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Intercalation and Exfoliation Mechanism of Kaolinite During the Emulsion Polymerization

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Layered clays have been used as reinforcement in polymer nanocomposites by having a structure of silicate layers, cation exchange capacity, organically modified and have high aspect ratios. The aspect ratio of these layers is defined by (ratio diameter/thickness) is particularly high, with values greater than 1000. In general, nanomaterials provide reinforcing efficiency because of their high aspect ratios. Kaolin is natural clay which is the characteristic clay mineral kaolinite that have chemical composition $Al_2O_3.2SiO_2.2H_2O$ and as a 1:1 dioctahedral phyllo-silicate in nature. The distance between the silicate layers is 0.72 nm and the layer thickness is 0.437 nm. Nanocomposites that use kaolin presented excellent thermal properties, flame retardant, barrier and mechanical. Concerning the methods for polymer nanocomposites synthesis, the most employedare melt blending and in situ polymerization. In this paper, we studied the mechanism of kaolinite during the in situ emulsion polymerization toproduction of polystyrene nanocomposites filled with kaolinite. The polymer nanocomposites were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

1. Introduction

Polymer nanocomposites is a class of material where the load is at least one of their dimensions in nanometric size (1-100nm) dispersed in a polymer matrix (Kim and Palomino, 2011). The morphology of nanoparticles used in nanocomposites is shaped like nano-spheres, nanofibers, nanotubes, nanowires and layered nanomaterial (Ma and Zhang, 2014; Chiu et al., 2014;Imai, 2010; Romero-Ibarra et al., 2012). Nano-fillers widely used in polymeric nanocomposites are natural layeredclays (Villanueva et al., 2014). Among the natural layeredclays, the kaolinite stands out to be abundant in nature and chemically inert. Clays present several advantages to the preparation of nanocomposites. They are thenano-filler most abundantly available, can be easily dispersed in the majority of polymers, present high chemical intercalation ability and can be organically modified. The resulting properties of the final material can be superior to the properties of other engineering materials, such as pure polymers, microcomposites and the traditional polymeric composites(Akinci et al., 2014). Compared to polymer composites, the nanocomposites that use clays as reinforcement can show better gas and membrane barrier properties (due to the high aspect ratio of the clays), flammability and thermal resistance (due to high energy binding of clay silicates and low thermal expansion in comparison to metals and polymers) and electrical properties (due to the ability to exchange cations or transfer protons from water in the interlayer) (Paul and Robeson, 2008).

In the production of polymer nanocomposites using clays as nano-reinforcement, the compatibility polymer-clay is fundamental to achieve desired properties for the nanocomposite and a stable latex. In this sense usually the clay needs to suffer a pre-treatment before being added. This pre-treatment consists in intercalate a substance such as dimethylsulfoxide (DMSO), 6-aminohexane acid (AHA), N-methylformamide and dodecilamina (NMF-DDMNA), carboxylic acid and functionalized ammonia and ureiain the clay. The amount and kind of organic modifier can have a direct effect in the stability of the latex(Wang et al., 2010; Itagaki et al., 2001; Ammala et al., 2007; Essaway et al., 2009; Yilmaz et al., 2012).

Besides compatibility, the dispersion of the clays in the matrix is important, because, in nanometric scale, leads to a better interaction between clay and polymer. The kinds of morphologies of the clays inside the polymer matrix are: tactoid (agglomerates), intercalated (aggregated) and exfoliated (dispersed). The amount of intercalated and exfoliated clay interacting with the polymer chains is responsible for the improvement in the mechanical, thermal and barrier properties, being the exfoliated morphology the preferred because it gives the best properties. Other factors affecting the stability of the latex are the amount of clay used and the presence of polymer stabilizing agents (Yılmaz et al., 2012).

In this paper showed the intercalation/exfoliation mechanism of kaolinite during *in situ* emulsion polymerization toproduction of polystyrene nanocomposites filled with kaolinite.

2. Experimental

2.1 Reagents

The kaolinite from the State of Amazon, Brazil and processed by Armil Union Northeast mining company (located in the State of Rio Grande do Norte, Brazil). Dimethylsulfoxide (DMSO, Synth), monomer styrene (St, Sigma Aldrich) washed four times with a 10 w/v% sodium hydroxide (Fmaia), potassium persulfate (KPS, Sigma Aldrich), sodium lauryl sulfate (SLS, Fmaia), hydroquinone (Sigma Aldrich). Distilled and deionized water.

2.2 Synthesis of the nanocomposite polystyrene / kaolinite

The synthesis of polystyrene/kaolinite nanocomposites was as follows: the desired amount of modified kaolinite was added into 133.90 g of styrene, and it was dispersed by a magnetic stirrer at 20 rpm at room temperature for 2 hours, followed by sonication for 24 min, the clay dispersion plus 537.94 g of water, an aqueous solution with 3.48 g of SLS and another with 0.57 g of KPS were added into a 1l batch reactor equipped (Figure 1) with a heating jacket, mechanical stirrer, reflux condenser, and purging tube. The stirring speed and nitrogen flux in the reactor were 60 rpm and 5 l/min, respectively. The reaction time was 90 minutes. To obtain samples in powder form for further characterization, the volatile liquids were evaporated in beakers in a laminar flow cabinet, and dried in an oven at 100 °C for 4 hours.

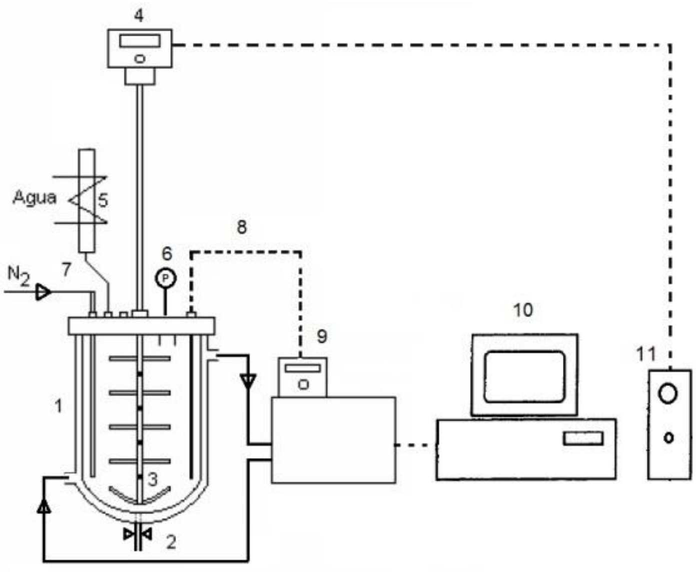


Figure 1. (1) Stainless steel reactor with heater jacket. (2) Sample collection valve bath (3/4) Stirrer, (5) Condenser, (6) Manometer, (7) Nitrogen line (g), (8) Thermocouple, (9) Thermostatic reactor bath, 10) Microcomputer with control and data capture system, (11) Agitation control.

2.3 X-ray Diffraction(XRD)

(Shimadzo, XRD 7000) with CuKα radiation k = 1.54060 Å with 2θ varying between 1.4-70º was utilized for characterization of clay and nanocomposites.

2.4 High Resolution Transmission Electronic Microscope(HRTEM)

For the present work, a High Resolution Transmission Electronic Microscope JEOL, JEM 3010 URP, Japan, equipped with a camera CCD, Gatan MSC794, was used. The images were obtained with image capturing software Gatan, Digital Micrograph. The conditions for HRTEM were 300 kV tension, spot size = 1μm and α-selector = 3, and beam current 111μA. Magnification was between 20,000-1,500,000.The powder nanocomposite samples were prepared and observed by HRTEM using an embedded method (Neto et al., 2015. In this method, the nanocomposite samples were macerated to obtain a thin and homogeneous powder, which was added and mixed into a solution of epoxy resin and catalyst. An ultramicrotome (Leica, Ultra Cutuct) was used to obtain thin sections (of around 120 nm in thickness) of cured epoxy resin containing the nanocomposite samples. The cut sections were placed on a carbon film coated copper grid of 3 mm of diameter.

2.5 Scanning Electronic Microscope (SEM)

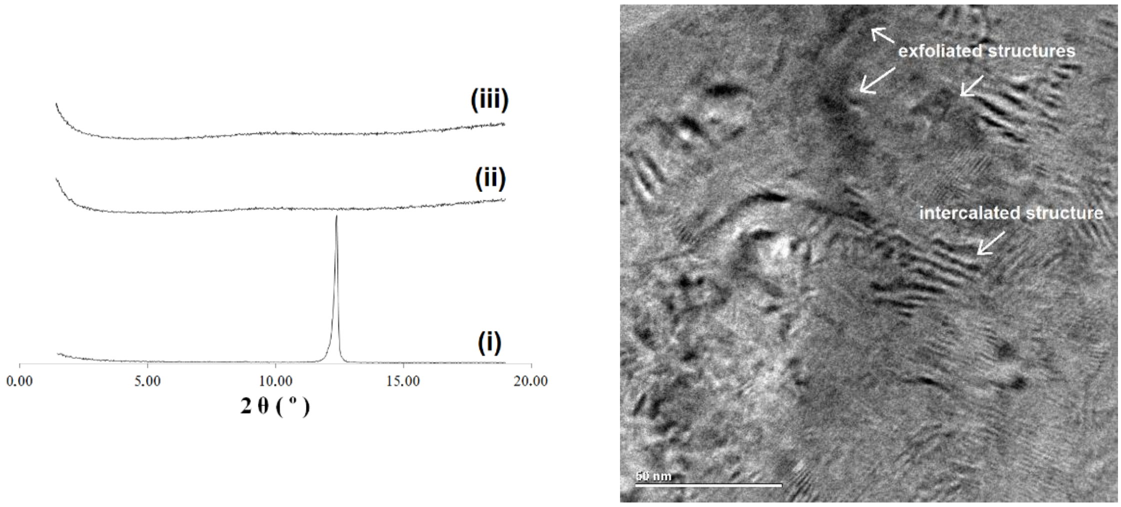
Was used the TM-3000 model by Hitachi with DPI=95.91, Pixel Size=3310.55 AcceleratingVoltage=15,000 Volt.Preparation of sample for analysis in SEM:In the preparation of the latex sample, an aqueous solution of 5 ml of water and 5ml of alcohol and 5ml of the latéx with 3% of clay was added. The mixture was added to a solution of Hand sprayer used to generate microdroplets. The microdrops were generated by the sprinkler to the sample holder. After addition of the microdroplets from the solution to the sample holder, the same was taken to a dissector for 24 hours prior to SEM analysis.

3 Results

The Figure 2a(i) shows XDR of kaolinite where it is observed the basal spacing (d_{001} = 0.72nm, 2θ = 12.33º) (14). The Figure 2a(ii) and 2a(iii) shows XDR of polystyrene and nanocomposite polystyrene/kaolinite, respectively. The XRD of the formed nanocomposites (Figure1a(iii)) illustrates the absence of any reflection pertaining to the presence of any remaining ordering of the kaolinite, this holds mainly for the layers that become exfoliated and/or intercalated within the polymer matrix (Essawy et al., 2009).

The clay, in intercalated form with ordered layers, as well as the polymer can be observed by Figure 2b. The monomer may have permeated between the layers of clay and polymerized, thus resulting in intercalation (Zhang et al., 2009).

Exfoliated clay morphologies are shown as dark lines in Figure 2b, randomly distributed, in the polymer matrix. These exfoliated structures show a total absence of order between clay layers. Even though kaolinite exfoliation is rare, due to the high cohesiveness between layers, it was possible to obtain a great amount of exfoliated clay in the polystyrene (Neto et al., 2015).



(a) (b)

Figure 2. (a) XRD patterns of (i) Kaolinite, (ii) Polystyrene, (iii) Nanocomposite. (b) HRTEM image Clay disposition in the polymer matrix (PS). Magnification of 200k.

3.1 Mechanism of intercalation and exfoliation of kaolinite during emulsion polymerization

Figures 3(i), (ii) and (iii) illustrate scheme of the emulsion polymerization mechanism of the polystyrene in the presence of the kaolinite modified with DMSO. Figure 3(i) shows, according to (Meneghetti and Qutubuddin, 2004), the drop of monomer with clay on its surface and inside the drop. The clay may have stayed on the surface of the monomer drops, making it resemble a polyhedron or pickering form (Ianchis et al., 2009; Sun et al., 2010). Due to the modification of kaolinite by DMSO, making it organophilic, the clay may have been located inside the drop of monomer during the polymerization (Meneghetti and Qutubuddin, 2004). The monomers migrate from the drop to the aqueous phase and then diffuse into the micelles and polymerize within the micelles(Lin, Di and Lin, 2009).

Figure 3(ii) shows the monomer intercalated in the clay and surrounded by surfactant with the hydrophobic part facing the clay (Lin et al., 2009;Wang et al., 2006; Meneghetti and Qutubuddin, 2002). After initiating the polymerization, the monomers that were in the water penetrate the micelles giving continuity to the polymerization as observed by Figure 3ii (Lin et al., 2009). The emulsifier was found on the kaolinite surface, making a locus of polymerization (Lin et al., 2009). According to as the polymerization reaction occurs, there is an increase in the size of the polystyrene molecule, causing the intercalation and exfoliation of the kaolinite, as observed by Figure 3iii (Lin et al., 2009; Meneghetti and Qutubuddin2004; Wang et al., 2006). After the polymerization the PS particles were found on the surface of the clay, as observed in Figure 2iii(Han et al., 2006; Liu et al., 2007; Hasegawa et al., 2003).

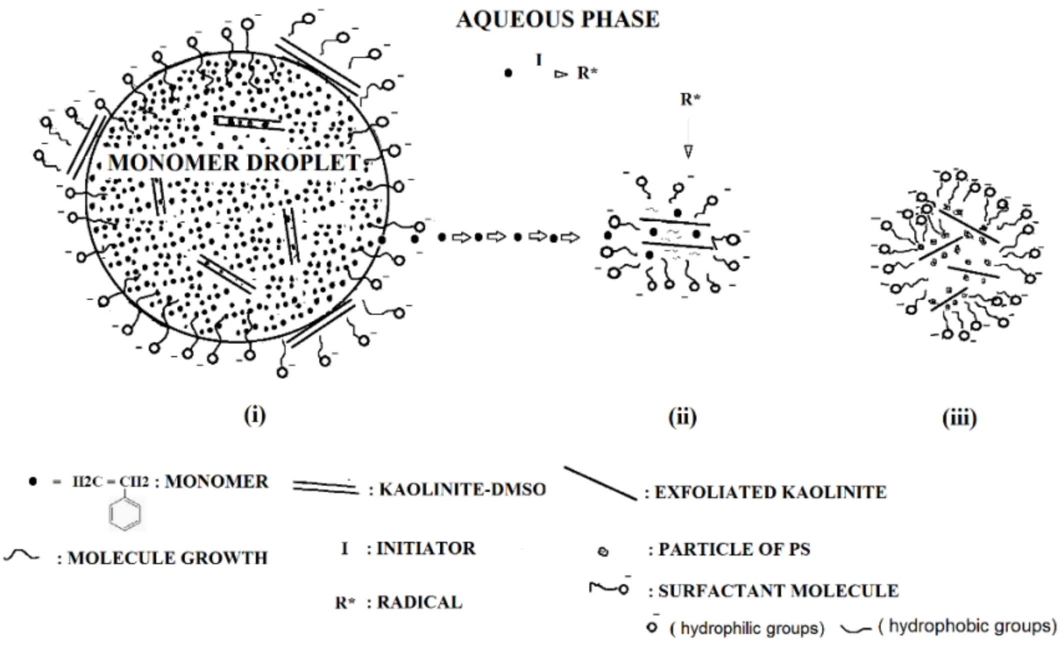


Figure 3. (i) drop of monomer with kaolinite modified on the surface and inside, (ii) Kao-DMSO intercalated with monomer. (Iii) Exfoliated Kao-DMSO layers and polymer particles on the surface of the layers.

3.2 Study of the morphology of nanocomposites by SEM

The image obtained by SEM is shown in Figure 4a and 4b. The Figure 4a illustrates the image obtained from the nanocomposite latex containing 3% Kao-DMSO. Layers kaolinite (hexagonal planar) along with precipitate latex (agglomerated forms) are observed on the surface of the layers. The images show that precipitate polystyrene particles are located on the surface of the kaolinite layers, which is in agreement (Sun et al., 2010). The chemical analysis performed by EDS-SEM shows the presence of aluminum and silicon from the kaolinite and the carbon from the polymer. The presence of gold was due to preparation of the sample for scanning microscopy. The gold film deposited in the sample improves the conduction of electrons. The Figure 4b shows the layers exfoliated with latex precipitate on the surface.

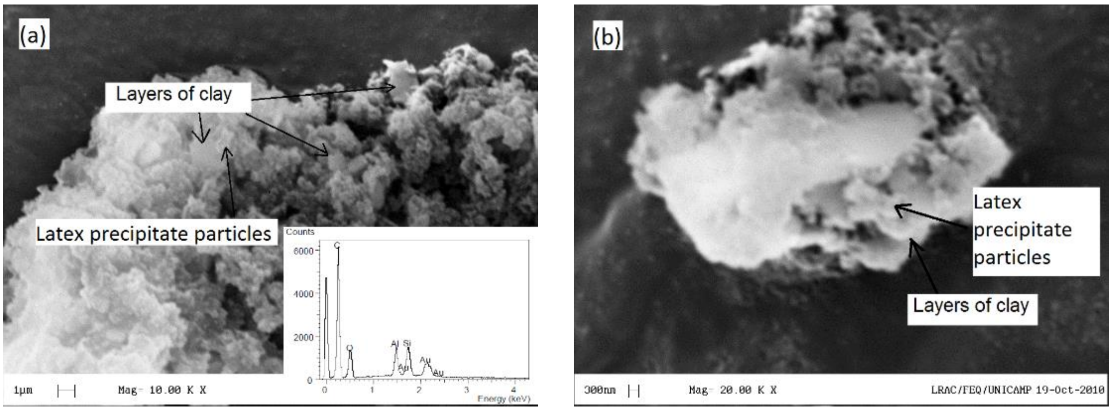


Figure 4.Latex precipitate 3% kao-DMSO-PS. (a) Magnitude: 10k and (b) Magnitude: 20k.

4. Conclusions

By means of the *in situ* polymerization technique it was possible to obtain polymer nanocomposite using kaolinite clay. The characterization by XRD and TEM showed that the layer morphology is intercalated and exfoliated. Through the study of several works it was possible to understand the mechanism of intercalation and exfoliation of the layers of the clay. The image by SEM proved the mechanism of intercalation and exfoliation of the clay layers.

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