

Comparative study of degradation of PP modified with an organic pro-degradant subjected to natural and artificial ageing

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ABSTRACT

In abiotic degradation the action of light radiation is one of the most important parameters, because polymers undergo degradation due to the action of light (natural or artificial). The aim of this study was to investigate the degradation rate for samples of polypropylene (PP) modified with an organic pro-degradant submitted to ageing in a natural environment and to accelerated ageing test. The degradation behavior of the samples exposed to the ageing processes was evaluated through changes in the degree of crystallinity (X_c), surface morphology (Scanning Electron Microscopy) and molecular weight. The results indicated that for the modified polypropylene samples natural ageing led to a 42.3% reduction in the molecular weight and the surface morphology showed evidence of erosion. In the accelerated ageing process the UV radiation was stronger, which led to a 94.3% increase in the degree of crystallinity and micro-voids were present on the surface of the modified polypropylene. **Polyolefins J (2016) 3: 93-101**

Keywords: Polypropylene; Degradation; Organic pro-degradant; Ultra-violet Radiation.

INTRODUCTION

Synthetic polymers like polypropylene are designed and manufactured to withstand environmental degradation, but these materials have a short useful life, in many cases of less than two years. Thus, the improper disposal of polymer waste, for instance, in dumps, landfills, rivers and the sea, leads to its persistence and accumulation in the environment [1, 2].

Abiotic processes such as photodegradation, are the most efficient occurring in the open environment, where the polymers undergo degradation through the action of sunlight resulting from direct exposure to solar radiation. However, the degradation behavior is dependent on the type of chemical ageing that occurs, since this is the principal factor in climatic ageing [3, 4, 5].

Neat polyolefins do not absorb UV light, but impuri-

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ties or defects remaining from the synthesis process or generated during thermal processing, such as hydroperoxide and carbonyl groups, can initiate the intensive photooxidation of such polymers [6]. This group of polymers is highly susceptible to photodegradation, which occurs faster in air than in an inert environment. Although, PP does not absorb energy at wavelengths above 290 nm, at which the oxidative radical may be generated through the absorption of sunlight, it strongly absorbs UV radiation at wavelengths shorter than 250 nm, which is well below the shortest wavelength reaching the earth's surface (around 290 nm) [7]. The explanation for this is that some impurities, such as hydroperoxide and carbonyl groups, act as initiators of photodegradation (chromophores).

Thus, the exposure of samples to weathering may cause changes in the chemical structure of the polymer, leading to a reduction in the molecular size and the formation of these groups as well as carbonyl hydroperoxides [8,9].

Photooxidation is considered to be the main process involved in polymer ageing and accounts for the failure of its useful properties in the later stages of the polymer lifetime. According to Yakimets et al. [8], this process consists of the degradation of the material by means of ultraviolet rays and is governed by the diffusion of O₂ in the polymer, which modifies irreversibly the structure and behavior of the material [10]. Oxidative degradation can modify the thermal, morphological, chemical and physical properties of polypropylene, due to impurities in the polymer which make it particularly sensitive to the presence of ultraviolet rays. Natural polypropylene without stabilizers and pigments is very sensitive to this type of degradation [11,12].

In abiotic degradation, the action of light radiation (sunlight or artificial) is one of the most important parameters. The Norrish I, II and III reactions can express photodegradation where the polymers are transformed by photoionization and chain scission. Photodegradation can occur through Norrish reactions, and/or crosslinking reactions, or oxidative processes [4,13,14].

In the study reported herein, the influence of the organic pro-degradant, free of transition metals, in PP samples exposed to natural and accelerated age-

ing was investigated. The organic pro-degradant additive is a potassium salt and benzoin with groups 1,2-oxo-hydroxy having both the ability to promote the degradation of polyolefin. According to Gijsman and Jansen [15] benzoin is an efficient catalyst and it undergoes molecular cleavage when under radiation, as described by Lewis [16].

The changes in the thermal, physical and morphological characteristics during the exposure period were studied using conventional techniques, such as differential scanning calorimetry (DSC) to observe the changes in the crystallinity, scanning electron microscopy (SEM) to analysis the surface modification of the samples before and after natural and accelerated photodegradation and measuring molecular weight by visometry to evaluate the decrease in the molecular weight of the samples.

EXPERIMENTAL

Materials

Polypropylene homopolymer (Grade: H125) (MI = 38 g/10min; d = 0.905 g/cm³) was kindly donated by Braskem, Triunfo/Brazil. Benzoin (2-hydroxy-2-phenylacetophenone) (98%) (Figure 1a) and octanoic acid (98%) were purchased from Sigma-Aldrich, and used as received. Potassium hydroxide was purchased from Synth. Potassium octanoate (Figure 1b) was synthesized from octanoic acid (7.2 mL) and potassium hydroxide (2.8 g) under water reflux as described in the literature [15]. The benzoin and potassium octanoate (1.0:0.1) were used, respectively, as catalyst and co-catalyst and together comprised the organic pro-degradant. Decalin (Vetec) was used to dissolve the PP for determination of the viscometric molecular weight.

Preparation of modified polypropylene

Samples of neat and modified (PP+1.25% organic pro-

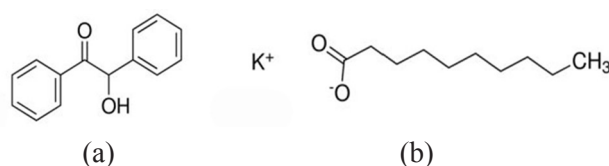


Figure 1. Chemical structure of compounds: (a) 1,2-oxo-hydroxy and (b) benzoin [15].

degradant) PP were extruded in a Ciola single-screw extruder ($L/D=22$), with a thermal profile from the feeding zone to the head of 210°C , 200°C and 190°C and a screw speed of 45 rpm, and then pelletized. The PP pellets with additive were ground in liquid nitrogen and oven-dried at 40°C for 24 h. Samples of PP with and without the organic pro-degradant in plate form (5×5 cm with 2 mm thickness) were obtained using a press at 220°C with a 2-ton loading for 5 min. These samples were exposed to natural ageing. The samples used in the accelerated ageing were injected in a molding machine (Minijet II) and molded at a processing temperature of 205°C and under a pressure of 450 atm. Samples of neat PP were submitted to the same treatment and used as a reference.

Photodegradation test

The degradation testing of the PP samples with and without modification was performed under ambient conditions for natural ageing and under UV irradiation for accelerated ageing. The samples were removed after different time periods.

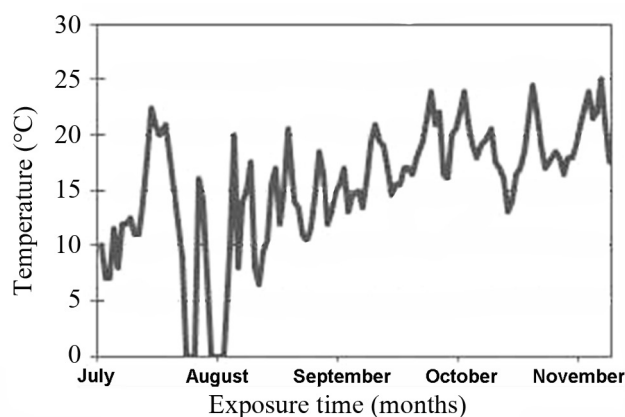
Natural ageing test

The test was carried out according to the method described in the standard ASTM D1435-13 [17]. The exposure of the samples to ageing in a natural environment (abiotic) was conducted from July to November 2011 (winter/spring), on platforms built with an inclination angle of 30° in relation to the ground, facing the equator, in Porto Alegre, Rio Grande do Sul State, Brazil (latitude $30^{\circ}05' \text{S}$; longitude $51^{\circ}11' \text{W}$).

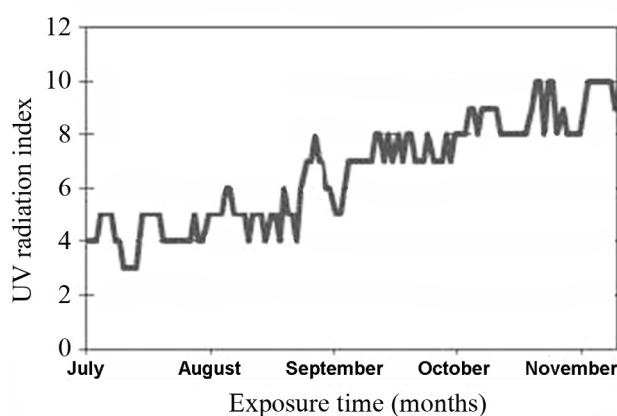
Data on the average UV radiation index, temperature and rainfall during the natural ageing test period were provided by the CPTED-INPE (Center for weather and climate studies - National Institute for Space Research), as listed in Figure 2. Also, the minimum and maximum temperatures were recorded on a daily basis throughout this period and were around 0°C and 25°C , respectively.

The response to the exposure of the material is dependent on these variables since higher values will accelerate the photodegradation and thus provide faster results. Another way to investigate the photochemical resistance of polymers is through exposure to specific environmental conditions, where the various compo-

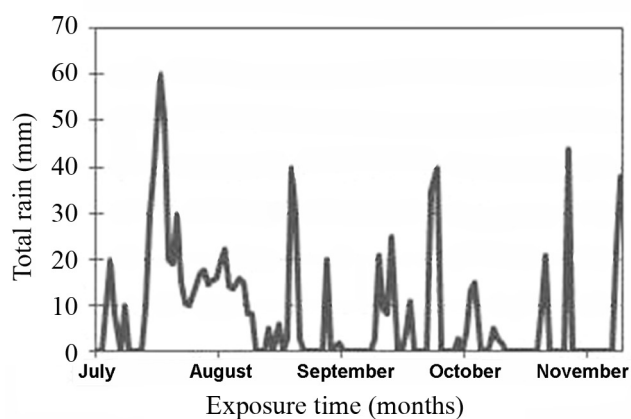
nents of the environment, such as ultraviolet radiation, visible light, temperature, humidity, wind, bacteria and the pH of rain, which can affect the chemical structure of the polymer and cause degradation, are investigated. The intensity of the elements of the natural environment varies significantly with the exposure



(a)



(b)



(c)

Figure 2. Environmental conditions during the test period from July to November 2011 in which the samples were exposed to natural ageing: (a) Temperature (b) UV radiation (c) Total rainfall.

process of the polymer, as confirmed by the results for the viscometric molecular weight, in which there is a significant decreasing in the M_v from 95,000 g/mol to 52,000 g/mol after exposure to natural ageing for 120 days and to 67,000 g/mol after being submitted the accelerated ageing for 63 days. This result indicates that an increased time of exposure enhances the degradation of the macromolecules of PP.

A more pronounced decrease in the M_v can be observed for both samples in the first 20 and 30 days of exposure, after natural and accelerated ageing, this being more evident for the samples containing the organic pro-degradant agent. This result is related to the degree of crystallinity, that is chemi-crystallization, where the molecules of a certain size are in an amorphous arrangement and after a certain period the crystallization tends to decrease, due to high levels of degradation. The same behavior was observed for the M_v , a decrease occurring within around 20 to 30 days followed by a stabilization of the values [8]. Note that during 60 to 90 days the modified PP samples showed a greater decrease, may be because the UV index was higher (Fig. 2-b), along with the temperature and frequency of rainfall during this time (Oct-Nov).

According Voght and Kleppe [25], the effects of ultraviolet radiation on the properties of PP are attributed to oxidative reactions that lead to chain cleavage mainly in the region of the molecules that participate in more than one crystalline lamellae (known as molecular knots), which together with the formation of surface cracks, lowers the resistance. The subsequent fission chain reaction reduces the polymer molecular weight on increasing the exposure time, this being the most significant effect on the modified samples exposed to natural weathering [25].

Table 1 shows the variation in the intrinsic viscosity of the PP samples before and after natural and accelerated ageing. A decreasing in the viscosity values can be observed as a function of the exposure time, this being more evident for the modified PP samples, due to the influence of the organic additive on the bond cleavage, decreasing the M_v and consequently the viscosity. It was noted that the artificial ageing affected the decrease in the viscosity more than the natural ageing, which indicates that the ultraviolet radiation conditions were more intense than those of natural

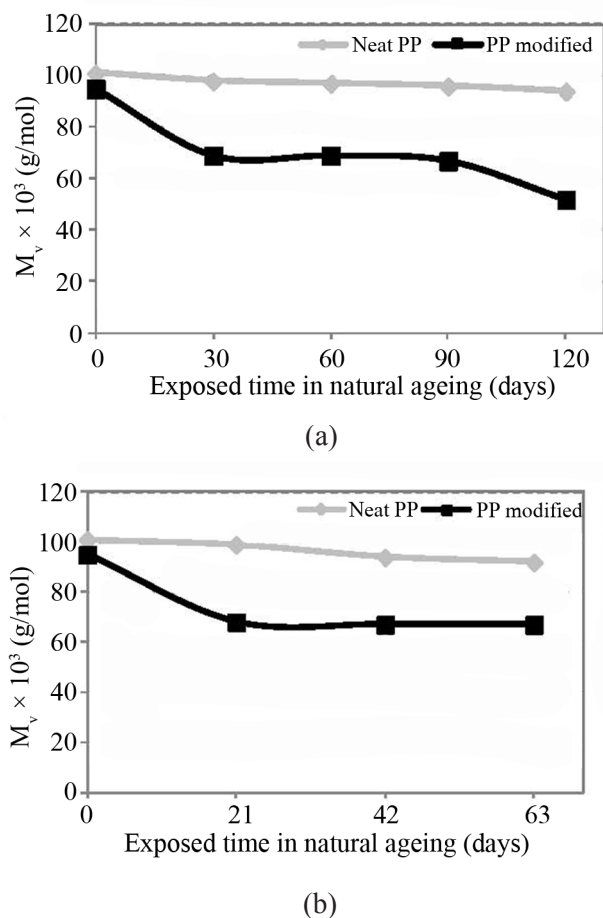


Figure 3. Viscometric molecular weight before and after exposed to: (a) natural ageing and (b) accelerated ageing.

sunlight, this decrease being directly proportional to the molecular weight.

Biodegradable polymers require the presence of oxygen and some form of activation energy such as light (UV) or heat for the initial oxidative degradation of the polymer [14]. In the DSC analysis changes in the crystallinity of the irradiated samples were detected in comparison with the control samples (unexposed samples). Figures 4 show the values for the degree of crystallinity (X_c) of the samples before and after exposure to the degradation processes of natural and artificial ageing.

On analyzing the results for the neat and modified PP samples before degradation, it can be observed that the crystallinity values for the modified samples are slightly lower than those for the unmodified samples (the difference being within the margin of error). This may be due to the presence of the organic pro-degradant in the modified samples, which influences the increase in the free volume, reducing the crystallinity, due to the inser-

Table 1. Intrinsic viscosity of the samples before and after exposure to the natural and accelerated ageing processes.

Exposure time (days)	Natural ageing (*h+ dL/g)		Exposure time (days)	Accelerated ageing (*h+ dL/g)	
	Neat PP	PP modified		Neat PP	PP modified
0	1.11	1.08	0	1.11	1.08
30	1.08	0.82	21	1.10	0.81
60	1.08	0.82	42	1.05	0.81
90	1.07	0.81	63	1.03	0.80
120	1.05	0.65	-	-	-

*According to the equipment manual, this period of the test (63 days) in the accelerated radiation was equivalent to approximately 600 days of exposure to natural weathering.

tion of side and/or functional groups [26].

The values for the X_c of the neat PP samples exposed to natural ageing for 120 days, showed an increase of 36.2%, and 28.8% after being submitted to accelerated ageing for 63 days. For the modified PP samples increases in the X_c value of 89.8% and 94.3% were observed for the natural and artificial ageing, respectively. However, the effect was more pronounced for the modified PP exposed to artificial ageing than the samples exposed to natural conditions.

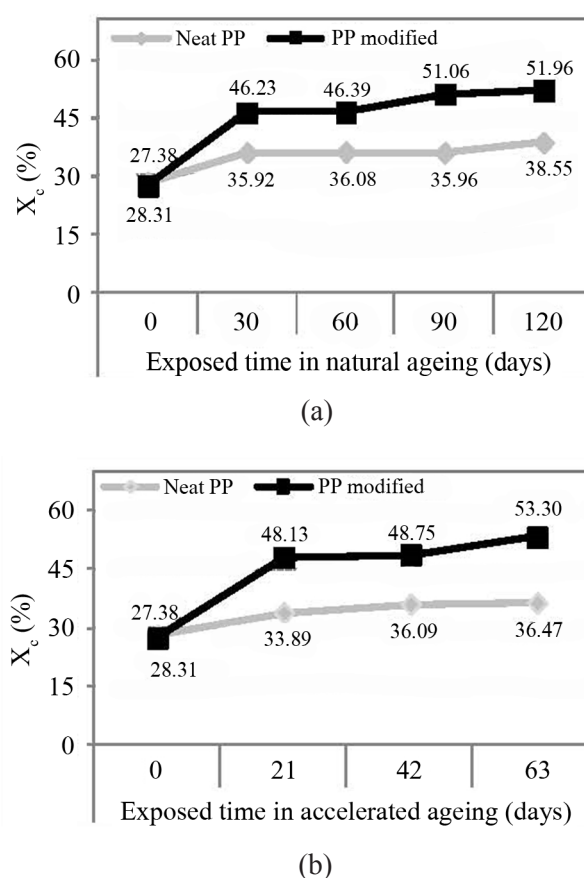
The initial reaction in PP photodegradation is a radical process, in that both stages (initiation and propagation) may result in chain cleavage and a subsequent increase in the crystallinity, due to the facile formation of crystalline regions with a greater number of smaller molecules [27]. When polyolefins are exposed to high energy radiation under oxygen atmosphere, the radicals generated by the scission of the C-H and C-C bonds can combine with the oxygen dissolved in the polymer and initiate chain reactions, the mechanism being a classical chain oxidation process involving peroxy and alkyl radicals [26].

On comparing the values for the degree of crystallinity of neat PP and PP modified, it can be observed that there was an increase in the X_c of the modified samples from 27.4% to 52.0% after natural ageing for 120 days and 53.3% after exposure to artificial conditions for 63 days. The pro-degrading agent favors the crosslinking of the PP molecules after exposure to environmental conditions such as UV radiation. The subsequent chain scission may have led to the production of molecules with molecular weight or size which is more favorable to crystallization, thus promoting the observed increase in crystallinity [1, 4, 23].

According to Yakimets et al. [11], these oxidation reactions occur predominantly in the non-crystalline

phase and produce small segments of the chains that crystallize within the pre-existing crystal due to the increasing crystallinity through chemi-crystallization, that is, a molecular rearrangement of the molecules of the amorphous region which are split. However, this rearrangement has certain limits, as it reaches a point where the exposure time is so long that the crystallization tends to decrease, due to high levels of degradation [11].

Figure 5 shows the surface micrographs of the neat PP and modified PP at the beginning of the test and af-

**Figure 4.** Effect of exposure time on the X_c : (a) natural ageing for 120 days and (b) accelerated ageing for 63 days.

site, season and time of day, and thus the results are often not reproducible.

Accelerated ageing

The samples molded in the injection process were subjected to accelerated ageing, according to ASTM G151-10 [18] and ASTM G154-06[19]. The samples were exposed to UV irradiation for 63 days at 30°C and 64% humidity, being turned every three days to obtain uniform radiation exposure on both sides of the sample. The UV equipment had eight fluorescent mercury lamps (Cleo Performance 80W - Philips), UVA = 22W and UVA/UVB = 0.8%. The radiation source was Philips fluorescent lamps of 80 W, with radiation at wavelengths of 310-400 nm (average around 340 nm), to simulate solar radiation, in accordance with ASTM G154-06 [19]. Under the conditions used the daily dose of ultraviolet radiation was around 0.77 Wh/m². According to the equipment manual, this period of the test (63 days) in the accelerated radiation was equivalent to approximately 600 days of exposure to natural weathering.

Methods for analysis

The thermal, physical and morphological changes which took place during the exposure of the samples to natural and accelerated ageing were monitored as described below:

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry analysis of the neat and modified PP samples exposed to two different degradation conditions was carried out with a DSC-Q20 calorimeter (TA Instruments). Scans were recorded using approximately 5- 6 mg of each sample at a heating and cooling rate of 10°C/min in a nitrogen atmosphere. The degree of crystallinity (X_c) was calculated according to Equation (1):

$$\%Crystallinity = 100 \times \frac{\Delta H_m}{\Delta H_m^0} \quad (1)$$

where ΔH_m is the melting enthalpy and ΔH_m^0 is the enthalpy of 100% crystalline polypropylene, previously reported to be 209 Jg⁻¹ [20].

Viscometric average molar weight

The viscometric average molecular weight (M_v) was

determined from the intrinsic viscosity $[\eta]$ of the samples, using the Mark-Houwink-Sakurada relationship $[\eta] = K M_v^\alpha$, where k and α are the constants for the polymer-solvent system, which are dependent on the polymer, solvent and temperature, according to reports in the literature [21], where $K = 11 \times 10^{-5}$ dL/g and $\alpha = 0.80$. The samples were dissolved in decalin at 135°C, at four different concentrations (0.2, 0.4, 0.6 and 0.8 dL/g). Viscosity measurements were carried out using an Ubbelohde-type capillary viscometer at a temperature of 135°C ($\pm 0.01^\circ\text{C}$) which was controlled by a circulating silicone bath (SOLAB, model 159 SL) [21].

Scanning Electron Microscopy (SEM)

To examine the surface morphology of the PP samples before and after being submitted to the natural and accelerated ageing for different periods of time, they were analyzed under a JEOL (Model JSM-6060) scanning electron microscope operating at 10 kV. The samples were sputter-coated with gold prior to the analysis.

RESULTS AND DISCUSSIONS

Figure 3 shows the results for the molecular weight of the neat PP and PP modified after 120 days exposed to natural ageing (Fig.3-a) and after 63 days exposed to accelerated ageing (Fig.3-b). On analyzing the viscometric molecular weight of neat PP, reductions of 6.9% and 8.9% were observed after exposure to natural ageing for 120 days and artificial ageing for 63 days, respectively. This reduction occurs because polypropylene does not absorb radiation at wavelengths above 290 nm, the radiation which reaches the earth's surface, so in the case of natural ageing the initiation of radiation photodegradation is attributed to the absorption of UV light by chromophores, such as catalyst residues and hydroperoxides, which are impurities incorporated during processing [22]. The absorption of UV light by these chromophores initiates a series of chemical photooxidation reactions which generate chemical groups, such as carbonyl and hydroperoxide, and cause chain scission and/or crosslinking [23, 24].

The addition of the organic pro-degradant agent to the polypropylene matrix accelerated the degradation

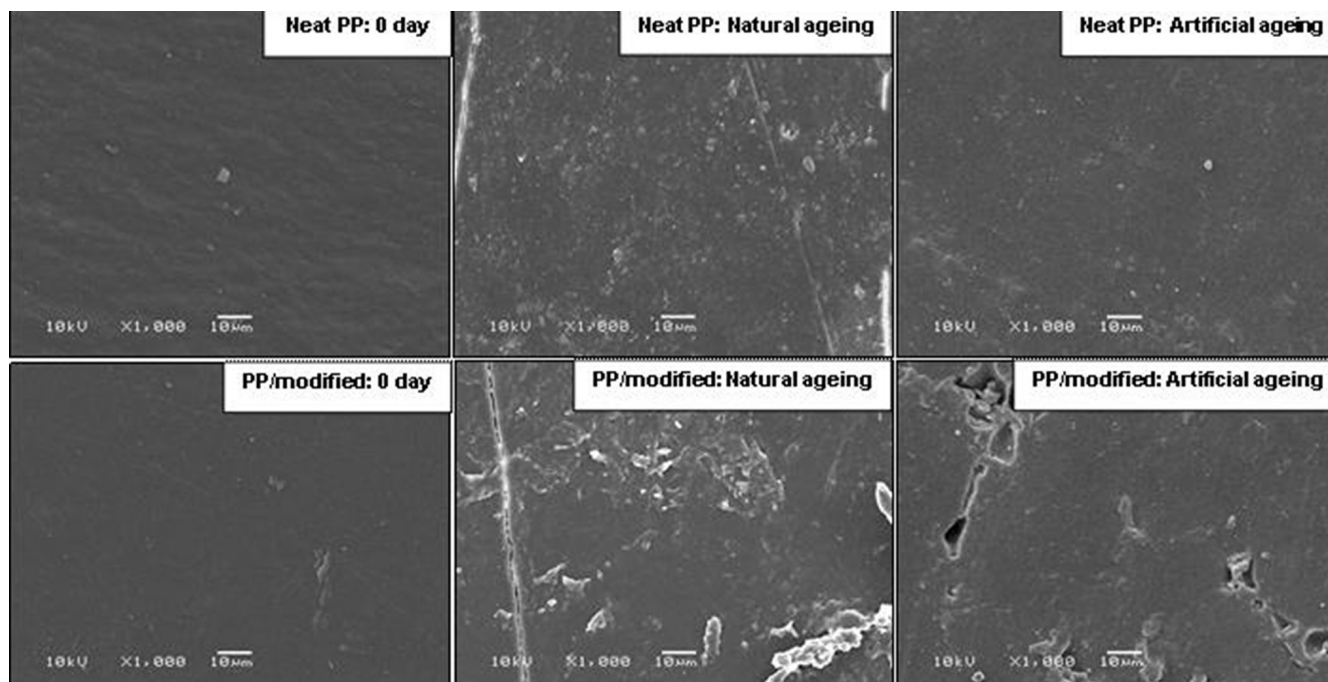


Figure 5. SEM micrographs of the neat PP and modified PP surfaces before ageing and after 120 days of natural ageing and 63 days of artificial ageing.

ter exposure to natural ageing for 120 days and accelerated ageing for 63 days. The samples of neat PP and modified PP at the start of the test present a uniform surface. Modification of the surface of the neat PP was more visible after exposure to natural ageing than accelerated ageing, presenting an irregular and deteriorated surface. On analyzing the surface of the PP modified with organic additive, cracks and pitting are clearly visible after ageing. This evidence of surface deterioration is most evident after exposing to natural ageing, because in the outdoor environment the samples are in contact with oxygen, acid rain, wind, bacteria and solar radiation. These factors, together with the possibility of the specific involvement of oxidizing atmospheric pollutions, initiate the degradation phase leading to the observed greater degree of erosion. On the surface of the samples modified through accelerated ageing, it is possible to observe micro-voids, due to the high frequency ultraviolet radiation [4].

During the photooxidation there are different reaction rates for the PP samples exposed to natural and artificial ageing conditions since the reactions are related to the diffusion of oxygen into the sample and the intensity of radiation emitted by the light. On exposure to artificial ultraviolet radiation the intensity is very high (UV-A-340nm and UVB-280) and the reac-

tion rate becomes excessively fast, with oxygen being most readily consumed in the reactions occurring in the superficial layers of the sample. This rapid consumption of oxygen at the surface leads to a shortage of oxygen and therefore the action of ultraviolet light inside the sample leads to crosslinking reactions. In the case of natural exposure the radiation intensity is lower and some of the oxygen can diffuse into the sample without reacting at the surface, leading to a lower degree of crosslinking. This occurs in early stages of degradation, while for a longer exposure time the oxygen can reach the interior of the samples (especially in the amorphous regions), and thus the chain scission reactions again dominate the photodegradation process [23,28,29].

CONCLUSION

The results obtained in this study indicated that exposure to UV irradiation (natural and artificial) led to an increase in the degree of crystallinity in both samples (neat and modified PP), but was more evident in the modified PP samples. This was because during the exposure of the modified PP to the artificial ageing for 63 days the ultraviolet conditions were more aggres-

sive and the organic additive enhanced the crosslinking of the PP molecules which was followed by chain scission and a consequent increase in the degree of crystallinity.

The factors associated with outdoor conditions (natural ageing), such as solar radiation, temperature, acid rain and humidity, influenced the viscometric molecular weight and the morphological properties. The modified PP samples exposed to natural ageing for 120 days showed a greater reduction in the molecular weight in comparison to those exposed to accelerated conditions. Morphological changes were observed on the surface of modified PP samples exposed to both natural and artificial ageing. However, these changes were more evident on the surface of the samples exposed to natural ageing, because the weathering factors present in the natural environment, together with the possibility of the specific involvement of oxidizing atmospheric pollutions, initiated the degradation phase leading to the deterioration of the sample surface. The conclusion should not be a repetition of the results, but a statement whether the aim of the research was reached.

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