2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
***ISBN:* 978-85-99141-05-2**

THERMOOXIDATIVE DEGRADATION OF HMSPP/CLAY NANOCOMPOSITE

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ABSTRACT

The objective of this study was evaluate the effects of thermal ageing in dumbbell samples of nanocomposites using stove at 110 ºC, with air circulation at different periods of time. The clay, Cloisite 20 A, was added to HMSPP to obtain nanocomposites in proportion of 5 and 10 wt%. The nanocomposites were processed in twin screw extruder to compatibilizer the HMSPP (high melt strength polypropylene), polypropylene graft maleic anhydride (PP-g-MA) and the Cloisite 20 A The effects were evaluated by carbonyl index determination (CI), Fourier transformed infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), scanning electron microscopy (SEM). The nanocomposites showed intense cracks and yellowing after thermal ageing.

Keywords: thermal ageing; HMSPP; Cloisite; gamma irradiation

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1. INTRODUCTION

Scientific research on preparation and characterization of polymer/clay nanocomposites has grown continuously in the last few years with the general aim to develop new polymeric materials with improved characteristics. Polypropylene/clay nanocomposites probably receive the highest interest owing to excellent cost/performance ratio and versatility of this polymer [1, 2]. Presently, this nanocomposites find their greatest application in the automobile industries [2].To understanding this application is very simple: the fillers commonly utilized such fiber glass or talc, need 20% or more in concentration to enhance the properties, since the nanoparticle needs 3% in concentration the enhance the properties, high mainly in the mechanical and gas permeability properties [3].

The clay utilized to develop nanocomposites is originated of montmorillonite. Naturally the montmorillonite as hydrophilic clay is difficult to exfoliate in the polymer matrix. The solution for this is the treatment with ammonium salt to render the clay more hydrophobic. This modification also leads to expand the layers distances of the clay due to the presence of alkyl chain intercalated in the interlayer [3].

Large varieties of polymers have been used as matrix for preparation of polymer nanocomposites. Among them the modified polypropylene by irradiation process [4] has been gained market in Europe through the production of foams and fibers. However, the molecular structure of this polymer is the same of the polypropylene: does not have any polar group that

could interact with the clay. To overcome this problem, diverse researchers have been called attention to the use of polypropylene graft maleic anhydride as compatibilizer agent. This compatibilizer agent has two groups: one polar and another nonpolar in the structure, [5] that facilitate the interaction between clay and polymer.

For industrial perspective the polymer/clay nanocomposites has more advantage because decrease the cost of the final product. However, to produce this material necessary to test in different formulations. Accelerated ageing tests are very usual, due the time shorter response than others such environmental ageing tests [6]. This work concerns to the ageing of modified nanocomposite processed by twin screw extruder under thermal ageing conditions and investigating of clay/HMSPP interaction in terms of stability comparison of the nanocomposite versus HMSPP.

2. EXPERIMENTAL PROCEDURE

The polypropylene pellets manufactured by Braskem and Maleic Anhydride used as a compatibilizer agent (PP-g-MA) polypropylene-grafted-maleic anhydride, Polybond 3200 by Chemtura (USA) was mixed with a sample of clay Cloisite 20 A by Southern Clay Products, in proportions of 5 and 10%, Tab. 1.
The HMSPP samples were obtained under ^{60}Co gamma source irradiation by CBE at dose of 12.5 kGy.

Table 1: Samples of legend

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

The samples were homogenized in the twin-screw extruder (Thermo-Haake Polymer Laboratory) to better incorporation of clay in polypropylene, the temperatures used were 170 to 200 ºC, with speed ranging from 30 to 60 rpm. The dumbbell samples for testing were obtained from thermal molding pressure at 80 bar and 190 ºC with the corresponding dimensions of the type IV, according to ASTM D 638-03. The accelerated ageing assay was performed in stove with air circulation at 110 ºC for period of 21 days.

2.1. Fourier transformed infrared spectroscopy

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

2.2. Differential scanning calorimetry

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}. Samples at about 8 - 12 mg were placed in closed aluminum pans. The cristallinity was defined according equation 1:

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

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} [7] and P was the PP fraction in the sample.

2.3. Scanning electron microscopy

Scanning Electron Microscopy was performed in equipment TableTop Hitachi model TM3000.

3. RESULTS AND DISCUSSION

In tab. 2, are presented the values of cristallinity, X_{c2} and melting point, T_{m2} in different periods of thermal ageing.

Table 2: **DSC values of melting temperature evaluated in the bulk of the samples**

Sample Time (days)	T_{M2}(ºC)		
	H1	NC1	NC2
7	162	163	164
14	162	163	164
21	160	140	166
	X_{C2}(%)		
7	48	50	45
14	48	43	48
21	46	46	46

The T_{m2} and X_{c2} values obtained in the center of the samples did not show that H1 any significant for H1 and NC2. However, in X_{c2} of NC1 the melting point has decrease of 163 to 140 ºC, fact connected to the chemicrystallization effect. For this sample formulation NC1 more intense surface cracks, were observed in the Fig. 1(H) SEM microscopy.

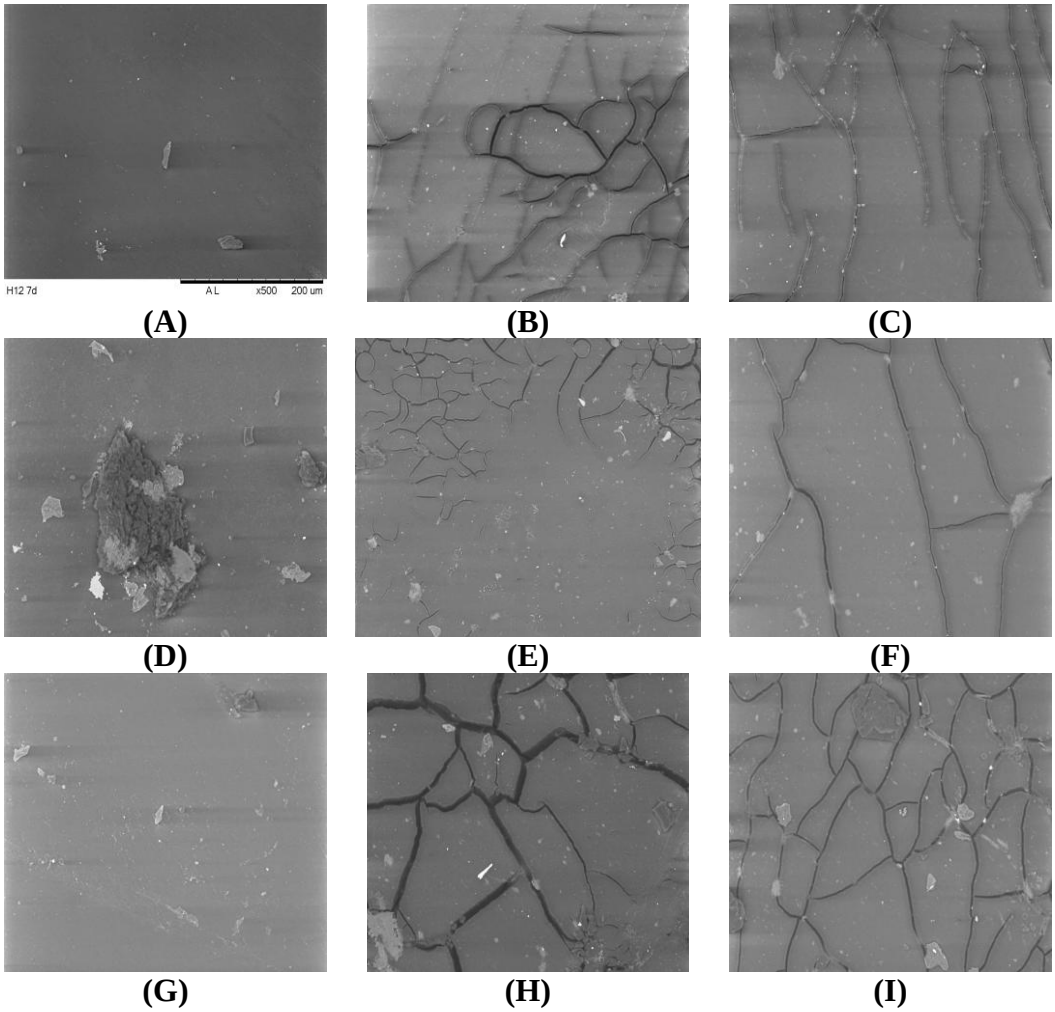

Figure 1: SEM of thermo-aged samples; 7 days: A(H1), B(NC1), C(NC2); 14 days: D(H1), E(NC1), F(NC2); 21 days G(H1), H(NC1), I(NC2).

The diffusion of oxygen is considered a significant in accelerated tests, especially in rapidly oxidizing polymers. Essentially all polyolefin, and particularly polyethylene and polypropylene, oxidize exclusively in the amorphous phase because the crystalline phase is impermeable to oxygen [8, 9].

The SEM of H1 after thermal ageing showed no changes in the surface, Fig. 1(A), (D), (G) therefore the H1 have more crystalline phase. However the nanocomposites after 7 days of ageing already demonstrated some cracks in the surface with higher exposition time, the cracks become more intense and deeper, as can be seen in Fig. 1(H). This fact can be explained by effect of chemicrystallization [10], in which cracks are promoted by contraction of surface layers. NC1 and NC2, are evidentially degraded with pronounced penetration of oxidation effect after 21 days. These surfaces, observed after ageig in stove, showed crack propagation increased with time. The alteration on H1 is more visible in the FT-IR analysis, Fig. 2 and in the carbonyl index, Tab. 3.

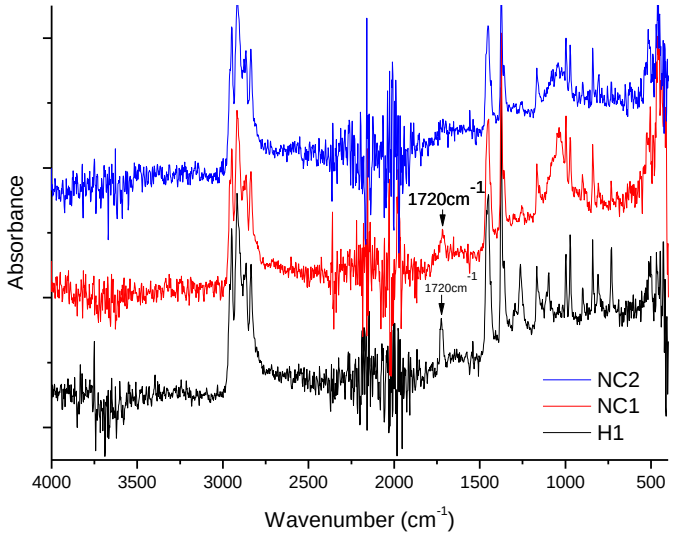

Figure 3 – FTIR of the samples thermal aged for 21 days

Time (Days) Samples	7	14	21
H1	0.018	0.204	1.05
NC1	0.009	0.071	0.128
NC2	0.017	0.102	0.125

Table 2 – Carbonyl index values

The carbonyl index (CI) was calculated from FT-IR spectra as the ratio of absorbance area in 2720 cm^{-1} using as reference and the carbonyl absorbance area at 1720 cm^{-1} that increases with oxidation [10, 11] according to the Equation 2:

$$CI = \frac{Abs(1720)}{Abs(2720)} \tag{2}$$

Although the H1 showed absence of any crack in the surface, changes are in the chemical structure occurred by oxidation according the carbonyl index determination. The large highest values in H1 at 14 and 21 days is connected with the induction time of oxidation while in the samples NC1 and NC2 showed relatively more stability to the ageing.

4. CONCLUSIONS

In terms of carbonyl index the less stable samples to thermal oxidation was H1. Although the nanocomposites showed lower carbonyl indexes they presented cracked surfaces with pronounced intensification in higher ageing time.

ACKNOWLEDGMENTS

The authors thanks CNPq for the grants, CCTM-IPEN for SEM analysis, Eleosmar Gasparin for DSC analysis, Nelson R. Bueno for extrusion of nanocomposites and CBE for irradiation of the samples, Braskem, Southern Clays and Chemtura.

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