

Elaboration and X-Ray Diffraction Techniques Characterization of clay-PEG 6000 Nanocomposites with clay Matrix

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Abstract

The aim of this experimental study is the elaboration of a low cost nanocomposite based on a natural clay (marl) and ecological polymer, in order to valorize the physical properties of the marls. Such a new nanocomposite is made of a clay matrix with inclusion of Polyethylene Glycol 6000 (PEG 6000), as reinforcement agent. We are focused on the study of the physical properties of the elaborated material. The use of X-Rays Diffraction (XRD) techniques enables us to measure an important parameter, which is the inter-sheet distance, d_{001} , for each crystalline phases (Kaolinite and Illite) that are present in the clay, for various PEG 6000 percentages.

Keywords: Clay matrix, Poly(ethylene Glycol) 6000, Intercalation, X-ray Diffraction characterization, Dry/grinding mixing, Humid mixing, Polytron device

1. Introduction

The exploration of the nanoclay doping has known, in the last decades, a very large interest, because of the deeper effect that the nanometer modifications can give to the corresponding matrix, compared to a macroscopic modification [1]. Nowadays, the surface modifications of the clays have become increasingly important, because it can be used to prepare the polymer/clay nanocomposites and applied in some new applications, such as adsorbents of the organic pollutants in soil, water and air, rheological control agents, paints and medicine [2].

In some previous work [3], one has studied some (macroscopic) physical properties of a clay-PEG 6000 composite elaborated by dry grinding method; and now, we develop some protocols to obtain the nanometric modification within the clay (nanoclay) matrix.

The feature here is that, the used clay (mostly hydrophilic) is not purified and it is not a commercial one. Our goal is to elaborate a low cost and ecological nanocomposite by the classical method and raw materials, in order to propose a new product for the construction industry. PEG 6000 is known for its pharmaceutical and cosmetically use. So, it is considered as ecological, biodegradable and thermal stable polymer [4]; that is why we were used it during all our experiments. PEG is a nonionic and water-soluble polymer with many applications, due to its flocculent,

thickening, sustained-release, dispersing and water-retention properties [5].

The main purpose of this paper is to discuss the elaboration of a new nanocomposite of a clay matrix with interaction of PEG 6000. The latter is introduced in order to reinforce the host matrix. This is why we adopt three different elaboration methods with six PEG 6000 percentages, in order to evaluate the effect of each method and also the effect of the reinforcement (PEG) on the clay matrix.

So, to evaluate the intercalation of the polymer within the inter-sheet spaces (nanocomposite construction), we have used X-Ray Diffraction analysis, which can inform us on the evolution of the inter-sheet distance for each elaborated sample. Collecting all these informations, we were able to measure the incidence of the inputs on the elaboration of new nanocomposites.

The same Design of Experiment will permit us, in future works, to estimate the evolution of the macroscopic behavior and the properties of new materials, as mechanical and geotechnical characteristics. This paper is organized as follows. The achieved experimentation protocol and discussion of the obtained results are the aim Section II. Some concluding remarks are drawn in the last section.

2. Experimental protocol and discussion of results

We adopted three elaboration methods, in order to produce our materials, dry processing, humid processing

Table 1: Input parameters of the composite/nanocomposite elaboration

Protocol	Input values						
	Polytron device		Simple dry grinding			Humid mixing	
PEG 6000 quantity (g/6g clay)	0	0.2	0.3	0.4	0.5	0.6	0.7 (for some essays)
Clay size	Constant						

and using a *polytron* device, for several PEG 6000 percentages.

In the next paragraph, we will present the plan of the used experiments and details of the elaboration protocols (methods).

2.1 Experiments plan

In Table 1, we present the experiments plan that was used to study the nanocomposite elaboration possibilities.

2.1.1. Process methods

a) Dry method

As pointed out in some previous paper [3], such a method consists in a simple grinding with three different sizes and several PEG 6000 percentage, in order to estimate the effect of each parameter on the studied physical properties, according to the mentioned paper.

b) Humid method

This method consists in the preparation of the composite (clay, PEG 6000) by mixing in deionized water, according to the following protocol :

- At fixed quantity in deionized water, we introduce slowly the clay powder at concentration 6g per 100ml of water. The mixing duration is about 6 hours in an ambient condition of temperature and speed using the standard magnetic bars.
- After 6 hours, we add the souhaitable percentage of PEG 6000. The mixing duration is about 48 hours.

Up to now, the protocol corresponds to the process protocol definition [5].

For the drying process, we modify a little that protocol described in Ref. [5] by three major modifications:

- accelerating the drying process using the centrifugation at 1500rpm for liquid (water) and solid (clay-PEG 6000) separation,
- the stove is used to evaporate the water quantity, which is still confined in the inter-sheets spaces (swelling),
- grinding is after used to obtain the souhaitable clay sizes to homogenize the propeties of the composites

and have a significant comparison of the processing methods.

c) Polytron device

This device permets to achieve very important speeds (about 30000rpm), in order to have a maximum of dispersion of the elements introduced on it. It can be used in biotechnology and in our domain [6]. In our case, we adopted 15000rpm as first essay, with 15mn as rotation duration.

The principal behind this technique is the increasng of the entropy of the system {water, clay, polymer}, in order to reach a certain level of nanoclay sheets separation (exfoliation) to enforce the introduction of the PEG 6000 chains, which are water soluble, into space between adjacent sheets (intercalation), obtaining so the intercalation of the polymer in the inter-sheets spaces.

2.1.2. XRD characterization

The classical way for the evaluation of the intercaltion of the polymer into the nanoclay sheets and also for the measurement of the inter-sheets spaces (according to Bragg formula (1) [7]), is XRD.

XRD anaysis at nanometrical scale informs on the eventual evolutions within samples presenting a minimum of cristallin phases.

We used an X'Pert PRO device from PANalytical using copper anticathod with a wave length of 1.54Å and a step size of 0.016°, where the samples are pouder type of the material we made, grinded on sizes according to our plan of experiments (constant for this study).

For more efficiency, we have overlayed XRD spectra to visualize the evolution of the graphs, according to the adopted parameters (PEG 6000 percentages and clay sizes), and we obtained the results we will describe in the following sections.

a) XRD analysis of the row material

According to Ref. [3], XRD spectrum of the row material (0% on PEG 6000) is done in Figure 1. The picks correspond to Kaolinite, Illite (mica), Quartz and Calcium Carbonate as major and apparent crystalline components.

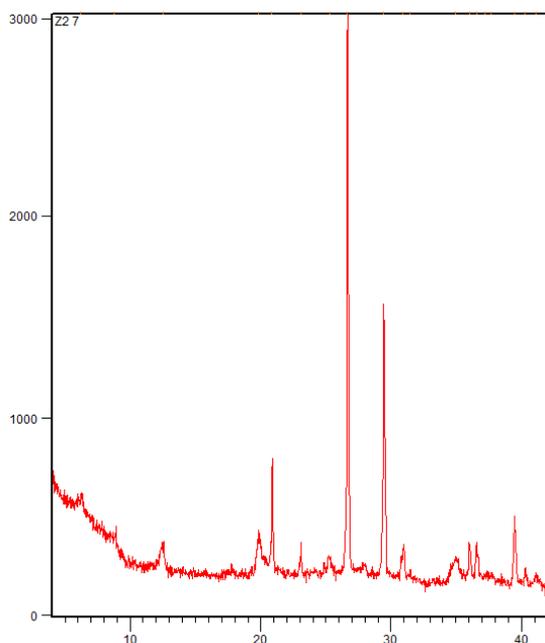


Figure 1: XRD spectrum of row clay materials

The results of XRD analysis are given in Table 2 describing the mineral that is present in the natural clay.

Table 2: XRD Results of the row clay material. We have used the abbreviations: M, for Mica (Illite), K, for Kaolinite, Q, for Quartz, and Ca, for Calcite.

Position [°2Th.]	Height [cts]	d-spacing (Å)	Mineral
8.7994	91.49	10.04950	M(001)
12.3466	26.07	7.16314	K(001)
19.8561	168.83	4.47149	K+M(02)
20.9208	528.89	4.24628	Q
23.1269	135.38	3.84598	Ca
25.3796	107.06	3.50948	K(002)
26.6980	2882.88	3.33909	Q+M
29.4753	1809.38	3.03049	Ca
31.4364	22.32	2.84577	Ca
34.9526	112.28	2.56713	M
36.0552	213.06	2.49111	Ca
36.5993	161.67	2.45532	M(131)
39.5140	437.35	2.28066	Q+Ca
40.3274	61.54	2.23652	Q

We note that, in this section, we fixed the clay size on one value in order to evaluate at first the effect of PEG 6000 percentage.

b) XRD Analysis Polytron method

As we said above, we have overlaid the XRD spectra for all elaboration methods.

Figure 2 presents seven spectra related to seven adopted PEG 6000 percentages or concentrations: from 0g to 0.6g of PEG 6000 per 6g of clay.

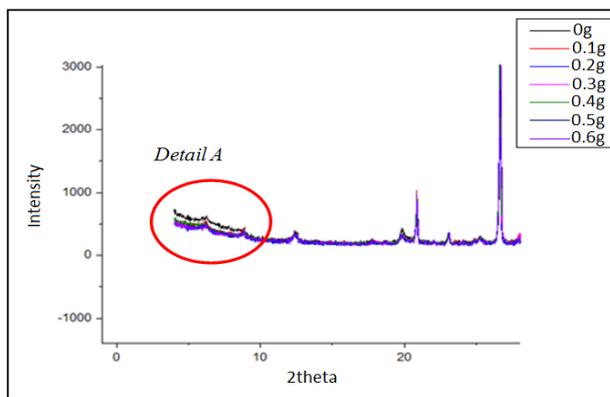


Figure 2: XRD spectra of polytron samples relatively to seven PEG 6000 percentages (from 0g per 6g of clay to 0.6g per 6g per clay).

For a best interpretation, we enlarged the scale of some parts of the above spectra that appear to be interesting. The importance information we can extract is related to the variation of the position of the peaks. The intensity and position '2θ' are the two parameters, related to the position, which permit to judge the success of the intercalation of a substance (eg. PEG 6000) into another (our clay composed of mica or Illite 001 (2θ = 8.7994°) and Kaolinite 001 (2θ = 12.3466°). Also, such a technique can be used for the exfoliation experiments of the nanoclay sheets into polymer matrices [8,9].

So, we have enlarged the scale of some parts in Figure 2 that are related to the position 2θ = 12.3466° of Kaolinite 001, and to the position 2θ = 8.7994° of Illite 00, according to Refs. [10] and [11], and we obtain Figure 3.

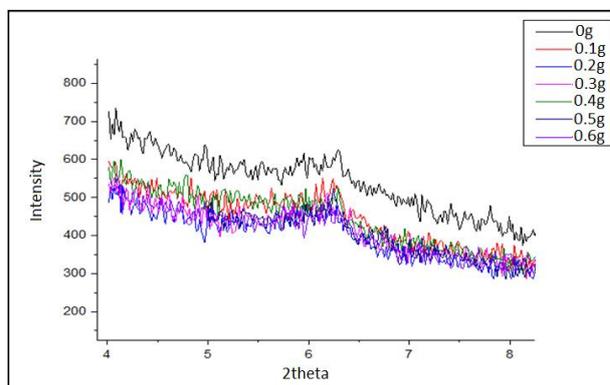


Figure 3 Part A of Figure 2.

We remark that, XRD spectrum of the row material (0% of polymer), drawn in black color, presents the highest values of intensity compared with all the samples where the clay is mixed to PEG 6000. In other words, the inserting of PEG 6000 causes the decreasing of the peaks intensity values of the XRD spectrum.

Starting from the same figure, we can observe that there is a kind of regroupment of spectra, depending on the value of PEG 6000 percentage:

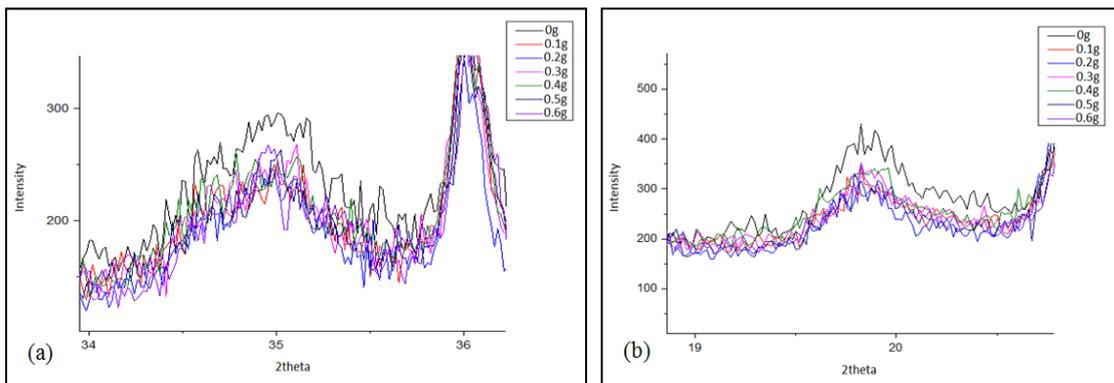


Figure 4: Other details: (a) Around $2\theta = 35^\circ$, and (b) around $2\theta = 20^\circ$ (see Table 1)

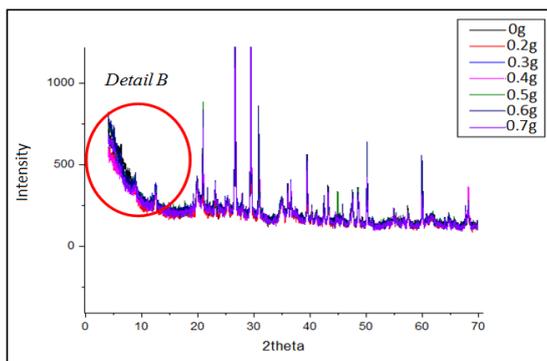


Figure 5: XRD spectra for dry method samples relatively to seven PEG 6000 percentages (from 0g per 6g of clay to 0.6g per 6g per clay)

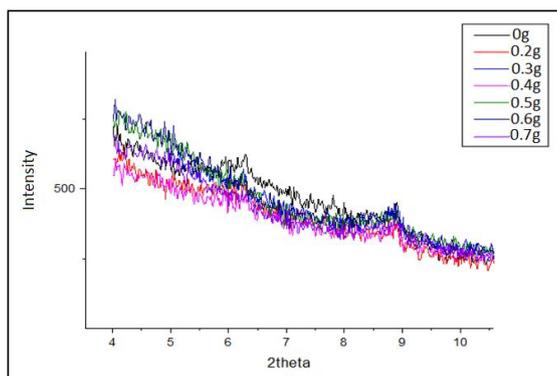


Figure 6: Detail B of Figure 5

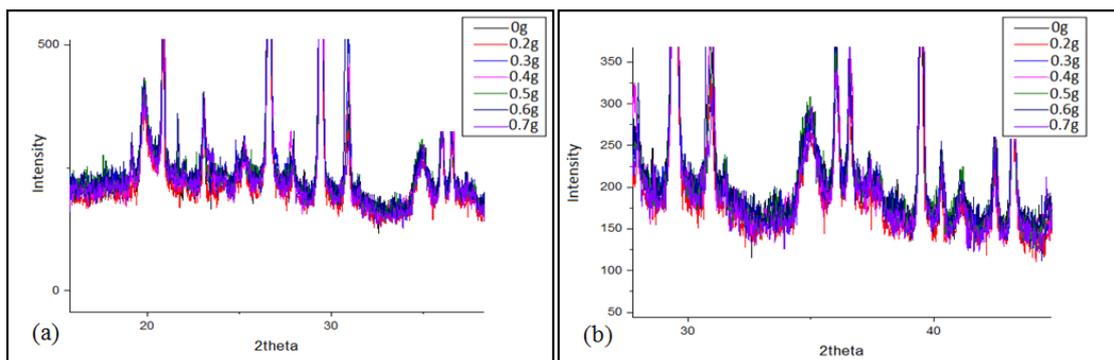


Figure 7: Other details: (a) In the interval $[20^\circ, 30^\circ]$ (a), and (b) in the interval $[30^\circ, 40^\circ]$

- group 1: 0g (row material in black) per 6g of clay.
- group 2: 0.1g (red) and 0.4g (green) per 6g of clay.
- group 3: 0.2g (blue), 0.3g (pink), 0.5g (dark blue) and 0.6g (purple) per 6g of clay.

The same phenomenon produces in other intervals of the angle 2θ , as shown in Figures 4(a) and 4(b).

c) XRD Analysis for dry grinding method

Also, for the dry grinding samples, XRD information allows the evaluation of the effect of PEG 6000 introduced into the clay matrix. We obtain the following graphs:

For a better description, we have tried to zoom on some areas that appear to be interesting, presenting roughly some gaps between spectra, as in the 2θ -interval $[4^\circ, 10^\circ]$ (detail B of Figure 5). We remark that, approximately, there is no difference between the seven signals, and then, the spectra are almost the same.

We also searched in other areas if there is any difference between the samples by zooming, for example, on the graphs in the 2θ intervals $[20^\circ, 30^\circ]$ and $[30^\circ, 40^\circ]$ (Figures 7(a) and 7(b)).

In conclusion, no considerable (nanometric) modification has been denoted about the effect of PEG 6000, according to the dry method.

In the next paragraphs, we will see the effect of humid mixing method on the intercalation of PEG 6000 into the inter-sheet spacing.

d) XRD analysis for humid mixing method

Figure 8 presents the overlaying of the spectra with several PEG 6000 percentages.

As we made in the previous XRD analysis, we focused on some interesting regions (Figures 9 and 10).

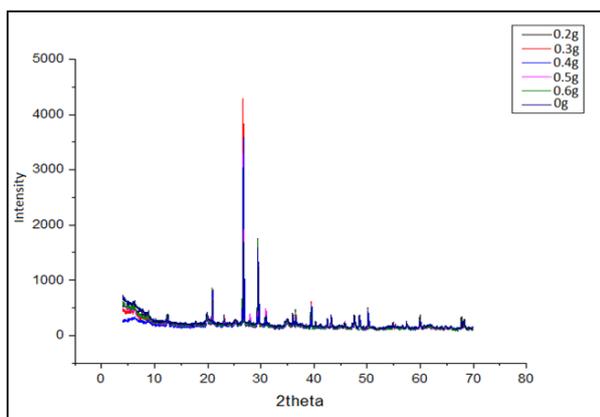


Figure 8: XRD spectra for humid mixing method samples, for seven PEG 6000 percentages (from 0g per 6g of clay to 0.6g per 6g per clay).

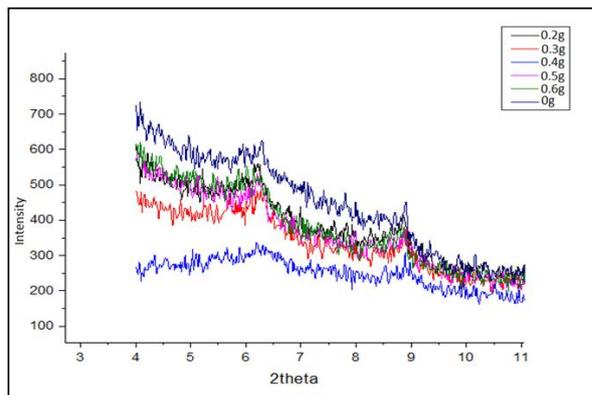


Figure 9: Zoom in the interval around $2\theta = 8^\circ$

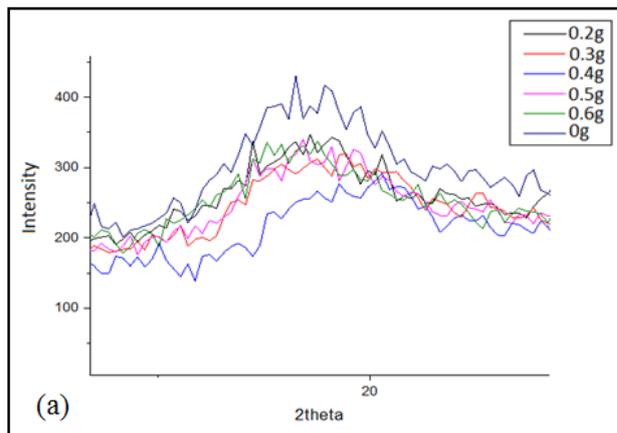
The shift between the intensity signals is clear in comparison with the two other methods (dry and polytron). Also, we can see, as mentioned for the polytron method, that the spectra are grouped, depending on the quantity of the added polymer (percentage).

XRD intensity of the row material (dark blue) is distinctly superior to those relatively to the other samples. By adding PEG 6000, the signal is diminished. Such a signal corresponds to a certain behavior, depending on the physics (thermodynamics [12]) of the nanometric transformations, that we will try to explain in the next sections.

At a first view, we can say that this diminution is caused by an additional X-ray absorption or dissipation in the amorphous phase that is PEG 6000, in our case, which could be intercalated into the clay nanosheets.

Moreover, it clearly appears that XRD spectra are grouped as follows:

- group 1: row material (dark blue)
- group 2: 0.2g (black), 0.5g (green) and 0.6g (pink) per 6g of clay,
- group 3: 0.3g per 6g of clay,
- group 4: 0.4g per 6g of clay.



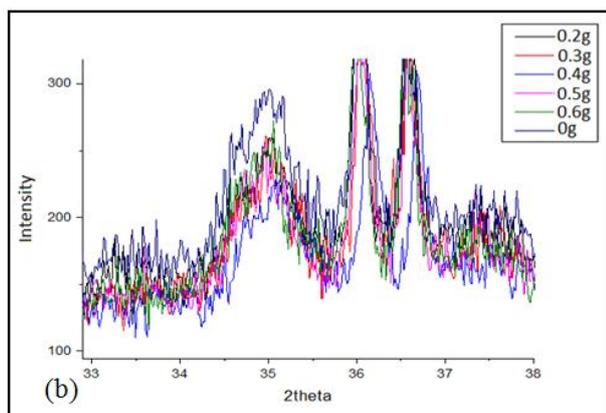


Figure 10: Zoom on the areas corresponding to 2θ around (a) 20° , and (b) around 35° .

Figure 10 shows almost the same configuration (groups) of XRD spectra of Figure 9.

2.1.3. Discussion: Comparison between the three methods

By this analysis, we want to study the influence of the elaboration methods on the intercalation of the adopted polymer that is PEG 6000 into the nanoclay layers.

For this, in the next sections, we will make several analysis by fixing one parameter and varying the other (polymer percentage and elaboration method). Also, we will see the influence on the basal distance 001 of each of the Kaolinite and Illite which compose the clay.

a) XRD analysis (effect of the method on the 0.4g PEG 6000 per 6g of clay)

In this paragraph, we study the influence of the method on the nanometric behavior of our marls, after the introduction of PEG 6000. So, we have fixed the percentage of PEG 6000 at the value 0.4g/6g clay, and plot the corresponding spectra of the three methods on the same graphs.

We note that, the quantity 0.4g is chosen, because of its important effect on the samples (XRD obtained by humid method). But the same analysis could be done for other specific rates if necessary.

Figures 12(a) and 12(b) show some zooms on zones around $2\theta = 8.7994^\circ$ (Illite 001) and around $2\theta = 12.3466^\circ$.

We remark that, it is the humid mixing method that gives more significant evolution, where the resulting XRD intensity is the most diminished, in comparison with the dry grinding and polytron methods.

For the dry method and polytron technique, compared with the XRD spectrum of the row material (black line), a little modification has occurred around the Illite, as shown in Figure 12(a), where the spectra of the two methods are merged a little bit under the spectrum of the row material.

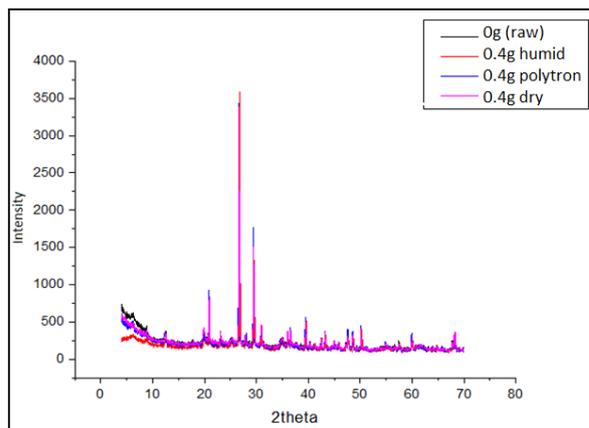


Figure 11: XRD spectra at 0.4g PEG 6000 / 6g clay for the three methods samples (dry grinding, humid mixing, polytron) and the row material (black line).

For the Kaolinite (Figure 12(b)), it is clear that no modification has been detected where the three spectra are merged (row material, dry grinding method and polytron technique).

The relative diminution of XRD spectrum, in the case of the humid mixing method, related to the other methods, means that the absorption or the additional dispersion of X-ray radiations were important. That proves that the quantity of PEG 6000 integrated within the nanoclay inter-sheets, was more important, and then, it causes the reduction of XRD signal intensity.

b) Basal distance d_{001} of Kaolinite and Illite

We have plotted the evolution of the basal distance of Illite at $2\theta = 8.7994^\circ$, and that of Kaolinite at $2\theta = 12.3466^\circ$, according to the elaboration methods, where the clay size is fixed, as we said above.

Figure 13 shows the evolution of the inter-sheet (basal) distance d_{001} of Kaolinite.

We remark that, for the dry grinding method, the distance d_{001} does not follow a significant evolution; it fluctuates around a middle value corresponding to the initial distance d_{001} of the row material inter-sheet spacing.

The Polytron technique, on the other hand, permits a very little increasing of the distance that is not too significant.

On the other side, for the two clay types, Kaolinite and Illite, we can see that the evolution of distance d_{001} corresponding to the humid mixing method, is intensified around PEG 6000 percentage of 0.4g per 6g of clay. The distance clearly decreases at this value, but it increases rather for higher percentages.

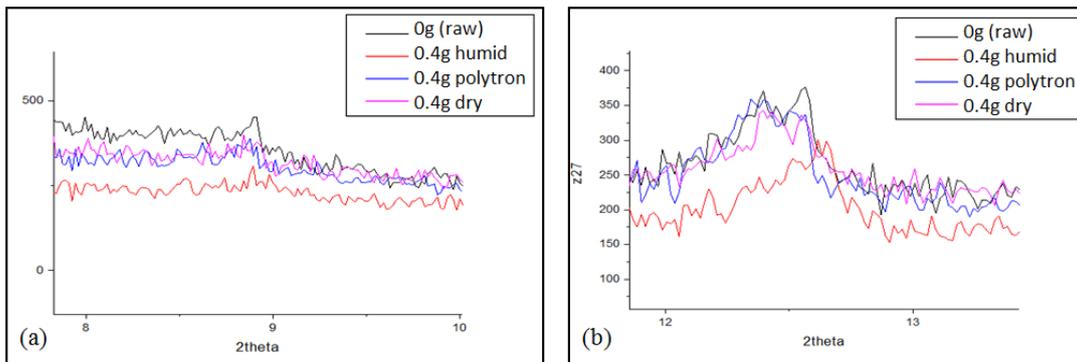


Figure 12: Zoom on the areas corresponding to (a) 2θ around 8.5° (Illite 001) and (b) 12.5° (Kaolinite 001)

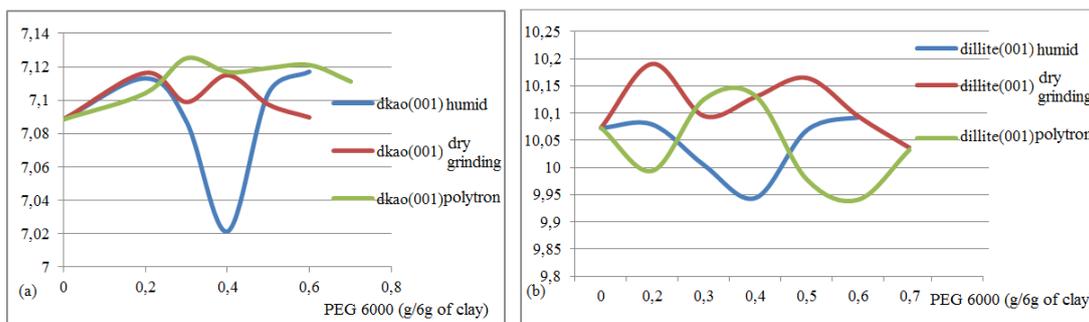


Figure 13: Basal distance d(001) of (a) Kaolinite, and (b) of Illite, according to the three methods.

2.2. Result and discussion

2.2.1. Thermodynamical interpretation

The intercalation of a polymer in the silicates was thermodynamically explained by Giannelis [10], according to which a nanocomposite could be formed if the Gibbs enthalpy G , during the formation process is negative. The Gibbs enthalpy variation is defined by: $\Delta G = \Delta H - T\Delta S$, where ΔH is the enthalpy variation, which expresses the intermolecular interactions, and ΔS is the variation of entropy, associated with the configuration variations of the system.

Starting from the above relation, Giannelis proved that the entropy loss at the separation of some parties of the polymer within the nanoclay sheets is approximately compensated by an entropy gain due to the increasing of the formation freedom of the organic molecules intercalated, which are liberated on the stage of the intercalation.

Consequently, the Gibbs enthalpy determines whether the intercalation takes place or not. Hence, we can interpret the enthalpy by the existence of the interactions between the polymer and the nanoclay sheets.

So, the intercalation ($\Delta G < 0$) is determined according to the nature of the forces that exist in the neighborhood of what we can call the effective molecule:

- Repulsive force between the excluded volume of the nanoclay layers (positive energy),

- Low van der Waals attraction (negative energy),
- Depletion forces due to the intercalation of the polymer in between the nanoclay layers (positive energy).

2.2.2. Critical value of polymer percentage and variation of the inter-sheet spacing

Denote by φ , the PEG 6000 percentage, and by d , the inter-sheet distance (basal distance d001) after intercalation.

There exists a critical percentage of PEG 6000, φ^* , such that:

- $\varphi < \varphi^*$: In this case, the inter-sheet distance d decreases, since the excluded volume forces are dominated by the attractive van der Waals ones. In this regime, the depletion force has no effect.
- $\varphi > \varphi^*$: For this case, the inter-sheet distance d rather increases, due to the excluded volume and depletion forces that dominate the attractive van der Waals ones.

In our case, we can observe that the critical value of the polymer percentage φ^* is equal to 0.4g per 6g of clay.

2.2.3. Repeatability of the humid mixing protocol and results validation

After studying the effect of the elaboration methods on the nanometric modifications of the clay structure, by XRD analysis, we saw that the used humid mixing protocol

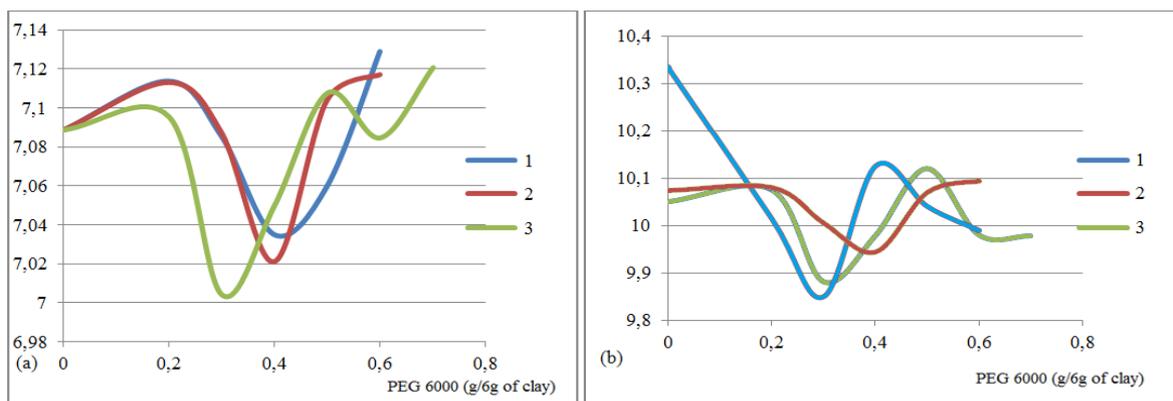


Figure 14: Basal distance evolution of three different samples (Kaolinite and Illite)

presented above, is the most influent elaboration method compared with the two others.

Moreover, Figure 13 shows that the critical value of the intercalation is clearly $0.4g$ of PEG 6000 per $6g$ of clay. Thus, we made two other experiments in order to obtain the so-called repeatability of the humid mixing protocol, obtaining so three different experimentations. Figure 14 plots the evolution of the inter-sheet distance d_{001} for Kaolinite (a) and Illite (b). From this figure, we can see that the critical distance is situated around $0.3g$ and $0.4g$ of PEG 6000 per $6g$ of clay. So, the repeatability of the protocol is ensured, because it permits us to obtain almost the same results for the three independent essays.

Conclusion and perspectives

We recall that the aim of this works is the elaboration of low-cost and ecological nanocomposites of clay matrix and polymer (PEG 6000) reinforcement for civil engineering uses.

We discussed three different elaboration methods which give typical modifications of the physico-chemical properties, from a macroscopic point of view. But, we focused on the nanometric variations, due to their strong effect on the macroscopic properties.

By XDR analysis, we were able to estimate the effect of each elaboration parameter. Hence, the results could be expressed by the choice of the optimal elaboration method, which is the humid mixing and the determination of the critical polymer quantity (between $0.3g$ and $0.4g$ per $6g$ of clay), above which we could have the strongest effect of the intercalation.

As perspectives, we project to elaborate further quantities of the considered nanocomposite, in order to estimate the effect of all kinds of parameters on its physical and mechanical properties, which are the polymer percentage, the clay size and other curing parameters (time, temperature...) of the modified clay.

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