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Microhardness and thermal study of the annealing effects in vinyl alcohol–ethylene copolymers

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The influence of annealing and thermal history on the microhardness, *MH*, of three vinyl alcohol–ethylene copolymers has been studied and the results compared with those for the corresponding homopolymers, poly(vinyl alcohol) and polyethylene. The results show that the microhardness of the copolymers increases with the vinyl alcohol content, although the degree of heterogeneity also seems to play an important role. Two thermal histories (fast quenching or slow cooling from the melt) have been imposed on the samples. The quenched (Q) specimens present lower values of *MH* than the corresponding slowly cooled (S) samples. Both Q and S samples were subsequently annealed at different temperatures. In the annealed samples, it has been found that the variation of *MH* is different for the two thermal histories. Thus, the Q samples show an increase of *MH* with the annealing temperature while the contrary is found for the S specimens. These results can be explained by the heterogeneous nature of these copolymers, as revealed by differential scanning calorimetry traces, which show an appreciable degree of material melting at temperatures well below the main melting peak.

(Keywords: vinyl alcohol–ethylene copolymers; microhardness; thermal history, heterogeneous composition)

INTRODUCTION

The annealing of polymer materials is a subject that has attracted both academic and industrial interest. The process has generally been used to improve the final properties of the material via reduction or elimination of defects and residual stresses and strains[1,2]. Moreover, for semicrystalline polymers, the size and perfection of the crystals can be improved by annealing, thereby influencing the mechanical properties.

The Vickers microindentation hardness test measures the resistance of a given material to plastic deformation produced by impact of an indentor. It is well known that semicrystalline polymers have three different regions: the ordered crystalline region, the amorphous region with chain sequences in disordered conformations and the interfacial region. It follows that the properties of semicrystalline polymers will depend on the balance between these regions, on molecular weight and on the thermal history. Microhardness, *MH*, measurements have been shown to be an appropriate means of studying the effects of annealing[3,4]. In addition, *MH* results can be related to mechanical parameters such as the elastic modulus and yield stress[5]. They have also been used to locate the glass transition temperature (T_g) in polymers[6] and, recently, to study the ageing of polymers[7].

Vinyl alcohol–ethylene (VAE) copolymers with a vinyl alcohol content higher than 60 mol% have recently attracted much interest in industry. They are currently used as barriers for the packaging of pharmaceuticals and food due to their impermeability to gases and vapours. Studies concerning the mechanical and dynamic mechanical properties of these copolymers have been carried out previously by our group[8,9].

One important characteristic of ethylene copolymers in general is that a very broad melting pattern is obtained when heterogeneous catalysts are used[10–13] in the copolymerization, showing more or less pronounced shoulders at temperatures well below the main melting peak. This is a very important feature to take into account for establishing adequate thermal histories, as will be discussed in this work.

The main aim of the present work was to study the influence of annealing and thermal history on the microhardness of VAE copolymers and the corresponding homopolymers. A parallel investigation of the changes in structure of the materials, as revealed by small-angle X-ray scattering (SAXS) and differential scanning calorimetry (d.s.c.), is also presented.

EXPERIMENTAL

Three commercially available VAE copolymers, VAE-1, VAE-2 and VAE-3, were used. *Table* 1 shows the

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Table 1 Composition in vinyl alcohol and distribution index (*DI*) of VAE copolymers

Copolymer	Composition (mol%) Nominal	 ^{1}H n.m.r.	 ^{13}C n.m.r.	*DI*
VAE-1	0.71	0.78	0.77	0.58
VAE-2	0.68	0.75	0.72	0.43
VAE-3	0.56	0.63	0.62	0.43

composition in vinyl alcohol determined by means of ^{1}H and ^{13}C n.m.r. spectroscopies. Sheet specimens were obtained as films by compression moulding in a Collin press of hot plates, at 210°C and at a pressure of 2.5 MPa for 15 min.

Each of the VAE samples was crystallized under two different conditions (Q and S). The first treatment, Q, consisted of fast cooling between cold plates after melting in the press. The S specimens were slowly cooled from the melt at a rate of $\sim 2°\mathrm{C\,min^{-1}}$.

The parent homopolymers, poly(vinyl alcohol) (PVAL) and a low density polyethylene (LDPE), were also studied in order to compare the results with those of the copolymers. Both homopolymers were commercial grades and, in the case of LDPE, the grade was that used for the production of the VAE copolymers studied.

The PVAL homopolymer samples were obtained by dissolving the powdered polymer in water and then evaporating the solvent at room temperature, until a film suitable for measuring microhardness indentations was obtained. On the other hand, LDPE films were obtained by melt compression at 140°C.

The different samples were subsequently annealed at different temperatures (T_a) in a Mettler FP82HT hot-stage for 15 min. After this time, the specimens were brought to room temperature.

A Vickers indentor attached to a Leitz microhardness tester was used to carry out microindentation measurements. All the measurements were undertaken at room temperature (22°C). A contact load of 0.98 N and a contact time of 25 s were employed. *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.

Each sample was investigated by d.s.c. In the case of the copolymers, some of the thermal histories were reproduced in the calorimeter to investigate the recrystallization of the material during cooling from T_a to ambient conditions. D.s.c. measurements were performed in a Perkin–Elmer DSC-7 calorimeter, at a scanning rate of $5°\mathrm{C\,min^{-1}}$. Melting points were identified with the maximum in the endothermic peak. To avoid differences in the melting temperature caused by variation in sample weight, the mass of the sample was fixed at approximately 6 mg in all experiments.

Selected samples were also studied by SAXS using synchrotron radiation in the Daresbury Laboratory (station 8.2). Rat-tail collagen (long spacing, $L = 67.0$ nm) was used for calibration.

RESULTS AND DISCUSSION

Figure 1 shows the variation of microhardness with annealing temperature. It is observed that, for the same thermal history, the microhardness increases with the vinyl alcohol content, although the values for VAE-1 and VAE-2 are very close.

Microhardness values of VAE copolymers containing <7 mol% vinyl alcohol (VAL) have been reported[14]. For these low contents in comonomer, microhardness increases as the vinyl alcohol content increases. This fact is explained by the small volume of the hydroxyl group, which allows the replacement of a hydrogen atom by the hydroxyl group without significantly disturbing the polyethylene lattice. In this case, single isolated VAL groups or other very short sequences can be built into the polyethylene lattice as point defects[15].

For the copolymers studied here, which have high VAL contents, the vinyl alcohol sequences are sufficiently long to permit crystallization of PVAL. Isolated ethylene units may be built in as defects in PVAL crystals. The results indicate that the peak melting temperature increases with vinyl alcohol content (*Table 2*). On the contrary, the enthalpy of melting and the long spacing (see *Table 2*) do not follow the same trend, as these parameters seem to present higher values for VAE-2 (although the differences are within experimental error). The reason for this behaviour lies in the heterogeneity of chemical composition distribution in the copolymers, as will be shown below.

It was pointed out in the Introduction that ethylene copolymers prepared with heterogeneous catalysts display a multimodal melting pattern due to higher comonomer content in the low molecular weight chains[10–13,16,17].

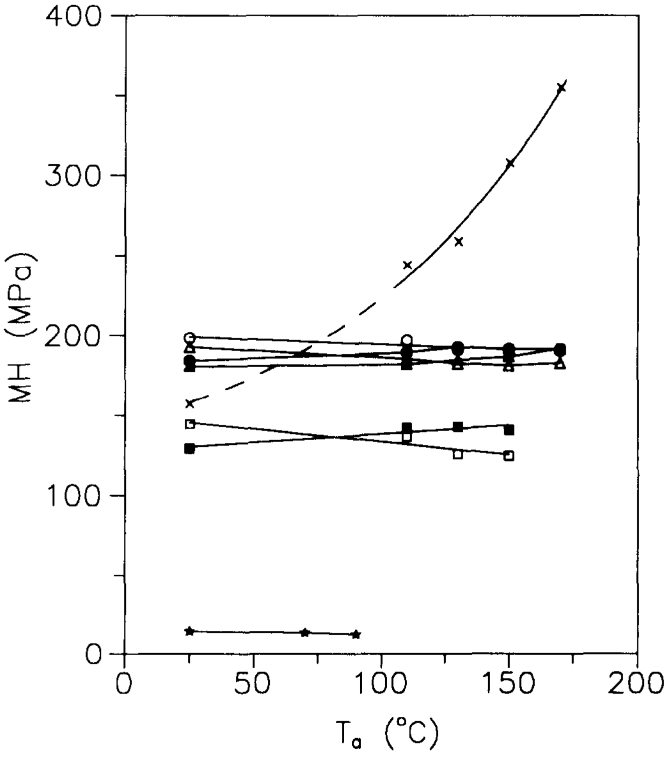

Figure 1 Plot of microhardness as a function of annealing temperature for the different samples: ×, PVAL; ○, VAE-1-S; ●, VAE-1-Q; △, VAE-2-S; ▲, VAE-2-Q; □, VAE-3-S; ■, VAE-3-Q; ★, LDPE-Q

Table 2 Peak melting temperatures (T_m), temperatures for a 50% enthalpy of melting ($T_{0.5}$), enthalpies of melting (ΔH) and long spacings (L) of Q and S VAE copolymer samples[a]

Sample	T_m (°C)	$T_{0.5}$ (°C)	ΔH (J g^{-1})	L (nm)
VAE-1-Q	187.5		86	13.3
VAE-1-S	186.8	174.3	86	14.3
VAE-2-Q	181.9		95	13.9
VAE-2-S	181.7	174.0	90	15.0
VAE-3-Q	165.0		80	12.7
VAE-3-S	165.1	157.3	82	15.2

[a] Estimated errors: temperatures ±0.5°C, enthalpies ±6 J g^{-1}, spacings ±0.5 nm

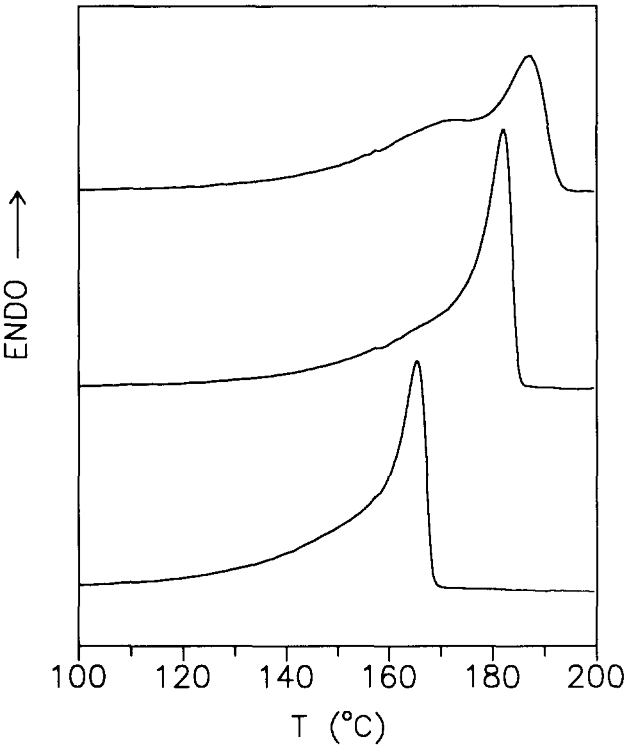

Figure 2 D.s.c. melting curves of the three copolymer samples slowly cooled from the melt: VAE-1-S (upper); VAE-2-S (middle); VAE-3-S (lower)

Differences in this distribution may alter the normal relation between composition and properties. This seems to be the case for our VAE copolymers, as can be deduced from *Figure 2*. This figure shows that VAE-1, with a higher vinyl alcohol content, exhibits a higher temperature for the main endotherm. However, its composition distribution clearly differs from that of VAE-2 and VAE-3. These two copolymers display a sharp endotherm which includes most of the total enthalpy of melting, while a more considerable spread is found in VAE-1. A measure of this heterogeneity is provided by the distribution index[11,12], *DI*, defined as the area of the low temperature tail of the d.s.c. melting curve over the total enthalpy of melting. A rough deconvolution of the profiles in *Figure 2* allowed us to obtain the values for *DI* shown in the last column of *Table 1*. This parameter is found to be considerably higher for the VAE-1 copolymer. It may be concluded, therefore, that peak temperatures are not a good choice for characterizing these copolymers. A better compromise is to work with the temperature $T_{0.5}$, where the partial enthalpy of melting is half of the total enthalpy. The corresponding values for this parameter are listed in the third column of *Table 2*. Virtually identical results are obtained for samples VAE-1 and VAE-2. It is not surprising, therefore, that similar values for microhardness are obtained for these two copolymers.

Broadly speaking, the melting patterns may be related directly to the distribution of crystal sizes in the samples. An idea of this distribution can be deduced from the long spacings derived from SAXS measurements. It has to be considered, however, that the non-crystalline component also influences the value of the long spacing. This could be the reason for our not observing clear differences in the total distribution of spacings between copolymers with the same thermal history (see *Figure 3* and *Table 2*), in spite of the distinct d.s.c. patterns.

The different behaviours of Q and S samples of the same VAE copolymer are determined by the two crystallization procedures (rapidly cooled or slow cooled from the melt). The crystallization of polymers takes place at conditions far from equilibrium, leading to the existence of a significant amorphous zone. For Q samples (the most rapidly crystallized specimens) the fast cooling limits development of the crystallites. Slow cooling (S samples), on the other hand, is more amenable to crystallite perfection. This is the reason for the higher microhardness values for slowly crystallized samples without further annealing. An estimation of the effect of cooling rate on crystal thickness can be obtained from *Figure 3*, which shows that the long spacing increases by about 1–2 nm when the samples are crystallized slowly (*Table 2*).

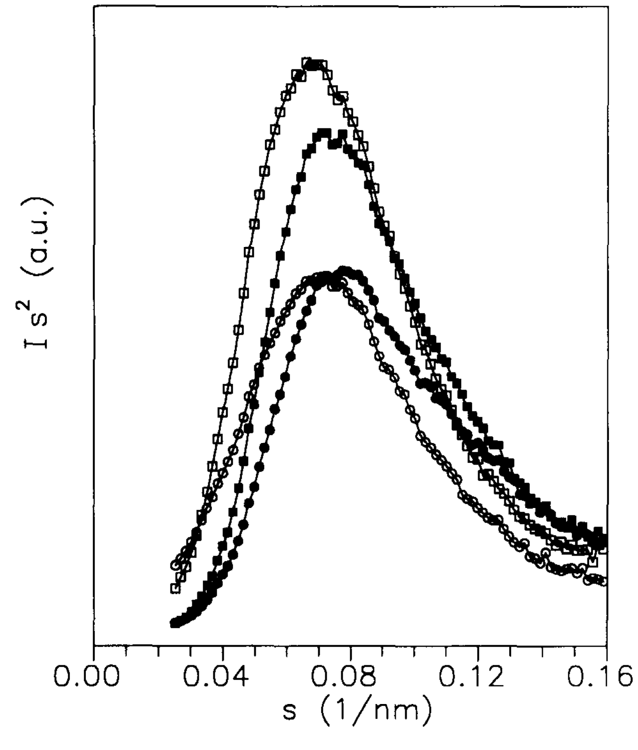

Figure 3 Lorentz-corrected small-angle synchrotron profiles as a function of the scattering vector, *s*, for several copolymer samples: ○, VAE-1-S; ●, VAE-1-Q; □, VAE-2-S; ■, VAE-2-Q

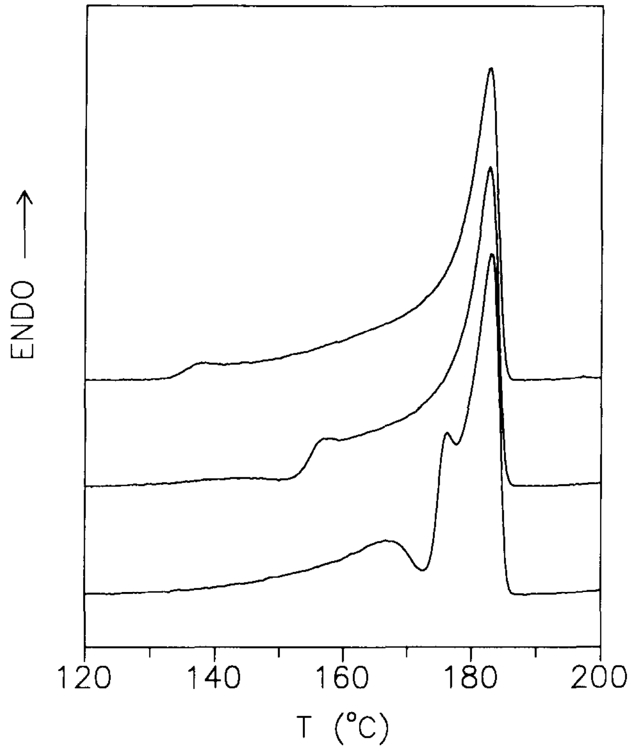

Figure 4 D.s.c. melting curves corresponding to sample VAE-2-S after annealing at different temperatures and subsequent quenching to room temperature. From top to bottom: $T_a = 130$, 150 and 170°C

In an attempt to obtain more ordered crystalline regions, the different samples were annealed at various temperatures. Focusing attention on the copolymer specimens, it can be deduced from *Figure 1* that the *MH* for Q samples increases with annealing temperature. Evidently, in this case, the annealing process has reduced the negative effect on crystallization of an initial fast cooling.

If no annealing is performed, Q samples have less microhardness than S samples, for reasons presented above. However, the microhardness of S samples decreases as the annealing temperature is increased. This result can be understood by taking into account the annealing procedure: the crystallites that melt at a determined crystallization temperature can crystallize in a later stage upon quenching from T_a. However, since they are less developed crystallites (of the Q type), their presence causes the overall microhardness to diminish. As observed in *Figure 1*, microhardness is decreased for the S samples with each successive treatment at higher annealing temperatures, because increasing amounts of samples are less perfectly crystallized when they are quenched to room temperature after the annealing process.

Thermal analyses of the samples provide a better understanding of the annealing effects. *Figure 4* shows the d.s.c. traces of the VAE-2 S samples at different annealing temperatures, T_a. It is observed that, for the three cases studied, the main melting peak remains unaffected, but a peak (or step) is obtained at a temperature about 10°C higher than T_a. It includes, presumably, the material with better formed crystals than the initial ones. Finally, the material molten at T_a crystallizes during quenching to low temperature and produces a broad melting peak below T_a. Obviously, this broad peak is more prominent as T_a increases, and, since it is now of the Q type rather than the initial S type, its microhardness should be reduced, thus overwhelming the original increase of *MH* due to annealing. A parellel and more complete d.s.c. investigation of the annealing effects has been performed on the VAE-2 Q sample, extending it to higher annealing temperatures. (Unfortunately these annealing temperatures produced appreciable degradation of the samples in air, and the intended *MH* measurements were not reliable.) The results of the d.s.c. study are presented in *Figure 5*. Again, a peak, or step, is produced at a temperature about 10°C above T_a, and the main melting peak is now appreciably shifted to higher temperatures when T_a is above 170°C.

One of the effects of annealing in these copolymers is, therefore, the appearance of a small peak at about 10°C above T_a. This result is general for heterogeneous ethylene copolymers and is due to the existence of material whose melting temperature is well below the main endotherm. In fact, in the case of ethylene copolymers with comonomer contents of the order of 10–20 mol%, the melting temperatures may extend even below room temperature and therefore the annealing proceeds at ambient conditions and leads to a melting peak at around 40–50°C. This should not be confused with the alpha relaxation of polyethylene crystals, which appears in the same temperature interval.

The amount of material molten at T_a can be monitored if, after the annealing, the sample is brought to low temperature at a controlled rate (although the sample will be different to the one employed for the *MH* measurements). *Figure 6* shows the results of cooling from different annealing temperatures, compared with the

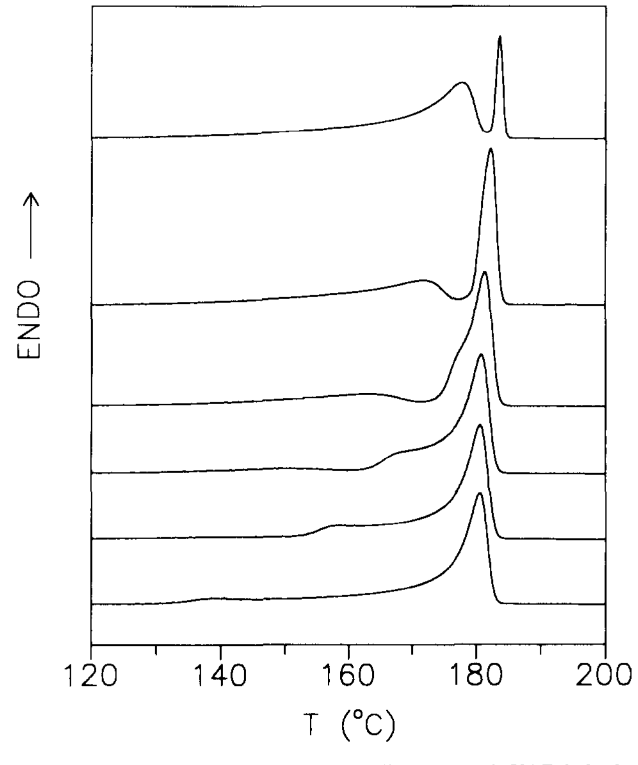

Figure 5 D.s.c. melting curves corresponding to sample VAE-2-Q after annealing at different temperatures and subsequent quenching to low temperature. From bottom to top: $T_a = 130$, 150, 160, 170, 175 and 178°C

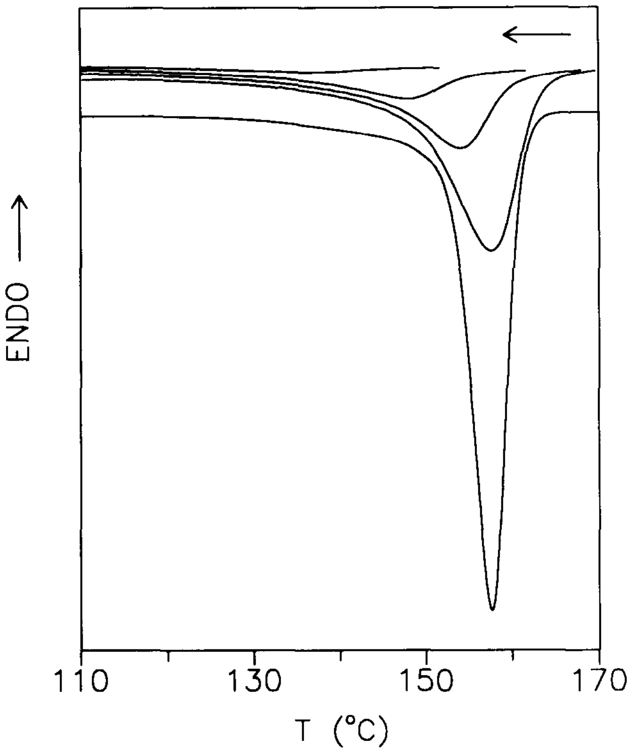

Figure 6 D.s.c. cooling curves corresponding to sample VAE-2-Q after annealing at different temperatures, cooled down from T_a. From top to bottom: $T_a = 160$, 170, 175, 178 and 200°C (melt state)

pattern corresponding to cooling from the melt. The subsequent crystallization of an appreciable quantity of material as T_a increases is observed in *Figure 6*. The thermal history imposed on this part of the sample will be an important factor for determining the *MH* (and the mechanical properties, in general) of the final material.

We now compare the annealing behaviour of the parent homopolymers with that of the VAE copolymers. *Figure 1* shows the effect of annealing on a sample of LDPE quenched from the melt. It is observed that the *MH* values for this sample are considerably lower than those of the VAE copolymers. In fact, the *MH* values of these copolymers are even higher than those of much perfect PE crystals[4] of a size of 40 nm. The second aspect deduced from the microhardness of the LDPE sample in *Figure 1* is that it remains practically constant in the analysed interval of T_a. The reason is that this interval corresponds to the so-called region I of annealing in PE[3], where a very small increase in *MH* (and in the long spacing) is found due to healing of crystalline defects. At higher temperatures, the approximate interval of 110–128°C (which, of course, will depend on the PE sample characteristics) is named region II, where a rapid increase in *MH* is found[3] due to an appreciable lamellar thickening. When the region of partial melting is reached (region III), *MH* falls to approximately the initial values and a second periodicity in the long spacing is observed[3] (together with a second melting endotherm at lower temperature).

The scheme of the dependence of *MH* on T_a is also valid for our VAE copolymers, but due to the very broad melting pattern of these samples, regions II and III overlap. The trend in *MH* variation then depends not only on the annealing temperature but also on the initial thermal history of the samples and on the form of cooling from T_a to room temperature.

The results for PVAL shown in *Figure 1* indicate a considerable increase of microhardness with T_a, and a surprisingly low microhardness for the untreated PVAL specimen. This latter result can be explained by the hydrophilic nature of the hydroxyl groups in the sample. Thus the films analysed can contain water molecules which act as a plasticizer in the polymer, reducing the resistance to plastic deformation quantified by microhardness measurements. However, above an annealing temperature of about 100°C, the microhardness increases and is in fact greater than that of copolymer samples, and this increase continues at higher annealing temperatures. This result is, therefore, attributed to a loss of water molecules by evaporation, together with a perfection of the crystallites. *Figure 7* shows the d.s.c. traces of poly(vinyl alcohol) specimens at different annealing temperatures. For lower values of T_a, an endotherm is observed, centred at about 120°C, followed by possible recrystallization. At higher annealing temperatures, this endotherm is not present, but the peak (step) at a temperature of 10°C above T_a is again obtained, as in the case of the VAE copolymers. For PVAL, however, the *MH* values show a very substantial increase as the annealing temperature rises.

CONCLUSIONS

The influence of annealing and thermal history on the microhardness of three vinyl alcohol–ethylene copolymers has been studied by microhardness measurements and the results compared with those of the corresponding

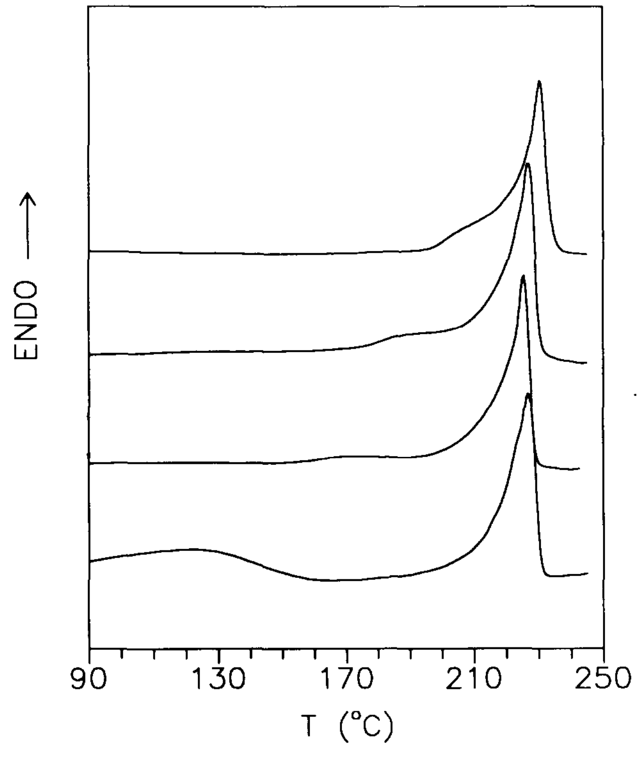

Figure 7 D.s.c. melting curves corresponding to homopolymer PVAL after annealing at different temperatures and subsequent quenching to low temperature. From bottom to top: $T_a = 110$, 150, 170 and 190°C

homopolymers, poly(vinyl alcohol) and polyethylene. The results show that the microhardness of the copolymers increases with the vinyl alcohol content, although the degree of heterogeneity also seems to play an important role.

Regarding the effect of the thermal history, the quenched, Q, specimens present lower values of *MH* (and of long spacing) than the corresponding slowly cooled, S, samples.

In the annealed samples, it has been found that the variation of *MH* is different for the two thermal histories. Thus, the Q samples show an increase of *MH* with the annealing temperature, while the contrary is found for the S specimens.

These results are explained by the heterogeneous nature of these copolymers, as revealed by the d.s.c. traces, which show an appreciable amount of material melting at temperatures well below the main melting peak. This behaviour, typical of ethylene copolymers obtained with heterogeneous catalysts, is shown to be of importance for the design of annealing strategies for these samples. Thus, from the present results, the best method to increase the *MH* value (and other related mechanical properties) of the copolymers is a slow cooling from the melt. If further annealing treatments are performed, it is important that the sample be cooled as slowly as possible after accomplishing the annealing.

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