular for the same ageing time the maximum of the endothermic peak (T_{max}) takes place at a temperature very similar for all blends analysed and for PET matrix. However increasing the TLCP content up to 30% w/w, DSC thermogram shows two ageing peaks corresponding to each of components, even though the ageing peak relative to TLCP phase is very small At this regard in Fig. 4 are reported the DSC curves of PET, Rodrun 3000, and 70/30 PET/Rodrun 3000 blend in the temperature range involving the enthalpy

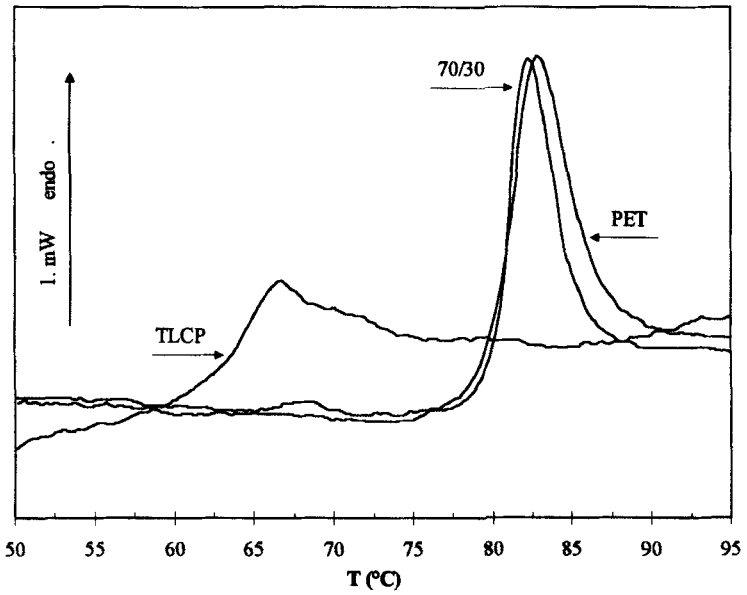

FIGURE 4 DSC curves of PET, Rodrun 3000, and 70/30 PET/Rodrun 3000 blend in the temperature range involving the enthalpy relaxation phenomena.

relaxation phenomena. The presence of two ageing peaks increasing the amount of TLCP confirms the immiscibility of the system. The enthalpy relaxation of the blends, normalised to the PET content, appears dependent on the TLCP percentage. In particular the peak area increases with the amount of TLCP in the blend, at equivalent time. The dependence of enthalpy relaxation on the ageing time for PET and blends is illustrated in Fig. 5. Comparing the slope of the curves at the beginning of ageing, it is evident that the blends show an increase in the ageing rate and approach a metastable equilibrium earlier than the pure PET. In particular at TLCP content of 30 weight percent a *plateau* value of enthalpy relaxation is reached for an ageing time of about 150 h. The blends at 2 and 10% w/w of TLCP do not show difference in the enthalpy relaxation behaviour and a *plateau* value is reached at about 360 h, while PET

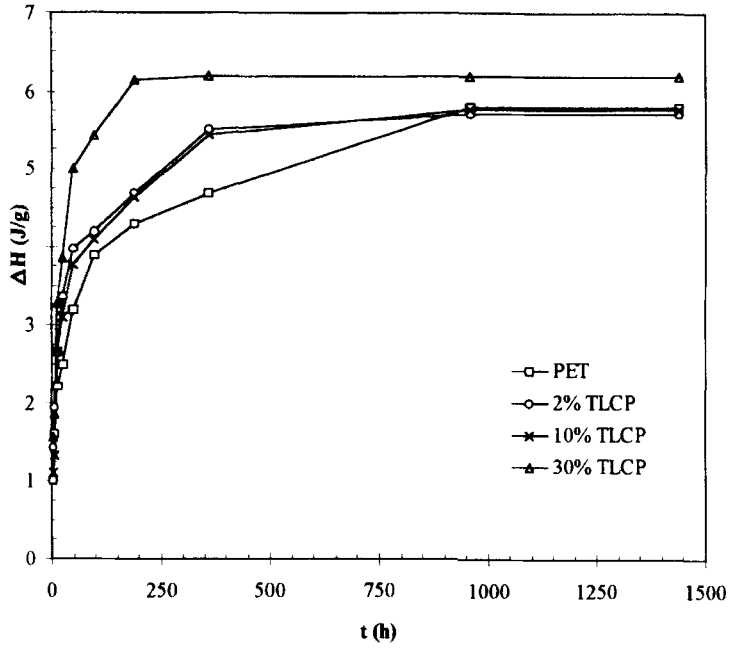

FIGURE 5 Enthalpy relaxation in function of ageing time for PET and PET/TLCP blends at 2, 10 and 30% w/w of TLCP.

needs an ageing time of 960 h.

According with these results in a study conduced on the ageing effects on the transport properties of this system, we have found that two days were enough to increase significantly the impermeability of the blends to the vapours at low activity while longer times were required for the pure PET. The decrease of permeability was attributed only to a lowering of sorption because the diffusion parameters for the aged samples coincide with those of unaged samples. The lowering of sorption was already observed for other systems[18-20] and was attributed to the presence of ordered regions that are impermeable to the vapours, behaving as crystalline phase. From these observations and the results reported so far we can hypothesise that the inclusion of TLCP in PET

promotes the formation of ordered structures in the amorphous phase during physical ageing, so that blends require shorter times of ageing to reorganise towards an equilibrium state.

Increasing the fraction of liquid crystalline component we also observed a continuous decrease in the cold crystallisation temperature (T_c). It was verified that the crystallisation temperature was not significantly influenced from the ageing time for all materials analysed. Representative DSC scans of blends and PET samples aged at 60 °C for 192 h are reported in Fig. 6.

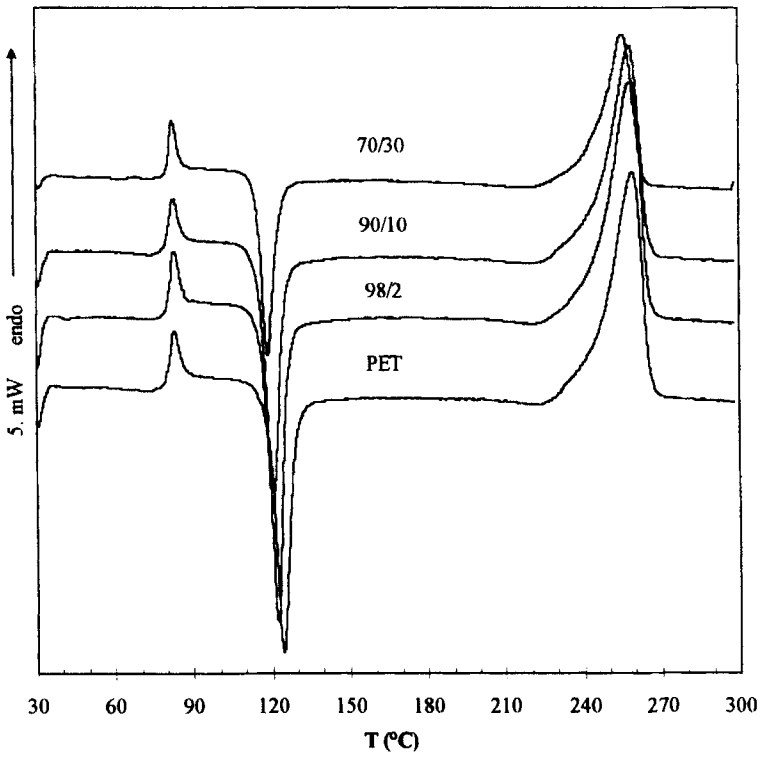

FIGURE 6 DSC thermograms of PET sample and PET/TLCP blends at 2, 10 and 30% w/w of Rodrun 3000.

Moreover the inclusion of TLCP influences also the enthalpies of crystallisation (ΔH_c). In fact, ΔH_c of the blends, normalised to the PET content, increases with increasing of Rodrun 3000 amount, as shown in Fig. 7. All the results obtained indicate that the cold crystallisation is favoured by the presence of the liquid crystalline component, confirming that the presence of nematic domains provides «nucleating» sites within the amorphous matrix that promote the formation of ordered structures.

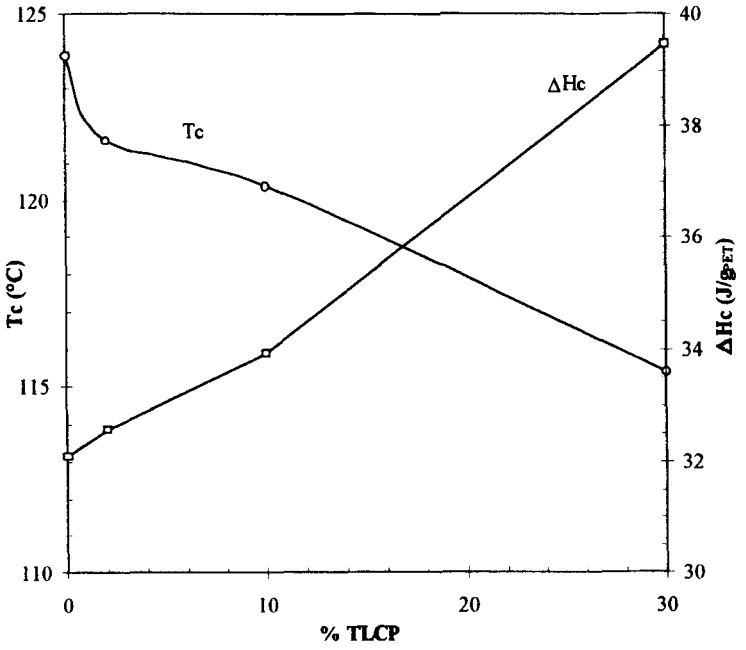

FIGURE 7 Crystallisation enthalpy (ΔH_c), normalised to the PET content, and crystallisation temperature (T_c) for the blends PET/Rodrun 3000.

CONCLUSIONS

The effect of the presence of a liquid crystalline polymer (Rodrun 3000) on the physical ageing of PET has been studied by DSC. It was found that respect to PET matrix, blends submitted to physical ageing show an increase in the ageing rate by a percentage that increase with the amount of TLCP. Increasing the fraction of liquid crystalline component we have also observed a continuous decrease in the cold crystallisation temperature and an increase in the crystallisation enthalpy. Analysing these results and the transport data obtained in a previous work[15] on this system we can hypothesise that the presence of TLCP domains promotes the formation of ordered structures withii the amorphous matrix during physical ageing.

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