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Photodegradation Mechanisms on Poly(ε-caprolactone) (PCL)

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Photodegradation of PCL was performed exposing injected specimens to ultraviolet radiation (UV-B) up to 9 weeks. Photodegradated PCL specimens were tested by Differential Scanning Calorimetry (DSC), Infrared Spectroscopy (FTIR), mechanical properties, Optical Microscopy (MO) and Scanning Electron Microscopy (SEM).Upon exposure decrease in elongation at break and increase of elastic modulus were verified, higher degree of crystallinity was observed for longer exposure what can be due to the chemi-crystallization mechanism. From IR spectra new carbonyl group (C=O) peaks were observed. Presence of micro cracks on specimens' surface was identified by MO. From morphological analyses is suggested that the photodegradation in PCL takes place by bulk erosion mechanism.

Keywords: *PCL, Phododegradation, Chemi-crystallization, Bulk erosion.*

1. Introduction

Synthetic plastics have been used for various purposes, especially in the packaging industrial sector; however, the majority of these materials presently cause serious problems with the waste management [1-4]. Focusing on potential solutions for this problem, polymer researchers have paid attention to biodegradable polymers, from petroleum and renewable sources, since they can be biologically degraded and therefore being considered as environmental friendly materials [5-12].

Among the biodegradable polymers, a special attention has been given by the scientific community to poly(ε-caprolactone) (PCL), that is a linear aliphatic semicrystalline polyester, synthesized by ring-opening polymerization of the cyclic lactone in presence of a catalyst. PCL has high ductility due to its chemical structure and low glass transition temperature of -60 ºC, it is thermally stable until 320 ºC, as a thermoplastic it is easily processed and recycled by conventional polymer processing, i.e., extrusion and injection [12-15]. PCL has been successful used in a wide range of industrial applications, including packing, food containers, agricultural films, biomedical applications, devices for automobile and electronic industries, and so on [16-18].

Nevertheless, to the best of our knowledge few works are dealt about the photodegradation of PCL. Tsuji et al. [19] suggested that photodegradation of PCL films proceeds via a bulk erosion mechanism with serious damages to the elongation at break, they observed that the effects are deeper in the amorphous phases; and the UV irradiation significantly increased the degree of crystallinity of PCL due to thickening of crystallites. Photodegradation of PCL was delayed upon blending with PVC as observed by Christensen et al. (2008) [20].Bei et al. (2000) [21] verified in poly(ε-caprolactone)-poly(ethylene glycol) block copolymer (PCE) that the pure poly(ethylene glycol) (PEO) cannot be photodegraded alone, but the carbonyl groups in PCL segment catalyze the breakage of PEO chains by a series of UV initiated free radical reactions.

In this work inject specimens of PCL were photodegraded by exposure to UV-B radiation, and their morphology, thermal and mechanical properties properly analyzed by optical microscopy (OM), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), infrared spectroscopy (FTIR) and mechanical properties. According to the DSC results further presented the chemi-crstallization process is suggested taking place and being the responsible for increasing the degree of crystallinity, and the photodegradation in PCL was evidenced by SEM images as occurring by bulk erosion mechanism.

2.Experimental

2.1 Materials

Poly (ε-caprolactone) (PCL) CAPA 6500, melting flow rate (MFR) = 28 g/10 min (190 °C/2.16 kg), was purchased from Perstorp Winning Formulas.

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2.2 Processing

Neat PCL was processed in a twin screw extruder Coperion-Werner&Pfleiderer ZSK 18. The temperature inside the extruder was kept between 80 °C and 100 °C and the screw speed was set up at 250 rpm. After extrusion, the material was granulated and oven dried for 24 hours at 40 ºC. Injected specimens for mechanical experiment were produced in Arburg Allrounder 270C machine at 80-100 ºC, according to ASTM D638 standard.

2.3 Radiation exposure

The radiation tests were performed using a Comexim (type C-UV) appropriate for non-metallic materials, operating with 40 W F40 UV-B fluorescent lamps with peak radiation at 313 nm. The samples were exposed to continuous radiation for periods up to 9 weeks, forwarding characterization experiments were performed.

3. Characterization

3.1 Differential scanning calorimetry (DSC)

DSC analyses carried out in a DSC-Q20 TA Instruments, samples weighting approximately 3 mg were heated from 25 ºC to 250 ºC, followed by cooling to 10 °C and reheating to 250 °C. The heating/cooling rate was 10 ºC/min, under nitrogen flow of 50 mL/min.

3.2 Mechanical tests

Mechanical properties in tension were measured according to ASTM D638; tests were conducted in an EMIC DL 2000 testing machine operating at 50 mm/min of elongation rate and 2000 kgf cell load. Tests were conduct at ambient temperature (~ 23 ºC) and presented results are an average of seven tests.

3.3 Fourier transformed infrared spectroscopy (FTIR)

FTIR analyses were performed in a Perkin Elmer Spectrometer Spectrum 400 FT Mid-IR, Attenuated Total Reflectance (ATR) mode was applied and scans ranging from 4000 to 650 cm^{-1} were computed.

3.4 Polarized optical microscopy (OM)

Photographs of PCL before and after exposure were recorded on a Carl Zeiss Polarized Optical Microscope equipped with a digital camera, AxioCAM MRc.

3.5 Scanning electron microscopy (SEM)

Scanning electron microscopy images were acquired in a VEGAN3 TESCAN machine with 30 KV. Fractured surface from mechanical test was covered with gold to avoid accumulation of charges.

4. Results and Discussion

Photographs of PCL specimens unexposed and exposed to UV-B radiation up to 9 weeks are illustrated in Figure 1. After exposure, there is light-yellowing on exposed specimen surface and micro cracks developed with exposition to radiation (Figure 1 from 1 week). According to the literature [15] the yellowing is evidence that photodegradation is taking place, its origin may be accessed to radiation absorption by chromophoric groups and formation of free radicals that absorb oxygen and start chemical and physical changes like chain scission, damaging the mechanical properties.

The texture of the specimen exposed surface becomes rougher and crumbles for longer exposure times. The presence of cracks and roughness in samples exposed to radiation has already been reported for other polymers like poly(3-hydroxybutyrate) (PHB), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP) [1,13,14,22,23].

Wellen et al.[24] studied the photodegradation and photostabilization of two commercial grades of PHB. The authors obtained the specimens by injection molding and the specimens were exposed to ultraviolet radiation (UV-A) for up to 12 weeks and then characterized by tensile testing, surface appearance, size exclusion chromatography (SEC) and scanning electron microscopy (SEM). According to the authors the exposure to UV-B radiation caused great damage on the surface color, reduction of molecular size and mechanical properties. However, it is important to note that for PHB changes in color can be not caused by chromophoric groups but by cracks on the specimen surface that increase its roughness and the diffuse reflectance of visible light.

Regarding the superficial changes originated upon exposition to radiation, according to Rabello and White[22] an important process called chemi-crystallization is observed in some semi-crystalline polymers, for instance in PP. In chemi-crystallization the chain scission occurs due to the degradation mechanism but these *broken* molecules reorganize in a crystalline phase, provided that they have enough mobility. The main characteristic of this process is the spontaneous crack formation on external surfaces by the contraction of the specimen layers, these cracks contribute to the embrittlement of ductile semi-crystalline

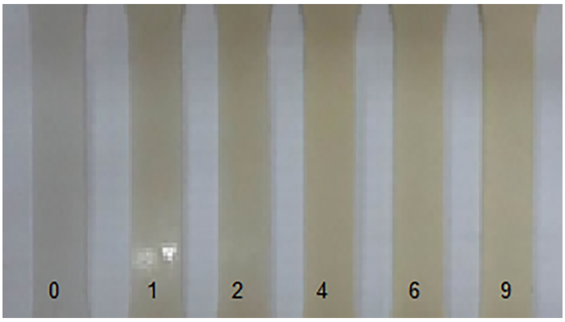

Figure 1. Photographs of PCL specimens illustrating light-yellowing after UV-B exposure. Exposing times in weeks are indicated

polymers promoting serious deterioration on polymer after short exposure.

Figure 2 shows DSC scans for melt crystallization and melting of PCL unexposed and exposed up to 9 weeks, and Tables 1 and 2 present thermal parameters computed from these scans. It is observed that the crystallization peak shifted lightly to higher temperatures, the degree of crystallinity (ΔX_c) decreased upon exposure. An interesting fact observed for 9 weeks of exposure is that the crystallinity was higher than for shorter intervals of exposure, somehow PCL molecular chains rearranged and crystallized, it may be seen as an effect of chemi-crystallization.

The melting peak temperature did not show significant changes, the degree of crystallinity (ΔX_m) measured from melting enthalpy presented a similar trend as that verified for melt crystallization, the degree of crystallinity decreased upon exposure and then it increased for longer exposure, i.e., 9 weeks, it also may be an effect of chemi-crystallization.

Polymer studiers have reported decrease in crystallinity upon degradation for other resins like PLA, PET and PEEK [25,26]. Santonja-Blasco et al.[25] investigated the effects of three types of degradation, thermo-degradation, photodegradation and biodegradation in PLA. At high temperature i.e., thermal degradation at 220 °C, random chain scission was faster followed by photodegradation and biodegradation. Photodegraded specimens presented around the half of molar mass compared to soil degraded ones, i.e. biodegraded. Chain defects such as the anhydride groups formed during photodegradation decreased the crystallization rate, but the extreme damages as higher chain scission and lower crystallinity were verified for thermal-degradation.

Vaughan and Stevens[26] analyzed the effect of gamma radiation on PET crystallization. Sample tests were experimented

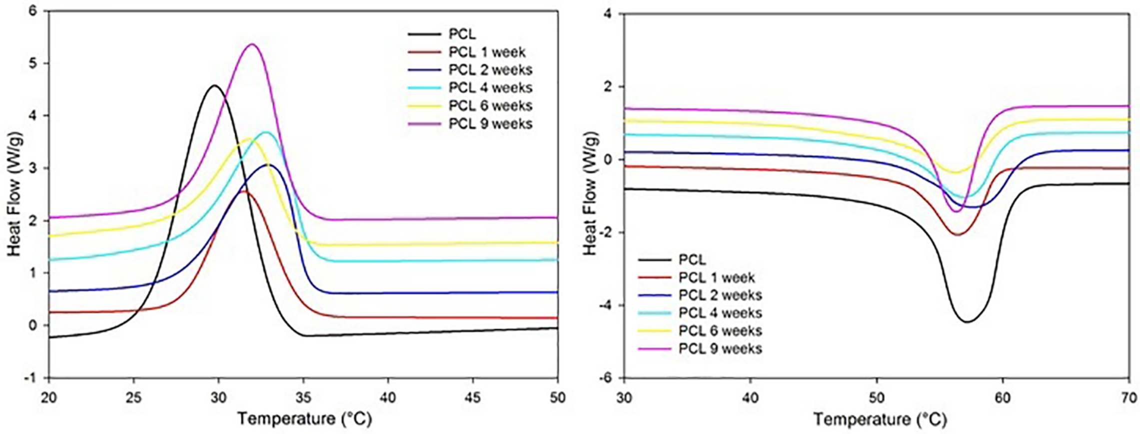

Figure 2. DSC scans for Melt Crystallization (left) and Melting (right), acquired during cooling and re-heating cycles, respectively

Table 1. Melt crystallization parameters computed from DSC scans during cooling for PCL exposed to UV-B radiation up to 9 weeks.

Compound	$T_{0,1\%}$	$T_{50\%}$	$T_{99,9\%}$	ΔT_c	T_c	c_{max}	$\bar{c}_{5\text{-}95\%}$	$\tau_{½}$	ΔH_c	ΔX_c
			(°C)			(min^{-1})		(min)	(J/g)	(%)
PCL	34.46	29.77	22.95	11.51	29.76	2.078	1.418	0.50	54.94	37.89
PCL 1 Week	36.06	31.35	24.36	11.70	31.46	2.263	1.504	0.47	13.49	9.30
PCL 2 Weeks	35.87	32.41	19.80	16.07	32.91	1.961	1.231	0.42	14.24	9.82
PCL 4 Weeks	36.16	32.21	19.87	16.30	32.79	1.921	1.021	0.46	16.84	11.61
PCL 6 Weeks	35.39	31.47	24.66	10.73	31.78	2.168	1.379	0.44	13.18	9.09
PCL 9 Weeks	35.81	31.84	22.42	13.39	31.97	2.306	1.380	0.46	27.03	18.64

$T_{0.1\%}$ (°C): temperature for 0.1% molten/crystallized fraction. $T_{50\%}$ (°C): temperature for 50% molten/crystallized fraction. $T_{99.9\%}$ (°C): temperature for 99.9% molten/crystallized fraction. T_p, T_c (°C): peak melting/crystallization temperatures. c_{max} (min^{-1}): maximum melting/crystallization rate. $\tau½$ (min): half melting/crystallization time (time to reach 50% molten/crystallized fraction from the start of the event). ΔH_m, ΔH_c: (J/g): latent heat of melting/crystallization. ΔX_m (%), ΔX_c (%): change in crystallinity during the event (the literature lists two slightly different reference values for the latent heat of fusion of PCL. Mandelkern[27,28] reports the value 142.4J/g in two of his textbooks, another textbook by Van Krevelen and Nijenhuis[29] quotes the value 148.1J/g. In the present work we decided to use the value 145J/g, an approximated mean value, as the melting enthalpy of 100% crystalline PCL).

Table 2. Melting parameters computed from DSC scans during the second heating for PCL up to 9 weeks.

Compound	$T_{0,1\%}$	$T_{50\%}$	$T_{99,9\%}$	ΔT_m	T_p	c_{max}	$\bar{c}_{5\text{-}95\%}$	$\tau_{1/2}$	ΔH_m	ΔX_m
			(°C)			(min^{-1})		(min)	(J/g)	(%)
PCL	49.02	56.91	61.67	12.65	57.22	1.887	1.217	0.81	45.43	31.33
PCL 1 Week	43.56	55.79	59.99	16.43	56.41	1.895	0.937	1.22	12.23	8.44
PCL 2 Weeks	41.68	56.50	63.36	21.68	57.73	1.332	0.725	1.52	13.06	9.01
PCL 4 Weeks	41.61	55.54	62.04	20.43	59.94	1.426	0.749	1.43	15.90	10.96
PCL 6 Weeks	42.22	54.87	61.56	19.34	56.33	1.319	0.724	1.29	15.92	10.98
PCL 9 Weeks	41.63	55.32	60.75	19.12	56.32	2.027	0.832	1.41	26.44	18.24

in amorphous state as well as after annealing. The gathered results were similar to those obtained for PEEK, i.e. as the radiation doses increased, the melt crystallization peak shifted to higher temperatures and the degree of crystallinity decreased.

Figure 3 shows results for elastic modulus (a), elongation at break (b), maximum stress (c) and tensile strength (d) for PCL before and after exposure to UV-B radiation.

Initially, PCL behaves as a ductile polymer, with low elastic modulus and high elongation at break (>418%). After exposure, its elastic modulus increased by 48% and remained almost unchangeable over the exposure time.

For elongation at break, a decrease of 80% was observed after the first week of exposure, in two weeks it decreased 94% in relation to unexposed PCL and 71% to PCL exposed for 1 week. Further exposure did not provide significant changes, specimens presented similar mechanical properties.

These events, increase in elastic modulus and higher decrease in elongation at break that occurred after exposure to radiation, modified PCL properties, making it a rigid and

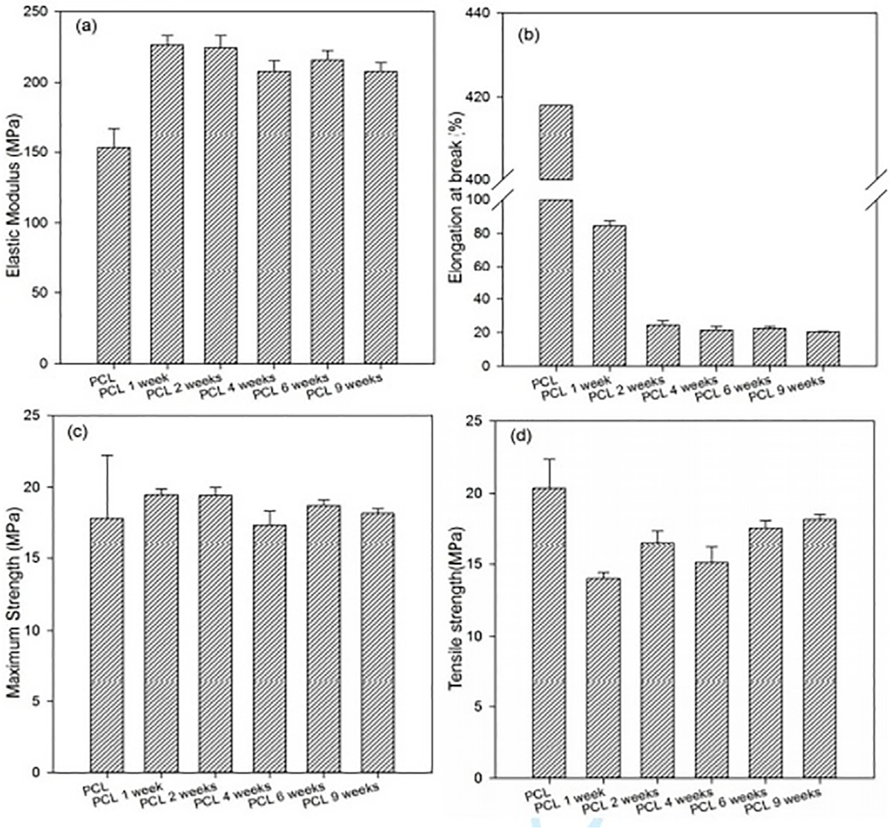

Figure 3. PCL mechanical properties before and after exposure. a) Elastic Modulus, b) Elongation at Break, b) Maximum Strength, d) Tensile Strength

brittle polymer, micro cracks, crazy development as well as chemi-crystallization are processes possibly linked to these changes [8].

Figure 4 shows FT-IR spectra of PCL unexposed and exposed. According to the literature [30,31], PCL presents infrared absorption bands which are relevant for polymer characterization and its changes. The spectra in Figure 4 presented in 2944 cm^{-1} and 2861 cm^{-1} referring bands to asymmetric and symmetrical stretching of CH_2 groups, respectively. The most intense peak at 1725 cm^{-1} is characteristic of carbonyl group C=O, the peak at 1300 cm^{-1} to the C-O and C-C groups of main chain, at 1243 cm^{-1} a symmetric elongation of C-O-C and at 1168 cm^{-1} a symmetrical elongation of C-O-C groups.

After exposure, the relative peak of carbonyl group (C=O), visualized at 1725 cm^{-1} broadened what may have been caused by formation of new radicals (C=O) localized in different regions in PCL macromolecules, for instance in terminal groups, this change is suggested as degradation evidence due exposure to UV-B radiation.

Optical microscopy images are presented in Figure 5, it is observed that before exposure PCL had a dense and non-porous surface, Figure 5 (Unexposed). After exposure,

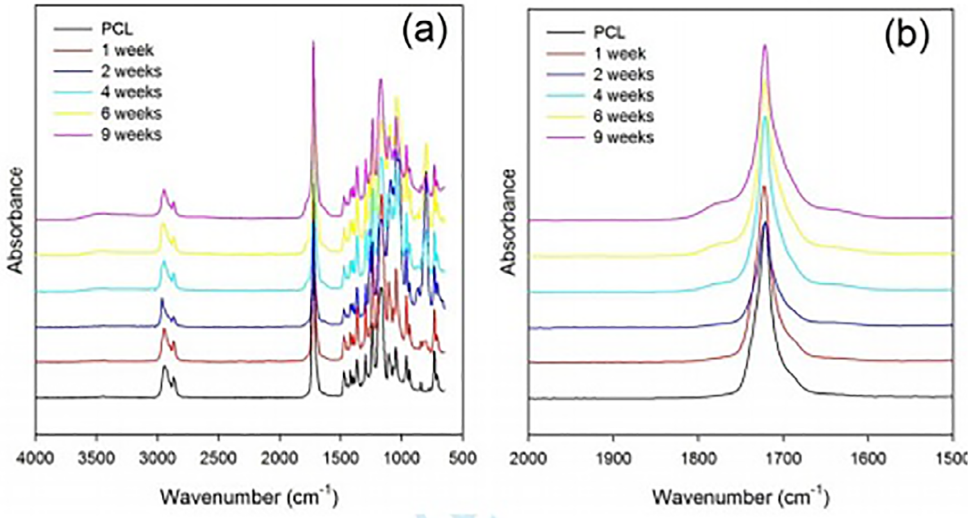

Figure 4. (a) FT-IR spectra of PCL unexposed and exposed to UV-B radiation and (b) zoom of Figure 5 (a) illustrating absorption wavenumber of carbonyl group

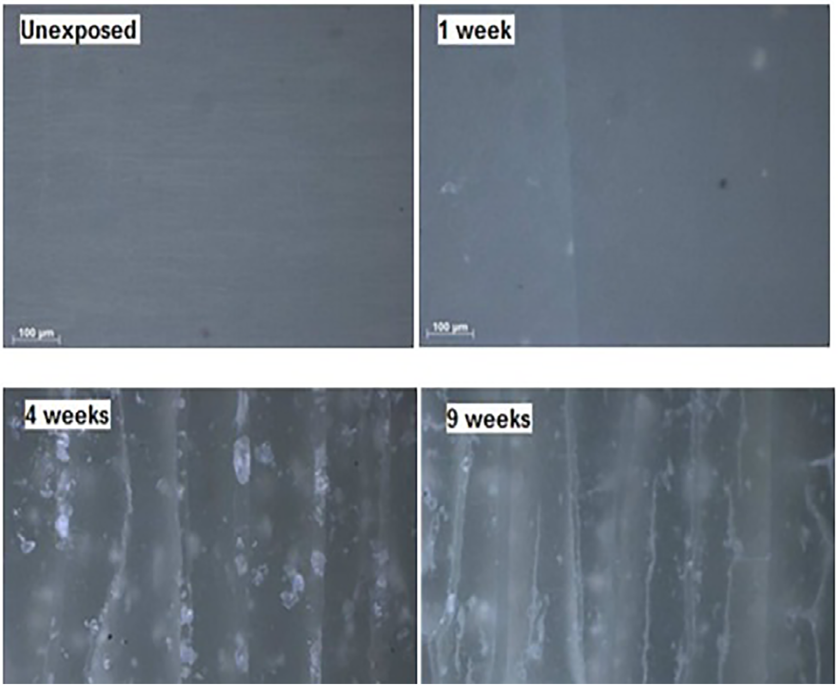

Figure 5. Optical microscopy images of PCL unexposed and exposed to UV-B radiation

Figure 5 for 1 week, presence of micro cracks on PCL surface is verifiable and they increase with exposure. It can be clearly seen in the micrographs (Figure 5 for 2 weeks exposure) presence of crystals inside and near of the cracks [32].

Regarding the cracks and roughness, the researcher groups Grigull et al., 2015 [32] and Narkis et al., 1985 [33], agree that these, probably, can be originated from chemi-crystallization as well as from degradation mechanism Norrish II. It is plausible assuming the observed decreasing in mechanical properties may be accelerated by these processes.

Figure 6 shows SEM images for PCL specimens upon UV-B radiation. Unexposed PCL presents ductile fracture with evidences of plastic deformation. After exposure the fracture surface changes and a fibrous morphology is observed. This behavior has been reported for PCL by Tsuji et al. 2006 [19], Castilla-Cortazár et al. 2012 [34] and França et al. 2016 [17] who related this morphological change due to degradation mechanisms called bulk erosion that is when the degradation occurs throughout the whole material, for this case, both the surface and the bulk of the material degrade. These authors observed initially surface erosion followed by the fibrous morphology, being both linked to PCL degradation, similarly to what was verified in the present work in Figure 6.

5. Conclusions

Photodegradation of PCL was analyzed by exposing injected specimens to UV-B radiation up to 9 weeks. From the gathered results was possible assuming that PCL is strongly affected by radiation, its mechanical properties such as elastic modulus and elongation at break changed considerably. FTIR spectra presented alterations related to the carbonyl groups; formation of micro cracks could be observed by optical microscopy. The degree of crystallinity increased for longer exposure time, as probable consequence of chemi-crystallization. In SEM images erosion and fibrous morphologies were verified what can be linked to loses in mechanical properties. Summing up 9 weeks of exposure are enough to considerably damage PCL products.

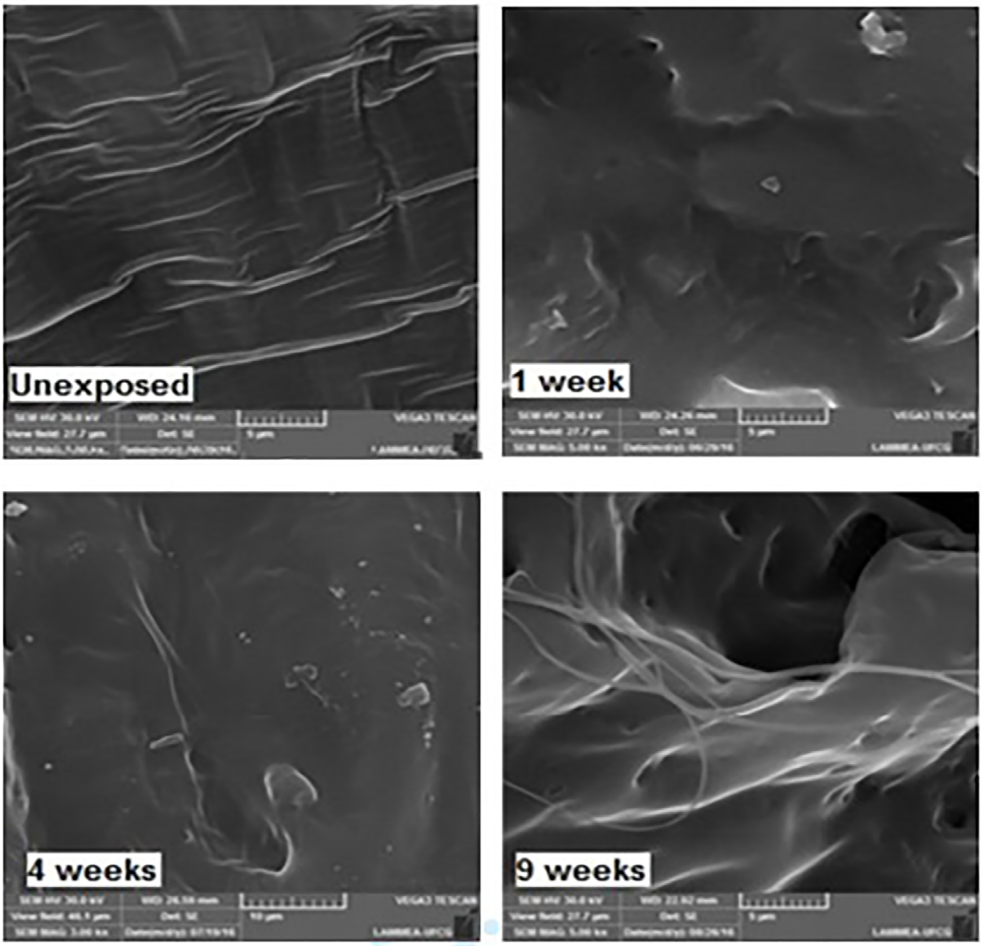

Figure 6. SEM micrographs of PCL fracture surface exposed to UV-B radiation. Exposure times up to 9 weeks

6. Acknowledgments

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