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Fracture toughness of controlled-rheology polypropylenes

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Abstract: The rheological, thermal, tensile and fracture properties of controlled-rheology polypropylene processed via organic peroxides have been evaluated. Different concentrations of di-tert-butylperoxide (DTBP) were used in this work. Both melt flow index and the crystallinity index increased slightly with the peroxide content while the melting temperature tend to decrease. This was attributed to the decrease in the molecular weight which mainly affects the amorphous region, especially the entanglement density of this semycrystalline polymer. As a consequence, the tensile stress and strain at break reduced as the peroxide content increased. The elastic-plastic response of the different polypropylenes at room temperature promotes the use of J-integral to determine the fracture toughness. A multiple specimens method was utilized. The crack initiation resistance and the crack propagation resistance were influenced by the molecular weight, decreasing as the peroxide content increased. The micromechanisms of failure were analyzed via scanning electron microscopy.

Introduction

Polypropylene (PP) is one of the most important commercial plastics due to its versatile properties such as its economy, low density, good thermal stability, mechanical properties, chemical and wear resistance, excellent humidity resistance, easily processing by wide techniques and environmentally friendly nature [1-2]. This is the primary reason of its popularity as a commodity in the food, automobile, furniture and toy industries.

Commercial PP produced in conventional reactors by Ziegler-Natta catalyst systems presents relatively high molecular weight (MW) and broad molecular weight distribution (MWD). These features cause high melt viscosity and elasticity which make them unsuitable for many commercial end-uses such as fiber spinning, blown film, extruded and injection moulding. In order to improve the polypropylene response during processing and to achieve specific grades, a post-reactor procedure that consists of degradation with organic peroxides is used to adjust and control the MW and MWD. Peroxide initiated scission reactions efficiently result in polymers with tailor made properties. The polypropylenes produced this way are termed “controlled-rheology polypropylenes” (CRPP) and they have improved melt flow characteristics due to reduced MW and narrowing MWD [3-9].

Reactor-made PP is a semicrystalline polymer which has been extensively investigated. The mechanical and fracture response of PP produced via catalysers is strongly influenced by the microstructure, especially the crystalline morphology [10-

19]. The ultimate properties of these polymers depend principally on the degree of crystallinity, the size and shape of spherulites, the lamellar thickness and the crystalline orientation. Crazing is the main micromechanism of deformation responsible of the failure of PP and the craze structure and extension are closely related to the molecular weight. Ibhadon [14] and Avella et al. [18] evaluated the impact fracture toughness of a set of reactor-made PP with different molecular characteristics meanwhile Sugimoto et al. [13] measured the quasi-static fracture toughness. In these studies, linear elastic fracture mechanics, (LEFM), with some modification was used to determine the fracture resistance of these polymeric systems. The results obtained showed a decrease of the fracture strength with the reduction on the molecular weight. Then, the crack initiation and growth, as well as the breakdown, are controlled by the amorphous interconnections among the spherulites; entanglement density improves as the molecular weight increases [13-14, 16-18].

While the different parameters that control the mechanical and fracture response of reactor-made PP are well established, there is little information on the fracture behaviour of peroxide degraded PP. Azizi et al. [9] measured the impact strength of controlled rheology PP using dicumyl peroxide (DCP). The results revealed the same tendency as in the case of reactor-made PP with different molecular mass; the impact strength reduces as the molecular weight decreases as a result of the addition of peroxide content.

Depending on the stress-strain relationship, the fracture mechanics parameters can be described on the basis of the linear elastic fracture mechanics (LEFM) or elastic-plastic fracture mechanics (EPFM). At room temperature and under low loading rates, PP presents a pronounced non linear elastic behaviour and an energy method as the J-integral is recommended to achieve the fracture toughness, J_C, in these materials.

In this study, the effect of peroxide content on rheological, thermal, tensile and fracture properties at room temperature of CRPP has been evaluated. The fracture toughness of a set of materials was determined through the J-integral method. The mechanical characterization was completed with a detailed analysis of the fracture micromechanisms in the scanning electron microscope. The effect of peroxide content and crystalline morphology on the toughness was discussed in the light of the test results and the fractographic information.

Results and discussion

Rheological properties

Table 1 presents the MFI and the GPC results for the polypropylene with 0, 154, 402 and 546 ppm of peroxide content termed as PP0, RCPP154, RCPP402 and RCPP546, respectively. Several conclusions can be drawn from the analysis of these data. First of all, rheology controlled polypropylene drops more abruptly the weight average molecular weight, M_W, than the number average molecular weight, M_n. As a consequence, the MWD described by the ratio M_W/M_n gets narrower [20]. This is represented in Fig. 1. Secondly, the main differences in M_W are found for a small concentration of peroxide, RCPP154, while there are non pronounced changes among the rheology controlled polypropylenes. Thirdly, MFI increases with the peroxide concentration. All these results confirm that increasing the amount of peroxide content drives more chain scission and therefore, reduces efficiently the length of the chains.

Tab. 1. Melt flow index (MFI) and molecular characterization data obtained from gel permeation chromatography (GPC) for polypropylene PP0, RCPP154, RCPP402 and RCPP546.

	PP0	RCPP154	RCPP402	RCPP546
MFI (g/10min)	11	26	48	59
M_n	51740	49510	45580	44050
M_W)	319060	238590	179410	172050
MWD	6.16	4.81	3.93	3.90

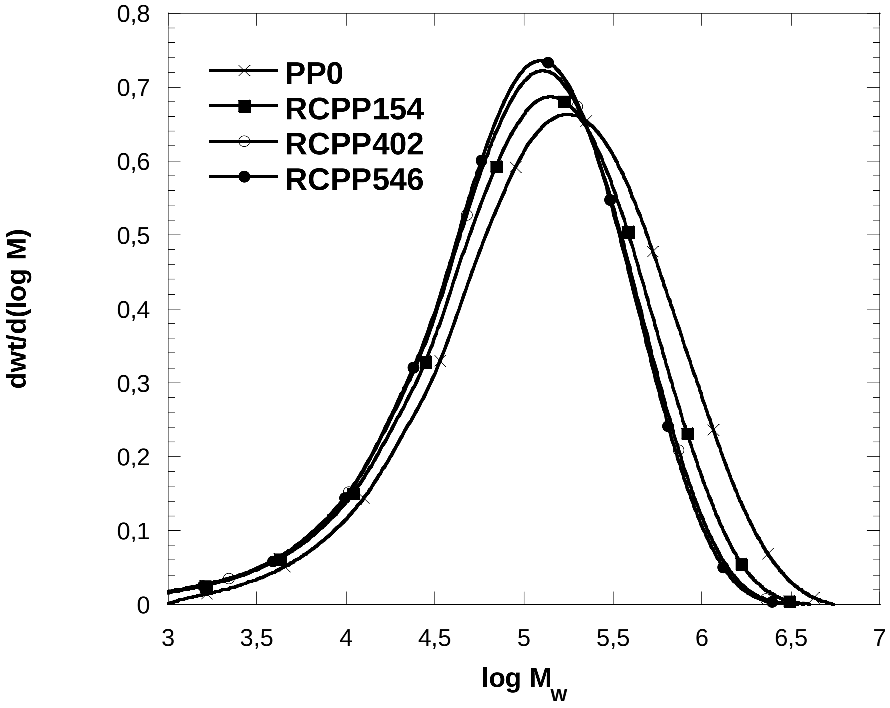

Fig. 1. Effect of peroxide content on the molecular weight distribution for polypropylene PP0 ×, RCPP154 ■, RCPP402 ○ and RCPP546 ●.

Thermal properties

Table 2 reports the apparent melting temperature, T_m, the crystallinity temperature, T_C, the apparent enthalpy, ΔH, and the crystallinity index, α, obtained by DSC and the crystallinity index, χ_c, obtained by X ray diffraction (XRD) for polypropylenes PP0, RCPP154, RCPP402 and RCPP546. All the values measured are in accordance with data reported in the literature [1-2]. T_m decreased with the peroxide content while T_c and α remained constant. The crystallinity index obtained by XRD, χ_c, was similar to that measured via DSC but the values seem to go up with the addition of a small amount of peroxide but are not affected by the increase in peroxide content. This is in accordance with the small differences in M_W as the peroxide content increases (Table 1). The decrease in T_m and the slight increase in χ_c with the reduction in M_W indicate that the entanglement density of the amorphous zone decreases. The principal reason is that the presence of a huge number of tie molecules can inhibit the internal rearrangement of the chains in a crystalline array.

Tab. 2. Thermal parameters obtained from DSC and XRD measurements.

	DSC				XRD
	T_m (ºC)	T_C (ºC)	ΔH (J/g)	α (%)	χ_c (%)
PP0	165	118	-112	56	54
RCPP154	163	118	-104	55	57
RCPP402	161	118	-104	55	56
RCPP546	161	118	-104	55	57

XRD patterns of PP0 and RCPP154 are shown in Fig. 2. Both patterns present peaks associated to monoclinic α-form of isotactic PP (iPP) (a=0.666 nm, b=2.078 nm, c=0.6495 nm, α=γ=90º and β=99.6º).

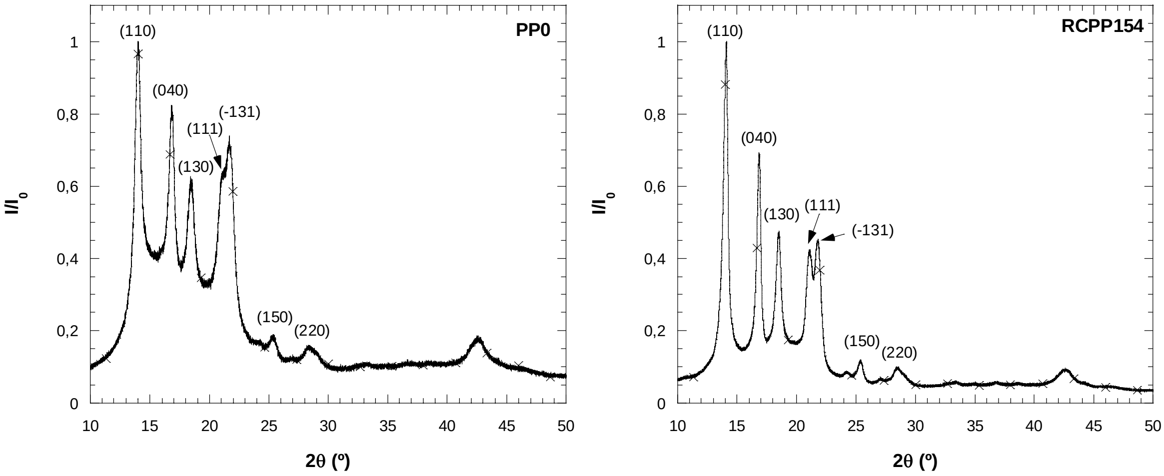

Fig. 2. XRD patterns of PP0 and RCPP154.

Tensile properties

The average yield strength, the tensile stress and strain at break of PP0, CRPP154, CRPP402 and CRPP546, together with their corresponding standard errors, is presented in Table 3. Attending to these results, the yield strength shows a light decrease with a small addition of peroxide but seems not to be influenced by the amount included. On the contrary, the stress and strain at break present a significant change with the peroxide content. Both magnitudes tend to diminish as the amount of peroxide increases. The strain at break of CRPP154 diverts from this tendency and the measurements obtained are incoherent. The values and the changes in the mechanical properties with the molecular weight are in accordance with those reported by Dasari et al. [10-11], Sugimoto et al. [13] and Ogawa [16]. The reduction in the molecular weight with the peroxide content involves changes in the amorphous part and the results obtained for the tensile stress at break and the strain at break are predominantly governed by this amorphous region.

Tab. 3. Tensile properties of polypropylene PP0, RCPP154, RCPP402 and RCPP546.

	Yield strength (MPa)	Stress at break (MPa)	Strain at break (%)
PP0	33.9 ± 0.3	20.4 ± 0.3	145 ± 50
CRPP154	31.5 ± 0.4	19.0 ± 0.5	320 ± 110
CRPP402	31.9 ± 0.3	17.5 ± 0.9	90 ± 60
CRPP546	31.1 ± 0.4	16 ± 2	44 ± 12

Fracture toughness

Fig. 3 shows the records of the load-load-line displacement curves associated with the single edge notch bending (SENB) specimens of PP070, CRPP154, CRPP402 and CRPP546. All the materials present elastic-plastic behaviour and this justifies the use of J-method to evaluate the fracture toughness. The curves were deviated from linearity and at a certain deflection level, sudden instability occurred and the specimen broke in two halves. The difference in stiffness is due to the different length of the initial cracks.

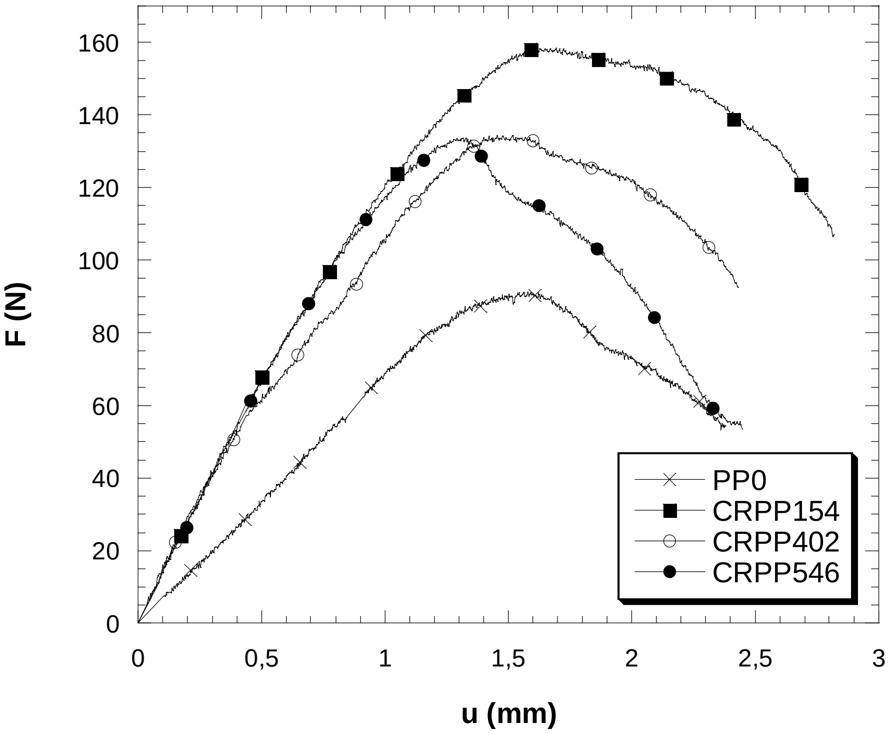

Fig. 3. Load (F)-load-line displacement (u) curves of PP0, RCPP154, RCPP402 and RCPP546.

Fig. 4 shows the R-curve in the form of J integral values versus stable crack growth, Δa, of PP0, CRPP154, CRPP402 and CRPP546. The analysis of the curves reveals that the reactor-made polypropylene is the toughest material and the increase of peroxide content acts in detriment of the toughness.

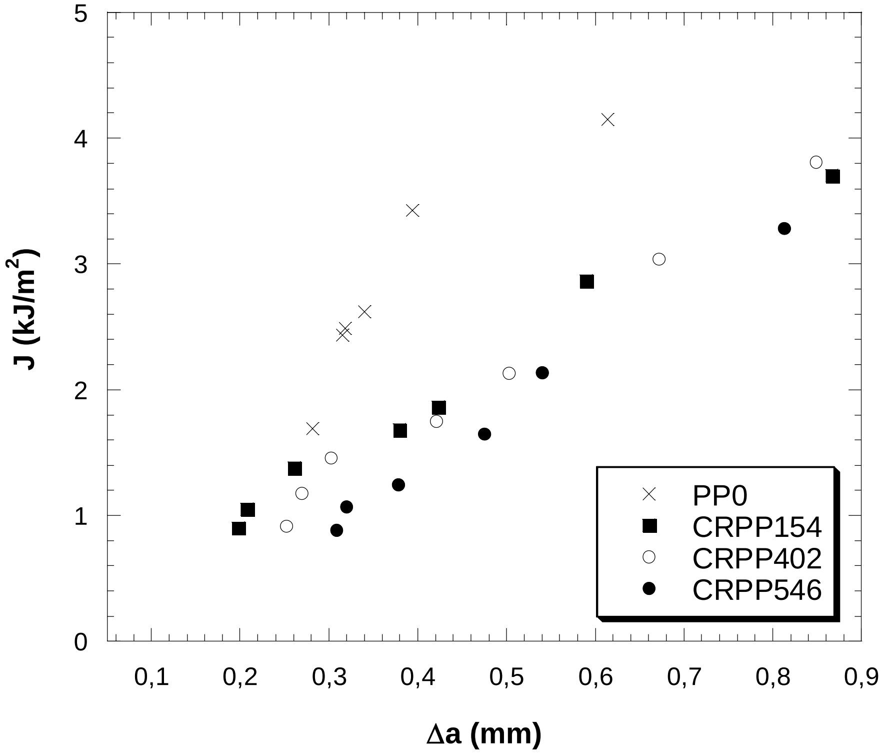

Fig. 4. J-R curve of PP0 ×, RCPP154 ■, RCPP402 ○ and RCPP546 ●.

This is indicated more clearly in Fig. 5. The crack initiation resistance, $J_{0.2}$, is reduced with the peroxide content (Fig. 5a) while the tearing modulus, T_J, drops abruptly with a small addition of peroxide and seems to be independent of the amount of peroxide included in the polypropylene (Fig. 5b).

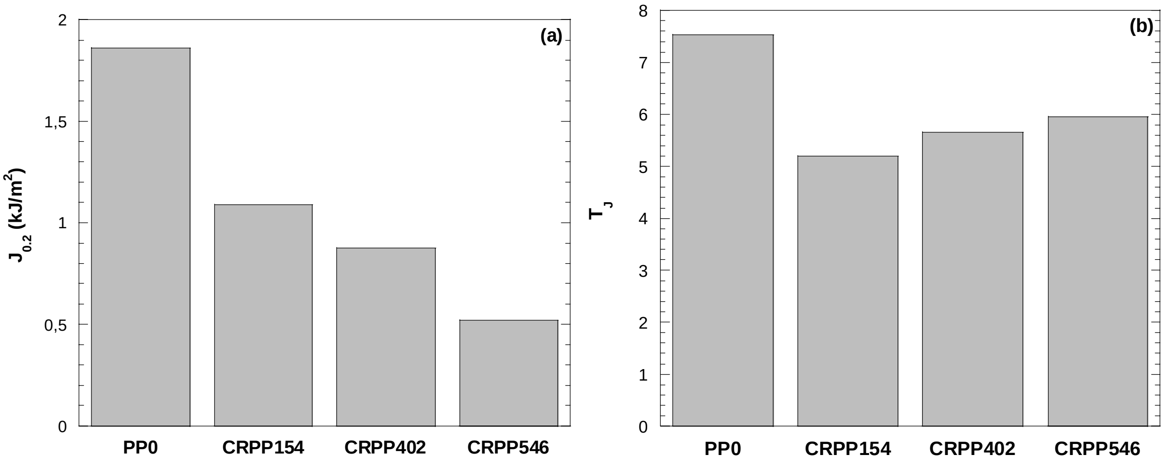

Fig. 5. (a) Crack initiation resistance, $J_{0.2}$, (b) Tearing modulus, T_J.

Independently of the material, the fractographic study of the fracture surfaces related to Fig. 3 also exhibited two distinguishable zones (Fig. 6). The one close to the notch is attributed to the stable crack propagation or subcritical crack growth. It was characterized by stress whitened and relatively smooth surface and was of about 2.5 mm in length. The remainder of the fracture surface was rough, un-whitened and uniform, reflecting unstable crack propagation of the specimens tested up to fracture (Fig. 7).

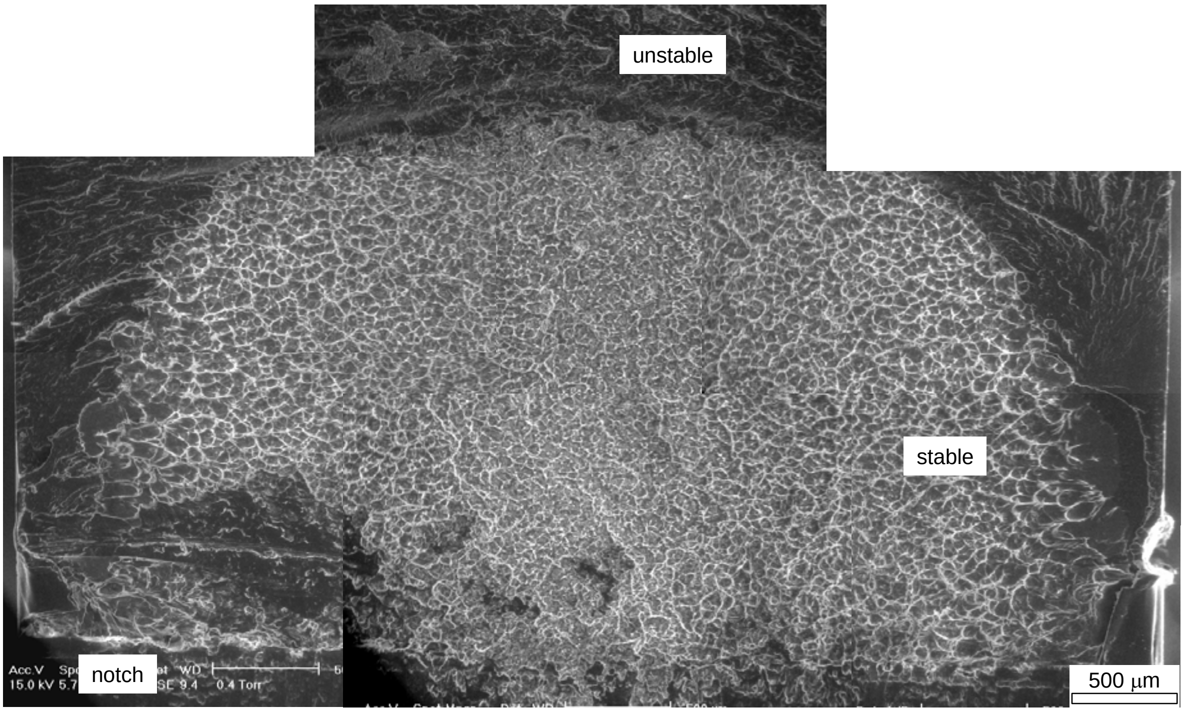

Fig. 6. Panoramic view of fracture surface of PP0 homopolymer close to the notch, detailing the different regions found in all the materials.

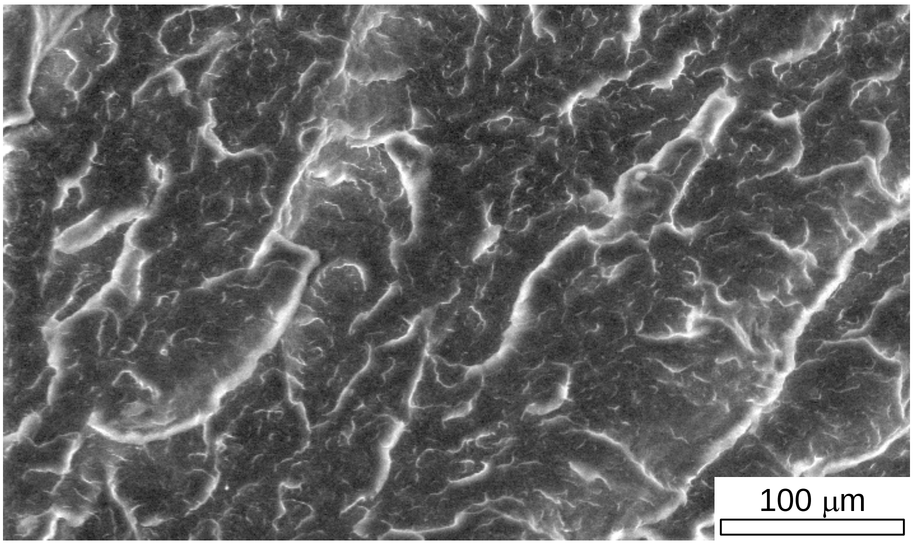

Fig. 7. Fractography of PP0 homopolymer showing details of the unstable crack propagation region.

A wedge effect could be also observed due to the presence of a skin (Fig. 6). Despite the different rheological properties of the 4 materials, no evident differences were found in the fractographic analysis as it is depicted in Fig. 8. A high magnification study of the crack stable region displayed spherulites interconnected by amorphous regions (Fig. 8). The spherulites consisted of an aggregate of lamellae that radiate from the centre outward, which is in accordance with the α-form PP (Fig. 2) [1-2, 12]. The size ranged from 30 to 70 μm. The morphology depicted indicates that crazing is the predominant micromechanism of strain. The spherulites are held together by tie molecules forming the amorphous region and can be easily separated from one another upon loading. This separation generates microvoids (stress-whitening) and this microporous structure is identified as crazes. With increasing loading, this craze area spreads out and propagates within the spherulitic and amorphous regions. When they fail, the cracks are formed [10-11, 14-15].

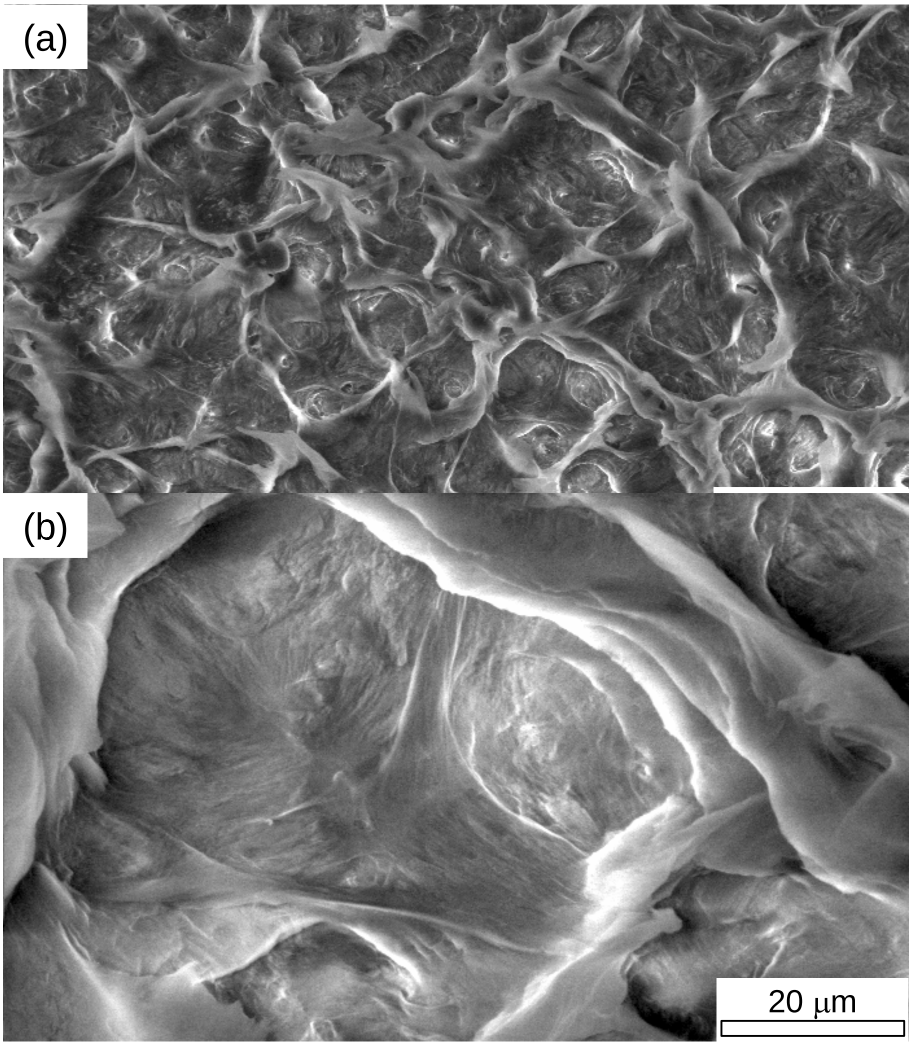

Fig. 8. (a) Stable crack propagation zone close to the notch of RCPP402. (b) Detail at a higher magnification showing a spherulite surrounded by amorphous region.

The results state that the fracture parameters are also dependent on the molecular weight, especially the crack initiation resistance seems to be more sensitive. These results are in accordance with those presented by Fukuhara [19]. The higher the molecular weight, the higher are the crack initiation resistance and the tearing modulus. More energy is necessary to form and propagate the crack through the crazing mechanism as the entanglement density increases with the molecular weight. Sugimoto et al. [13] pointed out that the increase of the fracture toughness with the molecular weight is related to the strength improvement of the craze before collapsing and forming a crack while Avella et al. [18] suggested that the formation of crazing, intimately related to the improvement in toughness, depended strongly on the molecular weight.

Conclusions

The influence of molecular weight on the rheological, thermal tensile and fracture properties of a set of rheology-controlled polypropylenes was investigated. The peroxide used was di-tert- butylperoxide (DTBP) and concentrations of 0, 154, 402 and 546 ppm were evaluated.

The peroxide content modified drastically the rheological properties of the PP, by reduction of the weight average molecular weight and narrowing the molecular weight distribution. This drop was primarily abrupt with small additions of peroxide content. As a consequence, the melt index increased and this was attributed to the efficiency of the process in promoting chain scissions.

The decrease in the molecular weight also tended to increase slightly the crystallinity of the polymer, especially when the amount of peroxide included was small. This indicates that the change in molecular weight mainly affects the entanglement density of the amorphous zone. The decrease in the molecular weight reduces the number of tie molecules and favours the crystalline arrangement.

The tensile properties, especially the stress and strain at break, are dependant on the molecular weight. The higher the peroxide content, the lower these magnitudes are. As the increase in peroxide content entails a decrease in the molecular weight which preferentially affects the amorphous region, this implies that the tensile properties are predominantly governed by the amorphous part.

The elastic-plastic behaviour of the different sets of polypropylenes at room temperature implied the use of J-integral to evaluate the fracture toughness. A multiple specimen method was employed. The crack initiation resistance and the crack propagation resistance increased with the molecular weight. The reactor-made polypropylene was the toughest of all the materials studied.

The micromechanism of failure of all the materials was crazing and no differences were found in the fracture surfaces among the different grades of polypropylene. All these results point to the influence of molecular weight which is related to the amorphous region. The increase of the entanglement density of the amorphous interconnections with reduction in peroxide content is directly associated to the improvement in the fracture behaviour.

Experimental part

Materials

The polypropylene was an ISPLEN homopolymer with high isotacticity (~90%) supplied by REPSOL-YPF. It was manufactured using a Spheripol process with a fourth generation Ziegler-Natta catalyst. The peroxide used was di-tert-butylperoxide (DTBP).

Sample preparation

The reactive experiments and sample preparation were carried out in the Technologic Centre REPSOL-YPF using a twin-screw extruder, Werner & Plfeiderer (model ZSK-30), with a length/diameter ratio of the dies, L/D, of 25. The peroxide and the PP were premixed to prepare a masterbatch using 0, 154, 402 and 546 ppm of peroxide content. Experiments were performed at profile temperatures of 190, 220, 240, 220, 200 ºC and at 150 rpm of screw rotation speed. Extrudates were cooled through a water bath and were granulated. Samples for mechanical and fracture properties were injection moulded.

Rheological measurements

Melt flow index (MFI) was measured following the ISO1133 standard using a Ceast 6932 extrusion plastometer at 230ºC/2.16 kg.

The molecular weight distributions are analyzed by Gel Permeation Chromatography (GPC) using Polymer Labs PL220 equipment. The samples are dissolved at 143 ºC in trichlorobenzene at a polymer concentration of 1.3 mg/ml. A phenolic antioxidant Irganox 1010 was added to the solution to prevent any degradation.

Thermal measurements

X ray diffraction (XRD) analysis was performed in a Philips PW3040/00 X´Pert MPD/MRD diffractometer using Cu-K_α. The minimum and maximum Bragg angles were 5º and 45º, respectively, with a $2\theta=0.004^o$ step. This technique was not only used to detect the different crystalline phases present in the materials, with the help of PDF software from the International centre for diffraction data, but also to determine the crystallinity index from the pattern using the following expression:

$$\chi_C = \frac{S_C}{S_C + S_a} \qquad (1)$$

where S_C is the total area associated to the crystalline peaks and S_a is the area of the amorphous halo.

The apparent melting temperature, T_m, the crystallinity temperature, T_C, and the crystallinity index, α, of all the samples were measured via differencial scanning calorimetry (DSC) using a Mettler-Toledo (model DSC822) equipment. Two scans were done at 10 ºC / min, from 0 to 200 ºC under nitrogen atmosphere, in aluminum pans with 10 mg of sample. The values of T_c were obtained from the maxima of the crystalline peaks meanwhile the values of T_m and the apparent enthalypy, ΔH, were calculated from the maxima and the area of the melting peaks, respectively. The crystallinity index via this technique was determined by:

$$\alpha = \frac{\Delta H}{\Delta H^0} \qquad (2)$$

where ΔH^0 is the heat of fusion per g of 100% crystalline α-PP taken as 190 J/g [1].

Tensile tests

The tensile tests were carried out, following the ISO527 standard, in order to measure the yield strength, the stress at break and the strain at break. Specimens with 10x115x4 mm in the narrow section were tested on an electromechanical testing machine (MTS Alliance RT/5), under displacement control at a cross-head speed of 50 mm/min. The strain was measured during the tests with a high strain extensometer attached to the sample (model MTS DX2000).

Fracture toughness

Fracture toughness tests were carried out on single edge notch bending (SENB) specimens obtained directly from the mould with 6x18x79 mm in size and an initial notch length of 8.1 mm. At the centre of the notch, a razor blade was inserted to create a sharp crack by tapping into the material. The resulting notch was ~ 9.0 mm in depth.

The tests were performed following the guidelines described by ESIS TC4 Protocol for the determination of J-fracture toughness of polymers at slow speed [21], and conducted on an electromechanical testing machine (MTS Alliance RF/100). All the materials were tested at room temperature and under displacement control at a cross-head speed of 1 mm/min using a three-point bend fixture of 72 mm loading span. The displacement at the centre of the sample was measured with a LVDT (linear variable displacement transducer) of ± 5 mm.

This method achieves the J-R curve of the polymers from multiple specimens. A set of nominally identical specimens is loaded to get different amounts of stable crack growth, Δa. For each specimen, J is calculated from the total energy required to extend de crack, U, which is determined from the area under the load versus load-point displacement curve, with the following expression:

$$J = \frac{2U}{B(W-a)} \tag{3}$$

where B is the thickness, W is the width and a is the crack length. The crack extension, Δa, is measured optically from the fracture surfaces. The specimens are cooled in liquid nitrogen and then broken by a high impact loading test.

Seven specimens were loaded to different crack extension lengths to characterize the J-R curve in the form of J versus Δa of each material. All these tests fulfilled the plain strain condition given by:

$$B = 25\frac{J}{\sigma_Y} \tag{4}$$

where σ_Y is the yield strength obtained from tensile tests.

The crack initiation resistance, J_C, is a difficult parameter to determine when blunting and notch deformation by yielding occur. That is the reason why J_C is defined as the value of J when the crack length is 0.2 mm of the total crack growth, $J_{0.2}$. Then, the initiation is calculated as the interception of the J-R curve with the blunting line at an offset of 0.2 mm defined as:

$$J = 2\sigma_Y(\Delta a - 0.2) \tag{5}$$

From the J-R curve, the tearing modulus, T_J, can also be obtained by the equation:

$$T_J = \frac{E}{\sigma_Y^2}\left(\frac{dJ}{d\Delta a}\right) \tag{6}$$

where E is the Young´s modulus.

After the fracture tests, the fracture surfaces of the broken specimens were examined by environmental scanning electron microscope, ESEM (Philips XL30), to determine the micromechanisms of failure.

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