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Reprocessability of high impact polystyrene/clay nanocomposites in extrusion

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ABSTRACT

Plastics' recycling contributes to society with economic, social and environmental benefits. Therefore, recyclability of a material is an important environmental factor to be considered in the development of new materials, such as nanocomposites. In this study, high impact polystyrene (HIPS) and its nanocomposites with 3 and 5 wt% of Cloisite 20A were processed within four extrusion cycles in a single screw extruder having Maddock mixing section. Changes in nanostructure, in thermal, flow and mechanical properties, and in morphology of neat HIPS and its nanocomposites with reprocessing cycles were investigated. X-Ray diffractograms showed that the basal interplanar distance of clay layers increased at the first extrusion cycle, indicating the formation of nanocomposites with intercalated structure, but remained almost constant along extrusion cycles. The MEV micrographs presented improved distribution and dispersion of clay agglomerates with extrusion cycles. The melt flow index and mechanical properties showed a tendency to increase and reduce or vice-versa along extrusion cycles due to competition between crosslinking and chain scission reactions. Since the degradation mechanisms of neat HIPS and its nanocomposites were similar, the observed differences between them were related to reinforcing and barrier effect of clay, content of agglomerates, and their distribution and dispersion along extrusion cycles. A distinct mechanical behavior was observed only for 5wt% clay nanocomposite due to the high proportion of agglomerates present in this composition.

1. Introduction

The life cycle of synthetic polymers traditionally ends their disposal in landfills, which leads to energy and material waste. Nowadays, in which the availability of raw materials are scarce, environmental issues become crucial in the product development process, especially with regard to improvement in the recovery of waste material [1]. In order to enable this process, mechanical recycling has proven to be attractive and environmentally friendly because it minimizes waste and it is a low polluting process with low energy consumption and economic benefits in reusing rejected parts in the production [1].

In general, recycled materials show loss of its properties due to degradation processes occurring during processing, life cycle and mechanical recycling [2]. The amount of degradation of a recycled plastic can vary from plastic to plastic, depending on among other factors their thermal history, their chemical structure and presence of impurities.

Various studies evaluating quality [1] and reprocessability [2,4–10] of neat HIPS have been developed. They observed that degradation of HIPS start in the double bonds of polybutadiene phase and proceeds by chain scission of PS chains. They also identified that elongation at break is the most affected mechanical property during recycling of HIPS [8–10].

Recycled plastics are usually associated with poor quality materials. In order to overcome this limitation, the development of highly valued new nanocomposite, nanoproduct or blend have been tried to expand their industrial applications. In this regards,

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researchers have tried to introduce the best modifications that can compensate the loss of properties. The addition of other components to the waste polymers seems to be the simplest and easiest way for reusing the recycled polymers.

The nanofillers present more excellent feature for improvement of mechanical, thermal, electrical, superparamagnetic, fire, optical and barrier properties, when compared with neat materials and regular composites [11–16]. Factors such as the nanometric size of dispersed phase and low concentrations of such filler, usually less than 5 wt%, contribute to the increasing use and study of these materials, since it assures large contact surface area between the fillers and the polymer matrix, good dispersion by avoiding the clay aggregation, and excellent properties without increasing the density and cost or reducing the light transmission properties of base polymer [13–15,17].

Among nanofillers, montmorillonite (MMT) clay is the most used for the development of new polymeric materials that is usually prepared by melt mixing [14,17,18]. In particular, a high shear mixer or twin screw extruder has been proven to facilitate clay delamination in the molten polymers [14,19,20].

Nevertheless, possible degradation processes associated with matrix, can be enhanced by the addition of these nanofillers due to: (a) undesirable side reactions that occur due to decomposition of surfactants used to chemically modify the clay [11,20–24]; (b) presence of metals impurities in clay structure that accelerate the generation of free radicals during decomposition of hydroperoxides [17,25–27]; (c) degradation by collapsing and re-aggregation of clay tactoids into agglomerates [13,25,28,29]. Provided that any of the aforementioned processes takes place to a significant extent, it should influence the mechanical properties of the nanocomposite. On the other hand, reprocessing may help dispersion, due to the longer exposition to the shear stresses. This occurred in the case of polyolefins [30] because exfoliation and dispersion are difficult to attain.

Although degradation processes of polystyrene [3,21,22] and high impact polystyrene [20] nanocomposites have been extensively studied, as reported previously, the effect of reprocessing on dispersion and on the final properties of high impact polystyrene based nanocomposites has not been performed yet. So, the aim of this study was to investigate at which extent clay content and multiple extrusion cycles affect its properties relative to neat HIPS, in order to evaluate the subsequent use of recycled HIPS/clay nanocomposites into second market applications. Furthermore, the effectiveness in preparing high-impact polystyrene/clay nanocomposites in a single screw extruder with maddock mixer was also evaluated.

The studied variables were (a) the number of extrusion cycles (1–4), and (b) the organoclay (Cloisite 20A) content (3 and 5 wt%). Neat HIPS was also reprocessed as a reference material. Changes in the structure, morphology and properties of HIPS nanocomposites were evaluated by X-ray diffraction (XRD), scanning electron microscope coupled with energy dispersive spectrometer (SEM-EDS), melt flow index (MFI), thermogravimetric analysis (TGA) and tensile test.

2. Materials and methods

2.1. Materials

It was used high impact polystyrene, Styron 478, donated by Unigel Chemical SA with melt index of 6 g/10 min (200 °C, 5 kg). Cloisite 20A (C20A), a montmorillonite clay modified by dimethyl di(hydrogenated tallow) quaternary ammonium [26], was provided by Buntech Technologia em Insumos Ltda.

2.2. Preparation of HIPS/Cloisite 20A nanocomposites and reprocessing cycles

The neat HIPS and its nanocomposites with 3 and 5 wt% of clay were prepared by melt compounding in a single screw extruder of AX Plastics (D = 16 mm, L/D = 26, 40 rpm) with Maddock mixing section between the compression zone and the flow control zone up to four times. Temperature profile used was: 190 °C, 200 °C and 210 °C. Before each extrusion, HIPS and the clay were dried in a vacuum oven for 16 h at 50 °C. Samples were coded according to the group title: HIPS (neat), HIPS − 3% (3 wt% of C20A) and HIPS − 5% (5 wt% of C20A), followed by the cycle number, such as, E1, E2, E3 and E4 for the 1st, 2nd, 3rd and 4 th of extrusion cycle, respectively.

2.3. Preparation of sheets by compression molding

Compression molded sheets of dimensions (150 × 150 × 1) mm were prepared in a hydraulic press (capacity of 24 kgf) at 200 °C for 1 min and 30 s at about 5 kgf, followed by quenching in an ice bath. The granules of each formulation were dried in a vacuum oven at 100 °C for 2 h before molding.

2.4. X-ray diffraction (XRD)

XRD analyzes were conducted at room temperature in a Panalytical equipment, X-Pert PRO, using CuKα radiation (λ = 1.5418 Å), 40 kV voltage and 20 mA current. Neat HIPS and HIPS/Cloisite 20A nanocomposites up to four extrusion cycles and Cloisite 20A were examined in a range of 2θ between 2.0 and 10.0° at a scan speed of 0.016° s^{-1}. The basal interplanar spacing d (001) of the nanocomposites were determined by Bragg's Law, as shown below in Eq. (1):

$$n\lambda = 2d\text{sen}\theta \quad (1)$$

Where: n = integer (order of diffraction); λ = wavelength of the incident radiation; d = interplanar distance for the set of planes hkl (Miller indices) of crystalline structure; θ = angle of incidence of X-rays.

2.5. Scanning electron microscopy with X-Ray microanalysis (SEM/EDS)

Cross sections of the sheets, fractured by immersion in liquid nitrogen and covered with gold to make them conductive, were analyzed in a FEI QUANTA 3D FEG model from secondary and backscattered electrons, using a 20 kV beam. Microanalysis was also *accomplished by* using Energy Dispersive X-Ray Spectrometry (EDS), which allows the identification of all elements present in the "standardless" condition.

2.6. Melt flow index (MFI)

Melt flow index (MFI) of neat HIPS and its nanocomposites after each reprocessing cycle were determined at 200 °C using a load of 5 kg, according to the ASTM D 1238. MFI corresponds to the mass of polymer passing through a capillary at an interval of 10 min at a given applied pressure.

2.7. Tensile test

Tensile strength test was performed using a universal machine Shimadzu AG-X 10 kN model, based on the ISO standard 527- 2. Test specimens, type 5A, were prepared by laser cutting from sheets prepared by compression molding. The test speed used was