

STUDY OF MODIFIED POLYPROPYLENE NANOCOMPOSITES BY GAMMA IRRADIATION WITH ADDITION OF CLOISITE CLAY

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ABSTRACT

Nanomaterials, and, in particular, nanoreinforcements for polymer composites have been the subject of intense research, development and commercialization. Clay-containing polymeric nanocomposites (CPNCs) are used as either functional or structural materials, large-volume CPNCs with a commodity or engineering polymer as the matrix, where the mechanical behavior is the main concern (followed by gas–vapor barrier properties, flammability, etc.). This work concerns to the study of the mechanical, thermal and morphological behavior nanocomposite, (HMSPP) Polypropylene High Melt Strength (obtained at dose of 12.5 kGy) and addition of 5 and 10 wt% of organoclay with Cloisite 20A nanocomposite. Agent compatibilizer polypropylene-graft, (PP-g-AM) was added at 3% concentration and the clay was dispersed through melt intercalation technique using a twin-screw extruder). We observed an increase in traction rupture. The mechanical behavior was evaluated by strength, the thermal behavior were evaluated by the technique of Differential Scanning Calorimetry (DSC), the morphology of the nanocomposites was studied by Scanning Electron Microscopy (SEM), Melt Flow Index (MFI) and Fourier Transformed Infrared Spectroscopy (FTIR) in nanocomposites Cloisite 20 A at 10% wt.

Keywords: Gamma irradiation, Polypropylene, Nanocomposites and Clay Cloisite

1. INTRODUCTION

Nanotechnology is one of the fastest growing new areas in science and engineering. The subject arises from the convergence of electronics, physics, chemistry, biology and materials science to create new functional systems of nano scale dimensions [1]. Nanocomposite is a new class of materials [2] that grow along with nanotechnology, both working with nanoparticles with a size of 0.1-100 nm [1].

Clay-containing polymeric nanocomposites (CPNCs) are used as either functional or structural materials [3]. Authors use clay when need to increase the mechanical strength [3 - 8], followed by improvement of gas–vapor barrier properties [3] among others.

The HMS-PP (high melt strength polypropylene), a polypropylene modified by grafting under high energy ionizing radiation is prepared in presence of acetylene atmosphere which promotes crosslinking [9], branching and/or chain scission. The properties of HMS-PP is unique; rheological properties are new; higher melt strength and higher resistance elongational [10, 11].

The nanocomposite of HMSPP/clay was obtained when the material is homogenised in a twin screw extruder. Due to the low polarity of PP, it is difficult to get the exfoliated and homogeneous dispersion of the silicate layer at the nanometer level in the polymer. This is mainly due to the fact that the silicate clays layers have polar hydroxyl groups and are compatible only with polymers containing polar functional groups. Consequently the matrix modification with polar oligomers is necessary prior to clay introduction in order to achieve nanometric dispersion of the Clay [12]. Several authors use the maleic anhydride as compatibilizer agent [3 – 8, 13] due to its polarity it increases the effect of compatibility of clay with the polymer matrix.

It is well reported that the efficiency of the clay as a reinforcing agent strongly depends on the extent of dispersion throughout the polymer matrix, while it is difficult to obtain the completely dispersed structure in polymer-clay nanocomposites [4].

When nanometric dispersion of primary clay platelets is obtained, the aspect ratio of the filler particle is increased and the reinforcement effect is improved [10].

In this work we evaluate the properties of high melt strength polypropylene with the addition of nanoparticles and also their mechanical and thermal properties.

2. EXPERIMENTAL

2.1. Materials and Methods

The PP H603 is manufactured by Braskem; the Maleic Anhydride is used as a compatibilizer agent (PP-g-MA) polypropylene-grafted-maleic anhydride, Polybond 3200) by Chemtura (USA) and the clay Cloisite 20 A by Southern Clay Products.

The samples of iPP (isotactic polypropylene) were placed in plastic bags with addition of acetylene. The bags were irradiated in a ⁶⁰Co gamma source at dose of 12.5 kGy in order to obtain the HMS-PP. In sequence two formulations 5wt% and 10 wt% of Cloisite 20A with 3wt% of PP-g-MA were prepared

The samples were homogenized in an twin-screw extruder (Thermo Haake Polymer Lab) to better incorporation of clay in polypropylene and also a sample HMS PP 12.5 kGy, the temperatures used were 170 to 200 °C, with speed ranging from 30 to 60 rpm, the material was pelletized.

The dumbbell samples for testing were obtained from thermal molding pressure at 80 bar and temperature of 190 °C with the corresponding dimensions of the type IV, according to ASTM D 638-03 [14].

2.2. Melt Flow Index (MFI)

The melt flow index was obtained in the Ceast Italy Melt Flow Modular Line at temperature of 230 °C and 10 min total time of test.

2.3. Mechanical Test

The samples were tested in a universal testing machine EMIC DL 3000 model with strain rate of $2 \cdot 10^{-2} \text{ s}^{-1}$.

2.4. FTIR (Fourier Transformed Infrared Spectroscopy)

Spectra of infrared spectroscopy were performed at Thermo Scientific (Nicolet 6700) Smart Orbit Diamond, in the range from 400 to 4000 cm^{-1} .

2.5. DSC (Differential Scanning Calorimetry).

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

$$X_c(\%) = \frac{\Delta H_f \times 100}{\Delta H_o}$$

ΔH_f = melting enthalpy of the sample, ΔH_o = melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg^{-1} .

2.6. SEM (Scanning Electron Microscopy)

Samples were fractured using liquid nitrogen. The fracture surface was analyzed by Scanning Electron Microscopy that performed in the equipment EDAX Philips model XR-30.

3. RESULTS AND DISCUSSION

3.1. Mechanical Test and Melt Flow Index

Obtained with the pellets, we obtained the results of Melt Flow Index:

Table 1: Melt Flow Index

Samples	iPP	HMSPP 12.5kGy	HMSPP 12.5 kGy 5wt% Cloisite	HMSPP 12.5 kGy 10wt% Cloisite
Melt Flow Index dg min ⁻¹	1.3	6.7	2.0	1.0

It was observed an increase in the processing flow of HMS PP 12.5 kGy, MFI = 6.7 dg min⁻¹ what reveals chain scission occurrence. With the addition of Cloisite 20A: HMS PP 12.5 kGy Cloisite 5wt%, the values changed for MFI = 2 dg min⁻¹ HMS PP and 12.5 kGy 10wt% Cloisite, MFI = 1.3 dg min⁻¹ respectively. These results agree with a good clay intercalation in the macro chains of HMS PP balancing the effects of chain scission Tab. 1.

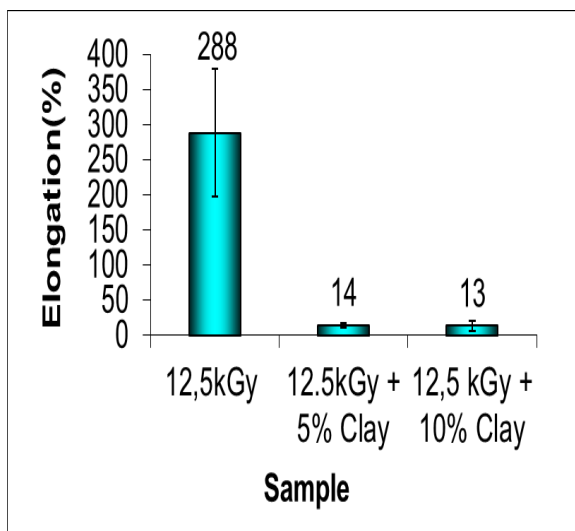


Figure 1: Elongation (%)

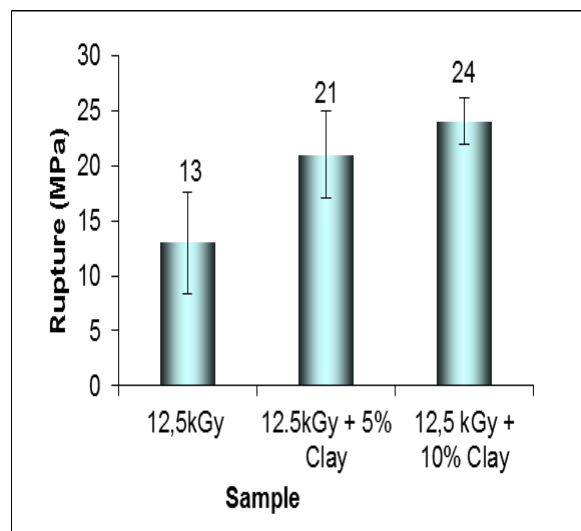


Figure 2: Tensile Rupture (MPa)

Due to intercalation of Cloisite into polypropylene, sample became stiffer causing their decreased deformation: HMSPP 12.5 kGy Cloisite 5 wt%: 14% elongation, HMSPP 12.5 kGy 10 wt% Cloisite: 13% elongation compared to HMSPP 12.5 kGy with has 288% of

elongation Fig. 1. The tensile rupture were demonstrated the reinforcing effect of the clay Fig. 2.

3.2. Differential Scanning Calorimetry

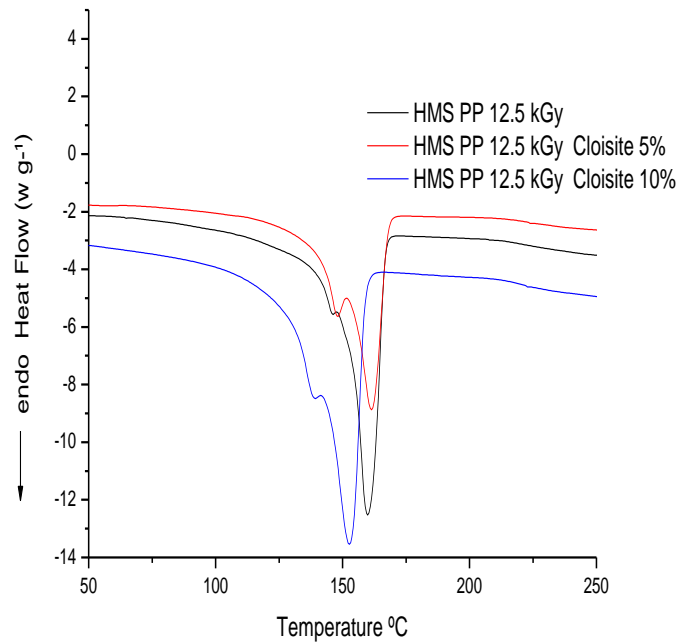


Figure 3: DSC in nitrogen atmosphere of pristine HMS PP 12.5 kGy and HMS PP/clay

Table 2: DSC , Tm_2 : Melting temperature secondary; X_c : degree of crystallinity

Samples	Tm_2 (°C)	X_c (%)
HMSPP 12.5 kGy	160	46
HMSPP 12.5 kGy Cloisite 5%	161	42
HMSPP 12.5 kGy Cloisite 10%	162	43

In Fig. 3, DSC results were reported. An increase in melting temperature of HMSPP 12.5 kGy and a decrease of crystalline concentration is related to the nucleation effect of the nanoclay.

3.3. Fourier Transformed Infrared Spectroscopy (FTIR)

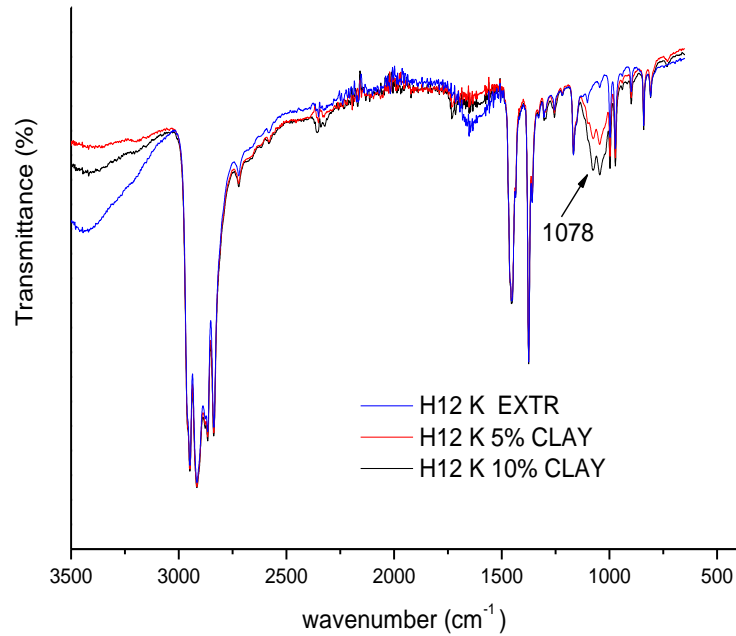


Figure 4: (FTIR) the pristine samples HMSPP 12.5 kGy and HMSPP/clay

The infrared spectroscopy is a sensitive method to monitor chemical changes in a polymeric material. When the tests were done, we realized that there were points that coincided with the irradiated sample only, but drew attention to a peak 1078 cm^{-1} .

The peak of 1078 cm^{-1} is in a range of $950\text{-}1150\text{ cm}^{-1}$ originating from vibrations of in-plane and out-of plane Si-O bonds [15,16].

3.4. Scanning Electron Microscopy (SEM)

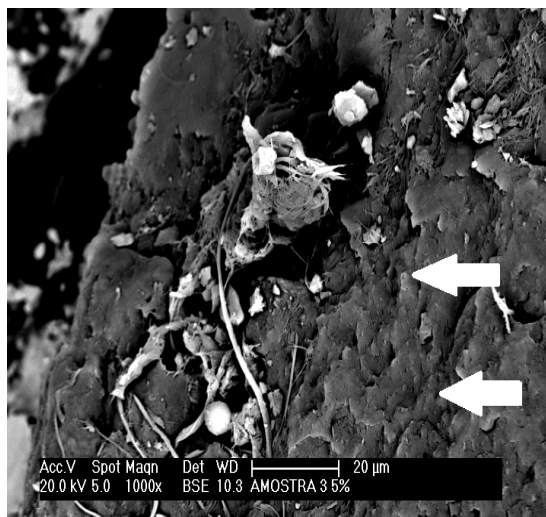


Figure 5: HMSPP 12.5 kGy Cloisite 5wt%

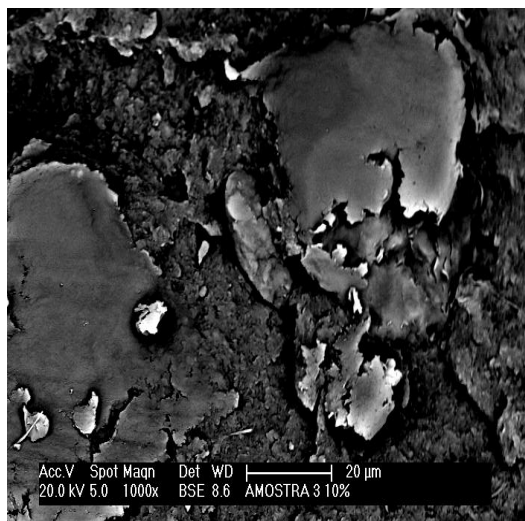


Figure 6 : HMSPP 12.5 kGy Cloisite 10wt%

The SEM is a method that was used in this work for a better view of the interaction of the two materials worked. The analyses were made on the fracture on scale of 20µm.

In Figure 5 have the HMSPP 12.5 kGy Cloisite 5wt% had a dispersion of clay better than in Fig. 6 where HMSPP 12.5 kGy Cloisite 10wt% had a higher occurrence of clusters

4. CONCLUSIONS

We obtained a decrease in elongation of the samples with Cloisite clay and reinforcement effect in the rupture tensile. With SEM we found a better dispersion in the samples with 5% compared to 10% Cloisite 20A. Nucleation and intercalation effects are observed in the processing of those samples.

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