Chemical Engineering and Processing 77 (2014) 66–76

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Preparation of high-impact polystyrene nanocomposites with organoclay by melt intercalation and characterization by low-field nuclear magnetic resonance

Jorge P. Chimanowsky Junior, Igor Lopes Soares, Leandro Luetkmeyer, Maria Inês Bruno Tavares*

Instituto de Macromoléculas Professora Eloisa, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco J, Cidade Universitária, Ilha do Fundão, CP 68525, Rio de Janeiro, RJ 21945-970, Brazil

ARTICLE INFO

Article history:
Received 29 May 2013
Received in revised form 9 November 2013
Accepted 29 November 2013
Available online 18 January 2014

Keywords:
Nanostructured materials
Recycling
HIPS

ABSTRACT

Recycled high-impact polystyrene nanocomposites with organoclay were prepared. Clay of the smectite group (montmorillonite) with two types of intercalated compounds was used (Viscogel S4 and Viscogel S7). The polymer nanocomposites were prepared by melt intercalation, applying two shear intensities in a twin screw extruder. The nanostructured materials obtained were characterized by NMR relaxometry, X-ray diffraction, thermogravimetric analysis, melt flow index and mechanical analyses. The results showed that the nanostructured materials presented a mixed intercalated/exfoliated morphology. The organophilic clay, Viscogel S7, generated polymer nanocomposites with better dispersion and distribution (at low concentrations) than those produced with the Viscogel S4. The shear rate was effective for dispersion of the nanoparticles. The materials processed at 600 rpm showed better dispersion than those processed at 450 rpm. The characterization techniques chosen were effective. They were complementary and permitted comparison among the polymer nanocomposites. The use of low-field NMR relaxometry allowed measurement of the spin–lattice relaxation time of hydrogen (T_1H), which provided more precise information on the mobility of the materials, thus complementing and explaining the results obtained by X-ray diffraction.

1. Introduction

The use of polymer materials to produce consumer goods or to replace other types of materials in various industrial processes has grown considerably in the past decade. Polystyrene (PS) is a thermoplastic widely used in various industrial segments, such as packaging and household articles (cups, pens) and electronics (appliances), due to its low cost and transparency. However, PS is a rigid material, making it hard to process, due to the aromatic rings present in the polymer chain, which is also responsible for its amorphous form [22,21,29]. This characteristic means this polymer requires modifications to facilitate its processing. High-impact polystyrene (HIPS), which is a grafted copolymer of polystyrene and polybutadiene obtained by solution polymerization of styrene with 5–15% polybutadiene, is often used due to its better processability. During co-polymerization, microscopic particles of rubber are formed, which disperse in the polystyrene matrix. The presence of these rubber particles alters the mechanical properties of the polystyrene, increasing its impact resistance. HIPS is widely employed for disposable packages, refrigerator parts, electrical–electronic goods, toys, furniture accessories and shoe soles, among others [6]. Because it is an amorphous material, it does not have a defined crystalline melting temperature (T_m) and its glass transition temperature (T_g) is near 100 °C [16]. Polystyrene is very important in the furniture and civil construction sectors because it combines low cost with high processability, performance and productivity. HIPS is suitable for a range of applications that require high impact resistance, such as large and thin molded parts for general use or items with more complex shapes, as well as for parts that require excellent surface finish [29].

The continuous growth in the use of polymer materials to make products that are disposable or have short lifetimes has been attracting attention from researchers and authorities throughout the world because of the generation of solid wastes and the consequent environmental problems [10,34]. Recycling is one of the main ways to control the environmental impact caused by these wastes. However, during recycling, polymers can undergo degradation of the polymeric chain [19,12,10]. Hence, one of the greatest challenges of this process is to keep the performance of these materials at a good enough level that they can be reused in the same

* Corresponding author. Tel.: +55 21 2562 8103; fax: +55 21 2270 1317.
E-mail address: mibt@ima.ufrj.br (M.I.B. Tavares).

0255-2701/$ – see front matter © 2014 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.cep.2013.11.012

application or other economically attractive applications defined according to the new characteristics [1,7,24].

Additivation of polymers is a procedure commonly employed in industry, to rectify or minimize the negative impacts of recycling on polymers. This technique can be applied to obtain polymer or while using it to make the final product. Two factors particularly influence the quality of the additive load and must be taken into consideration: particle size and distribution. The smaller and better distributed the particles are, the more effective their action and aspect ratio will be, and the higher this last property is, the better the reinforcement properties will be. Nanoparticles have all these characteristics, making their use an innovative way to significantly improve the properties of materials, due to the nanometric scale of the particles (0.1–100 nm) [13]. Polymeric nanocomposites based on lamellar silicates have attracted a good deal of interest because of their potential industrial uses [15,26]. The addition of up to 10% clay can alter the properties of these materials due to the large surface contact area between the clay and polymer [4,3]. These modifications include improvements in flame resistance and the gas barrier and mechanical properties [11,33,20]. However, the dispersion of clay in polymers poses some challenges, because there is a preferential interaction between them that favors the formation of agglomerates. In many cases the clay needs to be organically modified to make it compatible with the polymer and allow good dispersion [2,27]. Various studies have shown that the fusion method with use of mechanical force can improve the dispersion and exfoliation degree of the clay in nanocomposites, because the clay layers are opened due to the combination of shear force and diffusion of the polymer within these layers, increasing the mobility of the polymer [8,25].

The results of mechanical dispersion depend on the processing parameters, such as the equipment components, geometry of the shear elements and rheological characteristic of the polymer. However, the chemical affinity between the polymer matrix and the clay has the greatest influence on the resulting nanocomposite's morphology [14,18].

The mechanical force applied only reduces the size of the agglomerates in case of chemical incompatibility. On the other hand, when there is good chemical affinity between the clay and polymer, the processing parameters can be adjusted to attain an exfoliated morphology of the nanocomposite. Then the clay chemical processing conditions, except for those involving the single screw extruder, can be used to form an exfoliated nanocomposite [9,18].

The objectives of this work were to prepare polymeric nanocomposites via fusion, utilizing recycled HIPS and two organophilic clays, each with a specific intercalant, and to characterize the resulting materials by different techniques that permit assessing the mechanical and rheological properties and hence the type of morphology obtained.

2. Materials and methods

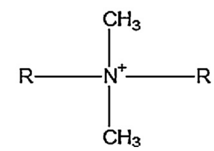
2.1. Materials

The description of the materials employed to prepare the nanocomposites are the following:

- High-impact polystyrene, supplied by the recycling firm Latasa Reciclagem.
- Viscogel S4 montmorillonite clay (Bentec)

Surfactant:

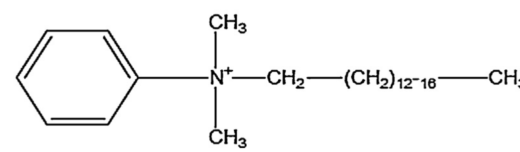
Bis(Hydrogenated Tallow Alkyl) Dimethyl Ammonium (BHTADMA)



- Viscogel S7 montmorillonite clay (Bentec)

Surfactant:

Dimethyl Benzyl Hydrogenated Tallow Ammonium (DMBHTA)



In the structure of bis(hydrogenated tallow alkyl) ammonium (BHTADMA), R represents the hydrogenated tallow groups with alkyl branches.

2.2. Methods

Fig. 1a and b presents the method used to prepare and characterize the materials. We used the powdered form of both polymer and nanocomposites for comparison of the results of the thermal analyses. For this purpose, we produced materials with the same granulometry.

2.2.1. Characterization of the HIPS

The material was donated by the recycler Latasa Reciclagem in flaked form, with three colors (green, black and white). The flakes were separated by color and analyzed by nuclear magnetic resonance in solution to determine the chemical structure and percentage of polybutadiene. Each sample was ground in a cutting mill and was also evaluated by X-ray diffraction, thermogravimetric analysis (TGA), low-field NMR and by calculating the melt flow index (MFI).

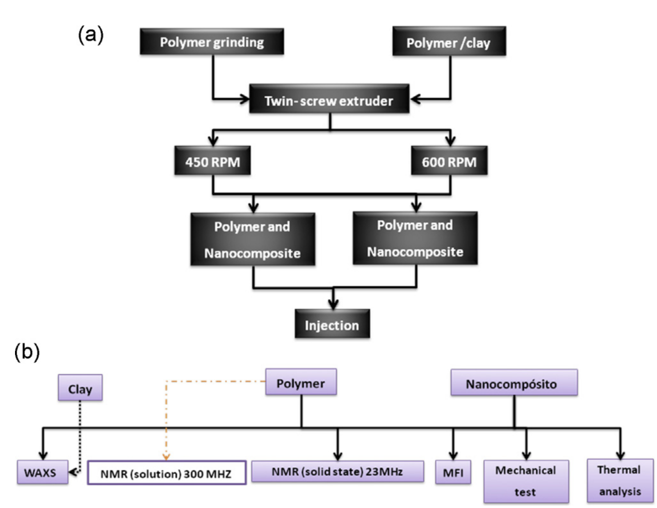


Fig. 1. (a) Method of preparation. (b) Method of characterization.