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# Microhardness and DSC measurements on liquid crystalline poly(diethylene glycol *p,p'*-bibenzoate) as a function of the ageing time

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**Summary**

The ageing process of the liquid crystalline glass of poly(diethylene glycol *p,p'*-bibenzoate), PDEB, has been studied by differential scanning calorimetry and microhardness measurements. The experiments have been performed on a sample of PDEB aged at 36°C during different times. The process was found to be rather fast at that temperature, and the results from both techniques are compared.

## Introduction

When a polymer melt is quenched from a temperature above the glass transition, $T_g$, to below it, the subsequent recovering of physical properties of the resulting glass towards equilibrium is termed as physical ageing (1). Several works (2-5) have been devoted to study the ageing process in amorphous and semi-crystalline polymers as well as in filled rubbers. To our knowledge, there is no such study on a liquid crystalline polymer glass.

Microhardness, MH, measurements are an adequate tool in order to detect transitions in polymers. These transitions can be located by means of temperature-dependent MH determinations (6). Moreover, this technique has been related to macroscopic parameters derived from stress-strain plots, namely elastic modulus and yield stress (7). Therefore, MH measurements can be used for studying the ageing of polymers, as this phenomenon involves changes of glass transition and modulus. On the other hand, the use of differential scanning calorimetry, DSC, for the study of the ageing process has been well established (8).

Poly(diethylene glycol *p,p'*-bibenzoate), PDEB, is a polyester which exhibits liquid crystalline character (9) and the presence of the central ether group in the spacer inhibits the transformation of the mesophase into a three-dimensional crystal found for similar polybibenzoates with all-methylene spacers (10-12). As usual in mesophase forming polymers, the liquid

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crystalline phase cannot be avoided with regular quenching conditions and PDEB displays a glass transition temperature which actually corresponds to a transition from the liquid crystalline glass.

This work is concerned with some preliminary results about ageing effects in the liquid crystalline glass of PDEB. Microhardness and DSC measurements have been performed for that purpose and the results from both techniques are compared.

**Experimental**

PDEB was synthesized by melt transesterification of the diethyl ester of *p,p'*-bibenzoic acid and diethylene glycol, using isopropyl titanate as catalyst. The polymer was purified by precipitating into methanol its solution in chloroform. The value of the intrinsic viscosity, measured at 25°C in chloroform, was 1.02 dL $g^{-1}$.

A Perkin-Elmer DSC7 calorimeter has been used for the DSC analysis of the ageing. The magnitude of this process has been estimated from the enthalpy of the endothermic peak appearing at the top of the glass transition, considering the baseline resulting from the prolongation of the specific heat curve above the glass transition temperature.

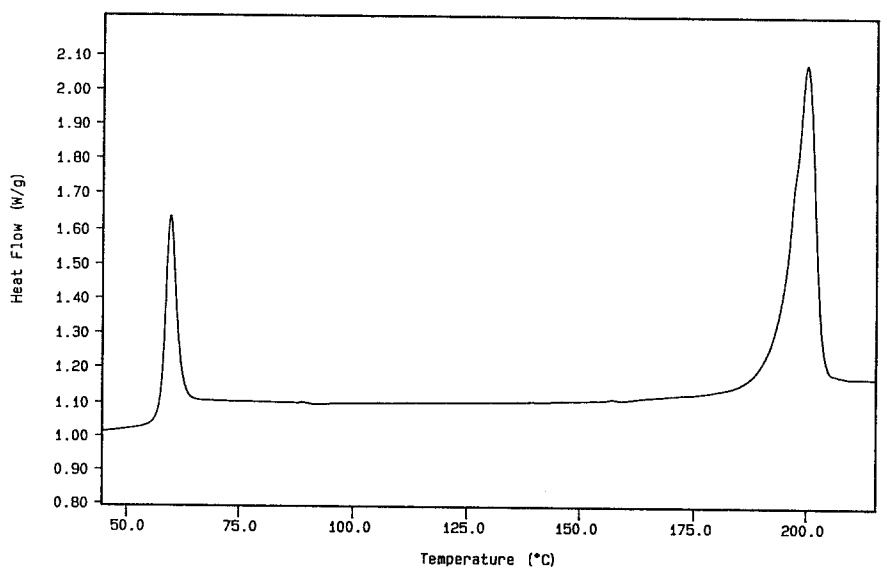


Fig. 1. DSC curve of a sample of PDEB aged at room temperature during ten months.

Microhardness measurements and ageing were carried out simultaneously by using a Vickers indentor attached to a Leitz microhardness tester and a Mettler FP2 hot stage. A load of 0.245 N was used, with a contact time of 5 s. This value was selected in order to avoid that the flow under the action of the indentor were affected by simultaneous ageing. MH values (in MPa) were calculated according to the relationship:

$$MH = 2 \sin 68° \, P/d^2$$

where P (in N) is the contact load and d (in mm) is the diagonal length of the projected indentation area.

Both DSC and MH measurements have been performed on a sample of PDEB aged at 36°C during different times.

**Results and discussion**

Fig. 1 shows the thermal transitions of a sample of PDEB quenched from the melt to ambient conditions and aged at room temperature during 10 months. The glass transition can be observed with an onset at 55°C, presenting an endothermic peak at the top centered at 60°C, with an apparent enthalpy of 4.3 J $g^{-1}$. The second peak, at 200°C, corresponds to the isotropization of the mesophase and exhibits an enthalpy of 17.6 J $g^{-1}$. That

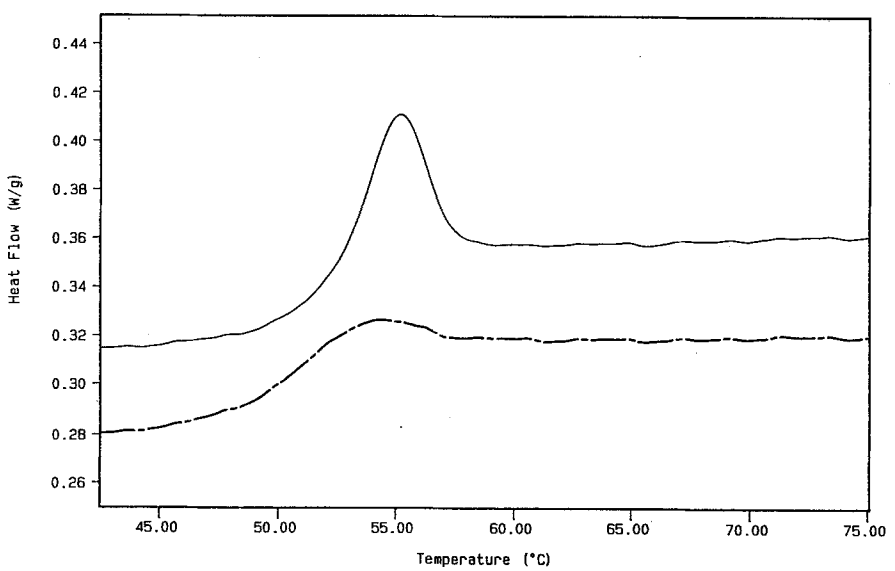


Fig. 2. DSC curves of PDEB aged at 36°C during 30 min (lower) and 215 min (upper)

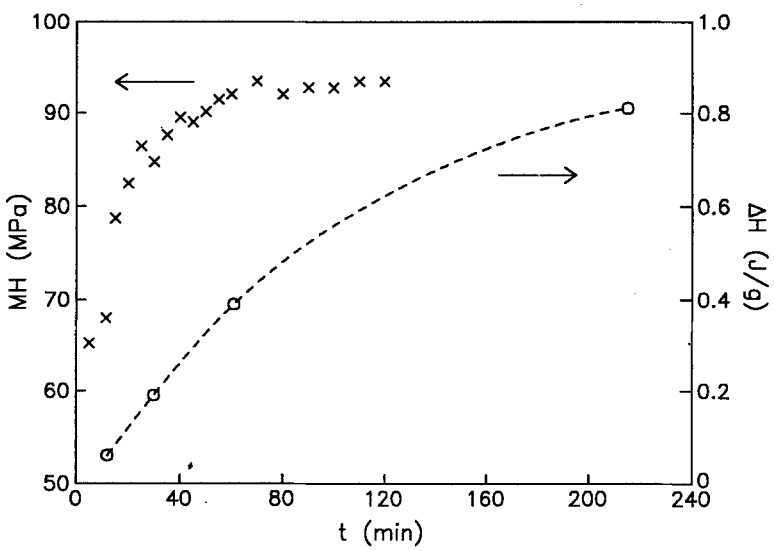


Fig. 3. Microhardness values and enthalpies of ageing as a function of time for a sample of PDEB aged at 36°C

the peak at 60°C is related to the ageing of the sample can be deduced from figure 2, where the glass transition corresponding to two different ageing times at T=36°C are presented. It can be observed that the endothermic peak appears in the region of the glass transition, at a temperature slightly higher, and it grows with the ageing time. Figure 3 shows the change of the enthalpy associated to the ageing peak as a function of the residence time at 36°C. Considering that the limiting value of the enthalpy of ageing is at least 4.3 J $g^{-1}$, as in figure 1, the process is still far from equilibrium in the experiments of figure 3.

Microhardness measurements have been also made on the PDEB sample in the first two hours of ageing at 36°C. The results are presented in figure 3 together with the DSC determinations. It is evident from this figure that the MH of the sample raises to a value almost two times higher after an ageing time of only two hours at 36°C, a clear evidence of the importance of this process for the final properties of the sample. The relative change on the microhardness appears to be higher than the enthalpy one. Thus, the MH increase is very slow after the first hour of ageing in contrast with the enthalpy values, which seem to display a smooth increase in the analyzed interval.

More experiments are in progress in order to analyze the kinetics of the ageing process from the measurements at different

temperatures and times. Furthermore, the correlation between MH and modulus will lead to a better understanding of the ageing phenomenon in this liquid crystalline sample.

**Acknowledgment**

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**References**

1. Struik LCE (1978) Physical aging of amorphous polymers and other materials. Elsevier, Amsterdam
2. Struik LCE (1987) Polymer 28: 1521, 1534
3. Petrie SEB (1976) J Macromol Sci Phys B12: 225
4. Tant MR, Wilkes GL (1981) Polym Eng Sci 21: 874
5. Montserrat S, Cortés P (1986) An Quim 82: 499
6. Lorenzo V, Benavente R, Pérez E, Bello A, Pereña JM (1991) J Non-cryst Solids 131-133: 584
7. Lorenzo V, Pereña JM, Fatou JG (1989) Angew Makromol Chem 172: 25
8. Ref 5 and refs therein
9. Pérez E, Benavente R, Marugán MM, Bello A, Pereña JM (1991) Polym Bull 25: 413
10. Watanabe J, Hayashi M (1988) Macromolecules 21: 278
11. Pérez E, Bello A, Marugán MM, Pereña JM (1990) Polymer Commun 31: 386
12. Pérez E, Riande E, Bello A, Benavente R, Pereña JM (1992) Macromolecules 25: 605

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