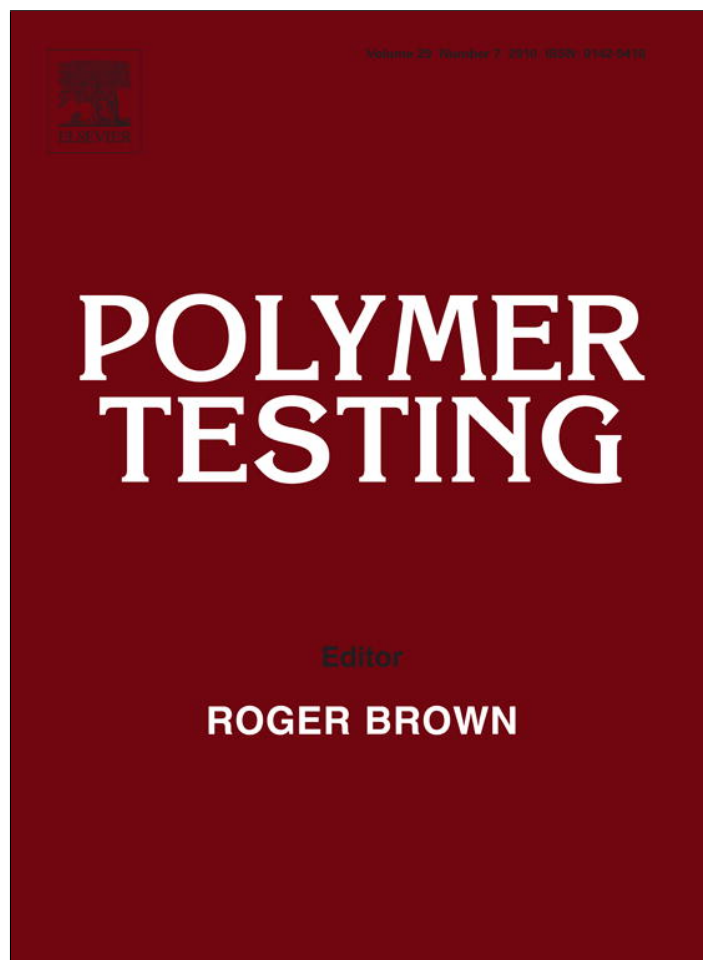


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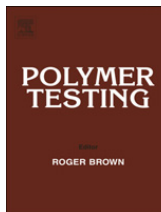


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Test Method

The role of notching damage on the fracture parameters of ethylene-propylene block copolymers

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ABSTRACT

The influence of the notching procedure on the fracture toughness measured via Elastic-Plastic Fracture Mechanics has been analyzed on four different ethylene-propylene block copolymers with two distinct dimensions, paying special attention to the morphology of the area surrounding the crack tip front. Two sharpening techniques were evaluated: the traditional steel razor blade and the femtolasers ablation process. The fracture toughness of the razor blade sharpened samples was always higher than that of the femtolasers sharpened specimens. Also, the fracture toughness of the razor blade samples was dependent on the thickness of the samples, whereas the fracture toughness of the femtolasers sharpened specimens was not influenced by the dimensions of the test specimens. The microscopic analysis of non-tested samples showed that the crack tip radii were similar for both type of sharpened samples but the damage and its extension ahead of the crack tip was dependent on the notching technique, the copolymer type and the dimensions of the analyzed specimen. The femtolasers sharpened samples presented a very tiny heat affected zone ahead of the crack tip, the size of which was independent of the copolymer type and the dimensions of the test specimen. On the other hand, the steel razor blade sharpened samples showed an area surrounding the crack tip formed by plastic deformation, the length of which increased for the smaller size of sample and for higher ethylene content in the copolymer.

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1. Introduction

Recently, some works have appeared in the literature reporting the relevance of the notch sharpening technique when evaluating the fracture toughness of polymeric materials [1–4]. It is a well-known fact that the quality of the notch is of deciding importance to determine well established fracture toughness values using Linear Elastic Fracture Mechanics (LEFM), J - R resistance curves using Elastic-Plastic Fracture Mechanics (EPFM) or Essential Work of Fracture (EWF) parameters using Post Yielding

Fracture Mechanics (PYFM). Therefore, the notch sharpening procedure is crucial and tackled by both ESIS (European Structural Integrity Society) [5–7] and ASTM International (Previously American Society for Testing and Materials) [8–10].

Martínez et al. [1,2] and Salazar et al. [3,4] have focused their research on the influence of the notch sharpening technique on the fracture parameters determined under LEFM [3,4], EPFM [3,4] and PYFM [1,2,4] conditions. The polymeric material utilized for their investigation was an ethylene-propylene block copolymer. The sharpening procedure was performed using steel razor blades and a femtosecond pulsed laser. The femtosecond pulsed laser ablation is characterized by very rapid creation of vapor

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and plasma phases, negligible heat conduction and the absence of a liquid phase [11,12]. Hence, this technique can remove the material of the notch tip by ablating it with almost no heat dissipation, preventing melting and thermal deformation of the surrounding area. These works proved that, independently of the fracture mechanics conditions, the fracture toughness of the specimens sharpened through femtosecond laser ablation showed lower values compared to those obtained on the samples sharpened using a steel razor blade. These differences could range from ~10% up to 90% under LEFM and PYFM conditions, respectively. The damage produced ahead of the crack tip through plastic deformation in the steel razor blade sharpened samples seemed to be the reason of this increase in the fracture toughness.

To date, the reports found in the literature concerning the influence of the notch sharpening technique on the fracture parameters have been focused on the experimental notching procedure, regardless of the type of polymeric material. Also, they do not quantify the damage facing the crack front. For these reasons, the objective of the present work is to evaluate if the differences found in the fracture parameters between femtolaser and sharp razor blade notched specimens are held independently of the morphological and structural properties of the ethylene-propylene block copolymer. Hence, four ethylene-propylene block copolymers with different structural properties have been chosen and the fracture parameters have been determined under EPFM conditions. Subsequently, the fracture toughness values are discussed in the light of the specimen thickness, the size and type of damage ahead of the crack tip and the structural parameters of the different copolymers.

2. Experimental procedure

2.1. Materials

The materials under study were four commercial grade ethylene-propylene block copolymers, EPBCs, supplied by Repsol in the form of pellets. The bulk specimens for fracture characterization were prepared by injection moulding.

The basic characteristics such as the ethylene content and the isotactic index determined from Nuclear Magnetic Resonance (NMR), the glass transition temperatures corresponding to the elastomeric particles, T_g EPR, embedded in the propylene matrix, T_g PP, measured via Dynamic Mechanical Thermal Analysis (DMTA), and molecular weights obtained by Gel Permeation Chromatography (GPC) are collected in Table 1.

The mechanical properties such as the Young's modulus, E , and the yield stress, σ_Y , were measured via tensile tests at a cross-head speed of 1 mm/min using ISO-527 bulk injected tensile samples (Table 2).

2.2. Sample preparation

Fracture toughness tests on bulk specimens were carried out on injected single edge notched bend specimens (SENB). For each copolymer, two specimen thicknesses, 6.35 mm and 9 mm, were analyzed, the overall dimensions being $6.35 \times 12.7 \times 55$ mm and $9 \times 18 \times 80$ mm, respectively. An initial straight-through slot with a depth to width ratio of 0.5 and terminating in a V-notch with 0.2 mm root radius was machined in all the specimens.

Two different procedures for the sharpening of the SENB specimens were carried out:

S-Type: The notch sharpening is performed with a fresh steel razor blade following the guidelines given by ESIS [6] and ASTM [10].

F-Type: The sharpening of the notch is produced through femtosecond pulsed laser ablation (Femtolaser) [11,12], using a commercial Ti:sapphire oscillator (Tsunami, Spectra Physics) plus a regenerative amplifier system (Spitfire, Spectra Physics) based on the chirped pulse amplification (CPA) technique. 120-fs pulses at 795 nm with a repetition rate of 1 kHz were produced. The scanning speed was 130 $\mu\text{m/s}$ and 8 passes were conducted with a pulse energy of 0.07 mJ. The sharp length inserted by the femtolaser was 500 μm .

The total initial crack depth, a_0 , to width ratio after sharpening was 0.55.

The morphology and dimensions of the crack tip after sharpening and the area beneath it of non-tested specimens were analyzed via light microscopy (Leica DMR) and scanning electron microscopy (Hitachi S-3400 N). Preparation prior to examination consisted of sectioning the bulk copolymer into films with thickness in the range between 6 and 10 μm with a microtome (Rotary Microtome Leica RM2265). The resulting sections were picked up and mounted on microscope slides to be analyzed via transmitted light microscopy or platinum sputter coated for scanning electron microscopy.

2.3. Fracture tests

The ESIS TC4 Protocol entitled "The determination of J -fracture toughness of polymers at slow speed" [2], was followed to achieve the J - R curves from multiple specimens. A minimum of seven samples was tested using an

Table 1

Basic properties of the copolymers under study.

	NMR		DMTA		GPC			
	Ethylene content (%wt)	Isotactic Index (%)	T_g PP ($^{\circ}\text{C}$)	T_g EPR ($^{\circ}\text{C}$)	M_w (kg/mol)	M_n (kg/mol)	M_z (kg/mol)	Polidispersity (M_w/M_n)
EPBC1	6.9	89.3	10.6	-45.8	816	161	2245	5.09
EPBC5	8.5	85.4	10.4	-49.3	353	66	1026	5.37
EPBC7	8.5	84.2	10.5	-49.4	302	56	882	5.39
EPBC12	11.2	81.0	10.5	-49.4	307	61	878	5.05

Table 2
Mechanical properties of the ethylene-propylene block copolymers.

	E (GPa)	σ_Y (MPa)
EPBC1	1.38 ± 0.06	26.1 ± 0.6
EPBC5	1.54 ± 0.03	23.9 ± 0.5
EPBC7	1.411 ± 0.008	23.03 ± 0.04
EPBC12	1.04 ± 0.26	21.2 ± 1.4

electromechanical testing machine (MTS Alliance RF/100) with a load cell of ± 5 kN. The tests were performed at room temperature and under displacement control at a cross-head speed of 1 mm/min using a three-point bend fixture of 50.8 and 96 mm loading spans for the SENB specimens with 6.35 and 9 mm in thickness, respectively.

3. Results and discussion

The mechanical response of the four copolymers at 23 °C and at a cross-head speed of 1 mm/min was highly

non-linear and the multiple specimen method was applied to determine the J -crack growth resistance curves [6]. Figs. 1 and 2 combine the R -curves of the S -Type and F -Type specimens with 6.35 and 9 mm in thickness, respectively. These plots also include the fit of the J -crack growth resistance curve to the power law $J = C \cdot \Delta a^N$, with $N \leq 1$. Independently of the copolymer type and specimen dimensions, the resistance curves of F -Type are always below those of S -Type. Moreover, the rising part of the R -curves shows little differences between the S -Type and F -Type samples. On the other hand, according to the fitted curves, for the same notch sharpening procedure, there seems to be no great influence of the thickness on the resistance curves.

Fig. 3 collects the fracture toughness, J_{IC} , obtained from the resistance curves of S -Type and F -Type specimens with 6.35 mm and 9 mm in thickness. For the computation of J_{IC} values, the guidelines described by Hale et al. [6] have been followed, where this critical value has been replaced by

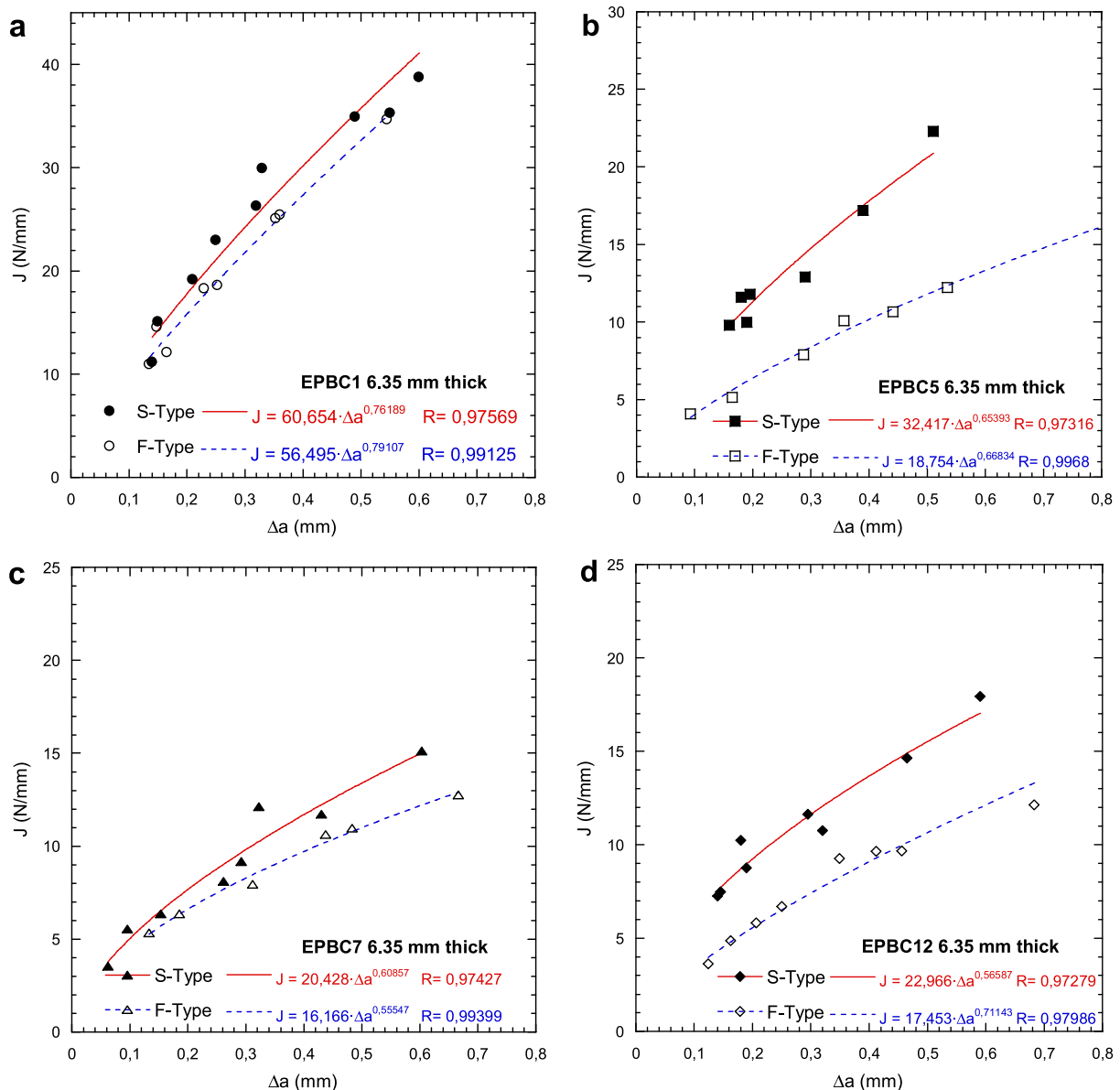


Fig. 1. J - R curves for S -Type and F -Type specimens of (a) EPBC1, (b) EPBC5, (c) EPBC7 and (d) EPBC12 determined from 6.35 mm thick samples.

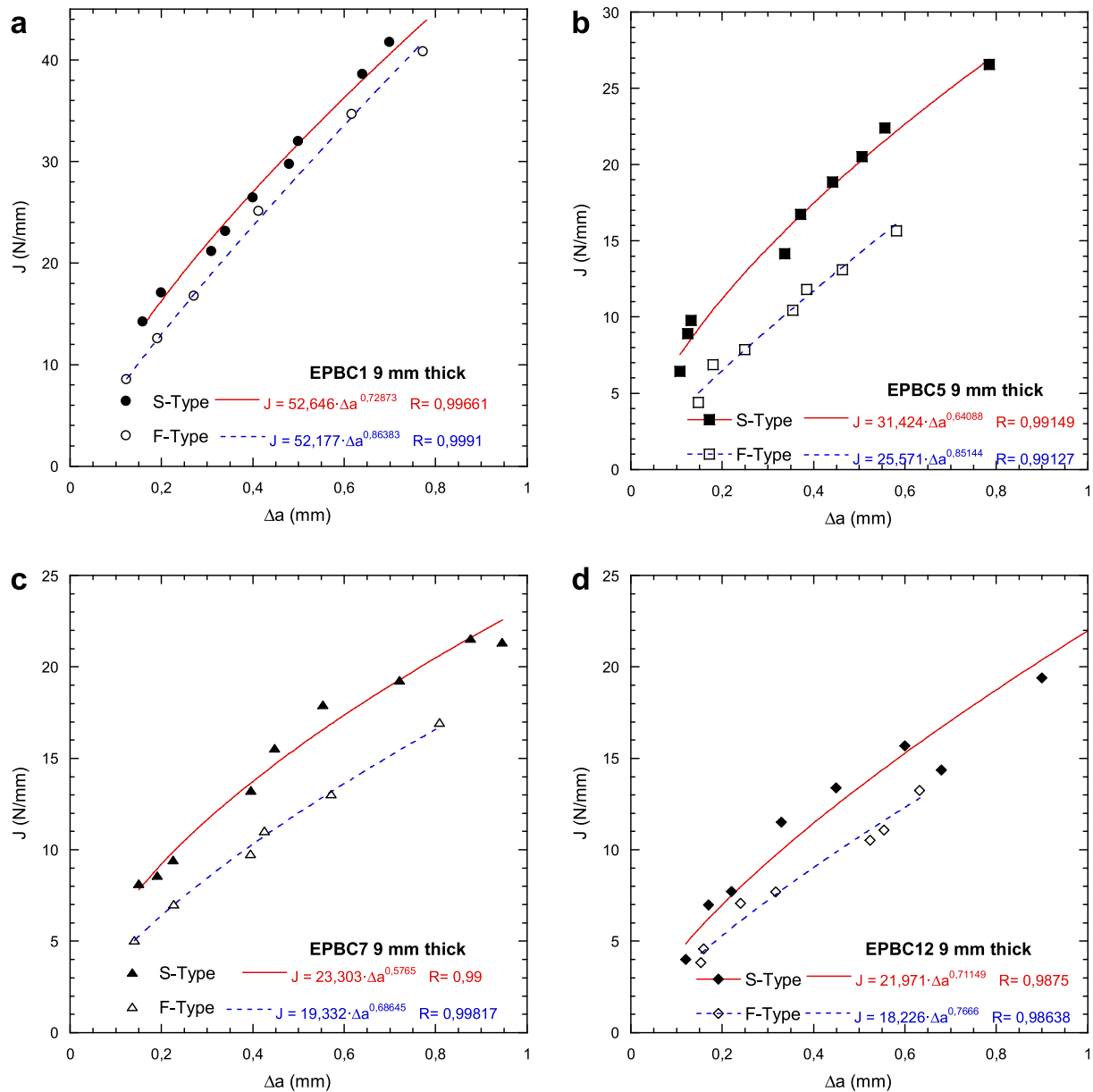


Fig. 2. J-R curves for S-Type and F-Type specimens of (a) EPBC1, (b) EPBC5, (c) EPBC7 and (d) EPBC12 determined from 9 mm thick samples.

a pseudo-initiation value $J_{0.2}$, which defines crack resistance at 0.2 mm of the total crack growth. The size requirements for plane strain J_{IC} are given by [13]:

$$B, a, W - a > 25 \frac{J}{\sigma_Y} \quad (1)$$

where B is the thickness, W is the width and a is the initial crack length. The fracture toughness values are not in plane strain except for EPBC12 S-Type 9 mm thick samples and EPBC5, EPBC7 and EPBC12 F-Type 9 mm thick specimens. The fracture values of the specimens sharpened with a steel razor blade, S-Type, showed in all cases higher values of the energy for crack growth initiation than the samples sharpened with the femtosecond laser, F-Type. The differences ranged from 13% for EPBC1 6.35 mm thick to 74% for EPBC5 6.35 mm thick.

Analysis of Fig. 3 yields further information. As regards the F-Type samples, for almost all the copolymers (EPBC5,

EPBC7 and EPBC12), the fracture toughness of the specimens with 6.35 mm in thickness is the same as that of 9 mm thick samples. However, this tendency is not followed by EPBC1. In the case of the S-Type samples, the fracture toughness of the 6.35 mm thick specimens is higher than that of the 9 mm thick samples except for EPBC7.

With the aim of evaluating the differences between F-Type and S-Type sharpened specimens, between 5 and 10 films with $\sim 8 \mu\text{m}$ in thickness were microtomed along the depth of the S-Type and F-Type sharpened samples for each copolymer before being tested. Figs. 4 and 5 show the micrographs obtained via transmitted light microscopy of the appearance of the crack tip and the area ahead of it for EPBC1 S-Type and F-Type sharpened specimens 6.35 and 9 mm thick, respectively. The crack tip has been marked with an arrow, and the measurements carried out at high magnification indicated that, independently of the copolymer,

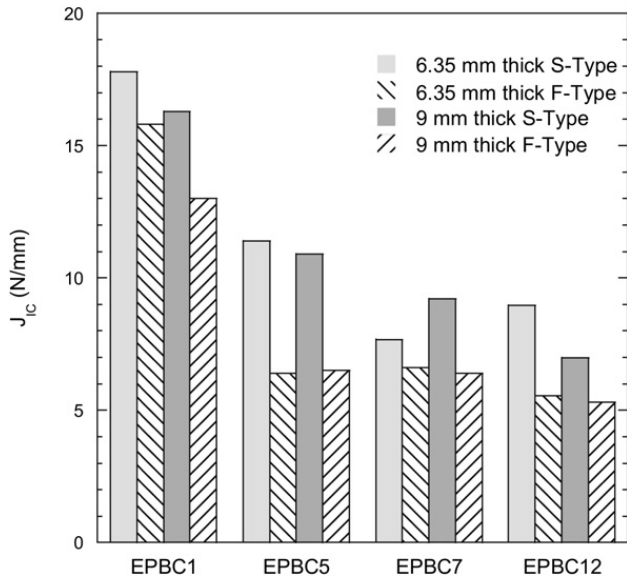


Fig. 3. Fracture toughness values, J_{IC} , of EPBC1, EPBC5, EPBC7 and EPBC12 as a function of the specimen's thickness and the notching procedure.

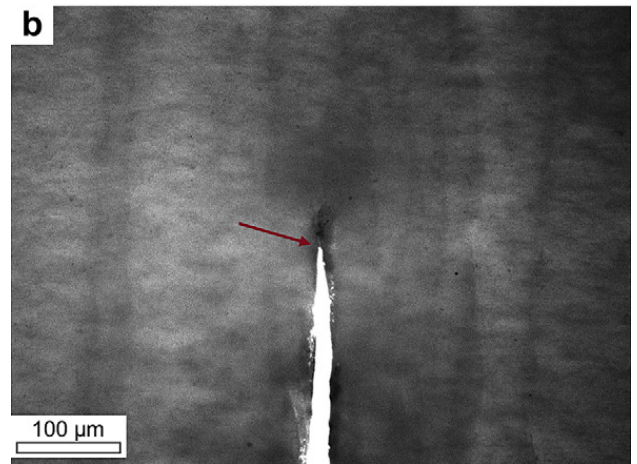
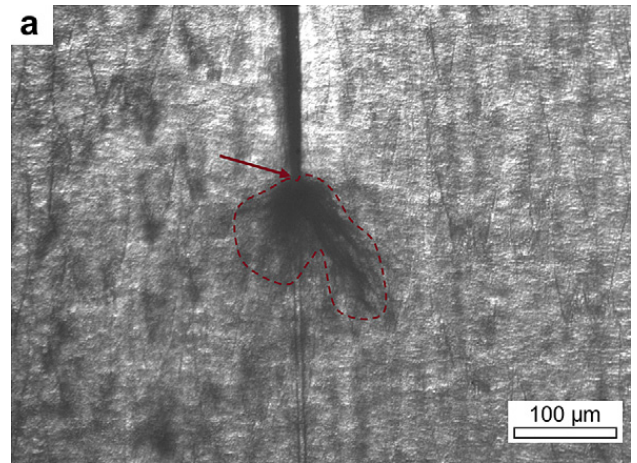


Fig. 5. Micrographs of EPBC1 showing the crack tip of non-tested (a) S-Type and (b) F-Type sharpened specimens with 9 mm in thickness. The arrow points out the end of the crack tip and the damage produced by plastic deformation is outlined by a dotted line.

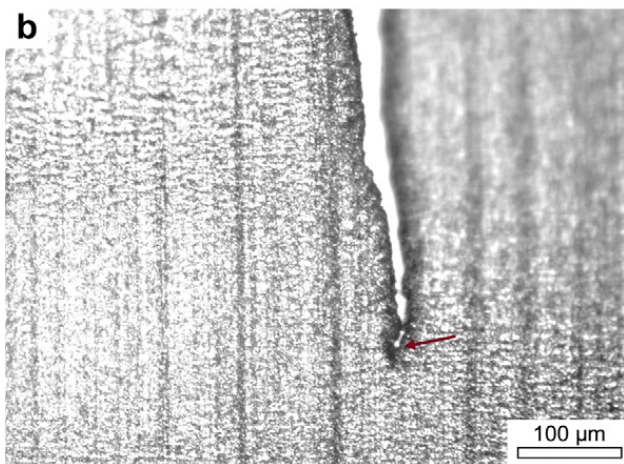
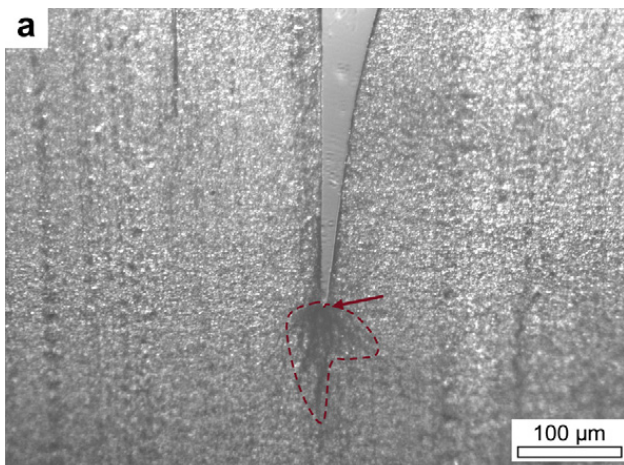


Fig. 4. Micrographs of EPBC1 showing the crack tip of non-tested (a) S-Type and (b) F-Type sharpened specimens with 6.35 mm in thickness. The arrow points out the end of the crack tip and the damage produced by plastic deformation is outlined by a dotted line.

sharpening procedure and dimensions, the values of the crack tip radius were similar and ranging between 1 and 2 μm . However, there is a dark area in the material facing the crack tip (outlined with dots) which extends deeper in the S-Type samples (Figs. 4a and 5a). This dark area is more difficult to observe in the F-Type specimens and, if it exists, it is confined to a very tiny region ahead of the crack tip (Figs. 4b and 5b). Moreover, the dotted zone of the S-Type 6.35 mm thick specimens (Fig. 4a) seems to be bigger than that of the S-Type 9 mm thick specimens (Fig. 5a). This contrasts with the analysis of the F-Type samples as a function of the thickness (Figs. 4b and 5b), because this tendency with the thickness could not be detected. To assess these trends, the damage length, measured as the length of a straight line going from the crack tip to the end of the dark area, was determined along the depth of the EPBC1 S-Type and F-Type specimens with 6.35 and 9 mm in thickness. The resulting profiles were plotted in Fig. 6a and b, respectively. As can be observed, the light microscopic inspection agrees with the measurements of the damage length. Independently of the specimen thickness and the analyzed depth, the damage length of the S-Type samples is always higher than that of the F-Type. Furthermore, the damage length of the S-Type 6.35 mm thick samples is greater than that of the S-Type 9 mm thick specimens, whereas for the F-Type

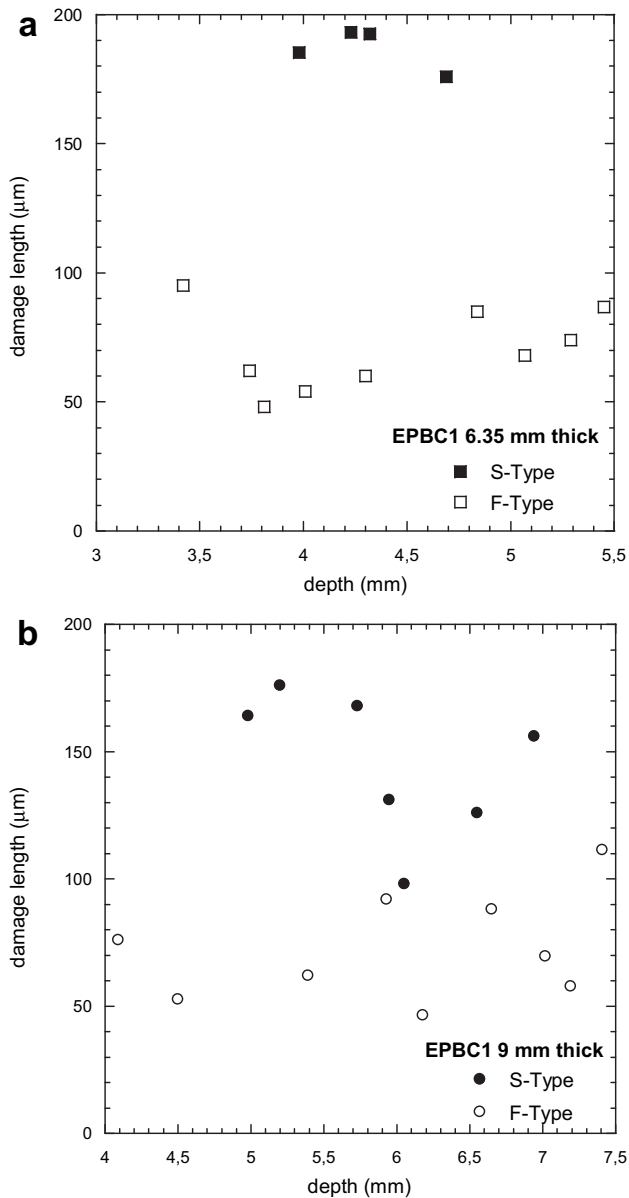


Fig. 6. Evolution of the damage length ahead of the crack tip through the specimen's depth with the notching procedure for non-tested EPBC1 copolymers with (a) 6.35 mm and (b) 9 mm in thickness.

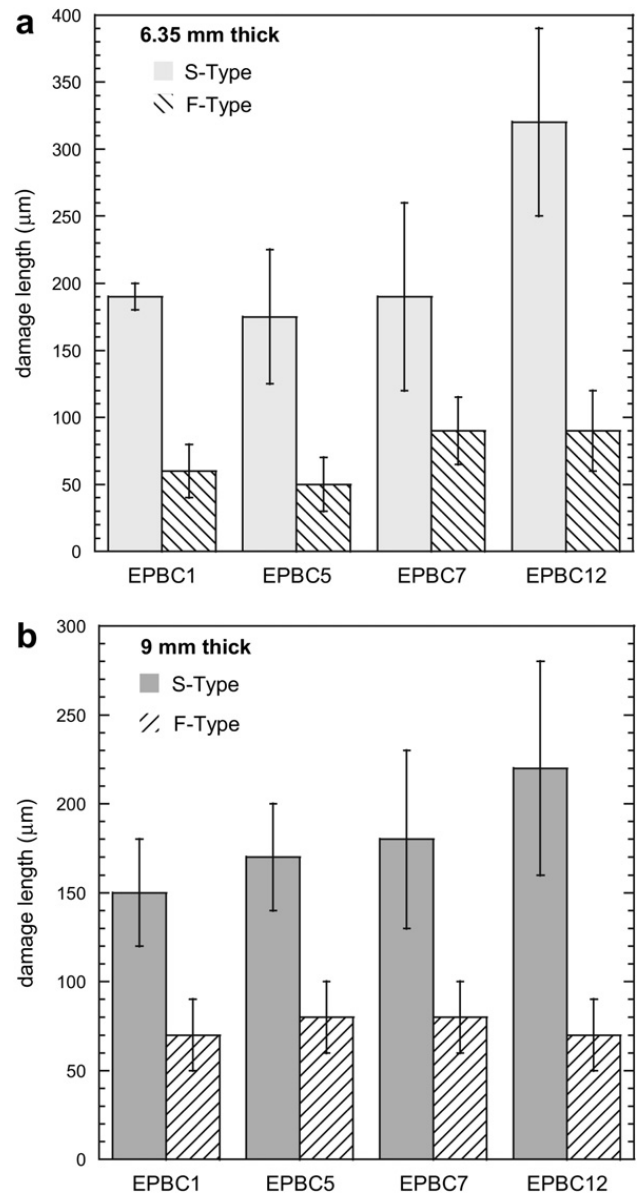


Fig. 7. Damage length as a function of the notching technique for non-tested EPBC1, EPBC5, EPBC7 and EPBC12 copolymers with (a) 6.35 and (b) 9 mm in thickness.

samples the damage length is not influenced by the specimen dimensions.

The evolution of the damage ahead of the crack tip for non-tested EPBC1, EPBC5, EPBC7 and EPBC12 as a function of the notching procedure is collected in Figs. 7a and b for the specimens with 6.35 and 9 mm in thickness, respectively. The plots represent the average damage length, obtained from the analysis of the films microtomed through the depth of the samples, together with their corresponding standard deviation. In the case of EPBC5, EPBC7 and EPBC12 copolymers, the damage ahead of the crack tip evolved similarly with the notching procedure and specimen thickness to that described for EPBC1. Several conclusions can be drawn from the analysis of these figures. Firstly, the length of the damage of S-Type is always higher than that of F-Type independently of the copolymer and specimen thickness. Furthermore, the damage length for

the F-Type specimens is influenced neither by the copolymer type nor the specimen dimensions. These quantitative results are in agreement with previous works [9,10]. It has been demonstrated that the region ahead of the crack tip with different texture to the rest of the virgin surface is caused during the notch sharpening.

To reach a better understanding of the nature of the damage ahead of the crack tip, S-Type and F-Type microtomed films were analyzed via scanning electron microscopy. Figs. 8 and 9 show the area surrounding the crack tip for EPBC5 S-Type and F-Type sharpened samples, respectively. The main difference in the zone beneath the crack is the morphology of the damage. In the S-type films, the area surrounding the crack tip is extremely deformed (Fig. 8a), with highly distorted holes left by the strained ethylene particles (Fig. 8b). These deformed particles can leave holes with up to 5 μm in length, which is a huge increase in size

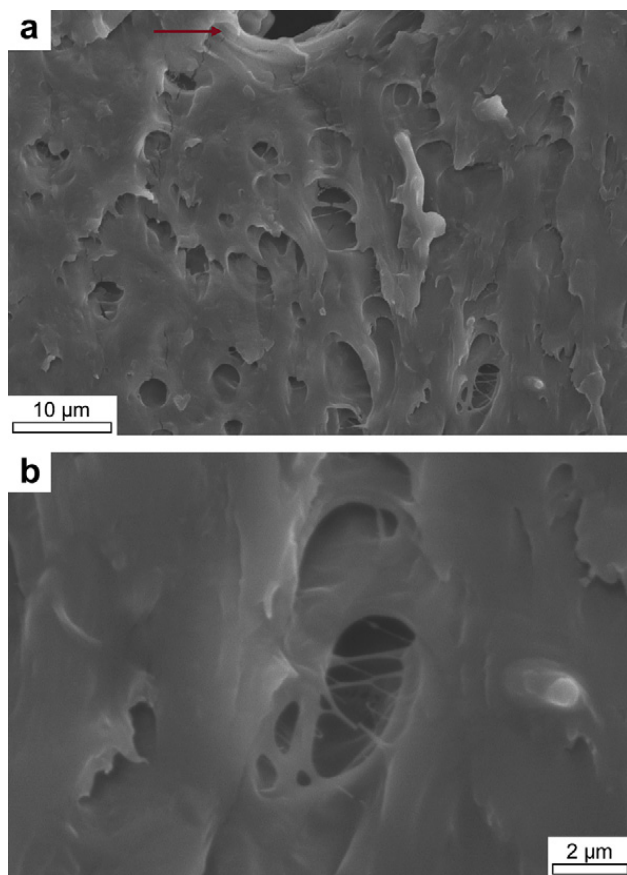


Fig. 8. Micrographs obtained via scanning electron microscopy showing the morphology of the damage beneath the crack tip in EPBC5 S-Type samples: (a) detail of the crack tip front and (b) damage ahead of the crack tip. The arrow points out the end of the crack tip.

taking into account that the non stressed elastomeric particle dimension is $\sim 0.4 \mu\text{m}$ [14]. On the other hand, the F-Type films present a very small area affected by the heat dissipation (Fig. 9a) where partially melted zones produced by the pulses of the laser ablation process can be discerned (Fig. 9b). It is worth mentioning that some of the F-Type analyzed films were characterized by complete absence of damage ahead of the crack tip (Figs. 4b and 5b).

During the sharpening procedure with the fresh steel razor blade, the force of tapping acts along the depth which leads to stresses which exceed the yield stress locally and generate wide plastic deformation areas. The extension of these areas is higher as the depth of the specimen decreases, assuming that roughly the same force is applied independently of the thickness of the sample.

Apart from that, the damage length seems to be related to the structural parameters of the copolymer, especially with the ethylene content. Interestingly, the damage ahead of the crack tip of the S-Type samples increased as the amount of ethylene content in the copolymer was raised (Table 1). As the ethylene content is increased, the stiffness and yield stress are reduced (Table 2). This implies a softening of the copolymer with the addition of ethylene. Hence, if the same force is applied for all the samples, independently of the thickness and the type of copolymer, the resulting damage will be larger for higher ethylene content. On the other hand, in the F-Type

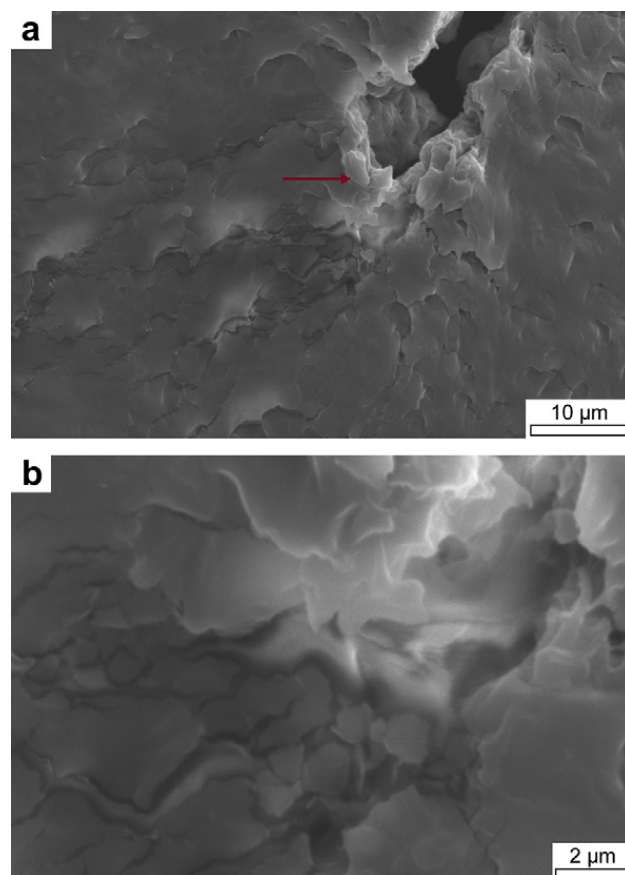


Fig. 9. Micrographs obtained via scanning electron microscopy showing the morphology of the damage beneath the crack tip in EPBC5 F-Type samples: (a) detail of the crack tip front and (b) damage ahead of the crack tip. The arrow points out the end of the crack tip.

specimens, there is no physical contact with the specimen during the notching procedure, which is the reason why the damage dimensions are held constant independently of the copolymer and thickness of the specimen. The nature of the damage is confined to a tiny heat affected zone.

Consequently, the presence of plastic deformation, either large (6.35 mm thick specimens) or small (9 mm thick specimens), accounts for the differences in the J_{IC} values of the distinct sharpened specimens when measured within the EPFM regime. The energy necessary to start crack growth is higher when the crack tip encounters a deformed area (S-Type) than when encountering almost virgin material (F-Type) because of the different mechanical properties of the crack front matter [9,10]. However, for the S-type samples, the extension of the plastic deformation damage ahead of the crack tip clearly plays an important role in the fracture toughness values. It seems that the higher the damage length beneath the crack tip, the more energy is needed for the crack to start growing because the area affected by strain hardened material with different properties to the virgin material is larger. This can partly explain the differences in the fracture toughness values between the S-Type samples with 6.35 mm and 9 mm in thickness (Fig. 3).

Finally, concerning the stable crack growth resistance, the similarity in the rising part of the resistance curves

between the *S*-Type and *F*-Type samples independently of the copolymer type and dimensions (Figs. 1 and 2) is indication that the notching procedure only influences the crack growth initiation and not its consequent propagation.

4. Conclusions

The influence of the notching procedure on the fracture parameters obtained via EPFM has been analyzed in four different ethylene-propylene block copolymers with two distinct dimensions. The crack growth initiation energy of the specimens sharpened via traditional steel razor blade was always higher than that of the samples sharpened via the femtolaser ablation technique. Furthermore, for the razor blade samples, the fracture toughness was dependent on the thickness of the samples, being lower in the thicker specimens; whereas for the femtolaser sharpened specimens the fracture toughness was not influenced by the dimensions of the test specimens. The damage in the crack front accounts for the fracture toughness values as all the test samples presented similar crack tip radii. The damage produced during the sharpening with steel razor blade consisted of a highly plastically deformed area surrounding the crack tip, the extent of which was larger as the thickness of the samples was reduced and the ethylene content in the copolymer was increased. On the contrary, the damage of the femtolaser sharpened samples was confined to a very tiny heat affected zone independently of the copolymer type and dimensions. Finally, the crack growth resistance was not affected by the notching procedure as the rising part of the *J*–*R* curves was similar independently of the notching technique and the thickness of the samples.

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