

## DEGRADATION STUDY OF HIGH MELT STRENGTH POLYPROPYLENE/CLAY NANOCOMPOSITES IN ENVIRONMENTAL AND ACCELERATED CONDITIONS

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### Abstract

The Polypropylene (PP) was initially modified by  $\gamma$  radiation or high melt strength PP. HMS-PP/ Cloisite 20 nanocomposites processed by melt mixing in twin-screw extruder derived samples to evaluate under environmental and thermal degradation conditions. PP-g-MA was the compatibilizing agent. The tests were conducted on dumbbell shaped samples under two different ageing conditions of degradation: environmental exposition and accelerated exposition. The morphology of aged samples was evaluated by XRD. TEM microscopy showed intercalation and exfoliation. Thermal degradation was studied by TGA. The DSC and the results showed decrease of melting point and increased crystallization under ageing conditions. The FTIR results showed the increase of carbonyl index related to the surface oxidation of the nanocomposites.

### Introduction

Polypropylene is a polymer widely used in many applications, and their thermal, rheological, mechanical, and gas permeation properties need to be improved. A large number of studies have been focused in the promotion of a range of capabilities for automotive industries and with great potential for use in the aeronautical field [1].

The Toyota group reported formation of Polypropylene (PP) nanocomposites by direct melt mixing of organoclays based on montmorillonite (MMT) and PP grafted with maleic anhydride (PP-g-MA) [1].

The ageing process of the PP nanocomposites under environmental conditions has been studied by diverse researchers. Through those studies it was found that incorporation of nanoclays does not change the ageing mechanism of the composite, but rather decreases its induction time, meaning that MMT can accelerates the oxidation process. In other hand, the thermo-oxidation is induced by temperature. Concerning the ageing kinetics of nanofilled PP there are only a small number of studies in the literature [2].

In the present work the synthesis of nanocomposite used the High Melt Strength Polypropylene (HMSPP), obtained by gamma irradiation under acetylene atmosphere

[3]. The HMSPP/ nanocomposites were prepared by melt-blending in order to solve the lack of compatibility between the HMSPP and the MMT [4].

The samples were submitted to environmental and accelerated assay. The UV – radiation would cause a serious degradation in the nanocomposites and consequently weaken the strength of the material. It leads to the formation of free radicals that react by scission, causing brittleness. Consequently, it lowers the molecular mass of chains [5, 6]. As a result, physical changes can be seen on the degraded specimens or products such as change of color to yellowish or brown and formation of cracks.

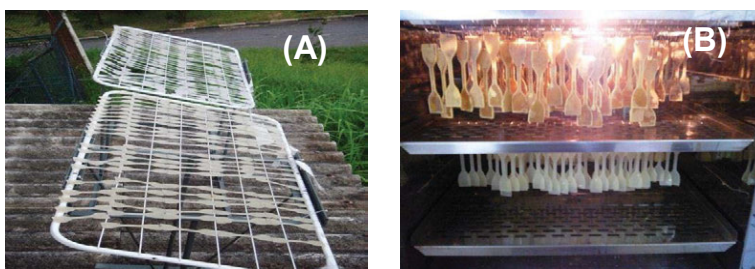
## Experimental

### Materials and methods

The iPP pellets were manufactured by Braskem and added of compatibilizer agent, propylene maleic anhydride graft copolymer (PP-g-MA) supplied by Addivant (Polybond 3200). The clay filler was Cloisite 20 by BYK Additives Company, a montmorillonite clay modified with quaternary ammonium salt (95meq/100g). The iPP was placed in plastic bags with acetylene and irradiated in  $^{60}\text{Co}$  gamma source at dose of 12.5 kGy in order to obtain the HMSPP. Two 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 operation 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 D638-2014 [7]. After molding, the dumbbell samples were mounted in appropriated device for environmental and thermal ageing, as illustrated in Figure.1.

**Table 1.** Content of clay and compatibilizer used in the samples

Samples	Matrix	PP-g-MA / %	Cloisite 20 / %
H1	HMSPP	-	-
NC1	HMSPP	3	1
NC2	HMSPP	3	10



**Figure 1.** Exposition conditions: (A) Device with dumbbell samples for environmental ageing exposed outside at the IPEN/CQMA, and (B) nanocomposite samples in air circulation stove at the temperature of 110 °C

### X-ray diffraction (XRD)

X-ray diffraction measurements were carried out in the reflection mode on a Rigaku diffractometer Mini Flex II (Tokyo, Japan) operated at 30 kV voltage and a current of 15 mA with  $\text{CuK}\alpha$  radiation ( $\lambda = 1,541841 \text{ \AA}$ ).

### Transmission Electronic Microscopy – TEM

Samples prepared by crioultramicrotomy using a diamond knife cooled at -60°C used Leica Ultra Crio Microtomo - Reichert Ultracuts FC S. The transmission electron microscopy (TEM) image was obtained at 80 kV with a JEOL JEM-2100 in samples of 50nm.

### Differential scanning calorimetry (DSC)

Thermal properties of specimens were analyzed using a differential scanning calorimeter (DSC) 822, Mettler Toledo. The thermal behavior of the films was obtained by the following program: heating from 25 to 280 °C at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere, according to ASTM D 3418-2015 [8]. The crystallinity was calculated according to the equation (1):

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

Where:  $\Delta H_f$  is melting enthalpy of the sample, P is the polymer fraction,  $\Delta H_0$  is melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg<sup>-1</sup> [9, 10].

### Thermogravimetric Analysis (TGA)

The TGA analysis was carried out in Mettler-Toledo TGA/SDTA 851 thermobalance under oxygen atmosphere of 50 mL min<sup>-1</sup>, in the range from 25 up to 650 °C at a heating rate of 10 °C min<sup>-1</sup>.

### Fourier transformed Infrared spectroscopy (FTIR)

Infrared spectroscopy was performed at Thermo Scientific (Nicolet 6700) with ATR accessory Smart Orbit Diamond, in the range from 400 to 4000 cm<sup>-1</sup>.

### X-ray fluorescence (XRF)

The sample of Cloisite 20 was placed in a crucible in a muffle furnace at 900 °C to eliminate volatile components. One pastille, by pressing under one layer of boric acid was analyzed in spectrometer Rigaku Fluorescence X-ray, model RIX.

## Results

In the X-ray Fluorescence was evidenced the composition of clay mainly as: SiO<sub>2</sub> (43%), Al<sub>2</sub>O<sub>3</sub> (16. 8%) and Fe<sub>2</sub>O<sub>3</sub> (3.6%). Those metallic ions act as pro-oxidant agents [11, 12].

The extrusion of PP and clay in presence of compatibilizer promoted the intercalation and exfoliation of the clay, according to the microscopy result, Figure 1.

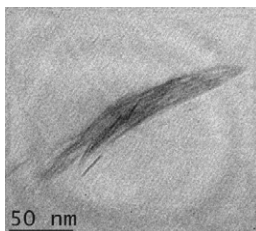


Figure 2: TEM image of NC1 at 50 nm scale.

The melting temperature ( $T_m$ ), and the crystallinity ( $X_c$ ) of the aged samples are presented in the Table 2 and Table 3, respectively, after environmental and thermal ageing. Two effects of the clay are operative on the nanocomposites ageing: one is the barrier effect; and the second is the catalytic effect of the clay on the oxidation process.

**Table 2:** DSC of samples aged in environment for 6 months

Months	$T_m / ^\circ\text{C}$				$X_c / \%$			
	zero	1	2	6	Zero	1	2	6
H1	160.1±0.11	161.2±0.14	160.5±0.13	153.4±0.11	46.1±0.1	45.2±0.6	45.1±0.4	45.0±0.5
NC1	159.4±0.12	152.1±0.13	146.2±0.13	145.8±0.13	44.1±0.4	47.6±0.7	39.9±0.6	45.5±0.6
NC2	162.8±0.13	161.5±0.15	163.7±0.15	156.1±0.14	48.2±0.5	45.0±0.5	46.2±0.7	43.1±0.6

$T_m$  = melt temperature;  $X_c$  = degree of crystallinity, as average of three samples.

**Table 3:** DSC of samples aged in stove with air circulation

Days	$T_m / ^\circ\text{C}$					$X_c / \%$				
	Zero	7	14	49	56	zero	7	14	49	56
H1	160.0±0.15	162.0±0.14	162.0±0.11	159.5±0.15	-	46.0±0.4	47.7±0.6	47.8±0.6	49.8±0.8	-
NC1	159.4±0.13	159.1±0.15	141.0±0.10	-	-	44.1±0.5	49.8±0.5	46.8±0.7	-	-
NC2	162.8±0.15	162.4±0.16	163.2±0.10	161.2±0.16	140.5±0.14	48.0±0.5	45.5±0.7	44.4±0.5	43.8±0.6	41.0±0.4

$T_m$  = melt temperature;  $X_c$  = degree of crystallinity, as average of three samples.

The catalytic effect of the clay, with chain scission and decrease of melt temperature, was more evident in the NC1, in both conditions. The crystallinity decreased mainly in the NC2 after 2 months of assay, as effect of dispersion of the clay in the matrix that difficult the chain segments to move from amorphous phase to crystallize. Also this result can be explained by formation of imperfect molecules; due to oxidation degradation and that defects difficult the crystallization.

Under these conditions the H1 was more stable compared to NC1, on attempt to catalytic effect of the ions in the clay. On the other hand the NC2 had more stability than NC1, in thermal degradation, owing to the barrier effect.

On TGA analysis, these two effects are observed by  $T_{\text{onset}}$ , represented in Table 4.

**Table 4:** Values of initial temperature of decomposition ( $T_{\text{onset}}$ ) in samples aged under environmental or thermal conditions.

Environment Assay/Months	H1	NC1	NC2
$T_{\text{onset}} / ^\circ\text{C}$			
Zero	251.9	234.3	297.6
1	238.9	207.4	232.0
2	229.1	214.4	224.3
6	225.2	213.2	215.0
$T_{\text{onset}} / ^\circ\text{C}$			
Thermal Assay/Days			
7	238.4	218.0	222.0
14	235.8	205.9	220.5
49	228.6	-	224.0
56	-	-	213.3

Considering that the main difference between NC1 and NC2 is the clay content and that thermal ageing is one drastic condition, in comparison with environmental condition,

the observed effects on DSC results corroborated with that of TGA analysis. In the environmental ageing, the barrier effect was more intense at 2 months in NC2 than in NC1. In NC1, the decrease of  $T_{\text{onset}}$  is due to the catalytic effect of the clay overlapping the barrier effect, according to Table 4.

In the thermal assay, the catalytic effect is more intense due to constant temperature and air circulation. In NC1, the assay stopped after 14 days, due to samples had disrupted in the stove. In the sample NC2, the catalytic effect of degradation occurs, however, the barrier effect was more intense. In fact, the higher content of clay can catalyze the oxidation on the polymer matrix. One explanation for this fact is that the sample has more exfoliated species than clusters [13].

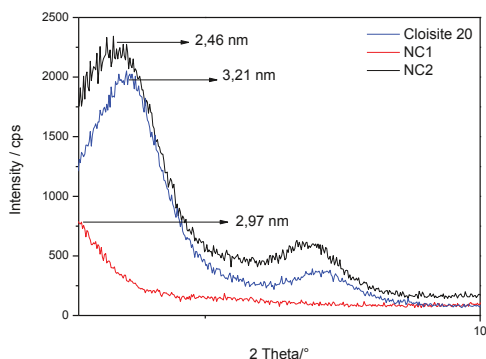
On the H1 the  $T_{\text{onset}}$  decreases as effect of the chain scission caused by environment condition (UV, rain, etc) and also by temperature effects (air circulation and constant temperature in the stove).

With degradation of the polymer matrix, the formation of carbonyl species occurs. It is usually measured by FT-IR in which carbonyl index is calculated by the ratio of the absorbance area of carbonyl stretching at  $1720\text{ cm}^{-1}$  and absorbance area at  $2720\text{ cm}^{-1}$  [14]. The calculated values are showed in the Table 5.

**Table 5:** Carbonyl index of the samples calculated in FT-IR spectra

Environmental assay/Months	H1	NC1	NC2
1	0.7	0.5	1.9
2	0.6	6.9	1.8
6	18.7	4.9	9.7
Thermal Assay/Days			
7	0	8.3	1.7
14	0	4.2	1.9
49	2.1	-	2.1
56	-	-	2.9

Comparing the nanocomposites NC1 and NC2 with the polypropylene H1 is observed that barrier effect of the clay protect against oxidation. On other hand, under thermal ageing, in NC1 the higher carbonyl index can be justified due to the effect of the clay ions while the barrier effect inhibits the formation of oxidative groups in NC2.



**Figure 3- XRD spectra of the samples H1, NC1 and NC2.**

The spectra of XRD of the samples, Figure 3, showed the comparison of NC1 and NC2 clay dispersion. In both occurred intercalation of polymer in the clay and exfoliation in the case of NC1 that corroborated with the TEM result (Figure 2).

### Conclusion

In the thermal properties the nanocomposites has showed the competition of the effects of the clay as barrier and oxidation promoter. In terms of dispersion, the NC1 has showed better dispersion, as observed in the TEM image. The effects of this better dispersion can be observed on DSC results, but on other hand, this lower content of clay, promoted the acceleration of the oxidation process in thermal assay by insufficient barrier effect.

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