

THERMAL ANALYSIS OF POLYPROPYLENE MODIFIED BY GAMMA IRRADIATION COMPOSITES UNDER OUTDOOR CONDITIONS

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ABSTRACT

This work reports the influence of the clay in the degradation process of the HMSPP. The polypropylene (PP) was irradiated under acetylene atmosphere in gamma irradiation source (⁶⁰Co) to obtain the HMSPP (high melt strength polypropylene). Composites of HMSPP were processed in twin-screw extruder with clay Cloisite 20A and Maleic Anhydride (PP-g-MA) as coupling agent. The obtained composites were exposed under outdoor conditions for 6 months. The ageing effects were characterized by Differential Scanning Calorimetry (DSC), Thermogravimetry Analysis (TGA). Chemical oxidation was evaluated by Carbonyl Index (IC) through infrared Spectroscopy (FT-IR). The results showed correlation between carbonyl index and ageing time.

1. INTRODUCTION

In recent days, polymer clay nanocomposites (PCNC) received a considerable scientific and technological interest. The most usual way to produce PCNC is melt-blending process in a twin-screw extruder. Nanocomposites synthesized on this way are expected to solve the lack of compatibility between the polymer and the clays [1].

Due to the application on automobilistic, paint and among others, the durability of PCNC, as well mechanical and thermal properties, is also of great importance for the application point of view [2].

Common natural clays like OMMT (organic modified montmorillonite) are hydrophilic. Prior to the introduction of the hydrophilic clay into the organophilic polymer matrices, the modification of the clay is essential, in order to obtain a good dispersion and a strong interfacial adhesion for the improvement in the mechanical properties [3].

In present study the polypropylene was modified by gamma irradiation to obtain the HMSPP (high melt strength polypropylene). This method was developed by polymer group of IPEN. This process causes in the polymer chain diverse different reactions as long chain branching and crosslinking formation [4].

The PCNC of HMSPP was obtained in molten state utilizing the twin screw extruder process. The obtained samples were exposed in environment for 6 months. That samples surface analysis resulted in the correlation between carbonyl index and ageing time.

2. EXPERIMENTAL

2.1 Materials and methods

The iPP pellets were manufactured by Braskem and compatibilizer agent, propylene maleic anhydride graft copolymer (PP-g-MA) was supplied by Addivant (Polybond 3200). The clay filler was Cloisite 20A by Southern Clay Products montmorillonite clay quaternary ammonium salt-modified (95meq/100g). The iPP was placed in plastic bags with acetylene that were irradiated in ^{60}Co gamma source at dose of 12.5 kGy in order to obtain the HMSPP. The iPP utilized in this work has no nucleating agent or stabilizing in its formulation. Two different formulations, Table 1, containing the clay were prepared in molten state using a twin-screw extruder (Thermo Haake Polymer Laboratory). The operated 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 D638-03. The dumbbell samples prepared and mounted in appropriated device for environmental and thermal ageing are illustrated in Fig.1.

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

Samples	Matrix	PP-g-MA /%	Cloisite 20A /%
H1	HMSPP	-	
NC1	HMSPP	3	0.1
NC2	HMSPP	3	5



Figure 1: Device with dumbbell samples for environmental ageing outside at the IPEN/CQMA

2.1.1. 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 crystallinity was calculated according to the equation:

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

Where: ΔH_f is melting enthalpy of the sample, ΔH_0 is melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg⁻¹ [5, 6].

2.1.2. Fourier transformed Infrared spectroscopy

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

2.1.3. X-ray fluorescence

The sample of Cloisite 20A was placed in a crucible and then placed in a muffle furnace at 900 °C to eliminate volatile components. The pastille was made pressing it on layer of boric acid and analysed in equipment Rigaku Fluorescence X-ray, model RIX [7].

2.1.4 Thermogravimetric Analysis (TGA)

TGA analysis was made in equipment Mettler Toledo-TGA/851, heating 25 – 650 °C at heating rate 10°C/min⁻¹.

3. RESULTS

Result of X-ray Fluorescence, analysis indicated the composition of the clay, Table 2:

Table 2: Composition of Montmorillonite clay

Components	Content /%
Loss on ignition	34.0 ±0.3
SiO ₂	43.0 ±0.4
Al ₂ O ₃	16.8 ±0.2
Fe ₂ O ₃	3.6 ±0.2
MgO	2.0 ±0.1
Na ₂ O	0.20 ±0.02
K ₂ O	0.023 ±0.002
Cl	0.19±0.01
CaO	0.11±0.01

Pro-oxidant elements as: Al, Fe and Mg are present in the clay. In the literature is reported that low quantities of these elements acts as oxidants of polymers by redox reactions with hydroperoxides [8].

Results of FT-IR, in Fig. 2, indicated presence of carbonyl group at 1720 cm⁻¹ and peak of 1048 cm⁻¹ is attributed to Si-O-Si bonds.

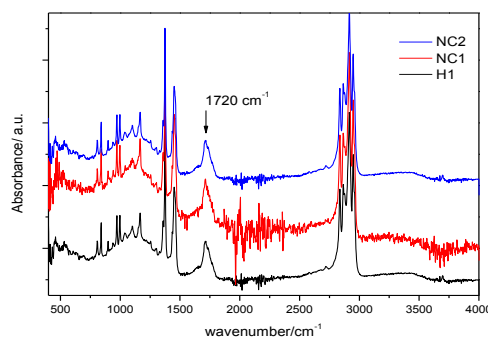


Figure 2: FT-IR of environmental aged samples after 6 months

Fig. 3 presents the carbonyl indexes (CI), calculated utilizing the areas of carboxylic acid peak (carbonyl stretching) at around 1720 cm⁻¹, and the peak at 2720 cm⁻¹, as reference. The C=O group is produced by alkyl radicals and oxygen reactions. To a certain extent, an alkoxide radical takes an electron from a carbon-carbon bond. This event transforms the oxidized group into carbonyl and the polymeric chain undergoes a mechanism called β -scission [9].

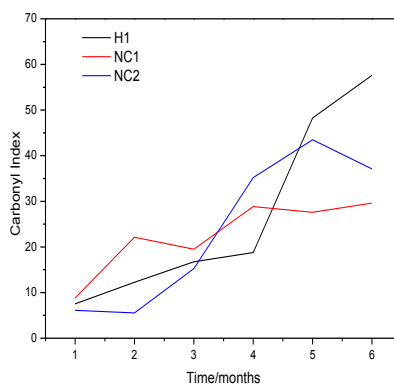


Figure 3: Carbonyl Index of samples environmental aged

Metallic ions present in the clay composites promote the oxidation of the surfaces in the early periods of exposition (up to 4 month). In the photo-oxidation phenomenon the competitive mechanism of the “screening effect” occurs. The clay lamellae acts as a filter to UV radiation, so in this case exfoliated clay can be more efficient, as observed with the 0.1% clay composite. Above to 4 months, H1, that has no oxidation protection, shows the CI continuously intensified.

Barrier effect is considered when assumed the diffusion of oxygen to the bulk of the composite. According to Bartolucci et al. [10], the clay layers act as barrier to the oxygen diffusion into the nanocomposite. So this effect can be evaluated in the interior of the sample by observing the crystallinity and melting temperature of the crystallites.

In the Tables 3, 4 and 5 are shown the effects of ageing assays on the crystallinity and melting temperature of the samples. In the sample NC2 the effect barrier was observed at 3 and 6 months, when the values of T_{m1} and X_c are almost constant. After this period of time the oxygen penetrates and accelerates the photo-oxidation condition on the nanocomposite NC2. The barrier effect was not observed in NC1 considering these properties

Table 3: Crystallization Temperature / T_c , Melting Temperature / T_{m1} , Crystallinity/ X_c and Decomposition Temperature / T_{onset} of sample H1

Time/Months	Zero	3	6
$T_{m1}/^{\circ}\text{C}$	165,7	158.7	156.9
$X_c/\%$	41.1	43.1	45.5
$T_{onset}(\text{O}_2)$	251.9	224.7	225.2
$T_{onset}(\text{N}_2)$	387.5	384.8	393.6

Table 4: Crystallization Temperature/ T_c , Melting Temperature/ T_{m1} , Crystallinity/ X_c and Decomposition Temperature / T_{onset} of sample NC1

Time/Months	zero	3	6
$T_{m1}/^{\circ}\text{C}$	167.6	152.3	148.6
$X_c/\%$	44.1	46.6	47.5
$T_{onset}(\text{O}_2)$	221.4	219.2	224.6
$T_{onset}(\text{N}_2)$	398.6	384.3	381.5

Table 5: Crystallization Temperature/ T_c , Melting Temperature/ T_{m1} , Crystallinity/ X_c and Decomposition Temperature / T_{onset} of sample NC2

Time/Months	zero	3	6
$T_{m1}/^{\circ}\text{C}$	167.7	178.0	159.2
$X_c/\%$	37.9	42.8	42.9
$T_{onset}(\text{O}_2)$	246.5	244.7	212.9
$T_{onset}(\text{N}_2)$	432.7	411.2	315.3

During environmental ageing the sample H1 suffers chain scission due UV components of the environmental sunlight, with decrease of T_{m1} in consequence and increase in crystallinity. The crystallinity tends to be higher after 6 months as for chemicrystallization effect, according to Mouzakis et.al. [11]. The amount of clay is not enough to prevent the chemicrystallization for long time.

Decreases of T_{m1} , the T_{onset} are more evident after 6 months in presence of higher clay concentration.

4. CONCLUSION

In terms of carbonyl index, the composites were more resistant's than H1. Although the composites showed more degradation effects by thermal analysis after 6 months.

5. ACKNOWLEDGEMENTS

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