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Characterization of Natural and Modified Clays to the Development of Polymeric Nanocomposites

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Summary: Bentonite is a technical term applied to layered silicates of very thin granulation, mainly composed by minerals of the smectites group. Montmorillonite, a phylossilicate with layers as thick as 1 nm, is the most common structure in the bentonite clay. The polarity of these materials is incompatible with most of the usual polymers and in order to overcome this problem, chemical modifications are often necessary. The purpose of this work is to evaluate the chemical and physical characteristics of different bentonites by comparing their product data sheets, their performance in the water Foster swelling and their response to chemical modifications of their surfaces structures. The samples were characterized by infrared spectroscopy and X-ray diffraction analysis. All bentonite samples showed effective intercalations of the modifying agent on their surface structures. This behavior showed the possibility of usage of these materials in the polymer layered silicates nanocomposites preparations.

Keywords: bentonite; clay; montmorillonite; nanocomposites; polymer

Introduction

Bentonite is a technical term applied to layered silicates of very thin granulation, mainly composed by minerals of the smectite group. Montmorillonite (which is the most common mineral in the bentonite structure), is a phylossilicate with layers as thick as 1 nm. Montmorillonite layered silicate belongs to the structural family known as the 2:1 phyllosilicates. The crystal structure of this mineral consists of layers made up of two silica tetrahedral sheets fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide, as illustrated in Figure 1. The stacking of bentonite layers leads to a regular van der Waals gap between them (the interlayer or gallery). Isomorphic substitution within the layers generates charge deficiency (i.e. Fe^{2+} or Mg^{2+} replacing Al^{3+}). The deficit charges are compensated by cations (usually Na^+ or Ca^+) absorbed between the three-layer clay mineral sandwiches. These are held relatively loosely and give rise to the significant cation-exchange properties. Hydration of the sodium or calcium ions makes an expansion in the galleries and the swelling of the clay; indeed, these platelets can be fully dispersed in water.[1–4] Bentonites can be classified in three types: sodic, calcic and policationic. The difference in the swelling of the sodic and calcic types is due to the attraction force between the layers, which is higher for calcic, reducing the amount of the water absorbed. In the sodic bentonite, this attraction force between layers is smaller, so that more water molecules are absorbed within its layers.[4,5]

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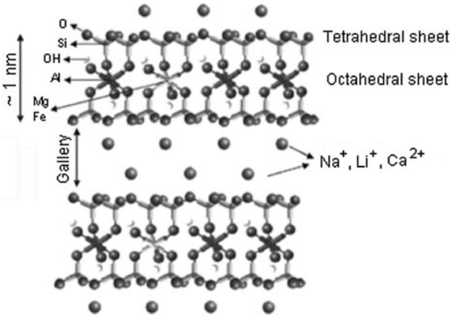

Figure 1.
Structure of sodium montmorillonite.

Due to the high aspect ratio, the high cation-exchange and water swelling abilities (responsible for the faster and complete intercalation of organic compounds), bentonites are usually employed in the preparation of organic modified layered silicates that is used in the polymer- based nanocomposites preparations.[6]

As the polarity of these layered silicates is incompatible with most of the usual polymers, they have to be chemically modified to improve compatibility between the inorganic (polar) and the organic (non-polar) phases. The compatibility with organophylic polymers is frequently attained by the alkaline or earth alkaline cation-exchange, from the interlayer layered silicate region (gallery), by cationic surfactants. This modification introduces a high hydrophobic character, decreases the superficial energy, making the silicate more compatible with organic polymers. Due to these properties, the layered silicate forms a miscible system, like a homogeneous nanocomposite.[7–14]

Polymer layered silicate nanocomposites have attracted great interest due to their improved properties compared with the pure polymer and conventional micro and macrocomposites. Some of these improvements include high module, increased strength and heat resistance, decreased flammability and gas permeability and increased biodegradability. Two particular characteristics of layered silicates are generally considered for polymer layered silicate nanocomposites. The first is the ability of the silicate particles to disperse into individual layers (totally delaminated or exfoliated). The second is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These two are, of course, interrelated, since the degree of dispersion of a layered silicate in a particular polymer matrix depends on the interlayer ionic species.[15]

Three different types of materials (Figure 2) may be obtained depending on the interactions of the components (polymer matrix and the layered silicate), the method of preparation and the strength of interfacial interactions between the polymer matrix and the layered silicate (modified or not).

In the first case, the nanoclay particles/platelets are uniformly distributed and dispersed in an aggregate form. This two phase material enhances mechanical or thermal properties, as in classical composite. This way, it can only be defined as a microcomposite. The second case is an intercalated nanocomposite in which polymer chains enters into the space between thin platelets of nanometer dimensions thereby resulting into huge reinforcement. However, in this case, platelets remain isolated in aggregates between which the matrix is intercalated. The last case is the nanocomposite with exfoliated structure. All the platelets of the aggregates are separated and dispersed within the matrix. This results into quantum jump in the reinforced area which should ideally cause a high enhancement in the properties. This effect usually occurs when very small quantities of nanoparticles are present in the matrix. The last two cases are the one which really reflect the effect of true nanocomposites partially or fully intercalated and/or exfoliated.[15–18]

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range ($1\,nm = 10^{-9}$ m). Nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monolithics, while posing preparation

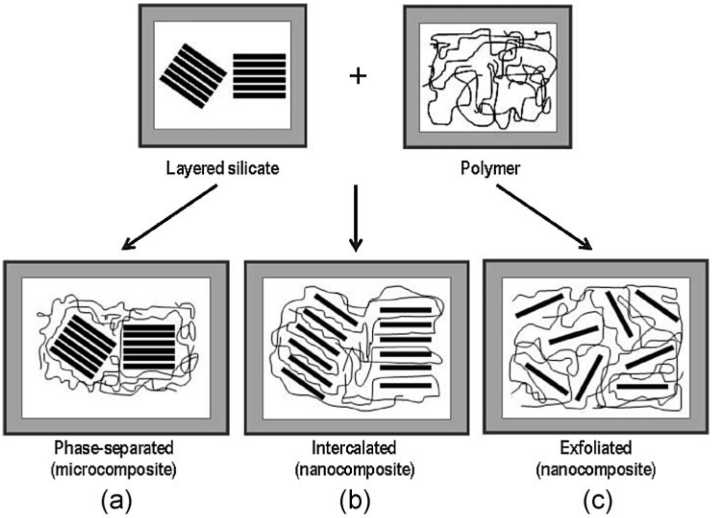

Figure 2.
Different types of composites arising from the interaction of layered silicates and polymers. a) Phase-separated microcomposite; b) Intercalated nanocomposite, and c) Exfoliated nanocomposite.

challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. They are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached,[19] even though the first inference on them was reported as early as 1992.[20]

The objective of this paper is to compare the chemical and physical properties of a number of bentonites, in order to study their potential for polymer layered silicate nanocomposite preparations. For this purpose, bentonite product data sheets (obtained from the suppliers) were compared, the samples were submitted to the swelling test and were also chemically modified. The modified products thus obtained were analyzed by infrared spectroscopy and X-ray diffraction.

Experimental Part

Materials

The bentonites evaluated in this work were from different suppliers: Natural Sodic Bentonite (VOLCLAY SPC), Light Yellow Bentonite (ARGEL CN 35), Brown Bentonite (BRASGEL FC and PERMAGEL), supplied by Bentonita União Nordeste S.A; Natural Sodic Bentonite (VULGEL CN 45), supplied by Aliança Latina Indústria e Comércio Ltda; Natural Light Yellow Bentonite (M 200), supplied by Mineração Vale do Juquiá Ltda; Sodic Montmorillonite (MN 4850/AV), supplied by J. Reminas Mineração Ltda and Enológica Barreal Bentonite, supplied by Schumacher Insumos. The clay polarity modifier agent employed in this work, AMS-32, supplied by Ioto International (this product is in the process of being patented).

Methods

Water swelling tests were carried out using Foster Method.[21] Accordingly, 1 g of clay was screened (ABNT 200 mesh) and slowly added to a graduated cylinder containing 50 cm^3 of water. After 24 h at room temperature, the volume of the swelled clay was measured. The swelled clay was left under stirring at room temperature for 5 min. After 24h, a new measure of the volume was taken.

A comparison between the different samples of clays employed in this work

Table 1.
Chemical compositions of bentonite samples (wt %). Product data sheets obtained from the supplier.

	VOLCLAY SPV	ARGEL CN 35	BRASGEL FC	PERMAGEL	VULGEL CN 45	M 200	MN 4850/AV	ENOLÓGICA BARREAL
Silica	63	60	64	60.2	64.75	60.0	63.12	58.4
Aluminium oxide	21	18	15	18.5	17.90	18.0	15.34	19.4
Iron oxide	3–4	3–4	6–7	7.2	3.55	5.0	5.77	3.2
Titanium oxide	<1	<1	<1	0.9	0.40	–	0.98	–
Calcium oxide	<1	<1	<1	2.4	0.60	2.0	0.99	1.5
Magnesium oxide	–	–	2–3	2.0	3.00	5.9	2.87	2.3
Sodium oxide	2–3	2–3	1–2	2.5	2.35	3.0	1.63	2.5
Potassium oxide	<1	<1	<1	0.53	0.15	1.0	0.45	0.8

was performed in the base of the bentonite product data sheets (obtained from the supplier, Tables 1 and 2).

Natural bentonite samples were swelled in water for 24 h, given 4% (wt) dispersions. The mixtures were left under stirring at room temperature for 20 min, and then kept at room temperature for 24 h. After that, water solution containing the AMS-32 modifier agent was added slowly to the dispersions, under stirring. After 24 h, the suspensions obtained were screened (ABNT 200 mesh) and kept at room temperature for more 24 h. The suspensions were filtered and the solids were dried at 60 °C for 48 h.

Pure and modified bentonites were characterized by infrared spectroscopy (FTIR), using a BIORAD spectrophotometer in the range of 400–4000 cm^{-1}. Samples were KBr pressed discs. Powder X-ray patterns for the samples were obtained in a Schimadzu XRD-6000 diffractometer, using a Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) in the 2θ range of 3–50 °. Instrument conditions were 40 mV, 40 mA and 2 ° min^{-1} scan rate in 2θ. Interlayer spaces were calculated from Bragg law.[22]

Results and Discussion

As can be seen from the data showed in Table 1, all bentonite samples tested have similar chemical compositions. The phyllossilicate nature of the clay samples can be seen by the comparison between the content of silica and aluminum oxide, since the higher content of silica is a characteristic of this kind of material.[23] Titanium oxide was present in almost all clay samples tested, since the content of this oxide was

Table 2.
Physical properties of bentonite samples. Product data sheet obtained from the supplier.

	VOLCLAY SPV	ARGEL CN 35	BRASGEL FC	PERMAGEL	VULGEL CN 45	M-200	MN 4850/AV	ENOLÓGICA BARREAL
Aspect	Thin powder	Thin powder	Powder	–	–	Thin powder	–	–
Coloration	Grey	Off white	Brown	Brown	Off white	Off white	Off white	Light yellow
Water content	Max 12%	Max 14%	Max 14%	Max 14%	8–15%	–	–	10–12%
pH	9	7	10–11	9.5	5.5	8.5	–	8.5–8.9
200 Mesh Granulation	Max 15%	Max 15%	Max 15%	Max 15%	Max 15%	–	–	–
Methyilene blue absorption	Min 50 mL/0.5 g	Min 50 mL/0.5 g	–	–	–	48–60 mL/0.5 g	–	–
Apparent viscosity, API Norm	<15 cP	<15 cP	<14 cP	<14 cP	–	–	–	–
Plastic viscosity, API Norm	<4 cP	<4 cP	<4 cP	<4 cP	–	–	–	–
Flame loss	8%	9%	7–8%	8.7%	7.11%	–	–	–
Apparent density	0.8 g/cm^3	0.7 g/cm^3	0.8–0.9 g/cm^3	2.6 g/cm^3	–	0.8–1.3 g/cm^3	2.9 g/cm^3	–

lower than 1%, it did not affect their main behavior.[24] The content of sodium oxide, higher than calcium oxide, confirmed that the samples were sodic bentonites.

The predominance of the sodium ion in these structures is responsible for their high cation exchange ability, swelling behavior, adsorption properties and large surface area.[25] The main aspect regarding to the iron oxide content is related to the color of the burned clays and to their flame retardance behavior.[24] There are no true natural sodic bentonites in Brazil, but just a number of occurrences of policationic montmorillonite clays, with different contents of ilitamontmorillonite minerals.[26] This fact explains the presence of magnesium, potassium, iron and aluminum in some samples.

Comparisons of the physical properties are shown in Table 2. Brasgel FC and Permagel clays are the darker samples. Their brown color is due to their high iron oxide content. Lower content of this oxide in the other samples resulted in lighter or grey color.

Plastic and apparent viscosity data are important to the material qualification and acceptance for use in petroleum exploration and production.[27] The flame loss behavior of the samples are probably due to the loss of the coordination and adsorption of water molecules, hydroxyl groups present in the mineral and loss of organic residues.[28]

The swelling water behavior of the sodic bentonites is an important characteristic which indicates the exfoliation of the layers of the clay when in contact with water. This property is important to promote organic molecules insertions, especially by the cation-exchange methodology. The results are shown in Table 3.

Values equal or less than 2 cm^3 were considered as ''no swelling''; between 3 to 5 cm^3 as ''low swelling''; between 6 to 8 cm^3 as ''medium swelling'' and up to 8 cm^3 as ''high swelling''. As can be seen from these results, all the samples showed a swelling behavior (with or without stirring) in accordance with the hydrophilic characteristic of the sodic bentonites.

Figure 3 shows the FTIR spectra of the natural and modified Permagel bentonite. All other samples presented similar spectra. The bands at 3625 and 3554 cm^{-1} are attributed to the structural O–H stretching mode. Interlayer and adsorbed water show O–H stretching bands between 3475 – 3413 cm^{-1} assigned to intra- and intermolecular hydrogen bonds. Water bending mode is observed at 1652 and 1634 cm^{-1} for natural and modified clay, respectively. Other vibrations modes characteristics of the clays structures were also observed and the assignments can be observed in Table 4. Modified Permagel bentonite shows CH axial symmetric and asymmetric stretching mode (CH_2 and CH_3 groups) at 2957, 2918 and 2846 cm^{-1}. Angular CH_2 and CH_3 bending mode is observed at 1470 cm^{-1}. Moreover, rocking $[CH_2]_n$ mode is observed at 718 cm^{-1}. These bands confirm the AMS-32 intercalation in the clays structures (Table 4).[6,28]

In order to confirm the effective intercalation of the AMS-32 modifier agent, the samples were analyzed by powder X-ray diffraction. All natural clays showed interlayer spaces between 12.20 and 14.95 Å. These values confirm their hydrated forms and swelling behavior, necessary character-

Table 3.
Swelling water results.

	VOLCLAY SPV	ARGEL CN 35	BRASGEL FC	PERMAGEL	VULGEL CN 45	M-200	MN 4850/AV	ENOLÓGICA BARREAL
Dried clay volume (cm^3)	1.2	1.3	1.6	1.4	0.5	1.6	1.1	1.2
Swelling (cm^3) after 24 h	13	9.0	13	15	13	12	4.0	14
Swelling (cm^3) after 24 h of stirring	ND[a)]	ND[a)]	40	49	ND[a)]	ND[a)]	5.0	ND[a)]

[a)] Not determined.

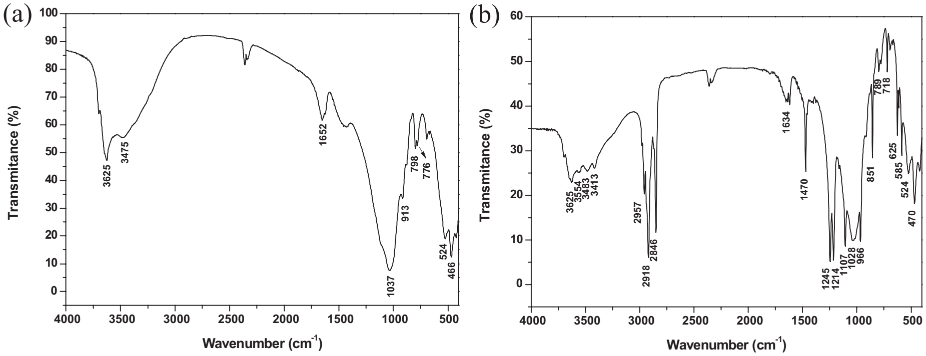

Figure 3.
FTIR spectra of Permagel bentonite: (a) natural; (b) modified with AMS-32.

istic to their use in reactions of structure modification.[1] Figure 4 shows the powder X-ray diffraction patterns of the samples.

The AMS-32 modifier agent, with exception of Permagel sample, causes a shift in the diffraction peak to lower angles, i.e., an increase in the interlayer space, d_{001}. This fact confirms the efficiency in the treatment applied to the clay surface. Values of the interlayer spaces calculated for the samples are shown in Table 5. More than one peak related to the interlayer spaces was observed in the powder X-ray data for modified clays. Other authors[29–31] have already implied that the presence of these multiple peaks are due to the formation of different modified clays structures.

For modified Permagel bentonite, the decrease in (001) peak intensity and the absence of peaks in lower angles can be attributed to a partial exfoliation of the clay. The surface modification of this clay was also confirmed by the IR data discussed above.

Conclusion

All samples analyzed showed similar chemical compositions and a high content of sodium oxide. This characteristic gives special colloidal properties to these layered silicates. The higher content of sodium ions allow the absorption of a great amount of water, which was confirmed by the swelling tests.

Infrared spectroscopy and powder X-ray diffraction analyses showed the effectiveness of AMS-32 intercalation into the bentonite structures. This is an important behavior, which can be explored in the polymer layered silicate nanocomposites

Table 4.
FTIR data for natural and modified Permagel bentonite. Values are given in cm^{-1}.

IR assignments	Natural	Modified
ν(OH)	3625	3625; 3554
ν(OH); hydrogen bond	3475	3483; 3413
δ(H—O—H)	1652	1634
δ(Si—O)	1037	1028
ν(Al—OH—Al)	913	966
ν(Si—O—M[a)])	798; 776; 524	851; 789; 625; 585; 524
ν(CH); CH_2 and CH_3 groups	–	2957; 2918; 2846
ν(S—O); AMS-32 structure	–	1245; 1214; 1107
$\delta(CH_2)$	–	1470
$\rho[CH_2]_n$	–	718

[a)] M = Al, Mg or Fe.

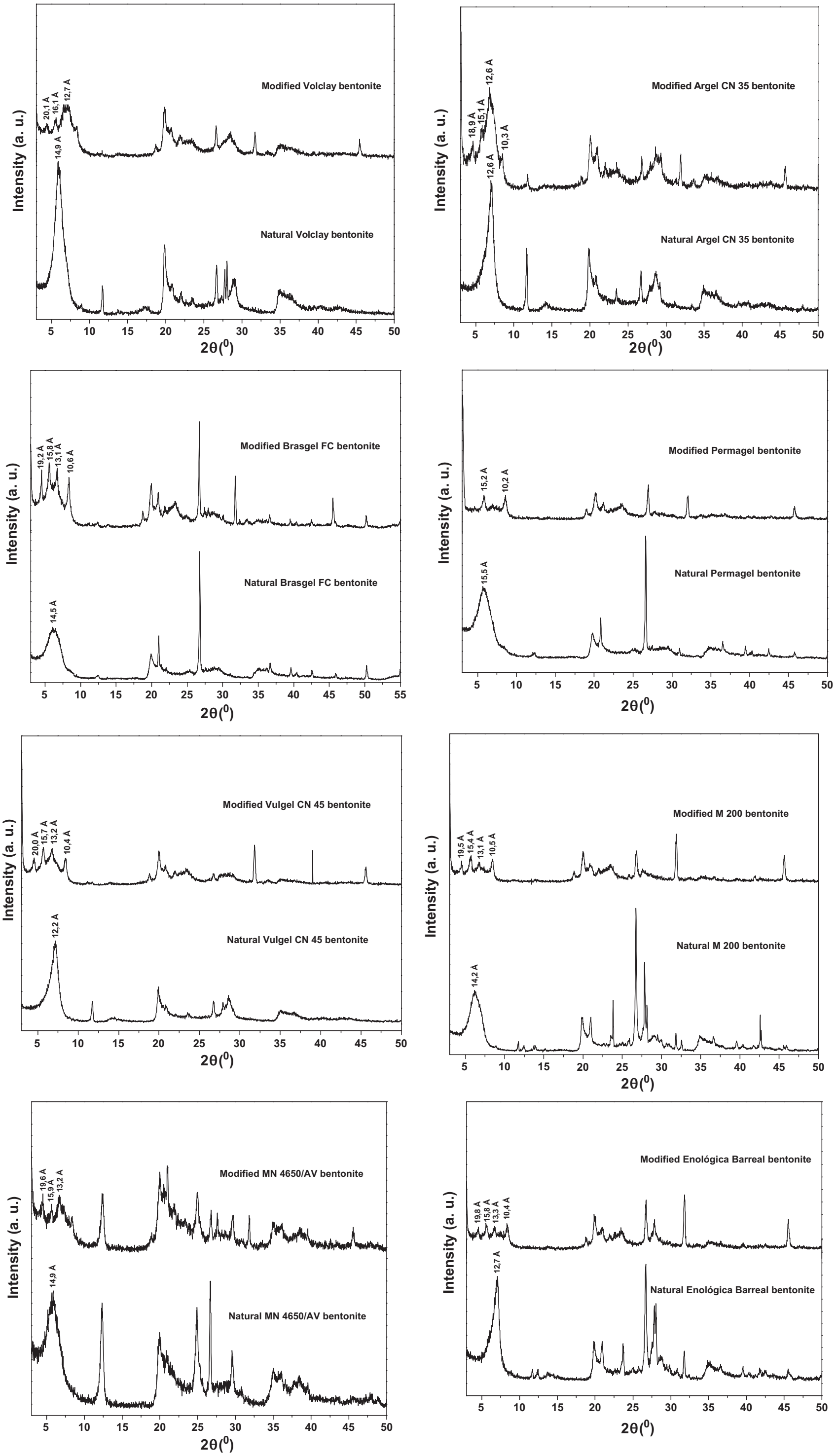

Figure 4.
Powder X-ray diffraction patterns of the natural and modified bentonite clays.

Table 5.
Interlayer spaces d_{001} for natural and modified bentonite samples.

Sample	Natural (Å)	Modified (Å)	
Volclay	14.90	20.15	16.10
Argel CN 45	12.60	18.90	15.10
Brasgel FC	14.53	19.25	15.87
Permagel	*15.55*	—	*15.23*
Vulgel	12.20	20.00	15.70
M 200	14.26	19.49	15.40
MN 4650	14.95	19.60	15.90
Enológica Barreal	12.70	19.80	15.80

synthesis. Modifier agents, like AMS-32, act lowering the superficial energy of the layers, thus enhancing the compatibility of layered silicates with polymers.

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