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Environmental ageing of irradiated polypropylene/montmorillonite nanocomposites obtained in molten state

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HIGHLIGHTS

- Nanocomposites of high strength PP (HMSPP) were aged under environmental conditions.
- HMSPP/MMT nanocomposites showed carbonyl index lower than the HMSPP.
- Concentration at 0.1% of clay promoted intense crystallization of β-phase.

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ABSTRACT

Nanocomposites of High Melt Strength Polypropylene (HMSPP) were obtained in organoclay concentrations of 0.1, 5 and 10 wt% using the montmorillonite (MMT). The clay was dispersed through the melting intercalation technique using a twin-screw extruder. The dumbbell samples were manufactured and settled in device for natural ageing assay. The mechanical properties (elongation and rupture strength) were evaluated and the thermal behavior was investigated by differential scanning calorimetry (DSC). The morphology of the nanocomposites was observed by scanning electron microscopy (SEM). Nanocomposites HMSPP/MMT showed intense cracks at the surface after 3 months of environmental ageing but not as deeply as in the HMSPP. The carbonyl index (CI) was calculated using infrared spectroscopy (FT-IR) technique in which the nanocomposites showed CI values lower than the HMSPP.

1. Introduction

Investigation in polymer clay nanocomposites was pioneered by researches from Toyota and has had considerable attention in consequence of their different characteristics (Mazrouaa, 2012; Hussain et al., 2006).

Polypropylene nanocomposites (PPNC) have remarkable utility in automobile and aircraft industries, agriculture, and others. But, one major problem associated with these applications is their stability to weathering. Various chemical reactions are responsible for the material degradation including the formation of oxidation products, rearrangements of the chemical structure, crosslinking and/or chain scission (Morlat et al., 2004; Oliani et al., 2010a).

Blend of polypropylene with clays to prepare nanocomposites is a practical tool to increase flammability resistance and permeability properties. In this sense melt intercalation was used to obtain nanocomposites of PP and organoclay in the molten state (Mazrouaa, 2012; Hussain et al., 2006).

The investigations of PPNC degradation were studied in laboratory, by thermal exposition in chambers, but, without consideration of important variables such as UV radiation intensity and luminosity cycle. The environmental ageing is a way to test the photochemical resistance of polymer when these variables affect the chemical structure by degradation mechanisms (Fechine et al., 2006; Diagne et al., 2007; Oliani, 2008).

Due to this demand, diverse researches have made studies about the behavior of photooxidation and degradation in PP nanocomposites (Morlat-Therias et al., 2005a, 2005b, 2008; Silvano et al., 2013). In some cases, the studies give the same conclusion: nanocomposites degraded faster than the pristine polymer. The relative instability of nanocomposites under UV ageing could constitute a major drawback for the applications of these materials in outdoor applications (Morlat-Therias et al., 2005a, 2005b).

In the present work was used the irradiation process of polypropylene that was developed by the polymer group of IPEN. The process consists of irradiation of the polymer matrix with acetylene atmosphere in gamma source. Some chemical changes were operated such as long chain branching and crosslinking (Oliani et al., 2010b, 2012).

The PPNC obtained by molten process showed the influence of the clay concentration in the degradation process of the chemical

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structure modified. The PPNC showed lost of rupture tension under the environmental ageing, as well as, reduction of the elongation property. Important results were the low carbonyl index present by the 0.1 wt% sample among higher concentrations tested.

2. Materials and methods

The isotactic polypropylene (iPP) pellets were manufactured by Braskem and compatibilizer agent, propylene maleic anhydride graft copolymer (PP-*g*-MA) was supplied by Chemtura (Polybond 3200). The clay filler was Southern Clay Products Cloisite 20 A quaternary ammonium salt-modified (95 meq/100 g) montmorillonite clay.

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. Three different formulations containing the clay were prepared and are represented in Table 1.

The samples were prepared in molten state using a twin-screw extruder (Thermo Haake Polymer Laboratory) to incorporate the clay in the polypropylene. 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. After molding, the dumbbell samples were mounted in appropriated device for environmental ageing, Fig. 1. The period of exposition was from January 2012 to June 2012.

2.1. Melt flow index (MFI)

Ceast Italy Melt Flow Modular Line was operated at temperature of 230 °C for 10 min of total time test.

2.2. Mechanical test

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

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	0.1
NC2	HMSPP	12.5	3	5
NC3	HMSPP	12.5	3	10

2.3. 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}.

2.4. Differential scanning calorimetry

The analysis was carried out in 822 Mettler-Toledo, under nitrogen atmosphere of 50 mL min^{-1} at a heating rate of 10 °C min^{-1}, in the temperature range from −50 to 280 °C, keeping in 280 °C for 5 min; from 280 to −50 °C at a cooling rate of 10 °C min^{-1} and from −50 up to 280 °C at heating rate of 10 °C min^{-1}. About 8–12 mg of sample was placed in closed aluminum pans. The cristallinity was defined as follows:

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

where ΔH was the measured melting enthalpy and ΔH_0 was the enthalpy of fusion at 100% crystalline PP, $\Delta H_0 = 209\ J\ g^{-1}$ (Mark, 2007) and P was the content of PP in the sample.

2.5. Scanning electron microscopy

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

2.6. X-ray diffraction (DRX)

X-ray diffraction was performed in Philips X'PERT equipment from 1 to 50 angle degrees.

3. Results and discussions

The sample HMSPP showed melt flow index value of 2.8 dg × 10 min^{-1} (Oliani, 2008). The H1 (without clay), NC1, NC2 and NC3 were processed in twin-screw extruder. The H1 degraded under processing to (MFI = 6.7 dg × 10 min^{-1}). The NC1 presented MFI = 6.2 dg × 10 min^{-1} similar to H1. The NC2 and NC3 showed more shear tension due to the clay concentration and MFI = 2 and 1 dg × 10 min^{-1}, respectively.

The DSC results for the aged samples in the period of 6 months are showed in Fig. 2.

The increase of melting temperature with addition of clay in H1, Table 2, occurred in consequence of compatibilizer agent used and also for the reprocessing of the composite. With increase of

Fig. 1. Device with dumbbell samples for environmental ageing exposed outside at the polymer processing laboratory IPEN/CQMA.