THERMAL-OXIDATION OF HMSPP NANOCOMPOSITES BASED ON MONTMORILLONITE CLAY

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Abstract *Nanocomposites based on high melt strength polypropylene (HMSPP) with montmorillonite clay were submitted to thermal assay. The samples were processed utilizing a twin screw extruder. The dumbbell samples were obtained by thermopressing and mounted in stove with air circulation. The effects of thermal assay on the nanocomposite were evaluated by Melt Flow Index (MFI), Energy Dispersive Scanning (EDS) and differential scanning calorimetry (DSC). It was observed that presence of clay can accelerate the process of thermal aging at lower content of 1wt%.*

Keywords: *HMSPP, polypropylene, nanocomposites, clay*

Introduction

The oxidation of polymers begins during processing and the hydroperoxides formed affects the rate of thermal-oxidation during subsequent use (aging and weathering). The degradation of polymers is like a double-edge sword: it has harmful aspects as well as beneficial aspects. If uncontrolled it can promote loss of polymer performance and lead to safety hazards of resistance and toxicity, but if properly controlled it can be used for producing new and better materials [1].

The polymer matrix used for this work was the HMSPP (high melt strength polypropylene) synthesized by gamma irradiation, according to the literature [2]. In the HMSPP was added the commercial montmorillonite clay, Cloisite 20. The method for mixing these materials was the molten state processing in twin-screw extruder. The focus of this study was to analyze the effects of clay addition in HMSPP under thermal assay.

Experimental procedure

The methodology followed Komatsu [3] with: isotactic polypropylene (iPP) pellets manufactured by Braskem and compatibilizer agent, propylene maleic anhydride graft copolymer (PP-g-MA) supplied by Chemtura (Polybond 3200). The clay filler was montmorillonite clay Cloisite 20 (BYK additives). The iPP was placed in plastic bags with acetylene gas and irradiated in ^{60}Co gamma source at dose of 12.5 kGy in order to obtain the HMSPP. The samples were prepared in molten state using a twin-screw extruder (Thermo Haake Polymer Laboratory) for incorporate the clay in the polypropylene. The operated temperatures were 170–200 ºC and speed ranging from 30 to 60 rpm. The dumbbell samples for testing were obtained from thermal molding pressure (80 bar and 190 ºC). After molding, the dumbbell samples were mounted in stove at 110 °C for thermal assay. In the table 1 are described the formulations of this work.

Table 1 - Content of clay and compatibilizer used in the samples

Sample	Matrix	PP-g-MA /%	Cloisite 20A /%
H1	HMSPP	-	-
NC0	HMSPP	3	-

NC1	HMSPP	3	1
NC2	HMSPP	3	10

Differential scanning calorimetry

Thermal properties of specimens were analyzed using a differential scanning calorimeter (DSC) 822, Mettler Toledo. The thermal behavior of the films was obtained by: heating from 25 to 280 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere, according to ASTM D 3418-08. The cristallinity was calculated according to the equation:

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

where: P is the PP fraction on the sample, ΔHf is melting enthalpy of the sample, ΔH0 is melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg^{-1}.

Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy was done using an EDAX PHILIPS XL 30. In this study, a thin coat of gold was sputter-coated onto the samples.

Melt flow index

The melt flow index was carried in Ceast Italy Melt Flow Modular Line and was operated at temperature of 230 ºC for 10 min of total time test.

Results and Discussion

Is very important to describe that some samples were totally degraded before the others, it was observed the detachment of those samples from the support inside the stove. For this reason the comparisons were made utilizing the pristine sample, 7 days, 21 days and the last resistant sample removed of the stove. In the table 2 was represented the values of DSC of thermal aged samples.

Table 2 – DSC values of the surface of aged samples

	Time/Days	T_{m2}/ºC	X_c /%
H1	0	159.9	46.1
	7	160.6	47.7
	21	158.5	48.5
	49	159.6	49.8
NC0	0	161,2	48,3
NC1	0	160.6	48.7
	7	159.1	49.1
	21	143.1	44.6
NC2	0	162.8	43.4
	7	162.4	45.5
	21	161.1	45.2
	56	132.6	40.6

On the sample NC0 (added of maleic anhydride), was observed an increase of crystallinity, as effect of nucleation owing to lower molecular weight of compatibilizer. This effect was observed considering the comparison of the sample H1 and NC0.

The decrease of Tm_2 is an effect of degradation and is pronounced in the NC1 after 4 days of ageing.

On this assay is very clear that lower amount of clay can catalyze the degradative process in condition of constant temperature and air circulation. In this case the sample NC1 has more degradation caused by chain scission and catalysis of metallic ions. The sample NC2, resisted for longer time showing the contribution of barrier effect of the clay. The clay galleries increase the tortuous path for oxygen diffusion to interior of the sample. In the interior of the sample the oxygen reacts for chain scission forming hydroperoxides and carbonyl, producing volatiles, that when leaving from interior of sample are trapped by clay galleries because these molecules are greater than oxygen.

As long of this assay, the volatiles products accumulate and become a physical barrier both to volatiles or oxygen diffusion to interior of the sample [4]. This can be observed in the sample with 10% of clay, were the assay extended until 56 days.

The oxygen diffusion is a key point to understand the process of degradation on polymer nanocomposites. In EDS, table 3, is observed the percentage of oxygen in the surface of the sample

Table 3 – EDS analysis on the surface of the thermal aged samples

Surface %	0	7	21	42	56 (days)
H1	2.8	2.8	5.8	7.4	--
NC1	2.5	2.5	9.7	--	--
NC2	3.4	3.4	7.9	9.6	22

The oxygen diffusion is very significant in thermal assay, especially faster in oxidized polymers. In polyolefins, and in particular the polypropylene, oxidation occurs mainly in the amorphous phase due to the crystalline phase to be impermeable to oxygen [5,6], as observed in DSC analysis.

The higher concentration observed on the sample with higher concentration of clay NC2 (10 wt%) can admit some hypothesis: the process of oxygen diffusion to interior of the sample where part of this oxygen is trapped on the clay galleries; higher superficial area with contact with oxygen, causing formation of cracks in the surface of the sample [7].

The presence of oxygen can promotes the process of chain scission on the polymer nanocomposite, as view on DSC and EDS results. The process of chain scission is more sensitive as observed in melt flow index, table 4.

Table 4 – MFI values

Sample	0 ($g.10min^{-1}$)	7d ($g.10min^{-1}$)	28d ($g.10min^{-1}$)	49d ($g.10min^{-1}$)	56d ($g.10min^{-1}$)
H1	6.4	9.3	8.1	36.7	-
NC1	5.1	21.5	39.6	-	-
NC2	1.0	3.7	4.3	-	48.2

The clay content can decrease the flow rate, due to the complexity of the structure of the clay. This effect is better observed when comparing H1 and the sample with clay NC2. The melt flow increases with time of assay due to the process of chain scission, caused by combination of diffusion of oxygen and the catalytic effect of metallic ions of the clay.

Conclusion

Based on those results, we concluded that clay can change the extension of degradation, but not change de mechanism of degradation. It was observed that sample with 1% of clay stoped at 21 days because the process of degradation is too fast. In the other hand the sample with 10% of clay assay resisted until 56 days. The quantity of clay could degrade more intensily but as a filler the clay promotes more mechanical stability and integrity.

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