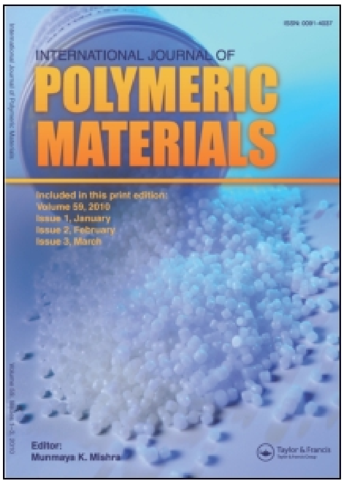

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Fatigue Crack Propagation Evaluation of Several Commercial Grade Propylene Polymers

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To cite this Article Wainstein, Jessica , Chapetti, Mirco , Montemartini, Pablo E. and Frontini, Patricia(2005) 'Fatigue Crack Propagation Evaluation of Several Commercial Grade Propylene Polymers', International Journal of Polymeric Materials, 54: 7, 575 — 587

To link to this Article: DOI: 10.1080/00914030390278707

URL: http://dx.doi.org/10.1080/00914030390278707

International Journal of Polymeric Materials, 54:575–587, 2005

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390278707

Fatigue Crack Propagation Evaluation of Several Commercial Grade Propylene Polymers

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Results of an experimental evaluation of commercial propylene polymers' performance under cyclic loading are reported. Experiments were conducted on one extrusion grade homopolymer and one impact block copolymer. The influence of thermal annealing was taken into account on the homopolymer. A laboratory-made mechanical fatigue unit capable of applying sinusoidal displacement was used to conduct fatigue tests on precracked specimens in three points bending at room temperature. Materials exhibit different crack propagation modes. The neat homopolymer *displays discontinuous-catastrophic crack propagation. Both copolymer and annealed homopolymer show longer fatigue lifetime but faster propagation rates than the neat homopolymer. The* annealed homopolymer *also propagates in a step-like way whereas the* block copolymer *displays a continuous crack propagation mode in which the crack advances regularly as cycling proceeds. A noticeable crack front damage (identified as stress whitening) is developed at the crack root, which seems to control the crack propagation rate*

Keywords: propylene polymers, fatigue, damage

Received 17 November 2003; in final form 29 November 2003.

The authors are grateful to the Agencia Nacional de Promoción Científica (PICTs 0063 and 12-04585), which partially supported this work; and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina. Comments on the manuscript by Dr. Witold Brostow are appreciated.

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INTRODUCTION

Commercial Polypropylene, PP, Polymers are available in various grades having different characteristics due to modifications done during polymerization (e.g., production of syndiotactic homopolymers, copolymers with different comonomer content or polymers with narrow molecular mass distribution) [1]. Their characteristics not only depend on molecular weight and comonomer content of the matrix, but also on tacticity, crystallinity, different crystallinity forms, supermolecular architecture and the processing history [2–7].

Although mechanical behavior of PP polymers has been extensively studied [7–15], many features are still unknown. Moreover, the use of PP is growing in new fields where an improvement of performance is required. For instance, components, and structures where cyclic loads are experienced [16–17], composite matrixes prosthetic devices machine components and piping [18–19], among others. In all these applications an understanding of the fatigue behavior is needed. Besides this, low frequency cyclic fatigue tests are more suitable for studying morphological effects than static and dynamic fracture tests [20]. To summarize, the evaluation of PP fatigue response appears interesting not only from a technological point of view but also from a scientific one. M. Kawanage et al. [20] studied fatigue process in neat PP and injection-molded blends of PP and Liquid-crystalline polyester in relation to the variation of viscoelastic properties. J. Karger Kocsis et al. [21] compared the damage mechanisms developed in fatigue process of filled and unfilled PP. J. A. Ferreira et al. [22] studied the effect of layer design on the fatigue behavior of glass-fiber-reinforced polypropylene composites, whereas N. A. Jones et al. [23] characterized the fatigue damage induced in PP. Despite these truly valuable efforts, many aspects of PP polymer fatigue behavior still remain unresolved. Moreover, the authors, previous results [24] have shown significant differences in the static and dynamic mechanical behavior of PP polymers. Under tensile experiments, for example, hormopolymers show a nonstable neck formation with localized stress whitening, whereas copolymer and annealed homopolymer show a diffuse stress whitening without necking.

The present article paper reports the mechanical behavior under cyclic loading of commercially available PP polymers. Two different polymers were assayed: one extrusion grade homopolymer, and one impact block copolymer. In order to enhance PP toughness below its glass transition temperature (Tg $\sim$ 0°C), propylene is copolymerized with ethylene [22]. However, copolymerization also induces a considerable loss in stiffness and strength characteristics. Another way of improving isotactic PP toughness is promoting further crystallization [2, 11] by thermal annealing over 140°C.

This article aims to investigate how the differences in the mechanical behavior of these polymers [24] are reflected in fatigue loading condition performance.

EXPERIMENTAL

Materials and Sample Preparation

Two different commercial grades of propylene polymers were assayed: isotactic polypropylene homopolymer 11O2KX Cuyolem^{TM} (PPH) and impact block copolymer 2300 PX Cuyolem^{TM} (PPC), kindly supplied by Petroquímica Cuyo SAIC. PP pellets were compression molded into plaques, annealed in an oven for h at 90°C, and slowly cooled in the oven to room temperature in order to avoid residual thermal stress PPH was also annealed at 150°C in order to change supermolecular structure [11, 25]; these samples were named PPH-150. PP is known to be polymorphic material with a number of crystal modifications such a monoclinic (α), hexagonal (β), and triclinic (γ) Commercial grades of iPP processed in laboratory or industrial scale crystallize essentially into the α modification [25–27]. Therefore, neither chemical composition nor thermal treatments used in this work are expected to be responsible for different crystal modifications.

Materials were previously fully characterized [24] and their main physical and mechanical properties are indicated in Tables 1 and 2. Bars were cut from the compression-molded plaques and machined to reach the final dimension 110 × 10 × 3 mm. Sharp notches were introduced by scalpel-sliding a razor blade having an on edge tip radius of 13 mm. The notch depth was 3.5 mm. Free surfaces, where plane stress conditions prevail, were removed by introducing 45° "V" Side-groove. Side-groove depth is critical; when they are too deep, lateral singularities are produced causing the crack to grow faster at the

TABLE 1 Physical Properties

Material	Commercial name	Annealing temperature [°C]	T peak [°C]	Cristalinity [%]
PPH	Cuyolem^{TM} 1102KX	90	166	46.8
PPH-150	Cuyolem^{TM} 1102KX	150	166	47.8
PPC	Cuyolem^{TM} 2300PX	90	168	37.3

TABLE 2 Materials Mechanical Properties

Material			Static Measurements[24]		
	E_t [GPa]		σ_y [MPa]		J_{IC} [MPa mm]
PPH	1.37		31.1		15.6
PPH-150	1.46		33.7		13.8
PPC	1.04		21.6		8.1
			Dynamic Measurements		
Material	$N_i 10^3$	$N_p 10^3$	ΔK_{th} [MPa·$m^{\frac{1}{2}}$]	α (Paris Law)	K_C at instability [MPa·$m^{\frac{1}{2}}$]
PPH	135	90	0.65	0.9 ± 0.04	2.27
PPH-150	40	#	0.90	2.0 ± 0.34	#
PPC	175	#	0.50	4.0 ± 0.62	#

#: Instability condition was not reached during the experiment.

outer edges. A straight crack front propagation was promoted by reducing the specimen's thickness by 30%.

Differential scanning calorimeter (DSC) measurements were taken at 10°C/min. The melting point was determined as the peak temperature and the degree of crystallinity was calculated from the enthalpy of fusion of iPP (209 J/g) [28].

FATIGUE CRACK-PROPAGATION EXPERIMENTS

A laboratory-made mechanical fatigue unit capable of applying sinusoidal displacements was used to conduct the fatigue tests. Experiments were carried out in three point bending at room temperature on precracked specimens. Materials and test configuration were chosen by an experimental trial and error procedure aiming to promote crack growing after a certain number of cycles but trying to render the creep damage at the lowest possible level. Stress levels at 30 percent of the yield stress have previously been shown to produce brittle failure in reasonable testing times [29]. At least five specimens, cut from the same compression-molded plaque, were tested in order to get reproducible results.

The minimum to maximum load ratio, R, in a fatigue loading cycle was maintained at 0.6 for an all-tension cycle. Maximum load was varied in the range of 250–300 N, which produced a maximum applied stress intensity factor at the notch tip $K_{l,max} = 2.0 - 2.3$ MPa·$m^{1/2}$.

The test frequency was 8 cycle·s^{-1}. For each test the maximum stress($\sigma_{\max}$) and the crack length (a) were recorded as a function of the loading cycle number. The load was recorded every 1000 cycles during the experiment. Crack tip position was monitored observing the edges of the testing sample by a traveling microscope. Because crack growth occurs with deformation at the crack tip, the effects of plastic yielding cannot be neglected. Therefore, crack length and associated ΔK values were calculated considering a plastic zone correction. The crack length, a_f,was taken to be $a_f = a + r_p$ where a is the original crack length and r_p is the plastic zone length. In order to evaluate r_p the validity of the Dugdale model was assumed [30]:

$$r_p = \frac{\pi}{8}\left(\frac{K}{\sigma_y}\right)^2 \tag{1}$$

Then, assuming the validity of Paris Law, fatigue data were plotted on log-log scale showing the crack growth rate per cycle, da_f/dN, vs. the oscillating stress intensity factor, ΔK [31].

$$\frac{da_f}{dN} = A(\Delta K)^m \tag{2}$$

ΔK values were calculated according to Eq. 3

$$\Delta K = \frac{\Delta F}{BW}(a_i)^{1/2} f(a_i/W) \tag{3}$$

where

$\Delta F = F_{\max} - F_{\min}$ is the load amplitude applied
B = specimen thickness
W = specimen width
a_f = actual crack length
$f(a_i/W)$ = shape factor given by ASTM 399 standard

In order to detect a possible hysteresis heating process, a thin thermocouple was placed in the side-groove. However, the temperature change was always negligible.

FRACTURE SURFACES AND DAMAGE CHARACTERIZATION

Some tests were interrupted at early stages of crack growth. In half of the samples, penetrating ink was introduced into the crack. Then, they were fractured in a Charpy pendulum to reveal the fracture surface and measure the crack length. Half of the sample was cut at its mid-thickness plane parallel to, the crack propagation direction and orthogonal to the fracture surface. After grinding and polishing, they were inspected by optical microscopy in order to examine the crack-tip profile and the damage zone surrounding the crack.

RESULTS

Fatigue Crack Propagation Phenomenology and Kinetics

Figure 1 shows a significant example of crack length as a function of the number of cycles for each material studied. Paris Plots calculated from different specimens are shown in Figure 2. Both plots demonstrate a subtle difference in the kinetics and mode of crack propagation depending on the chemical composition (homopolymer or copolymer) and the thermal history. The differences in the fatigue resistance behavior of PPH, PPH-150, and PPC are not expected to be due to different crystal modifications as was stated before.

In every case, two distinct phases of fatigue life having different characteristics could be identified. First, there is an initiation stage lasting N_i cycles during which the crack does not advance. Once a

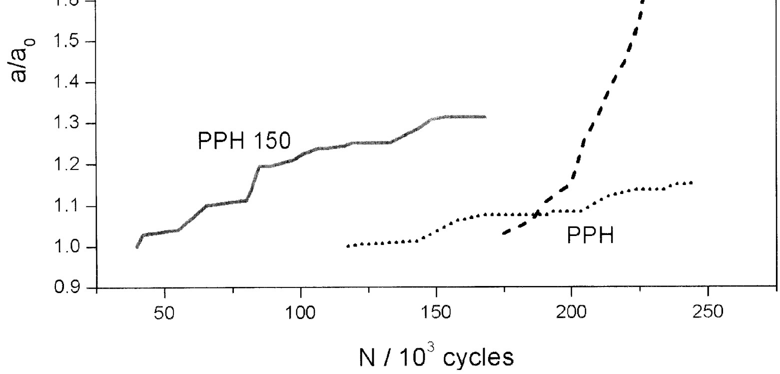


FIGURE 1 Crack length (a) vs. number of cycles (N).

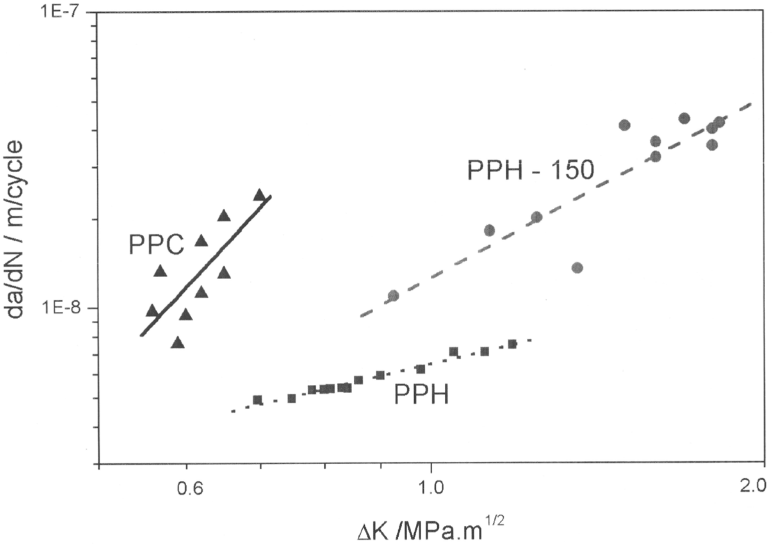


FIGURE 2 Paris plots log da_f/dN vs. log ΔK.

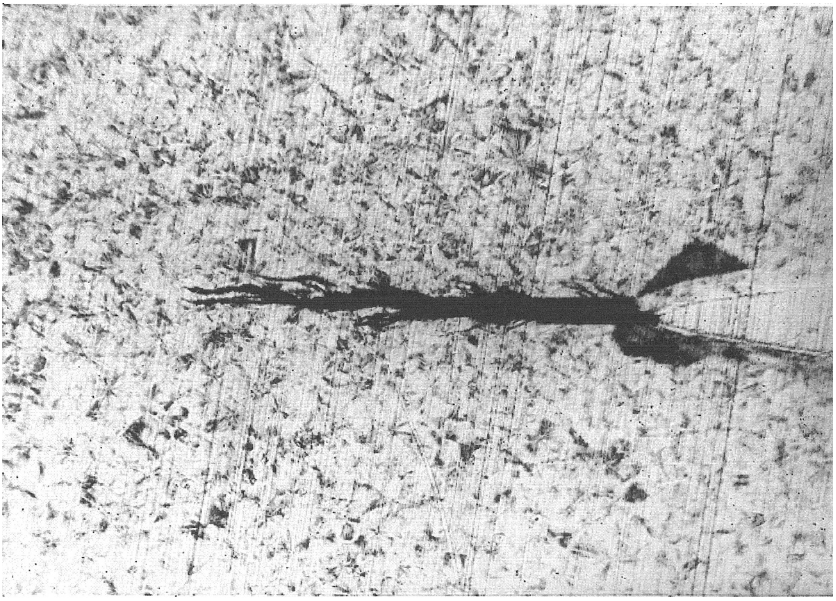
threshold of stress intensity factor (ΔK_{Th}) is reached, the stable crack propagation occurs. This propagation stage lasts N_p cycles (Table 2).

The *neat homopolymer* (PPH) *displays* a *discontinuous-stepwise-catastrophic crack propagation mode*. After a long initiation period (Table 2) the propagation stage is characterized by jumps, in which a continuous stable crack growth alternates with crack arrest periods giving a very low overall crack propagation speed (da/dN) (Figure 2). The crack growth rate for discontinuous step-wise propagation was calculated considering that the value of the stress intensity factor at the crack tip, K_I increase as the crack propagates. Every jump is presented on the Paris plot by only one separate point. The value of K_I was determined for each crack tip position by the standard expression K_I (Eq. 3). Despite the relatively high fatigue resistance, after a 15% of propagation (Figure 1) instability is reached and catastrophic failure occurs at a lower K_I value than the one reported in static experiments. This behavior is similar to the one found in static fracture experiments [11], where instability is reached after some stable propagation.

Thermal annealing clearly promotes a different behavior. The annealed homopolymer (PPH-150) displays *non catastrophic discontinuous step-wise crack propagation mode.* In comparison with PPH and under identical loading conditions it is clear that treatment at 150°C makes the initiation stage shorter (Table 2). Thermal annealing also induces faster propagation, as it emerges from Paris Plot (Figure 2, Table 2). However , a subtle difference in the crack propagation exists. The PPH-150 does not reach instability condition even though it also propagates in a step-like mode (Table 2, Figure 2). Thus, time to failure is really extended by annealing. A similar, although not exactly equal, propagation regime has been reported in literature for other polymers [32–33].

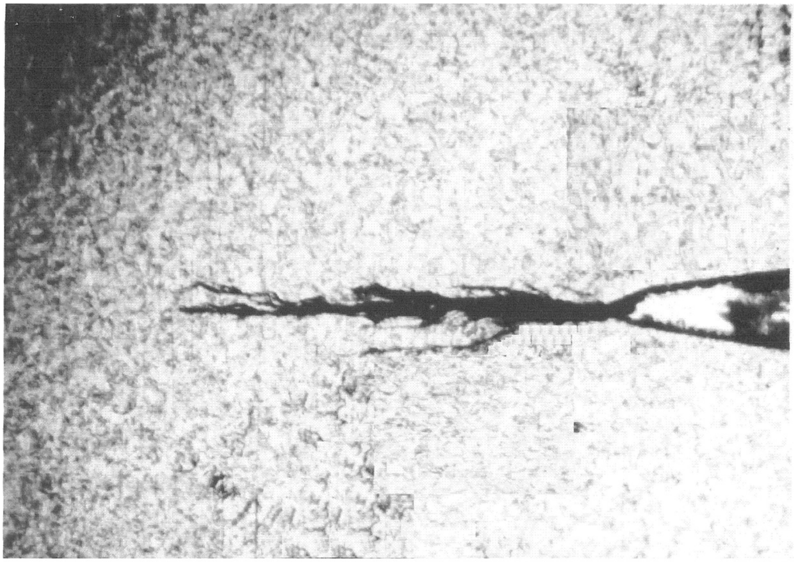
On the other hand, the copolymer behavior is different PPC shows, firstly, the longest initiation period. After that, it exhibits a *continuous crack propagation mode* in which the crack advances regularly during the fatigue test. Overall propagation rate (Figure 2) is high but fatigue lifetime (Table 2) is indeed enhanced by copolymerization with ethylene.

All three materials studied show a noticeable crack front damage, clearly identified as stress whitening developed at the crack root. This damage begins during the initiation stage and increases during propagation (Figure 3). Fatigue propagation appears as a discontinuous process that involves damage formation and the subsequent crack advance into the damaged material. The larger the size of the damaged zones

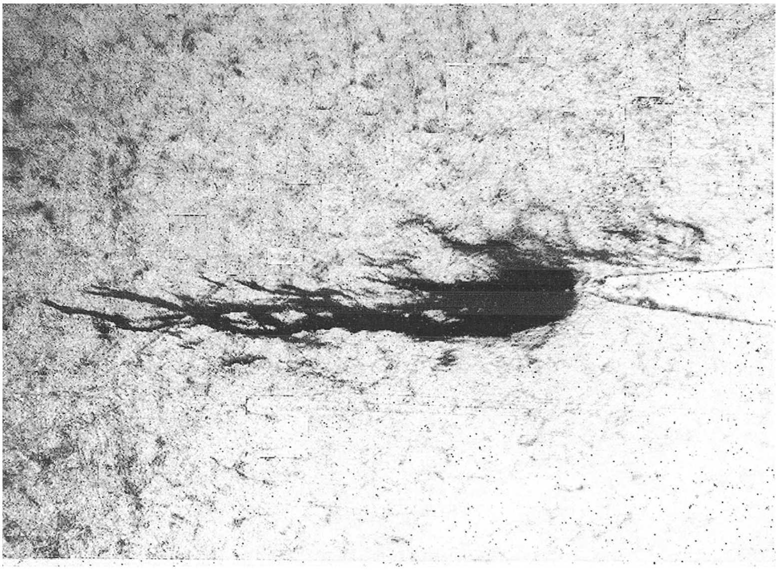


(a)

FIGURE 3 Side view sections removed from the center of specimens illustrating damage appearance (a) PPH, (b) PPH-150, (c) PPC.



(b)



(c)

FIGURE 3 Continued.

the higher the tendency toward a continuous propagation regime. The size of the damaged zone increases in the following order PPH, PPH-150, and PPC. For all of them, the size of the zone under plastic deformation did not meet the condition of being small in comparison to the initial crack length. Therefore, kinetic parameters may be considered only as comparative pseudo-quantitative because linear elastic fracture mechanics—LEFM—requirements could not be fulfilled under the large degree of plastic deformation developed during experiments.

DISCUSSION

In this article, fatigue crack propagation of one commercial extrusion grade PP homopolymer, as molded and after being thermally annealed (150°C), and one block copolymer were assessed.

The neat homopolymer displays discontinuous-catastrophic crack propagation. Continuous crack growth stages alternate with crack arrest periods at a very low overall crack propagation rate. However, instability condition is reached in a relatively short lifetime. Both copolymer and annealed homopolymer show a longer fatigue lifetime but faster propagation rate than the neat homopolymer. The annealed homopolymer also displays a step-like propagation mode but in the block copolymer the crack advanced regularly as cycles proceed. In consequence, a different rank among materials is obtained if initiation time, failure time, or the kinetics of crack growth are considered. In all three samples significant damage zone—identified as stress whitening—is developed at the crack tip.

In traditional materials, like steel, fatigue crack propagation occurs by the crack growth during each loading cycle. Then, when the driving force—generally characterized by the stress intensity factor or J-integral—is reduced below a critical threshold the crack growth stops. In some polymers, however, a cumulative damage mechanism enables crack growth after a multiple number of load cycles even if the driving force is unable to propagate the crack in each cycle [32]. This "sub-critical" fatigue crack propagation process was called discontinuous crack growth [33]. Besides this, in the literature the deformation of neat PP is attributed to crazing and brittle fracture that occurs with the breakdown of craze when the stress at the tip of the craze exceeds fibril-rupture stress. Previous investigations [32] on fatigue behavior of some ductile amorphous polymers reveal, in agreement with the present results on PPH, a unique crack propagation mode: a craze dominated sub-critical discontinuous crack growth mode, which leads to short fatigue lifetime. Therefore, PPH propagation appears consistent with the following model [33–34]: a craze zone grows continually with load cycling; when some critical condition is satisfied, the crack would suddenly strike through the entire craze before being arrested at the craze tip. The crack tip remains fixed until a new critical situation is reached. Under cyclic loading conditions, the most highly stressed fibrils are disentangled and fractured. This situation promotes a metastable equilibrium condition between fibril orientation—strain hardening—and void growth—strain softening. This process gradually thickens the craze leading to this so-called discontinuous crack growth [33]. In the case of neat PPH, after a number of cycles the instability condition is reached—similar to the results obtained in static measurements [11]—and the sample brakes. Craze initiation propagation, and coalescence occur simultaneously during fatigue, but as the number of cycles increases, craze propagation and coalescence become the primary mechanisms of fatigue damage. The softening due to craze void formation, which overwhelms fibril orientation hardening, weakens the material and promotes catastrophic failure. This is the reason why the K_{IC} value computed in fatigue experiments was lower than the one computed in static experiments, which corresponds to the undamaged material [24].

PPH-150 and PPC are more suitable to undergo plastic deformation, as can be deduced from the large degree of lateral penetration of the whitened zone (Figure 3). However, from the present authors' fatigue crack rate observations, it is clear that the damage zone is built up very rapidly in front of the initial crack. Then the damage zone offers an easy path for crack propagation, making it responsible for the decrease in fatigue resistant performance (N_i and da/dN). However, and surprisingly, in both PPH-150 and PPC, fatigue lifetime was definitely increased, suggesting the existence of a different mechanism, which impedes catastrophic failure even if the crack propagates easily. Spherulitic boundaries in iPP are widely accepted to be the weakest part of the structure They contain material rejected during crystallization—low MW or non-crystallizing chains and impurities. These weak boundaries can be strengthened by annealing or by adding less rigid phases like PE, which promotes matrix drawing and stretching [35] and prevents the void coalescence usually responsible for unstable fracture. It was said that annealing operates through partial melting and recrystallization processes that lead to the growth of thin crystallites and rearrangement of uncrystallized polymer chain mainly in the interspherulitic zones leading to a more interconnected physical network capable of impeding craze coalescence and allowing larger plastic deformation [3, 36]. The superstructure developed in this way is responsible for the longer fatigue lifetimes exhibited by the annealed samples.

Regarding PPC behavior, We may say that the relatively poor fatigue crack propagation resistant—high propagation rate—might arise from the considerable loss in stiffness and strength characteristics induced by ethylene modification. On the other hand, this modification may also lead to conditions that favor shear processes as well as crazing, which are expected to prevent brittle fracture and promote continuous crack propagation with longer fatigue lifetime [37].

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