

STUDY OF THE NATURAL AGING OF HIGH MELT STRENGTH POLYPROPYLENE (HMSPP) WITH ADDITION OF CLOISITE 20 A

Luiz G. H. Komatsu^{1*}, Washington L. Oliani¹, Duclerc F. Parra^{1*}, Maria J. A. Oliveira¹, Ademar B. Lugao¹

¹Nuclear and Energy Research Institute (IPEN/CNEN-SP),
Av. Prof. Lineu Prestes, 2242
CEP 05508-000 São Paulo – SP-Brasil
[*luizkomatsu@gmail.com](mailto:luizkomatsu@gmail.com)
dfparra@ipen.br

Abstract: Nanocomposites, particularly polymer/clay, has been the subject of research and developments with regard to intercalation in polymer matrix. Polypropylene is a commodity and when modified by gamma irradiation polypropylene with high melt strength (HMSPP) is obtained. In this work nanocomposite of HMSPP was obtained with nanoclay (Cloisite 20A), the nanocomposite was processed in twin screw extruder where the clay was homogenized in the melt. The material was pelletized and thermopressed to dumbbell samples submitted to natural aging for a period of four months. The aged dumbbell samples were characterized by Tensile Test, Differential Scanning Calorimetry (DSC), Scanning Electronic Microscopy (SEM) and Infrared Spectroscopy (FTIR) in comparison with a pristine HMSPP. After four months appears some superficial cracks and a decrease in the values of elongation and tensile stress was found in the nanocomposite with Cloisite 20A.

Keywords: *Polypropylene, HMSPP, Nanocomposite, Nanoclay and Cloisite*

1 Introduction

Polypropylene (PP) is one of most versatile commodity polymers. Owing to its low cost, relatively good properties, and steady improvement of physical properties, and new applications are continuously expanding [1]. Recent studies have been made adding clay to the polypropylene to nanocomposites, in particular, is focused attention on layered silicates (nanoclays) [2].

Nanocomposites formed from clay represent a potentially attractive approach for improving some performance characteristics (mechanical, thermal, etc) [3], and clays were considered to be an appropriate reinforcing agent [4].

Extensive efforts have focused on the performance of PP nanocomposites prepared by melt compounding. Temperature processing, shear rate, screw speed, resistance time, mixing strategies, and screw configuration have been the main challenges in the melt processing of polymer nanocomposites [5].

To merge the polymer chains into the clay layers is used a coupling agent, graft polypropylene with maleic anhydride (PP-g-MA). One of its main tasks is to improve the interaction of polymer/clay, another function is to assist in the exfoliation of the clay. When we analyze the dispersion of clay in the matrix two main phases are observed: Intercalated phase, when the polymer chains are intercalated between the clay layers forming a multilayer structure orderly; Exfoliated Phase: where the clay is uniformly dispersed in a polymeric matrix, maximizing the polymer-clay interactions.[6]

In this study the polypropylene was modified by gamma irradiation under an atmosphere of acetylene. With this modification the matrix performs greater resistance in the molten state. This new matrix is known as high melt strength polypropylene or HMSPP.

One major problem associated with the applications of polymers is their stability to weathering. Various reactions are responsible for the instability, including rearrangements of the chemical structure, formation of oxidation products, cross linking and/or chain scission [7].

When UV irradiation is strong, the changes caused by photo oxidation occur preferentially near to the surface. This is because the oxidation process is so rapid that oxygen is consumed near the surface before it can be diffused far in the interior of the polymer [7].

2 Methodology

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

The samples of iPP (isotactic polypropylene) were placed in plastic containers added acetylene and were irradiated in a ⁶⁰Co source (gamma) at dose rate of 12.5 kGy in order to obtain the HMS-PP. The formulations obtained are shown in a tab 1.

Samples	Matrix	Dose (kGy)	PP-g-AM (wt%)	Cloisite 20A (wt%)
H1	HMSPP	12.5	-	-
H2	HMSPP	12.5	3	5
H3	HMSPP	12.5	3	10

Tab 1 : Samples of the legends

The samples were homogenized in an twin-screw extruder (Thermo Haake Polymer Lab) to better incorporation of clay in polypropylene and HMS PP 12.5 kGy, at temperatures used of 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 [8, 9]

The dumbbell samples were arranged in a device for environmental aging, according to ASTM, and exposed in the period 2011/May to 2011/December.

2.1 Mechanical Test

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

2.2 FTIR (Fourier Transformed Infrared Spectroscopy)

Infrared spectroscopy was performed at Thermo Scientific (Nicolet 6700) Smart Orbit Diamond, range from 400 to 4000 cm^{-1} .

2.3 DSC (Differential Scanning Calorimetry)

Was carried out in a 822 Mettler-Toledo, under nitrogen atmosphere of 50 mL min^{-1} at a heating rate

of 10 °C min⁻¹, in the temperature range of -50 to 280 °C, keeping in 280 °C for 5 minutes and from 280 to -50 °C at a cooling rate of 50 °C min⁻¹ and reheating from -50 up to 280 °C at heating rate of 10 °C min⁻¹. The polymer samples at about 8 - 12 mg were placed in closed aluminum pans.

2.4 SEM (Scanning Electron Microscopy)

Scanning Electron Microscopy was performed in equipment EDAX Philips model XR-30.

3. Discussion and Results

In fig. 1 we have a graph of tensile test, it appears that there was a considerable improvement in tensile strength on the nanocomposite. Over time the sample with 5% of clay was more stable to aging than the comparative sample with 10% clay.

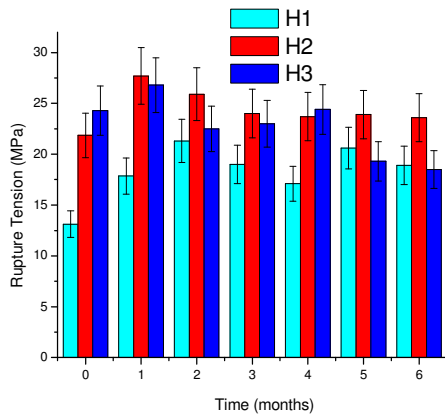


Fig. 1. Tensile Test of samples with environmental aging

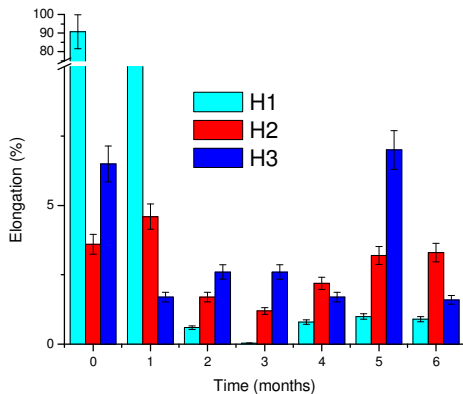


Fig. 2. Elongation of samples with environmental aging

Elongation clay samples had lower values therefore become more rigid. Over time, that values tend to fall because the samples became more fragile.

The following charts, tab. 2 and 3 show that the addition of the clay in HMSPP increases the melting temperature. Over time, the melting temperature decays due to chain scission mechanisms promoted by the weather and solar radiation.

T_{m2} (°C)				
Samples	zero	1 month	3month	6month
H1	160	161	159,5	153,4
H2	161,5	161,3	160,1	156
H3	162,8	161,5	160,3	156,1

Tab 2 : DSC - T_{m2} (°C) = Melting Point, of samples with environmental aging

X_c (%)				
Samples	zero	1 month	3month	6month
H1	46,1	45,6	42,3	45,5
H2	44,9	42,2	47,8	47,5
H3	48,2	44,1	49,2	43

Tab 3 : DSC - X_c (%) = Crystallinity, of samples with environmental aging

In tab. 3, sample H2 has become more crystalline due to effects of chain cleavage and segments crystallization in the amorphous phase. The sample H3 was more instable due to the high amount of clay dispersed without interacting with the polymer.

Studies indicated that layered silicates accelerate the photo-degradation of PP, but do not change its mechanism. Three possible explanations are considered: the adsorption of stabilizers on the silicate, the catalytic effect of ferric ions, and the decomposition of the surfactant used the modification of the silicate [10]. The SEM images on the first aging months exhibit signs of beginning degradation. With fourth month there is the formation of cracks which are clearly of degradation effect, fig. 4 and 5 in comparison with fig.3.

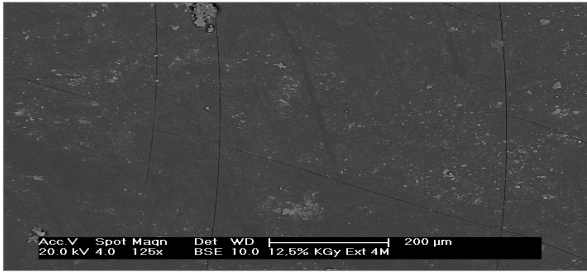


Fig.3 . SEM of HMSPP 12.5 kGy
 4 months of environmental aging

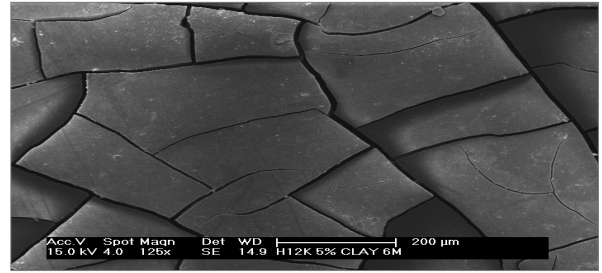


Fig.7. SEM of HMSPP + 5% Clay
 6 months of environmental aging

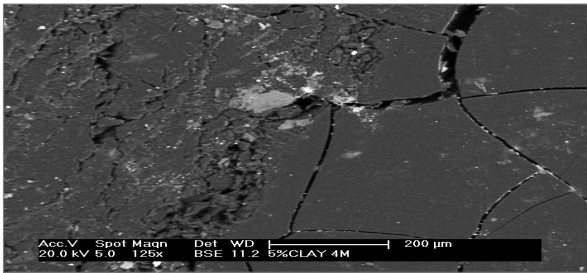


Fig. 4 . SEM of HMSPP + 5% Clay
 4 months of environmental aging

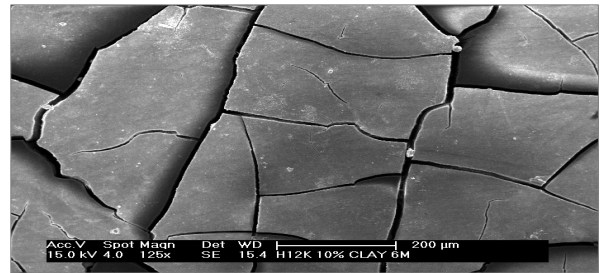


Fig. 8 . SEM of HMSPP + 10% Clay
 6 Months of environmental aging

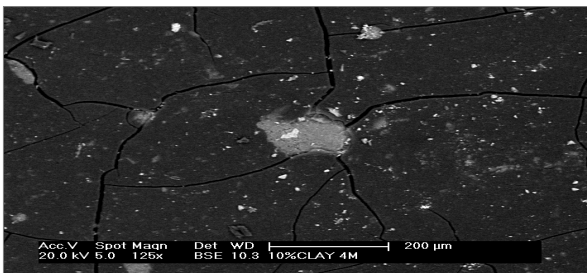


Fig.5. SEM of HMSPP+ 10% Clay
 4 months of environmental aging

The cracks became more intense in the sixth month of exposure fig. 7, in reference with aged HMSPP, fig. 6. It is also apparent that the sample with 10% clay, fig 8, reveals more intensely the presence of cracks than the others.

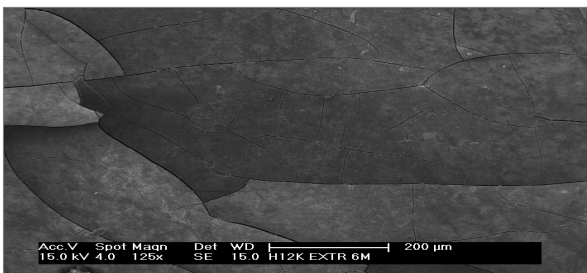


Fig. 6 . SEM of HMSPP 12.5 kGy
 6 Months of environmental aging

In the FT-IR spectra the band showed between 950 to 1150 cm^{-1} is characteristic of silica.[11, 12] The band, 1719 cm^{-1} [12], is attributed to carboxylic groups of oxidized products, that detected in the sample with 10% clay (at six months of exposure) and in the sample HMSPP 12.5 kGy at the fifth month of exposure is also attributed to carboxylic groups of oxidized species, Fig 9 to 11.

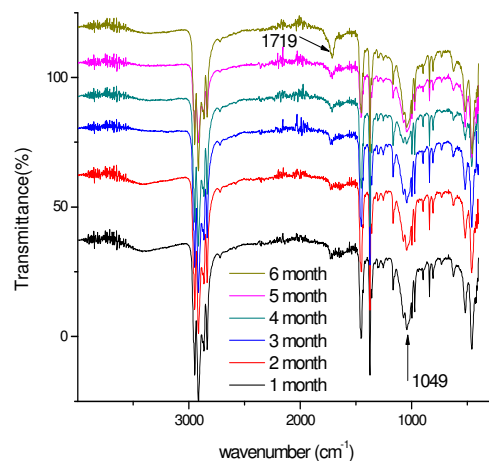


Fig. 9 . FT-IR HMSPP + 10% clay

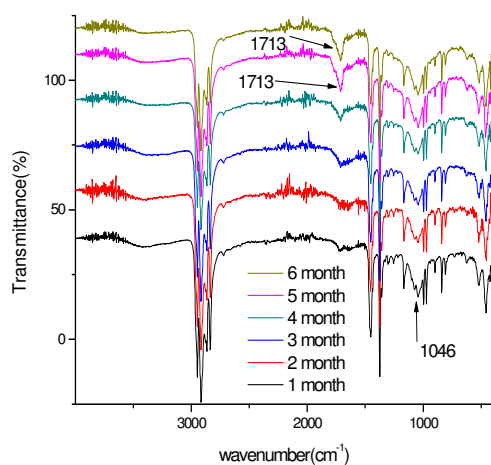


Fig. 10 . FT-IR HMSPP + 5%clay

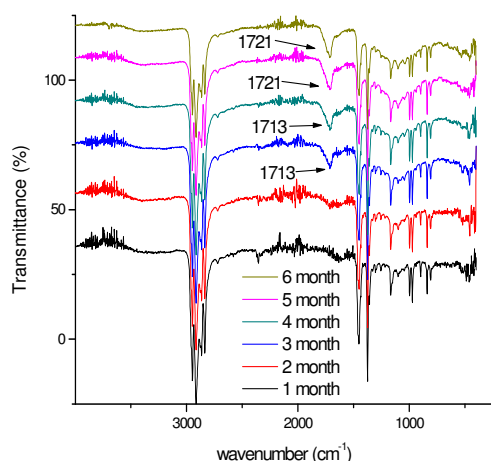


Fig. 11 . FT-IR HMSPP 12.5 kGy

4. Conclusion

The addition of clay has improved mechanical properties and thermal properties of the material. The sample with 5% of clay showed during aging, more stable than the sample with 10% clay.

Acknowledgments

The authors thank CNPQ for grant, Centre of science and Technology of Materials – CCTM/IPEN for microscopy analysis (SEM), Braskem, Chemtura, Southern Clay Products, Eleosmar Gasparim for DSC analysis, Nelson R. Bueno for extrusion of the samples and CBE for irradiation of the samples.

References

- [1] B. U. Nam, Y. Son “Evaluations of PP-g-MA and PP-g-HEMA as a compatibilizer for polypropylene/clay nanocomposites” *Polymer Bulletin* vol. 65 pp 837-847, 2010
- [2] D. Tabuani, S. Ceccia, G. Camino . “Polypropylene Nanocomposites, Study of the Influence of the Nanofiller Nature on Morphology and Material Properties” *macromol. Symp.* Vol 301, pp 114-117, 2011
- [3] S. K. Nayak, S. Mohanty, S. K. Samal “Effect of Clay Types on the Mechanical, Dynamic Mechanical and Morphological Properties of Polypropylene Nanocomposites” . *Polymer-Plastics technology an engineering*, vol 48, pp 976-988, 2009
- [4] M. Diagne, M. Guéye, A. Dasilva, A. Tidjani “Comparative Photo-Oxidation under Natural and Accelerated Conditions of Polypropylene Nacomposites Produced by Extrusion and injection Molding” *Journal of Applied Polymer Science*, vol 105 pp 3787-3793, vol 2007
- [5] S.R. Llamazares, B. L. Rivas, M. Pérez, F. P. Sarazin, A. Maldonado, C. Venegas “The Effect of Clay type and of Clay-Masterbatch Product in the Preparation of Polypropylene/Clay Nanocomposites” *Journal of Applied Polymer Science* vol 122 pp 2013-2025, 2011
- [6] L. B. Paiva; A. R. Moraes ; T. R. Guimarães . “Propriedades Mecânicas de nanocompósitos de polipropileno e montmorilonita organofílica” *Polímeros: Ciência e Tecnologia*, vol. 16 pp 136-140, 2006
- [7] W. L. Oliani, D. F. Parra, A. B. Lugao “UV stability of HMS-PP (high melt strength polypropylene) obtained by radiation process” *Radiation Physics and Chemistry* vol. 79 pp 383-387, 2010
- [8] L. G. H. Komatsu, W. L. Oliani, D. F. Parra, A. B. Lugao “Study of modified polypropylene nanocomposites by gamma irradiation with addition of Cloisite clay” INAC 2011
- [9] ASTM D 638 – 03 – *Standard test method for tensile properties of plastics.*
- [10] Z. Dominkovics, J. Hári, E. Fekete, B. Pukánsky, “Thermo-oxidative stability of polypropylene/layered silicate nanocomposites” *Polymer Degradation and Stability* vol 96 pp 581-587, 2011
- [11] A. Durmus, M. Woo, A. Kasgoz, C. W. Macosko, M. Tsapatsis . “Intercalated linear low density polyethylene (LLDPE)/clay nanocomposites prepared with oxidized polyethylene as a new type compatibilizer: Structural, mechanical and barrier properties” *European Polymer Journal*, **43**, pp.3737–3749 (2007).
- [12] C. Deshmane, Q Yuan , R. S. Perkins, R. D. K. Misra. “On striking variation in impact toughness of polyethylene-clay and polypropylene-clay nanocomposite systems: The effect of clay-polymer interaction”. *Materials Science and Engineering A*, **458**, pp.150-157 (2007).