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Characterization of pristine and purified organobentonites

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Abstract Pristine and purified Argel sodium bentonites were organically modified with quaternary ammonium and phosphonium surfactants by ion exchange reaction in order to investigate the effect of the chemical identity of the surfactant and of the clay purification procedure in the intercalation process, final structure and thermal stability of organobentonites. The bentonites were characterized by X-ray diffraction analysis, thermogravimetric analysis and Fourier transform infrared spectroscopy. The bentonite purification treatment and, especially, the chemical structure of surfactant affected the thermal behavior of the organobentonites. The phosphonium modified bentonites were thermally more stable than those modified with ammonium, particularly the purified bentonite. These results seem to be promising regarding to the potential application of phosphonium modified Argel bentonites for the melt processing preparation of nanocomposites with polymeric matrices requiring high processing temperatures.

Keywords Ammonium · Organoclay · Phosphonium · Thermal characterization

Introduction

Smectite clays such as montmorillonite (main constituent of the bentonite) are valuable minerals widely used in many industrial applications. Their natural abundance, low cost, high cation exchange capacity (CEC), swelling behavior, adsorption properties and large surface area are the driving force behind their widespread use [1–4]. Smectites are aluminum silicate materials composed of an aluminium or magnesium hydroxide octahedral sheet sandwiched between two silicon oxide tetrahedral sheets. The layer thickness of each platelet is around 1 nm, and their lateral dimensions may vary from 30 nm to several microns. The layers are located on top of each other like the pages of a book. Van der Waals gaps are created between the layers, called galleries. The isomorphic substitution of the tetrahedral or octahedral cations, e.g. the substitution of Al^{3+} with Mg^{2+} or Fe^{2+} with Li^{1+}, generates negative charges that are counterbalanced by alkali and alkaline earth cations located inside the galleries [5]. The inorganic cations present between the clay layers exchanged for organic ones, rendering the silicate surface organophilic and more compatible with organic liquids or polymers [5, 6]. Only then can a high degree of exfoliation be achieved once these clays are added to hydrophobic polymer matrices.

Modified montmorillonite (organoclays) can be used in a wide range of applications which include adsorbents, rheological control agents, paints, greases, cosmetics, personal care products, oil well drilling fluids, etc. [7–9]. More recently the performance-enhancing properties of

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these modified clays, used as a nanoscale additive in plastics to generate polymer nanocomposites has been widely celebrated. Nowadays nearly 70% of the organoclays produced are used for this kind of application [10–15].

Proper bentonite organic modification procedure is a key step for successful preparation of nanocomposites [6]. Quaternary ammonium cations of the general formula $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$ where R and R′ are hydrocarbon groups have been traditionally employed for the organophilic modification of montmorillonite by cation exchange [16–19]. However, the low thermal stability of these surfactants limits their use in polymer nanocomposites based on polymer matrices requiring high processing temperatures. The surfactant thermal degradation during processing could not only initiate/catalyze polymer degradation but also cause a variety of undesirable effects during processing as well as in the final product [20]. In order to overcome this limitation, thermally stable surfactants such as alkyl pyridinium [21], alkyl quinolinium [22], alkyl phosphonium [23–26], alkyl stibonium [27] or alkyl imidazolium [28–30] surfactants have been proposed as alternative routes to alkyl ammonium modifiers.

Although a great number of studies on montmorillonite modification with different organic surfactants have been published, results are highly dependent on clay geological localization, composition and purity. As yet, no reports on the thermal behavior of Argel bentonite clays modified with quaternary ammonium and phosphonium surfactants were published. Thus, the main goal of the present study is to analyze the effect of the chemical identity of the surfactant and of the clay purification procedure in the intercalation process, final structure and thermal stability of organobentonites.

Experimental

Materials

Pristine Argel sodium bentonite (AN) with CEC of 92 meq/100 g, as determined by Phelps and Harris method [31], was provided by Bentonit União Nordeste (BUN-Campina Grande, Brazil). This clay was purified with the purpose of removing organic matter, according to the procedure reported previously [32] and coded as AP. Since in this study our goal was also to study the influence of the surfactant chemical structure in the thermal properties of pristine and purified organobentonites, both pristine and purified bentonites were modified with cetyl trimethyl ammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$) and hexadecyl tributyl phosphonium bromide ($C_{16}H_{33}(C_4H_9)_3PBr$), supplied by Vetec and Aldrich, respectively.

Bentonite organic modification

Both pristine (AN) and purified (AP) bentonites were organically modified by cation exchange reaction with the quaternary ammonium (A) and phosphonium (P) surfactants following a previously described procedure [33] in which the individual organic surfactants were slowly added to a vigorously stirred aqueous bentonite dispersion kept at 70 ± 5 °C. The content of surfactant added was equivalent to the clay CEC. After 30 min under stirring the aqueous bentonite dispersion was allowed to stand at room temperature for 24 h, filtered and washed free of bromide anions, dried at 60 °C for 48 h and ground in an agate mortar to pass through a 325 mesh sieve. The AN and AP bentonites organically modified with alkyl ammonium (A) and alkyl phosphonium (P) were coded ANOA, APOA, ANOP and APOP, respectively. Pristine, purified and modified bentonites were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TG) and Fourier transform infrared spectroscopy (FTIR).

Characterization of the bentonites

X-ray diffraction

X-ray diffraction patterns were obtained using a Shimadzu XRD-6000 diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm, 40 kV, 30 mA) at room temperature. XRD scans were performed in pristine, purified and modified bentonites powder with a 2θ range between 1.5° and 30.0° at a scanning rate of 2° min^{-1} and a scanning step of 0.02°.

Thermogravimetric analysis

Thermogravimetric characterization of bentonites was performed on a Shimadzu TG apparatus, S1HA model, with samples of about 15 mg of material. The samples were heated at 10 °C min^{-1} under an atmosphere of air, 50 mL min^{-1}. TG and derivative thermogravimetry (DTG) curves were recorded from 30 to 900 °C.

Infrared spectroscopy

Fourier transform infrared spectroscopy characterization was conducted using a Nicolet Avatar TM 360 Fourier transform infrared spectrometer operating in the 400–4000 cm^{-1} range. KBr/clay pressed disks were used for bentonites characterization.

Results and discussion

X-ray diffraction analysis

X-ray diffraction patterns of pristine (AN) and purified (AP) bentonites (Fig. 1) confirm the major presence of montmorillonite (M) with reflections relative to the plans (001), (002) and (005) and also the presence of minerals such as kaolinite (K) and quartz (Q), designated as impurities [34]. Figure 1 also shows that clay purification favored the removal of kaolinite present in the AN bentonite without promoting the structure collapse.

Figure 2 shows XRD patterns of pristine (AN), purified (AP) and organically modified (ANOA, APOA, ANOP, and APOP) bentonites with a 2θ range between 1.5° and 10.5°. The data indicate that ammonium and phosphonium surfactants did intercalate within both AN and AP galleries as the *d*-spacing (d_{001}) of ANOA, APOA, ANOP and APOP were higher than that of AN (1.34 nm) and AP (1.37 nm). Although intercalation was successful with both ammonium and phosphonium surfactants, a comparison of the d_{001} spacing obtained for ANOA and APOA regarding to those of ANOP and APOP show that the peaks of phosphonium modified bentonites shifted to lower angles, i.e., displayed a larger increase of d-spacing for ANOP and particularly for APOP. This can be related either to the lower packing density of the alkyl phosphonium surfactant or to a higher conformational disorder of the alkyl phosphonium chains within the bentonite layers [35]. It is believed that the higher basal spacing obtained with phosphonium modified bentonites could facilitate the intercalation or even the exfoliation of the organoclay in a polymer nanocomposite.

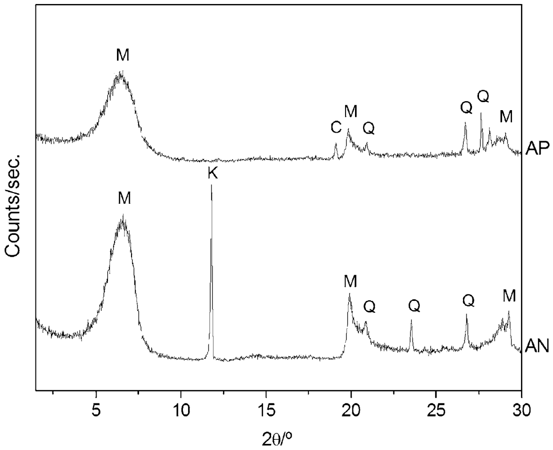

Fig. 1 XRD patterns for pristine (AN) and purified (AP) bentonites

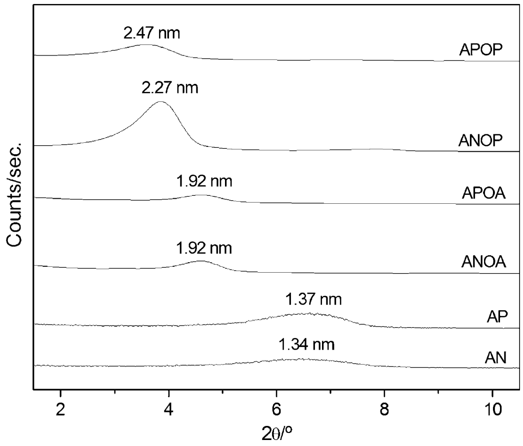

Fig. 2 XRD patterns for pristine (AN), purified (AP) and organically modified bentonites (ANOA, APOA, ANOP and APOP)

Thermogravimetric analysis

Thermogravimetric (Mass) and derivative thermogravimetry curves of the pristine (AN) and purified (AP) bentonites are shown in Fig. 3. Decomposition steps for these samples are presented in Table 1. Two thermal degradation transitions were observed for the AN clay. The first one (T_{H_2O}) occurred at 74 °C and is attributed to the volatilization of both free water (i.e., the water sorbed on the external surfaces of crystals) and water inside the interlayer space which forms hydration spheres around the exchangeable cations. The second transition (T_{OH}) took place at 720 °C and is

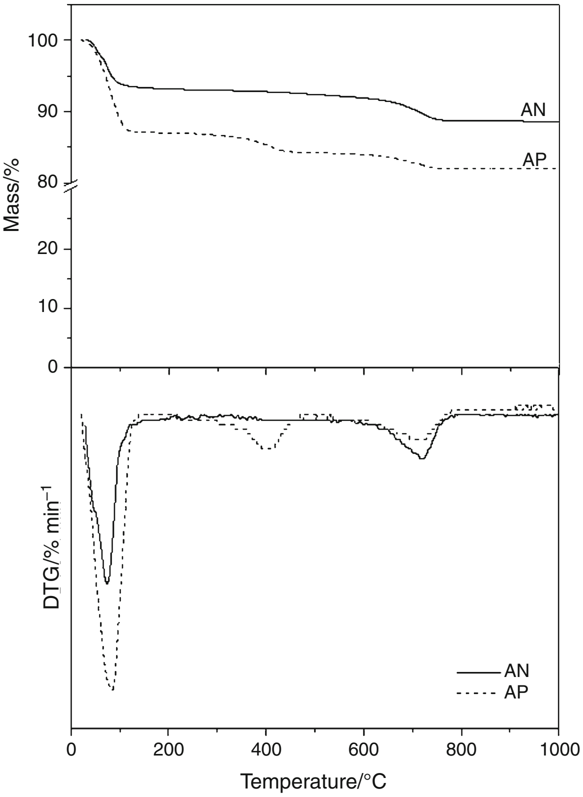

Fig. 3 TG and DTG curves of pristine (AN) and purified (AP) bentonites

Table 1 Decomposition steps for the neat surfactants and for pristine, purified and organically modified bentonites

Sample	T_{H_2O}/°C	Water/wt%	T_0/°C	T_{max}/°C	Intercalating agent fraction/wt%	T_{OH}/°C
A Surfactant	–	–	193	283	93.6	–
P Surfactant	–	–	230	393	98.5	–
AN	74	6.6	–	–	–	720
AP	82	10.2	–	–	–	730
ANOA	54	2.6	183	272	20.8	689
APOA	50	3.2	186	275	21.6	652
ANOP	46	0.7	193	343	13.9	665
APOP	47	1.1	232	346	14.4	588

attributed to the loss of structural water resulting from clay dehydroxylation [17, 36]. The purified clay (AP) displays T_{H_2O} at 82 °C, T_{OH} at 730 °C and an additional mass loss step at 420 °C (Fig. 3). This last step can be associated to residues from the purification process as evinced by FTIR (as shown below Fig. 6) where absorption band at 1558 cm^{-1} attributed to carbonate residues is observed [37, 38]. The absence of this band in the spectrum of purified organobentonites (APOA and APOP) (Fig. 6) suggests that this residue is removed during the bentonite organic modification, possibly during the washing step. The X-ray diffractogram of purified bentonite (AP) in Fig. 1 shows a peak at 2θ equal to 19° also attributed the carbonate residue (C) [34] corroborating FTIR data.

Figure 4 shows TG and DTG curves for organobentonites and Table 1 presents the decomposition steps for these samples. The amount of free water and interlayer water (T_{H_2O}) is reduced in the organobentonites (ANOA, APOA, ANOP, and APOP) compared as unmodified bentonites (AN and AP) reflecting the weaker hydration of organic cations [39]. The type of surfactant used in bentonite organophilization affected both the volatilization temperature values (T_{H_2O}) and the amount of water adsorbed (Table 1). Alkyl phosphonium modified bentonites (ANOP and APOP) showed smaller T_{H_2O} values and water content than alkyl ammonium modified bentonites (ANOA and APOA), which is consistent with the more hydrophobic nature of alkyl phosphonium ions [25].

The decomposition of ammonium surfactant (A surfactant) takes place in three steps at temperatures ranging between 193 and 554 °C. The maximum mass loss occurs at 283 °C and two small additional losses occur at 314 and 518 °C as shown in the DTG curve (Fig. 4). The alkyl ammonium intercalated within bentonite galleries displays the same thermal decomposition profile of the pure surfactant. Alkyl ammonium modified bentonites (ANOA and APOA) presented onsets surfactant decomposition temperatures (T_0) of about 183 and 186 °C and maximum surfactant decomposition temperatures (T_{max}) around 272 and 275 °C, respectively. The organic fraction in the organobentonites as determined by the total mass loss from 200 to 500 °C was 20.8% and 21.6%, corresponding to ca. 98.4% and 100.0% of the clay CEC, respectively (Table 1).

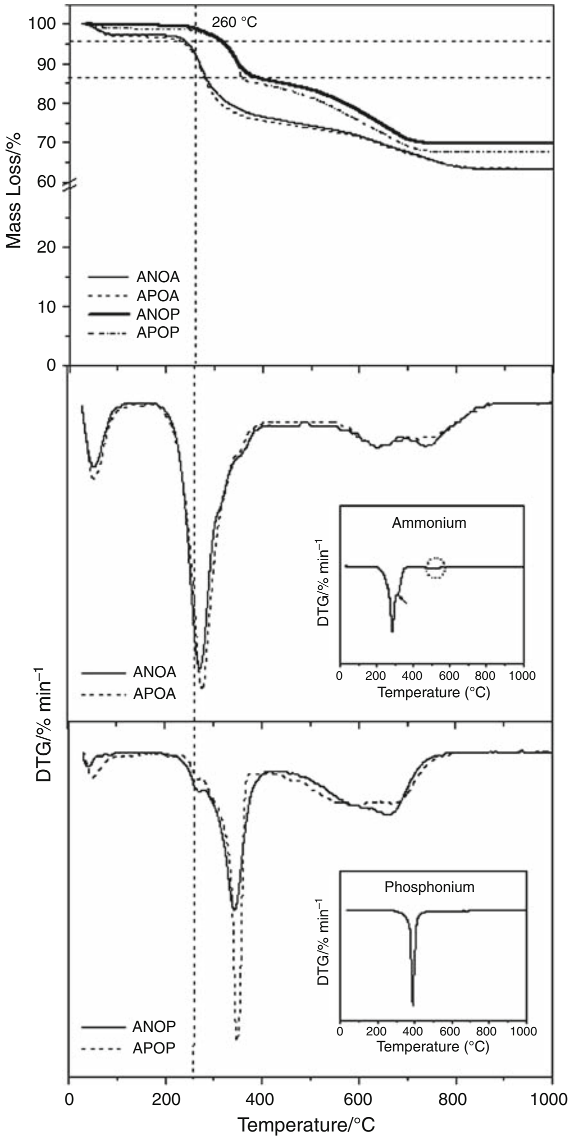

Fig. 4 TG and DTG curves of organically modified bentonites (ANOA, APOA, ANOP and APOP) and ammonium and phosphonium surfactants

On the other hand, the decomposition of phosphonium surfactant (P surfactant) takes place in one step, between 230 and 478 °C, with a maximum mass loss at 393 °C. Phosphonium modified bentonites (ANOP and APOP), displayed a second DTG peak, observed at lower temperatures (Fig. 4), which is absent in the TG curve of the surfactant alone. This second peak is associated with the surfactant adsorbed on the external surfaces of the clay [2, 39].

The adsorption of cationic amphiphilic substances at the clay/liquid interface is mainly ruled by two types of reactions, the cation exchange reaction and the surfactant adsorption reaction at sites that are nonexchangeable [39, 40]. The latter involves interactions between the hydrocarbon chains of these cations as well as interactions between the chains and the clay surface. It is believed that the phosphonium surfactant chains, unlike those of the ammonium surfactant, are arranged in a predominantly gauche conformation within the galleries of the clay [41–43]. This arrangement hinders the total exchange of organic cations with the Na^+ ions and free surfactant is adsorbed on the external surface of the clay. This hypothesis is confirmed by the data in Table 1, which shows that a smaller amount of phosphonium surfactant intercalated in the clays (ANOP and APOP) if compared to the amount of ammonium surfactant intercalated in these same clays (ANOA and APOA). The onset (T_0) and maximum surfactant decomposition temperature (T_{max}) is also presented in Table 1.

As expected, organoclays display a lower dehydroxylation temperature (T_{OH}) than unmodified clays. This can be attributed to the lower relative amount of inorganic material in the organobentonites. The data also shows that the type of surfactant employed practically did not affect this transition [17, 38].

In summary, the thermal behavior of organobentonites is affected by bentonite purification and, especially, by the chemical structure of the surfactant employed for organofilization. The thermal stability of purified bentonite modified with alkyl phosphonium surfactant was higher than that of alkyl ammonium modified clays. Although the surfactant decomposition maximum temperatures (T_{max}) for bentonites modified with the ammonium surfactant (ANOA and APOA) are higher than some polymer processing temperatures, these bentonites presented higher mass lost (~8.2%) than those modified with the phosphonium surfactant (~1.3%) at 260 °C (Fig. 4). The alkyl ammonium cations are reported to decompose following Hofmann elimination to produce α-olefins, amines or intermediates, leaving acidic protons on the silicate surfaces caused by *β*-carbon scission (Fig. 5). These protons can act as Brønsted acidic sites and thus promote polymer degradation [44–46]. Thus, phosphonium surfactant modified bentonites, especially the purified clay, seem to be best suited for the preparation of polymer nanocomposites by melt processing whenever polymeric matrices requiring high processing temperatures are to be employed.

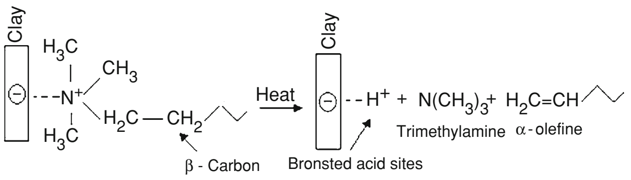

Fig. 5 Reaction scheme for the Hofmann elimination of organobentonite based on the general mechanism proposed by Fornes et al. [44]

Infrared spectroscopy

Thermogravimetric and derivative thermogravimetry data showed that the AP bentonite is more stable than the AN bentonite modified with the same surfactant. This suggests that the purification led to a lower amount of acidic sites as indicated in the FTIR data.

Figure 6 shows the typical spectrum of pristine (AN), purified (AP) and organically modified bentonites (ANOA,

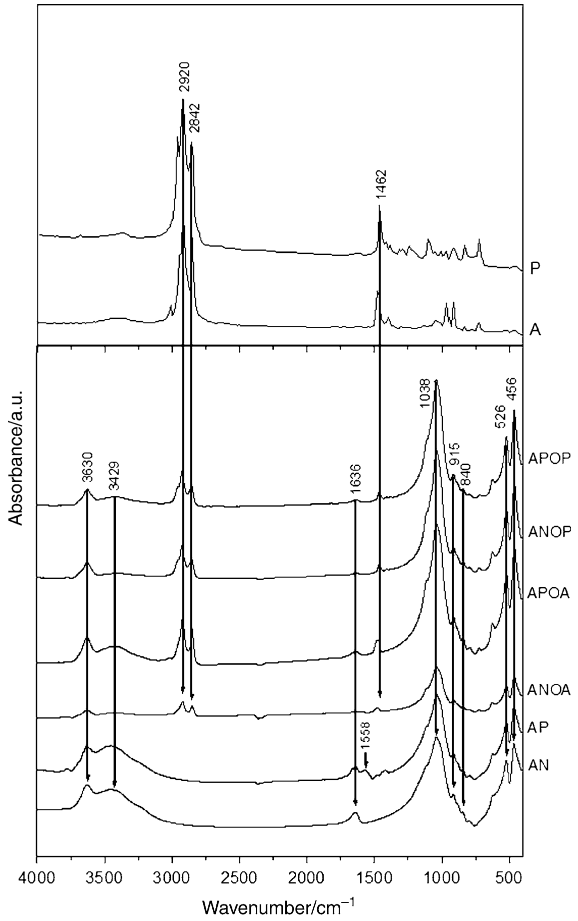

Fig. 6 FTIR spectra of pristine (AN), purified (AP) and organically modified bentonites (ANOA, APOA, ANOP) and of ammonium (A) and phosphonium (P) surfactants

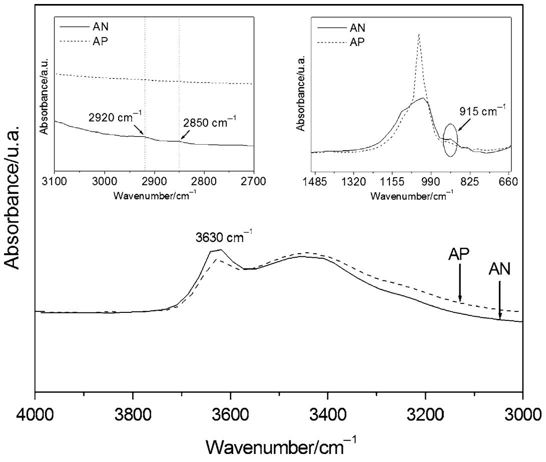

Fig. 7 FTIR spectra of pristine (AN) and purified (AP) bentonites in the regions of 4000–3000, 3100–2700 and 1485–660 cm^{-1}

APOA, ANOP and APOP) as well as of the ammonium and phosphonium surfactants (A and P) employed in this study. The major bands observed could be assigned to stretching vibrations of Al–OH (absorption near 3630 cm^{-1}) corresponding to inner hydroxyl groups, lying between the tetrahedral and octahedral sheets and are typical for smectites with a high amount of Al in the octahedral layer. The broad band near 3429 cm^{-1} is attributed to hydroxyl stretching vibrations (free and interlayer water molecules) and the band near 1636 cm^{-1} is related to the (H–O–H) bending vibrations of water molecules adsorbed on montmorillonite [47]. The band at 1038 cm^{-1} is attributed to the Si–O stretching vibrations, and those at 915 and 840 cm^{-1} are assigned to the bending vibrations of Al–Al–OH and Al–Mg–OH hydroxyl groups on the edges of the clay platelets. The peaks at 525 and 456 cm^{-1} are associated with Si–O–Al (octahedral Al) and Si–O–Si bending vibrations, respectively [47, 48]. The position of the band at 3429 cm^{-1} and of the peaks at 3630, 915, 840 and 526 cm^{-1} did not shift after purification and organophilization which is taken as an indication that these procedures did not modify the bentonite structure.

At a first glance it may seem that the surface acidity of both bentonites (AN and AP) is equivalent and that organic matter as impurities are absent from both clays. However, upon a scale expansion (Fig. 7) it is possible to see that the intensities of the FTIR bands at 3630 cm^{-1} (stretching vibrations Al–OH) and at 915 cm^{-1} (bending vibrations Al–Al–OH) are lower in the AP bentonite. This indicates that the purified clay (AP) has a smaller amount of aluminum and a lower concentration of hydroxyl groups (acidic sites) [48] than the pristine clay (AN). Figure 7 also shows that absorption bands at 2920 and 2850 cm^{-1}, which were assigned to organic matter [49], are present in the spectrum of pristine bentonite (AN) and absent in that of the purified bentonite (AP) indicating that the purification procedure was capable of effectively removing organic contaminants from the AN bentonite.

All organically modified bentonites (ANOA, APOA, ANOP and APOP) display two FTIR absorption bands at 2920 and 2842 cm^{-1}, which are attributed to, respectively, CH_2 asymmetric and symmetric stretching modes. These absorption bands are within the same spectral range for ammonium and phosphonium surfactants (Fig. 6) and indicate that both alkyl-ammonium and alkyl-phosphonium ions were incorporated within the galleries of the bentonites [23].

Conclusions

The thermal behavior of the organobentonites investigated was affected by bentonite purification and, especially, by the chemical structure of surfactant employed for clay organophilization. Although all organobentonites obtained might be used for the preparation of polymer nanocomposites by melt processing with polymeric matrices requiring high processing temperatures, those modified with phosphonium surfactant, particularly the purified bentonite, seem most appropriate for this application due their higher thermal stability.

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