Physical ageing and glass transition in amorphous polymers as revealed by microhardness

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Microhardness (MH) data as a function of temperature for two amorphous polymers [poly(methylmethacrylate) and poly(vinylacetate)] and two semicrystalline polymers [poly(ethyleneterephthalate) and poly(arylether ether ketone)] quenched into the amorphous state are presented. It is shown that MH can conveniently detect the glass transition temperature (T_g) for the above mentioned polymers. Molecular rearrangements taking place above and below T_g, such as physical ageing leading to a more compact molecular packing, and thermal expansion can also be followed by means of MH measurements. Finally, the presence of a crystalline phase in these materials has been shown to shift the T_g value towards higher temperatures.

1. Introduction
It is well known that microindentation hardness can provide a direct information on microstructure variations of semicrystalline polymers at various morphological levels [1-7]. Specifically crystal hardness (critical stress required to plastically deform the crystal) has been shown to depend on the average thickness of the crystalline lamellae and reflects its response to the intermolecular forces holding the chains within the lattice. Microhardness (MH) has also been proved to be capable to detect phase transitions in polymers. For instance, the glass transition [8] in isotactic poly(propylene) (PP) or the ferro-paraelectric Curie transition in the 70/30 poly(vinilydene fluoride-co-trifluorethylene [9] have been investigated by MH. However, the MH investigations carried out so far have been mainly restricted to highly flexible chain polymers such as poly(ethylene) (PE) and PP. The purpose of the present study is to extend the above investigations to the case of several amorphous polymers, including poly(methylmethacrylate) (PMMA), poly(vinylacetate) (PVAc) and two high melting semicrystalline polymers, poly(ethyleneterephthalate) (PET) and poly(aryletheretherketone) (PEEK) quenched into the fully amorphous state.

The specific aims of this paper are, first to show that MH can conveniently detect the glass transition temperature (T_g) of the above polymers and secondly that this mechanical property can adequately characterize the physical ageing of the polymer, below T_g, as a function of time. More specifically it will be shown that MH can detect the molecular relaxation of the nonequilibrium glassy state towards the corresponding state of the supercooled melt [10].

2. Experimental procedure
Commercial samples of PET and PEEK were supplied by ICI Plastics Ltd, Wilton, UK. An atactic PMMA sample prepared by suspension polymerization [11] was kindly supplied by Drs E. L. Madruga and J. San Roman and the PVAc material was prepared by Professor J. M. G. Fatou (Institute of Science and Technology of Polymers, Madrid). The above materials were compression moulded into 0.5 mm thick sheets at the following temperatures: 280° C (PET); 400° C (PEEK); 170° C (PMMA); 120° C (PVAc) and rapidly quenched well below their respective glass transition temperatures. Semicrystalline samples of PET and PEEK were obtained by slowly cooling from the above temperatures to room temperature. Microhardness was measured in the temperature range between room temperature and 150° C, using a MH tester with a square pyramidal diamond indenter. The MH value (in MPa) was calculated from the residual projected diagonal impression, using

$$H = kp/d^2 \qquad (1)$$

where d is the length of the diagonal (in mm), p the contact load (N) and k a geometrical factor equal to 1.854. A loading cycle of 0.1 min and a load of ~ 1 N were used. The glass transition temperature for PMMA and for the amorphous and semicrystalline PET samples was also determined using a differential scanning calorimeter (DSC). A heating rate or 20° C min⁻¹ was employed.

3. Results and discussion
Figure 1 shows the MH variation as a function of temperature for the four investigated polymers. In the case of the two amorphous polymers (PMMA and PVAc) MH decreases with T and the T_g value can be clearly identified with a bend in the H-T plot. However, the two semicrystalline materials quenched into the amorphous state (PET and PEEK) show an
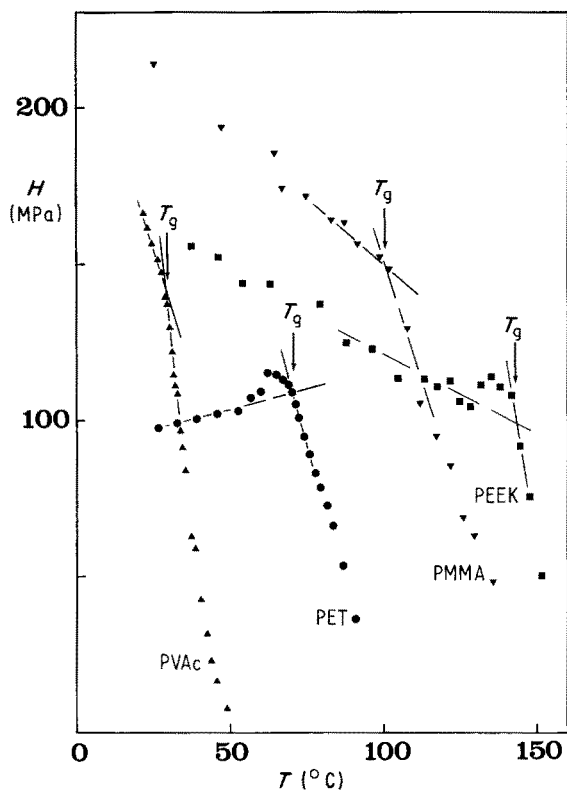
Figure 1 Microhardness H as a function of temperature for the four investigated amorphous polymers. Glass transition values are denoted by arrows.
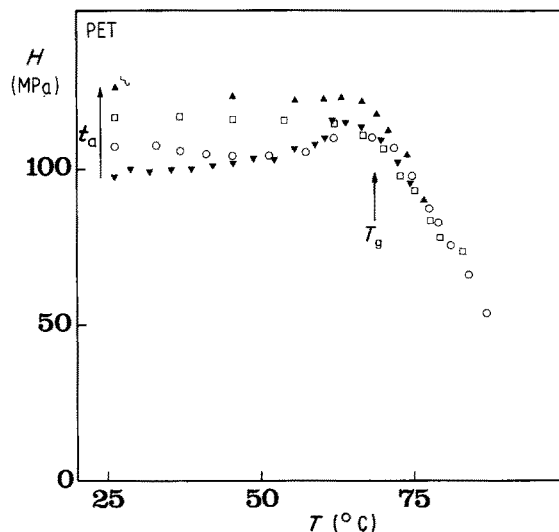

Figure 2 Microhardness as a function of temperature for various PET samples for different annealing times ranging from $t_a = 0$ h (lowest curve) up to $t_a = 100$ h (upper curve).

apparent maximum just before the glass transition takes place. Also, in the case of PET immediately tested after quenching it is observed that MH increases with T above room temperature. These phenomena will be later discussed in the light of the physical ageing undergone by the above polymers. In the general case, it is seen that MH follows and exponential decrease as a function of T given by

$$H = H_0 \exp\left[-\beta\left(T - T_0\right)\right] \qquad (2)$$

where H_0 is the hardness measured at a given reference temperature T_0, and β is the so called coefficient of thermal softening. Table I collects the β coefficients for the investigated polymers, below and above T_g (once the effect of physical ageing has been minimized). It is found that for $T < T_g$, $\beta \sim 1.2$–20×10^{-3} K^{-1} values are of the same order of magnitude than data obtained for the crystalline phase in other polymers [1, 12, 13]. On the contrary, for $T > T_g$, MH decreases at a much higher rate ($\beta = 33$–144×10^{-3} K^{-1}). As a consequence the hardness of the amorphous phase becomes negligible within a temperature range $\delta T = \sim 50°$C above T_g.

In the glassy state (below T_g) the critical stress required to plastically deform the amorphous molecular network (MH) involves displacement of bundles of chain segments against the local restraints of secondary bond forces and internal rotations. The intrinsic stiffness of these polymers below T_g leads to MH values which are 3–4 times larger than those obtained for typical flexible polymers. At the glass transition the onset of liquid-like motions involving longer chain segments takes place. These motions of larger bundles above T_g require more free volume, and lead to the faster MH decrease observed.

To investigate the origin of the anomalous behaviour of PET with respect to the other investigated polymers (positive slope of MH as a function of temperature below T_g), MH for PET quenched to a constant temperature below T_g was measured as a function of storage time (to be called annealing time). Figure 2 shows the obtained results, indicating that the slope of the H–T plot below T_g conspicuously depends on the
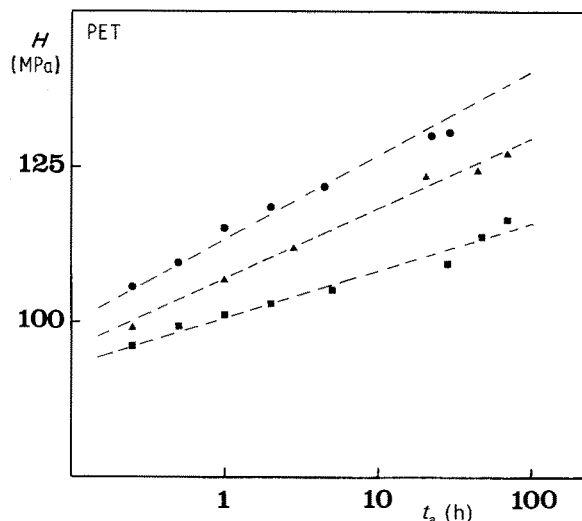
TABLE I Glass transition temperature (T_g) as measured by MH and coefficient of thermal softening (β) for the polymers investigated

Polymer	T_g (K)	$\beta \times 10^3$ (K^{-1})	
		$T < T_g$	$T > T_g$
PVAc	302	20.0	144
PMMA	373	4.6	33
PET	343	1.2	36
PEEK	416	4.0	56

Figure 3 Time-increase of microhardness H at different annealing temperatures T_a below T_g. Microhardness follows a law of the type: $H = A \log t_a + K$, where A and K are increasing functions of annealing temperature and t_a is the annealing time. T_a (°C): (●) 62; (▲) 45; (■) 29.
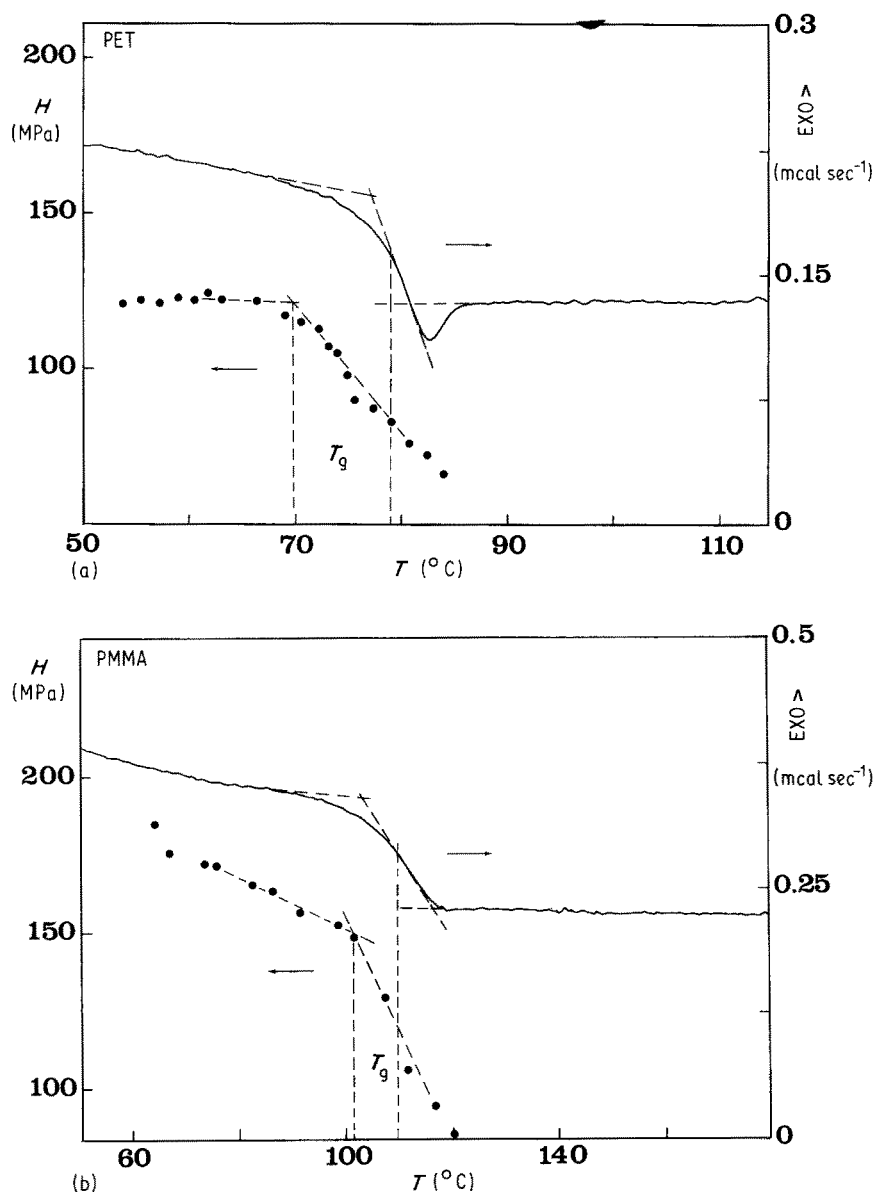
Figure 4 Comparison of DSC thermograms with the corresponding variation in microhardness as a function of temperature for a fully amorphous (a) PET and (b) PMMA.

thermal history of the samples. Beyond T_g all curves tend to similar MH values with a loss of memory of the previous thermal history. This reversible phenomenon which is commonly known as physical ageing reveals the influence of the molecular relaxation in the glassy state showing a tendency towards a more compact molecular arrangement, reducing segmental mobility and leading, as a result, to an increase of microhardness. For longer annealing times, the character of the H-T plot resembles that exhibited by the rest of the polymers from Fig. 1. We have investigated in detail the physical ageing for the PET sample as a function of $\log t$ for different $\delta T = T_g - T_a$ values where $T_a < T_g$ is the annealing temperature. The data of Fig. 3 follow a time-increase of MH of the type

$$H = A \log t + K \qquad (3)$$

in the range of 0–100 h, where the A and K parameters are increasing functions of the annealing temperature. This rate increase of physical ageing with temperature explains the apparent maximum near T_g observed in some of the investigated polymers (Fig. 1). The MH-

increase with time is correlated to the well-known free-volume decrease occurring up to very long periods of time [10]. This behaviour is characteristic for all types of glassy polymers, including other nonpolymeric materials [10]. An attempt to correlate the time-increase of microhardness with a possible variation in the average intermolecular distance and "cluster size" as derived from the position and integral breadth of the X-ray diffraction halo does not offer any definite answer. Apparently X-ray diffraction results are not sufficiently sensitive as to reveal the molecular relaxation motions which are detected by MH. A similar logarithmic MH-increase with t, has been shown to describe the annealing behaviour of semicrystalline polymers (near T_m, the melting temperature) [1]. However, the molecular mechanism involved in this case is evidently quite different, mainly entailing a thickening of the crystals [14].

It is interesting to compare the softening of the material near T_g measured by MH, as a function of temperature, with the corresponding DSC traces for amorphous PET and PMMA (Fig. 4). From these experiments it is conspicuously demonstrated that
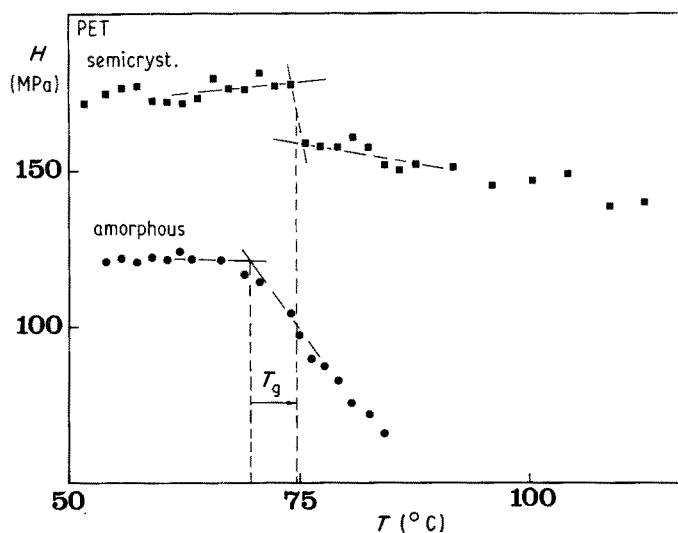
Figure 5 Microhardness H as a function of temperature for two PET samples: (top) crystallized and (bottom) quenched into the fully amorphous state. A shift of T_g towards higher temperatures for the crystalline polymer is observed.

both methods, MH and DSC, yield a similar measure of T_g. The apparent difference in the T_g value obtained ($\sim 10°$C) is a result of the fast heating rate used in the DSC determination in contrast to the quasi-static measurement in case of MH.

In order to examine the possible influence of the crystalline phase on the T_g value the MH of a sample of semicrystalline PET with a degree of crystallinity of 0.38 was studied. Figure 5 comparatively illustrates the hardness dependence upon temperature for amorphous and semicrystalline PET. To separate the ageing contribution from the pure temperature dependence of the amorphous material the hardness data for the former were taken after long annealing times ($t = 100$ h). The T_g value for crystalline PET is clearly evidenced by a sudden MH-decrease followed by a substantially slower temperature rate decrease than that obtained for the amorphous polymer. Most interesting is the fact that the T_g for the semicrystalline polymer is $\sim 5°$C higher than for the amorphous material. This result is in accordance with the concept that crystals disturb the amorphous phase and reduce segmental mobility [15]. As a consequence of this molecular immobilization the T_g range in the semicrystalline polymer is extended and shifted towards higher temperatures. Hence, ageing will persist at temperatures slightly beyond T_g. Figure 6 illustrates the thermograms of the PET samples of Fig. 5 near T_g.

For the semicrystalline sample the T_g is associated to a small change in the slope of c_p, T curve. The shift of T_g towards higher temperatures for the semicrystalline material parallels the MH behaviour suggesting the appearance of a "rigid amorphous phase" which is connected to the presence of the crystals [16].

For PET and PEEK it has also been possible to extrapolate the different contributions to MH of the crystalline phase (H_c) and the amorphous phase (H_a) at room temperature. The obtained H_c values (310 MPa for PET and 480 MPa for PEEK) fit well with data derived from *ab initio* calculations [1].

4. Conclusions

Microhardness has been shown to be a promising technique to detect accurately the glass transition temperature of amorphous and semicrystalline polymers. MH is additionally a method capable to measure the molecular reorganization taking place above and below T_g: on one side the contribution of chain mobility with increasing annealing time and temperature leading to a more compact structure (physical ageing) and on the other hand the influence of a thermal expansion. Finally, it has been also shown that T_g for a semicrystalline polymer is shifted towards higher temperatures when compared to the value obtained for the amorphous material.
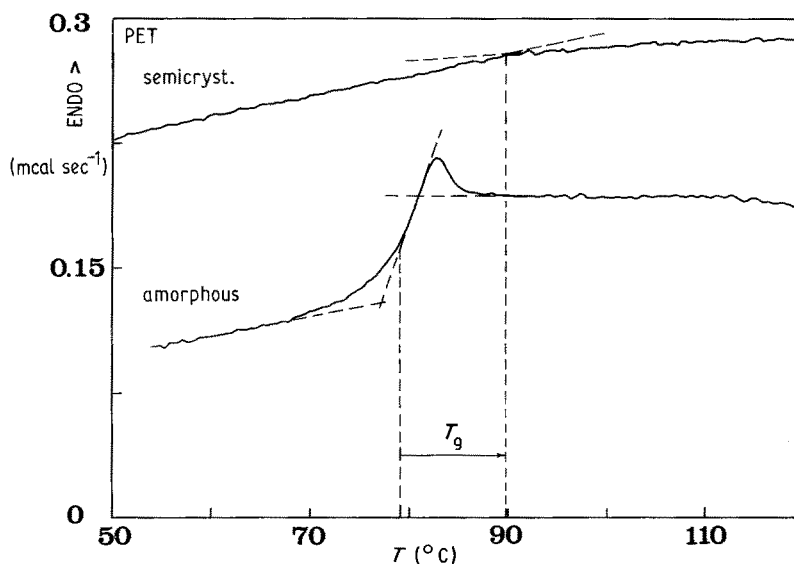

Figure 6 DSC thermograms of the same PET samples as in Fig. 5. A shift towards higher temperatures, for the crystalline polymer is also detected.

Acknowledgements

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