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Evaluation of Surfactants Addition as Compatibilizers for Halloysite Nanotubes Filled Polypropylene Nanocomposites

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Abstract - PP nanocomposites were obtained with halloysite nanotubes (HNT) by melting blending using a twin screw extrusion. Some additives were used for obtaining good mechanical and thermal properties, such as PP-g-MA and nonionic surfactants to increase the force of adhesion between the clay and the thermoplastic matrix. Three dimensional, edge-to-edge and face-to-edge interactions between HNT occurred, which are the main reasons for the simultaneous increases in Young modulus and impact Izod of PP/HNT nanocomposites. The use of PP-g-MA increases the formation of aggregates of the HNT in the matrix. On the other hand, the use of nonionic surfactants increase the dispersion of HNT in PP matrix and showed some individual HNT in the matrix. T_m and X_c were not affected by its presence, PP-g-MA or nonionic surfactants. The use of HNT showed a slight nucleation effect in the crystallization of PP. The use of PP-g-MA reduces the mechanical and thermal properties due to the larger-sized aggregates of HNT formed in the matrix. The use of the nonionic surfactants increase Impact Izod and larger amounts of surfactants acted as plasticizer showing a slight reducing the melt temperature and HDT.

Keywords: Nanocomposites; Polypropylene; Melt intercalation; Halloysite nanotubes

INTRODUCTION

Halloysite nanotubes (HNT) is a kind of mineral aluminosilicate clay with hollow nanotubular structure mined from natural deposits. Chemically similar to kaolin, halloysite has a molecular formula of $Al_2Si_2O_5(OH)_4$-nH_2O (n=0 or 2, dehydrated or hydrated form, respectively) [1-11]. Typically it is formed by rolling the kaolin sheet in preference to tetrahedral rotation to correct misfit of the octahedral and tetrahedral sheets and can adopt a variety of morphologies, the most common one is the elongated tubes [6]. The length of HNT varies in the range of 1–15 μm with inner diameter of 10–30 nm and an outer diameter of 50–70 nm, respectively, depending on the deposits [6, 12, 13]. In addition, different from most of clays, the hydroxyls groups of HNT are located in the inner side. Thus, the combination of siloxane surface and tubular geometry render them better dispersion property compared with other layered clay such as montmorillonite and kaolinite [3, 4]. There are obvious advantages in using HNT as filler for polymer composites. First, it is ease of processing because HNT are discrete nanoparticles with no or little surface charge. Such particles may eliminate the need for intercalation and exfoliation, as required by other two-dimensional nanoclay fillers such as MMTs, when it is mixed with polymers to produce homogeneous particle dispersion [1]. HNT were also used as bioreactors, time-release capsules, catalysts of polymer degradation, templates and for high-tech ceramic applications [9]. The objective of the present study was to evaluate the influence of the use of surfactant on the morphology, thermal and mechanical properties of the PP/HNT nanocomposites. Previous studies showed that use of 3 phr of HNT resulted in better ratio of HNT/mechanical properties of all nanocomposites obtained [13].

EXPERIMENTAL

Materials

Polypropylene homopolymer with a melt flow index (MFI (230 °C/2.16 kg)) of 6 g/10 min molecular weight (Mw) of 420 kg/mol, and density 0.905 g/cc (23 °C) was obtained from Braskem S.A. Poly(propylene-graft-maleic anhydride) Polybond 3150 (PP-g-MA) with 0.5 wt% of reactive MA modifier and MFI (230 °C/2.16 kg) of 50 g/10. Irganox B215 an antioxidant from Ciba was added to PP. The halloysite nanoclay was purchased from Sigma Aldrich with surface area 64 m^2/g and density 2.53 g/cm^3. HNT were used in this study as received. Nonionic surfactant based propoxylated and ethoxylated alkylphenol purchased from Oxiteno S.A. Trade name Ultrasol TEX 5049 BE

Nanocomposites Preparation

PP nanocomposites were obtained using a twin screw co-rotating extruder Coperion ZSK18 (screw diameter of 18 L/D = 38), operating at 350 rpm with constant feed ratio of 5 kg/h and temperature profile: 165- 170- 175- 175- 180- 185- 190ºC. The amount of HNT were fixed to 3 phr and the ratio of nonionic surfactants or PP-g-MA was 0.5:1 and 2:1 (surfactant/HNT).

Characterization

Samples for testing were prepared in a Battenfeld injection molding according to ASTM D 4101. Tensile testing according ASTM D638, specimen type 1, was

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carried out on a universal tensile machine EMIC DL 10000 at speed 50 mm/min.

Izod Impact tests were carried out at 23°C using a pendulum-type impact tester (Ceast, Resilimpact), according to ASTM D 256.

Thermal behavior of nanocomposites was studied by differential scanning calorimetry (DSC) using a 2100 TA Instruments, where linear heating and cooling experiments were obtained at 10°C/min under a constant flow of nitrogen and calibrated by an indium standard. The measurements were made in the second heating and cooling cycle. The degree of crystallinity was determined using ΔH_m^o 190 J/g for PP [15,16].

The thermal stability was measured using thermo gravimetric analyzer T.A. model QA 50. The samples (10.0 ± 0.5 mg in film form) were heated from 30 to 900°C at the rate 20°C/min under an inert atmosphere of nitrogen (50 ml/min).

The transmission electron microscopy (TEM) images were obtained at 80 kV with a JEOL JEM-1200 Ex II. Ultrathin sections (70 nm thickness) of the specimens, cooled at -80 °C, were obtained by cryoultramicrotomy with a glass knife. The cuts were placed on 300 mesh Cu grids.

A TA model QA 800 instrument was used for dynamic mechanical analyses (DMA) and the measurement of heat deflection temperature (HDT) behavior of the materials at a fixed frequency of 1 Hz. DMA analyses were performed in the single cantilever mode, and the injection-molded samples were heated from -30 °C to 130 °C at a rate of 3 °C/min. The conditions for the HDT analyses were adapted from the ASTM D-648 standard, and carried out in the three point bending mode, using specimens with approached dimensions of 50.00 x 3.2 x 12.77 mm, and a force of 0.79 N. The temperature range was from 30 °C to 120 °C using a heating rate of 2 °C/min. The HDT was recorded when the sample had suffered a deflection of 0.25 mm.

RESULTS AND DISCUSSION

Morphology nanocomposites

The microstructures of PP/HNT nanocomposites with 3 phr (Fig. 1), 0,5:1 and 2:1 PP-g-MA/HNT 3 phr of HNT and 0.5:1 or 2:1 5049/HNT of 3 phr HNT loading were observed by TEM. HNT were well dispersed in the matrix and some aggregates can be seen. The individually separated HNT are found in all the samples and aggregated of HNT appear in the sample with 3phr of HNT or when used PP-g-MA. Because of the special characteristics of HNT, there is low hydroxyl density on the surfaces and the HNT can be homogenously and easily dispersed inside the PP matrix [5,7]. Fig. 1 (F) illustrates the interaction between the HNT in the PP/HNT nanocomposites. The creation of edge-to-edge and face-to-edge structures is directly related to the chemical composition of HNT. Halloysite is chemically similar to kaolinite with a dioctahedral 1:1 layered aluminosilicate and consists of two different interlayer surfaces [5]. On the other hand, the chemical composition of halloysite indicates that HNT contain Fe_2O_3 which is positioned on the inner walls of tubules [5,6]. The inner and outer surfaces of tubules are covered by hydroxyl groups and oxygen atoms, respectively [5, 6]. The charge distribution caused by Fe_2O_3, hydroxyl groups and oxygen, unusual crystal shape and non-polar characteristics of PP are the main reasons for edge-to-edge and face-to-edge interactions between HNT [5]. The use of nonionic surfactant 5049, a more separated tubes of HNT were formed (Fig. 1 (E)). Due to the sledding of the sheets promoted by the surfactant 5049 into the layers, systems with ratio 2:1 5049:HNT showed homogeneous than systems with 0,5:1 5049:HNT.

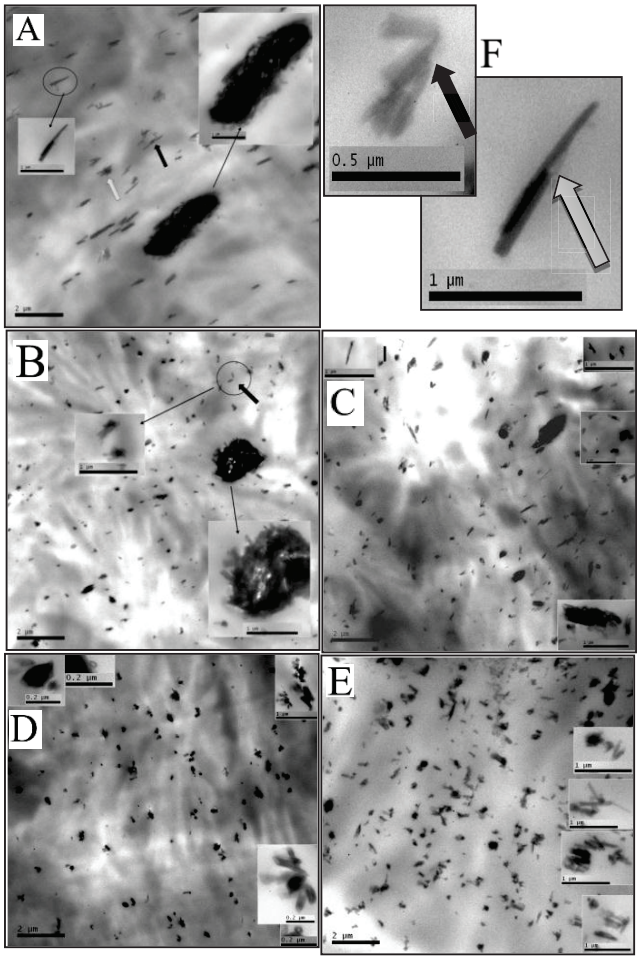

Fig. 1. TEM images of PP/HNT nanocomposites: (A) PP/HNT 3 phr; (B) 0.5:1 PP-g-MA/HNT 3 phr (C) 2:1 PP-g-MA/HNT 3 phr; (D) 0.5:1 5049/HNT 3 phr (E) 2:1 5049/HNT 3 phr. (F) Face-to-edge (black arrows) and edge-to-edge (white arrows) interactions between HNT.

Mechanical Properties

The increase in Young modulus was 28.5% the HNT content of 3 phr, Fig. 2. These results are attributed to several factors, as discussed on the morphology, good dispersion of HNT inside the PP, the edge-to-edge and face-to-edge interactions between HNT, and the three dimensional orientations of HNT inside the nanocomposites. Therefore the applied load can be easily transferred from matrix to HNT. The use of PP-g-MA or nonionic surfactant presented the values for Young modulus similar. The impact Izod values of the PP/HNT are slightly increased from 34.6 to 37.9 J/m. When PP-g-MA was used, the values of impact Izod showed a slight decrease, because formation of higher agregates of HNT, as seen in Fig. 1. Probably when PP-g-MA was used, HNT aggregates were formed, acting as tension concentrators and reducing the impact Izod. In Nan-Ying Ning's study [12], showed that the impact Izod slight increasing 11% and 26% with 1wt% and 10 wt% of the HNT content, respectively. In our study, the use of 5049 increase to 54 J/m (58% higher than neat PP). The increase value of impact Izod, is due to synergistic effect of the surfactant, which acted as a plasticizer and at the same time increased the dispersion of HNT in the PP matrix.

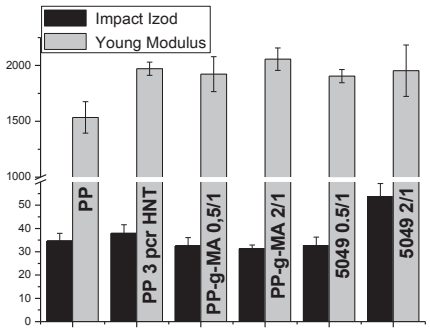

Fig. 2. Young modulus and Impact Izod of PP/HNT and modified PP/HNT nanocomposites.

Thermal Properties

The T_m, T_c and X_c results are show in Table 1. The values obtained for T_m and X_c are almost constant. The T_c value shifts to higher temperature with the presence of HNT. This result indicates the efficiency of HNT as a nuleating agent for PP crystallization. This behavior promoted changes in the crystal that may influence the reinforcement ability of the clay on the nanocomposites [13].

Table 1. DSC results for PP/HNT and modified PP/HNT nanocomposites.

Samples		T_m[a](°C)	T_c[a](°C)	X_c[b](%)
PP		170	119	62
PP 3 phr HNT		167	126	47
PP-g-MA	0.5:1 3 phr HNT	172	129	68
	2:1 3 phr HNT	165	125	55
5049	05:1 3 phr HNT	166	124	64
	2:1 3 phr HNT	164	117	65

[a] Standard deviation ± 1 °C.
[b] Standard deviation ± 10%.

The characteristic weight loss temperatures are summarized in Table 2. The data reveals that the loading of HNT show effects on the thermal stability of the nanocomposites. The addition of 3 phr of HNT increased the initial decomposition temperature at 10% and 50% weight loss compared to neat PP. Some previous investigations suggested that the barrier properties of the nanoscale fillers were responsible for the enhancement of thermal stability of nanocomposites [3, 5]. Barrier properties could include both the thermal barrier, which protects the polymer from contacting with fire, and the mass transport barrier, which slows down the escape of the volatile products during the process of degradation [3, 5]. Therefore it could be concluded that the barrier effects of HNT is not the leading factor in determining the thermal stability of PP/HNT nanocomposites. Some other investigations indicate that the iron oxides in the silicate fillers could act as flame retardant additives and lead to some radical trapping during the process of degradation, thus enhancing the thermal stability of nanocomposites [3, 5]. As reported, the degradation of PP in nitrogen is initiated primarily by the random thermal scissions of C–C chain bonds and the intermolecular transfer of hydrogen. During the initial degradation stage of PP/HNT nanocomposites, the degradation products of PP may considerably be entrapped into the lumens of HNT, resulting effective delay in mass transport and remarkably increasing thermal stability [3]. When PP-g-MA was used, the nanocomposites shows moderately improvement in thermal stability because of the formation of aggregates that deteriorate the interface between HNT and PP. However, the use of surfactant 5049 showed a little effect on the thermal stability, the similar behavior than PP occurred.

As shown in Fig. 2, the presence of ratio 2:1 of 5049 in the process caused increase in the impact strength of PP (from 34 to 54 J/m) because 5049 increased simultaneously the free volume between the polymer chains, thus reducing the thermal stability, Tm and Tg of the matrix (Table 3).

Table 2. TGA results for PP/HNT and modified PP/HNT nanocomposites

Samples		$T_{10\%}$[a](°C)	$T_{50\%}$[a](°C)
PP		375	432
3 phr HNT		458	492
PP-g-MA	0.5:1 3 phr HNT	385	443
	2:1 3 phr HNT	395	458
5049	05/1 3 HNT	376	444
	2/1 3 HNT	378	456

$T_{10\%}$ – temperature at which 10% of weight loss occurs.
$T_{50\%}$ – temperature at which 50% of weight loss occurs.
[a] Standard deviation ± 1 °C.

The behavior of the storage modulus was similar to that of the Young modulus. The β transition temperatures (Tg) of the nanocomposites were similar to the neat PP (Table 3). An exception was the system with 2:1 5049, which had a lower β transition value due to the interface adhesion between matrix and HNT, that was promoted by use of the surfactant. The addition of clay into the PP matrix caused a significant increase in the HDT from 39°C to 47°C for the individual HNT. The use of PP-g-MA increase 36% the values of HDT and the use of 5049 increase 15%.

Table 3. DMA results for PP/HNT and modified PP/HNT nanocomposites

Sample		Storage Modulus (E' 23°)	α Transition (°C)	β Transition (Tg °C)	HDT[c] (°C)
PP		1118	70	12	39
3 HNT		1571	75	12	47
PP-g-MA	0,5/1 3	1555	75	12	56
	2/1 3	1421	74	11	53
5049	05/1 3 HNT	1405	73	12	45
	2/1 3 HNT	1320	79	10	44

[c] Standard deviation ± 2 °C.

CONCLUSIONS

PP/HNT nanocomposites have been prepared by the incorporation of naturally occurring HNT.

The morphological investigations by TEM reveal that the dispersion of HNT in the PP matrix and the use of PP-g-MA, was homogenous with some aggregates of HNT.

The use of PP-g-MA increased the reinforcement ability of HNT in the PP matrix. However, the use of 5049 showed synergism effect, increasing the dispersion of the HNT and simultaneously acted as plasticizer. Thus, the nanocomposite obtained showed a gain for Young modulus without losing impact Izod and Thermal properties.

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