SUNTEXT REVIEWS

SunText Review of Material Science

ISSN: 2766-5100

Open Access

Review Article

Volume 2:1

Short Review on Bentonite Clays from Cubati (Brazil)

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Received date: 04 July 2021; **Accepted date:** 30 July 2021; **Published date:** 04 August 2021

Citation: Acevedo NIA, Rocha MCG, Oliveira CIR (2021). Short Review on Bentonite Clays from Cubati (Brazil). SunText Rev Mat Sci 2(1): 109.

DOI: https://doi.org/10.51737/2766-5100.2021.009

Abstract

The set of attractive properties is responsible for a wide range of applications for bentonite clays. In Brazil, around 62% of the reserves of this mineral are found in the State of Paraíba, mainly in the municipalities of Boa Vista and Cubati. There are several studies on the Boa Vista clays. However, the clay deposits in Boa Vista are running out. Therefore, it is interesting to evaluate the properties and possible applications of Cubati clays. The production of polymer/clay nanocomposites is one such application. This review aims to present some studies carried out with Cubati clays, in order to expand its field of application.

Keywords: Cubati clays; Bentonites; Nanocomposites; Organophilization

Introduction

Bentonite clays have a unique set of properties that combined with low cost and abundance, arouse great industrial interest. These minerals can be used in a wide range of applications due to their high swelling capacity and the ability to form gel in low concentrations, among others interesting features [1-6]. The development of polymeric nanocomposites is one such applications [4,7-15]. Bentonite is a 2:1 aluminosilicate, [$(Mg,Ca)O.Al_2O_3Si_5O_{10}.nH_2O$)], formed from the decomposition of volcanic ash, which in its natural form has the exchangeable cations Na^+, Mg^{2+}, Ca^{2+}, Al^{3+} and Fe^{3+} [1,16-18]. Montmorillonite is the most important mineral constituent of these minerals and is responsible by their properties [17,18]. The most important deposits of bentonite clays in Brazil (around 62%) are located in the state of Paraiba, mainly in the municipalities of Boa Vista and Cubati. The most common form of this occurrence is as a polycationic bentonite [1,19]. Although there are many studies on clays from Boa Vista, there are few works on production of nanocomposites by using clays from Cubati. Boa Vista deposits are running out. Therefore, our studies are focusing on evaluating the potential of Cubati clays [17-18]. Despite the numerous advantages associated with the use of bentonite clays in the production of nanocomposites, the natural hydrophilicity of these silicates hinders the interaction and the ability to blend them with hydrophobic polymeric matrices [1,18-20]. Therefore, an organophilization step is necessary to improve the interaction of the clay with the polymer. Different types of surfactants are often used. In this process, there is an exchange between the cations present in the clay with the cations of the surfactants [21-24]. Quaternary ammonium salts containing chains of different structures are the most widely used surfactants. The size of the alkyl chains has a significant role on the properties of the nanocomposites obtained, as the arrangement of the alkyl ammonium ions promotes different sizes of the basal spacing. Low d-spacing promotes strong interactions between the clays platelets, providing higher modulus values than those with higher basal spacing. On the other hand, high basal spacing allows the delamination of the clay layers during the production of the nanocomposites [21]. Organofilization is not enough to promote good adhesion properties between clays and hydrophobic polymeric matrices. In order to achieve nanometric dispersion of clay and a satisfactory interface, the use of compatibilizing agents is necessary. The nature and composition of the compatibilizers, as well as the processing conditions, have a significant influence on the properties of the materials obtained [19,25-34]. The most widely used compatibilizer for polypropylene/clay nanocomposites is the polypropylene grafted with maleic anhydride (PP-g-MA) [31-33]. There are many published studies on the evaluation of the effect of adding PP-g-MA on the properties of the obtained nanocomposites. The compatibilizing effect of PP-g-MA depends on its content, molecular weight and overall concentration in the polymer. The miscibility of this oligomer in the polymer has to be high in order to promote the achievement of an exfoliated or intercalated clay structure. Therefore, both the intercalation ability and the miscibility of the PP-g-MA in PP define the structure of the nanocomposite and its properties [23,25,27,28,32]. The dispersion of clay in the polymer matrix in a melt mixing process is also a function of the type of clay, the viscosity of the polymer and the operational conditions [27,31,33]. The reinforcing effect is a function of the surface contact area between clay and polymer and the interphacial adhesion. Therefore, an effective dispersion is required to increase both the aspect ratio of the clay particles and the surface contact area leading to obtaining good mechanical properties [25].

The industrial application of clays requires a complete identification of its nature and properties. Depending on the deposit from which the clay was extracted, there may be some difference in properties, even for a given clay variety. There are some published studies on the characterization and application of bentonite clays from Cubatí municipality in Brazil. Granulometric analysis by laser diffraction, wet granulometric analysis, X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermal analysis (DTA), chemical analysis by X-ray fluorescence (XRF) and cationic exchange capacity (CEC) are the most often-used characterization techniques [17,18,35,39]. The clay samples are named according to their source, such as: Campos Novos clays, specifying that these clays come from a deposit in Cubati called Campos Novos, or simply, Cubati clays. Sometimes, the samples are named after their color, such as: white, gray or green clay. These studies show that Cubati clays are polycationic bentonite clays, composed mainly of smectite, kaolinite, quartz, and the following cations: calcium (Ca), magnesium (Mn) and potassium (K) [17,35-40]. The clays from Boa Vista studied by Aranha show similar composition [41].

The growing demand for oil drilling fluids as well as the depletion of clay deposits traditionally used have generated incipient studies aiming at the use of Cubati clays in these applications [18,38,42,43]. To meet the necessary requirements, bentonite clays must perform some functions, such as acting as thixotropic, lubricant, permeability reducer and viscosity controlling agents in drilling fluids [44]. However, only the sodium bentonite clays partially meet these requirements. Therefore, the conversion of polycationic bentonites to sodium bentonites must be performed. Sodium carbonate is often used in this process. In our research group, we used sodium chloride [18] for the homoionization of the bentonite. This procedure, however, is not sufficient to obtain the required properties, as sodium bentonite is hydrophilic and is not compatible with hydrophobic oil fluids. As a result, the organofilization of clay becomes necessary. The surfactant most used in the organophilization process of Cubati clays is the quaternary ammonium salt, diesteryl dimethyl ammonium chloride [37,39,40]. This process involves the following steps: preparation of a clay/surfactant dispersion, stirring for 20 min at a given temperature, resting at room temperature for 24 h and washing and vacuum filtration. Silva et al., in a study of organofilization of two samples of Cubaty clays, respectively, gray and green clays, verified that there was an intercalation of the surfactant between the clays platelets [39]. The authors also observed that there was no effect of the following experimental variables; time of preparation of the clay/surfactant, rotor rotation used in the stirring process and resting time on the organofilization process. The ethoxylated amine surfactant TA50® was also used in the organophilization of Cubati clays [37,39]. Nonionic surfactants show greater stability and resistance to degradation than ionic surfactants. Costa et al. [38] compared the two types of surfactants and found that there was greater swelling capacity, measured by the Foster method, when the clays were organophilized with the ionic surfactant. The purification of the raw material is a very important step in the organophilization process. This step aims to eliminate or reduce the content of minerals that do not contribute to the plasticity of the clay as well as other impurities, which can interfere with the performance of the clay [23,43]. Most of the work carried out aiming at using clay in drilling fluids reports the use of hydrocyclone in the purification process. Studies aimed at applications of Cubati clays in the cosmetic area have shown promising results outlined the technological profile of the Cubati and Pedra Lavrada clays. Both clays have a low and narrow particle size range, appreciable oil adsorption capacity and good flow properties [40]. There are few studies related to the incorporation of Cubati clays in polymer composites or nanocomposites. Sales studied the effect of incorporating the variety of Cubati clay, named White clay on the properties of a thermoplastic acrylonitryle-butadiene-styrene copolymer (ABS) subjected to ionizing radiation. An acrylonitrile- styrene copolymer (SAN) was used as a compatibilizer. The clays previously activated with sodium carbonate were organophilized with the quaternary ammonium salt, cetyltrimethyl ammonium chloride (CCTMA). Initially, a masterbatch joint: SAN / 30% clay was prepared in a twin-screw extruder. After this stage, the composites were injection-molded. The ABS/clay composites showed superior values of modulus and resistance to rupture, both in tensile and in flexural stress. According to the authors, the clay particles act as barriers to the displacement of the chains. The results obtained indicated that there was a good dispersion of the clay particles and a satisfactory interaction between the clay particles and the matrix. The effects of adding the clay were more intense in the irradiated samples. The stiffness of the material increased due to the formation of crosslinks promoted by the irradiation of the polymer matrix. The impact resistance of the composites decreased with the addition of the clay, but this effect was less pronounced in the irradiated samples evaluated. Oliveira et al., the efficiency of PP graphted with maleic anhydride (PP-g-AM) as a compatibilizing agent for PP / clay nanocomposites [46]. The PP / clay nanocomposites were prepared in a twin-screw extruder. There were no significant changes in the tensile strength, nor in the Young's polypropylene modulus with the addition of the clay, even in the presence of PP-g-MA. These results indicated that there was no development of a good interface between polymer and clay. On the other hand, there was a significant increase in the elongation at break and in the toughness. This effect was attributed to the tactoids delamination after the yield point and, or a plasticizing effect of the compatibilizer on the polypropylene chains. However, a high d-spacing effect caused by the surfactant must be investigated. Rodriguez had also observed this behavior in PP composites with other Brazilian clays [47]. Calvancanti et al. prepared PP/clay nanocomposites using the Green and Gray varieties of Cubati clay. Ethylene-glycidyl methacrylate copolymer (E-GMA) was used as a compatibilizer [23]. The clays were organophilized with the non-ionic surfactant Ultramine TA50, after activation with sodium carbonate. The authors obtained two different structures. The PP/E-GMA/OGC (organophilized green clay) system presented the structure of a microcomposite, while the PP/E-MA/OGC (gray organophilized clay) gave rise to a nanocomposite with intercalated structure. According to the authors, the higher SiO_2 content allowed a greater adsorption of the compatibilizer, facilitating the intercalation of the polymer.

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