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Effects of Environmental Ageing on HMS-Polypropylene/Cloisite Nanocomposites

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Abstract - High melt strength polypropylene Nanocomposites (NC-HMSPP) were obtained with concentrations of 0.1 and 5 wt% of Cloisite 20A. The melt intercalation, using twin screw extruder was done to homogenize the nanocomposite in presence of polypropylene graft maleic anhydride (PP-g-MA) compatibilizer agent. In this work, the manufactured dumbbell samples were settled in device for natural ageing assay. The period of exposition was January to December of 2012. The effects of environmental ageing was determined by carbonyl index (FT-IR) and the results showed that nanocomposites were more stable than HMSPP. The mechanical properties (elongation and rupture strength) were evaluated and the thermal behavior was investigated by differential scanning calorimetry (DSC) and X ray diffraction (DRX). The morphology was observed by scanning electron microscopy (SEM) in which the nanocomposites showed intense cracks on the surface.

Keywords: *Nanocomposites, Polypropylene, Environmental Ageing*.

INTRODUCTION

The evaluation of photo-oxidative degradation in polymer matrix is one of principal elements subsides the development of product life time. The environmental investigation, such as ultraviolet radiation, visible light, temperature among others, shows how polymer structure is affected by degradation. During the degradation process occur chemical and physical changes in the polymer causing discoloration, surface cracking, loss of brightness, and loss of mechanical resistance. These phenomena often can be attributed to chain scission and, in some cases, also crosslinking [1].

Another interesting phenomenon reported in recent years is the changes in the material inherent crystallinity after the exposure. A possible explanation for this is the formation of new flexible chain segments by chain scission in the amorphous phase of the material by the UV-radiation [2].

For polypropylene (PP) nanocomposites, although in past decades, researches worked for good understanding about photodegradation mechanism and photo degradation products of PP, relatively few researchers reported on photo aging of PP nanocomposite [3].

This work focus in HMSPP/NC (high melt strength polypropylene nanocomposite), obtained by gamma irradiation process in acetylene atmosphere [4,5]. This process induces in material some chemical reactions such as chain scission and branching [6]. The high melt strength is very explored in industry for film extrusion due the stability under extrusion. Cloisite 20A is one type of clay utilized to obtain HMSPP/NC [4].

The samples are exposed in environment device for one year. In this time the samples are submitted to all weather seasons and concerning which accelerated degradation.

EXPERIMENTAL

The isotactic polypropylene (iPP) pellets was manufactured by Braskem and compatibilizer agent, propylene maleic anhydride graft copolymer (PP-g-MA) was supplied by Chemtura (Polybond 3200). The clay used was Cloisite 20A by Southern Clay Products. The iPP was placed in plastic containers added of acetylene and was irradiated in ^{60}Co gamma source at dose of 12.5 kGy in order to obtain the HMSPP (H1). Two different formulations containing the clay were prepared and are presented in Tab. 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

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

Melt flow index (MFI)
Ceast Italy Melt Flow Modular Line was operated at temperature of 230 ºC for 10 min of total time test.

Mechanical test
The samples were tested in a universal testing machine EMIC DL 3000 model with strain rate of $2.10^{-2} s^{-1}$.

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

Differential scanning calorimetry (DSC)
The analysis were carried out in 822 Mettler-Toledo, under nitrogen atmosphere of 50 mL min^{-1} at a heating rate of 10 °C min^{-1}, in the temperature range from -50 to 280 °C, keeping in 280 °C for 5 minutes; from 280 to -50 °C at a cooling rate of 50 °C min^{-1} and from -50 up to 280 °C at heating rate of 10 °C min^{-1}. About 8 - 12 mg of sample was placed in closed aluminum pans. The cristallinity was defined as follow equation 1:

$$Xc = P \times \frac{\Delta Hf \times 100}{\Delta Ho} \qquad Eq.(1)$$

Where ΔH was the measured melting enthalpy and ΔH_0 was the enthalpy of fusion at 100% crystalline PP, ΔH_0= 209 J g^{-1} [6] and P was the fract content of PP in the sample.

Scanning electron microscopy (SEM)
Scanning Electron Microscopy was performed in equipment EDAX Philips model XL-30. The Balzers SCD 050 Sputter Coater was used to cover the samples with Au

X ray Diffraction (DRX)
X ray diffraction was performed in Philips X'PERT equipment from 1 to 50 angle degrees.

RESULTS AND DISCUSSION
In tab. 2 is showed the MFI values of the samples.

TABLE 2 – MFI of H1 nanocomposites

Samples	H1	NC1	NC2
MFI (dg 10 min^{-1})	6.7	6.1	2

The sample H1 (without clay) showed high melt flow index owing to the process in extruder. The NC1 presented little significant difference while in NC2 is verified intercalation of the clay in the polymer matrix. The DSC results for the aged samples in the period of 1 year are showed in Fig. 2.
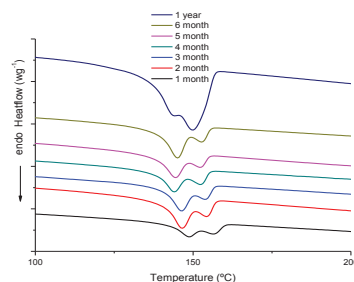

FIGURE 2 - Heating thermogram of DSC for sample NC1 in the period of 1 year

The increase of melting temperature with addition of clay in H1, Tab. 2, occurred in consequence of compatibilizer presence and the reprocessing to the composite. With increase of clay concentration, the melting temperature decreases suggesting a reduction of spherulites size because the clay retards the growing of individual lamellae [8].

TABLE 2 - Melting point values (T_{m2}) and crystallinity of samples after ageing

	Tm_2(°C)			Xc(%)		
Time Sample	0	4 month	1 year	0	4 month	1 year
H1	160	157	145/ 152	46	47	46
NC1	159	143/ 152	146/ 154	40	38	46
NC2	162	159	156	44	47	45

The NC1 curve showed double peak characteristic of β-phase. Some researchers reported that β-phase can melt and recrystallize during DSC experiment [8]. The β-phase is thermodynamically unstable and can be obtained under some special conditions such using temperature gradient, flow-induced crystallization and adding special nucleating agent. Nano-sized fillers such montmorillonite (in this case the Cloisite 20A) have been reported to have β-nucleating ability [10].

UV-radiation causes scission of the backbone chain and/or formation of radicals, the smaller amorphous chain segments tend to rearrange themselves into higher ordered chains resulting in higher material crystallinity. This effect referred to as "cold – or chemi-crystallization" [2].

Crystallization is affected by clay addition since nanoclays serve as nucleating agents. In consequence of higher clay content, the cristallinity was higher. After exposure, the crystallinity of nanocomposites increased, similar to that observed by Rabello et. al. [9]. 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 five ageing moths as a general effect. In the samples after 1 year, is observed increase in crystallinity due to the chain scission process and crystallization of free radicals.

During the environmental ageing occurred displacement of T_m owing to chain scission mechanism caused by temperature (thermo oxidation) and solar radiation (photo oxidation).

The results of the tensile test and elongation are represented in Fig.3. For samples recently produced the clay was reinforced the nanocomposites in comparison with H1.
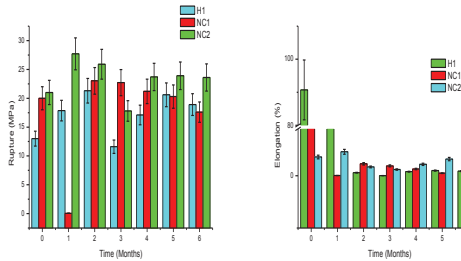
**FIGURE 3-** Rupture tension and elongation of dumbbell samples

It is well known that the clay addition 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 in the case of using PP-g-MA as a compatibilizer, which is the proof of the higher interaction between HMSPP-PP-g-MA-clay. In general, property decreasing is thought to be caused by clay agglomerates formation as result of increase of clay amount [8].

From the second 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 the stable tension of rupture and elongation showing a satisfactory interaction of the polymer in the clay.

Studies indicate that nano clays accelerate the photodegradation of PP, without changing the degradation mechanism. Three mechanisms were proposed: absorption of stabilizants, catalytic effect of ferric ions and the decomposition of active agent utilized in the modification of clay [11]. In Fig. 4 A – C showed the iniating of cracking in the surface.
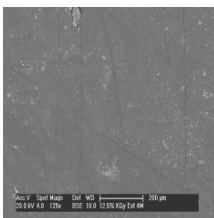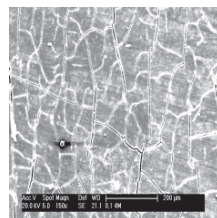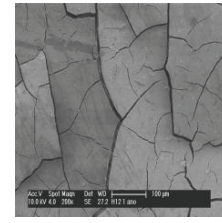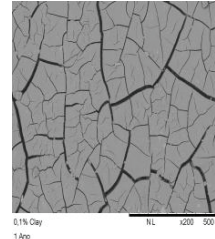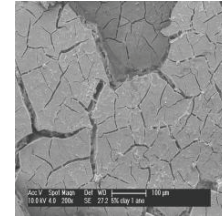
(A) 4 months   **(B) 4 months**
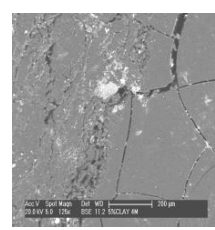
(C) 4 months   **(D) 1year**

(E) 1 year   **(F) 1year**

FIGURE 4 – Surface micrograph after environmental ageing – (A) H1; (B) NC1; (C) NC2; (D)H1 ; (E) NC1; (F) NC2

This cracking can be associated with the practical consequence of chemi-crystallization where the spontaneous formation of surface cracks cause contraction of surface layers and crack opening [9]. With the tendency of material become more fragile, the intensity of cracks increases, as showed in Fig. 4 D - F after 1 year of exposition.

The FT-IR spectra along the ageing time showed increase of peak intensity at 1720 cm⁻¹ attributed to the surface oxidation products, Fig. 5.
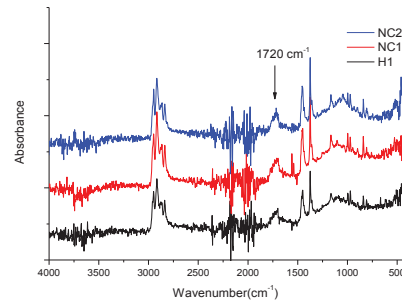
FIGURE 5 - FT-IR spectra of samples environmentally aged after 1 year

The carbonyl index was calculated from FT-IR spectra from the ratio of absorbance area increasing in 1720 cm⁻¹, using, as reference, the carbonyl absorbance area at 2720 cm⁻¹ [12- 14] according to the equation 2:

$$Ic = \frac{Abs(1720)}{Abs(2720)} \qquad \text{Eq. 2}$$

TABLE 4 - Carbonyl index values

Time	H1	NC1	NC2
1	0.74	0	1.36
2	0.58	0.12	1.26
3	3.58	0.23	2.42
4	5.68	0.31	4.50
5	11.61	0.33	5.48
6	18.71	0.34	12.88
1 year	19.19	18.55	24.17

At initial ageing time, all the nanocomposites presented carbonyl indexes values higher than the H1. In fact their preparation processed by extrusion of HMSPP and clay, in air atmosphere justified these initial oxidized state. In despite of chain scission in the composite containing Cloisite the formed radicals have more difficult to combine with oxygen than those formed in the polypropylene, H1. This fact can be explained by difficult of O_2 penetration owing to the Cloisite platelets barrier, remembering that H1 has also an morphology more resistant to O_2 penetration [15].

TABLE 5 – Interlamelar distances values

Samples	$d_{001}(\text{Å})$
Cloisite 20A	24,4
NC2	30,8

The results of DRX are shown in Tab. 5. The intercalation of the clay is evident in the matrix due to the increase in interlamelar distances. Those results corroborated with the literature [16]

CONCLUSIONS

The nanocomposite NC1 showed more stability under environmental ageing. This is evident in carbonyl index values and in rupture tension. In SEM analysis the sample NC1 showed more intense surface cracks than NC2. However in NC2 the cracks are larger and deeper than NC1. After 1 year of exposition the samples showed the higher intensity of cracks.

ACKNOWLEDGEMENTS

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