Materials Research. 2015; 18(4): 763-768
DOI: http://dx.doi.org/10.1590/1516-1439.010115

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Effect of Weathering and Accelerated Photoaging on PET/PC (80/20 wt/wt%) Melt Extruded Blend

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Received: April 16, 2015; Revised: May 27, 2015

In this study we investigated the natural weathering of a catalyzed blend of poly(ethylene terephthalate)/polycarbonate PET/PC (80/20wt/wt%). The results were compared to the accelerated photoaging tests. The specimens were characterized by wide angle X-ray diffraction (WAXD), optical microscopy (OM), thermogravimetry (TG/DTG), medium infrared spectroscopy (FT-IR) and stress-strain analysis. The OM analysis revealed the coexistence of at least three phases – one rich in PET (matrix), the other rich in PC (dispersed droplet) and an interfacial region between them, made of PET/PC copolymer (compatibilizing agent) produced *in situ*. The TG/DTG curves showed that UV radiation acted mainly on the PET-rich phase and the PET/PC copolymer. The OM and TG/DTG results indicated that the degradation of the compatibilizing agent has had a critical effect on the mechanical properties. For both types of aging (natural and accelerated), the PET's carbonyl index decreased with the exposure time. The FT-IR results corroborated what was seen in the OM images, showing that the PET phase acts as a shield against the PC degradation. Under accelerated aging, the mechanical properties decreased abruptly - mainly the stress-strain at yield and break - due to the degradation of the *in situ* compatibilizing agent.

Keywords: *weathering, accelerated photoaging, PET/PC blend, properties*

1. Introduction

Despite the extensive investigation over the past four decades, polymer blends continue to be an interesting matter for academy and industry. In particular, poly(ethylene terephthalate) (PET) and polycarbonate (PC) can be found in several commercial blends. Each one of these polymers has noteworthy intrinsic characteristics that allow their use in engineering applications. Aiming to combine their qualities, blends have been widely studied. Pesetskii et al.[1] investigated the effect of an chain extenders and impact modifier on a PET/PC blend. They mentioned the effect of the chain extenders on the morphology, and the increase in the impact strength. Nanocomposites of PET/PC were prepared by Mubarak[2]. He highlighted the blends immiscibility, the increase of Young's modulus and the decrease of melting temperature in blends containing 1-2 wt% of nanofiller. PC/PET blends rich in PC, in the presence and absence of three different transesterification catalysts, were studied by Al-Jabareen et al.[3]. The presence of the catalyst reduced the interfacial tension between the two immiscible components and improved the fracture behavior. Mendes & Pereira[4] discussed the effect of solid state polymerization on rheological and thermal properties of PET/PC blends. Peng et al.[5] blended recycled PET/PC/terpolymer and showed that different sequences, through low temperature solid state extrusion, resulted in the improvement of impact strength. The effects of the catalyst and residence time on PET/PC blends were studied. The authors noticed an increase in impact strength, modulus, thermal stability and melt flow index properties[6]. Oscillatory shear flow in the molten state was used to study the effect of exchange reactions on various samples of some immiscible blends of PET/PC[7]. Sonication was used to a PET/PC melt blend and the effect on impact strength and miscibility were observed[8]. Although PET/PC blends have been widely investigated, studies on their natural weathering or accelerated aging are scarce. This study explores the weathering in Rio de Janeiro city and accelerated photoaging of a PET/PC blend. The effect of UV radiation on the thermal, mechanical properties and morphology were described.

2. Experimental

2.1. Materials

The materials used were PET (Mossi & Ghisolfi, IV = 0.8 dl.g^{-1}), PC (GE Plastics, MFI = 2.5 g.10min^{-1}) and cobalt acetylacetonate (J.T.Baker Chemical Co.).

2.2. Composites and specimens preparation

Initially the polymers were dried at 120 °C for 8 hours. The reactive blend was processed in a co-rotating twin-screw extruder (L/D = 36, screw diameter = 22 mm) with a vacuum

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system, within a temperature range of 190-255 °C and a speed of 200 rpm. The 80/20 (wt/wt%) blend was chosen, and 500 ppm of cobalt acetylacetonate II – transesterification catalyst – was added to the blend[9]. The injection-molding process was performed using a Ray-Ran model RR300, and the specimens were obtained according to the ASTM D-638[10]. The barrel temperature was set to 275 °C and the mold temperature was set to 70 °C. The injection pressure and the holding pressure used were 7.5Bar.

2.3. Aging test

Natural aging was performed according to ASTM D-1435[11]. The exposure time was until 2,000 hours. The minimum temperature was 14 °C and the maximum temperature was 34 °C, and the relative humidity was 59%. The accelerated photoaging was performed according to ASTM G-155[12]. We used a Q Sun model Xe-1-B xenon test chamber, equipped with a xenon lamp. The UV protocol was: wavelength of 340 nm, light intensity of 0,35 W/m² and relative humidity of 50%. In both cases, 10 specimens were tested for each exposure time.

2.4. WAXD

Wide-angle X-ray diffraction (WAXD) analysis was performed using a Rigaku Miniflex diffractometer, with CuKα radiation ($\lambda = 1{,}5418$ Å) and experimental conditions of 30 kV, 15 mA, ranging the 2θ angle from 2° to 35°, using the resolution of 0.01°.

2.5. OM

The blend morphology was observed using a Zeiss THMS 600 microscope, over a film placed between two round glass coverslips. The assembly was inserted into the microscope hot stage and heated from 25 to 280 °C. It was kept for 2 minutes to erase the thermal history of the sample, and then cooled to identify the phases. We took pictures recording the matrix, dispersed phase and interfacial region.

2.6. TG/DTG

The thermogravimetry (TG/DTG) was carried out using a TA Q500 thermogravimetric analyzer from 30 to 700 °C at 10 °C/min, under nitrogen atmosphere. The initial degradation temperature (T_{ONSET}), temperature of maximum degradation (T_{max}) and final degradation temperature (T_{end}) were robserved.

2.7. FT-IR

Fourier-transform infrared spectroscopy combined with thermal analysis was used by Holland & Hay[13] to investigate the thermal degradation of PET, and we did the same in this study. The infrared spectroscopy of theparent materials and composites was performed using a FT-IR Varian Excalibur model, within the range of 4000-400 cm^{-1}. The spectrum was obtained by attenuated total reflectance (ATR) method, using 100 scans and resolution of 2 cm^{-1}. The effect of UV radiation on PET (1720 cm^{-1}) and PC (1780 cm^{-1}) carbonyl groups was observed. We determined the carbonyl index - the ratio between absorbance of both carbonyl groups and the absorbance of an unalterable band (1508 cm^{-1}, aromatic ring C=C bond) at each exposition time.

2.8. Tensile test

The tensile text was performed in an Instron tester model 4204, according to the ASTM D-638[10] using a load cell of 10 kN, test speed of 10 mm/min and type V dumbbell-shapped specimens. The Young's modulus, stress-strain at yield and at break values were assessed. The results consider the mean of 5 specimens at each UV exposition time.

3. Result and Discussion

3.1. WAXD

Figure 1 shows the WAXD patterns of the neat polymers and the PET/PC blend, after different types of aging. The diffraction angles (2 θ) of PET at 17, 23 and 27° are ascribed to the crystallographic planes HKL (010), (110), (100), respectively[6,13,14]. The WAXD pattern of the PC resembled an amorphous material. The WAXD pattern of the unexposed PET/PC blend did not show the crystallographic planes of PET, meaning the total absence of crystalline or paracrystalline regions. After the UV exposure, the shape of the WAXD diffractograms was similar, but with different values of the peaks' areas. Progressively, for both aging types, the area of the amorphous portion raised according to the exposure time. This can be ascribed to the degradation of the remaining paracrystalline regions in the PET phase.

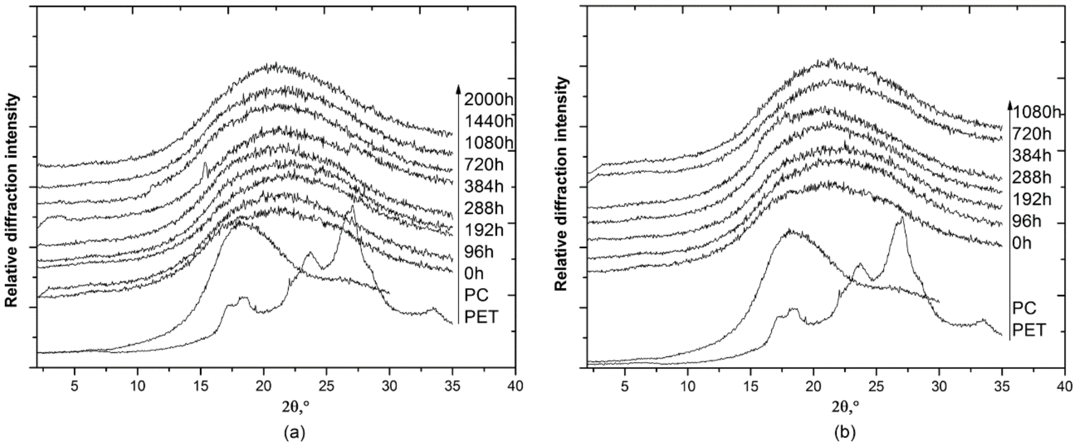

Figure 1. WAXD curves of the PET/PC blends, exposed to (a) natural aging and (b) accelerated aging.

3.2. *OM*

The OM image of the unexposed PET/PC blend in the molten state is shown in Figure 2. The morphology is matrix/droplet. At least three phases were detected. The matrix was PET and the dispersed phase was PC. The interfacial region (thickness 0.0077-0.0088 µm) seemed to be comprised of a PET/PC copolymer, which acted as a compatibilizing agent between the PET and PC phases. The copolymer was formed *in situ* by a transesterification (reaction between PET ester groups and PC carbonate groups), acidolysis (reaction between PET terminal carboxyl groups and PC carbonate groups), and alcoholysis (reaction between PET terminal hydroxyl groups and PC carbonate groups). The image of the blend exposed for 2,000 hours (Figure 3) revealed an increase in the droplet size (coalescence effect) and a decrease of the interfacial region thickness (0.0022-0.0055 µm). The degradation of the PET/PC copolymer (compatibilizing agent) was made easier by its oligomeric nature and higher mobility at the aging temperature. The size reduction of the interfacial region – which could have been beneficial - resulted in a negative effect, mainly on the mechanical properties. The breaking of the copolymer chain decreased the blend compatibility, inducing larger immiscibility in the blend. This event, associated with the UV attack on the high molar mass chains of PET and PC, probably caused the significant deterioration of the mechanical properties.

3.3. *TG/DTG*

Concerning to the TG and DTG curves of the blends, before exposure to UV radiation they showed three stages of degradation, as seen in literature[15]. The first DTG peak was ascribed to the low molecular mass of PET/PC copolymer produced *in situ* through reactive extrusion, as seen by Pereira and co-workers[6]. The next peak was an intense peak and a shoulder. The prominent portion was due to the weight loss of the PET phase and the shoulder corresponded to the mass loss of the PC phase. After weathering and accelerated UV exposure, the TG/DTG curves showed the same general outline of the unexposed blend, but slight changes could be observed at different exposure times. The values of Tonset, Tend and Tmax are shown in Table 1. For both aging conditions, the Tonset decreased with exposure time. In the accelerated aging, initially there was a sudden drop in T_{max}; it ranged between 424 and 428 °C from 96 to 720 hours, and increased to 434 °C after 2000 hours. For natural aging, it has also occured a sharp drop in T_{max}; from 96 to 384 hours the temperature ranged between 422 and 424 °C, and increased sharply from 720 hours on, reaching values close to the unaged PET. Due to the test temperature and its low molar mass, the copolymer had higher molecular mobility inside the blend, allowing progressive degradative action of UV radiation with exposure time. During the UV exposure, the PET is attacked by the combined action of

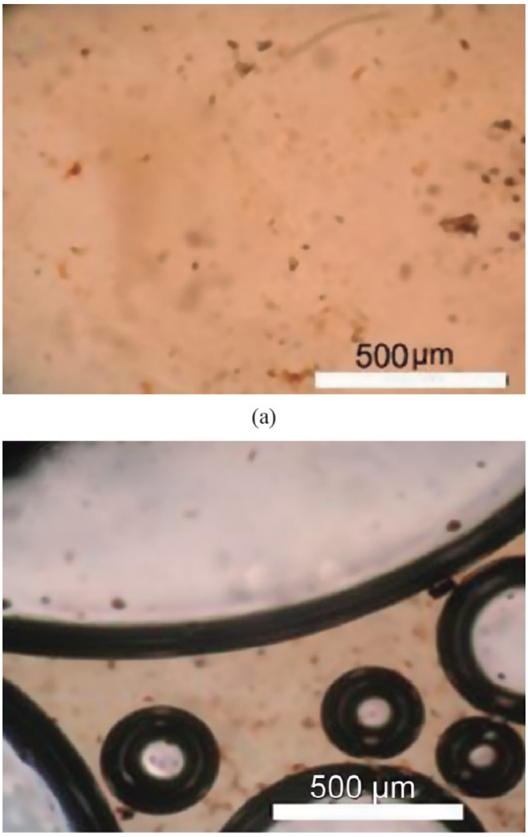

Figure 2. OM images of PET/PC (80/20 wt/wt%) (unexposed): a) 25°C; b) 280 °C.

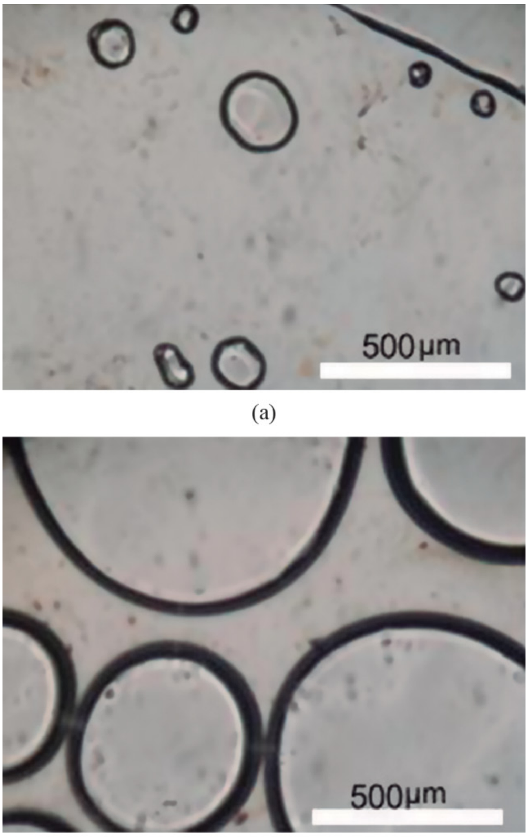

Figure 3. OM images of PET/PC (80/20 wt/wt%) (exposed 2000 h): a) 25 °C; b) 280 °C.

thermal and photo-oxidative degradations, as also reported by Fechine et al.[16,17]. The chain scission occurred at the ester bond, resulting in a decrease of molar mass and embrittlement of the polymer chain. For this blend, the PET phase was the matrix and it was more easily degraded by the UV radiation. This was the reason for the predominant decline in the T_{max} with exposure time for both aging types. The T_{max} of the PC phase did not show significant changes regardless of exposure time and type of aging. According to Diepens et al.[14,18], PC is degraded by photodegradation and the deterioration initiates with heterolytic scission of the carbonate bond (forming primary free radicals), producing structures like aromatic hydrocarbons, ether and aromatic alcohol of low molar mass. In this work, the integrity of the PC was related to the protection by the PET matrix. PET degraded and acted as a shield against PC degradation. We noticed that during the weathering the T_{end} showed a general increasing trend with longer exposure times. We can assume that fragments of the PET or PC released by the degradative action of UV radiation might have recombined, resulting in a new stable chemical structure. Actually, both types of aging caused substantial changes in the thermogravimetric properties of the blend.

3.4. FT-IR

Figure 4 shows the effect of the UV radiation on PET and PC carbonyl indices as a matter of exposure time. Considering the weathering, the carbonyl index of PET showed a slight trend to decrease. The PC carbonyl index remained practically constant. For accelerated aging, the decline of the PET carbonyl index was more pronounced, while the PC carbonyl index was constant. Fraisse et al.[19] investigated recycling of PET/PC blends. In their study, aging was not made on PET/PC blends but rather individually on PET and PC waste materials, in order to produce PET/PC blends. Both homopolymers degraded by action of UV radiation in an accelerated photoaging test. As seen in the TG/DTG analysis, the PET degradation occurred more quickly and affected the homopolymer and the PET/PC copolymer. PET acted as a

Table 1. Representative TGA data of the PET, PC and the blend, under natural and accelerated aging.

Sample	Degradation Temperature (°C)		DTG (°C)	
	Onset	End	Maximum Temperature (T_{max})	
			PET phase	PC phase
PET	402	450	426	-
PC	482	540	-	504
PET/PC 0h	296	521	438	494
PET/PC[n].96h	295	519	422	483
PET/PC[n].192h	294	519	424	490
PET/PC[n].288h	291	520	423	485
PET/PC[n].384h	287	524	424	494
PET/PC[n].720h	286	530	436	500
PET/PC[n].2000h	282	524	437	500
PET/PC[a].96h	291	506	424	496
PET/PC[a].192h	296	519	428	487
PET/PC[a].288h	289	513	424	473
PET/PC[a].384h	292	514	427	495
PET/PC[a].720h	282	506	426	499
PET/PC[a].2000h	285	497	434	500

[a]accelerated. [n]natural.

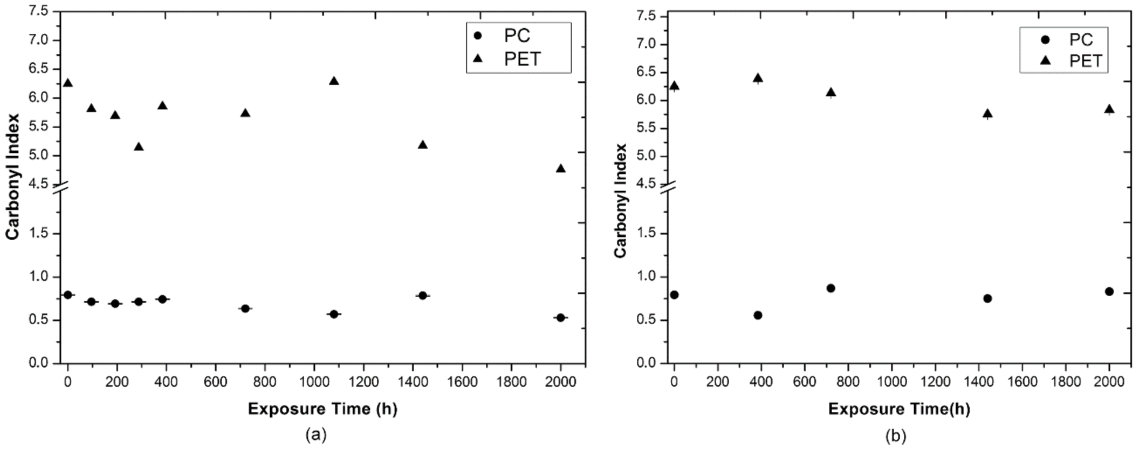

Figure 4. Carbonyl index as a function of exposure time for (a) natural and (b) accelerated photoaging.

kind of covering on the blend. Thus, the results found for carbonyl index and thermogravimetry are corroborative.

3.5. Tensile test

As mentioned before, there has been relatively little investigation on aging of PET/PC blends. In general, the mechanical properties of the blend combine the characteristics of both homopolymers. Our mechanical evaluation concerned the elastic modulus, stress strain at yield and stress-strain at break. The elastic modulus (Figure 5) was steady for both kinds of aging. The stress-strain at yield showed the same trend (Figures 6 and 7). For weathering, both properties were practically unchangeable as the exposure time increased. In contrast, the yield properties obtained from accelerated photoaging revealed an abrupt drop after 384 hours of exposure. The ductility was lost (values near zero) at longer exposure times. Although under accelerated photoaging the standard deviation was large, the stress at break (Figure 8) showed a trend to increase as a function of exposure time. The values of that property for weathering were nearly constant. Even considering the variation of the standard deviation, the decrease of strain at break was large (Figure 9). Since the beginning, the decrease of the strain at break was huge. The effect was more pronounced under accelerated conditions. The values dropped to nearly zero in the early stage of UV exposure. The abrupt loss

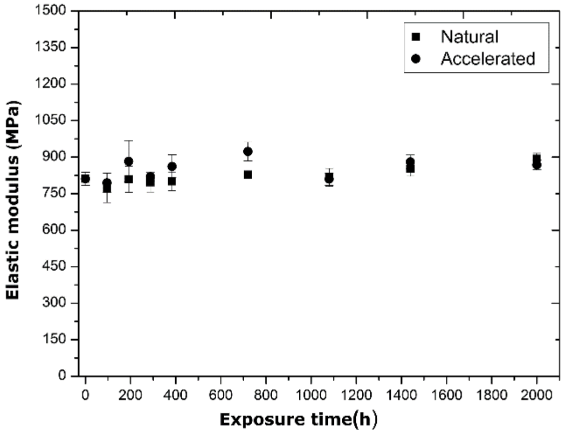

Figure 5. The elastic modulus as a function exposure time for natural and accelerated photoaging.

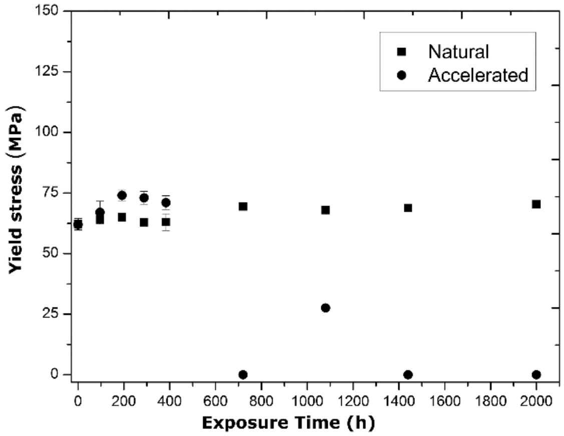

Figure 6. The yield stress as a function exposure time for natural and accelerated photoaging.

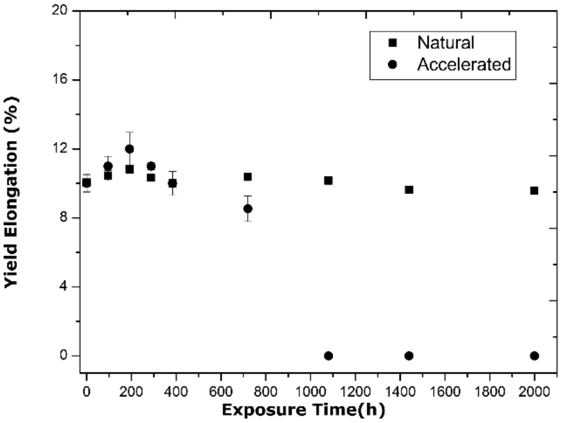

Figure 7. The yield elongation as a function exposure time for natural and accelerated photoaging.

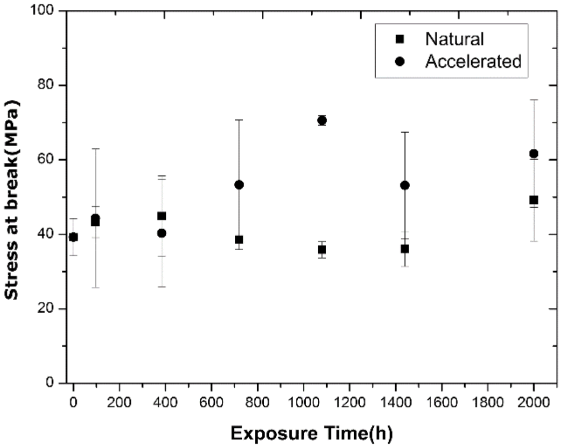

Figure 8. The stress at break as a function exposure time for natural and accelerated photoaging.

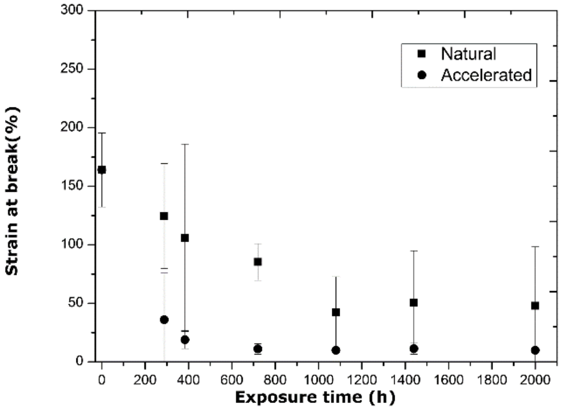

Figure 9. The strain at break as a function exposure time for natural and accelerated photoaging.

of physical properties - mainly stress-strain at yield and break - during the accelerated photoaging was ascribed to an increase of the carbonyl index. The ester bond along the PET homopolymer and copolymer backbone did no resist the UV attack. Therefore, for outdoor applications, virgin and recyclable PET must contain an additive against the UV radiation.

4. Conclusions

Similar to what happens to living beings, homopolymers and blends are also susceptible to the action of ultraviolet radiation. In particular, the action of UV irradiation on the blend was negative. The OM and TG/DTG results allowed inferring that the degradation of the compatibilizing agent (the PET/PC copolymer) has a decisive effect on the mechanical properties. The evaluation of the WAXD diffractrogram areas indicated that in the PET phase, there were still structures with some degree of organization. The carbonyl index values were in agreement with FT-IR and OM results. The PET was the matrix and acted as a kind of shielding against the PC degradation. The mechanical properties at yield and break seemed to be greatly affected by the degradation of the compatibilizing agent.

Acknowledgements

The authors strongly thank to Conselho Nacional Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Universidade Federal do Rio de Janeiro (UFRJ) for supporting this research. Also thank Mossi & Ghisolfi Co and GE Plastics for supplying the precursor homopolymers.

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