Microhardness and dynamic mechanical measurements in polyethylene near the β relaxation

J. M. PEREÑA
Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

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

In a previous paper we have reported that microhardness is a technique capable of detecting very precisely the glass transition of isotactic polypropylene [1], showing a sharp maximum in the temperature range of this transition, which was also investigated by parallel dynamic mechanical measurements. The close agreement between the results obtained by means of both techniques has encouraged us to study the possible use of the temperature dependence of microhardness for locating the secondary relaxations of polymers, which are customarily investigated by dynamic mechanical techniques.

Among the secondary relaxations of polymers, the β relaxation of polyolefins is particularly interesting. This relaxation results from motions of chain units located in the interfacial region, and its existence is not universal in the different types of polyethylene, being conditioned by the presence of an interfacial content higher than about 7% [2]. Because of this, the β relaxation has been clearly detected in branched polyethylene and has not been detected at all in linear polyethylene of medium molecular weight, by using dynamic mechanical methods.
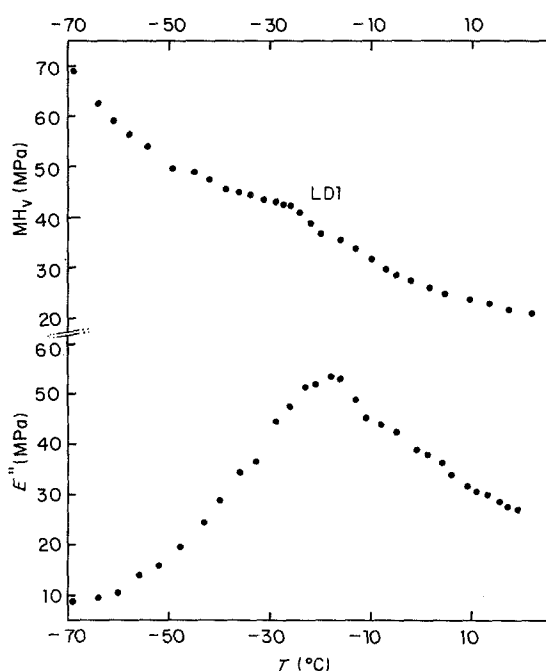

Figure 1 Variation of microindentation hardness (MH_v) and dynamic loss modulus (E'') of low-density polyethylene as a function of temperature.

Five commercial samples of polyethylene, two of them of high density (HD) and the other three of low density (LD), were placed between stainless steel plates, heated at 5° C above the melting point and hot pressed at 15 MPa for 10 min. The mouldings were cooled by quenching in ice water and the thickness of the specimens was around 0.2 mm, which is adequate for performing the microhardness measurements as well as the dynamic mechanical ones.

Determinations of Vickers microhardness (MH_v) were carried out by means of a square-pyramidal indentor in Zeiss Universal equipment. MH_v values were calculated according to $MH_v = K(P/d^2)$, d being the length of the diagonal of the projected area of identation (μm), P the contact load applied (g) and K a constant equal to 18 191. Suitable test conditions have been established previously in relation to the load and time of application of the indentor (10 g and 30 sec, respectively). The samples were situated on a temperature cell adapted to the shape of the microscope [3] and the measurements performed with temperature increasing in steps smaller than 1° C over the range from −60 to 25° C.

Dynamic mechanical moduli were determined with a Rheovibron model DDV-II-B viscoelastometer, at 3.5 Hz and temperatures ranging from −60 to 25° C. The same samples were used for the dynamic mechanical measurements and later for the microindentation hardness ones. The working temperatures for both techniques ensure that no further crystallization takes place during the measurements.

Figs 1, 2 and 3 show the temperature dependence of microhardness and dynamic mechanical results of the studied samples. As was to be expected, the low-density polyethylenes (Figs 1 and 2) exhibit a clear β relaxation, represented by a maximum of the loss modulus as a function of temperature, whereas the temperature dependence of dynamic loss modulus shows no increase for the high-density polyethylenes at the temperature location (around −20° C) of the β relaxation (Fig. 3). The loss modulus against temperature plots for high-density polyethylenes also show a pronounced increase, starting above 0° C at the low frequency used (3.5 Hz), due to the near presence of a strong α relaxation with a comparatively low activation energy value (around 100 kJ mol^{-1}).

The parallel measurements of microindentation hardness reveal a decrease of this parameter as
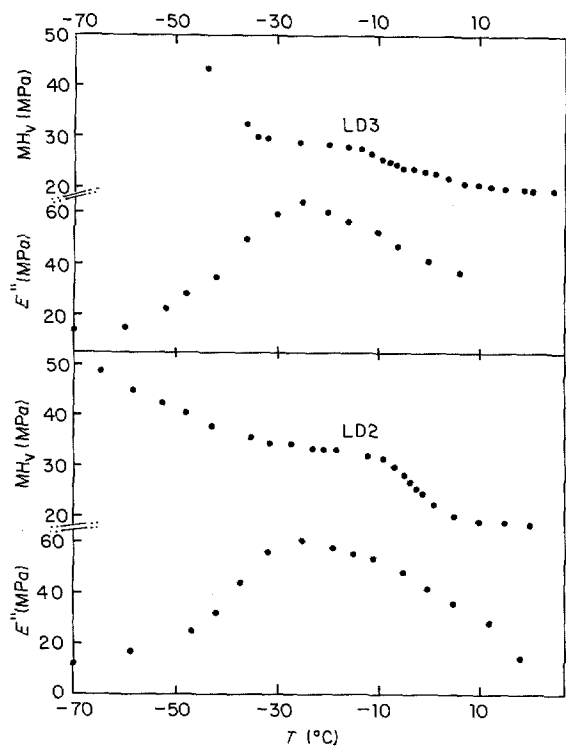
Figure 2 Variation of microhardness (MH$_v$) and dynamic loss modulus (E'') of two different low-density polyethylenes as a function of temperature.

Figure 4 Ratios of microhardness to dynamic loss modulus (MH$_v$/E'') of various samples of high-density (HD) and low-density (LD) polyethylenes.

temperature increases. The decrease passes through a clear plateau in the case of low-density polyethylenes (Figs 1 and 2) while the high-density polyethylenes (Fig. 3) show a gradual change of slope. Moreover, at the lowest temperatures (below $-30°$ C), the latter group of samples display a small temperature dependence of microhardness, in contrast to the steeper decrease of this parameter for low-density polyethylenes at the same temperature interval.
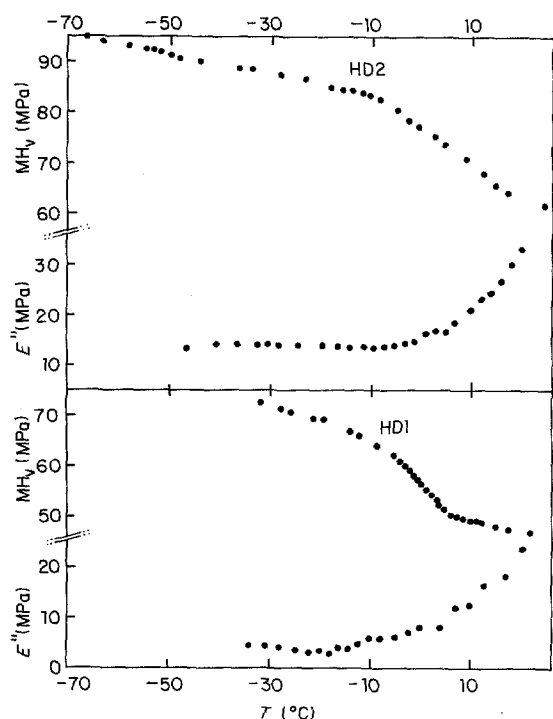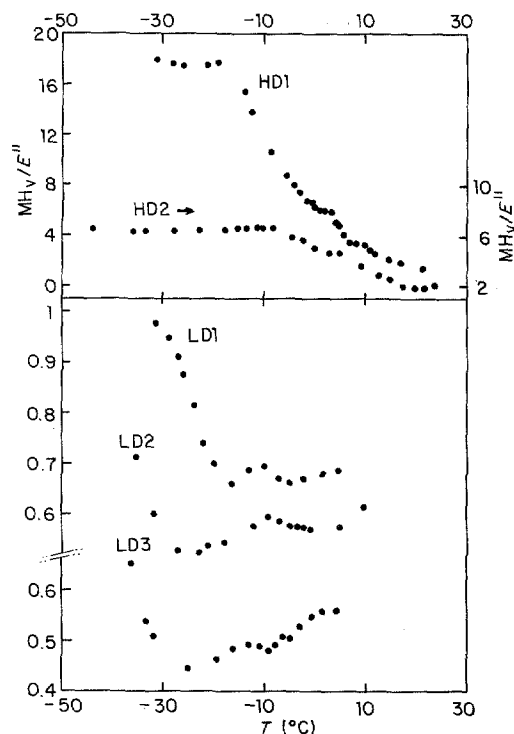

Figure 3 Variation of microhardness (MH$_v$) and dynamic loss modulus (E'') of two different high-density polyethylenes, plotted against temperature.

Notwithstanding this, inspection of Figs 1 and 2 does not allow a precise location of the β relaxation temperature in the low-density polyethylenes, which is quite different from the behaviour of the temperature dependence of microhardness in the T_g region [1].

The ratio between microhardness and modulus of elasticity has been taken as a useful guideline for the energy dissipated by a polymer undergoing a micro-indentation [1, 4, 5]. Thus, in this work we have measured the real (storage) and imaginary (loss) parts of the complex elasticity modulus, E' and E'', respectively. Owing to the low values of loss tangent in polymers, E' is much higher than E'' and the former can be taken as the dynamic elasticity modulus of the samples. The variations of the ratios MH$_v$/E' as a function of temperature (not plotted) for the polymers studied, leave no ambiguity with regard to the different behaviour of low- and high-density polyethylenes in the β relaxation range. For the low-density polyethylenes, the MH$_v$/E' ratio increases from $-40°$ C up, whereas it is practically constant for the high-density polyethylenes.

When the MH$_v$/E'' ratio is considered (Fig. 4) the high-density polyethylenes show continuous decreases whereas the low-density polyethylenes exhibit clear minima. Moreover, at temperatures below $-35°$ C the values of the MH$_v$/E'' ratio substantially exceed the scale of the plot for the low-density polyethylenes, in sharp contrast to the practical constancy for the high-density polyethylenes. The main relative minimum for LD1, LD2 and LD3 samples, which takes place at the low temperature side of each plot, points to the temperature of the β relaxation in the branched poly-ethylenes. The temperatures determined in this way ($-25°$ C for the polyethylenes LD2 and LD3 and $-16°$ C for polyethylene LD1) show a close

agreement with those obtained by dynamic mechanical measurements at 3.5 Hz ($-25°$C for LD2 and LD3 and $-18°$C for LD1).

In conclusion, the use of only microhardness indentations for recognizing the secondary relaxations in polyethylene, does not allow their precise temperature location, in contrast to the easy placing of the glass transition by means of microhardness against temperature plots, but the joint use of microhardness and dynamic mechanical techniques shows that the variation of the microhardness/modulus of elasticity ratios leads to the clear detection of the existence of the secondary relaxation and its temperature location.

Acknowledgements

References

1. B. MARTIN, J. M. PEREÑA, J. M. PASTOR and J. A. DE SAJA, *J. Mater. Sci Lett.* **5** (1986) 1027.
2. R. POPLI, M. GLOTIN, L. MANDELKERN and R. S. BENSON, *J. Polym. Sci. Polym. Phys. Edn* **22** (1984) 406.
3. J. M. PASTOR, A. MONTIEL, F. RULL and J. A. DE SAJA, *J. Phys. E Sci. Instrum.* **14** (1981) 71.
4. B. R. LAWN and V. R. HOWES, *J. Mater. Sci.* **16** (1981) 2745.
5. V. LORENZO, J. M. PEREÑA, J. M. G. FATOU, J. A. MENDEZ-MORALES and J. A. AZNAREZ, *J. Mater. Sci. Lett.* **6** (1987) 756.