

TEMPERATURE DEPENDENCE OF THE FRACTURE BEHAVIOUR OF POLYPROPYLENE FILMS

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ABSTRACT

In this work, the fracture of films of one Polypropylene (PP) Homopolymer and three Ethylene-Propylene (EPBC) Block Copolymers with different ethylene content (EC) at temperatures around their glass transition (T_g) is investigated by means of the Essential Work of Fracture (EWF) Method. The fracture behaviour is studied at low speeds (2 mm/min) for the different materials, in the range from -40 to +70°C. The materials are tested in the form of extruded films of 90 μm thickness, in a DENT geometry, and annealed 1h at 120°C. The homopolymer is found to be much more temperature-sensitive than the EPBC with lower EWF values at $T < T_g$ and the opposite trend at $T > T_g$. The ductile-brittle transition of the homopolymer that occurs below its T_g is suppressed for the EPBC in the temperature range studied. The variations of the EWF fracture parameters with T are consistent with those of a previous study in LDPE, and are explained in terms of molecular relaxation, ethylene phase content, and changes in the yield and fracture stresses. Some limitations of the EWF method are found with the more ductile materials, which show the necking phenomenon with DENT specimens at the higher temperature studied.

INTRODUCTION

Polypropylene (PP) is one of the most used plastics at present in a very wide range of applications [1]. Apart from moulded pieces and fibres, a high percentage of its use is in the form of films and sheets, and it is of most importance to find a reliable method to measure their toughness properties. As polypropylene is brittle at temperatures under its glass transition (from 0 to 20°C) or at impact speeds, EPBC (ethylene-propylene block copolymers or impact copolymers) are used in some applications where an increase in toughness is required. However, a previous study [2] on the fracture behaviour of films by using the Essential Work of Fracture (EWF) concept showed that at room temperature (RT) PP is tougher than EPBC. There is hence a need to understand the fracture toughness behaviour of these toughened systems tested under low molecular relaxation conditions (ie. low temperatures and/or high strain rates). It is the purpose of this work to contribute to this understanding by performing and analysing the EWF tests at different temperatures around T_g (and in the service temperature range) with the materials selected.

THEORY

Recent papers have shown that the EWF procedure can be a very useful tool for studying the fracture properties of thin films and sheets of ductile materials [3-8]. The EWF concept was developed initially by Cotterell and Reddel [9] on the basis of Broberg's idea [10], who suggested that the total work of fracture (W_f) dissipated in a pre-cracked body could be divided into the work consumed in two distinct zones, the inner and the outer regions. This method of work partitioning gives rise to the essential work of fracture (W_e) and the non-essential (or plastic) work of fracture (W_p), respectively. The former corresponds to the work dissipated in the fracture process zone which is a material property for a given sheet thickness; and the latter to the yielding work in the outer surrounding region which depends on the geometry of the specimen tested. Thus, the following relation can be written:

$$W_f = W_e + W_p = w_e l t + w_p \beta l^2 t \quad (1)$$

where w_e is specific essential work of fracture (per unit ligament area), w_p specific non-essential work of fracture (per unit volume), l ligament length, t specimen thickness and β is plastic zone shape factor. The specific work of fracture, is then:

$$w_f = W_f / l t = w_e + \beta w_p l \quad (2)$$

According to this equation, the plot of w_f as a function of l should be a linear relation, whose intercept with the Y-axis and slope would give w_e , and βw_p respectively. Thus, the EWF method consists in testing specimens with different ligament lengths, registering W_f for each (area under the force-displacement curve), plotting the w_f - l diagram and calculating the best-fit regression line. More details about the restrictions on the ligament length and its discussion, according to the European Structural Integrity Society (ESIS) EWF protocol [11] are given elsewhere [8] (and in the references therein).

It has already been demonstrated theoretically that w_e is equivalent to J_C (and thus to G_C) [3], which has also been supported experimentally by different authors [3,12-14]. Thus, the advantage of the EWF method compared to the J -Integral procedure is, in many cases, its experimental simplicity.

MATERIALS

The PP commercial grades chosen were one homopolymer (called H0) and three low-EC block copolymers (EPBC), with 5.5, 7.4 and 12 % ethylene (called C1, C2 and C3, respectively), as determined by Fourier Transformed Infra Red (FTIR) Spectroscopy. The material was received as pellets, and cast-extruded to obtain 90 μm nominal thickness (t) non-oriented films. In order to homogenise the crystal microstructure of the material, which is basically smectic (or "quenched") after rapid cooling [2], the films were annealed for 1 h in a fan-assisted oven at 120°C (controlled to $\pm 2^\circ\text{C}$), producing a transformation of the smectic phase into a monoclinic state.

EXPERIMENTAL

Dynamic Mechanical Analysis

The evolution of the dynamic storage modulus (E') and the loss factor ($\tan \delta$) with temperature was studied in tensile mode on a Dynamic Mechanical Analysis TMA Instruments DMA 2980 apparatus, at 1 Hz and 3 $^\circ\text{C}/\text{min}$, from -100 to 150 $^\circ\text{C}$. The sample dimensions were 10 and 5 mm in gauge length and width, respectively.

Mechanical and Fracture Properties

Tensile tests were conducted on an universal testing machine (Instron 5567) equipped with a 1000 N load cell and an environmental chamber, at different temperatures comprised between -40 and +70 $^\circ\text{C}$ ($\pm 2^\circ\text{C}$) and a

crosshead speed of 2 mm/min. With the aim of increasing the accuracy of the results, the *dumbbell* specimens, tested according to ASTM D638-91 standard, were individually measured in their thickness with an induction based coating measurer (precision of 1 μm). The yield stress (σ_y), considered as the maximum stress, and the elastic modulus were calculated from the engineering stress-strain curves.

The EWF tests were performed on the same equipment and at the same temperature range as the tensile tests at a crosshead speed of 10 mm/min. Deeply double edge-notched samples (DENT, Mode I) were prepared by cutting the sheets into rectangular coupons of total length $Z_t=90$ mm (with a length between the grips of $Z=60$ mm) and a width $W=60$ mm (inset in Figure 1). Initial notches were made perpendicularly to the tensile direction (which coincided with the extrusion direction) with a fresh razor blade, obtaining for each set at least 20 specimens with ligament lengths varying between 5 and 25 mm. The ligament lengths and the thickness were measured before the test using a travelling binocular lens and the same apparatus described above, respectively. The load-displacement curves were recorded, and the absorbed energy calculated by integration of the area under the curve (Figure 1). The ligament length range was selected so that the films fractured in a plane-stress state, what was checked by plotting the net-section maximum stress (σ_{net}) versus ligament length, and observing if the values were consistent with the Hill's prediction of $\sigma_{\text{net}} = 1.15\sigma_y$ in plane-stress [15].

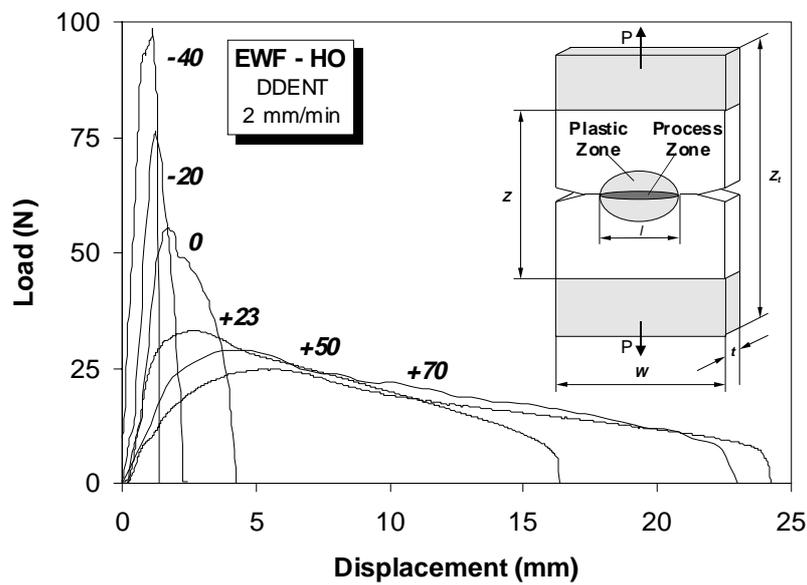


Figure 1: Effect of test temperature on the load-displacement curves of H0 DENT specimens (inset), with a ligament length of around 14 mm.

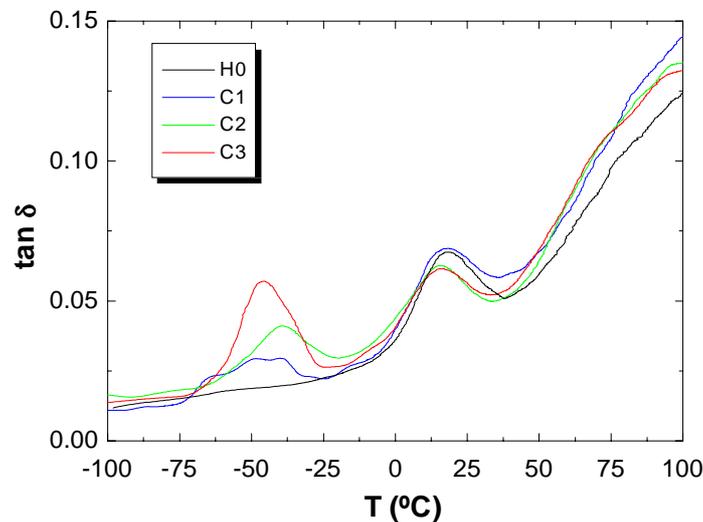


Figure 2: Evolution of $\tan(\delta)$ as a function of temperature for the four materials.

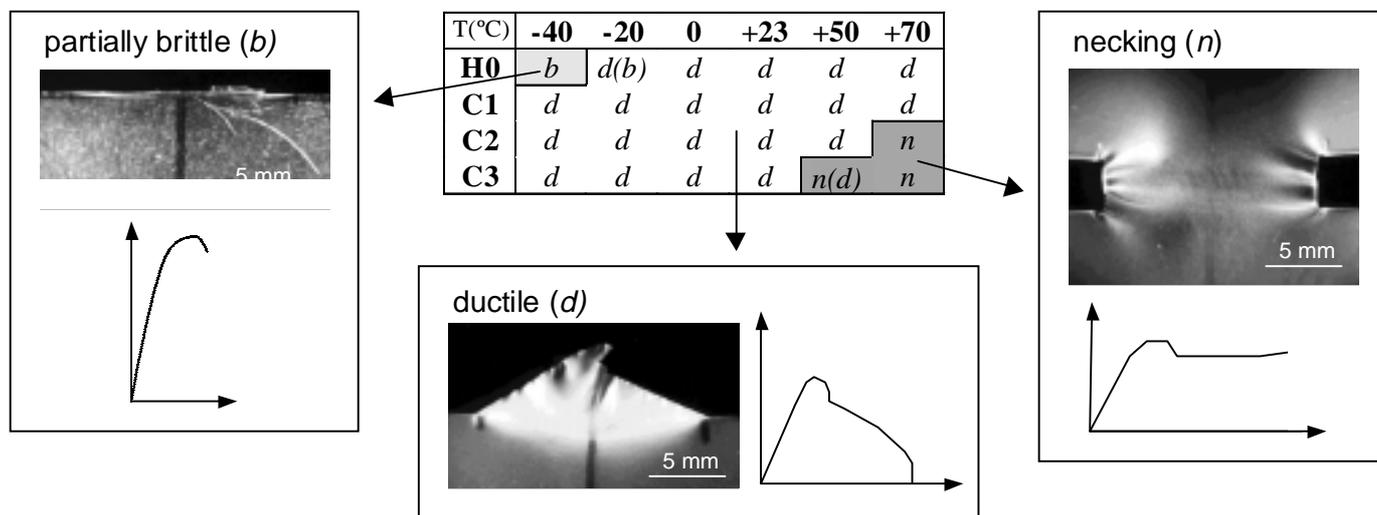


Figure 3. Schematic of the types of fracture of the materials studied as a function of test temperature. The table indicates the failure mode (*b*: semi-brittle; *d*: ductile; *n*: necking). The photomicrographs show the ligament area after fracture and corresponding load-displacement curve for each type.

RESULTS

Viscoelastic Behaviour

In Figure 2, $\tan(\delta)$ is plotted against temperature for the four materials studied. Two clear transitions can be observed around -40°C and 20°C , and these correspond to the glass transition (or β relaxation) of ethylene (T_g^E) and propylene (T_g^P) blocks, respectively [16]. It can be observed that the area of the ethylene transition peak increases sharply with the EC, and that of the propylene peak decreases slightly as the EC increases.

Fracture Behaviour

Three types of fracture behaviours were observed during the tests of the DENT samples: *partially brittle* (*b*), *ductile* (*d*) and *necking with no fracture* (*n*), as summarised in Figure 3. The *partially brittle* fracture was only observed on the H0 samples tested at -40°C and for the longer ligaments samples tested at -20°C , giving a load-deflection curve with a maximum and a load-drop occurring after it. This behaviour discards the use of the EWF for the treatment of the data, since a basic requirement of the theory is that the ligament is fully yielded before the propagation starts [9]. Clearly, this condition is not met in these samples. Neither is Linear Elastic Fracture Mechanics (LEFM) applicable, because the basic requirements of the standard is not satisfied [17]. For the majority of the specimens, the fracture was stable and *ductile* showing the typical behaviour of polypropylene films in a DENT configuration, already described in our previous works [7, 18] as shown in Figure 3. Here, the EWF procedure is applicable. From Figure 1, it can be observed that, as the temperature is raised, the load level decreases but the total deformation is increased. *Necking* is reflected by the very strong crack-tip blunting mechanism that prohibits crack initiation and propagation. This only occurred in the C2 and C3 samples tested at 70°C and some C3 samples at 50°C (Figure 3). As can be seen in Figure 3, the test was closer to a tensile test than to a fracture test, and thus the use of the EWF method of analysis was discarded for samples that showed high degree of crack-tip blunting. It is noted that similar observations have already been found in PP with high ductility and reported in the literature [2, 19].

By plotting the w_f vs. l diagrams of the sets that showed ductile fracture (examples of H0 and C2 are shown in Figure 4), very good linear relationships were obtained (except H0 samples at 50°C , where more scatter was observed). From these straight lines, the values of w_e and βw_p were calculated. It can be seen that, in a wide temperature range, an increase in T produces a progressive raise of the w_f values, giving an increase of the Y-axis intercept (w_e) and the slope (βw_p). However, this trend is much less pronounced as the EC is increased, and the regression lines tend to merge to a single line. In the H0 diagram (Fig. 4a), the data at set -40°C was not used to calculate the fracture parameters because the samples showed unstable fracture, though they are plotted

here for comparison purposes. The results of the fracture parameters for the four materials as a function of T are summarised in Figure 5. However, the trends as shown are only approximations and have to be taken carefully.

Temperature Effect on the Specific Essential Work

It can be seen in Figure 5a that w_e is very sensitive to the temperature for the homopolymer, compared to the copolymers. For H0, w_e increases sharply with T, reaching a maximum at around 40-50°C. Conversely, the copolymers have similar w_e values (~ 45 kJ/m²) up to a threshold temperature (T_{th}). This T_{th} , above which w_e starts to decrease, is found to exist in all materials except C2 (possibly attributed to experimental error). It is noted that T_{th} decreases as the EC increases (ie. 50-60°C for H0 and C1, and 20-30°C for C3).

Temperature Effect on the Specific Non-Essential Work

The dependence of βw_p on temperature is plotted in Figure 5(b). For the homopolymer, βw_p increases dramatically as T increases, reaching a maximum at around 40°C (similarly to the w_e results) and dropping beyond that temperature. Obviously, no βw_p data are available for H0 at -40°C, but one could estimate that this term tends to zero as T decreases, since the plastic zone is almost non-existent at very low T [3]. The steep rise of the data for H0 gradually disappears for EPBC as the EC increases, although the same trend but clearly less marked is apparent. We cannot, however, extrapolate confidently the dependence of βw_p to lower temperatures (T<-40°C), or higher temperatures based on these results.

DISCUSSION

The temperature dependence of the fracture toughness has been treated widely in the literature [20-27]. Sims [22], and particularly Williams and collaborators [23-25] have treated the case of PP systems, basically at impact rates. Much of the work has focussed on the question of whether or not the energy absorption mechanisms have a direct correlation with the molecular relaxation processes occurring in the material. It should however be realised that adiabatic heating at the crack-tip, which produces a blunting phenomenon [26,27], may also increase the toughness. Nevertheless, in the present work, this second consideration may be dismissed as the test rate and the reduced sample thickness do not allow heat accumulation. Hence, an explanation based on molecular relaxation seems useful to understand the experimental results.

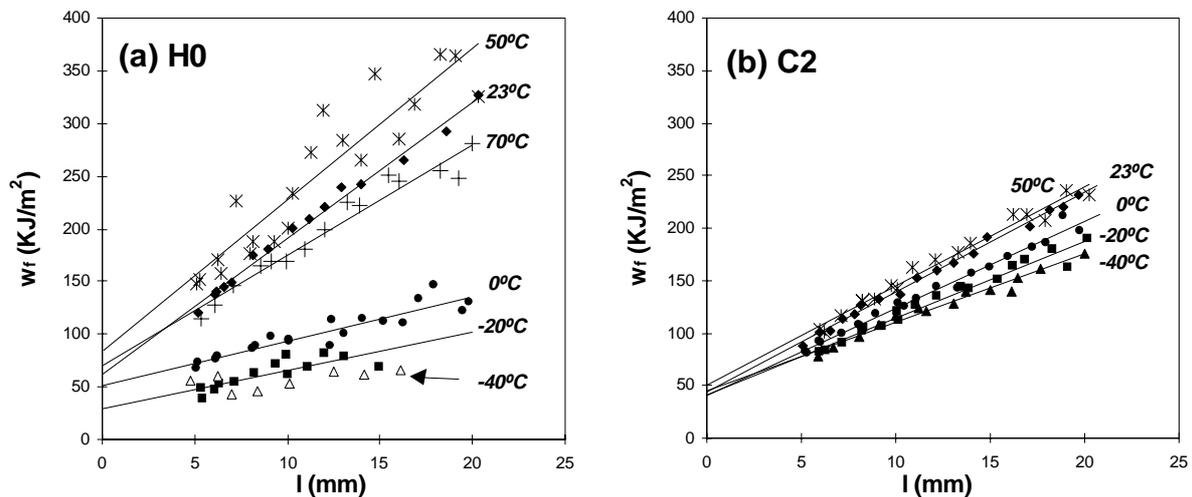


Figure 4: Plots of w_f against l for H0 and C2 at different test temperatures. [+: 70°C, *: 50°C, ◆: 23°C, ●: 0°C, ■: -20°C, ▲: -40°C (Δ: brittle)]

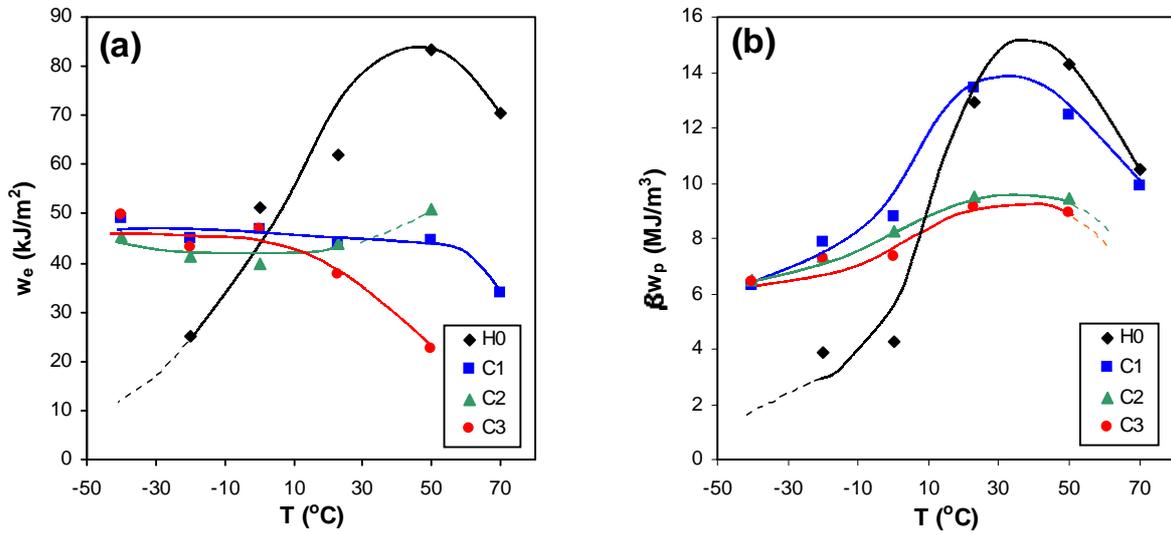


Figure 5: Evolution of w_e and βw_p with temperature for the different materials studied.

Concerning H0, the dependence of w_e can be related to its glass transition. The inflection point in the curve matches fairly well the T_g^P measured by DMA. (Note that T_g is a temperature range, not a fixed value of T). Thus, it is convincing to explain the maximum toughness results in terms of the molecular relaxation activated at that temperature. The ductile-brittle transition that occurs at low T can be explained by the Ludwik-Davidenkov-Orowan criterion [28], which states that the fracture changes from ductile to brittle if the fracture stress drops below the yield stress. It is known that with decreasing T (or increasing test speed), the yield stress increases more rapidly than does the fracture stress.

On the other hand, the copolymers show no increase in w_e near T_g^P or T_g^E , despite the PP blocks (that are nevertheless predominant in the material) and the ethylene segments that show important relaxation at 20 and -40°C, respectively, as seen by DMA. A possible explanation for the absence of a w_e maximum for the EPBC at 20°C could be that an increase in the energy dissipation due to T_g^P is offset by a decrease in the toughness attributed to the ethylene phase well above its T_g^E . A previous EWF study gave a value of $w_e = 24.3$ kJ/m² for LDPE films at room temperature and 2 mm/min [29], which is consistent with the results presented here. This same reasoning may explain why at RT the homopolymer shows higher w_e values than the EPBC. Another interesting feature is that T_{th} at which w_e starts to decrease clearly depends on the EC, and can be related to the minor mechanical resistance to temperature of polyethylene than polypropylene. These results, however, deserve of more work that is in progress.

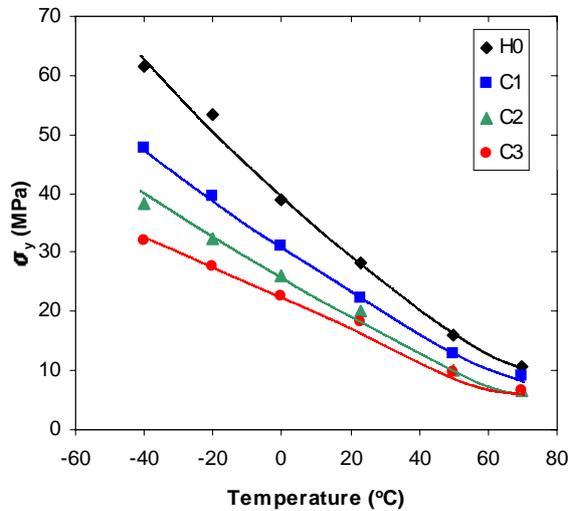


Figure 6: Temperature dependence of σ_y for the four materials.

It can be derived from Fig. 5(b) that the effect of the molecular relaxation on the plastic item is even more important than on w_e , especially in the EPBC. A competition between the shape factor (β) and the plastic energy

density (w_p) is the key to understand the plastic term temperature dependence. At $T < T_g$, β tends to 0 and the whole term tends to 0 independent of the value of w_p (which is certainly higher at RT). On the contrary, at high T, β is high but w_p decreases (due to a decrease in σ_y with T as shown in Figure 6), and thus βw_p decreases. Considering H0, it is clear that at $T < T_g^P$, the frozen structure of the PP blocks restricts the plastic deformation, and therefore βw_p tends to zero. In that situation, much of the energy is stored elastically and may be released suddenly in an unstable fracture. After the maximum, the decrease in βw_p is due to the decrease in σ_y at this T (Fig. 6). By adding a small amount of ethylene, plastic reorganisation in the bulk material is allowed to take place at low T (easier as the EC is higher), thus giving higher β (and βw_p) values. Indeed, the trend of the data shown in Fig. 5(b) reflect this supposition, and it can be seen that an EC threshold may exist, above which the ethylene phase effect is negligible (as shown by the similarity of the data for C2 and C3, despite their EC is clearly different). Higher EC than this threshold can be detrimental to other properties (σ_y , E, w_e , transparency, etc.) An optimum EC should therefore be selected to optimise these properties. Above T_g^P , the EPBC present lower βw_p values than H0. This is caused by the decrease in σ_y (Fig. 6) due to the presence of ethylene. (For LDPE films, a value of $\beta w_p = 5.1 \text{ MJ/m}^3$ has been reported [29], which is less than half the H0 value and is consistent with the results obtained).

It is interesting to compare the copolymers to the homopolymers. As discussed in [2,19], to improve the ductile failure behaviour it is necessary to increase simultaneously w_e and βw_p , since this brings about an increase of the total fracture work. However, it has been shown that, in some cases, the variation of a morphological characteristic (filler content [30], crystallinity [19] or crystal perfection [2]) produces an opposite effect on the EWF fracture parameters. That is, when one parameter increases the other decreases, and vice-versa. But if we consider EC as the material variable, then this is not the case in this study. On one hand, it should be observed that at $T > RT$ (and therefore above T_g^P), H0 has better fracture properties (both w_e and βw_p) than the copolymers. On the other hand, at T under T_g^P , the scenario is reversed. In the range of the low temperatures studied, C1 shows the best fracture properties amongst the EPBC studied. It has to be emphasised that the main interest of the EPBC at low temperatures is that they do not break in a brittle manner, which is a more desirable behaviour for many applications.

CONCLUSIONS

The EWF method has been successfully used to characterise the temperature effect on the plane stress fracture properties of PP and EPBC. The results show that the homopolymer is found to be much more temperature sensitive than the EPBC. At temperatures above RT, the homopolymer has greater energy dissipation than the copolymers. In contrast, at low T, the homopolymer presents a ductile-brittle transition, which is suppressed in the range studied by copolymerisation with only a small EC. The variations of the EWF fracture parameters with T are consistent with those of a previous study in LDPE, and can be explained in terms of molecular relaxation mechanisms, ethylene phase content, and changes in the yield and fracture stresses. Some limitations of the EWF method were found with the more ductile materials, which showed a necking phenomenon without fracture propagation in DENT specimens at high T.

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