Macromol. Symp. ***180,*** *23–31 (2002)*

Cast-Extruded Syndiotactic Polypropylene Films: Preliminary Structural and Mechanical Results

*Liberata Guadagno**, *Carlo Naddeo, Concetta D'Aniello,*
Luciano Di Maio, Vittoria Vittoria, Domenico Acierno§

Department of Chemical and Food Engineering
University of Salerno
Via Ponte Don Melillo 84084 Fisciano - SA, Italy

§ Department of Materials and Production Engineeering
University of Naples "Federico II" – Piazzale Tecchio 80100 Napoli, Italy

Summary: Syndiotactic polypropylene (sPP) was cast-extruded with a laboratory single screw extruder, obtaining a crystalline and still highly transparent film.

The structural studies showed that the film crystallized at room temperature in the disordered helical form I, containing a fraction of a mesophase with the chains in trans-planar conformation. X-ray patterns, taken either along the extrusion direction (MD) or along the orthogonal directions (TD and ND), indicated a low orientation of the *c* axis parallel to the machine direction (MD) and a partial orientation of the *a* axis along the transverse direction (TD). Mechanical properties performed in either direction showed a very similar behaviour, but a different strain at the breaking point. The mechanical parameters were derived in both directions.

Introduction

The use of new metallocene catalysts in recent years has allowed a very rapid development of polymers with a wide range of structures and related properties,

---

*Corresponding author: Dipartimento di Ingegneria Chimica e Alimentare - Università di Salerno - via Ponte don Melillo, 84084 Fisciano (SA), Italy. *E-mail address: lguadagno*@unisa.it

CCC 1022-1360/00/$ 17.50+.50/0

depending on the processing conditions. Among them syndiotactic polypropylene (sPP), recently obtained with high tacticity and high molecular weight[1-3], is receiving a great attention owing to its new properties respect to the isotactic isomer. In the case of sPP the difficulty of correlating the physical properties to the structural organization, as determined by the processing procedures, is principally due to its very complex polymorphic behavior, not yet fully clarified[4-15] .

Four crystalline forms of sPP have been described so far, characterized by either different chain conformation or crystalline packing. Form I and form II are characterized by chains in helical conformation[4-7], whereas form III and form IV present chains in trans-planar and $(T_6G_2T_2G_2)_n$ conformations, respectively[8-9]. Furthermore, depending on degree of stereo-regularity and on the mechanical and thermal history of the sample, different amounts of disorder in the crystalline packing can be evidenced[16-17].

Beside the crystalline phase structure, and the presence of disordered phases, an important parameter to be taken into account is the orientation state of either the crystalline or the amorphous phase. This parameter largely dictates the performance of semi-crystalline samples, processed in conditions in which orientation can develop[18-21].

In this paper we present some preliminary experimental results about the structure and the mechanical properties of sPP films obtained by “cast-extrusion” process. This is an industrial process in which some orientation and better properties can be achieved.

Experimental

Syndiotactic polypropylene (sPP) was cast-extruded with a laboratory single screw extruder at 200°C into a film 30 μm thick (sample CE).

Fiber X-ray diffractions spectra were obtained using a PHILIPS PW 1710 Powder Diffractometer (Ni-filtered Cu K_α radiation) operating under vacuum by means of a cylindrical camera with a radius of 57.3 mm. The imaging plate FUJI BAS-1800 system was used to record the diffraction patterns.

The infrared spectra were obtained in absorbance by using a FT-IR BRUKER IFS66 spectrophotometer with a resolution of 4 cm^{-1} (32 scans collected).

Differential scanning calorimetry (DSC) results were obtained using a METTLER TA 4000-DSC 30 thermoanalyzer purged with nitrogen and chilled with liquid nitrogen for sub-ambient measurements. Temperature range was –100°C/200°C at a heating rate of 20°C/min.

Birefringence results were obtained using a polarizing optical microscope JENAPOL equipped with Eringhause compensator.

Mechanical tensile properties were analyzed with an Instron 4301 Dynamometer. Samples of film of 120 x 10 mm x mm were cut in both machine and transverse direction. Cross head speed and grip distance were set at 50 mm/min and 100 mm respectively.

Results and Discussion

Structural Organization

In some cases, the cast-extrusion can produce a film with an uniplanar orientation: to investigate this possibility, the X-ray patterns have to be taken along the extrusion direction (machine direction, MD) and along the orthogonal directions (through direction ND and transverse direction TD). The X-ray diffraction pattern of the cast-extruded sample (CE) obtained along the MD direction shows only Debye-Sherrer rings. In Fig.1 we show the X-ray diffraction pattern of the cast extruded sample (CE) taken along the ND direction. The same pattern is obtained along TD direction.

All the reflections, the spacing and the diffraction angles 2ϑ correspond to the disordered form I. In both patterns, Debye-Sherrer rings from (200) reciprocal plane are the most prominent, showing a maximum of intensity along the equatorial plane. As a matter of fact, only the (200) reflection of the helical form I, corresponding to 12.3° of 2ϑ is polarized along the equator, indicating a partial orientation of the *a* axis along the transverse direction (TD) perpendicular to the machine direction (MD). The second reflection, indexed as 010 of form I and corresponding to 15.9° of 2ϑ is not polarized, whereas the third reflection corresponding to 20.8° of 2ϑ and indexed as (111) of form I shows a very low polarization along the first layer, corresponding to the helical identity period of 7.45 Å. This indicates a low orientation of the *c* axis parallel to the machine direction.

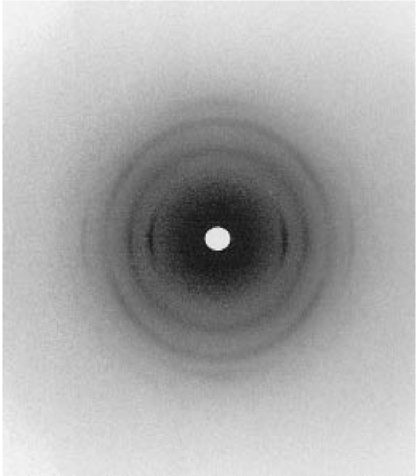

Fig 1. X-ray diffraction pattern of sample CE along ND direction

It is worth noting that the second reflection, at 15.9° of 2ϑ, is not sharp, showing a diffuse halo at 17° of 2ϑ. This reflection, already found in samples crystallized at low temperatures[22-25], was attributed to a trans-planar mesophase, containing lateral disorder in the packing of the chains. This phase was probably formed, in a small fraction, during the rapid cooling of the cast-extruded film at room temperature.

To confirm the partial presence of chains in trans-planar conformation, in Fig.2 we show the FTIR spectrum in absorbance (1300-700 cm^{-1}) of sample CE.

Infrared analysis is very sensitive for the chain conformation determination: as a matter of fact helical and trans planar bands have been evidenced since the first preparation of the syndiotactic isomer of polypropylene[26-27].

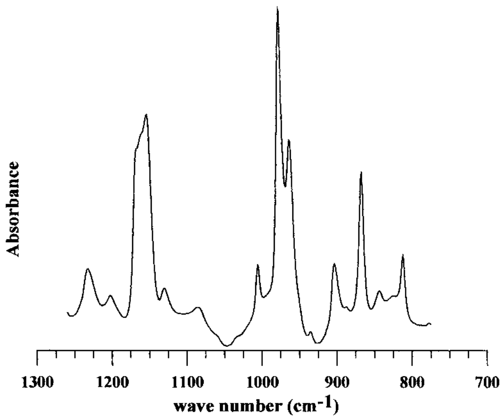

Fig 2. Infrared spectrum of sample CE

We observe that the bands of the helical form of sPP, appearing at 810, 868, 977, and 1005 cm^{-1}, are present and well developed, but the trans-planar bands at 831, 963, and 1132 cm^{-1} are evident too, although of reduced intensity, indicating that a small fraction of chains organized in a different conformation. Therefore, during the extrusion process, the film crystallizes at room temperature prevalently in the helical form I, and still containing a fraction of mesophase with the chains in trans-planar conformation.

In Fig.3 the thermogram obtained in the differential scanning calorimeter (DSC) is reported.

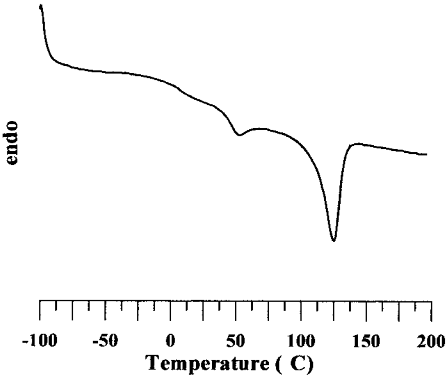

Fig 3. d.s.c. thermogram of sample CE

The curve shows the melting peak with the maximum at 124.5°C, and a melting enthalpy, $\Delta H_m = 30.5$ J/g. This value corresponds to a crystallinity of 16% , obtained using for ΔH_0 the value of 8 kJ/mol[28]. At lower temperatures we observe the deflection from the baseline, due to the glass transition, appearing at about 5.2°C. Afterwards, a second deflection, appearing as a small endothermic peak, centered at 52.8°C, is evident in the curve. It was already associated to the melting of the mesophase[23-25] : also in this case the X-ray diffractograms as well as the FTIR spectra suggest that there is in the sample a fraction of material neither in the helical crystalline nor in the amorphous state.

The orientation of the cast extruded film was investigated by birefringence measurements, performed on different strips cut along the film width. This procedure was followed because in the cast extrusion process a different orientation can be achieved in the central part of the film, respect to the lateral strips.

In Fig.4 we show the birefringence, Δn, as a function of the distance from the center of the film.

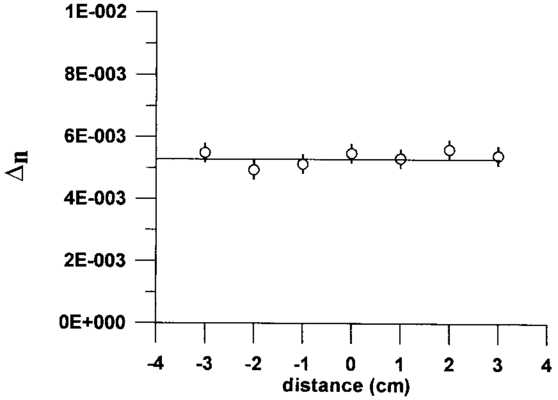

Fig 4. Birifrangence index along the width of the film

We can observe that the experimental points fit the same straight line, whose mean value is 5.3×10^{-3}. This result indicates that the orientation is not very high, as already shown by the X-ray patterns, and it is uniformly distributed along the width of the film.

Mechanical Properties

Representative stress-strain curves, performed both in the machine direction (MD) and in the transverse direction (TD), are shown in Fig.5.

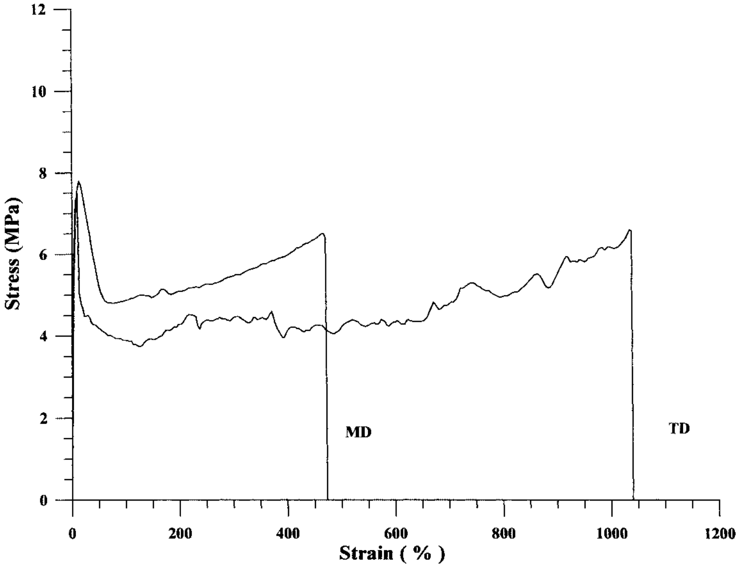

Fig 5. Sress-Strain curves along MD and TD directions

In Table 1 we report the average mechanical parameters of the material. We can observe that almost all the mechanical parameters are very similar in either direction. In particular the elastic moduli are the same, in the experimental error, and the yield stress is very near in the two directions. Only the strain at break is very different, being 5% for sample CE-MD and 11% in the transverse direction (sample CE-TD), indicating that the chain arrangement is different in the two directions.

In spite of this large difference, the stress of breaking is just the same, that is 6.4 MPa.

Table 1

The elastic modulus, E (Mpa), the yield stress σ_y (Mpa), the breaking stress σ_b (Mpa) and the draw ratio of breaking λ_b for sample CE tested along the machine direction (CE-MD) and in the transverse direction (CE-TD).

Sample	E (MPa)	σ_y (MPa)	σ_b (MPa)	λ_b
CE-MD	234	7.8	6.4	5
CE-TD	228	7.5	6.4	11

This work was supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica MURST (PRIN 2000 *"Catalizzatori di coordinazione e polimeri a struttura mirata"*).

References

[1] Ewen, J.A.; Jones, J.A.; Razavi, A.; Ferrara, J. D.; *J. Am. Soc.* **1988**, *101*, 6255.

[2] Longo, P.; Proto, A.; Grassi, A.; Ammendola, P.; *Macromolecules* **1992**, *24*, 462.

[3] Grisi, F.; Longo, P.; Zambelli, A.; Ewen, J. A.; *J. Mol. Cat. A: Chemical* **1999**, *140*, 225.

[4] Lotz, B; Lovinger, A. J.; Cais, R. E.; *Macromolecules* **1988**, *21*, 2375.

[5] Lovinger A.J.; Lotz, B.; Cais, R.E. ; *Polymer* **1990**, *31, 2253.*

[6] Lovinger, A. J.; Davis, D.D.; Lotz, B.; *Macromolecules* **1991**, *24, 552.*

[7] Lovinger, A.J.; Lotz, B.; Davis, D.D.; Padden, F.J.; *Macromolecules* **1993**, *26, 3494.*

[8] Chatani, Y. ; Maruyama, H.; Noguchi, K.; Asanuma, T.; Shiomura, T.; *J Polym. Sci. Part C* **1990**, *28*, 393.

[9] Chatani, Y. ; Maruyama, H.; Asanuma, T.; Shiomura, T.J. ; *J. Plym. Sci. Poly. Phys. Ed.* **1991**, *29*, 1649.

[10] De Rosa, C. ; Corradini, P.; *Macromolecules* **1993**, *26*, 5711.

[11] De Rosa, C.; Auriemma, F.; Vinti, V.; *Macromolecules* **1997**, *30*, 4137.

[12] De Rosa, C.; Auriemma, F.; Vinti, V.; *Macromolecules* **1998**, *31*, 7450.

[13] Lacks, D.J.; *Macromolecules* **1996**, *29*, 1849.

[14] Palmo, K.; Krimm, S.; *Macromolecules* **1996**, *29*, 8549.

[15] Nakaoki, T.; Ohira, Y.; Hayashi, H.; *Macromolecules* **1998**, *31*, 2705.

[16] Auriemma, F.; Lewis, R.H. ; Spiess, H. W.; De Rosa, C. ; *Macromol. Chem. Phys.* **1995**, *196*, 4011.

[17] De Rosa, C.; Auriemma, F.; Corradini, P.; *Makcromol. Chem.* **1996**, *29*, 7452.

[18] Uehara, H.; Yamazaki, Y.; Kanamoto, T.; *Polymer* **1996**, *37*, 57.

[19] Loos, J.; Buhk, M.; Petermann, J.; Zoumis, K.; Kaminsky, W.; *Polymer* **1996**, *37*, 387.

[20] Loos, J.; Petermann, J.; Waldofner, A.; *Colloid Polymer Sci.* **1997**, *275*, 1088.

[21] D'Aniello, C.; Guadagno, L.; Naddeo,C.; Vittoria,V.; *Macromolecular Rapid Commun.* **2001**, *22*, 104

[22] Vittoria, V.; Guadagno, L.; Comotti, A.; Simonutti, R.; Auriemma, F.; De Rosa, C.; *Macromolecules,* **2000**, *33,* 6200.

[23] Guadagno, L.; Fontanella, C.; Vittoria, V.; Longo, P.; *J. Polym. Sci., Part C* **1999**, *37*, 173

[24] Guadagno, L; D'Aniello, C; Naddeo, C.; Vittoria, V; *Macromolecules,* **2000**, *33*, 6023.

[25] L. Guadagno; L. D'Arienzo; V. Vittoria; P. Longo; G. Romano; **2000**, *J. Macromol. Sci. Phys. Ed., B39,* 425

[26] Corradini, P.; Natta, G.; Ganis, P.; Temussi, P.; *J. Polym. Sci.C,* **1967**, *16*, 2477.

[27] Natta, G.; Corradini, P.; Ganis, P.; *Makromol. Chem.* **1960**, *39*, 238.

[28] Rodriguez-Arnold, J.; Zhang, A.; Cheng, S.Z.D.; Lovinger, A.J.; *Polymer*, **1994**, 25, 1884.