Manufacturing of Polypropylene Laminates and Related Structural Reorganization in the Crystalline Phase

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Synopsis

The conditions for obtaining recrystallization in more ordered modifications are described for an uniaxially oriented sample of isotactic polypropylene, annealed with fixed ends. These recrystallization conditions are related to the conditions of a lamination process.

INTRODUCTION

Processes of preparing oriented polyolefin laminates, through annealing treatments under pressure, from piles of oriented films (ends constrained), are described in the patent literature.[1-5] Such lamination procedures, in nearly all the reported examples, are performed on isotactic polypropylene (*i*-PP) and conducted at temperatures lower than, but not far from, the melting of the polymer.

Annealing treatments of oriented *i*-PP samples with fixed ends have been extensively studied. A large part of such studies refer only to low-temperature conditions ($T_a < 160°C$),[6-11] but some high-temperature annealing experiments are also described.[12,13] In particular, Wyckoff[12] pointed out, for isometric annealing at high temperatures ($T_a < 172°C$), the occurrence of partial melting and recrystallization phenomena with maintenance of crystalline orientation. Evidence for recrystallization phenomena in the melting temperature region for *i*-PP disoriented samples (α-form) has been presented in the literature[14-18], and some kinetics for these recrystallizations have been recently described by us.[19] It has been also shown that these recrystallizations imply transitions to more ordered modifications (of the α-form), in terms of the orientation of the chains in the crystal structure.[20,21]

In this article we shall describe the conditions for obtaining recrystallizations in more ordered modifications, for an *i*-PP uniaxially oriented sample, annealed with fixed ends. The aim is to examine whether such recrystallization conditions are related to the lamination process conditions.

EXPERIMENTAL

The uniaxially oriented *i*-PP films are the commercial MO produced by Moplefan S.p.A., 38 μ in thickness. The material is highly isotactic, being approximately 97.5% insoluble in *n*-heptane. It has an intrinsic viscosity of 2.5 dL/g.

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The thermal treatments and measurements were carried out in a Perkin-Elmer differential scanning calorimeter (DSC-2), in a flowing N_2 atmosphere. The heating rates during the measurements as well as the cooling rates from the annealing temperatures were fixed at 10°C/min. The restrained conditions were obtained using the method described by Samuels.[22]

The sample support was made from an aluminum sample-pan lid, supplied by Perkin-Elmer for use in their DSC instruments.

Film samples were tightly wound on the support and knotted. The sample was then placed into a sample pan and a second lid crimped over the tied film to further restrain movements.

The X-ray diffraction patterns were obtained using an A.E.D. Siemens automatic X-ray diffractometer with Ni-filtered CuKα radiation, at room temperature. Film packs, as obtained after the DSC treatments, were placed perpendicular to the X-ray beam; the diffracted intensity was collected with a Geiger counter moving in the 2θ circle. No corrections were applied to measured intensities.

It has been shown[23-25] that the crystalline structure of the α-form may show various degrees of disorder in the "up" and "down" positioning of the chains, while the unit cell and the ordered disposition in it of threefold right- and left-handed helical chains remain substantially unchanged. Two limiting structures may be postulated for the α-form: an ordered limiting structure (henceforth denoted α_2) with a well-defined disposition of "up" and "down" helices in the unit cell and a disordered limiting structure (henceforth denoted α_1), with a random distribution of "up" and "down" chains in each site of the unit cell.

As previously described,[23,24] the two limiting modifications α_1 and α_2 have substantially identical X-ray spectra. However, while, in the α_1 modification, only reflections with $(h + k)$ even are allowed, in the α_2 modification reflections with $(h + k)$ uneven also may be present, though generally associated with a lower intensity.

The ratio of the areas below the peaks located nearly at $2\theta = 35°$ and $2\theta = 36.5°$, on the first layer line (that is, the peaks indicated by D and E in fig. 1 of ref. 24 and thereafter referred as I and II) has been taken by us as a quantitative index of the degree of ordering.

The lamination experiments were performed in a Carver Laboratory press. The film was cut into squares, and 10 squares were superimposed to form an assembly. The assembly was placed in the cold press between two chrome plates, and a pressure of 1000 psi was applied. The temperature was raised to the fixed value and held for 20 min; then the press heaters were turned off, and the assembly was allowed to cool, under pressure.

RESULTS AND DISCUSSION

The DSC scan for the uniaxially oriented film, in restrained conditions, is reported in Figure 1(a).* DSC scans for film specimens (again restrained), after two different annealing procedures with fixed ends, at various temperatures,

*As is well known,[22,26] the restrained conditions produce higher melting peak positions (T_m) than unrestrained conditions (T_m in our case increases from 165 to 173°C).

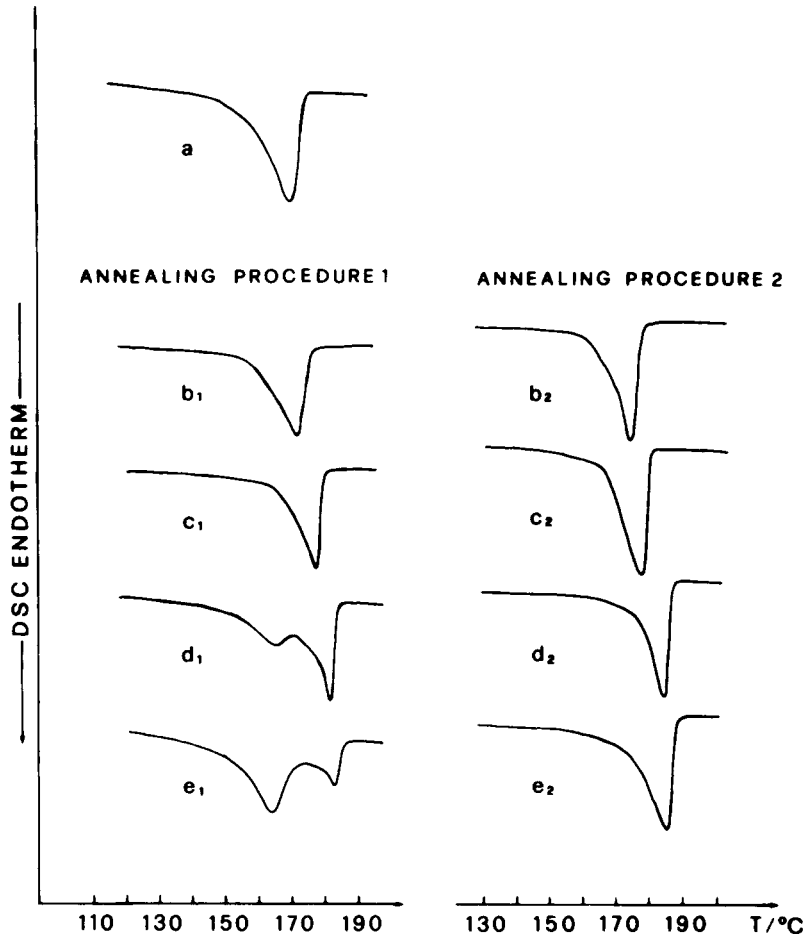


Fig. 1. DSC curves (at heating rate 10°C/min) of restrained uniaxially oriented isotactic polypropylene films. The annealing procedures 1 and 2 are described in the text: (a) as received samples; (b) T_a = 155°C; (c) T_a = 162°C; (d) T_a = 168°C; (e) T_a = 171°C.

are also reported in Figure 1. In procedure 1 the annealing temperature (T_a) was reached at the rate of 10°C/min, and the annealing time was 20 min. For temperatures higher than 168°C, double melting peaks are obtained, the lower peak being below the annealing temperature and hence corresponding to the melting of species crystallized during the cooling, which follows the annealing procedure.

In procedure 2, T_a was reached at the rate 0.3°C/min and the annealing time was 14 h. In such conditions, in the considered T_a range, only samples characterized by single peak melting endotherms are obtained.

On the basis of the comparison between scans analogous of that of Figure 1 (procedure 1 vs. procedure 2), it is possible to infer that, as in disoriented samples,[20] recrystallization processes are involved.

The melting peak positions (T_m), obtained by scans analogous to that of Figure 1, are reported in Figure 2 vs. T_a, for both the annealing procedures. The observed behavior is analogous to that pointed out for disoriented

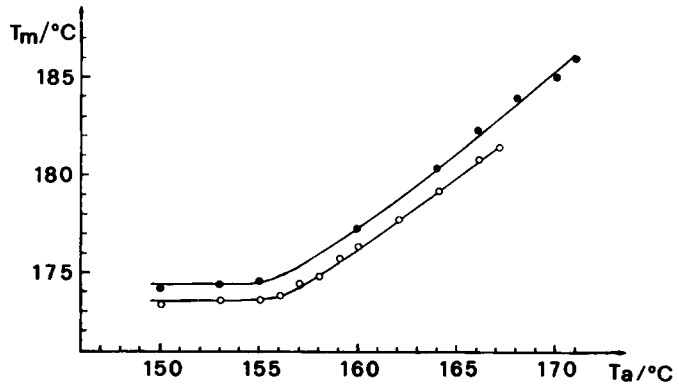


Fig. 2. Temperatures T_m of the endothermic single maxima of the kind of Figure 1 (b, c, d_2, e_2) as functions of the annealing temperature T_a: (○) annealing procedure 1; (●) annealing procedure 2.

samples[20,21]: The T_m values are nearly constant up to a given T_a value (in the present case $T_a \simeq 155°C$), then T_m increases with T_a.

X-ray diffraction patterns, in the form described in the experimental part, for some of the samples of Figure 2, are reported in Figure 3. The ratio of the areas below the peaks indicated by I and II in Figure 3 is nearly unchanged for T_a value up to 155°C [compare Fig. 3(a) and 3(b)] and is typical of a modification near to the limiting modification α_1.[24] For higher T_a values the

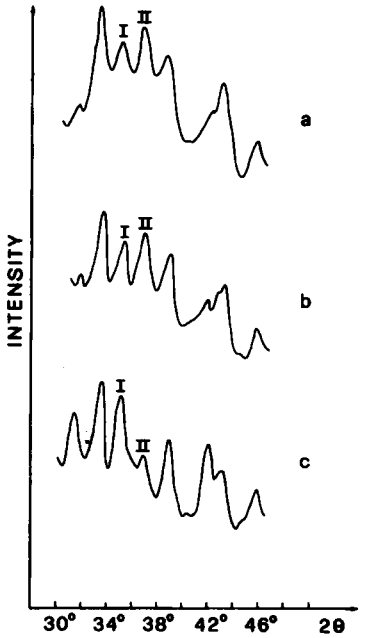
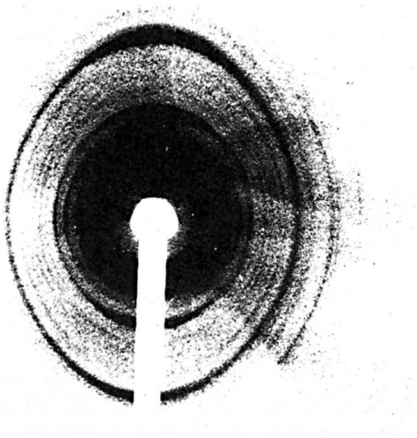


Fig. 3. X-ray diffraction patterns in the 2θ interval 30–46° (CuKα) for the first layer line: (a) as received sample; (b) sample annealed with procedure 2 at T_a = 155°C; (c) sample annealed with procedure 2 at T_a = 171°C. The ratio between the areas below the peaks indicated by I and II was taken as a qualitative index of the degree ordering.

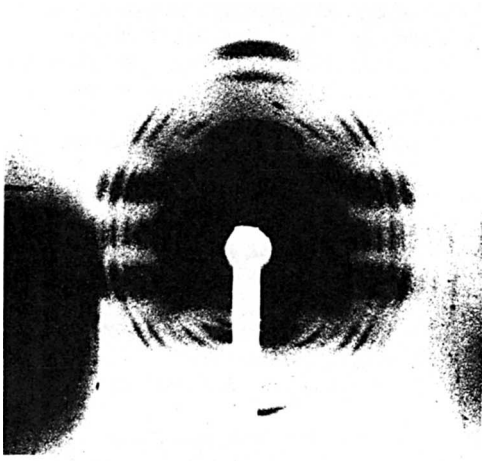
"up–down" degree of order increases with T_a; the high ratio between peaks I and II for T_a = 171°C indicates the formation of a modification not far from the α_2 limiting modification.

Hence, also for this oriented sample, the relevant increases of the melting temperature and the disorder–order transition occur in the same annealing temperature range, which, as established for disoriented samples,[21] is the range in which partial melting and recrystallization occur.

It is worthwhile to note that, when the recrystallization process is complete at the annealing temperature, no or only a little disorientation is produced, as observed in the Wyckoff experiments.[12] Just as an example, the X-ray diffraction patterns of the samples, whose DSC scans are shown in Figures 1(e_1) and 1(e_2), are reported in Figures 4(a) and 4(b), respectively. Figure 4(a) shows



(a)



(b)

Fig. 4. X-ray diffraction patterns in a cylindrical camera of the samples annealed at T_a = 171°C: (a) with procedure 1 [see also Fig. 1(e_1)]; (b) with procedure 2 [see also Fig. 1(e_2)].

that the incomplete recrystallization at T_a and the rapid crystallization on cooling produce partial disorientation.

On the other hand, lamination experiments on the films, according to the procedure described in the Experimental section, produce negligible adhesion between the films for $T_a < 155°C$, and generate at least partial disorientation for $T_a > 170°C$; hence the temperature range useful for the lamination process corresponds to the range for which a significative recrystallization in a more ordered modification occurs, provided that that is complete in the time of isothermal annealing.

Our experiments suggest that the increase of the "up–down" degree of order in the oriented films which constitute the laminates could be related to the adhesion between the films; in such a way nondestructive test for the laminates could be provided.

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