Materials Science Forum Vols. 408-412 (2002) pp. 1579-1584

Planar Texture Developed in Plasma Treated Polypropylene Films

M. Aouinti[1], D. Chateigner[2], A. Gibaud[3] and F. Poncin-Epaillard[1]

[1] Laboratoire de Cristallographie et Science des Matériaux, ISMRA, 6 Bd. du Maréchal Juin, FR-14050 Caen, France

[2] Laboratoire de Physique de l'Etat Condensé, Université du Main, BP 535, FR-72085, Le Mans

[3] Polymères Colloïdes et Interfaces, Université du Maine. Av. O. Messiaen, FR-72085, Le Mans

Keywords: Crystallization, Plasma, Polymer, Polymer Film, Polypropylene, Surface, Texture

Abstract. The QTA analysis of plasma-treated polypropylene films revealed the stabilisation of a planar texture with the long axis at random but in the plane of the treated films. This texture development is associated to the crystallisation of the polypropylene film under plasma irradiation, and to the increase of the crystallite sizes, as seen from the x-ray peak profiles.

Introduction

Plasma modification of polymer surfaces has a great interest in many application fields like painting, adhesion, biomaterials, electronics...Until now, this technique may be considered as a green method as no solvent is necessary, rapid as in few minutes the treatment is achieved, and universal since with the same apparatus, hydrophilic or hydrophobic surfaces is obtained. One of the most important claims of the technique is that this modification affects only few layers of the materials. However with polymers, this assumption must be carefully verified.

In a previous work, a bulk structure of isotactic polypropylene modified in a nitrogen plasma was reported [1] in specific conditions. These conditions were corresponding to drastic ones, i.e. high discharge power (more than 80 W) and long treatment time (more than 5 min). The initial polymers, composed mostly of smectic and amorphous phases, crystallized under irradiation in the so-called α phase. If a thermal effect is not excluded to explain such a transformation, the phenomenon is associated to VUV absorption.

Polypropylene finds most applications as thin films (typically in the 100μm thickness range), as in food industry for instance. Since the crystallized phases of polypropylene are of low symmetry, their mechanical behavior will be different when amorphous or crystallized. Furthermore, in the crystallized form(s), the stabilization of a texture may influence considerably the mechanical responses, giving anisotropic macroscopic deformations and stresses in the materials, which could backward be of importance for their optimized use. It becomes then of major importance to examine how crystal phases develop under plasma irradiation in thin films of polypropylene, and if eventually this crystallization is accompanied by a texture development.

In this work we concentrate on the characterization of CO_2 plasma treated films of polypropylene. The amount, structure and crystallite sizes of the crystalline phases grown under irradiation are characterized by x-ray diffraction. The preferred orientation of the crystallites are quantitatively determined using x-ray diffraction peaks deconvolution.

Experimental details

The polypropylene films used were supplied by the Institut Textile de France ITF. They are isotactic semi-crystalline polymers synthesized by heterogeneous Ziegler-Natta catalysis. The initial crystalline phase is estimated to 38% approximately in volume and corresponds to the smectic state. Before plasma treatment, the 100 μm thick films were successively washed with ethanol then acetone, and dried under vacuum for one day.

A microwave plasma generator (SAIREM, 433 MHz) with variable power (from 0 to 250 W), coupled to a resonant cavity was used for irradiation. The gas (Carbon dioxide, purity > 99.995 %)

flow control was ensured by a MKS mass flow meter, and the pressure measured with Penning and Pirani gauges. The films were plasma treated using a gas flow of 20 sccm under a pressure of 7.5 10^{-1} mbar. Films were located at a distance of 4 cm from the plasma discharge. We selected a plasma power of 100W and varied the irradiation time from 0 to 11 min in order to follow the crystallization process. Then, on the more crystallized film, we operated quantitative texture analysis.

The x-ray structure and crystallite size characterization was operated on an X'PERT Philips diffractometer in the Bragg-Brentano mode. Silicon standard was used to calibrate for instrumental aberrations, and Rietveld refinement was practiced with the help of the Rietquan program. X-ray QTA was measured on a 4-circles diffractometer equipped with a CPS 120 from INEL as detailled elsewhere [2]. The use of such a detector is essential for polypropylene films since broad diffraction peaks are present, with strong overlaps. We first controlled by regular φ-scans that the texture was axially symmetric around the normal to the film plane. Then we measured one χ-scan with 5° steps and 1800 seconds of counting time per χ postion, using an incidence angle ω = 10°, approximately the Bragg position for the {111, 041, 131} triplet. The films were large enough to ensure that the x-ray beam was fully intersecting the sample up to χ = 65°. The amorphous part was remove by assuming a linear variation under each of the peaks. Data reduction (volume/absorption, localisation corrections) was operated in our program Pofint [3], while the OD refinement was operated using the WIMV direct method as implemented in the Beartex package [4].

Results

Structural and microstructural evolution. The observed crystallographic structures of blank and treated polypropylene correspond to the smectic [5-9] and monoclinic ( ) [9,10] phases respectively (Fig. 1). The blank sample pattern exhibits two principal reflections, (100) and (101), at respectively 2θ values of 15° and 21°. These reflections are associated to the smectic phase of isotactic polypropylene [11,12]. A third broad reflection (2 = 17°) is identified as the amorphous phase [12]. We neatly observe a phase transition from the smectic to the monoclinic phase beginning after 1 min of treatment. After 11 min the transformation is fully achieved at this plasma power. As a consequence of the increase in crystallization with irradiation, we observe that peak intensities increase with time. Furthermore, their full width at half maximum decreases, indicating an overall growth of the crystallite sizes. The Rietveld refinements of the diagrams indicate crystallographic structures very close to the ones of literature [13-17]. We obtain on the most crystallized film: a = 6.66Å; b = 6.5Å; c = 20.86Å; = 98.7Å. The refined phase abundance increases slowly for short duration, less than 5 % up to 6 min of treatment (Fig. 2, left), then increases rapidly, reaching more than 63 % of crystallized phase for 11 min of treatment. The crystallite sizes (Fig. 2, right) vary in a similar fashion, reaching approximately 150 Å for 11 min of treatment.

Quantitative Texture Analysis. Looking at the evolution of diffraction lines with the tilt χ orientation angles (Fig. 3), one can see that the intensities of the reflections {110/011}, {040} and {-111/130/031} decrease with χ, while the {111/-131/041/121} group remains almost constant (due to defocusing, its maximum decreases while its integrated value increases). We used all the four indicated groups and the refined values of the cell parameters to refine the OD, which gives an OD completion with numbers of paths in OD cells from 3 to 17 (Fig. 4). These values may be enhanced taking account of weaker diffraction lines, but with our counting times reflections at larger 2θ were to much noisy. Experimental and recalculated pole figures compare favorably (Fig. 5), with averaged $RP_{0.05}$ of only 1.4% and RP_1 as low as 1%. The texture strength is relatively low with a texture index of 1.35 m.r.d.^{2}. The orientation corresponds to the alignment of c axes randomly in the plane of the film, with a random orientation of the a and b axes around c, as denoted by the recalculated low indices pole figures (Fig. 6). This orientation type corresponds to a planar texture with only 1 degree of rotation freedom for the crystallites.

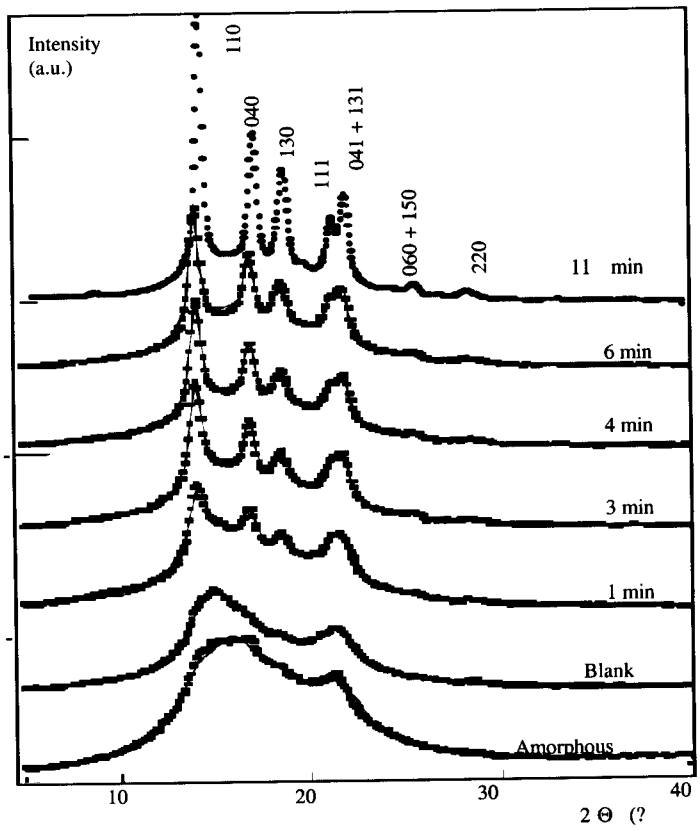

Fig. 1. XRD diagrams of the plasma treated polypropylene films

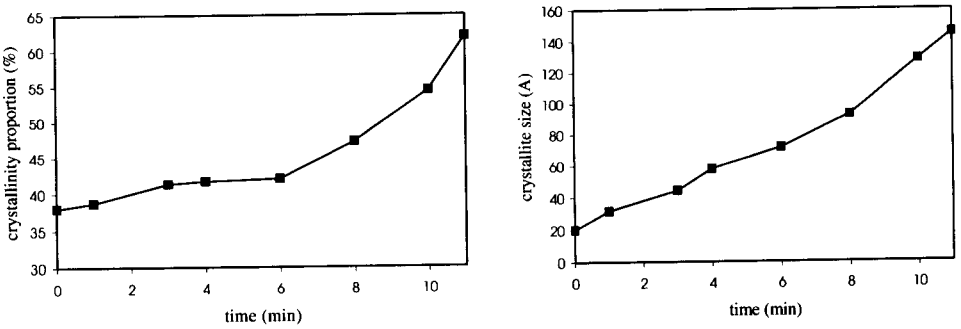

Fig. 2. Phase abundance (left) and crystallite sizes (right) versus irradiation time.

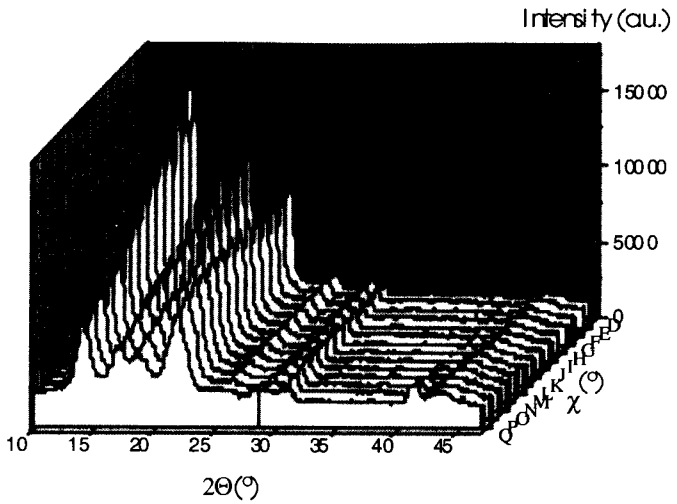

Fig. 3. XRD diagrams of the 11 min plasma treated film, measured in function of the χ angle. $\chi = 0$ is the back plane, $\chi = 65°$ in front, 5° steps

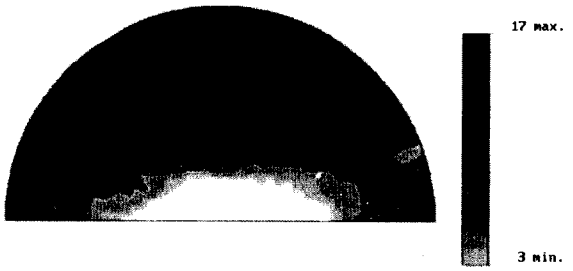

Fig. 4. OD completion represented as number of paths in each OD cells (MIMA subroutine of Beartex program). Linear scale, equal area projection.

Discussion

The structural transformation observed under plasma irradiation appears as a successive occurrence of 2 different phenomena. In the first minute of irradiation, the complete crystallization of the smectic phase is achieved in the as-furnished initial films and transformed into the α polypropylene phase. Then an additional slow crystallization and growth process of the α phase takes place at the expense of the amorphous phase. The transformation appears as a continuous process, with a progressive chain organization, which incidences is the texture formation. It implies lateral motions, macromolecular chains turn over to set up the helices of the α phase in the observed orientation, as was previously supposed [12].

The alteration, initiated by the plasma energy source, may be promoted either by a direct energy transfer bombardment from ions (in the 0 - 100 eV range) and metastable species (0 – 20 eV) on a thickness scale of 10-20Å, or by indirect radiative absorption, particularly visible orUV photons, whose action is known to be effective on a thickness scale higher than 10 μm in this kind of materials. The latter is probably responsible of such a transformation, by analogy to previous works on polypropylene treatments under nitrogen plasma [1], which could also apply for the CO_2 treatment. However, if the thermal relaxation resulting from a too low excitation energy would not

be enough to break polymer bonds efficiently, the corresponding energy may be used for local chain rearrangements and promotion of the texture.

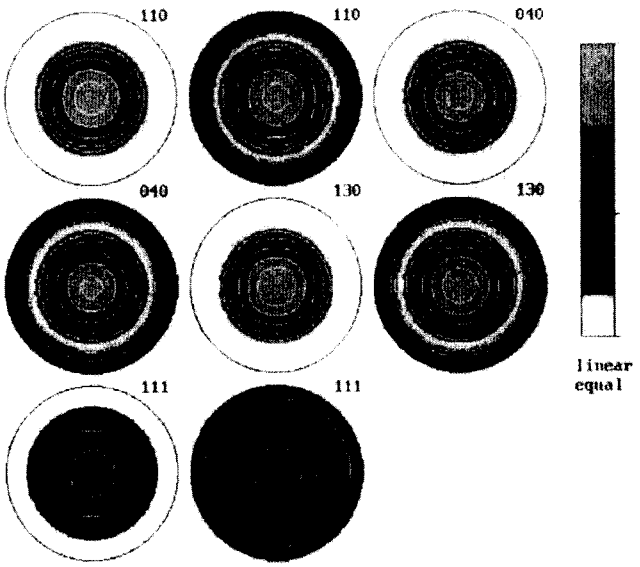

Fig. 5. Experimental and recalculated normalized multipole figures showing the quality of the refinement. Linear density scale, equal area projection. max = 1.6 m.r.d., min = 0.6 m.r.d.

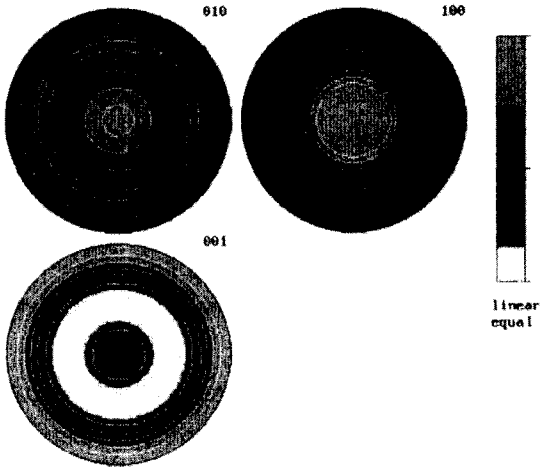

Fig. 6. Recalculated {010}, {100} and {001} normalized pole figures showing the alignment of the c axes of polypropylene in the film plane (planar texture). Linear density scale, equal area projection. max = 1.7 m.r.d., min = 0.4 m.r.d.

Conclusion

The structural and microstructural modifications of 100 m thick polypropylene films by specific CO_2 plasma conditions (high power and long treatment times) has been characterized using x-ray diffraction. The polypropylene film structure is modified in the bulk through mostly VUV absorption and thermal relaxation. This structural change is associated to a phase transition from the smectic + amorphous phases into the monoclinic phase, with rapid, then slower kinetics respectively for the first transformation and a slower rate of the latter one. During both these transformations, the mean crystallite size is increasing and the stabilization of a planar texture is achieved in the film. The texture strength is moderated, with the longest cell parameter at random in the plane of the film, for the most treated film.

Acknowledgements

This work has been funded by the European Union project under the Growth program (G6RD-CT99-00169) ESQUI: "X-ray Expert System for Electronic Films Quality Improvement".

References

[1] F.Poncin-Epaillard, J.C. Brosse, T.Falher: *Macromolecules* **30** (1997) 4415.

[2] J. Ricote, D. Chateigner: *Boletín de la Sociedad Española de Cerámica y Vidrio*, **38[6]** (1999) 587.

[3] POFINT: "Pole Figure Interpretation", D. Chateigner, CNRS-INEL licence (2002).

[4] H.R. Wenk, S. Matthies, J. Donovan, D. Chateigner: *J. Applied Crystallography* **31** (1998) 262.

[5] G. Natta: *Makromol. Chem.*, **35** (1960) 94.

[6] J. A. Gailey, R. H. Ralston: *SPE Trans.*, **4** (1964) 29.

[7] R. L. Miller: *Polymer* **1** (1960) 135.

[8] D. M. Gezovich, P. H. Geil: *Polym. Eng. Sci.* **8(3)** (1968) 202.

[9] G. Border, M. Grell, A. Kallo: *Faserforsch. Textil-Tec.* **15** (1964) 527.

[10] N. Kawamoto, H. Mori, K. H. Nitta, S. Sasaki, N. Yui, M. Terano: *Macromol.Chem.Phys.* **199** (1998) 261.

[11] H.Tanaka: *Eur. Polym. J.* 27(7) (1991) 565.

[12] P. B. Mc Allister, T. J. Carter, R. M. Hinde: *J. Polym. Sci.* 16 (1978) 49.

[13] Z. Mencik: *J. Macromol. Sci.* B6(1) (1972) 101.

[14] D.R. Ferro, S. Bruckner, S.V. Meille, M. Ragazzi: *Macromolecules* 25(20) (1992) 5231.

[15] W. Stocker, S.NB. Magonov, H.J.C. Wittmann, B. Lotz: *Macromolecules* 26(22) (1993) 5915.

[16] A. Turner-Jones, J.M. Airzlewood, D.R. Becket: *Macromolules* 75 (1964) 134.

[17] S. Nishimoto, T. Kagiya: "Handbook of polymer degradation", Ed. S. Hamid, M.B. Amin, A.G. Maadhad, Dekker Inc., New York, 3 (1992).