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# Determination of fracture toughness of propylene polymers at different operating temperatures

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## ABSTRACT

The influence of the temperature on the fracture parameters of three types of polypropylenes under static loading conditions has been analyzed. Single-phase polypropylene homopolymer and random ethylene–propylene copolymer were tested slightly above their glass transition temperatures (within the ductile-to-brittle transition region), and well below and above them; heterophasic ethylene–propylene block copolymers were tested on the range of temperatures from above the glass transition temperature of propylene matrix to below the glass transition temperature of the elastomer phase. Attending to the mechanical response, suitable Fracture Mechanics approaches were used. Fracture toughness increased with temperature for single-phase polymers but block copolymers were not temperature sensitive for the range of temperatures above the glass transition temperature of the elastomeric phase despite their variation on the mechanical properties.

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## 1. Introduction

Low manufacturing costs, ease of recycling and possibility of tailoring properties are some of the reasons why isotactic polypropylene, PP, has been enjoying the fastest growth in consumption since its discovery [1]. There are three typical types of PP: homopolymers, random copolymers and block (or impact/heterophasic) copolymers. The copolymers are usually of ethylene and butane. Random copolymers usually contain up to 6 wt% of ethylene or other comonomers inserted randomly within the chain, reducing the crystallinity and the melting point by introducing irregularities into the chain. They are used where clarity, lower melting point or lower modulus is desirable. The low content in ethylene provides a continuous and monophase structure with one single glass transition temperature,  $T_g$ , slightly below that of the PP homopolymers because of the presence of ethylene. Block copolymers, also known as impact or heterophasic copolymers, contain up to 40% ethylene–propylene rubber (EPR), uniformly dispersed within the homopolymer matrix [1–3]. They show two distinct glass transition temperatures, associated with the PP matrix,  $\sim 23^\circ\text{C}$ , and with the elastomeric phase,  $\sim -50^\circ\text{C}$ . As implied in the name, those copolymers are used where impact strength is important, especially at low temperatures [1]. The toughening mechanism is related to the generation of many small crazes, which absorb significant energy, and the interruption of a propagating fracture in the matrix [4–11]. This mechanism operates above the glass transition temperature of the dispersed phase, and its effectiveness is determined by one side, the nature of the elastomeric phase, which defines the deformation

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### Nomenclature

$a_0$	initial crack length
$a$	crack length
ASTM	American Society for Testing and Materials
$B$	specimen thickness
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
$E$	Young's modulus
EPBC	ethylene–propylene block copolymer
EPR	ethylene–propylene random copolymer
ESIS	European Structural Integrity Society
EWf	Essential Work of Fracture
$F(J)$	cumulative probability
$G_{IC}$	critical energy release rate
GPC	Gel Permeation Chromatography
$J$	$J$ -integral
$J_{Cmin}$	lowest fracture toughness
$J_{Cmax}$	highest fracture toughness
$J_{IC}$	fracture toughness at crack initiation
$J_{med}$	mean fracture toughness
$J_0$	threshold toughness
$J_{0.2}$	crack resistance at 0.2 mm of the total crack growth
$K_{I_{max}}$	critical stress intensity factor
LEFM	Linear Elastic Fracture Mechanics
$m$	shape parameter
$M_n$	number average molecular weight
$M_w$	weight average molecular weight
$M_z$	z-average molecular weight
NLEFM	Non Linear Elastic Fracture Mechanics
NMR	Nuclear Magnetic Resonance
$P$	cumulative probability
PP	polypropylene homopolymer
SENB	single edge notched bend specimens abbreviation
$T_g$	glass transition temperature
$W$	specimen width
$\Delta_a$	crack extension
$\sigma_Y$	yield stress
$\chi$	degree of crystallinity
3P-W	three-parameter Weibull model

behaviour of the dispersed particles and their ability to absorb and redistribute the energy; and by the other side, the concentration and particle size, which establishes the probability of both initiating crazes and intercepting the fracture line.

The influence of the structural and morphological parameters (content, size and interparticle distance of the rubber modifiers [4–14], molecular weight, tacticity, crystallinity index, shape, size and distribution of crystalline regions of the PP matrix) on the fracture behaviour of PPs has been widely analyzed specially under high loading rates and at low temperature [2–4,6–17,18–25]. The main reason is that these polymeric materials, especially the block copolymers, exhibit a wide range of properties and structures with a great performance in the high strain field.

Apart from the typical high strain rate applications, the propylene polymers are also particularly suitable for hot and cold water distribution systems, heating and air conditioning for residential and industrial networks and transport of agricultural and industrial fluids as well as food substances. In service and in most of these applications, the polymers are to bear temperatures that go from  $-30\text{ }^{\circ}\text{C}$  to even  $100\text{ }^{\circ}\text{C}$  under static loading conditions. Previous works by Pooler [26] and Kobbe [27] illustrated vastly different behaviours over a practical in-service range of temperatures for HDPE and polypropylene formulations under compressive, tensile and flexural testing configurations, respectively. However, under quasi-static conditions there is lack of systematic studies in the literature of the evolution of the fracture parameters of bulk PPs with the temperature.

Santarelli and Frontini showed that it was very difficult to determine the fracture toughness of PP homopolymers at room temperature and under static loading conditions [28]. The fracture toughness data were highly scattered and showed a strong sensitivity to notch [19–31] and geometry dimensions [4,5,28] and strain rate [5,12,15,16,30,31]. In addition, some

load–displacement records displayed excessive nonlinearity and the presence of stable crack growth extension prior to instability [4,12,19,33,34,35]. This so-called ductile to brittle transition regime behaviour complicated the application of the LEFM methodologies and was explained in terms of the nearness of the testing temperature to the  $T_g$  of the PP homopolymer [1]. To avoid taking into account these difficulties, some authors [4] studied the fracture far away from the ductile to brittle transition temperature which comprises the range that goes from  $\sim 0^\circ\text{C}$  to  $\sim 40^\circ\text{C}$ . The reason is that PP homopolymers became completely ductile above  $40^\circ\text{C}$  and entirely brittle below  $\sim 0^\circ\text{C}$ . However, Santarelli and Frontini [28] and Cocco et al. [34,35] demonstrated that a statistical approach based on the weakest-link model such as the three-parameter Weibull model could be successfully applied to characterize the fracture behaviour of polymers in the ductile to brittle region without the need of lowering temperature. From the statistical parameters, a toughness threshold can be determined and Cocco et al. demonstrated that this parameter is an actual representative material toughness [34,35].

The copolymers, especially the block copolymers, have been extensively analyzed under the combination of high rate and low temperatures. The conventional impact strength determined by either Charpy or Izod tests were normally used to investigate the influence of the morphology and the structural parameters on the mechanical and fracture behaviour [2,6–14,19,20,23,24]. In few cases, the Fracture Mechanics theory was applied to determine the fracture behaviour, and always under temperature and strain rate conditions that allowed the use of LEFM approach [6–9,12,15,16,19,20,22,25]. Certainly, over the full range of temperatures and test speeds, the conditions for strictly valid LEFM testing were not met, but even though, this approach was used defining an apparent critical stress intensity factor,  $K_{I\max}$ , calculated from the maximum load reached during the test [22,25]. The results showed that the impact strength rose with both ethylene content and test temperature, and above all, the brittle to ductile transition temperature was shifted to lower temperatures with the increase in the ethylene content [4,11,21,24–26]. The presence of elastomer enhanced the stability of a growing crack [6] and moreover, the ductile-to brittle transition temperature reduced with increasing the test speed or strain rate [22,25]. Also, the microstructure plays an important role in the behaviour at high rate. The reduction of the dispersed phase particle size and interparticle distance led to a systematic increase of the impact strength and a decrease of the brittle to ductile transition temperature of the materials [13,21].

Very few analyses of these copolymers can be found in the literature under quasi-static conditions. Fernando and Williams [4] showed that at low testing speeds, the copolymers presented a linear elastic behaviour which allowed the use of the concepts of the LEFM only at very low temperatures, as the ductile–brittle region was in the range between  $-100$  and  $-45^\circ\text{C}$  depending on the ethylene content. At high temperatures, the non-linear response of these polymeric materials requires the use of elasto–plastic methodologies based on the  $J$ -integral to construct the  $J$ - $R$  curve [12,19,36,37]. Fasce et al. [12,19] proved that the  $J$ - $R$  curves of the PP homopolymer was above those of the copolymers, and as a consequence, showed better fracture toughness, and this was consistent with the high yield stress of the former. For thin films at low rate tests, the Essential Work of Fracture (EWF) methodology [9,19,38–40] to characterize PP homopolymers and copolymer. In these studies, the EWF parameters of the homopolymer were found to be more temperature-sensitive than the copolymers with lower EWF values at temperatures below the glass transition temperature of the PP matrix ( $T_g \sim 0^\circ\text{C}$ ) and the opposite trend at temperatures above the  $T_g$  of PP. Besides, the ductile to brittle transition temperature of the homopolymer that occurs below its  $T_g$  was suppressed for the copolymers. The variations of the EWF parameters with the temperature were explained in terms of molecular relaxations, ethylene content, and changes in the yield and fracture stresses.

As shown, most of the works in the literature prefer to analyze the influence of the morphology and structural parameter on the conventional impact strength at high strain rates over the use of the Fracture Mechanics theory. However, there are many industrial and technologic applications where relatively thick components of bulk propylene polymers are submitted to a range of in service temperatures under static loading conditions. Therefore, to assess the effect of temperature on mechanical properties and fracture behaviour of the propylene polymers is essential. So, this paper presents the results of a wide experimental study on the influence of the temperature on the mechanical properties and the Fracture Mechanics parameters obtained under quasi-static conditions of the three types of propylene polymers: a PP homopolymer, an ethylene–propylene random copolymer and four different ethylene–propylene block copolymers. Special attention will be paid to the employed Fracture Mechanics methodology to determine the fracture parameters attending to the mechanical response of each polymer as a function of the testing temperature. In addition, the effect of the structural parameters and morphology on the mechanical and fracture behaviour will be investigated.

## 2. Theory

At low loading rate, the fracture behaviour of the propylene polymers with increasing temperature goes from the brittle to the ductile behaviour. In case of complete brittle behaviour, LEFM is applicable and the basic guidelines of ISO 13586 standard were followed [41]. For the ductile response, fracture characterization is attained with the help of Elasto Plastic Fracture Mechanics (EPFM) methodologies such as the multiple specimen method [42] and the normalization method [43]. Both methodologies allow the construction of the whole  $J$ - $R$  curve, which is described by a power law  $J = C \cdot \Delta a^N$ , with  $N \leq 1$ . For the computation of  $J_{IC}$  values, the guidelines described by Hale and Ramsteiner [42] have been followed, where the initiation toughness is defined as the lower value of a  $J_{0.2}$  parameter, which defines crack resistance at 0.2 mm of the total crack growth, or a  $J_{BL}$  value, specified as the intersection of the blunting line with the  $J$ - $\Delta a$  curve.

Under those experimental conditions within the ductile-to-brittle region, where the fracture behaviour of polymers is neither completely brittle nor entirely ductile, a statistical approach based on the weakest link model was applied. This theory states: (1) fracture toughness is variable, differing throughout the given material and particularly along the specimen crack front, (2) the fracture toughness of any specimen is governed by the point or region having the lowest toughness along the crack front. The experimental results were fitted by a three-parameter Weibull model (3P-W) given by the following expression [34,35]:

$$F(J) = 1 - \exp \left\{ - \left[ \frac{J - J_0}{C - J_0} \right]^m \right\} \quad (1)$$

where  $F(J)$  is the cumulative probability that can be calculated by means of an estimator,  $J$  represents the toughness value,  $C$  is the scale parameter,  $m$  is the shape parameter, and  $J_0$  is the threshold toughness parameter independent of size. In this way a minimum toughness value is obtained implying that there is null probability of failure for driving forces lower than  $J_0$ . The Weibull parameters ( $J_0$ ,  $m$  and  $C$ ) are calculated following the methodology described below:

- (1) Results are arranged from the lowest to the highest fracture toughness values, and an order number was assigned to each value,  $i$ .
- (2) Cumulative probabilities were calculated by using the following estimator:

$$F(J_i) \approx P_i = \frac{i - 0.5}{N} \quad (2)$$

where  $i$ :  $i^{\text{th}}$   $J$  fracture value and  $N$ : the total number of data.

- (1) The cumulative function was re-arranged by taking logarithms twice, obtaining the expression of a straight line:

$$\ln \left[ \ln \left[ \frac{1}{1 - P} \right] \right] = m \cdot \ln(J - J_0) - m \cdot \ln(C - J_0) \quad (3)$$

the parameter  $m$  is the slope of the straight line;  $C$ , the ordinate  $y$  at  $x = 0$ .  $J_0$  is obtained as the value that best fitted the straight line for the experimental points.  $J_0$  can assume values between 0 and  $J_{\text{Cmin}}$ , the lowest fracture toughness value; values smaller than zero lack physical meaning and  $J_0$ , by definition, has to be lower than  $J_{\text{Cmin}}$ . This method is perfectly stated for stationary crack. In growing cracks the peak stress samples a higher volume of material than in a stationary one, thus the probability of brittle fracture increases [44]. There exists also a reduction of constraint, which lowers the peak stress, and therefore the probability of brittle fracture [45]. These two factors cause a change in the probability function. Since the interest is determining a fracture toughness threshold, a censoring strategy is usually used to avoid these effects [44]. Data was then censored according to the criterion proposed elsewhere [34]: any specimen presenting a crack growth larger than 10% of the original remaining ligament:

$$\Delta a > \Delta a_{\text{max}} = 0.1(W - a_0) \quad (4)$$

was excluded in the regression analysis. To estimate Weibull function parameters, probability was recalculated using only valid data.

### 3. Experimental procedure

#### 3.1. Materials

The materials under study were a PP homopolymer, PP, an ethylene–propylene random copolymer, EPRC, and four ethylene–propylene block copolymers, EPBC9-1, EPBC9-2 EPBC12-1 and EPBC12-2, supplied by Repsol in form of pellets. The specimens for mechanical and fracture characterization were prepared by injection molding. The basic characteristics such as the ethylene content 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), the degree of crystallinity of the PP matrix,  $\chi$  PP, measured by Differential Scanning Calorimetry (DSC) and molecular weights obtained by Gel Permeation Chromatography (GPC) are collected in Table 1.

**Table 1**

Basic properties of the propylene polymers under study.

	NMR	DMTA		DSC		GPC		
	Ethylene content (wt%)	$T_g$ PP (°C)	$T_g$ EPR (°C)	$\chi$ PP (%)	$M_w$ (kg/mol)	$M_n$ (kg/mol)	$M_z$ (kg/mol)	Polydispersity ( $M_w/M_n$ )
PP	0	10.6	–	52.0	396	53	1254	7.5
EPR	3.1	0.6	–	33.0	263	49	688	5.4
EPBC9-1	8.5	18.1	–48.0	40.0	353	66	1026	5.4
EPBC9-2	9.0	12.8	–45.7	38.5	551	94	1757	5.9
EPBC12-1	11.2	10.6	–49.4	40.6	307	61	878	5.05
EPBC12-2	12.0	12.4	–45.9	36.5	531	100	1601	5.30

In case of the block copolymers, two of them presented an ethylene content of 9 wt%, EPBC9-1 and EPBC9-2, and the other two were characterized by an ethylene content of 12 wt%, EPBC12-1 and EPBC12-2. The main difference between EPBC9-1 and EPBC9-2 or EPBC12-1 and EPBC12-2 is the molecular weight, that is, EPBC9-1 and EPBC12-1 had higher molecular weights than their corresponding partners EPBC9-2 and EPBC12-2.

### 3.2. Mechanical performance

In order to assess the performance of the propylene polymers at different temperatures under quasi-static conditions, tensile and fracture tests were conducted on an electromechanical testing machine (MTS Alliance RF/100) with a load cell of  $\pm 5$  kN, at a cross-head speed of 1 mm/min and at different testing temperatures depending on the type of polymer. The testing temperatures were chosen to attain different types of fracture going from the ductile to the brittle behaviour for all the materials under study and also, going through the ductile to brittle transition zone in the single-phase polymers. Thus, the monophasic polymers as the PP and EPR were tested at temperatures close to their glass transition temperatures, that is, at 23 and 45 °C; well above their  $T_g$ s, at 60 °C, and well below them, at –20 °C. In case of the block copolymers, the tests were carried out at four different temperatures to cover all the possible fracture behaviours, that is, at room temperature (above the glass transition temperatures of both PP matrix and the elastomeric phase), at 0 and –40 °C (between the glass transition temperatures of the PP matrix and the elastomeric phase), and at –80 °C (well below the glass transition temperatures of the copolymers). In this way, all possible in service fracture patterns were achieved.

Tensile tests were performed to determine the mechanical properties, such as the Young's modulus,  $E$ , and the yield stress,  $\sigma_y$ , at different testing temperatures of these polymers. The guidelines described by ISO 527 standard [45] were followed and all the specimens presented a narrow section with  $4 \times 6 \times 33$  mm<sup>3</sup> in size.

Fracture tests were performed on single edge notched bend specimens (SENB) with 6.35 mm in thickness, being the overall dimension of  $6.35 \times 12.7 \times 55$  mm<sup>3</sup> for the PP, EPR and the block copolymers with high molecular weight, EPBC9-2 and EPBC12-2; and of  $26.35 \times 24 \times 105$  mm<sup>3</sup> for the copolymers with low molecular weight, EPBC9-1 and EPBC12-1. An initial straight-through slot with a length to width ratio of 0.5 and terminating in a V-notch with 0.15 mm in root radius was machined in all the samples. The notch was sharpened by sliding a razor blade across the notch to achieve a total crack depth,  $a_0$ , to width,  $W$ , ratio of 0.55. A three point bend fixture was used with a span to width ratio of 4.

The cryogenic and high temperature tests were conducted placing the load train (hinges, grips or bending fixture and sample) inside an environmental chamber (MTS 651.06E-03), which was connected to a dewar flask containing liquid nitrogen in case of the low temperature tests. The cooling process consisted of adding liquid nitrogen continuously until the load frame ceased to move to balance the thermal contractions while maintaining a constant load of 15 N on the specimen. The same procedure was followed during the heating process. Once the target temperature was reached and before starting the test, conditioning was held 30 min more to guarantee that the specimen was in thermal equilibrium.

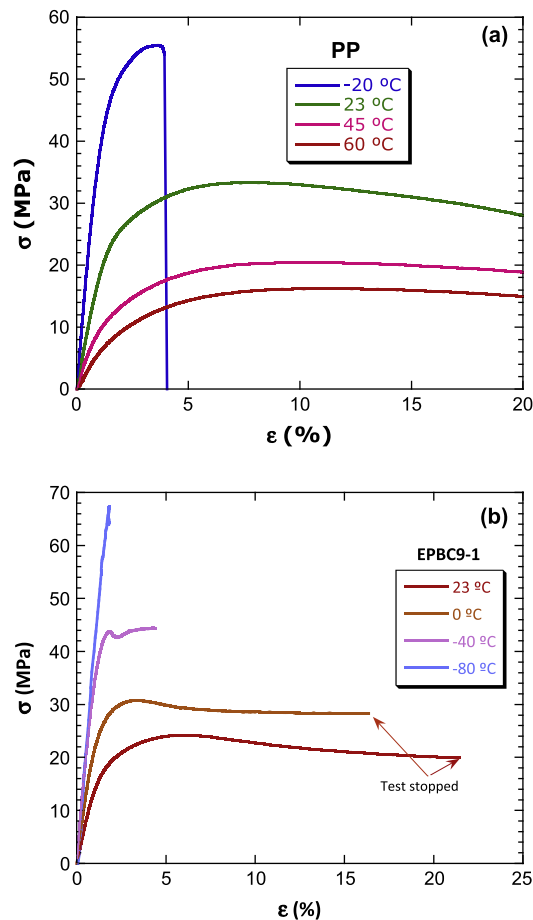
Finally, fracture surfaces of the broken specimens were analyzed via light microscopy and scanning electron microscopy (Philips XL30 and Hitachi S-3400 N) to analyze the differences in the fracture surfaces with the temperature.

## 4. Results

### 4.1. Mechanical properties

By way of illustration, Fig. 1a and b show typical stress–strain curves obtained from the tensile tests at –20, 23, 45 and 60 °C for the single-phase polypropylene homopolymer, PP; and at –80, –40, 0 and 23 °C for the heterophasic block copolymer EPBC9-1, respectively. The random copolymer, EPR, displayed analogous records to those shown by PP while the rest of block copolymers, EPBC9-2, EPBC12-1 and EPBC12-2 presented similar curves to those of EPBC9-1. The mechanical response of both monophasic and heterophasic polymers depended strongly on the testing temperature. The monophasic polymers presented completely ductile behaviour as the range of testing temperatures was above their glass transition temperatures and semi-brittle behaviour for the testing temperature below their glass transition temperatures, that is, at –20 °C (Fig. 1a). On the other hand, all the block copolymers displayed a ductile behaviour for temperatures above the glass transition temperature of the elastomer phase, that is, at –40, 0 and 23 °C, but they became entirely brittle below the glass transition temperature of the ethylene phase, that is, at –80 °C (Fig. 1b). As expected, as the temperature is reduced, the ductility decreased but the stiffness and yield stress rose.

With the aim of analyzing more deeply the mechanical response of the different materials, the evolution with the temperature of the Young's modulus,  $E$ , and the yield stress,  $\sigma_y$ , are collected in Table 2 for the single-phase polymers, in Tables 3 and 4 for the heterophasic copolymers with 9 wt% and 12 wt% ethylene content, respectively. In the single-phase polymers as PP and EPR, the increase in the mechanical properties with the reduction of the temperature was more accentuated in the pure polymer, PP, than in the random copolymer, EPR, by the lack of elastomer phase of the former (Table 2). For the block copolymers, the increase in the mechanical properties as the temperature decreased resulted more abrupt when the temperature was reduced below the glass transition temperature of PP matrix, 0 °C. By the decrease of temperature from 23 °C to 0 °C, a transition from a complete ductile behaviour of the two constituent phases to a ductile behaviour of the elastomer particles embedded in a PP matrix under deformation constraint within its amorphous zones was attained. With further



**Fig. 1.** Stress–strain curves obtained from the tensile tests at: (a)  $-20$ ,  $23$ ,  $45$  and  $60$  °C for the monophase PP and (b)  $-80$ ,  $-40$ ,  $0$  and  $23$  °C for the heterophasic EPBC9-1.

**Table 2**

Evolution with the temperature of the tensile properties, such as the Young's modulus and the yield stress, of the single-phase polymers PP and EPR.

	PP				EPR			
$T$ (°C)	$-20$	$23$	$45$	$60$	$-20$	$23$	$45$	$60$
$E$ (MPa)	$4120 \pm 300$	$1910 \pm 30$	$1080 \pm 80$	$641 \pm 4$	$3500 \pm 300$	$1040 \pm 30$	$590 \pm 20$	$350 \pm 30$
$\sigma_Y$ (MPa)	$54.5 \pm 1.4$	$33.2 \pm 0.2$	$20.9 \pm 0.4$	$16.2 \pm 0.1$	$51.4 \pm 2.2$	$26.3 \pm 0.4$	$14.5 \pm 0.1$	$11.3 \pm 0.1$

**Table 3**

Evolution with the temperature of the tensile properties, such as the Young's modulus and the yield stress, of the heterophasic block copolymers with 9 wt% of ethylene content, EPBC9-1 and EPBC9-2.

	EPBC9-1				EPBC9-2			
$T$ (°C)	$-80$	$-40$	$0$	$23$	$-80$	$-40$	$0$	$23$
$E$ (MPa)	$3600 \pm 300$	$2700 \pm 200$	$1690 \pm 50$	$970 \pm 40$	$3100 \pm 200$	$2430 \pm 20$	$1510 \pm 50$	$1000 \pm 300$
$\sigma_Y$ (MPa)	$69 \pm 4$	$44 \pm 1$	$29.7 \pm 0.3$	$23.9 \pm 0.5$	$52 \pm 5$	$40 \pm 2$	$27.5 \pm 0.1$	$25.9 \pm 0.5$

**Table 4**

Evolution with the temperature of the tensile properties, such as the Young's modulus and the yield stress, of the heterophasic block copolymers with 12 wt% of ethylene content, EPBC12-1 and EPBC12-2.

	EPBC12-1				EPBC12-2			
$T$ (°C)	$-80$	$-40$	$0$	$23$	$-80$	$-40$	$0$	$23$
$E$ (MPa)	$2900 \pm 200$	$1900 \pm 200$	$1180 \pm 50$	$1000 \pm 300$	$2770 \pm 90$	$2000 \pm 100$	$1650 \pm 90$	$750 \pm 20$
$\sigma_Y$ (MPa)	$41.7 \pm 0.3$	$31.7 \pm 0.1$	$24.7 \pm 0.5$	$21 \pm 1$	$55 \pm 5$	$37 \pm 2$	$21.2 \pm 0.2$	$20.1 \pm 0.1$



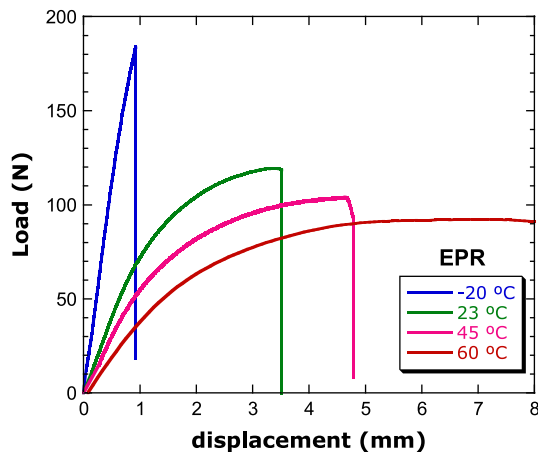


Fig. 2. Load–displacement records of fracture tests at  $-20$ ,  $23$ ,  $45$  and  $60$  °C for EPR.

reducing the temperature, the glassy state spread out through the polymer, stiffening the material as a whole and nullifying its deformation capability [18,20,25,32,46,47].

In general, the well known trends were attained, that is, the increase in ethylene content implied a decrease in both the Young's modulus and the yield stress (Tables 2–4). The only worth mentioning result in this sense is that for the block copolymers with similar ethylene content, the Young's modulus of the copolymers with higher molecular weight showed lower values, being these differences more accentuated close and below the glass transition temperature of the elastomeric phase (Tables 3 and 4). The copolymers with higher molecular weight presented lower degrees of crystallinity (Table 1), which accounts for the reduction of the elastic modulus as this parameter is highly dependent on the hardest part of the structure, that is, the crystalline region [18,20,32,46,47].

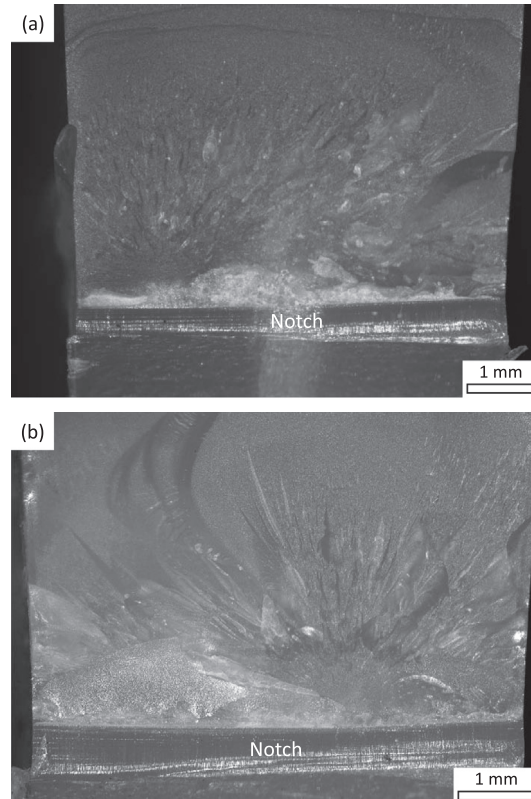


Fig. 3. Fracture surfaces at  $-20$  °C of (a) PP and (b) EPR. Tiny stress whitening region close to the notch is discernible due to craze formation.

#### 4.2. Fracture characterization

According to the similitude of behaviours displayed by the materials, the following analysis is divided into two groups: fracture behaviour of monophasic polymers such as PP and EPR, and fracture behaviour of heterophasic polymers such as EPBCs.

#### 4.3. Monophasic polymers

The load–displacement curves in the temperature range between  $-20$  and  $60$  °C were similar for the propylene homopolymer, PP, and the random copolymer, EPR. By way of illustration, Fig. 2 shows the load–displacement records obtained at different temperatures for EPR. Both PP and EPR fractured in an entirely brittle mode at  $-20$  °C and in a completely ductile manner at  $60$  °C, but the fracture at  $23$  and  $45$  °C was unstable displaying nonlinear load–displacement records. The combination of non-linearity and fracture instability at  $23$  and  $45$  °C indicated that under quasi-static conditions, these two testing temperatures are within the ductile-to-brittle transition region. Moreover, the wide difference between these two testing temperatures and these, in turn, with the glass transition temperatures of the PP and EPR denotes that the brittle–ductile transition is a gradual transition [11]. Accordingly, the three-parameter Weibull mode was applied to determine the fracture behaviour. On the other hand, the brittle behaviour displayed at  $-20$  °C met the requirements of the LEFM approach while the ductile response at  $60$  °C with the entire fulfilment of the EPFM hypothesis allowed the construction of the  $J$ – $R$  curve with the help of the normalization method. Next, the fracture characterization of PP and EPR in the brittle region,  $-20$  °C, within the ductile-to-brittle transition region,  $23$  and  $45$  °C, and in the ductile zone,  $60$  °C, is described.

#### 4.4. Brittle behaviour

The fracture behaviour at  $-20$  °C of both PP and EPR was completely brittle (Fig. 2) and the application of the LEFM method described in ISO13586 standard provided values of the critical energy release rate,  $G_{IC}$ , of  $3.5 \pm 0.1$  and

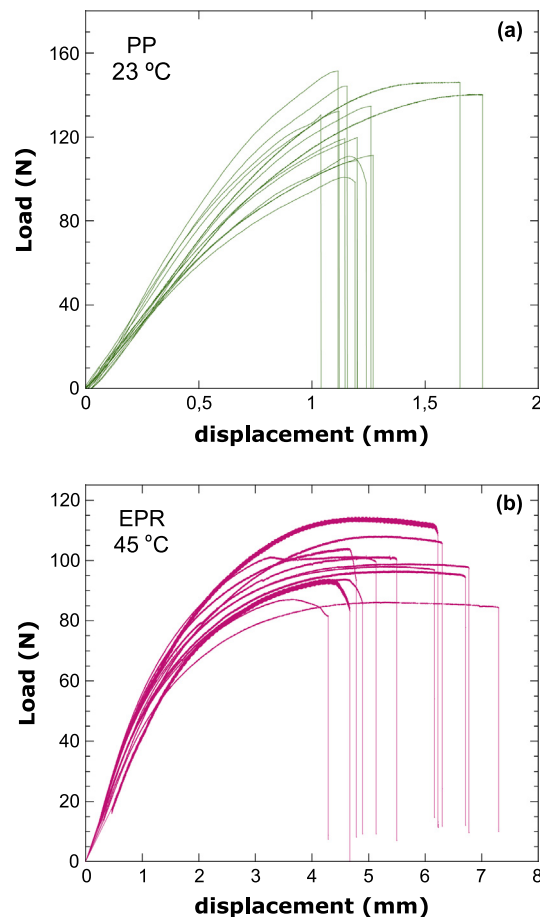


Fig. 4. Typical load–displacement curves of fracture tests (a) at  $23$  °C for PP and (b) at  $45$  °C for EPR.



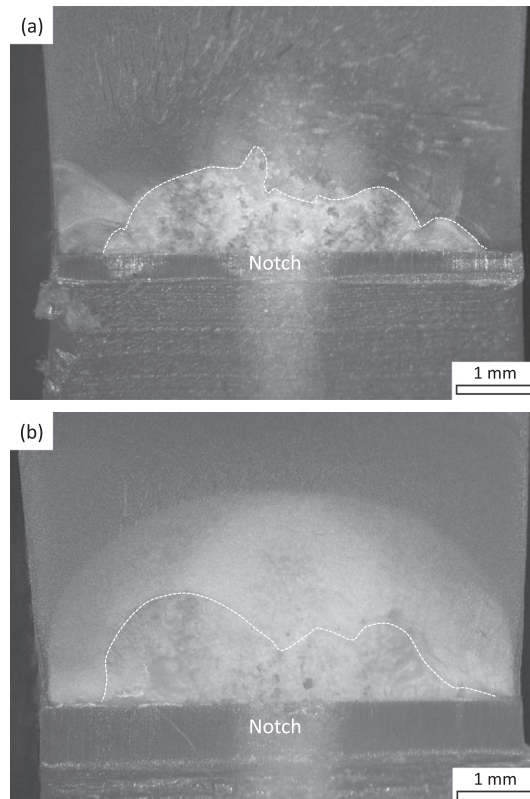
$3.8 \pm 0.2 \text{ kJ/m}^2$ , respectively. The crack initiation energy of the random copolymer was slightly higher than that of the pure polypropylene but not significant enough because of the low ethylene content in the copolymer and the glassy state of the polymer at this testing temperature.

Fig. 3a and b shows the fracture surface of the PP and EPR at  $-20^\circ\text{C}$ , respectively. The micrographs display a rough surface, typical of the brittle mode. Even though a small stress whitened region is discernible next to the notch in the polypropylene homopolymer (Fig. 3a) indicative of the development of crazes during the fracture process even at temperatures well below its glass transition temperature [12,19,28].

#### 4.5. Brittle-ductile transition region

Sets of 60 and 38 identical specimens were tested at 23 and  $45^\circ\text{C}$  for PP, while fracture toughness tests of sets of 58 and 57 samples were performed at 23 and  $45^\circ\text{C}$  for EPR. Fig. 4a and b shows typical load–displacement records from completed fracture tests at  $23^\circ\text{C}$  for PP and at  $45^\circ\text{C}$  for EPR, respectively. Analogous curves were obtained for EPR at  $23^\circ\text{C}$  and for PP at  $45^\circ\text{C}$ . As observed, the curves of identical samples appeared widely scattered and the general trend is that the unstability was prone to occur before the maximum load plateau at  $23^\circ\text{C}$  and after it at  $45^\circ\text{C}$  for both polymers.

Fig. 5a and b shows the fracture surfaces of PP at 23 and  $45^\circ\text{C}$ , respectively. Three regions were distinguishable. Next to the notch, there is a stress-whitened rough region with an irregular profile related to stable crack growth, followed by a smooth stress-whitened zone with a very diffuse boundary associated with plastic deformation, and behind it, the remainder surface, completely plain and unwhitened. The main deformation mechanism in PP is crazing, and this brittle behaviour occurs when the multiple crazes that appear to develop both in transpherulitic and interspherulitic modes surrounding the crack tip are not able to proceed further [12,19,20,22,28,34]. The deflected crack path observed within the stress-whitened region was attributed to a combination between a plane strain state in the centre of the specimen to a plane stress state in the surface, that is, contributions from both crazing and shear yielding [4,5,22,28,42]. Even though, this polymer was sensitive to the testing temperature within the ductile-to-brittle transition region as the areas related to both stable crack growth and plastic deformation of the specimens tested at  $45^\circ\text{C}$  were larger than those corresponding to the samples tested at  $23^\circ\text{C}$ . Thus, the testing temperature of  $45^\circ\text{C}$  was close to the ductile behaviour region while the temperature of  $23^\circ\text{C}$  was near the brittle behaviour zone. Since stable crack growth did not exceed the 10% of the remaining ligament (Eq. 4) no censoring strategy was applied [34,44].



**Fig. 5.** Fracture surface of PP: (a) at  $23^\circ\text{C}$  and (b) at  $45^\circ\text{C}$ . The irregular profile of stable crack growth has been outlined with white dots.

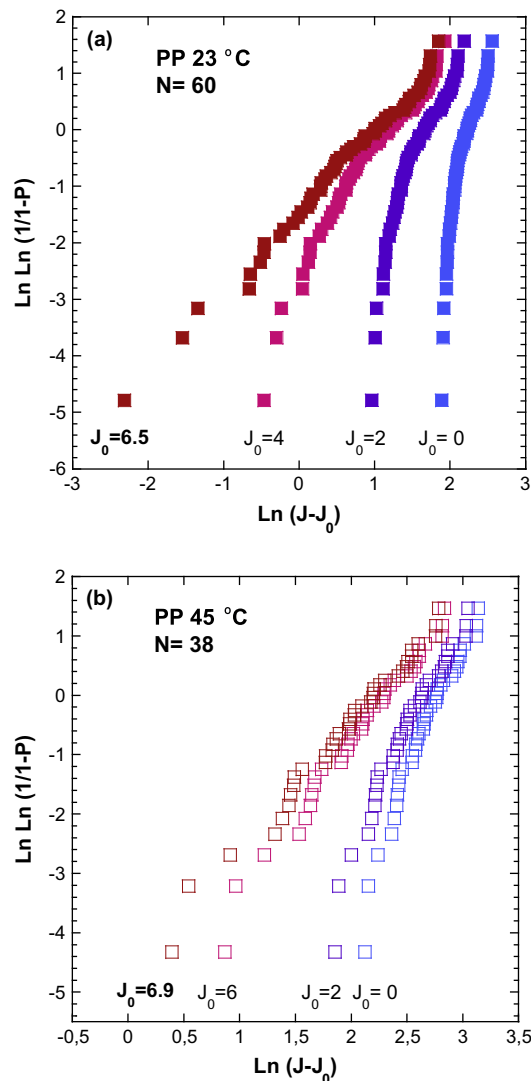
The toughness values displayed by individual replicas of PP ranged from 6.6 to 12.9 kJ/m<sup>2</sup> at 23 °C, and from 8.4 to 23.1 kJ/m<sup>2</sup> at 45 °C (Table 5). The mean values, together with their standard deviations, were  $9.0 \pm 1.7$  and  $15.0 \pm 3.9$  kJ/m<sup>2</sup> at 23 and 45 °C, respectively. Fig. 6a and b shows the straight-line regression evolution of PP homopolymer taking different  $J_0$  values at 23 and 45 °C, respectively. The numeric values of the calculated parameters and the regression coefficients are shown in Table 5. The toughness lower bound values were 6.5 and 6.9 kJ/m<sup>2</sup> at 23 and 45 °C, respectively. The value of the fracture toughness at 23 °C is in accordance to those found in the literature for similar pure polypropylenes [12,28,34,35].

Fig. 7a and b shows the fracture surfaces of EPR at 23 and 45 °C, respectively. Again three regions were evident. The failure also occurred in a brittle manner caused by crazing [19]. Some stable crack growth was detectable, with lengths of 300 and

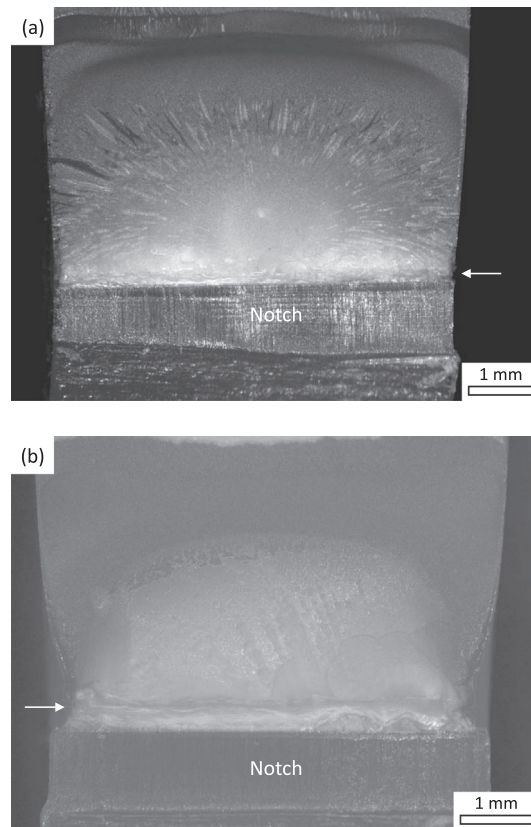
**Table 5**

Weibull parameters for PP and EPR sets at 23 and 45 °C.

	<i>T</i> (°C)	Experimental data set				3W-P model parameters			
		<i>N</i>	<i>J</i> <sub>cmin</sub> (kJ/m <sup>2</sup> )	<i>J</i> <sub>cmax</sub> (kJ/m <sup>2</sup> )	<i>J</i> <sub>med</sub> (kJ/m <sup>2</sup> )	<i>m</i>	<i>C</i>	<i>J</i> <sub>0</sub> (kJ/m <sup>2</sup> )	<i>R</i>
PP	23	60	6.6	12.9	$9.0 \pm 3.9$	1.44	9.26	6.5	0.9879
	45	38	8.4	23.1	$15.0 \pm 3.9$	2.19	16.07	6.9	0.9922
EPR	23	58	10.7	34.9	$19.2 \pm 4.7$	2.51	20.60	8.5	0.9817
	45	57	17.0	57.0	$31.6 \pm 9.2$	2.25	33.76	11.4	0.9915



**Fig. 6.** Weibull statistical approach:  $J_0$  determination by 3P-W fit to experimental points of PP at (a) 23 °C and (b) 45 °C.



**Fig. 7.** Fracture surface of EPR: (a) at 23 °C and (b) at 45 °C. The boundary between the stable crack growth region and the stress-whitening zone has been marked with an arrow.

500  $\mu\text{m}$  utmost at 23 and 45 °C, respectively. Thus, no censoring criterion due to stable crack growth was needed. Finally, the length and strength of the stress-whitened region were larger and more intense at 45 than at 23 °C.

The toughness values of identical replicas of EPR ranged from 10.7 to 34.9  $\text{kJ/m}^2$  at 23 °C, and from 17.0 to 57.0  $\text{kJ/m}^2$  at 45 °C (Table 5). The mean values, together with their standard deviations, were  $19.2 \pm 4.7$  and  $31.6 \pm 9.2$   $\text{kJ/m}^2$  at 23 and 45 °C, respectively. Fig. 8a and b shows the straight-line regression evolution of random copolymer taking different  $J_0$  values at 23 and 45 °C, respectively. The toughness lower bound values were 8.5 and 11.4  $\text{kJ/m}^2$  at 23 and 45 °C, respectively.

As expected, the fracture toughness enhanced for both PP and EPR with raising temperature with improvements of 6% and 34%, respectively. When the temperature was increased, the deformation within the amorphous phase became less and less restrained, and this resulted in a tougher behaviour [1,19]. In addition, the well-known trend that the ethylene–propylene random copolymer presented higher fracture toughness than the pure polypropylene independently of the testing temperature because of the presence of the ethylene phase was also attained [1].

#### 4.6. Ductile behaviour

At 60 °C, both PP and EPR were entirely ductile and the EPFM normalization method allowed us to calculate easily the  $J$ – $R$  curves under static loading conditions. Fig. 9 shows the  $J$ – $R$  curves, together with the fit of the  $J$ -crack growth resistance curve to the power law  $J = C \cdot \Delta a^N$  with  $N < 1$ , and the corresponding fracture toughness values,  $J_{IC}$ . The resistance curve of the random copolymer was above that of the pure polypropylene and consequently, the fracture toughness of the former was higher than that of the latter.

Fig. 10a and b shows the fracture surface features of PP and EPR at 60 °C, respectively. Both polymers displayed a completely stable fracture where crack growth was clearly discernible from the highly stress whitened region. In case of EPR, shear leaps generated during stable crack propagation reflected the predominantly plane stress conditions at these experimental conditions (Fig. 10b).

#### 4.7. Heterophasic copolymers

Typical load–displacement records of fracture tests carried out at 23, 0, –40 and –80 °C on EPBC9-1 are combined in Fig. 11. For all the copolymers, the mechanical response for temperatures above the glass transition temperature of the

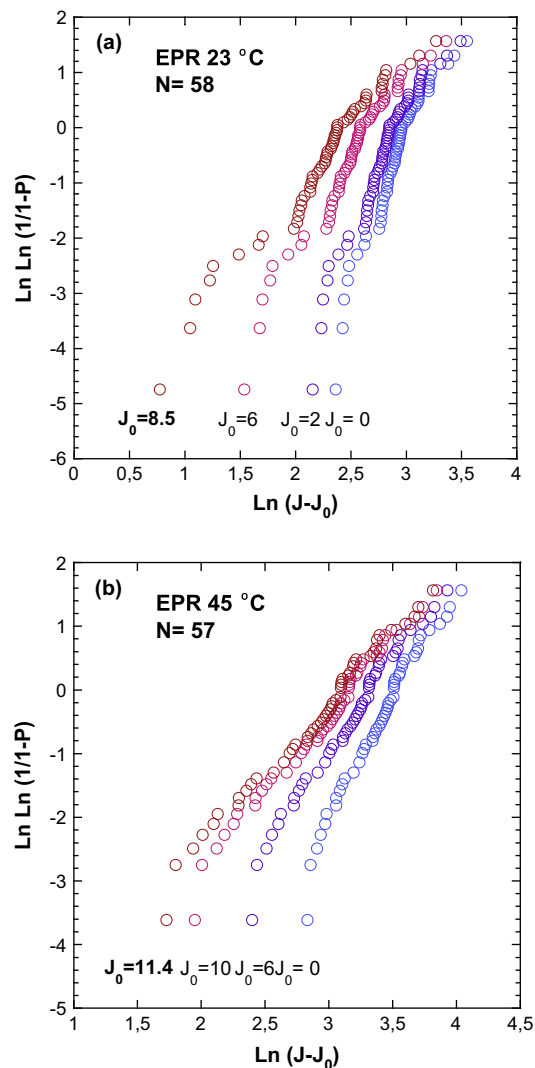


Fig. 8. Weibull statistical approach:  $J_0$  determination by 3P-W fit to experimental points of EPR at (a) 23 °C and (b) 45 °C.

elastomeric phase was clearly non-linear and below it, that is, at  $-80$  °C, the load–displacement diagrams were mainly linear and elastic till rupture.

The representative resistance curves at 23, 0 and  $-40$  °C for the copolymers with 9 wt% ethylene content, EPBC9-1 and EPBC9-12, and with 12 wt% ethylene content, EPBC12-1 and EPBC12-2, are gathered in Figs. 12 and 13, respectively. Power law fits of  $J = C \cdot \Delta a^N$  type were also included. Attending to the fittings, small differences could be appreciated among the  $J$ – $R$  curves at 23, 0 and  $-40$  °C for every copolymer. Even those curves obtained below the glass transition temperature of the PP matrix, at 0 and  $-40$  °C (glassy state), scarcely differed from those determined at 23 °C. Not even a tendency could be drawn, as the  $J$ – $R$  curves at the lowest temperature were not always below those determined at higher temperatures (Fig. 12a and 13a).

Fig. 14 displays the evolution of the fracture toughness,  $J_{IC}$ , with the testing temperature for all the block copolymers under study. Fracture toughness values,  $J_{IC}$ , followed the same trend as the  $R$ -curves. This parameter determined under static loading conditions was not influenced by the temperature as long as the testing temperature was higher than the glass transition temperature of the elastomer phase. By contrast, well below the glass transition of the elastomeric phase, at  $-80$  °C, there was an abrupt drop in the fracture toughness, more noticeable as the molecular weight of the copolymer was lower. Under the glass transition temperature of the elastomer phase, this behaves like solid particles and does not provide the necessary dispersed phase/matrix stiffness difference required to induce a stress concentration and to promote further toughening effects [13].

Attending to the influence of the supramolecular parameters (ethylene content and molecular weight), the fracture toughness is clearly governed mainly by the molecular weight: the higher the molecular weight the larger the fracture

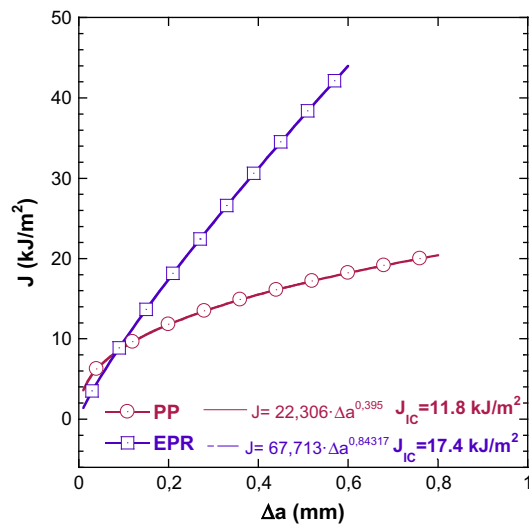


Fig. 9.  $J$ - $R$  curves for PP and EPR at 60 °C determined via the normalization method [44].

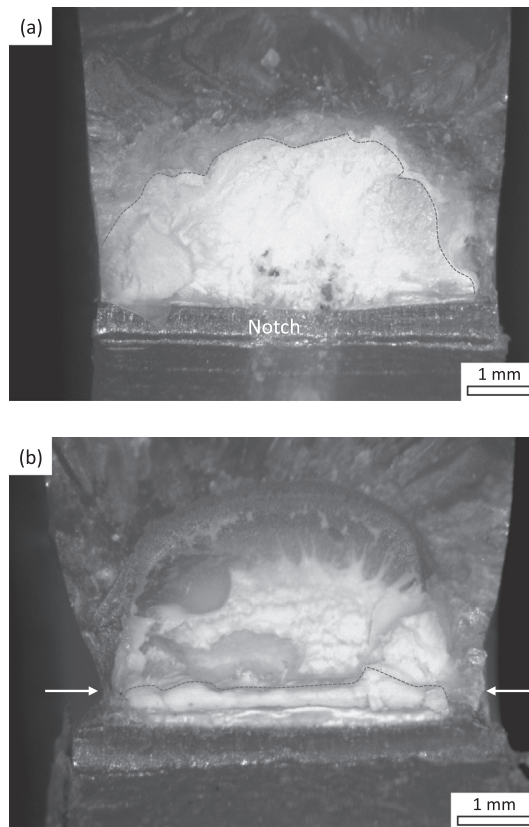
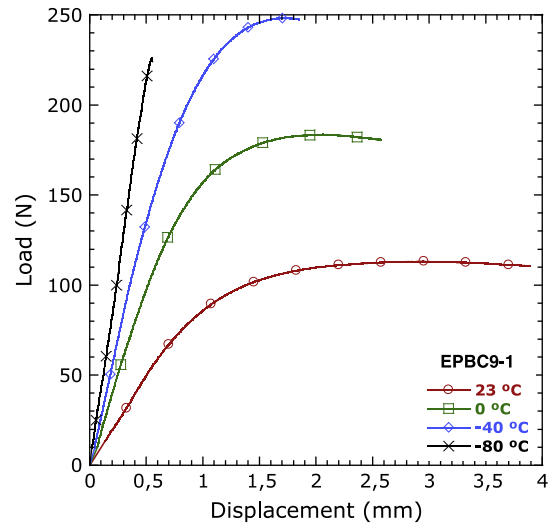
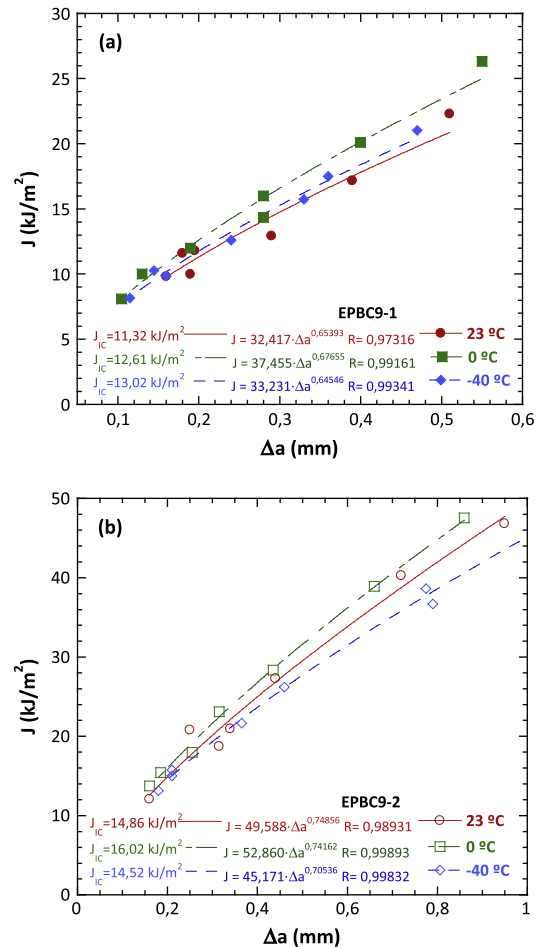


Fig. 10. Fracture surfaces at 60 °C of (a) PP and (b) EPR. The arrows in (b) point out the shear lips created during stable crack propagation and the stable crack growth zone has been outlined with grey dots.

toughness independently of the testing temperature for polymers with similar ethylene content. Moreover, the deterioration in the fracture toughness values below the glass transition of the elastomeric phase is less severe as the molecular weight is increased (EPBC9-2 and EPBC12-2). In case of semicrystalline copolymers, the strength of the fibrils which join the crystalline areas is enhanced with the molecular weight. This strength increase leads to the improvement on the fracture behaviour [9,18,32]. However, these differences with the molecular weight contrast with the analysis as a function of the ethylene

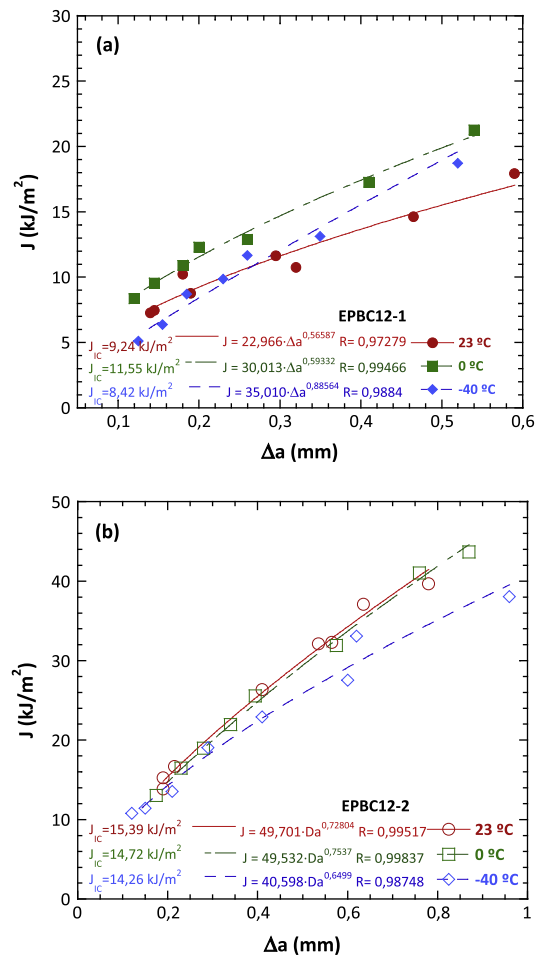


**Fig. 11.** Load–displacement records of fracture tests at 23, 0, –40 and –80 °C for EPBC9-1. The only tests brought till rupture were those carried out at –80 °C.

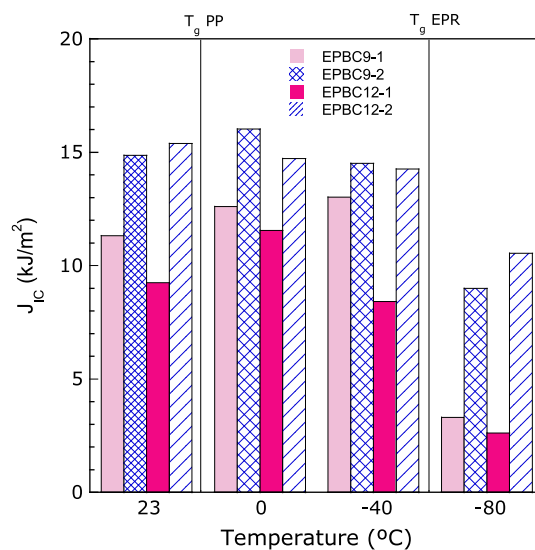


**Fig. 12.** Resistance curves at 23, 0 and –40 °C of copolymers with an ethylene content of 9 wt%, EPBC9-1 and EPBC9-2 obtained via the  $J$ -integral multiple specimen method [43].

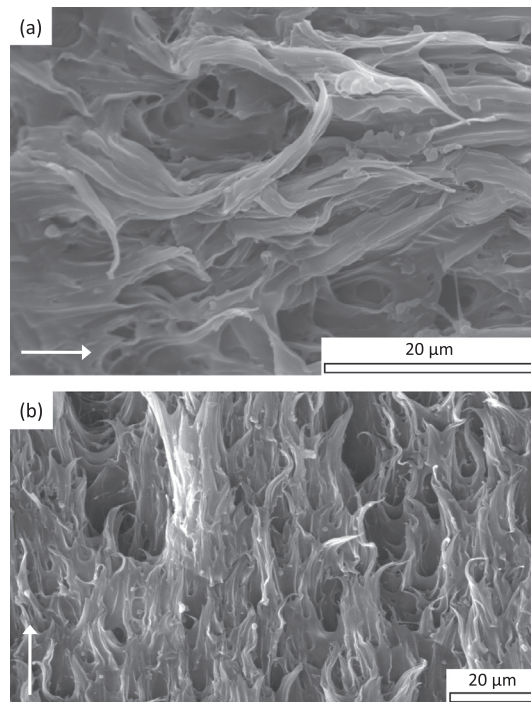




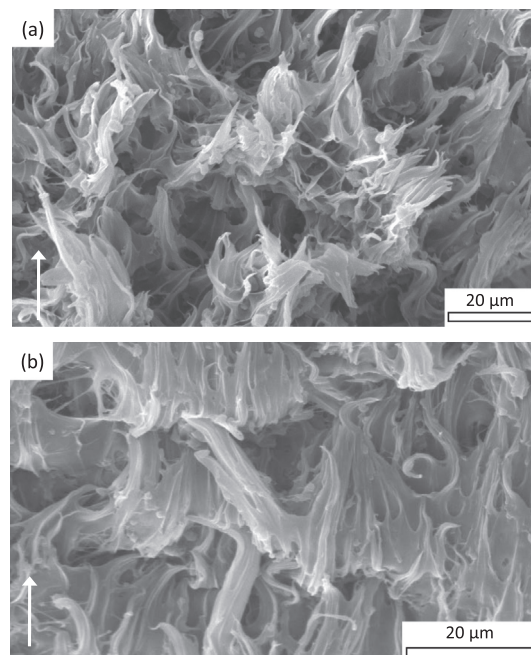
**Fig. 13.** Resistance curves at 23, 0 and  $-40$  °C of copolymers with an ethylene content of 12 wt%, EPBC12-1 and EPBC12-2 obtained via the  $J$ -integral multiple specimen method [43].



**Fig. 14.** Evolution of the fracture toughness,  $J_{IC}$ , with decreasing temperature for EPBC9-1, EPBC9-2, EPBC12-1 and EPBC12-2 copolymers.

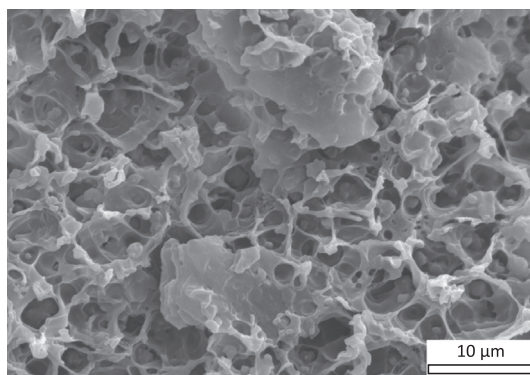


**Fig. 15.** Fracture surfaces associated to the stable crack growth region obtained from the SENB fracture toughness tests on copolymers with 9 wt% ethylene content at 23 °C via scanning electron microscopy: (a) EPBC9-1 and (b) EPBC9-2. The arrow points out the crack growth direction.



**Fig. 16.** Fracture surfaces associated to the stable crack growth region obtained from the SENB fracture toughness tests on copolymers with 12 wt% ethylene content at 23 °C via scanning electron microscopy: (a) EPBC12-1 and (b) EPBC12-2. The arrow points out the crack growth direction.

content. As for similar molecular weight, the fracture toughness values were not so remarkable modified with the ethylene content, and the copolymers with 12 wt% ethylene content even showed slightly lower values than those with 9 wt%, except for the case between EPBC9-1 and EPBC12-1 at  $-40$  °C (Fig. 17). In any case, the range of ethylene content under study was so reduced that tiny changes were expected in the fracture values.



**Fig. 17.** Stress whitening region ahead of the stable crack growth zone obtained from the post-mortem fracture surfaces of EPBC9-1 tested at 23 °C.

Figs. 15 and 16 show the morphology of the stable crack growth region associated to the fracture surfaces tested at 23 °C of the copolymers with 9 wt%, EPBC9-1 and EPBC9-2, and with 12 wt% ethylene content, EPBC12-1 and EPBC12-2, respectively. It is worth mentioning that all the copolymers suffered intense whitening due to plastic deformation before any crack growth. The fracture surfaces displayed a macroductile tearing formed by broken stretched filaments oriented in the direction to the crack propagation. Attending to previous works [9,13,14,19,21], upon loading, small cavities are nucleated at the weak points of the copolymer such as the boundary between the EPR particles and the PP matrix (Fig. 17) or the intercrystalline zones in the PP matrix. These voids are stabilised by fibrillar bridges of PP filaments which are plastically deformed and orientated. With consequent increase in deformation, excessive plastic flow occurs at these PP filaments and a stable crack nucleates and propagates through the closely PP bridges giving rise to the fibrillated morphology with ductile pulling of ligaments left behind.

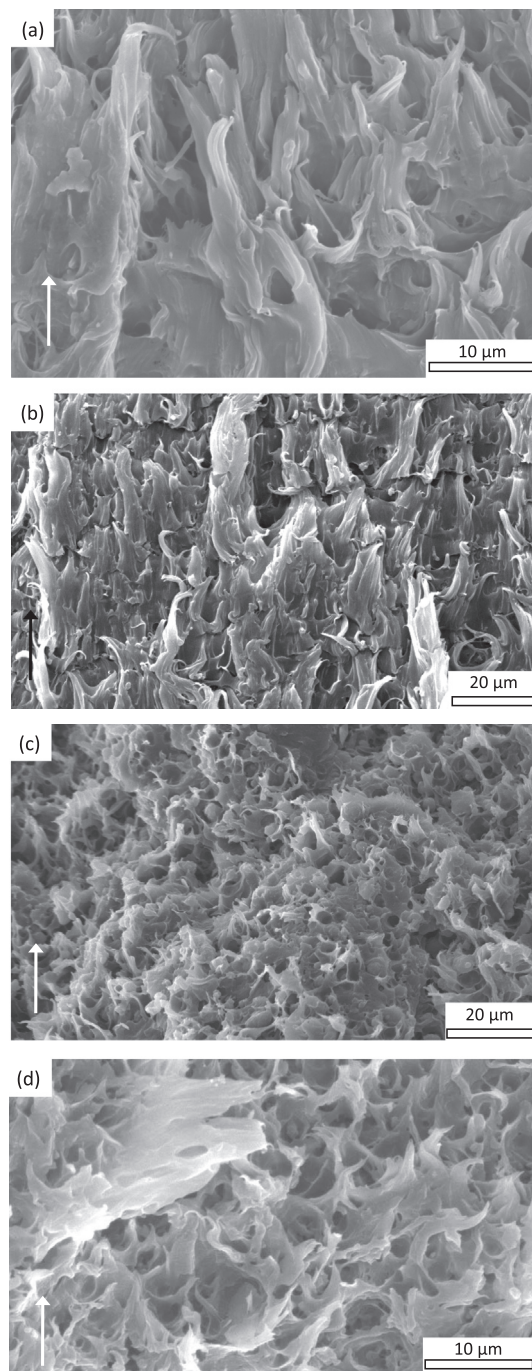
The fractographic study carried out on the post mortem fracture surfaces of every copolymer tested at 0 (Fig. 18) and –40 °C revealed the reasons why at these testing temperature and under quasi-static conditions a pronounced non linear response occurred despite the glassy state of the PP matrix, with fracture parameters very similar to those obtained at room temperature. At 0 °C, the copolymers presented a macroductile tearing (Fig. 18) although the degree and extension of plastic fibrillation of the PP matrix is less accentuated than at 23 °C (Figs. 15 and 16). The very same occurred at –40 °C, being the plastic flow of the matrix much less enhanced than at 0 °C. At both temperatures, it was visible the presence of voids through the ductile tearing of the PP matrix. Attending to the works by Doshev et al. [13] and Starke et al. [14], below the glass transition temperature of the PP matrix, the fracture behaviour falls on the EPR particles: these elastomeric particles relieve the volume strain by cavitation. At the particle/matrix interface as well as within the EPR particles themselves, plastic deformation is induced around the glassy PP matrix, with mechanical properties at 0 °C and –40 °C higher than at 23 °C. On the other hand, only qualitative differences could be appreciated between the fracture surfaces for copolymers with the same ethylene content and different molecular weights at 0 °C and –40 °C: The ductile tearing of the PP matrix seemed to be more pronounced in case of the copolymers with higher molecular weight, EPBC9-2 (Fig. 18b) and EPBC12-2 (Fig. 18d) than in those with lower molecular weight, EPBC9-1 (Fig. 18a) and EPBC12-1 (Fig. 18c). In turn, among the fracture surfaces of the copolymers with similar molecular weight but different ethylene content, no differences were detected at the distinct testing temperatures.

At –80 °C, well below the glass transition temperature of the EPR phase, the appearance of the fracture surfaces was completely brittle, although a closer examination of the zone next to the initial sharp notch evidenced the presence of a small plastic deformation area (Fig. 19). Some PP fibrillation due premature developing cavitation of EPR particles in all the copolymers was noticeable in this area. The diminish, to almost its total disappearance, of the craze area and the surrounding plastic region, and thus the reduction of the deformation energy [6,13,36], is the reason of the drastic drop in the fracture toughness values (Fig. 14).

As in the analysis realized at higher temperatures, only qualitative differences could be observed among the copolymers with different molecular weight. As the small plastic deformation of the copolymers with high molecular weight, EPBC9-2 (Fig. 19b) and EPBC12-2 (Fig. 19d) showed an initial plastic pulling of the PP matrix a bit more marked than that of the copolymers with low molecular weight, EPBC9-1 (Fig. 19a) and EPBC12-1 (Fig. 19c). No changes were also appreciable between the fracture surfaces of the copolymers with the same molecular weight and distinct EPR content.

## 5. Discussion

While the fracture toughness of the monophasic polymers raised with increasing temperature, the fracture toughness of the block copolymers was not sensitive to the temperature under static loading conditions when the testing temperature is above the glass transition temperature of the elastomer phase. This contrasts with the mechanical properties which varied strongly. No marked change either in the fracture toughness or the fracture surfaces was observed when going under the

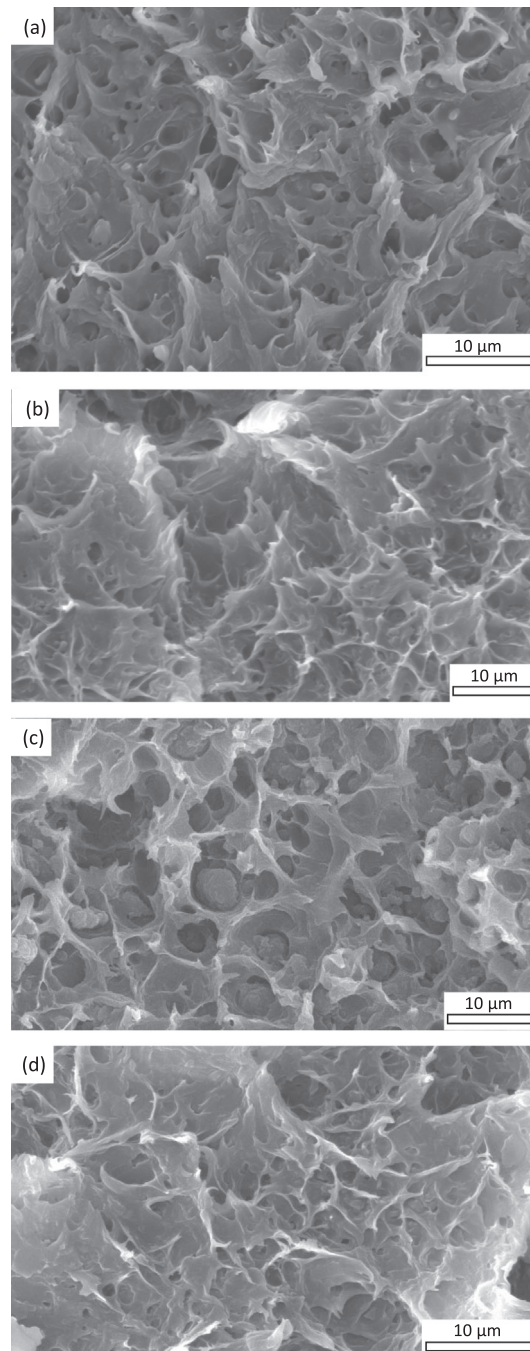


**Fig. 18.** Fracture surfaces associated to the stable crack growth region obtained from the SENB fracture toughness tests at 0 °C via scanning electron microscopy: (a) EPBC9-1, (b) EPBC9-2, (c) EPBC12-1 and (d) EPBC12-2. The arrow points out the crack growth direction.

glass transition temperature of the PP matrix. The elastomer particles were responsible of the no loss of integrity in this temperature range via two additive mechanisms. First of all, they acted as stress concentrators and relieved the volume strain by cavitation, but at the same time, through the well bonded particle/matrix interface, load transfer occurred which was capable of promoting plastic deformation in a stiffer and glassy PP matrix before initiation of stable crack propagation.

Under quasi-static conditions, the fracture toughness increased with ethylene content. The copolymers presented improved fracture toughness with respect to the pure polypropylene despite the lower mechanical properties of the former. This contrasts with the results obtained by Fasce et al. [12,19]. In this case, the presence of the elastomer not only enhances





**Fig. 19.** Fracture surfaces associated to the zone close to the initial sharp notched obtained from the fracture toughness tests on SENB at  $-80^{\circ}\text{C}$  via scanning electron microscopy: (a) EPBC9-1, (b) EPBC9-2, (c) EPBC12-1 and (d) EPBC12-2.

the stability of a growing crack improving the high rate response but also retards the crack growth initiation. At low loading rates, the toughening mechanisms via cavitation of the particles and plastic deformation are developed completely before the crack reinitiates its growth. Consequently, the fracture toughness is improved as the ethylene content is increased.

Concerning the influence of the supramolecular properties, the fracture behaviour of the copolymers was more dependent on the molecular weight than on the ethylene content. The reason is that for the chosen copolymers, the differences on the molecular weight were as high as 73% over the 33% on the ethylene content. As known, the strength of PP filaments occurring during the macroductile tearing of the PP matrix during the deformation process is directly proportional to the molecular weight. Hence, the higher the molecular weight the bigger the strength and deformation capability of PP filaments before

their breakage [10,12,13,32]. This accounts for the improvement of the fracture toughness of copolymer with lower ethylene content but higher molecular weight. However, this is not the general trend. The random copolymer presented enhanced fracture toughness compared to the PP homopolymer despite the molecular of the former was 50% lower.

## 6. Conclusions

Under static loading conditions, propylene based polymers may exhibit a wide mechanical response and fracture behaviour depending on the type, morphology and temperature range.

For temperatures above the glass transition temperatures of single-phase polypropylenes as neat polypropylene and random copolymer, the behaviour was completely ductile. However, the fracture behaviour did not follow the same deformation response, that is, it was not entirely ductile. This compelled the use of different Fracture Mechanics methodologies to determine the fracture toughness. For the temperatures closer to the glass transition temperature, the scatter and semi-brittle behaviour of these polymers caused the use of a statistical approach for the determination of the fracture toughness; while at higher temperatures, the EPFM methodologies could be applied. On the other hand, although the mechanical response was semi-brittle below the glass transition temperatures, the fracture behaviour was entirely brittle which allowed the use of LEFM approach.

For block copolymers, a wide range of temperature going from below the glass transition temperature of the elastomer phase to well above the glass transition temperature of the PP matrix was analyzed. In this case, the deformation and fracture patterns coincided. The response was entirely ductile above the glass transition temperature of the elastomer phase and completely brittle below it, allowing the application of the EPFM and LEFM methods, respectively.

Polypropylene homopolymer and random copolymer presented enhanced fracture toughness with increasing the temperature for temperatures above their glass transition temperatures. However, the fracture toughness of the block copolymers was not influenced by the temperature at low loading rates as the temperature remains above the glass transition temperatures. This contrasted with the varying mechanical properties with the temperature of these copolymers. The toughening mechanisms promoted via the load transfer generated through the interface between a glassy stiffened matrix and a ductile elastomer explained these results.

In relation to the influence of the structural parameters, the fracture toughness increased with the ethylene content generally. However, in case of the copolymers with similar molecular weight, the fracture toughness of the copolymers with higher ethylene content did not always showed clearly improved fracture toughness. Hence, the molecular weight seemed to control the fracture behaviour of the copolymers even more than the ethylene content, especially at low temperatures. Indeed the strength of the PP filaments developed during the deformation process depends upon molecular weight.

## Acknowledgement

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