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## Environmental ageing of irradiated polypropylene/montmorillonite nanocomposites obtained in molten state



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### HIGHLIGHTS

- Nanocomposites of high strength PP (HMSPP) were aged under environmental conditions.
- HMSPP/MMT nanocomposites showed carbonyl index lower than the HMSPP.
- Concentration at 0.1% of clay promoted intense crystallization of  $\beta$ -phase.

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### ABSTRACT

Nanocomposites of High Melt Strength Polypropylene (HMSPP) were obtained in organoclay concentrations of 0.1, 5 and 10 wt% using the montmorillonite (MMT). The clay was dispersed through the melting intercalation technique using a twin-screw extruder. The dumbbell samples were manufactured and settled in device for natural ageing assay. The mechanical properties (elongation and rupture strength) were evaluated and the thermal behavior was investigated by differential scanning calorimetry (DSC). The morphology of the nanocomposites was observed by scanning electron microscopy (SEM). Nanocomposites HMSPP/MMT showed intense cracks at the surface after 3 months of environmental ageing but not as deeply as in the HMSPP. The carbonyl index (CI) was calculated using infrared spectroscopy (FT-IR) technique in which the nanocomposites showed CI values lower than the HMSPP.

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### 1. Introduction

Investigation in polymer clay nanocomposites was pioneered by researches from Toyota and has had considerable attention in consequence of their different characteristics (Mazrouaa, 2012; Hussain et al., 2006).

Polypropylene nanocomposites (PPNC) have remarkable utility in automobile and aircraft industries, agriculture, and others. But, one major problem associated with these applications is their stability to weathering. Various chemical reactions are responsible for the material degradation including the formation of oxidation products, rearrangements of the chemical structure, crosslinking and/or chain scission (Morlat et al., 2004; Oliani et al., 2010a).

Blend of polypropylene with clays to prepare nanocomposites is a practical tool to increase flammability resistance and permeability properties. In this sense melt intercalation was used to obtain nanocomposites of PP and organoclay in the molten state (Mazrouaa, 2012; Hussain et al., 2006).

The investigations of PPNC degradation were studied in laboratory, by thermal exposition in chambers, but, without consideration of important variables such as UV radiation intensity and luminosity cycle. The environmental ageing is a way to test the photochemical resistance of polymer when these variables affect the chemical structure by degradation mechanisms (Fechine et al., 2006; Diagne et al., 2007; Oliani, 2008).

Due to this demand, diverse researches have made studies about the behavior of photooxidation and degradation in PP nanocomposites (Morlat-Therias et al., 2005a, 2005b, 2008; Silvano et al., 2013). In some cases, the studies give the same conclusion: nanocomposites degraded faster than the pristine polymer. The relative instability of nanocomposites under UV ageing could constitute a major drawback for the applications of these materials in outdoor applications (Morlat-Therias et al., 2005a, 2005b).

In the present work was used the irradiation process of polypropylene that was developed by the polymer group of IPEN. The process consists of irradiation of the polymer matrix with acetylene atmosphere in gamma source. Some chemical changes were operated such as long chain branching and crosslinking (Oliani et al., 2010b, 2012).

The PPNC obtained by molten process showed the influence of the clay concentration in the degradation process of the chemical

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structure modified. The PPNC showed lost of rupture tension under the environmental ageing, as well as, reduction of the elongation property. Important results were the low carbonyl index present by the 0.1 wt% sample among higher concentrations tested.

## 2. Materials and methods

The isotactic polypropylene (iPP) pellets were manufactured by Braskem and compatibilizer agent, propylene maleic anhydride graft copolymer (PP-g-MA) was supplied by Chemtura (Polybond 3200). The clay filler was Southern Clay Products Cloisite 20 A quaternary ammonium salt-modified (95 meq/100 g) montmorillonite clay.

The iPP was placed in plastic bags with acetylene that were irradiated in  $^{60}\text{Co}$  gamma source at dose of 12.5 kGy in order to obtain the HMSPP. Three different formulations containing the clay were prepared and are represented in Table 1.

The samples were prepared in molten state using a twin-screw extruder (Thermo Haake Polymer Laboratory) to incorporate the clay in the polypropylene. The operated temperatures were 170–200 °C and speed ranging from 30 to 60 rpm. The dumbbell samples for testing were obtained from thermal molding pressure (80 bar and 190 °C), for type IV dimensions according to ASTM D638-03. After molding, the dumbbell samples were mounted in appropriated device for environmental ageing, Fig. 1. The period of exposition was from January 2012 to June 2012.

### 2.1. Melt flow index (MFI)

Ceast Italy Melt Flow Modular Line was operated at temperature of 230 °C for 10 min of total time test.

### 2.2. Mechanical test

The samples were tested in a universal testing machine EMIC DL 3000 model with strain rate of  $2 \times 10^{-2} \text{ s}^{-1}$ .

**Table 1**  
Formulations of the samples.

Samples	Matrix	Dose (kGy)	PP-g-AM (wt%)	Cloisite 20A (wt%)
H1	HMSPP	12.5	–	–
NC1	HMSPP	12.5	3	0.1
NC2	HMSPP	12.5	3	5
NC3	HMSPP	12.5	3	10

### 2.3. Fourier transformed infrared spectroscopy

Infrared spectroscopy was performed at Thermo Scientific (Nicolet 6700) with ATR accessory Smart Orbit Diamond, in the range from 400 to 4000  $\text{cm}^{-1}$ .

### 2.4. Differential scanning calorimetry

The analysis was carried out in 822 Mettler-Toledo, under nitrogen atmosphere of 50  $\text{mL min}^{-1}$  at a heating rate of 10 °C  $\text{min}^{-1}$ , in the temperature range from –50 to 280 °C, keeping in 280 °C for 5 min; from 280 to –50 °C at a cooling rate of 10 °C  $\text{min}^{-1}$  and from –50 up to 280 °C at heating rate of 10 °C  $\text{min}^{-1}$ . About 8–12 mg of sample was placed in closed aluminum pans. The cristallinity was defined as follows:

$$X_c = P \times \frac{\Delta H_f \times 100}{\Delta H_0} \quad (1)$$

where  $\Delta H$  was the measured melting enthalpy and  $\Delta H_0$  was the enthalpy of fusion at 100% crystalline PP,  $\Delta H_0 = 209 \text{ J g}^{-1}$  (Mark, 2007) and  $P$  was the content of PP in the sample.

### 2.5. Scanning electron microscopy

Scanning Electron Microscopy was performed in equipment EDAX Philips model XL-30.

### 2.6. X-ray diffraction (DRX)

X-ray diffraction was performed in Philips X'PERT equipment from 1 to 50 angle degrees.

## 3. Results and discussions

The sample HMSPP showed melt flow index value of  $2.8 \text{ dg} \times 10 \text{ min}^{-1}$  (Oliani, 2008). The H1 (without clay), NC1, NC2 and NC3 were processed in twin-screw extruder. The H1 degraded under processing to (MFI=6.7  $\text{dg} \times 10 \text{ min}^{-1}$ ). The NC1 presented MFI=6.2  $\text{dg} \times 10 \text{ min}^{-1}$  similar to H1. The NC2 and NC3 showed more shear tension due to the clay concentration and MFI=2 and 1  $\text{dg} \times 10 \text{ min}^{-1}$ , respectively.

The DSC results for the aged samples in the period of 6 months are showed in Fig. 2.

The increase of melting temperature with addition of clay in H1, Table 2, occurred in consequence of compatibilizer agent used and also for the reprocessing of the composite. With increase of



**Fig. 1.** Device with dumbbell samples for environmental ageing exposed outside at the polymer processing laboratory IPEN/CQMA.

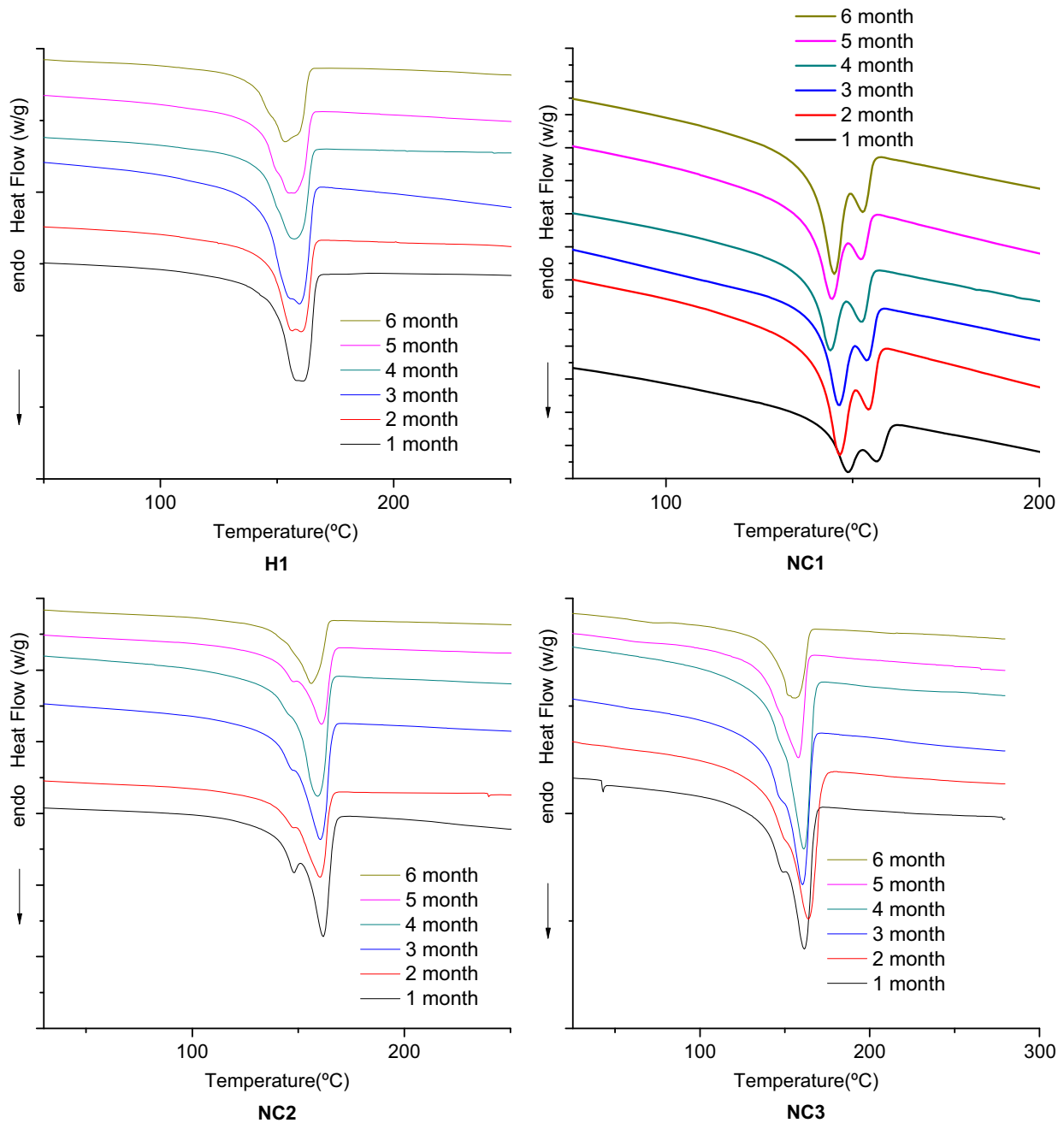


Fig. 2. DSC curves of the samples melting.

**Table 2**  
Melting point values ( $T_{m2}$ ) of samples after ageing.

Samples	$T_{m2}$ (°C)						
	Time (month)						
	0	1	2	3	4	5	6
H1	160	162	161	160	157	155	153
NC1	159	148/156	146/153	146/153	143/152	144/152	145/152
NC2	162	161	160	160	159	161	156
NC3	163	162	164	160	161	158	156

clay concentration, the melting temperature decreases suggesting a reduction of spherulites size because the clay retards the growing of individual lamellae (Perprnicek et al., 2009).

The mechanism of photooxidation of PP can be explained from the formation of hydroperoxides, which can decompose to produce alkoxy radicals that abstract hydrogen from the polymeric backbone or undergo a  $\beta$ -scission. Alcohol and ketone are formed with a macroradical. The macroradical is further oxidized, generating carboxylic acids with scission of the macromolecular backbone, and some other carbonylated products. Because the carboxylic acids are final stable products, the increase of their concentration can be used to quantify the rate of photooxidation (Morlat et al., 2004). Scission reaction contributed to  $T_m$  decreasing.

In Table 2 the samples NC1 shows values attributed to two peaks of  $T_m$ , one of them is characteristic of  $\beta$  phase. The  $\beta$  phase is thermodynamically metastable and can be obtained under some special conditions as temperature gradient, flow-induced crystallization and nucleating agent addition. Nano-sized fillers such as

montmorillonite (in this case the Cloisite 20A) have been reported to have  $\beta$ -nucleating ability (Mingxian et al., 2009).

With the environmental ageing occurred displacement of  $T_m$  to lower values, owing to chain scission mechanism caused by temperature (thermo oxidation) and solar radiation (photooxidation).

Table 3 shows the influence of clay on the crystallinity of processed composites.

Crystallization was affected by clay addition since nanoclays serve as nucleating agents. In consequence of higher clay content, the crystallinity was higher. After exposure, the crystallinity of nanocomposites increased, similar to that observed by Rabello and White (1997). In effect, small segments generated by chain scission of the molecules were crystallized in the amorphous phase as effect of the chemi-crystallization. This was evident after 5 ageing months as a general effect. For NC2 sample crystallization rate was stabilized at 3rd month which can be associated to efficient intercalation of the polymer in the clay galleries.

The results of the tensile test and elongation are represented in Fig. 3. Before ageing the nanocomposites were reinforced in comparison to H1.

It is well known that the clay causes an increase of the modulus in the case of satisfactory adhesion between the clay and polymer matrix. The highest value of the modulus was reached when using PP-g-MA as a compatibilizer, which is the proof of the higher interaction between HMSPP-PP-g-MA-clay. In general, property values decreasing is thought to be caused by clay agglomerates formation as the result of increase of clay amount (Peprnicek et al., 2009).

From the 2nd month of aging, losses of mechanical property confirmed the mechanism of chain scission. They were also observed losses in elongation values. However, NC2 showed the

better results of stable tension of rupture and elongation showing a satisfactory interaction of the polymer in this clay percentual.

Previous studies indicated that nanoclays accelerate the photo-degradation of PP, without changing the degradation mechanism. Three mechanisms were proposed: absorption of stabilizants, catalytic effect of ferric ions (contaminants) and the decomposition of active agent used in the modification of clay (Morlat et al., 2004; Morlat-Therias et al., 2005b). In the SEM micrographs, no surface degradation was shown at the 1st month. The surface cracking of H1, Fig. 4, started in the 4th month of ageing, and during the ageing it became the more deeply cracked sample.

The FT-IR spectra after the ageing time showed increase of intensity at  $1720\text{ cm}^{-1}$ , peak attributed to surface oxidation products, Fig. 5.

The carbonyl index was calculated from the FT-IR absorbance spectra increasing with the absorbance area increase, in  $1720\text{ cm}^{-1}$ , and, as reference, the carbonyl absorbance area unchanged at  $2720\text{ cm}^{-1}$  (Deshmane et al., 2007; Babetto and Canevarolo, 2000; Cáceres and Canevarolo, 2009) according to the following equation:

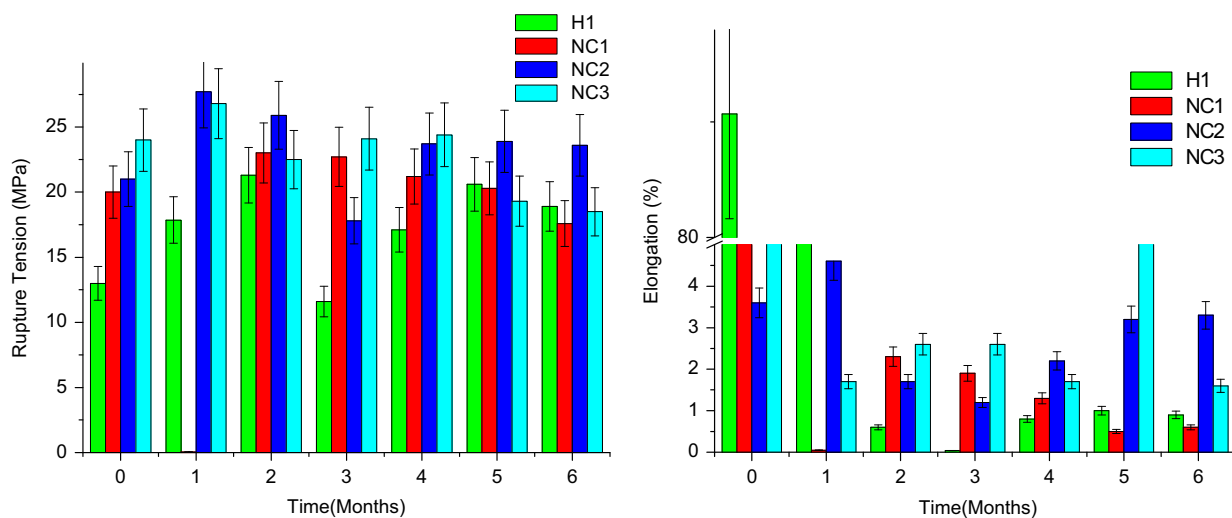
$$IC = Abs(1720)/Abs(2720) \quad (2)$$

At initial ageing time, all the nanocomposites presented carbonyl indexes values higher than the H1, Table 4. In fact, their preparation by extrusion process of HMSPP and clay, in air atmosphere, justified these initial oxidized state. But the values were inverted after the 2nd ageing month, Table 4. Despite of the chain scission in the composite containing Cloisite, the radicals had more difficulty in combining with oxygen than those formed in the polypropylene, H1, one factor is the barrier effect of clay lamellae, which prevents macroradicals from reacting with oxygen (Silvano et al., 2013) that can be better observed in NC1, if occurs exfoliation of the clay.

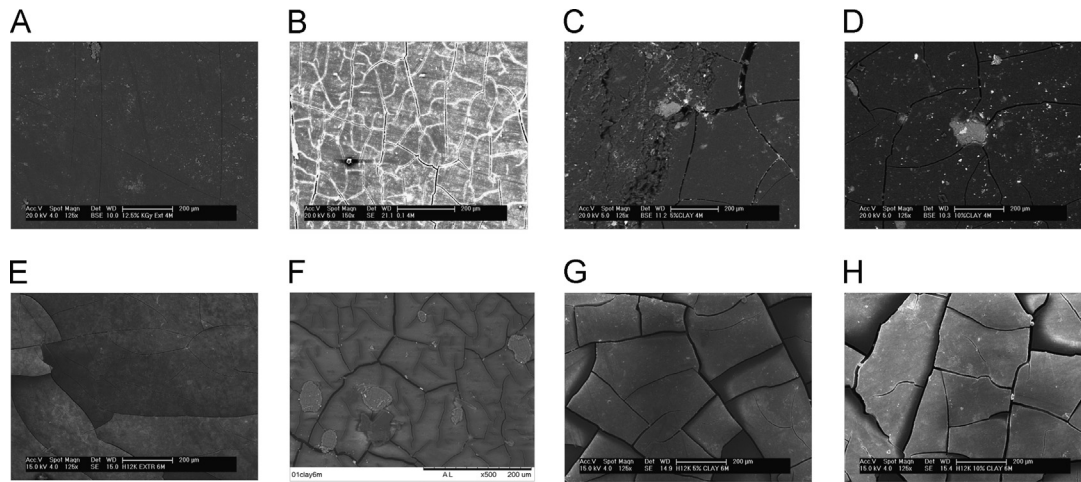
On the other hand the effect of clay concentration was favorable to the oxidation. The chemical composition of the nanocomposites was obtained in the EDS spectra, both highlight two principals elements that form the clay: silicon (1.80 keV) and aluminum (1.68 keV), these elements were present due to the nature of the clay (Lamontagne et al., 2001; Xie et al., 2001) and showed iron as contaminant. This contaminant promotes oxidation of the polymer, except for NC1 in which the efficiency of blocking effect seems to superimpose the effect of clay contaminants. After 6 months the carbonyl index for NC2 and NC3 reveals

**Table 3**  
Crystallinity values ( $X_c$ ) obtained by DSC analysis.

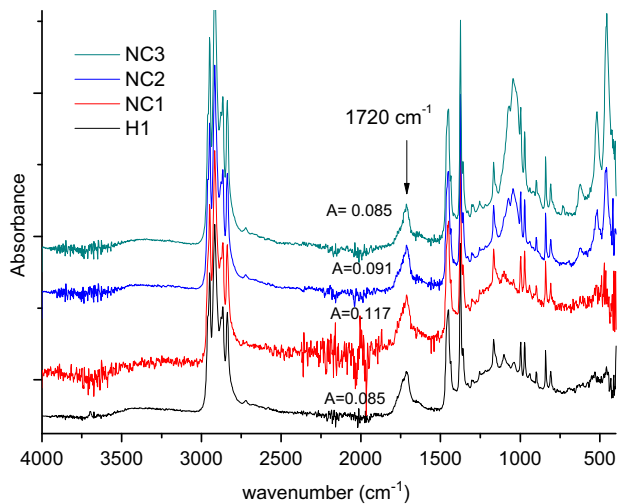
Samples	$X_c$ (%)					
	Time (month)					
	0	1	2	3	4	5
H1	46	45	45	42	47	48
NC1	40	42	34	35	38	38
NC2	44	46	50	47	47	47
NC3	48	45	46	49	47	52



**Fig. 3.** Rupture tension and elongation of dumbbell samples.



**Fig. 4.** Surface micrograph after environmental ageing – (A) H1; (B) NC1; (C) NC2; (D) NC3; (E) H1; (F) NC1; (G) NC2; (H) NC3. (A) 4 months (B) 4 months (C) 4 months (D) 4 months (E) 6 months (F) 6 months (G) 6 months (H) 6 months.



**Fig. 5.** FT-IR spectra of the samples environmentally aged for 6 months.

**Table 4**  
Carbonyl index values.

Time	H1	NC1	NC2	NC3
1	0.74	0	1.36	1.92
2	0.58	0.12	1.26	1.78
3	3.58	0.23	2.42	3.91
4	5.68	0.31	4.50	4.09
5	11.61	0.33	5.48	5.08
6	18.71	0.34	12.88	9.69

the blocking effect persistence through the lower CI values compared with H1.

The results of DRX are shown in Table 5. Owing to the increase in interlamellar lamellae distances in the clay. It is evident that occurs the intercalation of the clay in the matrix. This result corroborated with that of the literature (Fermino, 2011).

In the sample NC1 exfoliation of the clay with total separation of the lamella was occurred, when no signal of DRX was observed.

#### 4. Conclusion

The addition of clay has improved mechanical properties and thermal properties of the irradiated polymeric material. Nano-

**Table 5**  
Interlamellar distances values

Samples	$d_{001}$ (Å)
Cloisite 20A	24.4
NC2	30.8
NC3	29.7

composite NC2 showed superior mechanical stability compared with HMSPP (H1). At 0.1% of clay the intense crystallization of  $\beta$ -phase probably due to exfoliation and intercalation of the clay was verified. The samples with clay showed more intense cracks on the surface but not as deeply as in the HMSPP surface. Concerning the carbonyl index, the NC1 has showed more stability during the ageing, this fact can be connect to the probable exfoliation of the clay in the polymer matrix regarding it blocking effect.

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