

Daniel Resende¹, Camila Dornelas¹, Maria I. B. Tavares¹, Lucio Cabral²,
Luis Simeoni³ and Ailton Gomes¹

PREPARATION OF MODIFIED MONTMORILLONITE WITH BENZETHONIUM AND BENZALKONIUM CHLORIDE FOR NANOCOMPOSITES PREPARATION

¹Instituto de Macromoleculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil; mibt@ima.ufrj.br

²Laboratorio de Tecnologia Industrial Farmaceutica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil

³Laboratorio de Farmacologia Molecular, Universidade de Brasí lia, Brasí lia, DF, Brazil

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Abstract. Modified clays were intercalated with benzethonium chloride and benzalkonium chloride by exchanging the sodium ions. The organoclays obtained were characterized by X-ray diffraction (XRD); thermogravimetric analysis (TGA) and low field nuclear magnetic resonance (NMR), through proton spin-lattice relaxation time measurements ($T_{1\rho}$). From the characterization data, the formation of organically modified clays was confirmed. These products can probably be used to prepare PVC nanocomposites with superior processing characteristics due to better chemical structure of clay surfactants.

Keywords: clay, montmorillonite, modifications, characterization.

1. Introduction

The polyvinyl chloride (PVC) is one of the most consumed thermoplastics in the world and it is considered as one of the most versatile plastics among the others. The great versatility of PVC is due to its properties and suitability to a variety of thermo processes. Considering that this resin is non toxic and inert, the choice of additives with such characteristics enables the production of films for packaging for foods, drugs and medical-products for hospital use [1-4].

Normally, PVC is widely used in blister with aluminum laminates for packaging drugs. A characteristic that limits the PVC processing is its instability compared to other plastics – it degrades when exposed to heat, oxygen, light, and mechanical energy [5]. Generally, PVC is not processed alone, in most of the cases it is mixed with primary and secondary plasticizers and blends with

other polymers such as polyethylene [5] and polychloroprene [6], which are normally used to improve and/or modify mechanical and thermal properties of PVC. Taking into consideration the necessity of the use of plasticizers in PVC manufacture and knowing that these compounds are hazardous to health, the development of new materials based on PVC is of paramount importance. One of such materials is PVC nanocomposite.

Composites can be defined as a material that contains two or more substances combined, producing a material with functional and structural properties different from those of individual constituents. They are heterogeneous and multiphase with a batch component (structural or reinforcement) that provides resistance for material, and another phase, which transfers this effort, named matrix or continuous phase. When the dispersed particle is in the nanometer scale, a nanocomposite material is produced [7].

Nanotechnology involves the addition of low quantity of nanoparticles [8-12]. Layered silicates have been widely used as a nanoparticle in obtaining polymeric nanocomposites. Clays like montmorillonite, mica, hectorite, and saponite are the most commonly used filler material for polymers due to their unique characteristics of intercalation and exfoliation [8].

Generally, the use of inorganic materials does not provide proper interaction with organophilic polymers because of inadequate dispersion and adhesion. The changes of surface are commonly used to make the interaction much better between the surfaces of clay with the polymeric matrix. The exchange of sodium and calcium ions present in the clay lamellar space by alkylammonium is one of the alternatives used to modify the hydrophilic characteristic between lamellae to hydrophobic. It also

reduces physical and electrostatic interactions in interlayer space, facilitating the polymer chain intercalations between the lamellae, forming nanocomposites, with nanostructure that can be intercalated and/or exfoliated [9-15].

The preparation of PVC nanocomposites using modified commercial clay with octadecylamine is done to increase their mechanical and barrier properties. However, these clays do not have proper thermal stability or acceptable dispersion of clay in the PVC matrix. Therefore, taking into account problems with PVC stability due to its degradability facility [16-17], this work deals with the clays modification to prepare organoclays with surfactants that will permit to obtain PVC nanocomposites with higher degree of thermal stability.

According to the exposition done before, the focus of this work was to modify organically the homoionic clay with the two types of surfactants – benzalkonium and benzethonium chloride – to obtain organophylic clays with intercalated surfactants that will probably make PVC nanocomposites more thermal stable.

2. Experimental

2.1. Nanomaterials Preparation

The nanoparticles preparation was by solution mode. The amino surfactant was solved in the chosen solvent and after that it was added the sodium clay solution. Both effects of reaction time and solvent nature were evaluated. After the products were obtained by filtration, the precipitate obtained was dried for a few days in an oven with circulating air and then pulverized.

The modified clays were prepared with the ratio of approximately 3:1 (w/w) of silicate : surfactant, by solution. The surfactant value was based on an excess of 20 % of the CEC clay. Reactions were performed at room temperature, varying with the reaction time in a range of 1 to 24 hours.

2.2. Characterization

These nanoparticles were characterized by X-ray diffraction, low field NMR and thermogravimetric analysis (TGA). The techniques of X-ray diffraction (XRD) and TGA have been extensively used for characterization of nanoparticles and nanomaterials. The nanocomposites and nanomaterials can be detected by X-ray diffraction, observing the changes in the interlayer clay distance.

One of the new techniques that can be used to observe the formation of nanoparticles is low field NMR, which permits to detect their formation and homogeneity.

2.2.1. X-ray diffraction (XRD)

The samples were analyzed using an X-ray diffractometer, XRD 6000, Shimadzu, with nickel-filtered

CuK α ($\alpha = 1.54$ E) radiation operated at 40 KV and 30 mA. The data were recorded at 2 θ rates from 2 to 20° at 2° per minute. The basal spacing of nanomaterial was calculated using the Bragg's [9] equation: $\alpha = 2d\sin\theta$.

2.2.2. Low field NMR

Low field NMR MARAN ultra 23 spectrometer, operating at 23 MHz (for protons), and equipped with an 18 mm variable temperature probe, was used for the determination of relaxation measurements. Proton spin-lattice relaxation times (T_{1H}) were determined directly by the traditional inversion recovery pulse sequence ($180^\circ - \tau - 90^\circ$) the 90° pulse of $4.6\mu s$ was calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty τ data points, ranging from 0.1 to 5000 ms, with 4 scans for each point and 5s of recycle delay. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the program WINFIT. Distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using the software WINDXP. All measurements were done thrice.

2.2.3. Thermogravimetric analysis (TGA)

The samples were analyzed in nitrogen flow, with a flow rate of 50ml/min with heating rate of 293 K/min for 323 K until 1023 K. Results are shown as a curve Thermogravimetric (TG), which records the variations in weight depending on the temperature.

3. Results and Discussion

3.1. X-ray Diffraction Analysis (XRD)

From the X-ray diffractograms showed in Figs. 1 and 2 it was observed that the reaction times to obtain an intercalation of the clay with benzethonium (BZT) and benzalkonium (BZK) chloride varied from 1 to 4 h. After 24 h no significant change in the clay basal distance was detected due to the maximum capacity of clay exchange.

The basal spacing observed for different reaction times with benzethonium and benzalkonium clay is presented in Tables 1 and 2.

Table 1
Basal spacing values for organophylic clay prepared with benzethonium chloride

Reaction time, h	2 Theta value, θ	Basal spacing, \AA
Sodium Clay	6.55	13.5
1	3.75	23.6
2	3.65	24.2
4	3.75	23.6
24	3.75	23.6

XRD - BENZETONIUM CLAY

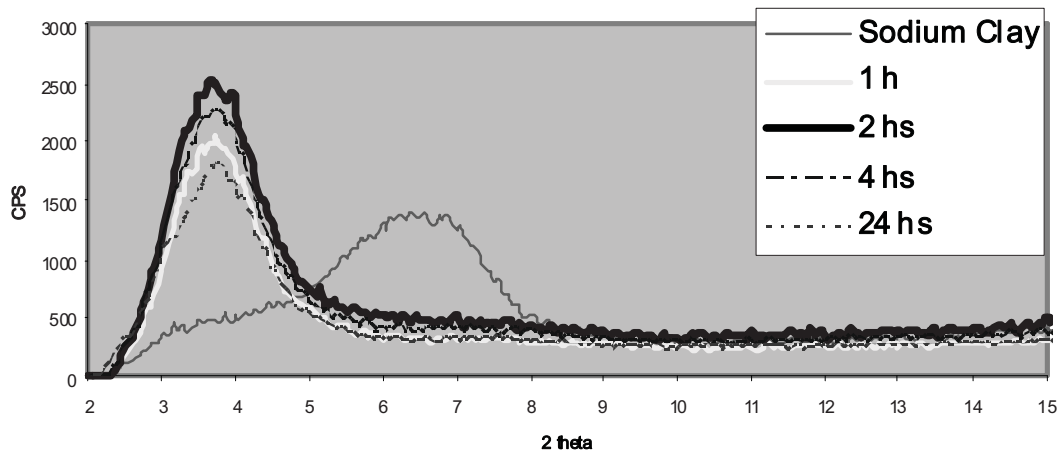


Fig. 1. Modification of sodium clay with benzethonium chloride

XRD - BENZALCONIUM CLAY

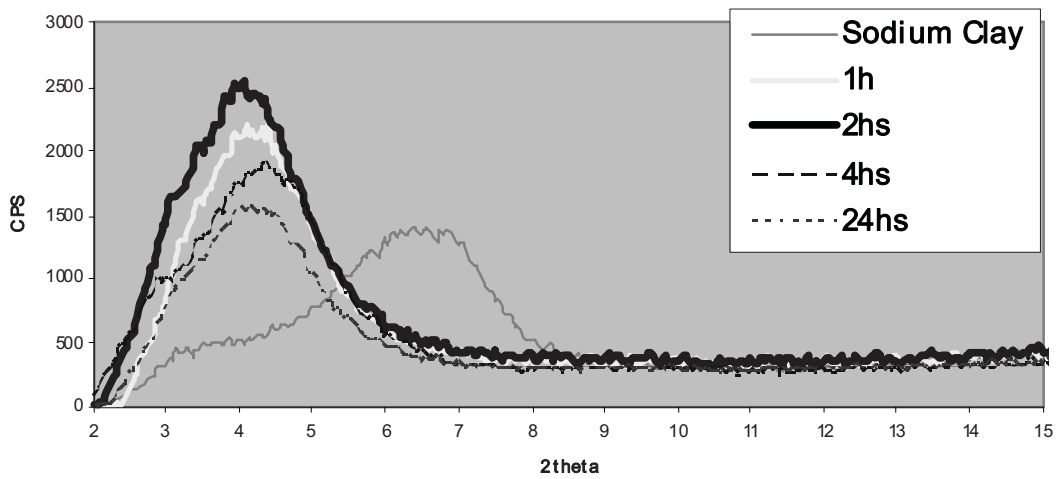


Fig. 2. Modification of sodium clay with benzalkonium chloride

Table 2

Basal spacing values for organophylic clay prepared with benzalkonium chloride

Reaction time, h	2 Theta value, θ	Basal spacing, Å
Sodium Clay	6.55	13.5
1	4.10	21.6
2	4.00	22.1
4	4.35	20.3
24	4.15	21.3

3.2. Thermogravimetric Analysis (TGA)

Analyzing the TGA data, it was discovered that the onset temperature values are higher than those measured for PVC processed, which is lower than 453 K. Fig. 3 shows the TGA curves for two modified clays. The clay modified with benzethonium appeared to be more stable and hence it seems to be more interesting for PVC.

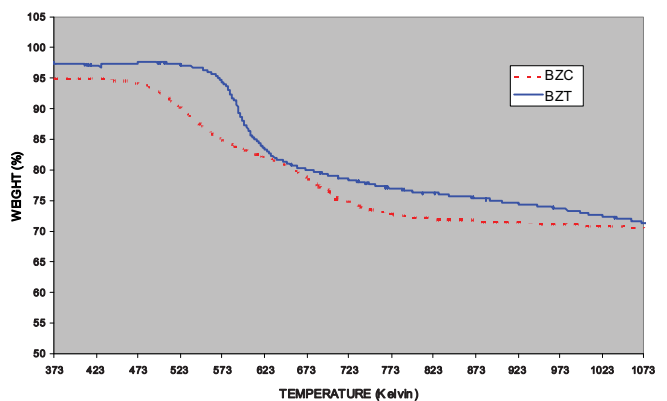


Fig. 3. Onset of clay modified with benzethonium chloride (a) and with benzalkonium chloride (b); reaction time is 2 h

3.3. Low-field NMR Analysis

Table 3 shows the low-field NMR data obtained for the raw materials and Table 4 the relaxation measurements for the modified clays prepared.

Table 3

T_1H values of the raw materials determined by the low-field NMR

Raw material	T_1H for the raw materials, ms			
	0.01	0.5	14	----
Sodium clay	0.01	0.5	14	----
BZT	----	2	----	111
BZK	----	16	55	----

Table 4

T_1H values of modified clays determined by low-field NMR

Modified clay (reaction time)	T_1H , ms Domains		
	0.6	52	199
BZT (1h)	0.6	52	199
BZT (2h)	0.5	14	----
BZT (4h)	0.6	---	115
BZK (1h)	0.4	54	
BZK (2h)	0.5	20	---
BZK (4h)	0.5	18	160

From low-field NMR data no evident differences in relaxation values (0.50 ms) for both sodium clay and after clay modification was observed. This result showed that the process of clay modification was appropriate, since the absence of other domains and a predominance of a single domain confirms the homogeneity of the nanoparticle formed.

4. Conclusions

The low-field NMR relaxation data has appeared to be a powerful clays modification tool. From XRD diffraction it was observed that both agents presented sufficient intercalation in 1 or 2 h of reaction and from TGA the benzethonium surfactant is more stable.

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ПРИГОТУВАННЯ МОНТМОРИЛОНІТУ МОДИФІКОВАНОГО ХЛОРИДОМ БЕНЗЕТОНІЮ ТА БЕНЗАЛКОНІЮ ДЛЯ ОДЕРЖАННЯ НАНОКОМПЗИТІВ

Анотація. Реакцією обміну між йонами натрію та хлоридами бензетонію та бензалконію модифіковано глини. Одержані органоглини охарактеризовано з використанням рентгенодифракційного і термогравиметричного аналізу та в низькій області ЯМР. Показано, що одержані продукти можна використовувати для приготування полівінілхлоридних композицій з покращеними характеристиками завдяки кращій хімічній структурі поверхнево-активних речовин глини.

Ключові слова: глина, монтморилоніт, модифікація, характеристика.