



Research paper

Preparation and characterization of soy lecithin-modified bentonites

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ABSTRACT

In this work, a study of exchange of soy lecithin, a natural product, in bentonite was performed in order to synthesize bio-organoclays. The effects of initial amount of modifier and reaction time were studied at a fixed reaction temperature. Organoclays thus obtained were characterized by means of X-ray diffraction (XRD) analysis, X-ray fluorescence spectrometry (XRF), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and water absorption tests. An effective intercalation of soy lecithin between the clay layers was obtained. The ionic exchange reaction was completed at short times whereas variations in the initial amount of modifier produced organoclays with different final properties. At low ratios of soy lecithin to bentonite, a slight increment in basal spacing of organoclays was observed due to intercalation of the organic modifier between the clay layers and a significant diminution on water absorption was achieved. When the organic content increased, the inter-layer spacing increased but thermal stability of organoclays decreased compared to the samples with low organic content, whereas the water absorption was not affected. The obtained bio-organoclays are potential environmental-friendly fillers for the development of clay/biopolymer nanocomposites.

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1. Introduction

Clays have been used for the last 30 years as nanometric fillers to reinforce polymeric matrices (Fornes et al., 2001; Hedley et al., 2007) with the aim of improving specific properties, mainly thermal, barrier, impact and mechanical, for an important number of applications (Limpanart et al., 2005; Roelofs and Berben, 2006; Xie et al., 2002). Bentonite (Bent) is one of the most commonly used clays in polymer nanocomposites technology due to its low cost and natural abundance (Bergaya et al., 2012). Montmorillonite, a clay mineral of the smectite group, is the primary component of Bent and determines its defining properties, such as high specific surface area and swelling capability (Bergaya et al., 2011). It is composed of layers of about 1 nm which are held apart mainly by electrostatic forces. Each layer is characterized by a 2:1 structure with a central octahedral sheet of alumina which is attached to two external tetrahedral sheets of silica (Alexandre and Dubois, 2000; Mandalia and Bergaya, 2006; Picard et al., 2007). The net negative charge of the layers, which is generated due to isomorphous substitutions of Al^{+3} with Fe^{+2} or Mg^{+2} in the octahedral sites and of Si^{+4} with Al^{+3} in the tetrahedral sites, is compensated by the presence of cations, mainly as Na^{+} and Ca^{+2} , situated in the interlayer space (Bergaya et al., 2011).

It is known that in the pristine state, Bent is compatible only with hydrophilic polymers, such as poly(vinyl alcohol) (Ollier et al., 2013). However, a large number of polymeric matrices are hydrophobic. In

those cases, in order to increase chemical compatibility between both components, and then, improve the dispersion of Bent inside the polymer matrix, it is necessary to modify one of them (Čapková et al., 2006; Pavlidou and Papaspyrides, 2008). Generally, this can be accomplished by the appropriate conversion of these hydrophilic clays in organophilic ones, via ion exchange reactions (Picard et al., 2007; Xi et al., 2007; Xie et al., 2002). Modified clays prepared by cation exchange with long-chain quaternary alkylammonium or phosphonium salts have been widely studied and the resulting organoclays have been used in the preparation of clay/polymer-nanocomposites, mainly for industrial applications (Ruiz-Hitzky and Van Meerbeek, 2006). Nevertheless, the application of these clays in biological fields is limited by the toxicity and poor biocompatibility presented by these kinds of modifiers (Wicklein et al., 2010). However, during the last years, the application of organoclays has been extended to these fields including drug delivery systems (Dong and Feng, 2005; Lin et al., 2002; Park et al., 2008; Zheng et al., 2007), excipient and active substances in pharmaceutical products (Lee et al., 2005; Wang et al., 2008), antithrombogenic materials (Zhou et al., 2009), immobilization host for biological species like enzymes, amino acids, proteins, nucleic acids and phospholipids (Mallakpour and Dinari, 2012, 2013; Nagy et al., 2013; Ruiz-Hitzky and Van Meerbeek, 2006; Songurtekin et al., 2013; Wicklein et al., 2011; Yu et al., 2013).

Moreover, phospholipids have been scientifically studied since the 1700's and became commercially available as lecithin in the 1930's (Szuhaj, 2003). They have a basic structure of a diacylglycerol backbone with a phosphate ester on the α or third carbon of the glycerol molecule (Szuhaj, 2003). Usually, another compound is attached that

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characterizes the phospholipid. The main commercial source of lecithin today is the soya bean, but phospholipids can be found in all living cells as part of the cellular membranes. The International Lecithin and Phospholipid Society defines lecithin as “a complex mixture of glycerophospholipids obtained from animal, vegetable or microbial sources, containing varying amounts of substances such as triglycerides, fatty acids, glycolipids, sterols, and sphingophospholipids” (Szuhaj, 2003). However, the composition of lecithins and their phospholipids will vary depending on their source. Vegetable lecithins are high in phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, and phosphatidic acid, but very low in phosphatidylserine and sphingomyelin (Macrae et al., 1993; Szuhaj, 2003). Phosphatidylethanolamine and phosphatidylcholine are neutral, zwitterionic phospholipids with an amphiphilic character. These possess a net positive charge at pH lower than the isoelectric point (Nagy et al., 2013), which allows the cationic ion exchange with clays and, on the other hand, the presence of the hydrophobic chains allow interactions via Van der Waals forces with the other components of soy lecithin. For these reasons, soy lecithin (SL) could act as a natural bio-surfactant and environment-friendly bio-modifier that can be used for the preparation of organoclays. Thus, the resulting bio-organoclays are potential reinforcements of biodegradable polymers for the development of bio-nanocomposites applicable to cosmetic, biomedical and food industry, among other fields. In the specific case of melt compounding and injection molding of thermoplastic polymer nanocomposites at high processing temperatures, it is important to know the thermal stability of the clay to avoid its thermal degradation during the processing of the material. When the organoclay is degraded during processing, the compatibility with the polymer matrix, as well as the final performance of the nanocomposite are affected (Ludueña et al., 2013).

In this work, Bent was modified via cation exchange reactions with SL and the effect of reaction time and the initial amount of SL on the modification of Bent were analyzed. The effectiveness of each modification was discussed in the light of the characterization results by X-ray diffraction analysis (XRD), X-ray fluorescence spectrometry (XRF), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and water absorption tests. In order to choose the most potential organoclays for the preparation of clay/polymer nanocomposites, the organic content, the degree of hydrophobicity, the interlayer space and the degradation temperature of the organoclays were studied. These parameters will determine the type of polymer to be employed and also the processing conditions (or processing window).

2. Experimental

2.1. Materials

The clay employed in this work was a bentonite supplied by Minarmco S.A. (Neuquén, Argentina); it was used as received. The cation exchange capacity (CEC) of bentonite, measured by the methylene blue method, was found to be 105 meq/100 g clay. Granular soy lecithin was obtained from Melar S.A. (Buenos Aires, Argentina).

2.2. Modification of bentonite with soy lecithin

A 4 g sample of Bent was dispersed in 100 ml of distilled water and the adequate content of aqueous solution of SL, acidified with hydrochloric acid (pH = 1), was added in order to obtain samples with g SL/g bent = 0.25, 0.50, 0.75, 1.00 and 1.20. The dispersion was kept under stirring at 75 °C for different times. The exchanged clay was then filtered and washed several times with a 1:2 mixture of ethanol-distilled water. Finally, the wet product was frozen for 24 h and then lyophilized at 100 mTorr and –50 °C for 72 h using a VirTis 2KBTES-55 freeze dryer in order to obtain a free flowing product.

2.3. Characterization

X-ray diffraction (XRD) tests were performed on the clay powder using an X-Pert Pro diffractometer, operating at 40 kV and 40 mA, with CuK α radiation ($\lambda = 1.54 \text{ \AA}$). Powders of finely ground samples were put in horizontal glass holders, then passed over several times with a glass slide in order to eliminate texture. Diffractograms were recorded at a scanning speed of 1°/min from $2\theta = 2^\circ$ to 15° in steps of 0.0167°; 0.5° was selected for the divergent slit and scatter slit.

X-ray Fluorescence spectroscopy (XRF) was performed for elemental analysis, by using a PANalytical MiniPal 2, equipped with CrK α radiation ($\lambda = 0.2291 \text{ nm}$) and a Si-PIN detector. Measurements were carried out at 20 kV and 5 μA , in helium flow. Light elements (below Na in periodic table) could not be detected. Samples were analyzed in powder form without any additional preparation. Each powder was put into a XRF plastic sample cup with a thin polypropylene window measuring 76 mm in diameter.

Thermogravimetric analysis (TGA) was carried out with a TG HI-Res thermal analyzer (TA Instruments) at a heating rate of 10 °C/min from room temperature to 900 °C in air flow. The specimen weight was in the range of 7–15 mg. Organic mass contents were determined subtracting the mass loss between 150 °C and 500 °C from the bentonite to the modified clays. Degradation temperatures were obtained from the maximum of each event at the derivative curves of TG (DTG).

Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 6700 Thermo Scientific instrument equipped with a diamond ATR probe, over the range 400–4000 cm^{-1} from 32 co-added scans at 4 cm^{-1} resolution. About 10 mg of finely ground clays were placed on the sample holder.

Water absorption tests were carried out at 90% RH (relative humidity). To control the humidity level during testing, clay samples were enclosed in a small chamber containing an aqueous solution of glycerine (34 wt.%) which fixes the relative humidity (RH) within $90\% \pm 1\%$ (Greenspan, 1977). Before tests, all the samples were dried under vacuum until constant weight. Samples were weighted at prefixed times until the equilibrium mass (M_{eq}) was achieved and water absorption at each time was calculated as:

$$M_t(\%) = \frac{M_t - M_0}{M_0} \cdot 100 \quad (1)$$

where M_t is the mass of the sample at a time t and M_0 is the initial mass of the sample (dried). Triplicate measurements were conducted for each sample and the average values were used for water absorption calculation.

3. Results and discussion

The bentonite used in this study consisted predominantly of montmorillonite as evidenced by XRD analysis (D'Amico et al., 2014). Also, it contained quartz and feldspar as major impurities, as well as traces of gypsum and sepiolite. The main chemical composition was obtained by XRF and the results are shown in Table 1. This Bent has high content of Fe, which can be attributed to the location of the deposit from which it was extracted (Murray, 2006).

Table 1
Chemical composition of Bent.

Sample	Composition (wt.%)							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	TiO ₂	Others ^a
Bent	52.3	13.1	22.1	1.9	4.7	1.3	2.0	2.4

^a Others = % SO₃ + % Cl.

3.1. Effect of reaction time

The effect of reaction time on the final properties of the organoclays was studied. The concentration of soy lecithin was set at 0.5 g SL/g Bent and the temperature was fixed at 75 °C, then, the reaction time was varied from 0.5 h to 18 h.

X-ray diffraction patterns of the modified bentonites at different reaction times are displayed in Fig. 1. The 001 basal reflection of raw Bent (13.2 Å) shifted to lower angles after the chemical treatment with SL, suggesting an increase of the basal spacing as intercalated molecules were introduced into the bentonite interlayer space (Ouellet-Plamondon et al., 2014). Upon intercalation, an increment of around 2 Å was found and the basal spacing remained practically constant with the increase in reaction time (Table 2).

Bent and SL FTIR spectrums were recorded in order to compare them with the SL-Bent organoclays (Fig. 2). The FTIR spectra of pristine Bent had an important band centered at 3641 cm⁻¹ corresponding to the structural OH groups of the clay whereas the bands centered at 3440 and 1656 cm⁻¹ (OH stretching) correspond to free water adsorbed in the clay. The absorption band centered at around 1004 cm⁻¹ is attributed to Si in plane vibration. AlAlOH, AlFeOH and AlMgOH bending vibrations show absorption bands at 916, 880 and 800 cm⁻¹, respectively (Farmer and Russell, 1964; Madejova and Komadel, 2001; Nayak and Singh, 2007). The presence of SL in the modified bentonites was evidenced by the appearance of two bands centered at 2922 and 2852 cm⁻¹, respectively, that correspond to the CH₂ asymmetric and CH₂ symmetric stretching vibrations, and another one centered at 1467 cm⁻¹ that corresponds to the deformation vibrations of CH₂/CH₃. The bands centered at 1200–970 cm⁻¹ related to the vibrations of PO₂ and C–O bonds (Nagy et al., 2013) are not visible in the spectrum due to the superposition with the Si band previously mentioned. The clear shift of the CO stretching band at 1737 cm⁻¹ in neat SL to 1702 cm⁻¹ in SL modified bentonites indicates possible interactions with the clay layers surface.

The highest organic content, calculated from TGA curves, was achieved early at 0.5 h and after that there was only a low rearrangement of intercalated surfactant (Fig. 3A). The initial greatest organic content can be explained considering the strong electrostatic interaction between the clay and the phospholipids (Neumann et al., 2000). Then, at intermediate reaction times, rearrangements of these molecules may have occurred. In addition, the organic content slightly decreased and the phosphorus content present in the modified bentonites, listed in Table 2 (obtained by XRF), decreased with the reaction time, remaining constant after 4 h, which implies that the phospholipids present in SL interact with each other through Van der Waals

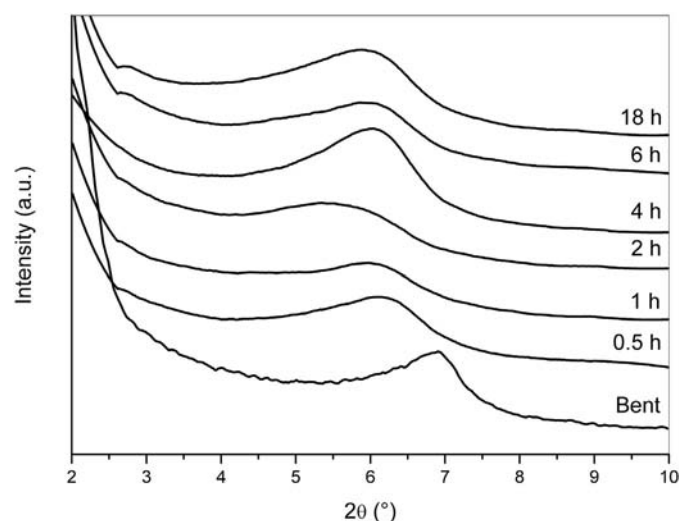


Fig. 1. XRD spectra of Bent, neat SL and modifications with SL at different reaction times.

Table 2

Organic content, basal spacing, phosphorous content and moisture absorption after 24 h of the SL-modified bentonites as function of reaction time.

Reaction time (h)	Organic content (wt.%)	d_{001} (Å)	Phosphorous content (wt.%)	Moisture absorption (wt.%)
0	0	13.2	0	18.3 ± 0.1
0.5	27.7 ± 0.3	14.4	3.31 ± 0.03	6.6 ± 0.3
1	25.9 ± 0.3	14.8	3.13 ± 0.03	5.8 ± 0.2
2	23.1 ± 0.2	16.3	1.74 ± 0.02	6.4 ± 0.3
4	25.8 ± 0.3	14.7	1.52 ± 0.02	6.0 ± 0.3
6	22.9 ± 0.2	14.8	1.54 ± 0.02	6.2 ± 0.1
18	24.1 ± 0.2	15.0	1.53 ± 0.02	6.7 ± 0.3

forces and the amount of interactions increases as a function of reaction time leading to a rearrangement of its molecules (Wicklein et al., 2010). In general, the organic content achieved at equilibrium was around 24 wt.%, and there was not a wide variability within the reaction times studied.

Considering the future application of the organoclays obtained in the present work in the development of melt compounded or injection molded nanocomposites, it is important to focus the study on the analysis of their thermal stability. The derivative thermograms (DTG) of the modified bentonites with different reaction times, the raw clay and SL are compared in Fig. 3B. Thermal decomposition of raw Bent occurred in three steps. The first one, from room temperature to approximately 150 °C, corresponds to dehydration of adsorbed water molecules; the second one, between 150 and 450 °C, is the slow loss of interlayer water; and the third one, at temperatures up to 650 °C, corresponds to the dehydroxylation of the structural OH groups of the clay. Thermal decomposition of SL occurred in a wide range of temperatures, with a series of events mostly overlapped at 180, 255, 325 and a very small one at 540 °C. SL-modified bentonites were thermally decomposed in three main steps (Ouellet-Plamondon et al., 2014; Zhu et al., 2011). First, the removal of physically adsorbed and intercalated water molecules, which shifted to lower temperatures compared with raw Bent, between room temperature and 120 °C (Wicklein et al., 2010; Zhu et al., 2011), because water molecules weakly interact with the organoclays which possess lower surface energy. In addition, the intensity of this peak was significantly reduced in all SL-modified bentonites, indicating an increase in the hydrophobic nature (Hedley et al., 2007). Then, the decomposition of SL which also occurs in three steps, was centered at around 190, 250 and 450 °C; and finally the dehydroxylation of the structural OH at around 600 °C. The multiple stages of decomposition of the organic modifier suggest the existence of different conformation states and environments of lecithin in the organoclay (as was

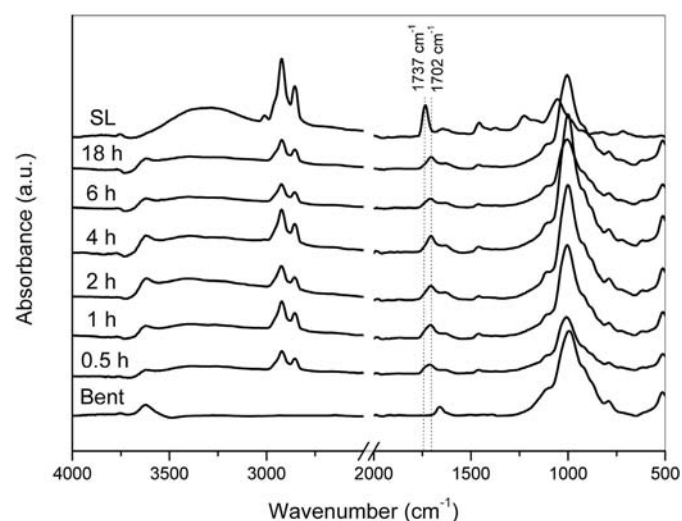


Fig. 2. FTIR spectra of Bent, neat SL and modifications with SL at different reaction times.

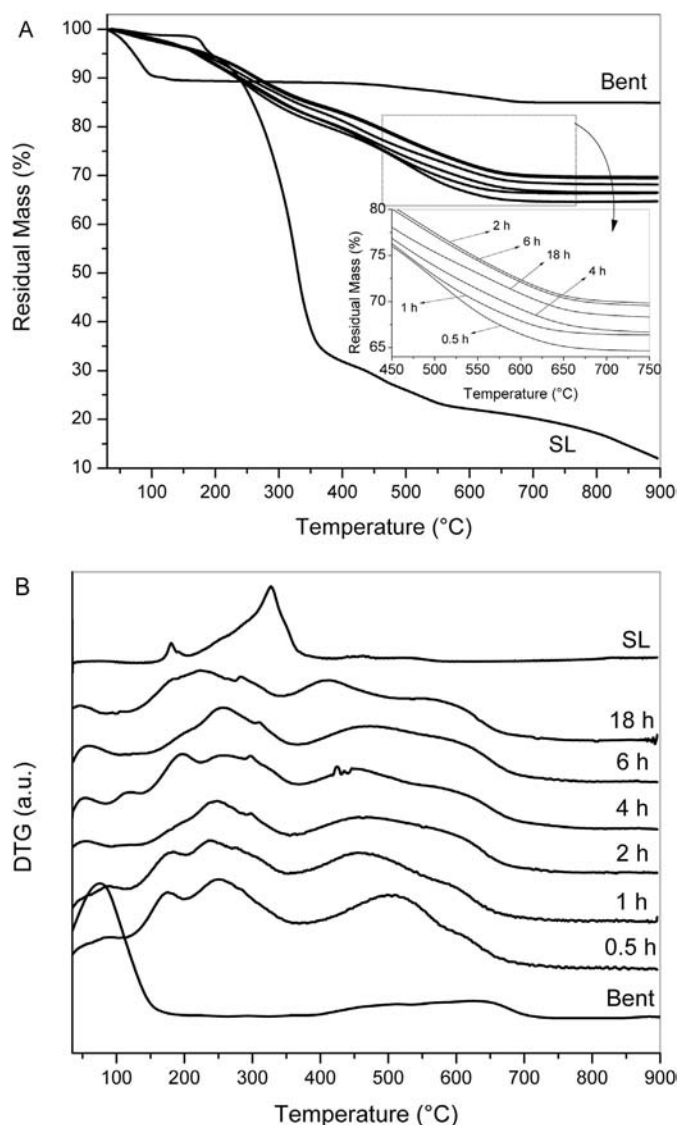


Fig. 3. TGA (a) and DTG (b) curves of Bent, neat SL and modifications with SL at different reaction times.

corroborated by XRD) (Silva et al., 2014). In addition, organoclays started degrading at slightly higher temperatures as the reaction time increased, probably due to different arrangements of SL molecules.

Finally, water absorption tests were performed and the hydrophobicity of organoclays could be estimated by this measurement. The moisture absorption of the raw Bent was 18 wt.% and this value was reduced by a factor of three for SL-modified bentonites (Table 2), as evidenced in DTG curves. This result was independent of the reaction time, which shows that the ion exchange reaction was completed after short times. The subsequent increase in time had no significant effect, except for the possible accommodation of the molecules, which is in agreement with all the results presented above.

3.2. Effect of SL amount

The effect of soy lecithin amount on the final properties of organoclays was also studied. The temperature and reaction time were fixed at 75 °C and 2 h, respectively. Bent was modified using 0.25, 0.50, 0.75, 1.00 and 1.20 g SL/g Bent ratios.

The basal spacing of the resulting organoclays increased with the amount of adsorbed surfactant (Fig. 4). The original basal spacing of Bent (13.2 Å) shifted to 15.1, 16.5, and 20.3 Å after modification of

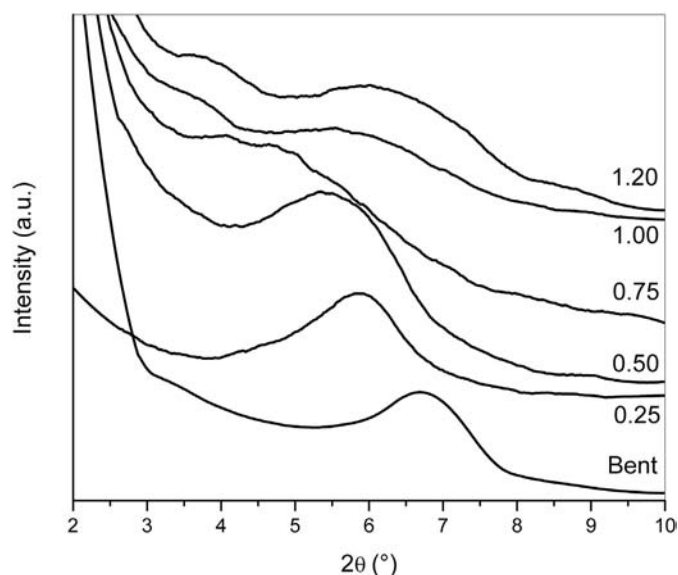


Fig. 4. XRD spectra of Bent, neat SL and modifications with different amounts of SL.

bentonite with 0.25, 0.50, and 0.75 g SL/g Bent ratios, respectively (Nagy et al., 2013; Zhu et al., 2011). When the g SL/g Bent ratios were 1.00 and 1.20, the basal spacing increased to 24.5 and 24.3 Å respectively, which is larger than that of raw Bent. These values and the occurrence of a secondary reflection at 16.0 Å and 14.7 Å suggest that multiple arrangement models of surfactant-molecule interlayer were formed (Zhu et al., 2011). Another interpretation could be that, influenced by the heterogeneous charge distribution in layers, some of them are more readily intercalated, while others are less easily intercalated, thus generating different basal spacings (Silva et al., 2014; Zhou et al., 2009; Zhou et al., 2007). These reflections are broader compared with those of raw Bent. The broadening was caused by the disordered structure, in which the orientation of alkyl chains in the interlayer space corresponds to at least two arrangements (Ouellet-Plamondon et al., 2014; Zhu et al., 2011).

The bands that appeared in the FTIR spectrums (Fig. 5A) are in accordance with the ones detailed in the previous section (i.e., effect of reaction time). The intensities of SL-modified bent bands increased as a function of the initial g SL/g Bent ratio, indicating that the amount of modifier increased. Moreover, the unperturbed ν_{CO} band of SL, which appeared at 1737 cm^{-1} , shifted to 1708 cm^{-1} for the SL-modified bentonites (Fig. 5B), suggesting that SL interacted with the Bent surface. This is in accordance with the observations made in the previous section. However, the conservation of the band at 1735 cm^{-1} in the spectrum of the organobentonites with higher SL contents can be explained considering that the additionally adsorbed molecules are not able to be in direct interaction with the adsorption centers because they are already occupied and their intermolecular interactions are like in the original SL (Wicklein et al., 2010).

The organic content increased concomitantly as a function of the initial g SL/g Bent ratio and it did not stabilize within the studied range of concentrations (Fig. 6A). Moreover, the phosphorous content, measured by XRF, was in accordance with this trend, as resumed in Table 3.

DTG curves of the modified bentonites as a function of initial g SL/g Bent ratio are plotted in Fig. 6B. The decomposition of SL in the modified bentonite was a two- to three-step process and the initial temperatures of degradation were higher than raw SL ones. In DTG curves of the organoclays, the event that appeared in Bent, at 73 °C, corresponding to adsorbed water, decreased its intensity or disappeared completely with the intercalation of different amounts of SL molecules within the clay, as previously described. Furthermore, the temperature of dehydration for the organoclays was slightly higher than the temperature for Bent. This can be attributed to the hindered escape of the interlayer

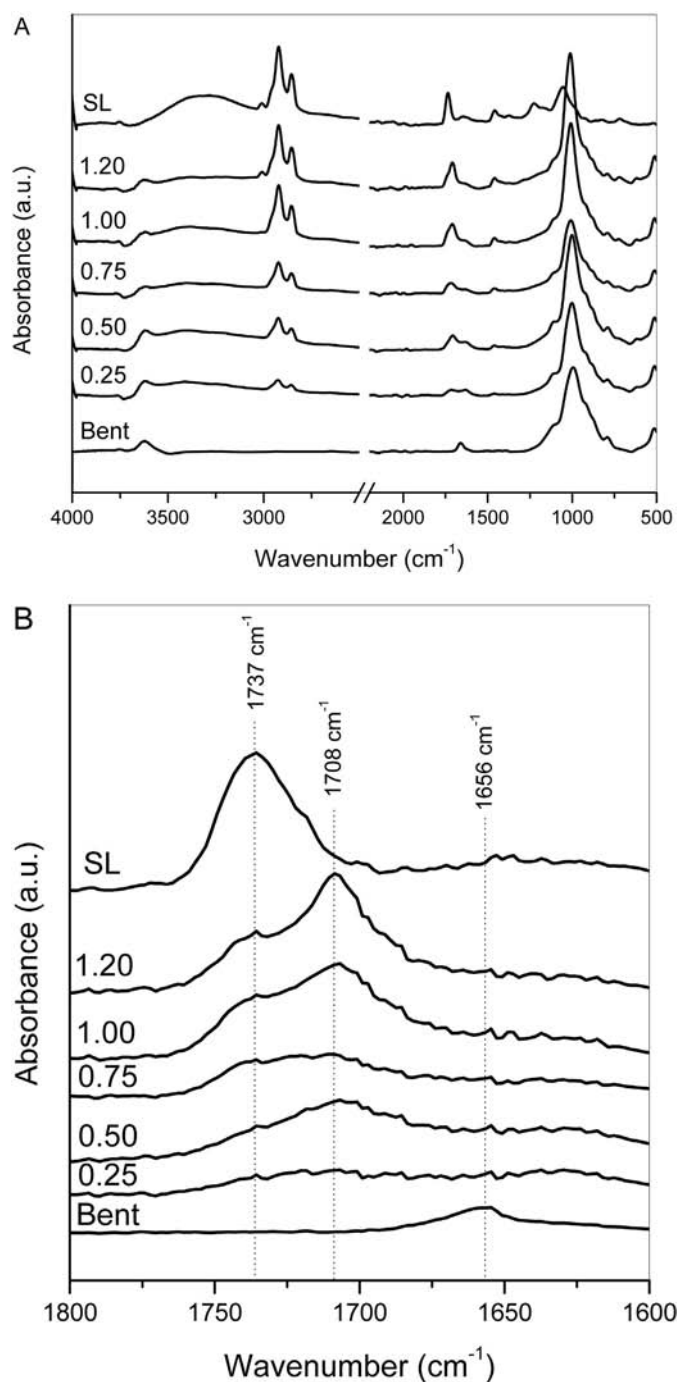


Fig. 5. FTIR spectra (a) and analysis of carbonyl vibration (b) of Bent, neat SL and modifications with different amounts of SL.

water as a result of the presence of intercalated SL molecules (Wicklein et al., 2010). In addition, there was a slight shift in the dehydroxylation peak of SL-modified bentonites to a lower temperature as reported by other authors (Zhang et al., 2012; Zhu et al., 2011).

In the case of 0.25 and 0.50 g SL/g Bent ratios, only two peaks of decomposition of SL were observed. However, with increasing surfactant amount, a new degradation peak at lower temperature appeared, which can be attributed to the decomposition of adsorbed SL molecules that interact via Van der Waals forces with the layer surface, because this interaction is weaker than the electrostatic ones and therefore, the event requires lower energy and thus occurs at lower temperatures. Additionally, the intensity of this peak increased, whereas the intensity of the second peak decreased. This suggests that the Van der Waals

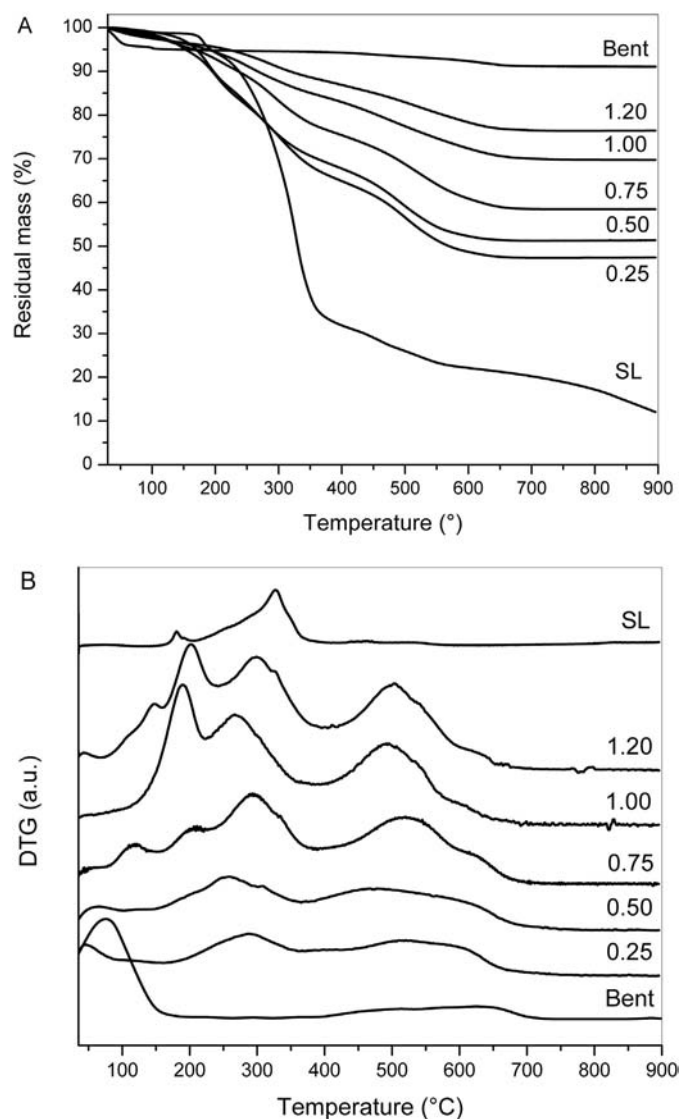


Fig. 6. TGA (a) and DTG (b) curves of Bent, neat SL and modifications with different amounts of SL.

interactions became more important at higher ratios of g SL/g Bent (Wicklein et al., 2010; Zhang et al., 2012; Zhu et al., 2011).

As depicted in DTG curves in Fig. 6B, the maximum temperature of decomposition of all SL-modified bentonites (at around 200 °C) remained below that of neat lecithin (at 329 °C). Thus, the conformational changes due to the adsorption via Van der Waals forces of surfactants may reduce the thermal stability of organobentonite (Zhang et al., 2012).

All the organoclays absorbed much less moisture than neat Bent (Table 3). However there were practically no differences among the

Table 3

Organic content, basal spacing, phosphorous content and moisture absorption after 24 h of the SL-modified bentonites with different initial g SL/g Bent ratios.

g SL/g Bent ratio	Organic content (wt.%)	d_{001} (Å)	Phosphorous content (wt.%)	Moisture absorption (wt.%)
0	0	13.2	0	18.3 ± 0.1
0.25	16.2 ± 0.2	15.1	1.72 ± 0.02	8.6 ± 0.4
0.50	22.8 ± 0.2	16.5	1.74 ± 0.02	6.4 ± 0.3
0.75	33.4 ± 0.3	20.3	4.71 ± 0.05	6.1 ± 0.8
1.00	41.9 ± 0.4	24.5–16.0	5.03 ± 0.05	6.3 ± 0.5
1.20	44.0 ± 0.4	24.3–14.7	5.10 ± 0.05	7.2 ± 0.3

organoclays with different organic contents, possibly because the adsorption centers were already occupied or the path for the water entry was impeded by the adsorbed organic molecules, as seen in TGA and FTIR analyses (Wicklein et al., 2010).

4. Conclusions

In this work, a novel environmental-friendly modification of bentonite by using a natural and economical product, soy lecithin, and the effects of reaction time and modifier content were analyzed and established. Reaction time had not a great effect on the final properties of the organoclays and it can be considered, based on the results of TGA, DTG, FTIR, XRD and water absorption tests, that the equilibrium conditions were achieved at short times (0.5 h); after that there was only a low rearrangement of SL molecules. On the other hand, initial SL/Bent ratio determined the final properties of each organoclay. Considering the DTG curves and FTIR spectra, the intermolecular interactions became more important at higher ratios of SL/Bent and these interactions caused a detriment on the thermal stability of the organoclays. For low initial g SL/g Bent ratios (until 0.75) only one diffraction peak for organoclays was observed, whereas for higher concentrations (1.0 and 1.2 g SL/g Bent) an increment in the interlayer space and a new diffraction peak was registered, suggesting a different molecular orientation of SL molecules inside Bent.

The organoclays developed in this work, mainly those with lower organic content, could be used as promising environmental-friendly fillers for the formulation of clay/biopolymer nanocomposites due to their thermal stability, increased interlaminar space and markedly lower degree of hydrophobicity than that of Bent. Work is in progress in this direction.

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