

Characterization of the Isothermal Crystallization of Poly(ethylene Terephthalate) by Microhardness Measurements

J. M. PASTOR,* A. GONZÁLEZ, and J. A. DE SAJA, *Física de la Materia Condensada, Facultad de Ciencias, 47011 Valladolid, Spain*

Synopsis

The two-stage isomerization isotherms of poly(ethylene Terephthalate) have been followed through microhardness analysis. A great variation in microhardness values seems to prove the increase of the strength and stiffness of the samples produced by the secondary isomerization. A smaller variation is observed for the primary isomerization.

INTRODUCTION

In the last years the influence of the crystallinity degree in discussing the physicochemical behavior of the semicrystalline polymers has been largely considered. Diffraction measurements, thermal analysis, electron microscopy, and vibrational spectroscopic studies are the standard tools in academic laboratories for characterizing this parameter, but the industrial use and interpretation of the results obtained by these techniques is in general long and complicated. That is why a new test necessarily has to be found so that the value of the crystallinity levels or its evolution versus several thermal and mechanical treatments can be supplied in a simple and effective way.

This challenge is part of a continuing program of our laboratory dealing with the application of the microhardness measurements in the study of chemistry and physical structural transformations.¹⁻⁴ This technique is a very interesting nondestructive test, of difficult microscopic interpretation, but whose simplicity and high sensitivity make it suitable for industrial purposes, if it has previously been correlated with the above microscopic indicated techniques.

In an early investigation² we have proved the validity of this method in the study of the crystallinity changes which occur during the annealing of a stabilized PVC under different conditions, and in this paper we try to extend these results to other interesting semicrystalline polymer: the poly(ethylene terephthalate) (PET), in samples with different times and temperatures of crystallization. This compound is a well-known polymer with important industrial applications and with an additional interest for our purposes since it shows a wide range of crystallinity as a result of thermal treatment above the glass transition temperature ($T_g \sim 75^\circ\text{C}$). The isomerization isotherms (as

*Author for correspondence.

a function of annealing time) allows one to distinguish two stages in the transformation process.⁵ The first one corresponds to a transformation from the gauche conformation of the amorphous phase to a trans conformation of the crystalline form. This evolution corresponds to the sigmoidal curve of the isomerization isotherm.⁵ A later linear evolution of this curve is a consequence of a secondary crystallization process.

Several kinetic measurements using FTIR, DSC, optical measurements, etc.⁵⁻¹¹ have been carried out in order to clarify the mechanism of the gauche-trans isomerization process and its time and temperature dependence.

This paper is concerned mainly with the analysis of the microhardness results on samples with a variety of temperatures and times of crystallization in order to follow the evolution of the two-stage isomerization process, previously contrasted by intensity Raman measurements.

EXPERIMENTAL

Materials

A commercial PET with a molecular weight M_n of 20,000 was used in this work. Unoriented amorphous samples of 1 mm thickness were obtained by melt-pressing the blend for 30 s at 250°C and quenching in ice-water. X-ray diffraction diagrams showed no crystallinity after this treatment.

Samples of 6 × 6 mm cut from the above sheets were crystallized at various temperatures above the glass transition temperature (75°C) until 225°C for times ranging from 5 min to 7 days and then cooled in an ice-water bath. Thermal treatments were made in a forced draft oven which was nitrogen-purged to avoid degradation during the experiments.

Apparatus

Vickers microhardness (MHv) measurements were carried out at room temperature by means of a square-pyramidal indenter in a Zeiss Universal equipment.¹ In order to make the MHv measurements serviceable for PET, suitable test conditions have to be established previously in relation with the load and time of application of the indenter (40 g and 30 s, respectively).

Raman spectra were obtained using the Dilor XY spectrometer with multi-channel detection (512 intensified diodes). Spectral slit widths were ca. 1.5 cm^{-1} for all measurements. The spectra were recorded with 50 accumulations using the spectrometer in the high dispersion mode. The 514.5 nm exciting line of a Spectra Physics argon-ion laser (mod. 2020/5 w) was utilized as the source of illumination. The laser power was approximately 150 mW at the sample.

RESULTS

Raman Measurements

Thermal treatments in PET cause an essential change in the crystallinity of this material and consequently in the vibrational behavior. Therefore, the vibrational spectrum of this compound has been largely studied.^{5,12-22} These

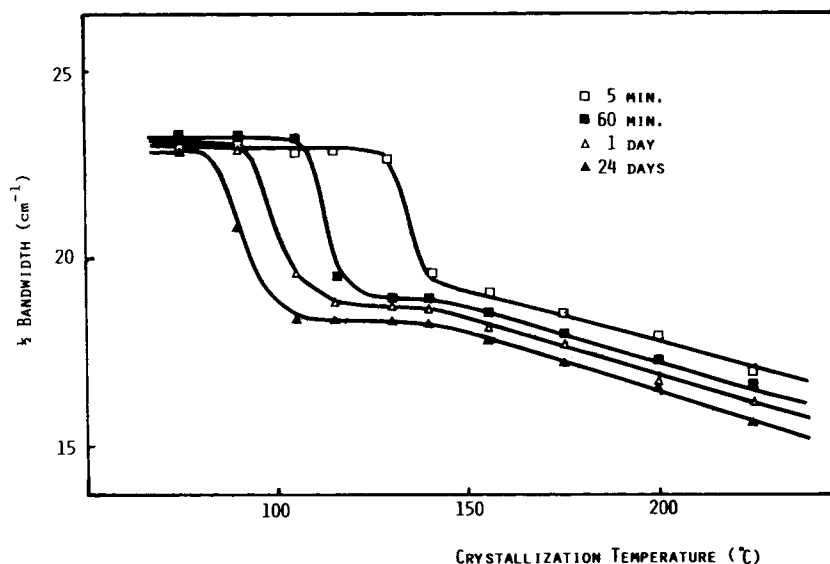


Fig. 1. Raman bandwidth at half maximum intensity of C=O stretch as a function of the annealing temperature for PET samples.

changes, though related to the crystallinity, are explained as being due to the conformational changes.

Crystallization has been correlated with the width of the carbonyl band at 1730 cm^{-1} . Melveger¹⁷ showed a correlation between the density of a PET sample and the half width of the carbonyl band situated at $1725\text{--}1730\text{ cm}^{-1}$. On the other hand, the Raman peaks measured between 900 and 1220 cm^{-1} correlate with conformational changes and interchain effects rather than with amorphous-crystalline differences. This means that information about the crystallinity and conformation through the analysis of the Raman data from these two spectral regions can be found. In Figure 1 the carbonyl band half-width is presented for samples with different crystallization temperatures and times. In the same way Figure 2 represents the intensity ratio of the 1092 cm^{-1} to that at 1117 cm^{-1} . The peak at 1092 cm^{-1} appears in the crystalline material and it is characteristic of trans conformers, and 1117 cm^{-1} is a peak unchanged by these transformations. These figures show a similar sigmoidal curve and a later linear variation to that obtained by Infrared spectroscopy.⁵

Microhardness Measurements

As shown in Figure 3, substantial variations occur on the MHv behavior with the time and crystallization temperatures of the samples. In effect a variation of microhardness values is observed for the samples crystallized below 140°C at different times of crystallization. These results are similar to these previously observed by Raman spectroscopy.

Furthermore, a very strong change of microhardness is detected for all the samples at about 140°C and only slightly observed in Figure 1.

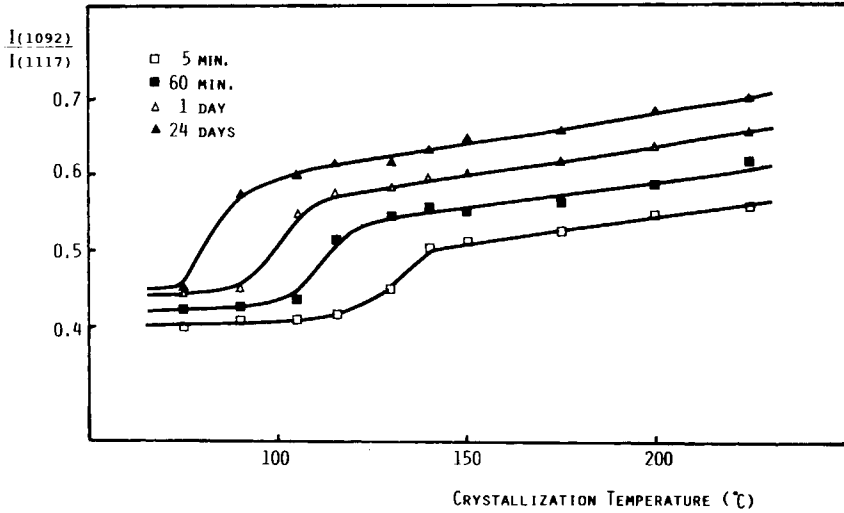


Fig. 2. Relative Raman intensity $I(1092 \text{ cm}^{-1})/I(1117 \text{ cm}^{-1})$ as a function of the annealing temperature for PET samples.

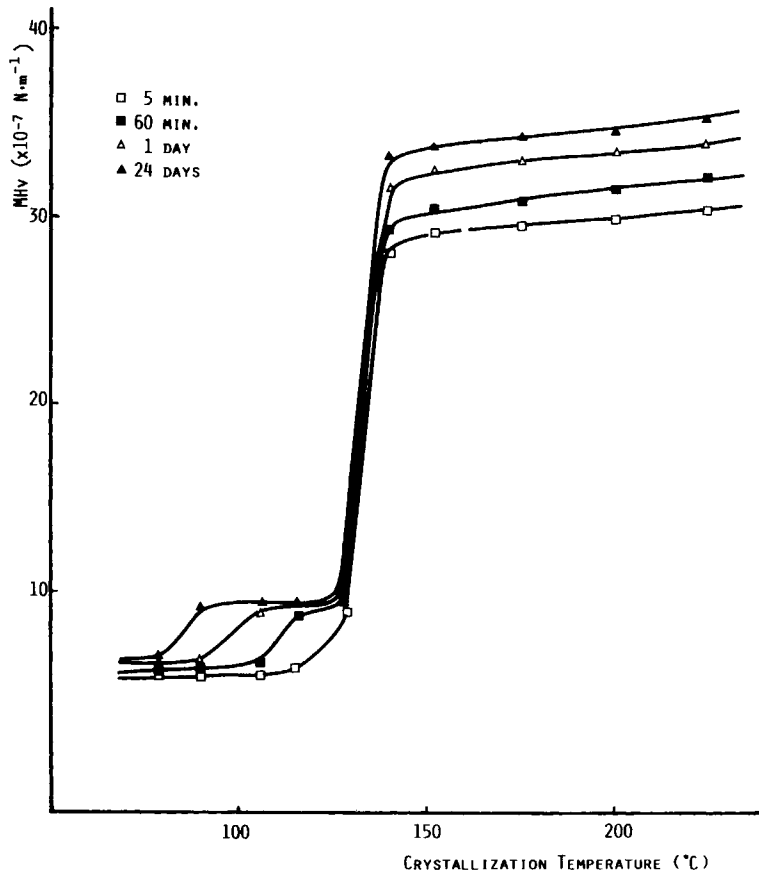


Fig. 3. Variation of the microhardness with the annealing temperature for PET samples.

DISCUSSION

The conformational studies made on the PET by infrared, Raman and NMR^{5,23-27} lead to a gauche structure in the amorphous phase and a trans conformation for the crystalline phase. Amorphous trans isomers, which are associated with interlamellar links and affect the tenacity of the PET fibers, are also observed.²⁷

It is detected that the amorphous trans content decreases as the crystalline trans content increases.^{5,20} In this way the 900–1100 cm^{-1} region from the Raman spectra has been analyzed for the PET with the purpose of identifying the bands corresponding to the different phases and studying their variation with the temperatures and times of crystallization. The sigmoidal curves (Fig. 2) occurring below 140°C are in agreement with Infrared experiments^{5,20} and correspond to the transformation from the amorphous phase to the crystalline one, or the increase of the crystalline phase (Fig. 1). The increase of this morphological change taking place above 140°C shown in Figures 1 and 2 means a continuous transformation from the amorphous to the crystalline phase.

This evolution is also followed through the microhardness technique, showing values with a similar behavior and can be interpreted as a low variation of the mechanical properties. However, at about 140°C a very important increase of the microhardness values is obtained, reflecting a great variation of the mechanical behavior.

This transformation is connected to the secondary isomerization process. In effect, it has been well characterized as a change of structure at crystallization temperatures above 140°C.^{11,28,29} The amorphous regions between the side faces of the micellar blocks begin to crystallize and the stacking of the lamellae becomes very clear at these high crystallization temperatures. As a consequence, the crystallites formed are higher, producing an increase of the strength and stiffness of the polymer. This last process can be clearly observed by the microhardness evolution (Fig. 3) but obviously it will be poor on the vibrational observation since the configurational change is less than the one produced on the primary isomerization.

CONCLUSIONS

The crystallization process of the PET compounds takes place in two stages. The amorphous phase is transformed to a crystalline phase, where imperfectly small crystallites are formed, through rotational gauche–trans isomerization. With crystallization temperatures above 140°C a loss of intercrystalline tie molecules occurs, and the crystallites become much larger. The Vickers microhardness (MHv) measurements reflect a great sensitivity to these morphological changes.

Detailed correlation between MHv results and the data obtained by all the other available physical method is necessary. From a more practical viewpoint, however, this research shows the microhardness testing as a very useful and sensitive tool which could be used to control the crystallization processes in PET.

The authors gratefully acknowledge financial support from the Dirección General de Investigación Científica y Técnica (PA86-0198).

References

1. A. González, J. M. Pastor, J. A. De Saja, and A. Pérez, *Angew. Makromol. Chem.*, **130**, 201 (1985).
2. A. González, B. Martín, M. Muñoz, and J. A. De Saja, *Polym. Testing*, **6**, 361 (1986).
3. A. González, J. Martín-Gil, J. A. De Saja, and R. Rodríguez, *J. Appl. Polym. Sci.*, **31**, 717 (1986).
4. B. Martín, J. M. Pereña, J. M. Pastor, and J. A. De Saja, *J. Mater. Sci. Lett.*, **5**, 1027 (1986).
5. S. B. Lin and J. L. Koenig, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 2277, 2365 (1983).
6. A. Jeziorny, *Acta Polym.*, **37**, 237 (1986).
7. G. Groeninckx, H. Reynaers, H. Berghmans, and G. Sonets, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1311 (1980).
8. G. Groeninckx and H. Reynaers, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1325 (1980).
9. P. Colomer, S. Montserrat, and G. Martín, *Polymer*, **26**, 423 (1985).
10. S. A. Jabarin, *J. Appl. Polym. Sci.*, **34**, 85, 97 (1987).
11. M. V. S. Rao, J. Kumar, N. E. Dweltz, *J. Appl. Polym. Sci.*, **32**, 4439 (1986).
12. A. J. Miyake, *Polym. Sci.*, **38**, 479 (1959).
13. C. Y. Liang and S. J. Krimm, *Spectroscopy*, **3**, 554 (1959).
14. W. O. Statton, J. L. Koenig, and M. J. Hannon, *Appl. Phys.*, **41**, 4290 (1970).
15. A. Cunningham, I. M. Ward, H. A. Willis, and J. V. Zichy, *Polymer*, **15**, 749 (1974).
16. G. E. McGraw, *Polym. Prepr.*, **11**, 1122 (1980).
17. A. J. Melveger, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 317 (1972).
18. F. J. Boerio, S. K. Bahl, and G. E. McGraw, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1029 (1976).
19. F. J. DeBlase, M. L. McKelvy, M. Lewin, and B. J. Bulkin, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 109 (1985).
20. Sh. B. Lin and J. L. Koenig, *J. Polym. Sci., Polym. Symp.*, **71**, 121 (1984).
21. B. J. Bulkin, M. Lewin, and F. J. DeBlase, *Macromolecules*, **18**, 2587 (1985).
22. F. Adar and H. Noether, *Polymer*, **26**, 1935 (1985).
23. T. R. Manley and D. A. Williams, *Polymer*, **10**, 339 (1969).
24. L. D'Esposito and J. L. Koenig, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1731 (1976).
25. R. Daubeney, C. W. Bunn, and C. J. Brown, *Proc. Roy. Soc.*, **226**, 531 (1954).
26. J. Stokr and B. Schneider, *Polymer*, **23**, 714 (1982).
27. S. Nagou and S. Oba, *J. Macromol. Sci. Phys.*, **B18**, 297 (1980).
28. K. H. Illers and H. Breuer, *J. Colloid. Sci.*, **18**, 1 (1963).
29. J. Petermann and U. Rieck, *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 279 (1987).

Received December 15, 1988

Accepted January 6, 1989