

Crystalline modifications of ethylene–vinyl acetate copolymers induced by a tensile drawing: effect of the molecular weight

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The influence of a tensile drawing on the crystalline organisation of ethylene–vinyl acetate copolymers (EVA) of different molecular weights has been investigated by differential scanning calorimetry (d.s.c.). The consequence of the crystalline organization changes on the mobility of the amorphous phase has been also investigated, through the study of the glass transition. The results show that more disorganized crystals appear after the tensile test, specially for the higher molecular weight. These more disorganized crystals constitute physical ties reducing the mobility of the amorphous chains which link them, as shown by the significant increase of the glass transition temperature of these high molecular weight EVA after tensile drawing. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The yielding behaviour of polymers has been studied for years because it plays an important role in leaving inherent good properties of the polymer in the final product¹. Drawing is able to induce alignment of polymer chains in the drawing direction and promotes, in some cases, resultant crystallization.

The aim of this work was to investigate the influence of tensile drawing on the crystalline organization of ethylene–vinyl acetate copolymers (EVA) with different molecular weights. Polymer films have been elongated until break during a tensile test and crystallinity of the copolymer films has been studied before and after testing by differential scanning calorimetry (d.s.c.). Changes of crystallinity after the tensile test have been analysed as a function of the molecular weight of the EVA. The consequence of the crystalline organizational changes on the mobility of the amorphous phase has also been investigated, through the study of the glass transition temperature.

EXPERIMENTAL

Five ethylene–vinyl acetate copolymers have been studied. The vinyl acetate content is the same for all the EVA and is equal to 28% w/w. The copolymers, of various grades (or melt index) differ in their molecular weight. A high melt index corresponds to a lower molecular weight.

Molecular weights were determined by means of gel permeation chromatography (g.p.c.), except for the EVA A, which was insoluble in the solvent used (THF). *Table 1* gives the melt index and molecular weights (M_w and M_n) of the different EVA.

EVA films were obtained in a press at 150°C. A pressure of 1.5 MPa was applied for 3 min. Circulating water in the press platens ensures the cooling of the films to room

temperature in 5 min. A thickness equal to 300 μm is obtained by inserting spacers under the platens. Tensile tests were performed on the EVA films using a tensile test machine (DY 34 from MTS), at a speed equal to 300 mm min^{-1} . The geometry of the sample corresponds to the H1 geometry specified in the French standard NFT51-034, equivalent to the ISO standard ISO/R527 (gauge total length equal to 110 mm and width at the centre equal to 6 mm). The force is measured as a function of the elongation until the breakage of the sample. Films of EVA have been analysed by d.s.c. before testing and after breakage.

Differential scanning calorimetry was carried out on a Mettler instrument from -150 to 150°C at a scanning rate equal to 10°min^{-1} .

RESULTS AND DISCUSSION

The degree of crystallinity of the copolymers was calculated from d.s.c. measurements using the melting enthalpy of polyethylene ($\Delta H_f = 280 \text{ J mol}^{-12}$). Polyethylene is indeed the only crystallisable comonomer in EVA copolymers. In *Table 2* is given the degree of crystallinity of the EVA copolymers before elongation.

We consider first the effect of the molecular weight of the EVA on the degree of crystallinity before stretching. EVA of lower molecular weight (samples C, D and E) exhibit a similar degree of crystallinity. For EVA A and B, the value is higher, due probably to the fact that for longer chains, longer sequences of PE are present, favouring the crystallisation³. This effect is evidenced by the more pronounced contribution, for these EVA, of the high temperature melting peak, corresponding to best organized PE crystals.

The d.s.c. curves of the EVA before tensile drawing will be presented successively in *Figures 1–7*. It can be noted that the melting endotherm is rather complex and wide-spread in all cases, starting around 20°C up to about 70°C , indicating that a large continuum of crystal morphologies is involved. The aspect of the d.s.c. curves of the non-stretched

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Table 1 Melt index and molecular weight of the EVA copolymers

Reference	EVA A	EVA B	EVA C	EVA D	EVA E
Melt index (/g (10 min) ⁻¹)	03	25	150	420	800
<i>M_n</i> (/g mol ⁻¹)	–	18 900	15 600	15 700	9800
<i>M_w</i> (/g mol ⁻¹)	–	41 600	39 500	34 000	23 500

films is dependant on the molecular weight of the copolymer. Globally, two major components can be distinguished, related to the existence of two predominant crystal morphologies—one at low temperature around 40°C, due to less perfect crystals, and a second one at higher temperature, corresponding to crystals of the best organized PE chains in the copolymers (the value for the melting temperature of pure PE is equal to 120°C²). A broadening or a third component can be observed between 60 and 40°C, depending on the molecular weight of the EVA. The complexity of the EVA crystalline organization is due to the fact that the VA groups introduce disorder into the polyethylene chains. Vinyl acetate sequences perturb the crystallization of perfect PE crystals, and can be included into the poorly organized structures.

Concerning the differences between the d.s.c. curves of the non-stretched EVA, it can be noted that the proportion of the high temperature peak (located around 70°C) decreases when the molecular weight of the EVA decreases. More numerous disorganized crystals are present for the lower molecular weights, and more perfect crystals are observed for the higher molecular weights (EVA A and B). Longer chains also favour the formation of best organized crystals, probably due to the fact that less defaults or irregularity (for example chain ends or branched sequences) are present, compared with shorter chains.

We now consider the effect of tensile orientation on crystalline organization. In *Figure 1* are compared the results from the d.s.c. analysis for EVA A before and after testing. It can be seen that the high temperature peak whose melting temperature is located at 78°C is more intense before the mechanical testing, compared with the other

Table 2 Melting enthalpy ΔH_m and degree of crystallinity of the EVA films before tensile testing

Reference	A	B	C	D	E
ΔH_m (/J g ⁻¹)	49.8	38.4	29.7	26.3	27.8
Degree of crystallinity (/%)	17.8	13.7	10.6	9.4	9.9

crystalline contributions, occurring at lower temperature. Furthermore, the contribution of the low temperature peak, located around 40°C is much more pronounced after the tensile test, contrary to the crystals melting between 50 and 65°C, which are less numerous after the mechanical test. There is therefore an enrichment of the less perfect crystals (melting at 40°C).

For EVA B, whose d.s.c. curves are presented on *Figure 2*, quite similar observations can be made. The contribution of the low temperature becomes the more important after the tensile test. However, the differences between the d.s.c. curves before and after elongation are less pronounced for EVA B compared to EVA A.

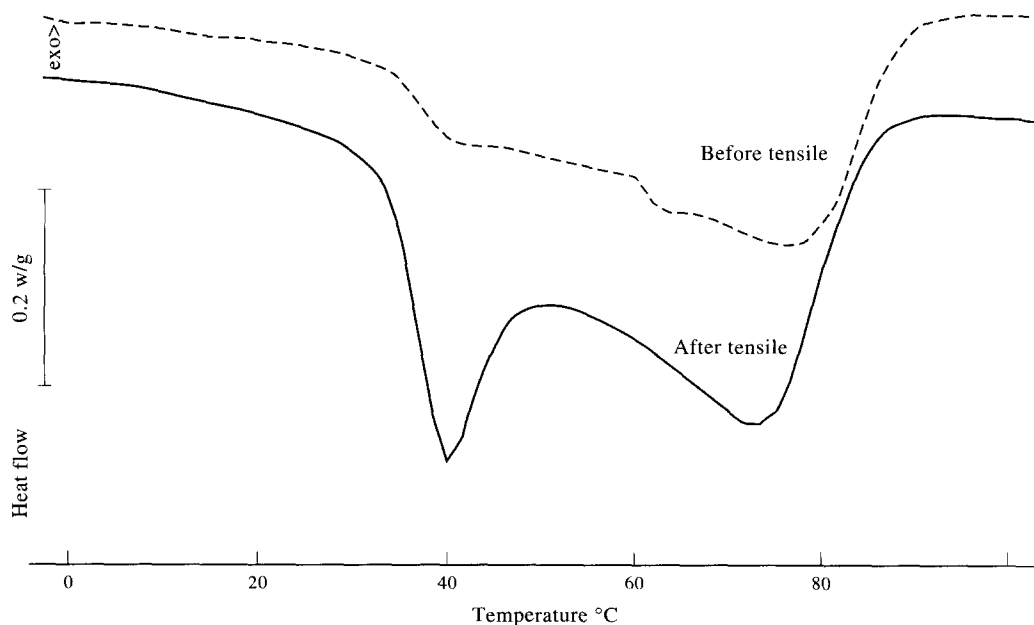
Figure 3 presents the d.s.c. curves of EVA C before and after elongation. A similar trend is observed, i.e. the appearance of more numerous disorganized crystals after the tensile test, as proved by a more intense peak at low temperature.

Figure 4 shows the d.s.c. curves of EVA D. After the tensile test, the magnitude of the low temperature peak (related to the less perfect crystals) is increased.

d.s.c. curves of EVA E are presented in *Figure 5*. It appears that the curves before and after tensile drawing are only slightly different. Indeed, the intensity of the peak located at low temperature is slightly higher after the tensile test. Fewer crystalline modifications have occurred during tensile drawing for these low molecular weight EVA, compared to the higher molecular weight.

A decreasing crystallinity change is also observed when the molecular weight is decreased: the lower the molecular weight, the lower crystalline organization changes occur.

Also of interest is the evolution of the degree of

**Figure 1** d.s.c. curves of EVA A before and after stretching

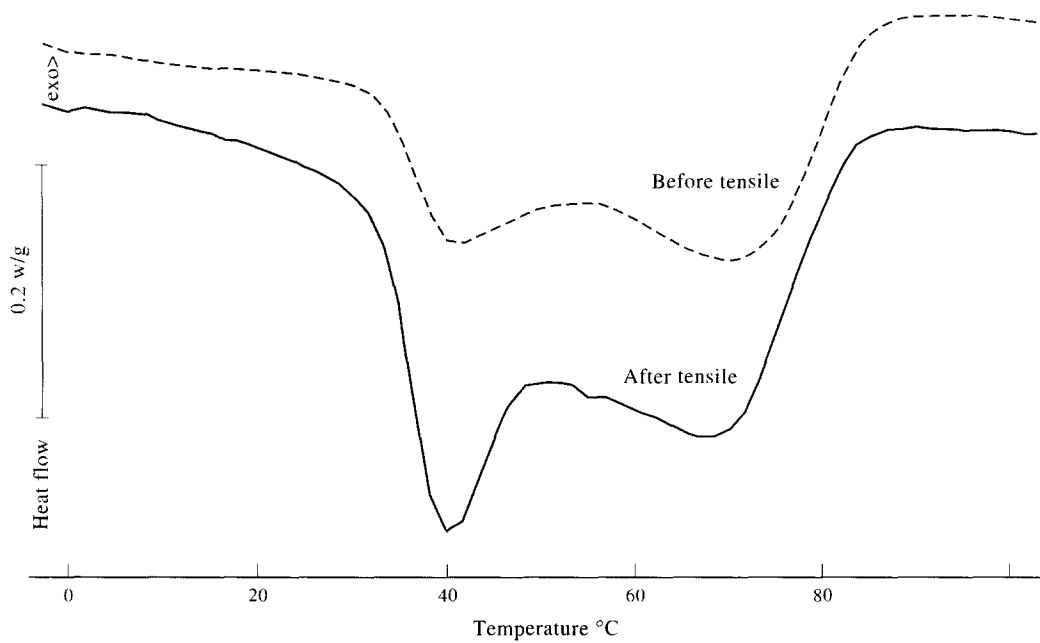


Figure 2 d.s.c. curves of EVA B before and after stretching

crystallinity of the EVA after the mechanical test and the consequence of the crystalline changes on the mobility of the amorphous phase. This can be studied by investigation of the glass transition.

Table 3 presents the results concerning the degree of crystallinity after tensile drawing, and the percent of elongation at break.

Concerning the influence of tensile orientation on the degree of crystallinity, it can be observed that the degree of crystallinity is increased after the tensile test, except for the EVA E, for which the evolution is negligible. Figures 6 and 7 present the tensile curves of the EVA copolymers, using two different force axis scales. For the EVA E, no stiffening after the yield was observed on the tensile curve, in contrast with the other copolymers, for which a stiffening appears before the break, especially for EVA A, B and C. For these polymers, the important film elongation (until 800% elongation) induces chain orientation, favouring the

crystallisation and increasing the tensile resistance. For EVA E, the shorter chains slide doubtless after the yield point, and no stiffening is observed. So, the stiffening under tensile drawing is responsible to the increase of the degree of crystallinity observed for some EVA.

Consequences on the amorphous phase

The previous results have evidenced some major changes in the crystalline organization and degree of crystallinity after tensile drawing, depending on the molecular weight. It is now interesting to investigate the consequences of these changes on the mobility of the amorphous phase. The glass transition of the EVA has been studied before and after the tensile test. Table 4 presents the values of the glass transition temperature and the specific heat of the EVA copolymers, before and after stretching.

The variation of the specific heat ΔC_p , before tensile drawing, as a function of the molecular weight is globally in

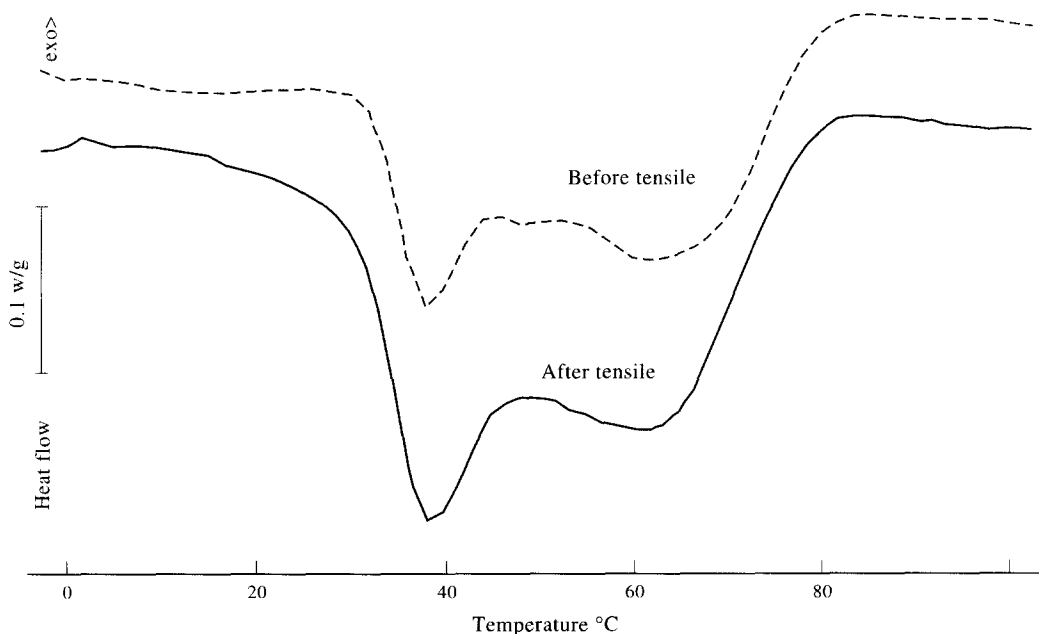


Figure 3 d.s.c. curves of EVA C before and after stretching

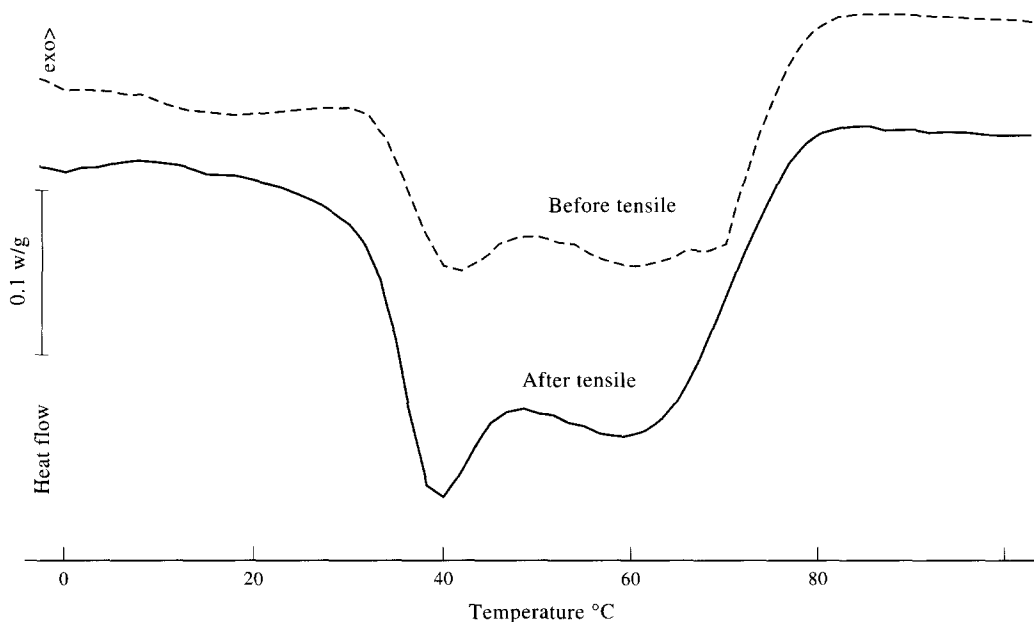


Figure 4 d.s.c. curves of EVA D before and after stretching

agreement with evolution of the degree of crystallinity. ΔC_p represents the amount of matter affected by the glass transition (i.e. the amorphous phase). Before tensile drawing, the values of ΔC_p are quite similar for EVA C, D and E, and lower for EVA B and particularly for EVA A. The proportion of the amorphous phase is therefore greater for the lower molecular weights, in agreement with a lower degree of crystallinity.

After the tensile test, the specific heat is globally decreased (excepted for EVA E), indicating a decrease of the amount of amorphous phase, in agreement with the increase of the degree of crystallinity observed after the mechanical test.

The values of T_g before tensile drawing are quite similar for the studied EVA and are close to the values given by Nielsen⁴ or Reding et al.⁵. Reding et al. suggest that the glass transition observed is related to the motion of isolated $-\text{CH}_2-\text{CHR}-\text{CH}_2-$ groups, where R represents the acetate group.

Concerning the effect of the tensile orientation on the

glass transition temperature, it appears that the values of T_g are still constant after the tensile test for EVA C, D, and E. It is interesting to notice that a significant increase of T_g (of 6–7°C) is observed for EVA A and B. This increase of the T_g value is the consequence of a reduction of the mobility of the amorphous phase, induced by the crystalline modifications.

Discussion

d.s.c. analysis of the EVA films before and after tensile testing have evidenced the complex crystalline organization of these copolymers, composed of a rather wide distribution of crystal sizes. Two major components can be distinguished, related to the existence of two predominant crystals sizes: one at low temperature around 40°C, due to less perfect crystals, and a second at higher temperature, corresponding to crystals of the PE chains the best organized in the copolymers⁶. Multiple endotherms have been reported by several authors and several explanations have been proposed. Bell et al. attributed the double melting

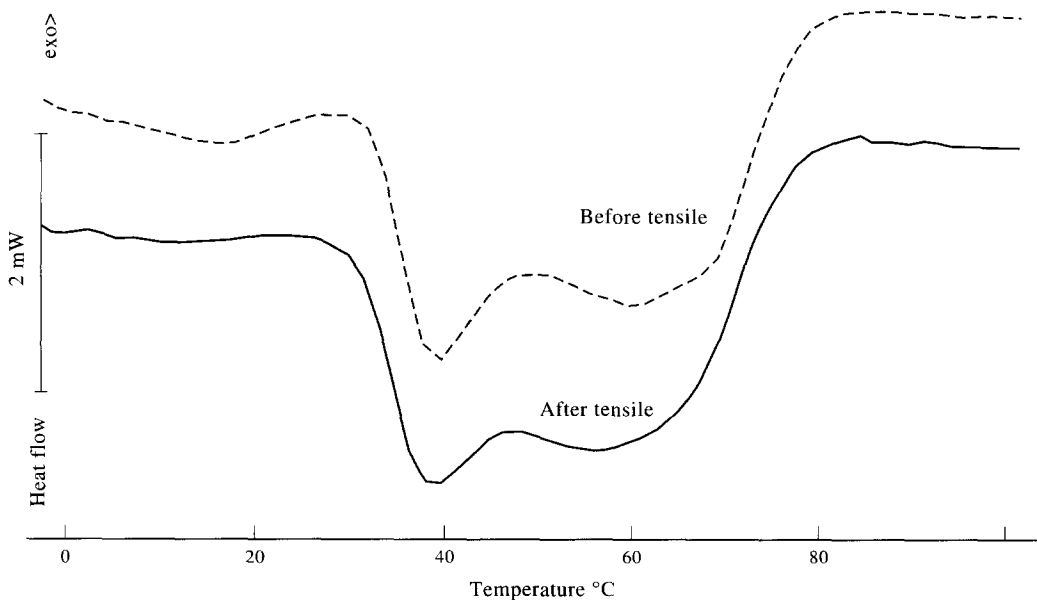


Figure 5 d.s.c. curves of EVA E before and after stretching

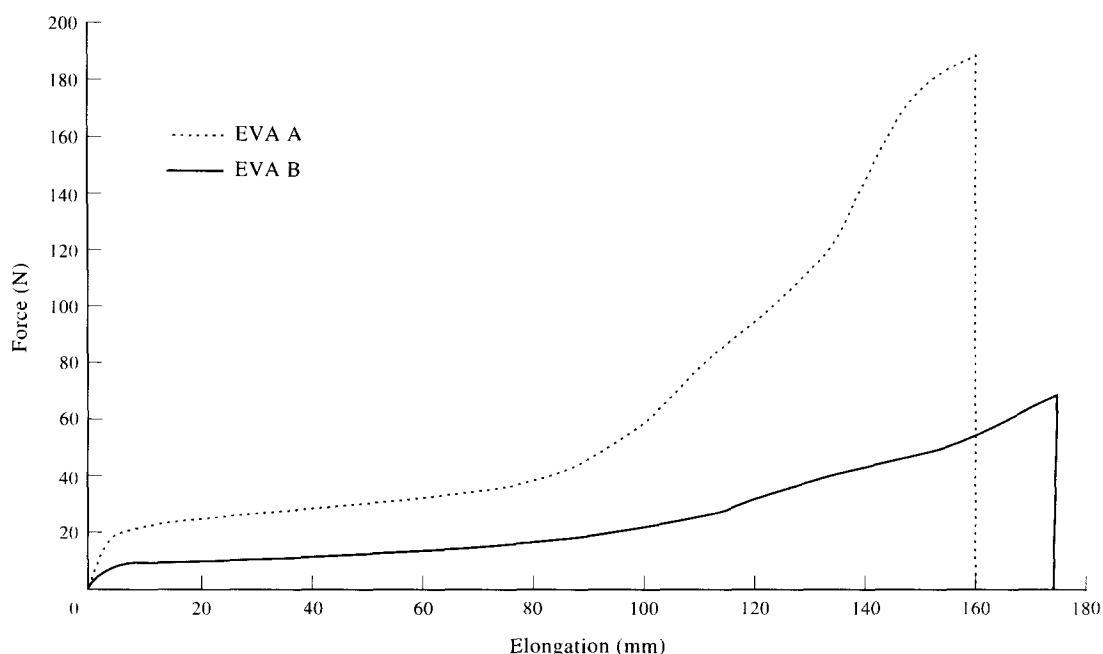


Figure 6 Tensile curves of EVA A and B

peak in nylon 66 and polystyrene to folded-chain crystals, on the one hand, and to less perfect bundle crystals, on the other hand⁷. Crystal perfection difference has also been proposed by Mandelkern et al.⁸. The PE sequences are quite strongly hindered in their crystallisation by the vinyl acetate groups either by their effect on the length PE sequences or by their association due to their polarity when present as pendant chains. Bugada et al have treated the vinyl acetate units essentially as isolated, single unit³. However, Raffield considers that there is an increase tendency for sequences of vinyl acetate to be present in the crystalline phase when the concentration of the comonomer rises⁹.

d.s.c. results have also shown that decreasing the molecular weight favours the amorphization of the copolymer and the formation of more numerous poorly organized crystals, due probably to the fact that for longer chains, longer sequences of PE are present, favouring the

crystallisation³. The distribution of crystallizable comonomer sequences seems to govern crystallization even if melt viscosity decreases as molecular weight does. This behaviour is in full agreement with Flory¹⁰ and Burfield¹¹ theories of copolymer crystallization that relate the crystallinity to the fraction of crystallizable comonomer.

d.s.c. analysis performed after tensile testing until break have provided evidence that polymer elongation induces significant crystalline modifications. These modifications are traduced by an increase of the degree of crystallinity and, above all, by an increase of the contribution of the low temperature melting peak, related to disorganized crystals, compared to the high temperature peak (melting of more perfect PE crystals).

However, the modifications are greater for the higher molecular weights, especially EVA A and B, for which an important increase of the contribution of the lower

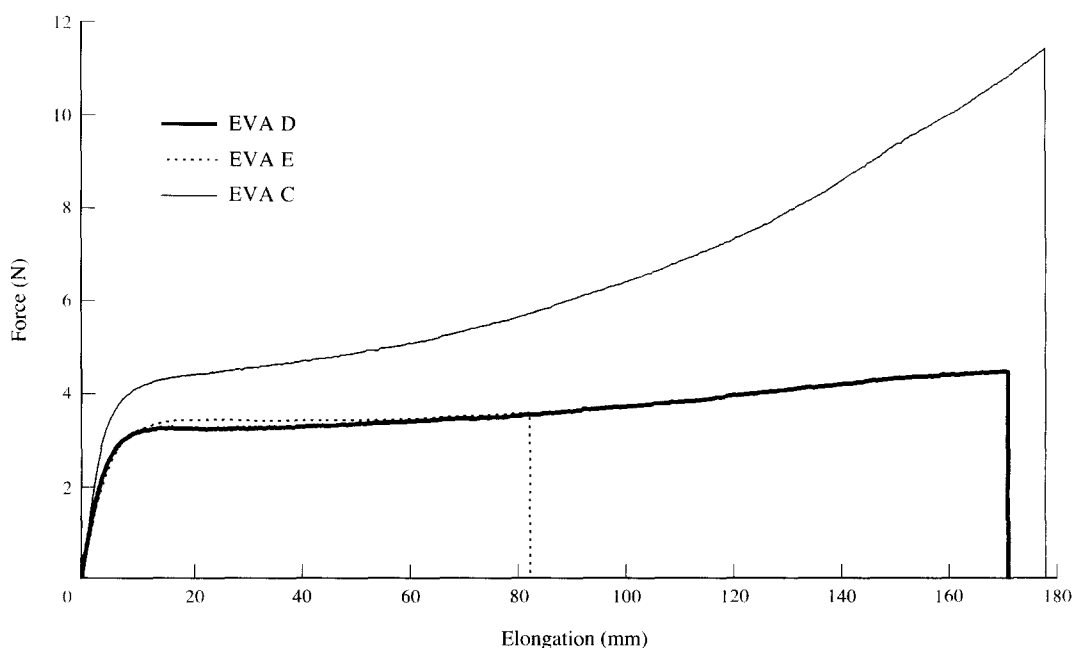


Figure 7 Tensile curves of EVA C, D and E

Table 3 Melting enthalpy, degree of crystallinity after tensile testing (in brackets is indicated the degree of crystallinity before tensile testing, for comparison) and elongation at break of EVA films

Reference	A	B	C	D	E
ΔH_m ($J g^{-1}$)	66.1	57.0	47.0	41.4	28.0
Crystallinity (%)	23.6	20.4	16.8	14.8	10
after tensile testing	(17.8)	(13.7)	(10.6)	(9.4)	(9.9)
Elongation at break (/ 805 %)	875	890	860	400	

temperature peak is observed. When the molecular weight is decreased, the changes of the crystalline organization and the increase of the degree of crystallinity become smaller. For the lower molecular weight, EVA E, changes of degree of crystallinity and crystalline organization tend to be negligible. Capaccio and Ward^{12,13} have already shown that the thermal properties of drawn polymers are related to the draw ratio, but also to the molecular weight, which can affect the melting temperature.

Parallel to the crystallinity evolution, some important variations of the glass transition temperature have been observed after the tensile test. More precisely, a significant increase (+ 6–7°C) is observed for EVA A and B, indicating a decrease of the mobility of the amorphous chains. This mobility reduction is certainly induced by the presence of more numerous disorganized crystals. These crystals constitute physical ties reducing the mobility of the amorphous chains which link them and explain the increase of the glass transition temperature. Similar results have been obtained during the study of steel/EVA/steel assemblies by dynamic mechanical measurements and d.s.c., showing a decrease of the amorphous phase mobility induced by a crystalline modification¹⁴. The study of the influence of the crystalline phase on the molecular mobility of PVDF has also evidenced some mobility reduction of the amorphous chains located in the vicinity of the crystals after stretching¹⁵. Zipper et al. have studied the effect of crystallinity on chain mobility in the amorphous regions of a miscible polycarbonate/polyester blend and have concluded that the glass transition behaviour suggests that mobility in the amorphous phase is decreased by increasing the crystallinity of the surrounding regions¹⁶. These authors have proposed that the crystalline regions impose constraints (tensile or compressive) on the amorphous regions, which reduce mobility by affecting the free volume distribution. Results obtained by Talhavani et al. suggest also that stretching of PE increases the degree of crystallinity and reduces the average amount of free volume¹⁷.

So the new crystalline structures of the EVA formed during stretching impose restrictions on segmental mobility of some amorphous chains, by placing the amorphous zones under tension. After elongation, the amorphous phase can be compared to an intercrystallite pseudo-oriented amorphous phase. The crystalline regions can be considered to act as thermoreversible 'cross-links'.

The important increase of T_g observed for EVA A and B is therefore due to the formation during elongation, of more numerous small crystals, increasing the constraint of the neighbouring amorphous chains.

For copolymers C, D and E, a crystalline modification, with the formation of disorganized crystals, is also observed but is not sufficiently important to induce a detectable mobility reduction of the amorphous phase.

The existence, for EVA A and B, of substantial stiffening during tensile testing, before the break, explains the formation of these more numerous disorganized crystals,

Table 4 Specific heat ΔC_p and glass transition temperature T_g of the EVA films before and after tensile testing ($\Delta T_g = \pm 1^\circ$)

Reference	A	B	C	D	E
ΔC_p before tensile testing ($J g^{-1} K^{-1}$)	0.53	0.75	0.80	0.77	0.78
ΔC_p after tensile testing ($J g^{-1} K^{-1}$)	0.37	0.43	0.62	0.37	0.88
T_g before tensile testing ($^\circ$)	-26.2	-26.8	-24.4	-22.1	-26.1
T_g after tensile testing ($^\circ$)	-20.0	-20.0	-24.1	-21.4	-25.5

compared with the other polymers, for which a smaller or non-existent stiffening is observed during tensile drawing. During the tensile test, chains are stretched and oriented. This stretching and orientation enables the formation of new poorly organized crystalline structures. Liu et al. have also observed an additional peak on the low temperature side of the endotherm peak of iPP after tensile testing¹⁸.

CONCLUSION

By studying the influence of tensile drawing on the crystallinity of EVA copolymers of different molecular weights, it is clearly seen that some important changes of crystalline organization and degree of crystallinity appear after stretching, depending on the molecular weight. The results obtained are able to lead to the following conclusions:

- All the EVA copolymers studied present a rather complex multiple melting endotherm, indicating that a large continuum of crystal morphologies is involved.
- The crystalline organization before stretching depends on the molecular weight. More small and disorganized crystals (melting at low temperature) are present for the lower molecular weights, for which the degree of crystallinity is lower compared to the higher molecular weights.
- After the tensile test, more disorganized crystals appear, specially for the higher molecular weight. For the lower molecular weight, less crystalline modifications can be seen.
- The degree of crystallinity is increased after the tensile test, except for the lowest molecular weight EVA, for which the evolution is negligible. These crystallinity modifications (both crystalline organization and degree of crystallinity) are induced during the stretching of the EVA films, and more precisely during the yielding and the stiffening of the samples, specially observed for the higher molecular weights.
- These great changes of the crystallinity have a significant consequence on the mobility of the amorphous phase. The important increase of the glass transition temperature observed for the two highest molecular weight EVA are related to a decrease of the mobility of the amorphous chains. More numerous disorganized crystals, present after stretching for the higher molecular weight EVA, constitute physical ties reducing the mobility of the amorphous chains which link them.
- Finally, it appears that the molecular weight of ethylene vinyl acetate copolymers plays a major role in the tensile behaviour and crystalline organization of these copolymers, even the vinyl acetate content is identical.

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