JOURNAL OF MATERIALS SCIENCE LETTERS **8** (1989) 1418-1419

Temperature dependence of microhardness indentations and dynamic mechanical moduli of polyesters in the vicinity of the glass transition

C. C. GONZÁLEZ, J. M. PEREÑA, A. BELLO
Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain

B. MARTÍN, J. C. MERINO, J. M. PASTOR
Física de la Materia Condensada, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

The hardness of polymers was one of the early quality-control tests for characterizing these materials. The later use of small loads and the consequent measurements of the indentations by means of a microscope have led these tests to be considered non-destructive, and have brought about a revival of microhardness studies of polymers, mainly polyolefins. These works have aimed to detect the textural, morphological and surface changes in these polymers [1], to measure the geometry and recovery of the indentation [2], to relate these parameters to the macroscopic mechanical properties [3, 4], to study the structural uniformity of poly(vinylidene chloride) powder compacts [5], to measure the orientation of hot-drawn poly(ethylene terephthalate) by evaluating the microhardness anisotropy [6] and to assess the parellelism between the temperature dependences of microhardness and dynamic mechanical moduli near the main and secondary relaxations of polypropylene [7] and polyethylenes [8].

Following these initial works [7, 8], the study of the temperature dependence of coupled measurements of microhardness indentations and dynamic mechanical moduli has been focused on polymers and copolymers derived from terephthalic acid and trimethylene glycols. The main relaxation of these polymers is the glass transition, which presents different intensities (measured as the maximum value of the loss modulus at the temperature of the relaxation) [9]. Thus, the aim of this work was to study the similarity between the sharp increase of the microhardness and the maximum of the loss modulus at the glass transition temperature and the quantitative parallelism of both values.

The polymers used in this work were poly(ditrimethylene terephthalate) (PDTMT) and a copolymer (COP) of this and poly(trimethylene terephthalate). Polyterephthalates were obtained by transesterification and polycondensation in the melt phase using dimethylterephthalate and the corresponding glycols with tetra-isopropyl titanate as the catalyst. The glycols used were trimethylene glycol (Merck), ditrimethylene glycol and a mixture of these (for the copolymer). Ditrimethylene glycol was synthesized by ring-opening polymerization of trimethylene oxide, initiated by sulphuric acid with methylene chloride as the solvent and trimethylene glycol as the transfer agent. A detailed study of these reactions is reported in [10].

Vickers microhardness measurements were carried out by means of a square-pyramidal indentor attached to Zeiss Universal equipment. In order to obtain reproducible microhardness values at the different temperatures of the samples, suitable test conditions in relation to the load and time of application of the indentor were established previously (20 g and 30 sec for COP, and 10 g and 30 sec for PDTMT, for the experimental temperature range). Moreover, the limited range of temperature allowed by the optical system of the microscope in order to avoid damage to the lenses must be borne in mind. A continuous flow of nitrogen gas, at a controlled temperature, through the variable-temperature cell allows working between −70 and 70° C with an accuracy of 0.5° C. The gas is expelled from the upper part of the cell creating a dry atmosphere around the sample in order to avoid the formation of frost on its surface [11]. The microhardness measurements were performed with temperatures increasing in steps smaller than 1° C, and the values correspond to the average on different positions of the sample.

The dynamic mechanical behaviour was determined with a Rheovibroin DDV II-B dynamic viscoelastometer (Toyo Measuring Instruments Co.). The complex modulus and the loss tangent were measured at 3.5 Hz and the storage (E') and loss (E'') parts of the complex elasticity modulus were calculated at temperatures ranging from −20 to 20° C, with the same specimen used for indentation microhardness measurements. The temperature range was scanned in steps smaller than 2° C, in order to visualize clearly the viscoelastic behaviour in the vicinity of the glass transition. In the case of the micro-indentations the temperature interval between consecutive measurements was smaller still, since the increase in microhardness at the glass transition is very sharp. Moreover, it has previously been reported [9] that there is no crystallization at the working temperatures of the present sets of measurements.

Fig. 1 shows the variation of the microhardness as a function of the temperature for PDTMT and COP samples, presenting a sharp maximum at 1 and 18° C, respectively. Similar behaviour of the temperature dependence of microhardness has been detected in

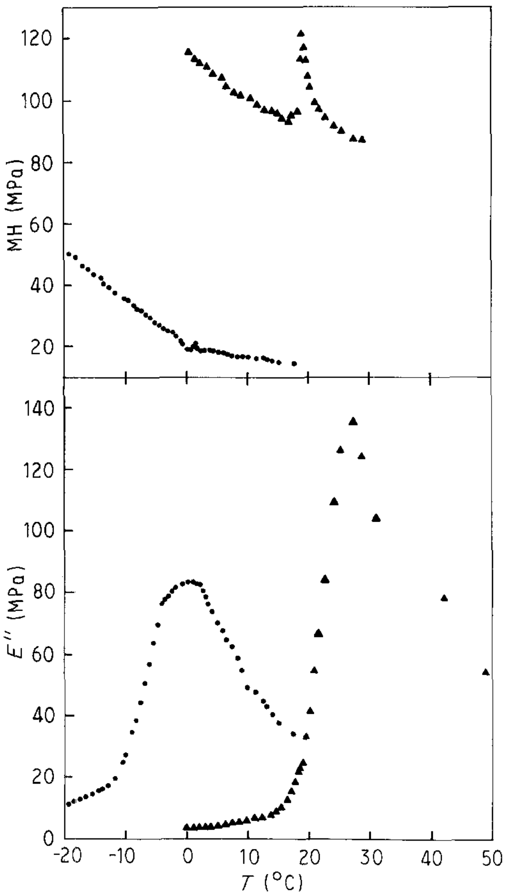

Figure 1 Temperature dependence of microhardness (MH) and dynamic mechanical loss modulus (E'') of (●) PDTMT and (▲) COP.

studies of the Curie points in ferroelectric materials [12–15]. Moreover, the parallel viscoelastic behaviour of the polyesters is also shown in Fig. 1, showing a maximum of the loss modulus of the polymers at 0 and 26° C, respectively.

The increases of the relative intensity for the loss modulus, calculated on a percentage basis from the maximum E''-values corresponding to the glass transitions and referred to the minimum values taking place at around -50° C, are 3300 and 730% for COP and PDTMT, respectively. Similarly the percentage increments of the maximum value of microhardness, referred to the near minimum at lower temperatures, are 29 and 7% for COP and PDTMT, respectively. Both pairs of values show that the intensity increments measured by dynamic mechanical and microhardness measurements are quantitatively comparable, even though the intensity increases of dynamic mechanical measurements are mush higher than those of the microhardness ones. Moreover, the change of microhardness in the vicinity of the glass transition is very pronounced, as reported for the T_g of polypropylene [7], whereas that change is weaker and does not present a maximum for the secondary relaxations [8].

In conclusion, the variations of microhardness with the temperature provides insight into the viscoelastic properties, allowing precise establishment of the position of the glass transition temperature measured by dynamic mechanical techniques and quantitative comparison of the relative intensity of the corresponding maxima. These results will be confirmed and enlarged for other polymer series.

Acknowlekdgement

The financial support of the Comisión Interministerial de Ciencia y Tecnología (Grants MAT 88-0220 and PA 86-0198) is gratefully acknowledged.

References

1. F. J. BALTÁ-CALLEJA, J. MARTÍNEZ-SALAZAR and D. R. RUEDA, in "Encyclopedia of Polymer Science and Engineering" Vol. 6, 2nd Edn (Wiley, New York, 1986) p. 614.
2. V. LORENZO, J. M. PEREÑA, J. M. G. FATOU, J. A. MÉNDEZ-MORALES and J. A. AZNÁREZ, *J. Mater. Sci. Lett.* **6** (1987) 756.
3. V. LORENZO, J. M. PEREÑA and J. M. G. FATOU, *Angew. Makromol. Chem.* in press.
4. V. LORENZO, J. M. PEREÑA, J. M. G. FATOU, J. A. MÉNDEZ-MORALES and J. A. AZNÁREZ, *J. Mater. Sci.* **23** (1988) 3168.
5. R. CRAWFORD, D. PAUL and Y. ADEEBNIA, *Eur. Polym. J.* **16** (1980) 401.
6. V. LORENZO and J. M. PEREÑA, *J. Appl. Polym. Sci.* in press.
7. B. MARTÍN, J. M. PEREÑA, J. M. PASTOR and J. A. DE SAJA, *J. Mater. Sci. Lett.* **5** (1986) 1027.
8. J. M. PEREÑA, B. MARTÍN and J. M. PASTOR, *ibid.* **8** (1989) 349.
9. C. C. GONZÁLEZ, J. M. PEREÑA and A. BELLO, *J. Polym. Sci., Polym. Phys. Ed.* **26** (1988) 1397.
10. C. C. GONZÁLEZ, A. BELLO and J. M. PEREÑA, *Makromol. Chem.* **190** in press.
11. J. M. PASTOR, A. MONTIEL, F. RULL and J. A. DE SAJA, *J. Phys. E: Scient. Instrum.* **14** (1981) 71.
12. J. M. PASTOR, F. RULL, B. MARTÍN and J. A. DE SAJA, *Ferroelectrics* **34** (1981) 227.
13. B. MARTÍN, J. C. MERINO, J. M. PASTOR and J. A. DE SAJA, *J. Phys. C: Solid St. Phys.* **15** (1982) 1067.
14. B. MARTÍN, J. M. PASTOR, F. RULL and J. A. DE SAJA, *Solid St. Commun.* **44** (1982) 1047.
15. B. MARTÍN, J. C. MERINO, J. M. PASTOR and J. A. DE SAJA, *Ferroelectrics* **55** (1984) 261.

Received 19 May
and accepted 7 July 1989