

THERMAL-OXIDATION BEHAVIOUR OF MODIFIED POLYPROPYLENE NANOCOMPOSITES OBTAINED IN MOLTEN STATE

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Abstract

The thermo-oxidation behaviour of modified polypropylene nanocomposites obtained in molten state, in accelerated conditions are studied in this work. The nanocomposites were processed in twin-screw extruder, and the dumbbell samples were obtained by thermopressing. The montmorillonite clay, Cloisite 20A was added in modified polypropylene at concentrations of 5 and 10 wt% in presence of the PP-g-MA (polypropylene-graft-maleic anhydride) as compatibilizer agent. The samples were mounted in device and placed in stove at 120 °C with air circulation. The thermoxidative stability of the HMSPPNCs were investigated using the characterization techniques: spectroscopic (ATR-FTIR), microscopy (SEM) and calorimetry (DSC). The oxidation induction time viewed through carbonyl index (CI) calculation has initiated after 14 days in all the samples. The chemocrystallization effect was observed in the results of crystallinity and in the SEM images where cracks are intensified in the samples with clay after 21 days of exposition.

Keywords: Montmorillonite, PP-g-MA, Nanocomposites, Polypropylene

1 INTRODUCTION

In the past years, different methods have been proposed to prepare polymer nanocomposites, such as melt compounding, in situ polymerization and solvent-assisted process. Among them the melt compound approach results to be more economical and simpler and appears to be valuable method for industrial application¹.

Nanocomposites prepared by melt blending are synthesized almost exclusively from organoclay to solve the lack of compatibility between the polymer and the clays². This process was utilized by Toyota group to develop polypropylene nanocomposites with organoclay³.

Organoclay usually are montmorillonite (MMT) in which the interlayer sodium counterions have been replaced by organic cationic surfactants, mostly alkylammoniums salts. The introduction of surfactants increases the interlayer spacing and lowers the clay surface energy, thus facilitating the separation and dispersion of the clay layers into the polymer matrix².

Polypropylene (PP) as nanocomposite matrix, is particularly interesting because of its low cost and good mechanical properties. This polymer has been used in conventional composites for a long time and, in

combination with even low amounts of filler⁴. However, PP usually has relatively low melt strength which limits its use in applications, such as thermoforming, foaming, and blow molding. To make PP with good mechanical properties and high melt strength, scientists have explored different methods to prepare high melt strength polypropylene (HMSPP)^{5,6}. The present work concerns to the thermal ageing of HMSPP obtained by the gamma irradiation process in acetylene atmosphere⁷.

In the literature, Bhattacharya et al.⁸, has worked with commercial type of HMS-PP, and studied the dispersion of clay in foams of HMS-PP nanocomposite. In previous works^{9,10} Komatsu et al. reported the effects of clay addition in the environmental ageing of nanocomposites. In both of cases the nanoclay was the montmorillonite (Cloisite 20A).

The HMSPP nanocomposite (HMSPPNC), was obtained in twin-screw extruder process, with maleic anhydride as compatibilizer agent. The dumbbell samples were prepared and mounted in stove with air circulation evaluate the thermal stability of polypropylene-clay nanocomposites.

2 MATERIAL AND METHODS

The isotactic polypropylene (iPP) pellets 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 a ^{60}Co gamma source at dose of 12.5 kGy in order to obtain the HMSPP. Three different formulations were prepared according Table 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	5
NC2	HMSPP	12.5	3	10

The samples were prepared by melt mixing using a twin-screw extruder (Thermo Haake Polymer Laboratory). Temperatures used were 170 to 200 °C, at speed ranging from 30 - 60 rpm. The dumbbell samples for testing were obtained from thermal pressing at 80 bar and 190 °C, in type IV dimensions according to ASTM D638-03. The samples was mounted in device on stove with air circulation at 120 °C.

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} .

Differential scanning calorimetry

The analysis were carried out in DSC 822 Mettler-Toledo, under nitrogen atmosphere of 50 mL min^{-1} at a heating rate of 10 $^{\circ}\text{C min}^{-1}$, in the temperature range from -50 to 280 °C, keeping in 280 °C for 5 minutes; cooling from 280 to -50 °C at a cooling rate of 10 $^{\circ}\text{C min}^{-1}$ and reheating from -50 up to 280 °C at heating rate of 10 $^{\circ}\text{C min}^{-1}$. Samples at about 8 - 12 mg were placed in closed aluminum pans. The crystallinity was calculated according to equation 1:

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

Where ΔH was the measured melting enthalpy and ΔH_0 was the enthalpy of fusion at 100% crystalline PP, $\Delta H_0 = 209 \text{ J g}^{-1}$ [11] and P was the PP fraction in the sample.

Scanning electron microscopy

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

3 RESULTS AND DISCUSSION

In the table 2 are showed the values of crystallinity and the melting temperature.

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

Sample Time (days)	$T_{M2} (^{\circ}\text{C})$		
	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

In the sample NC2 the lower temperature can be related to the vulnerability of the sample to temperature and oxygen, thus accelerating the thermo-oxidation process. It was verified chemy-crystallization process. This process is more evident in the sample NC2, where the temperature decreased to 140 °C. Figure 1, shows the visual process of chemy-crystallization: formations of cracks on the surface of the sample that increased with time of degradation becoming deeper.

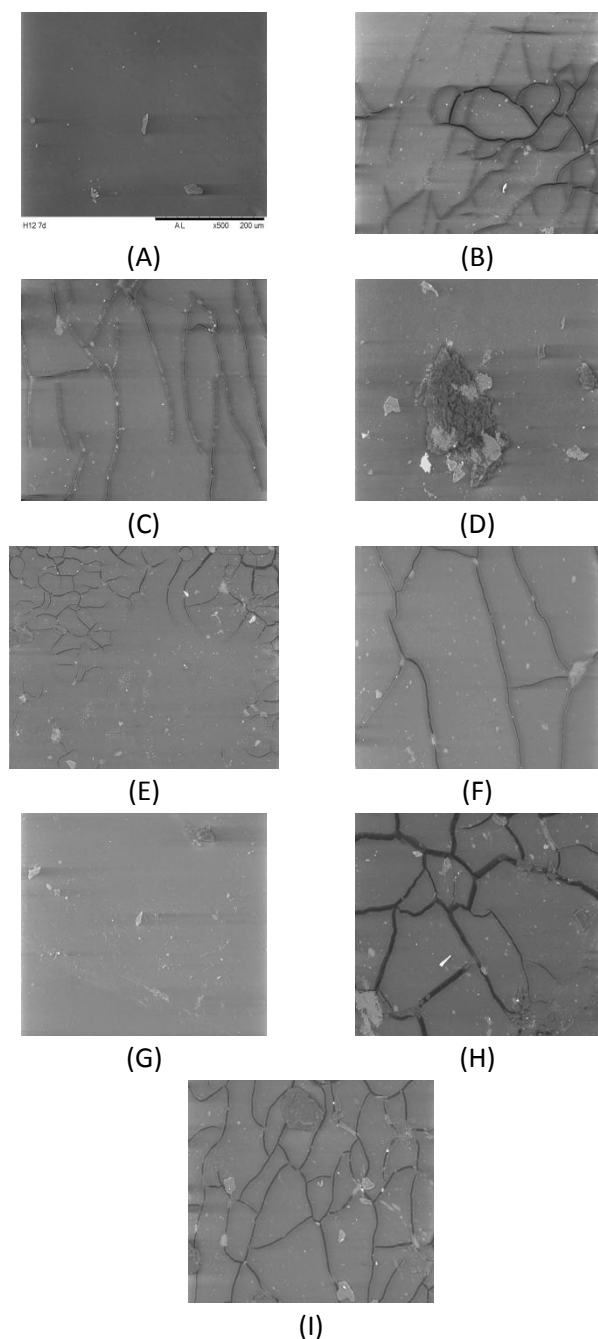


Figure 1: SEM of thermo-aged samples; 7 days: A(H1), B(NC1), C(NC2); 14 days: D(H1), E(NC1), F(NC2); 21 days G(H1), H(NC1), I(NC2).

The diffusion of oxygen is considered a significant promoter in accelerated tests, especially in rapidly oxidizing polymers. Polyolefin, and particularly polyethylene or polypropylene, oxidize exclusively in the amorphous phase because the crystalline phase is impermeable to oxygen^{12, 13}.

In the sample H1, figure 1 (A)(D)(G) cracks were not observed in the surface, cracks were observed in the surface of nanocomposites after 7 days of thermal ageing. However increasing of time of degradation, the

cracks become deeper due the contraction of the surface layers by the chemy-crystallization effect¹⁴, as showed in the samples NC1. Figure 1 (B)(H), NC2 Figure 1 (C)(F)(I). In the other hand carbonyl index reflect significantly the surface oxidation of H1.

TABLE 3: Carbonyl Index

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

During the oxidation process, the polymer macromolecules degrade leading to the formation of alkyl radicals. These unstable alkyl radicals combine with oxygen to form hydroperoxides, which can decompose to produce alkoxy radicals. These alkoxy radicals may either abstract hydrogen from polymer backbone or undergo β -scission. As a result of these propagation steps, the polymer matrix is degraded further leading to the production of a mixture of carbonyl and hydroxyl species¹⁵.

The carbonyl index (CI) was calculated using areas of FT-IR spectra at 2720 cm^{-1} , as reference and the carbonyl absorbance area at 1720 cm^{-1} that increases with oxidation time^{14,16}, Equation 2:

$$CI = \frac{Abs(1720)}{Abs(2720)} \quad \text{Equation (2)}$$

The nanocomposites showed chemical stability terms of carbonyl index. The H1 demonstrated more degradation with time, however after 14 days, the nanocomposites degradation process became accelerated.

4 CONCLUSIONS

Comparing the nanocomposites with the HMSPP, crack propagation was more intense in the HMSPPNC surfaces although oxidation propagation in the surface was higher in the HMSPP.

5 ACKNOWLEDGMENT(S)

The author thanks Capes for the grants, CNPq, FAPESP (process 2012-0236-1). Braskem, Southern Clays and Chemtura for the samples. Eleosmar Gasparim for the thermal analysis and Nelson R. Bueno for the extrusion of the samples.

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