Influence of the stirring time on the exfoliation of the Cloisite 30 B clay in PVC composite: structural characterization by XRD.

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ABSTRACT

This study aims to evaluate the influence of the stirring time on the exfoliation efficiency of the montmorillonite clay in PVC composites, prepared by the polymerization "in situ" process. The work was performed in 2 steps. In 1st. stage: tests of expansion with Cloisite 30B clay in MVC, which was used to assess the degree of expansion in MVC of each of them at different stirring times: 2, 4 and 6 h. After stirring, each system was kept in observation for 3 days to evaluate the changes in the decanted volume of the clay in the reactor. 2nd. stage: the Influence of the stirring time for the clay exfoliation. Cloisite 30B clay was used to compare the influence of the stirring time for exfoliation and characterized by X-ray diffraction (XRD).

Keywords: Organoclay, nanocomposite, XRD

Introduction

The preparation of nanocomposites with polymeric matrix is a recent high-impact area, mainly because at least one of the components is in nanometric scale. Specifically, the inorganic load, which gives to the materials some interesting properties such as: greater mechanical strength, higher thermal stability and better magnetic, optical or electric properties, due to a higher surface area structure, promoting a better dispersion in the polymeric matrix and therefore improvement of the physical properties of the composite which depend on the homogeneity of the material [1, 2]. Additionally, the preparation of nanocomposites within a polymeric matrix allows a compromise between low-cost and a high level of performance, resulting from the synergy between the components [1].

In function of the application, several types of load can be used and the difference between them is, for instance, the morphological property or properties such as the thermal resistance or chemical reactivity. The most common loads include the carbonates, the sulphates, the aluminium-silicates and the metallic oxides [3]. Between these loads, the aluminium-silicate clays are the most studied due to its technological importance in the area of high-performance materials. These loads are two-dimensional systems consisting of lamellar units with interstitial sites corresponding to their interlamellar regions, where monomers can be merged and, subsequently, polymerized by *in situ polymerization reaction.* This is mainly due to the important advantages of the lamellar silicate such as: (a) consistent lamellar structure of two layers of tetrahedrical silica, (b) galleries normally occupied by hydrated cations, and (c) property of easy ionic exchange. The host inorganic material, being inactive, without redox character, allows an easy control of the polymerization [4].

Among all the potential nanocomposite precursors, those based on clay and lamellar silicates have been the most widely investigated, probably due to the fact that the starting material (clay) can be easily found and that their intercalation chemistry have been investigated since a long time [5].

A strong interfacial interaction between the polymeric matrix and the area of the lamellar silicates is the main reason that is observed in the excellent properties of the nanocomposites formed by polymer-lamellar silicates, when compared to conventional composite [6, 7].

In this work, the emphasis is given to the process of nanocomposites (PVC/clay) preparation through “in situ” polymerization methodology. Therefore, the main objective is to study the influence of the stirring time on the exfoliation of the Cloisite 30 B clay in PVC composite by XRD characterization.

Experimental part

The clay used was Cloisite 30B montmorilonite modified with surfactant (Mt $_2$, containing EtOH), quaternary ammonium chloride and hydroxyl groups (Southern clay products, Texas/USA).

Influence of the stirring time on the Clay exfoliation

At this stage, the influence of the stirring times during the clay expansion with MVC and during the dispersion in water and other additives was studied.

Planning of experiments was carried out using Minitab, as shown in table 4, where 4 hours is considered the best agitation time, giving the best expansion of the clay.

Initially, the clay was expanded with the MVC, and then, after adding water and other additives, the composite is obtained by “in situ” polymerization process. Then the samples were analyzed via DRX, with the aim of assessing the level of clay exfoliation in the polymeric matrix.

The experimental procedure is: the clay (12 g) is added in a reactor. Then the vacuum is made and 400 g of MVC are added under pressure (4.0 $kgf.cm^{-2}$). The mixture was kept under pressure and temperature constant for a period defined in planning experiments (table 1). Then water and other additives are added and the mixture is kept under stirring conditions at constant pressure and temperature during the time defined in table 1.

After this period, the system is overheated to begin the MVC polymerization reaction.

At the end of the polymerization, the sample was collected, filtered, and after drying in fluid bed dryer, analyzed by DRX.

Table 1 – planning of experiments

Run order	10	1	9	6	8	2	3	4	5	7
Sample	1	2	3	4	5	6	7	8	9	10
Agitation (h)										
MVC + clay	2	0	0	4	4	2	2	0	0	4
H_2O + additives	1	0	2	0	2	0	2	1	0	1

Run order	11	12	13	14	15	16	17	18
Sample	11	12	13	14	15	16	17	18
Agitation (h)								
MVC + clay	0	2	2	2	4	4	4	0
H_2O + additives	1	2	1	0	0	2	1	2

Clay ratio was estimated with basis of the description of the methodology of in situ polymerization of PVC-clay nanocomposites cited by Pan *et al.*[9]. The PVC nanocomposites were prepared through the process of emulsion and the presence of nanostructures merged and exfoliated in the material for clay concentrations ranging from 2.0 and 3.5%wt. For the process of in situ polymerization via suspension, Hayan *et al.* [10] used a ratio of 2%wt modified clay and changed the grouping clay (Cloisite ® 6A, Cloisite ® 10A and Cloisite ® 30B).

Results

Figure 1 displays the Cloisite 30B clay X-ray diffratogram in the following conditions: stirring time (Clay + MVC) = 4 h; stirring time (water + additives) = 2 h. The presence of a small characteristic peak of diffraction is observed, denoting a non-embedded state [10].

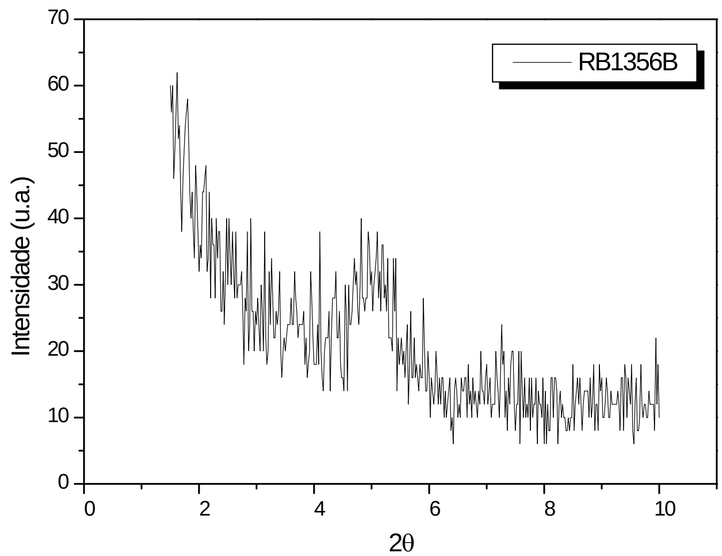

Figure 1: Cloisite 30B clay X-ray diffratogram; stirring time (Clay + MVC) = 4 h; stirring time (water + additives) = 2 h.

Figure 2 shows the Cloisite 30B X-ray diffratogram, in the following conditions: stirring time (Clay + MVC) = 4 h; stirring time (water + additives) = 4 h.

Through the Figure 2 no characteristic diffraction peaks are detectable. This indicates that the clay layers were exfoliated and dispersed in the PVC matrix at nanometric scale, as confirmed by literature [10].

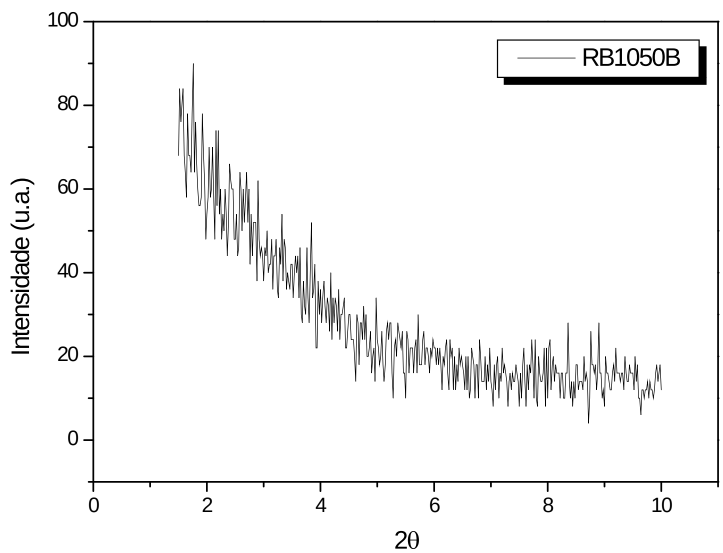

Figure 2: Cloisite 30B clay X-ray difratogram; stirring time (Clay + MVC) = 4 h; stirring time (water + additives) = 4 h.

From the results obtained, the stirring time is identified as an important parameter which evidenced a modification of the composite structure when this time is changed.

Conclusions

From XRD analyses, it was possible to identify the importance of the stirring time on the clays exfoliation in PVC array, because it promotes clay expansion, causing better dispersion in polymeric matrix.

DRX analyses indicated also the influence of the stirring time on the exfoliation of the clay under study: Cloisite 30B.

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