Essential Work of Fracture of photo-oxidized LDPE/EVA Films

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Summary: The Essential Work of Fracture approach (EWF) was used to determine how UV-C irradiation alters the fracture behaviour of LDPE/EVA films. Complementary characterization was performed by FTIR, DSC, TOM, and uniaxial tensile testing. The crosslinking reactions that govern photo-oxidation process at initial stage of exposure stiffened the amorphous phase of the polymer, leading to films with enhanced elastic modulus, yield stress and ultimate strength, but impaired strain at break. In the fracture experiments carried out on films irradiated within 0 and 5 days, EWF methodology requirements were met and the corresponding fracture toughness parameters (w_e and βw_p) turned out to be sensitive to UV-C irradiation. Longer irradiation time triggered the development of microcracks, which not allowed further stable crack growth and invalidated the application of EWF approach.

Keywords: Essential Work of Fracture; fracture toughness; irradiation; plastic films; polyethylene

Introduction

The vulnerability of polymeric materials to degradation in a wide variety of environments and conditions limits their applications and extensive long use. Due to their reduced thickness it is expected that plastic films quickly degrade.[1] Such degradation results from changes of morphology and even chemical structure and it is induced by several factors including ultraviolet radiation, high temperature, external applied strains, internal tensions generated during processing, oxygen, corrosive chemical substances and micro-organisms.[1–5] When plastics films are exposed to photo-oxidative conditions such as UV-irradiation, the change of the primary structure of the polymer can lead to concomitant yellowing discoloration and loss in mechanical integrity.[4,6–8]

Uniaxial tensile tests are commonly employed for the assessment of the effects of UV-irradiation on the mechanical response of polymers. [3,6,7,9–13] Particularly, strain at break has been found to be the most sensitive property. However, it is well known that strain at break is not an intrinsic property of the material and it is generally widely scattered. On the other hand, fracture mechanics concepts yield inherent toughness values and they are suggested to be more reliable and practical for quality control purposes. Surprisingly, this alternative has been rarely adopted to study the susceptibility of polymers to UV-irradiation.

The currently accepted method to evaluate the fracture toughness of ductile films is the Essential Work of Fracture (EWF).[14] EWF defines a fracture para-

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meter called specific work of fracture (w_e), which may be considered a material constant for a given thickness. This method has gained popularity owing to its experimental simplicity and it was used to study the fracture behaviour of a wide range of polymeric films.[15–25] In particular, it has been pointed out the suitability of the EWF method to characterize degradation embrittlement in thermal oxidized PP [21] and to study physical ageing in PET films.[20]

In this paper, the results of a deep investigation regarding the fracture behaviour of commercial LDPE/EVA films as a function of UV-C radiation exposure using the EWF approach are presented and discussed.

Theoretical Background: The Essential Work of Fracture Concept

According to Broberg,[26] when failure of a test specimen is preceded by extensive yielding and slow crack growth, the non-elastic region at the tip of crack may be divided into two regions: an inner fracture process zone and an outer plastic deformation zone. The total work of fracture, W_f, is then partitioned into two terms [13]:

$$W_f = W_e + W_p \tag{1}$$

W_e is termed the ‘‘essential work of fracture’’ and it is the energy expended in the fracture process zone, whose value is proportional to the ligament area (lB). W_p is termed the ‘‘nonessential work of fracture’’ and it is the work dissipated in the plastic deformation zone, whose value is proportional to the volume of the yielded zone (Bl^2). Hence:

$$W_f = w_e Bl + w_p \beta B l^2 \tag{2}$$

w_e is the specific essential work of fracture, w_p is the specific non-essential work of fracture and β is a shape factor related to the feature of the outer plastic zone. Dividing Eq. 2 by the ligament area (lB) results the specific work of fracture, w_f:

$$w_f = w_e + \beta w_p l \tag{3}$$

Under plane stress conditions, w_e is regarded as a material constant (for a given film thickness) and provided the βw_p term remains independent of the ligament length, a linear relationship is expected between w_f and l as suggested by Eq. 3. The intercept of this line with the w_f -axis gives w_e while its slope provides βw_p.

The applicability of the EWF relies on the following conditions being satisfied: 1) geometrical similarity exists between specimens of different ligament lengths during crack growth and 2) ligament length is fully yielded prior to the onset of crack propagation.[27]

Experimental Part

Materials

A film made of low-density polyethylene LDPE modified with 5% of an ethylene–vinyl acetate copolymer EVA (Agrotileno®-LTD; 150 μm in thickness) was provided by IPESA SA. This work involved the characterization of original films and one-side UV-irradiated during 2, 5, 10 and 16 days films. The exposure intensity in the ultraviolet part of the spectrum was 36 W/m^2 for UV-C (253.7 nm), 1 W/m^2 for UV-B (290– 315 nm) and 2 W/m^2 for UV-A (315– 400 nm). The temperature was kept at 37 ± 1 °C and the humidity level at 52%.

Analytical Characterization

Two usual techniques: FTIR and DSC[3,28,29] were used to corroborate photo-oxidation of LDPE/EVA films. FTIR spectra in the range of 4000 to 600 cm^{-1} were obtained using a Genesis II Mattson spectrometer equipped with an attenuated total reflectance (ATR). DSC measurements were carried out in a Pelkin Elmer Pyris 1 at a heating rate of 10 °C/min from 0 °C to 160 °C. In crystalline fraction calculations, the heat of fusion of PE pure crystalline phase was taken as 285 J/g,[30] while the experimental heat of fusion was determined by using a base-line construction between 7 °C and full melting.

Microscopy

The inspection of films feature was done by transmission optical microscopy (TOM) using a Leica DM-LB Microscope.

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Uniaxial Tensile Test

Uniaxial tensile experiments were carried out in an INSTRON 4467 testing machine at 100 mm/min using dumbbell-shaped specimens. Samples with a gauge length of 30 mm and a width of 5 mm were stamped on the films using a mallet handle die. At least five specimens of each film were tested. Elastic modulus (E), yield stress (σ_y), ultimate stress (σ_{max}) and strain at break (ε_b) were determined. Since it is expected that films display anisotropic behaviour due to the stretching experienced in the blowing manufacturing process,[18] mechanical parameters were determined both along the machine direction (MD) and along the transverse direction (TD).

Fracture Experiments

The EWF tests were performed in an INSTRON 4467 testing machine at a crosshead speed of 10 mm/min using double edge notched tensile (DENT) samples with different ligament lengths. Samples were prepared following the recommendations of ESIS procedure.[14] In order to examine the features of the fracture process zones, tests were recorded using a video camera equipped with macro-lens and cross-polarized light.

The absorbed energy until failure (W_f) was calculated by numerical integration of the load-displacement traces. Experimental w_f values were plotted against ligament lengths, l. A linear relationship was obtained by the usual practice that establishes a linear regression confidence limit of at least 95%. βw_p parameter was evaluated from the slope while w_e was determined by extrapolating the straight line to zero ligament length.

Results

Chemical Structure and Morphological Changes

The feature of the spectra obtained by infrared analysis confirms that photo-oxidation of LDPE/EVA films occurred due to UV-C irradiation (Figure 1-*a*). The characteristic sharp band (around 1740 cm^{-1}) associated with the carbonyl ester group of the EVA copolymer broadened with increasing exposure time. This effect has been explained by oxidation reactions, which change the primary struc-

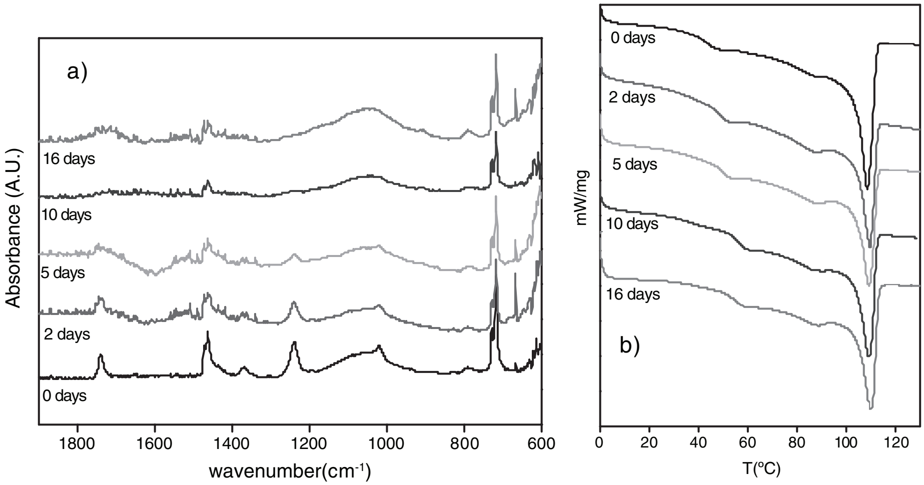

Figure 1.
Analytical characterization *a*) FTIR spectra and *b*) DSC thermograms.

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Table 1.
Crystalline fractions of LDPE/EVA films arisen from DSC analysis.

Irradiation time	X_c (%)
0 days	40.7
2 days	37.7
5 days	38.6
10 days	39.7
16 days	39.7

ture of the polymer leading to chain scission and crosslinking.[1,4,9]

Results of the thermal analysis by DSC indicate that morphological changes also occurred (Figure 1-*b*). Original films exhibited a melting endotherm that showed two melting temperatures centred at 88 and 108 °C. Melting was preceded by a crystalline relaxation process, known as α' transition, appearing at about 50 °C. The onset of α' transition shifted to higher temperature with increasing exposure time, being especially evident in those films longer irradiated. This phenomenon has been attributed to the increasing degree of crystals perfection with irradiation time.[3,31,32] In the amorphous domains of photo-oxidized samples, the molecular chains possessing higher mobility owing to chain scission gathered into crystals.

Irradiation slightly affected the bulk crystalline fraction of films, which achieved an almost constant value around 40% (Table 1) demonstrating that changes occurred mainly in the amorphous phase.[3]

Uniaxial Tensile Behaviour

The tensile stress-strain (σ–ε) curves in Figure 2 demonstrate that LDPE/EVA specimens failed in a ductile manner and exhibited the typical behaviour of oriented films.[7,33,34] MD samples displayed a broad yield behaviour reminding rubber-like deformation pattern; strain hardening occurred right after yielding with no-necking development. On the contrary, TD samples exhibited a double yield point pattern associated to the partial melting-recrystallization phenomenon.[35] Necking formation followed yielding and a cold drawing process occurred up to strain hardening and failure. Mechanical parameters determined in MD were higher than those evaluated in TD, except for the strain at break (Figure 3).

The uniaxial tensile response of the films was altered by irradiation but kept its anisotropic character.

The elastic modulus (*E*) slightly increased with exposure time (Figure 3-a). The yield stress (σ_y) -that was taken as the extrinsic point in TD samples and as the value corresponding to 20% of deformation in MD samples- showed an abrupt raise at 2 days of irradiation and remained practically unchanged with further exposure (Figure 3-b). The strain at break (ε_b) did

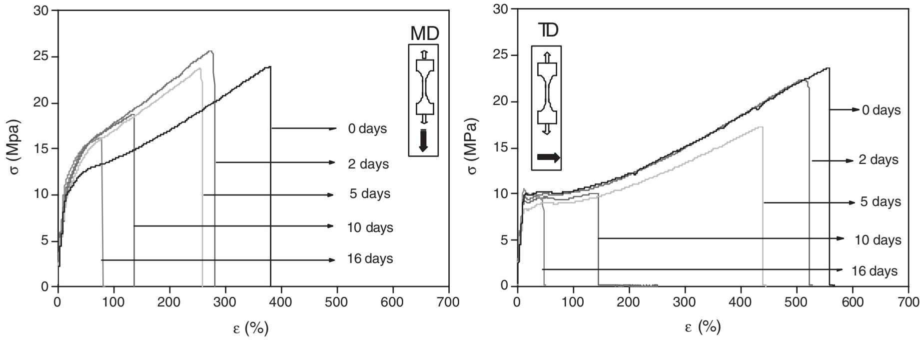

Figure 2.
Typical uniaxial tensile stress-strain curves of irradiated LDPE/EVA films.

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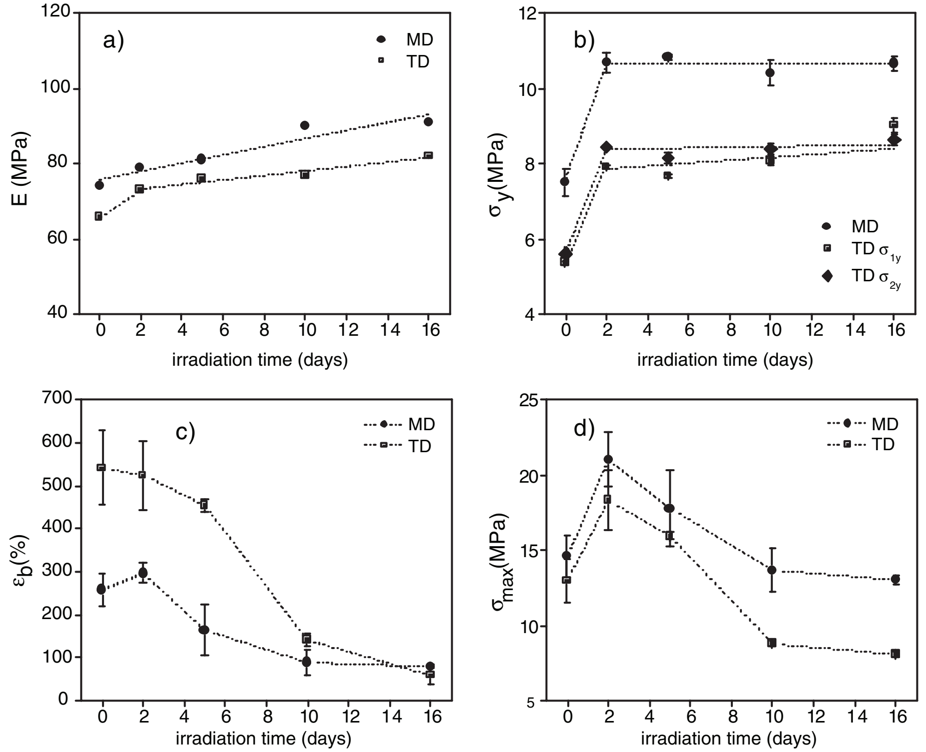

Figure 3.
Uniaxial Tensile parameters as function of exposure time. *a*) Elastic modulus, *b*) Yield stress, *c*) Strain at break, *d*) Ultimate strength.

not showed a clear trend with irradiation time up to 5 days of exposure. But a pronounced reduction in the film stretching capability occurred in samples irradiated longer than 5 days (Figure 3-*c*). The ultimate stress (σ_{max}) also increased at 2 days of irradiation. Strain hardening did not occurred in samples incapable of stretching and consequently σ_{max} attained the corresponding yield stress values.

It is known that each tensile parameter depends in a different way on many concomitant factors such as crystallinity, crystal dimensions and orientations, number and tautness of the molecules connecting crystalline blocks, cross-links and defects in the structure.[9,35] The tensile behaviour at low deformation levels of films irradiated up to 5 days may be due to the appearance of crosslinked structures that stiffened the amorphous phase of the polymer. Enhanced tensile parameters have been already reported in other studies regarding radiation crosslinking on LDPE, LLDPE and LDPE/EVA blends.[36–37]

Transmission light optical images of Figure 4 show that 10-days irradiated films presented several microcracks along the machine direction (MD) and also that they grew in number and size with further irradiation. Consistently, surface parallel and superficial networks of microcracks as well as superficial pores has been previously detected by SEM in UV irradiated LLDPE, *i*PP, *s*PP and PP/EPR. [8,9,31,38,39] The formation of such defects on the polymer surface has been attributed to two different phenomena: One is related to the higher volume of photo-oxidized macromolecules that causes stresses and strains on the film

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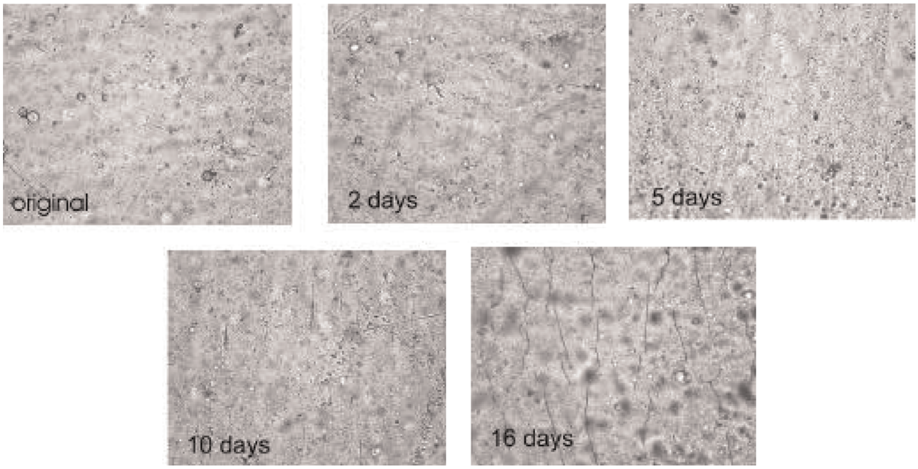

Figure 4.
TOM images showing original and irradiated LDPE/EVA films features.

surface.[8] The other is associated with the contraction of surface layers during crystalline changes (chemi-crystallization).[8,31]

It is worth noting that the abrupt drop in the strain at break appeared in agreement with the build-up of microcracks even if they were or not superficial. This result is in accord with Rosa and co-workers observation in which a drop in the strain at break correlates with the appearance of microcracks in *i*PP subjected to natural and accelerated ageing.[39]

Fracture Behaviour

Testing of DENT specimens produced load–displacement curves at various ligament lengths of the types shown in Figure 5-a and plastic zones features like those of Figure 5-b. Original film curves indicate that the failure of the specimens in both directions occurred by ductile tearing of the ligament region. However, in MD samples the maximum load and its extension reached considerably higher values than those achieved by TD specimens and larger plastic zones developed. Films irradiated up to 5 days also exhibited stable crack growth by ductile tearing and displayed load-displacement traces similar to the ones of original films (Figure 5-*a*). On the other hand, in curves of films further irradiated load dropped unsteadily after reaching its maximum value. In such cases, it was observed that crack grew via a ‘‘step-wise’’ tearing mechanism up to final fracture. This mechanism seems to be the result of ductile tearing alternating with growth and coalescence of microcracks located inside the ligament region.

In EWF plots of original film and films irradiated up to 5 days the variation of w_f with l appeared linear (Figure 6). Consequently, w_e and βw_p values could be determined from the fitted straight line (Eq. 3). The regression coefficients (R^2) were higher than 0.95 (Table 2).

MD samples yielded higher fracture parameters than the ones showed by TD specimens. Effectively, previous investigations carried out on other plastic films showed that EWF parameters are sensitive to molecular orientation.[40–41] Since the fragmentation of crystal lamellas dissipates much more energy than disentanglement and scission of tie molecules in the amorphous regions between the crystals, the resistance to crack propagation is higher for cracks growing transversely to MD than for cracks growing parallel to it.

Even if both EWF parameters increased with irradiation, w_e showed the most pronounced changes (Table 2), exhibiting

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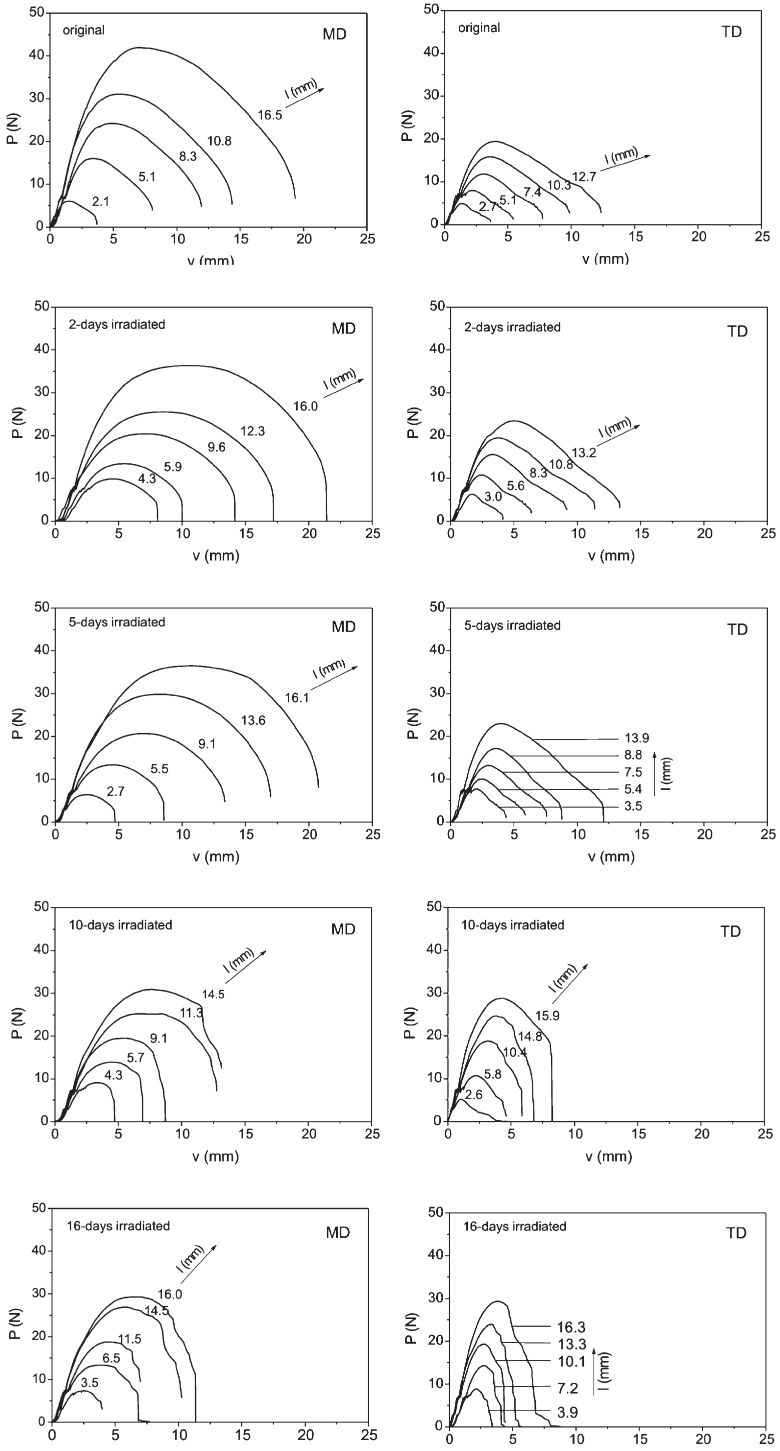

Figure 5.

Fracture Test results. *a*) Typical load-displacement curves and *b*) Photographs took during loading of DENT samples showing the plastic deformation zones developed before to crack initiation.

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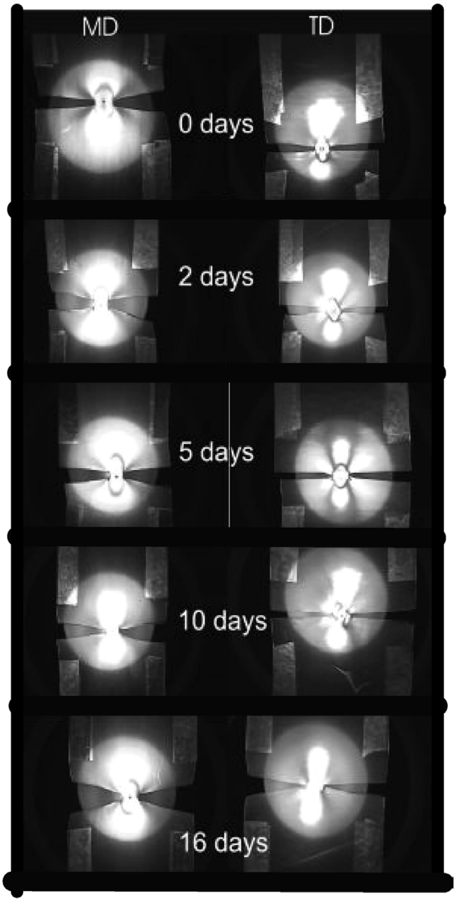

b)

Figure 5.
(*Continued*)

a maximum at 2 days of irradiation. The stiffening of the amorphous phase mentioned in the previous section, may also be responsible for the fracture toughness enhancement.

On the other hand, w_f vs l data points of films irradiated longer than 5 days appeared widely scattered (Figure 6). The linear regression coefficients (R^2) resulted lesser than 0.8 (Table 2) and errors in intercepts and slopes values were about 40% and 20%, respectively. Hence, in these cases the EWF approach was not more valid and so that fracture parameters could not be inferred. It is worth noting that at these irradiation levels the total energy to fracture of the films drastically diminished as judge from low values of the total specific work of fracture (see open dots in Figure 6).

Discussion

In a large number of investigations the strain at break is reported as the most sensitive of the mechanical properties to UV degradation.[3,5–7,38,42,43] and it is used in practice as an indicator of degradation degree.[2] However, it is known that this parameter responds in a pronounced way to localized structure irregularities and defects. The strain at break is generally widely scattered and it is linked to tensile

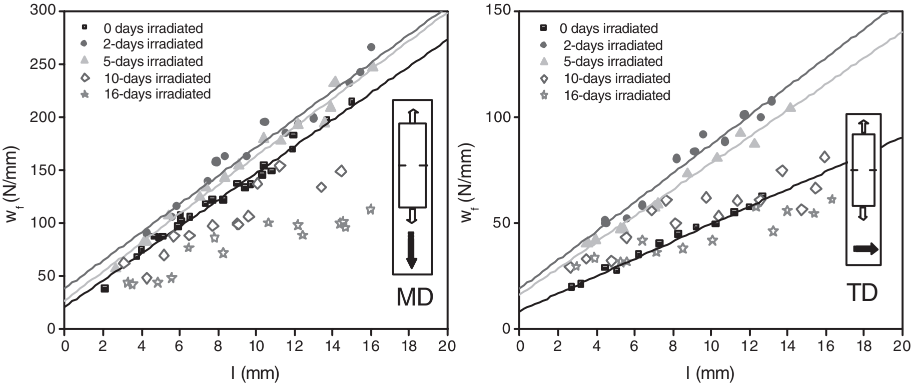

Figure 6.
Specific work of fracture versus ligament length plots of irradiated LDPE/EVA films.

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Table 2.
Fracture toughness parameters yield by EWF approach.

Irradiation Time	MD			TD		
	$w_{e(MD)}$ (N/mm)	$\beta w_{p(MD)}$ (N/mm^2)	R^2	$w_{e(TD)}$ (N/mm)	$\beta w_{p(TD)}$ (N/mm^2)	R^2
0 days	20.6 ± 3.1	12.6 ± 0.3	0.98377	8.4 ± 1.0	4.1 ± 0.1	0.99144
2 days	37.9 ± 8.1	13.3 ± 0.7	0.96372	18.9 ± 4.1	6.8 ± 0.1	0.96214
5 days	27.0 ± 5.2	13.6 ± 0.5	0.98192	16.1 ± 2.7	6.2 ± 0.3	0.97653
10 days	–	–	0.84748	–	–	0.76894
16 days	–	–	0.83881	–	–	0.68196

test artefacts such as sample necking. That is why the lone use of this parameter to characterize polymeric films subjected to any kind of ageing condition is questioned.[4,21,44] At this point, the EWF appears as an alternative methodology to study originally ductile plastic films. In fact, a previous study regarding thermal oxidation in PP films demonstrated that while elongation at break did not allow to clearly detect ageing effects, the βw_p term of the EWF varied significantly, revealing a true progressive loss of toughness linked to a decrease of the polymer molar mass. [21] In our investigation the strain at break changed significantly with irradiation time only at large times of exposure.

During EWF experiments, DENT samples of 0, 2 and 5 days irradiated films underwent full ligament yielding prior to crack propagation (Figure 5-*b*) and load-displacement curves displayed excellent self-similarity within the whole ligament length range (Figure 5-*a*), meeting the basic requirements of the EWF approach. An adequate linear relationship was found in each w_f vs l plot and fracture toughness parameters could be determined. Both parameters resulted sensitive to irradiation time and also reflected the anisotropic nature of the films (Table 2).

DENT samples of films irradiated during 10 and 16 days also displayed fully yielded ligaments prior to crack advance (Figure 6) indicating that the initial steps of deformation were not altered. The corresponding load-displacement curves showed self similarity in the pre-maximum load range (Figure 5) as it was corroborated applying the partition analysis of the EWF that is presented in what follows.

Although it is not the main objective of the EWF, the partition of the total essential work of fracture (w_f) between two components: the specific work of fracture for yielding (w_y) and the specific work of fracture for subsequent tearing (w_t), can be done: [40,45,46]

$$w_f = w_y + w_t \tag{4}$$

In analogy with Eq. 3, the variation of w_y with l is expressed as:

$$w_y = w_{e,y} + \beta' w_{p,y} l \tag{5}$$

where $w_{e,y}$ represents the yielding related part of the specific essential work of fracture (w_e) and $\beta' w_{p,y}$ is the yielding component of the specific non-essential work of fracture (βw_p). When applying this concept in our analysis, the peak of the load-displacement curves was taken as the cut-off point. w_y varied linearly with the

Table 3.
Yielding related components of the specific work of fracture.

Irradiation Time	MD			TD		
	$w_{e,y(MD)}$ (N/mm)	$\beta w_{p,y(MD)}$ (N/mm^2)	R^2	$w_{e,y(TD)}$ (N/mm)	$\beta w_{p,y(TD)}$ (N/mm^2)	R^2
0 days	13.2 ± 1.5	4.1 ± 0.1	0.98206	5.2 ± 0.8	1.2 ± 0.1	0.96688
2 days	23.2 ± 4.8	5.6 ± 0.4	0.99891	7.9 ± 1.1	2.2 ± 0.1	0.98132
5 days	17.5 ± 2.9	5.5 ± 0.4	0.98345	7.6 ± 1.9	2.1 ± 0.2	0.96139
10 days	13.3 ± 3.4	4.5 ± 0.3	0.98222	7.3 ± 1.5	2.0 ± 0.1	0.96756
16 days	12.8 ± 2.1	2.6 ± 0.2	0.98060	7.2 ± 1.8	1.4 ± 0.1	0.96068

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ligament length for all the studied films including those longer irradiated (see linear regression coefficients in Table 3). While the yield stress resulted insensitive to irradiation time after the raise displayed at 2-days of exposure (Figure 3-*b*), both yielding related parameters $w_{e,y}$ and $\beta' w_{p,y}$ showed significant variations. Results further proved that $\beta' w_{p,y}$ decreased in a pronounced way with increasing irradiation time from 10 to 16 days.

At long time of exposure, irradiation changed the crack growth manner of the films from completely stable to unstable ‘‘step wise’’ mode. It is appropriate to suppose that when crack extension occurred by microcracks coalescence, the associated fracture energy had very little contribution to the total work of fracture of the specimen. Obviously, films showing this type of crack growth behaviour did not meet EWF requirements. Similar cases are discussed in literature: the ductile to brittle transition described for PBT [47], the partially brittle fracture observed in PP films at low temperature[48] and the limited yielding exhibited by UV-aged *s*PP.[22]

Conclusions

In fracture experiments of original films and those exposed to UV-C radiation up to 5 days, EWF methodology requirements were met. The specific essential work of fracture (w_e) and the specific non-essential work of fracture (βw_p) parameters reflected the anisotropic character of films, being the ones determined in MD higher than those evaluated in TD. Up to these time of exposure, the strain at break showed variations within the order of its scattering while EWF parameters appeared more sensitive to the changes in molecular structure and morphology that took place in the films. Irradiated films displayed enhanced fracture parameters due to the stiffening of the amorphous phase via crosslinking reactions.

Sometime between 5 and 10 days of exposure microcracks developed in the films. These defects appeared responsible for the abrupt loss in the film drawing capability (ε_b). In fracture experiments, EWF requirements were not met since microcracks also unstabilised the crack front advance behaviour. However, the initial stage of deformation was not altered showing the remaining ductile nature of the films. The yielding parts of the specific essential work of fracture ($w_{e,y}$) and of the specific non essential work of fracture ($\beta w_{p,y}$) were still sensitive to UV-C irradiation time. Both parameters went to a maximum at 2-days of irradiation and then decreased with increasing exposure time indicating the detriment of film fracture toughness. The impair of the yielding related parts of the specific work of fracture was not evidenced by the tensile yield stress, which remained unaltered.

According to our results, the lone use the uniaxial tensile test was not enough to describe the effect of UV-C irradiation on the mechanical behaviour of LDPE/EVA films while the EWF approach appeared as a more complete tool. When the change in the propagation mode from complete stable by ductile tearing to ‘‘step-wise’’ occurred, the film became mechanically useless.

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