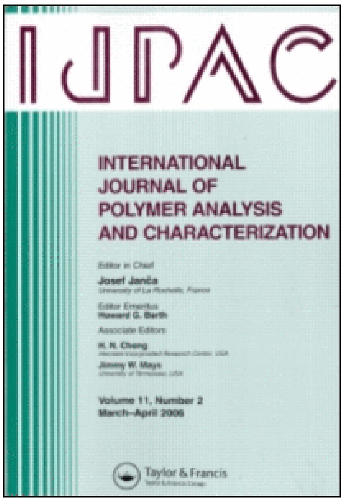

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Shear-Induced Crystallization of Syndiotactic Polypropylene

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Abstract: Syndiotactic polypropylene (PP) was synthesized using Ph_2 C(Flu)(Cp)$ZrCl_2$ catalyst in a homogeneous system and supported on silica/methylaluminoxane. With the aim of studying the crystalline and fracture morphologies, these polymers were hot pressed and cooled. The plaques were cryofractured and the fracture surfaces were investigated by scanning electron microscopy. Syndiotactic PP synthesized by the homogeneous catalyst showed a brittle deformation micro-mechanism in association with crazing/tearing, while results obtained with the supported catalyst showed brittle fracture accompanied by ductile pulling of fibrils. A highly oriented crystalline morphology, a shish-kebab structure, was observed only for the sPP obtained with the silica/MAO supported metallocene catalyst.

Keywords: Metallocene-supported catalyst; Syndiotactic polypropylene; Shish-kebab morphology

INTRODUCTION

Taking into consideration that almost a third of all polypropylene production is processed by injection molding,[1] great attention has been paid to the impact of this processing method on the crystallization

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conditions of this semicrystalline polymer. It is very important to mention that injection-molded parts are formed by a complex anisotropic morphology ranging from a highly oriented skin to a spherulitic central core.[2] As is well known, processing conditions greatly influence the crystalline morphology and ultimate properties of semicrystalline polymers. Moreover, it is necessary to consider the intensive shear and elongational flow fields that the polymer chains are subjected to in the molten state during processing operations such as fiber spinning, injection molding, and film blowing.

Semicrystalline polymers subjected to shear conditions in the molten state may crystallize in a very different morphology when compared with polymers crystallized under quiescent conditions. A highly oriented crystalline structure called shish-kebab morphology can be obtained in the first case.[3–9] This structure has been carefully investigated by rheo-SAXS (small-angle X-ray scattering) and rheo-WAXD (wide angle X-ray diffraction) techniques.[5] According to these studies, SAXS patterns showed strong meridional reflections due to the rapid development of oriented polymer structures within the melt. This result indicates that during the flow, orientation causes alignment of chain segments of the polymer molecules and results in the formation of primary nuclei in the flow direction. Furthermore, it was also observed that these nuclei induce a second crystallization, in other words, induce the growth of a large quantity of lamellae radially outward from the central core of the structure.[4–7]

Kalay and Bevis[3] observed that a controlled orientation of isotactic polypropylene (iPP) by shearing during injection molding resulted in a final product with a higher Young's modulus. This increase in the mechanical properties was attributed to the shish-kebab morphology developed by the shearing that the polymer was subjected to during solidification from the molten state. In addition, self-reinforced iPP sheets presenting higher values of melting temperature, tensile strength, and light transmittance were also obtained from continuous melt extrusion of polypropylene under controlled processing conditions.

Somani et al.[4] investigated by SAXS the influence of a shear strain of 1,428% at different shear rates (10, 57, and $102\,s^{-1}$) on Ziegler-Natta isotactic polypropylene (ZN-iPP), in the subcooled melt (140°C) under isothermal conditions, on the overall crystallization and on the crystalline morphology. The authors observed that the crystallization kinetics was found to increase by two orders of magnitude as compared to quiescent crystallization. According to this work, the major fact governing the overall dynamics in the polymer molecules at the melt state under shear is the influence of the relaxation behavior on polymer chains. The authors observed that the polymer molecules only above a critical orientation molecular weight (M^*) could become oriented at a given shear rate. Both a minimum strain and strain rate values have to be imposed at shear flow to induce crystallization. This is a prerequisite for a certain degree of molecular extension to be achieved in order to induce the formation of stable primary nuclei.

The development of shish-kebab morphology is also related to the processing temperature as well as to the weight-average molecular weight and molecular weight distribution (MWD).

In the present study, crystalline morphology and micro-mechanism of deformation of syndiotactic polypropylenes with different crystalline degrees synthesized through $Ph_2C(Flu)(Cp)ZrCl_2$ metallocene catalyst, in a homogeneous system and supported on silica/methylaluminoxane (MAO), were investigated by scanning electron microscopy (SEM).

EXPERIMENTAL SECTION

Chemicals

All operations were carried out in a dry nitrogen atmosphere. Propylene and nitrogen were purified by sequential passage through columns containing 4 Å molecular sieves and copper catalyst to remove oxygen, carbon dioxide, and moisture, respectively. Toluene was refluxed over metallic sodium/benzophenone and was distilled under a nitrogen atmosphere prior to use. Diphenylmethylene (fluorenyl, cyclopentadienyl) zirconocene ($Ph_2C(Flu)(Cp)ZrCl_2$) was obtained from Boulder Scientific Company; commercial silica gel (Grace Davison, Sylopol 948), with a surface area of 309 m^2/g, and methylaluminoxane (MAO 10 wt% solution in toluene) from Crompton GmbH (Germany), were used without further purification.

Catalyst Preparation

Homogeneous System

Homogeneous solution of $Ph_2C(Flu)(Cp)ZrCl_2$ in toluene was prepared, and 0.005 mmol Zr was directly employed in the propylene polymerization reaction.

Heterogeneous System

Silica Pretreatment with MAO. Silica gel was heated at the temperature of 400°C for 4 h under a nitrogen atmosphere. After calcination, silica was pretreated with MAO (5 mmol Al/g silica) at room temperature in toluene. The solid material was separated and washed three times with toluene at 90°C.

Immobilization of Metallocene Catalyst on Silica/MAO. $Ph_2C(Flu)(Cp)ZrCl_2$ solution in toluene reacted with MAO-pretreated silica (0.05 mmol Zr/g silica) in an Schlenk flask under vigorous stirring for 4 h. After the metallocene immobilization, the heterogeneous catalyst was washed by flotation three times with 30 mL of toluene at room temperature and dried until no weight loss was observed.

Propylene Polymerization

Polymerization reactions were performed in a 0.5 L doubled-walled round-bottom glass autoclave equipped with vacuum pump and thermostatic bath. The stirring speed was 600 rpm. At 0.2 bar flow of nitrogen, the diluent (toluene) was transferred into the reactor. After that, part of the MAO was introduced in the reactor and the other part was kept in contact with the catalyst suspension for the heterogeneous system (containing toluene and the supported catalyst) or solution (homogeneous system) for about 10 min. The nitrogen in the reactor was purged, and the toluene, at 20° or 40°C of polymerization temperature (Tp), was saturated with 2 bar of propylene monomer. For some reactions the monomer pressure was increased until 4 bar immediately after catalyst addition. Then the heterogeneous catalyst was introduced into the reactor, starting the polymerization. The polymerization was stopped after 1 h by stopping the stirring, degassing the reactor, and adding a solution of 5% acid chloridric in ethanol. The polymer was washed with ethanol and distilled water, filtered, and dried by vacuum at 60°C.

Polymer Characterization

The syndiotactic polypropylenes were characterized by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 Differential Calorimeter. Three runs (heating, cooling, and second heating) were performed at a heating rate of 10°C/min in the temperature range of 40°–190°C. The second-heating melting peak temperature was taken as the melting point. The crystallinity degree (%) was calculated using the melting enthalpy $\Delta H_m^{100\%}(sPP) = 166$ J/g.[10]

Sample Preparation

The syndiotactic polypropylene samples were prepared by compression molding at 135°C and 15,000 Kgf/cm^2, followed by cooling to room temperature by running water under pressure (15,000 Kgf/cm^2). Then, the samples were cryofractured and one of the surfaces was treated with concentrated H_2SO_4 solution containing $KMnO_4$ (1%). After the etching the surface was washed with H_2SO_4/water solution (10%), distilled water, and ketone. After the washing procedure, the sample was kept at room temperature in order to dry.

A scanning electron microscope (JEOL JSM, model 5610LV) was employed in order to study both the etched and not-etched fracture surfaces. The crystalline morphologies and the micro-mechanism of deformation were investigated. Multiple images were taken at different locations of the fracture surfaces to ensure that the results are indeed typical of the samples. This procedure was carried out in order to confirm that the images are a true representative of the topography of the surface and are not characteristics of artifacts.

RESULTS AND DISCUSSION

Table I shows the results of propylene polymerization using the metallocene catalyst $Ph_2C(Flu)(Cp)ZrCl_2$ in homogeneous and in heterogeneous systems and the characteristics of the obtained sPP. It can be observed that the activity for the supported catalyst was around the half of the activity obtained with the homogeneous system at polymerization temperatures (Tp) between 40° and 80°C. It was also noticed that only the syndiotactic polypropylene synthesized with the homogeneous metallocene at 20°C presented crystallinity by DSC analysis. In addition, by

Table I. Propylene polymerization with the syndiospecific catalyst (homogeneous and heterogeneous systems)

Condition	Homogeneous catalyst				Supported catalyst			
$T_{polym.}$ (°C)	Yield (g)	A^a	$T_m{}^b$ (°C)	$X_c{}^c$ (%)	Yield (g)	A^a	$T_m{}^b$ (°C)	$X_c{}^c$ (%)
20	82.25	53.4	135	5	9.12	5.9	141	24
40	60.37	67.4	—[d]	—	27.81	31.1	120/132	17
60	76.72	133.7	—	—	45.74	79.7	118	12
80	92.49	239.0	—	—	40.14	103.7	86/93	10
90	99.94	314.0	—	—	31.05	97.4	—	—

100 mL of toluene; 0,005 mmol of homogeneous $Ph_2C(Flu)(Cp)ZrCl_2$ catalyst; 0,1 g of heterogeneous catalyst; 5,8mL of MAO 10% p/v.

[a] Catalytic activity: Kg PP/mmolZr mol Ph.

[b] Melting temperature.

[c] Crystallinity degree considering$H_m^{100\%}$(sPP) = 166 J/g.[10]

[d] Amorphous PP.

supporting this syndiospecific catalyst on silica/MAO and using higher polymerization temperatures (40°–80°C), it was possible to obtain crystalline PP. This clearly shows that the metallocene has its stereospecificity increased when fixed on silica support.

Figure 1 shows the SEM micrographs of different regions of the not-etched and etched fracture surfaces of the syndiotactic polypropylene synthesized with the homogeneous catalyst at 20°C of Tp.

According to the micrographs shown in Figures 1(a) and 1(b), it can be seen that the deformation micro-mechanism was brittle in association with crazing/tearing. The micrographs of Figures 1(c) and 1(d) show that different crystalline structures were formed. Spherulitic morphologies are clearly seen in these micrographs. Furthermore, it can be seen that crystalline structures oriented in a specific direction were also developed, as pointed out by the arrow on Figure 1(d). These micrographs suggest that the highly oriented supermolecular morphology might be the shish-kebab

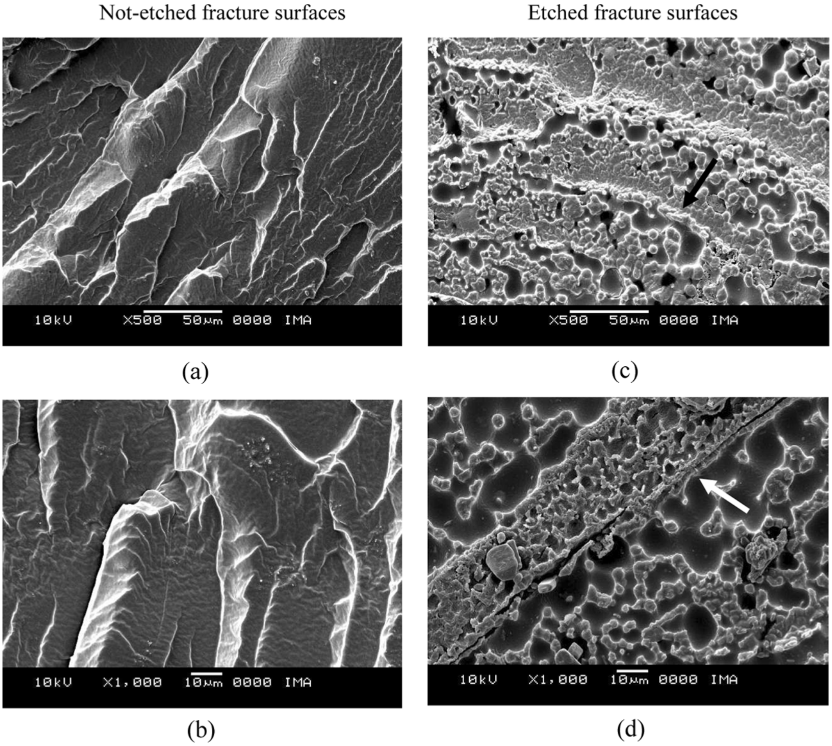


Figure 1. SEM micrographs of different regions of the not-etched ((a), (b)) and etched ((c), (d)) fracture surfaces of the syndiotactic polypropylene synthesized with the homogeneous catalyst at 2°C of Tp ($X_c = 5\%$).

structure once neither a nucleant agent nor a fiber was used in order to induce some orientation. This phenomenon is possible once the sample was subjected to successive shear fields during the initial steps of the compression molding.

Figure 2 shows the SEM micrographs of different regions of the not-etched and etched fracture surfaces of the syndiotactic polypropylene synthesized with the homogeneous catalyst at 40°C of Tp.

In the micrographs shown in Figures 2(a) and 2(b), it can be seen that the fracture morphology of the sample was brittle with crazing-tearing, opposite to the fracture morphology of polypropylene synthesized with the homogeneous catalyst at 20°C of Tp. Despite the lack of crystallinity obtained in DSC analysis of this polymer, micrographs of Figures 2(c) and 2(d) show that the sPP crystallized in a different morphology than the one obtained with the homogeneous catalyst at 20°C of Tp. This might be due to the different molecular characteristics of the polymer such as molecular weight and stereoregularity.

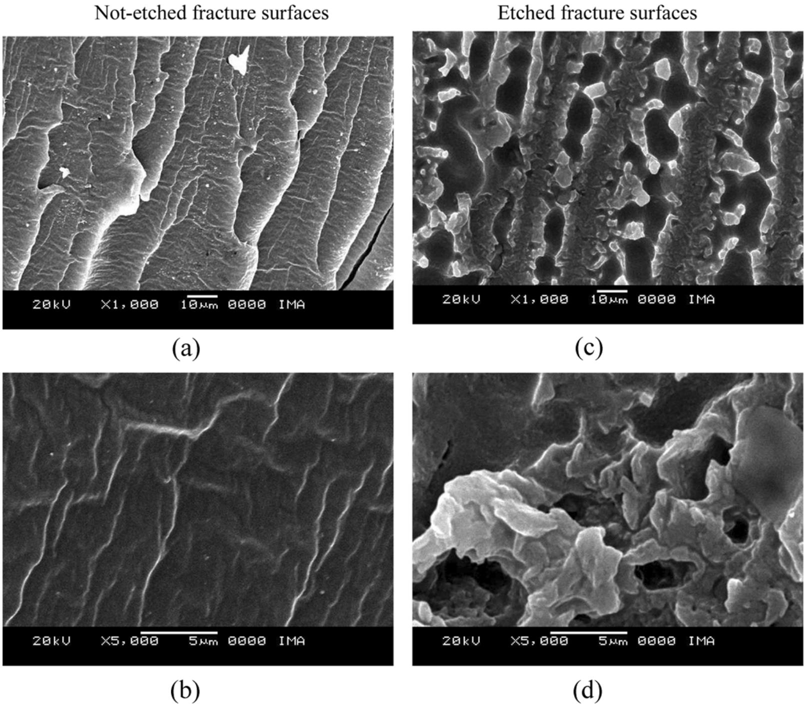


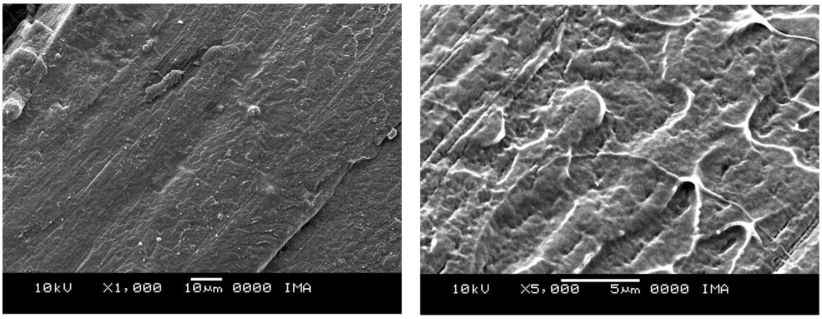
Figure 2. SEM micrographs of different regions of the not-etched ((a), (b)) and etched ((c), (d)) fracture surfaces of the syndiotactic polypropylene, synthesized with the homogeneous catalyst at 40°C of Tp.

Figure 3 shows the SEM micrographs of different regions of the not-etched fracture surfaces of the syndiotactic polypropylene synthesized with the silica/MAO supported catalyst at 40°C of Tp. The micrographs show that the sPP obtained with the syndioespecific metallocene catalyst supported on silica/MAO presented brittle fracture morphology together with ductile pulling of fibrils.

Figure 4 shows the SEM micrographs of different regions of the etched fracture surface of the syndiotactic polypropylene synthesized with the silica/MAO supported catalyst at 40°C of Tp.

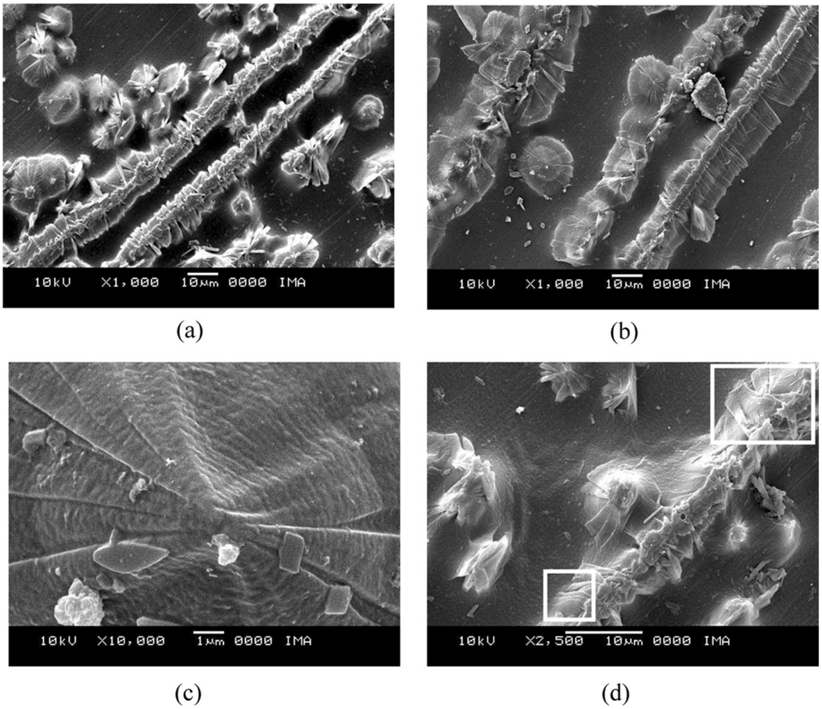
According to the micrographs in Figures 4(a) and 4(b), it can be seen that the sPP crystallized in both the spherulitic morphology and in a highly oriented cylindrical supermolecular structure, unlike the shish-kebabmorphology mentioned in the literature for ZN-iPP.[3,4] It can also be observed that the morphology is very different from that observed for the sPP obtained with the homogeneous catalyst. This difference might be related to the fact that the sPP obtained with the homogeneous catalyst did not present any crystallinity, according to the DSC analysis.

It is interesting to mention that, in spite of the low crystallinity ($X_c = 17\%$) of the sPP obtained with the heterogeneous catalyst, it was possible to observe the development of shish-kebab structures. This phenomenon can be attributed to the presence of chains with molecular weight sufficiently high to contribute to the formation of stable row nuclei (shishmorphology), because of the heterogeneization of the metallocene catalyst. However, it is very important to consider that the compression molding conditions such as shear strain and shear rate manually employed also contributed to the development of this crystalline structure.



(a) (b)

Figure 3. SEM micrographs of different regions of the not-etched fracture surfaces of syndiotactic polypropylene synthesized with silica/MAO-supported catalyst at 40°C of Tp ($X_c = 17\%$).



(a) (b)

(c) (d)

Figure 4. SEM micrographs of different regions of the etched fracture surfaces of syndiotactic polypropylene synthesized with silica/MAO-supported catalyst at 40°C of Tp (X_c = 17%).

The micrograph illustrated in Figure 4(c) shows that the sPP presented a crystalline morphology very similar to the ring-type spherulite.[11] The ring spherulites are composed of lamellar crystals that change orientation continuously in the radial direction. Furthermore, lamellar morphologies in different views edge-on (smaller box) and flat-on (larger box) can clearly be seen in the micrograph shown in Figure 4(d).

CONCLUSIONS

SEM micrographs of the syndiotactic polypropylene synthesized with the $Ph_2C(Flu)(Cp)ZrCl_2$ metallocene catalyst in homogeneous system, at 20°C of Tp, and in silica/MAO supported system, at 40°C of Tp, showed that these polymers crystallized both in a spherulitic morphology and also in a highly oriented crystalline structure called shish-kebab morphology.

Furthermore, fracture morphologies typical of semicrystalline polymers, such as brittle fracture with crazing/tearing and brittle fracture with ductile pulling of fibrils, were observed for the sPP obtained with the homogeneous and supported metallocene catalysts, respectively. The SEM micrographs also showed that ring-type spherulites were observed for the sPP obtained with the supported catalyst.

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