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Preparation and thermal properties of organically modified bentonite with ionic liquids

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Abstract : Local bentonite clay was organically modified via cation exchange reaction using four ionic liquids (ILs: MPrPI, MPrPPI, BMIM and BrPrMIM) differing in their chemical architecture. In order to confirm the insertion of these ILs in layered silicates, basal spacings of interlamellar structure, have been characterized using X-ray diffraction (XRD) analysis, results indicate that the interlayer spacing of the piperidinium organo-bentonite ranged from 14.46 to 14.86 Å, while it ranged between 13.10 and 14.46 Å in imidazolium organo-bentonite. More specifically, a monolayer configuration of ILs within the interlayer space was indicated by XRD results. To obtain information on the thermal stability and degradation products, thermal properties of these imidazolium and piperidinium ions exchanged on the surface of bentonite were investigated by using differential scanning calorimetry

(DSC) and thermogravimetric analysis (TGA/DTG) from room temperature to 400°C. These thermal measurements revealed that organobentonite showed two distinct regions; (I) from 50 to 150°C corresponds to the removal of adsorbed water and the elimination of the water species coordinated to the interlayer cations; (II) thermal degradation of ionic liquids took place in the temperature range of 150 - 350°C, also, the imidazolium modified bentonites were thermally more stable than those modified with piperidinium. These results seem to be promising regarding to the potential application of these modified bentonites as adsorbents or for the melt processing preparation of nanocomposites. © Trade Science Inc.

Keywords : Organoclay; Ionic liquids; Thermal characterization; XDR; ATG/DTG.

INTRODUCTION

Organoclays have drawn much attention from the academe to the industrial communities for a long time^[1]. Many researchers have investigated these products because of their interesting properties^[2]. They represent a new generation of adsorbents for both organic and inorganic pollutants; this is due to their small particle size, swelling capacity, anisotropic shape, reactive

surfaces, large specific surface area and high ion exchange capacity^[3]. The advantage that the organoclays present is the possibility of changing their properties by varying the structure of the intercalated organic species^[4], the combination of the hydrophobic nature of the organic species and the layered structure of the silicate layers leads to unique physicochemical properties. As a consequence, a number of previous studies have demonstrated that the interlayer spacing

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distance is a function of the lengths of intercalated molecules^[5]. In these applications, it was noticed that such organic modification alters the nature of clay from hydrophilic to hydrophobic, imparting enhanced interaction of the clay products towards hydrophobic pollutants in the environment^[6].

Nevertheless, the surface treatment of clay minerals has received great interest, for example, ion exchange of the inorganic cations with organic cations, usually with quaternary ammonium compounds, can change the surface properties^[7].

In the same way, and in order to determine the utility of ionic liquids as surfactants, previous studies have shown that the intercalation of interlayer space by a series of substituted imidazolium^[8], phosphonium^[9], ammonium^[10], pyridinium^[11] or pyrrolidinium^[12] ionic liquids not only changes the surface properties from hydrophilic to hydrophobic but also greatly increases the basal spacing of the layers.

As reported previously by Siao et al^[13], the interlayer spacing values of these materials were an important parameter for the intercalation of the polymers in the preparation of clay polymer nanocomposites. On another aspect, organoclays have found many applications as adsorbents of hazardous compounds, catalysts and precursors for the preparation of porous heterostructure clays^[14].

Inspired by the previous research, the present work focuses on the preparation and characterization of imidazolium and piperidinium ions differing in their chemical architecture, exchanged on the surface of bentonite, with the objective of preparing organoclays with higher thermal stability. Three modes of thermal analysis, thermogravimetric analysis (TGA), differential thermal (DTG), and differential scanning calorimetry (DSC) were used to determine this stability. Also, X-ray diffraction (XRD) angles were performed to characterize the basal spacings of interlamellar structure of these novel organically modified clays. The novelty of this work is the fact that we use a low cost local clay from Algeria and ionic liquids synthesized by us that have never used in this type of study.

EXPERIMENTAL

Materials and methods

1. Reagents and materials

The reagents used in this study are: 1-methylimidazole (99 wt.%), N-methyl piperidine (95 wt.%), 1-bromopropane (99.5 wt.%), 1-bromobutane (99.5 wt.%), ethyl acetate, diethyl ether and N,N-dimethylformamide. They were purchased from Fluka and used as received. Deionized H₂O was obtained by using a Millipore ion-exchange resin deionizer.

2. Bentonite sample

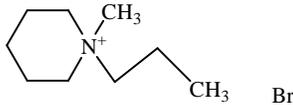
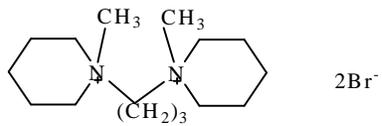
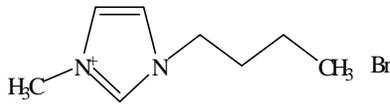
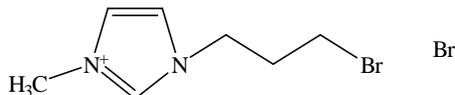
The bentonite used in this study was mined from the Hammam Bouhrara deposit (Maghnia, Algeria) was kindly supplied by ENOF (the National Company for Non-ferrous Mining Products, Algeria). The chemical composition was found to be as follows: 62.4% SiO₂, 17.33% Al₂O₃, 1.2% Fe₂O₃, 3.56% MgO, 0.8% K₂O, 0.81% CaO, 0.2% TiO₂, 0.33% Na₂O, 0.05% As, 13.0% loss on ignition at 900 °C. The mineralogical analysis showed that the native crude clay mineral contains preponderantly montmorillonite (85%). The clay composition also includes quartz (10%), cristoballite (4.0%) and beidellite (1%). The bentonite was purified according to the method published in a previous study^[15]. The cation exchange capacity (CEC) of the bentonite has been given by the research of Makhoukhi et al.^[16] and was found to be 67.5 meq/100 g clay.

Synthesis of ionic liquids

Synthesis of 1-methyl-1-propyl piperidinium bromide and bis-methyl piperidinium propylidene bromide was reported earlier and the synthesis conditions and characterization of these two piperidinium ILs were given in our previous published studies^[17,18].

The ionic liquid, 1-butyl-3-methylimidazolium bromide and 1-butylbromide-3-methylimidazolium bromide were synthesized as described in the literature^[19,20]. Briefly, 1-methylimidazole (6.79 ml, 85.26 mmol), and 1-bromobutane (9.87 ml, 89.03 mmol) were combined in a 1:1 ratio for [BMIM⁺][Br⁻] and in a 1:2 ratio for [BrBMIM⁺][Br⁻] before being stirred at 70°C for 6 hours. The removal of residual volatile compounds from the ionic liquid was made in vacuum using a rotary evaporator and washed then with fresh ethyl acetate (100 mL). The obtained products were analyzed by ¹H, ¹³C NMR (DRX 400 MHz spectrometer) and FTIR (Perkin-Elmer Spectrum BX)

TABLE 1 : Chemical structures of prepared ILs

ILs	Formula /Molecular weight	Structure
1-Methyl-1-propyl piperidinium bromide	[MPrPI ⁺][Br ⁻] 222.17	
Trimethylene bis-methyl piperidinium bromide	[MPrPPI ⁺][2Br ⁻] 400.24	
1-Butyl-3-methylimidazolium bromide	[BMIM ⁺][Br ⁻] 219.12	
1-Propyl bromide-3-methylimidazolium bromide	[BrPrMIM ⁺][Br ⁻] 283.99	

to confirm the absence of any major impurities.

The intercalation of the layered clays by ionic liquids (named: [MPrPI], [MPrPPI], [BMIM] and [BrPrMIM]) was undertaken in order to determine the utility of ionic liquids as surfactants for exfoliating these layered clays. Their names and structures are given in TABLE 1.

Preparation of ionic liquids modified bentonites

The intercalation of the ILs ionic liquids into the bentonite galleries was carried out by cationic exchange reaction following a previously described procedure^[16, 21], briefly; aqueous solutions of ionic liquids were prepared by dissolution in 100 ml of distilled water of each IL. The ionic liquids intercalated bentonites were prepared during 24 h by slow addition of 10 g of bentonite (1g/h) to ionic liquids in a reactor under medium speed stirring at room temperature. The products were then separated by filtration, washed several times with distilled water, dried in a convection oven at 80°C during 24 h and finally crushed in a mortar.

Characterization of raw and modified bentonites

X-ray diffraction (XRD) analyses were performed with a fine-focus Cu anode source (Diffractis 586 Enraf Nonius) by selecting the CuK α radiation line (wavelength λ of 1.54 Å), focused by a multilayer mirror and collimated by slits. Diffraction patterns were captured using an X-ray tube voltage and current of 40 kV and 20 mA, respectively and an exposure time of 300 s.

The ranges of scattering vector $q = 4 \pi \sin\theta/\lambda$ (θ

being half the scattering angle) were 0.08–0.50 Å⁻¹. The repeat distances d characteristic of the structural arrangements were given by q (Å⁻¹) = $2\pi/d$ (Å). Silver behenate and highly pure tristearin were used as standards to calibrate detector^[22]. The measurement accuracies of the q -values have been estimated at 0.0005 Å⁻¹.

In order to evaluate the thermal stability of the raw and modified bentonites, as well as the amount of intercalated ionic liquids products, thermo-gravimetric analysis (TGA) and differential thermal analyses (DTG) were performed with a NETZSCH STA 449 C instrument using 4 ± 0.001 mg samples. The samples were heated at a rate of 5°C/min from room temperature to 400°C in an argon atmosphere. The temperature reproducibility of the TGA instrument was $\pm 3^\circ\text{C}$.

In the same conditions, differential scanning calorimetry (DSC) thermograms were recorded by using a NETZSCH DSC 204 F1 instrument, which operated at a ramp of 10°C/min from room temperature to 400°C flowing argon atmosphere, temperature controller with an accuracy of $\pm 0.001^\circ\text{C}$ achieved in the entire range of measurements.

RESULTS AND DISCUSSION

Spectral data for ionic liquids

The details of spectra (¹H, ¹³C NMR and Ftir) of ILs were found to be identical with those reported in the literature and are given below:

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TABLE 2 : Spectral data of prepared ILS

IL	Spectral data
[MPrPI ⁺][Br ⁻]	¹ H-NMR (CDCl ₃) δ _H (ppm) : 0.93 (t, 3H, J = 7, CH ₂ CH ₃), 1.47-1.64 (m, 8H, 4×CH ₂), 3.23-3.29 (m, 6H, 3×N ⁺ CH ₂), 3.31 (s, 3H, N ⁺ CH ₃); ¹³ C-NMR (CDCl ₃) δ _C (ppm) : 15.13, 19.51, 20.40, 24.30, 47.70, 59.63, 61.63, 123.75; IR (ν̃ /cm ⁻¹): 2950 [ν(C-H)], 1467 [δ(C-H)], 1261 [ν(C-N)], 949,750 [ν(C-H)].
[MPrPPI ⁺][2Br ⁻]	¹ H-NMR (D ₂ O) δ _H (ppm) : 1.63 (m, 4H, 2·CH ₂ CH ₂ CH ₂), 1.85 (m, 8H, 4·CH ₂ CH ₂ CH ₂), 2.29 (m, 2H, CH ₂ CH ₂ CH ₂), 3.05 (s, 6H, 2·N ⁺ CH ₃), 3.34-3.36 (t, 12H, 6·N ⁺ CH ₂ CH ₂); ¹³ C-NMR (D ₂ O) δ _C (ppm) : 15.13, 19.51, 20.40, 47.70, 59.63, 61.63; IR (ν̃ /cm ⁻¹) : 2956 [ν(C-H)], 1466 [δ(C-H)], 1227 [ν(C-N)], 755 [ν(C-H)].
[BMIM ⁺][Br ⁻]	¹ H-RMN (CDCl ₃) δ _H (ppm) : 10.12 (1H, s, N ⁺ CHN), 7.62 (1H, s, N ⁺ CHCHN), 7.46 (1H, s, N ⁺ CHCHN), 4.28-4.24 (2H, t, J=2.6 Hz, NCH ₂ CH ₂ CH ₂), 4.06 (3H, s, N ⁺ CH ₃), 1.86-183 (2H, m, J=6.4 Hz, NCH ₂ CH ₂), 1.27-1.21 (2H, m, J=2.8 Hz, NCH ₂ CH ₂ CH ₂), 0.81 (3H, t, J=6.8 Hz, N ⁺ (CH ₂) ₃ CH ₃). ¹³ C-RMN (CDCl ₃) δ _C (ppm): 13.53, 19.50, 32.22, 36.80, 49.87, 122.30, 123.88, 137.20; IR (ν̃ /cm ⁻¹) : 3068 [ν(=C-H)], 2958, 2872 [ν(C-H)], 1632 [ν(C=C)], 1463 [δ(C-H)], 1168 [ν(C-N)], 751 [ν(C-H)].
[BrPrMIM ⁺][Br ⁻]	¹ H-RMN (CDCl ₃) δ _H (ppm) : 7.58 (1H, s, N ⁺ CHN), 7.47 (1H, s, N ⁺ CHCHN), 6.96 (1H, s, N ⁺ CHCHN), 4.29-4.25 (2H, t, J=7.8 Hz, NCH ₂ CH ₂ CH ₂), 4.05-4.01 (2H, m, J=2 Hz, NCH ₂ CH ₂ CH ₂ Br), 1.82(2H, t, J=7.6 Hz, N(CH ₂ CH ₂ CH ₂)). 1.77-1.72 (3H, s, N ⁺ CH ₃); ¹³ C-RMN (CDCl ₃) δ _C (ppm) : 30.02, 31.67, 36.06, 48.62, 121.20, 122.94, 143.49; IR (ν̃ /cm ⁻¹) : 3071 [ν(=C-H)], 2958, 2873 [ν(C-H)], 1632 [ν(C=C)], 1462 [δ(C-H)], 1137 [ν(C-N)], 753 [ν(C-H)], 652 [ν(C-Br)].

Characterization of modified bentonites

1. X-ray diffraction analyses

The X-Ray Scattering measurements represent a powerful way to understand the changes in the structure of the clay environment. Figure 1 exhibits XRD pattern of raw and modified bentonites. The range period (d) was calculated from $d = 2\pi/q$, where q is the position of the peak at maximum of the bragg reflections. XDR patterns showed reflections at $q = 0.488, 0.416, 0.434, 0.422, 0.434$ and 0.479 \AA^{-1} , which correspond to the interlayer distances of $d = 12.86, 15.08, 14.46, 14.86,$

14.46 and 13.10 \AA for the raw bentonite, purified bentonite, B-[MPrPI], B-[MPrPPI], B-[BMIM] and B-[BrPrMIM], respectively, located at 2θ between 4° and 8° (see Figure 1 (b)).

Firstly, this figure clearly shows the increase in the basal spacing of bentonite from 12.86 \AA for the raw bentonite to 15.08 \AA for purified bentonite, these values confirming that the raw bentonite is hydrated with one monolayer, while the purified bentonite has two layers of interlayer water, which is consistent and identical with other values reported in the literature^[23,24].

It can be noticed that in the purification step there is

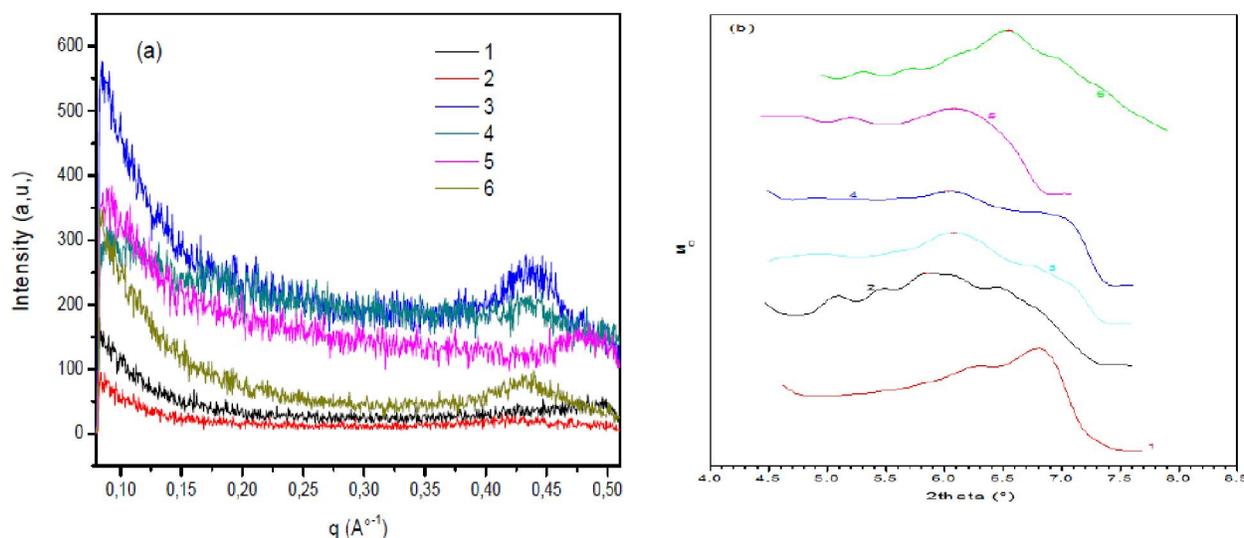


Figure 1 : X-ray diffraction patterns of the raw and modified bentonite at 20°C (1) BN, (2) BP, (3) B-[MPrPI], (4) B-[MPrPPI], (5) B-[BrMBIM], (6) B-[BrMBIM]. (a) in the q range 0.08-0.50, (b) in the 2θ range 4-8°

an increase of the basal spacing of clay, which indicates that some water molecules remain between the bentonite layers during washing of bentonite.

The basal spacing values of the raw and modified bentonite are shown in TABLE 3. From this data, the basal spacings for the four organoclays prepared, are between 13.10 and 14.86 Å. In other words, the thickness of the bentonite layer is 9.6 Å. Therefore, the interlayer distance is 0.24-0.22 Å. This shift is a clear signature of the intercalation of the ILs between the layers of bentonite^[25]. Nevertheless, the d_{001} values indicate that the exchanged [MPrPI⁺], [MPrPPI⁺] and [BMIM⁺] ions adopt monolayer arrangements in the interlayer depending on the amount of the modifier loading and on its orientation.

TABLE 3 : d-Spacings of the raw and modified bentonite calculated from XRD patterns

Clay/Organo-bentonite	2θ°	d-Spacing (Å)	Change in d spacing Vs bentonite (Å)
BN	6.86	12.86	-
BP	5.85	15.08	+ 02.22
B-[MPrPI]	6.10	14.46	+ 01.60
B-[MPrPPI]	6.04	14.86	+ 02
B-[BMIM]	6.10	14.46	+ 01.60
B-[BrMBIM]	6.73	13.10	+ 0.24

In this way, bentonite intercalation with dicationic piperidinium is more important to that obtained by a monocationic piperidinium; this difference can be explained by the molecular weight of the IL and its arrangement into the bentonite galleries.

Previous studies by Gu et al. have studied bis-pyridinium dibromides modified organo-bentonite. These authors demonstrated that this dicationic ionic liquid ion lies parallel to the siloxane surfaces and forms monolayers^[26].

On the other hand, the intercalation of bentonite with [BMIM⁺] provides access to the basal spacing ($d=14.46$ Å) is more important to that obtained by [BrPrMIM⁺] (13.10 Å), this difference can be explained by the intercalation mechanism and by the chemical structure of IL ions exchanged on the surface of bentonite, also, with their arrangement into the bentonite galleries. In the fact, the B-[BrPrMIM] physically adsorbed on the external surface of the clay had bromide atom attached with the chain propyl, where this bromide

was keyed and clogged into the surface and established a physical adsorption. Thus, it can be concluded that the intercalation of the [BrPrMIM⁺] into narrow interlayer spacing is difficult due to the steric hindrance caused by the large size of bromine atoms, leading to a significant decrease in the d-spacing of organoclay.

This result is compare to that published by Reinert et al^[27] who studied the intercalation of the same IL salt [BMIM⁺] with chloride anion on montmorillonite and found a value of 13.69 Å. Also Abdallah and Yilmazer^[28] who, when studying the adsorption of same IL [BMIM⁺] salt with bromide hexafluorophosphate anions on sodium montmorillonite, found that the intercalated organoclay presented basal spacing of 13.4 Å.

Generally, the molecular weight of [MPrPPI⁺] was larger than that of [MPrPI⁺] by 1.69%, than that of [BMIM⁺] by 1.72% and by 1.17% for [BrPrMIM⁺], meaning that the amount of the exchanged [MPrPPI] in the bentonites interlayers was larger than that of the exchanged [MPrPI⁺], [BMIM⁺] and [BrPrMIM⁺]. The d-spacing of the organobentonites increased in the following order:

B-[MPrPPI] > B-[MPrPI] H⁺ B-[BMIM] > B-[BrPrMIM]. These results suggest that the swelling of the clay is directly related to the steric size and molecular weight of the intercalated molecule, and are in good agreement with previous studies^[29].

2. Thermogravimetric analysis (TGA, DTG and DSC)

As mentioned before, one of the objectives of this organomodification by using ILs is to produce organoclays with improved thermal stability, which is an important feature for further applications. For this reason, and in order to evaluate thermal properties of these organoclays, three mode of thermal analysis were used: TGA, DTG, and DSC.

TABLE 4 : Temperatures decomposition of raw and modified bentonites discernible from curve DTG

Clay/Organo-bentonite	Temperature at step I (°C)	Temperature at step II (°C)
BN	94	-
PB	112	-
B-[MPrPI]	78	255
B-[MPrPPI]	61	261
B-[BMIM]	65	290
B-[BrMBIM]	83	306

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The results are reported in terms of the maximum decomposition temperature which was found from derivative peaks (TABLE 4). The raw and purified bentonite show mass losses of 9.4% and 10.2% respectively below 150°C due to the removal of the bounding, physisorbed water around metal cations in the exchangeable sites of bentonite; there is no further degradation thereafter.

The four organobentonites (B-[MPrPI], B-[MPrPPI], B-[BMIM] and B-[BrPrMIM]) showed 7.7%, 8.1%, 8.2%, 8.5% weight losses, respectively, in the TG curve (Figure 2). However, in the case of the B-[MPrPI], the weight loss, which is attributed to the decomposition of the IL, was observed as 13.20% and total weight loss of the B-[MPrPI] was 22.08%. In the case of the B-[MPrPPI], weight loss, which is also attributed to the decomposition of the IL, was observed as 12.08% and the total weight loss of the B-[MPrPPI] was 18.48%. For the B-[BMIM], the weight loss, which, again, is attributed to the decomposition of the IL, was observed as 6.78% and the total weight loss of the B-[BMIM] was 17.63%.

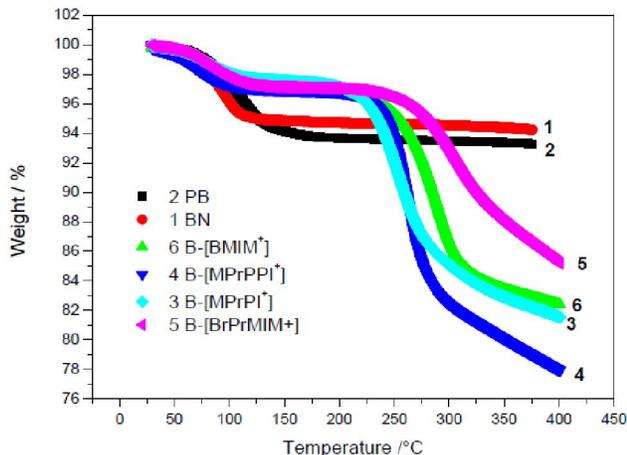


Figure 2 : TGA curves of the raw, purified and modified bentonites

On the other hand, The DTG curves of raw and purified bentonite show one endothermic peak: the peak at 94°C is ascribed to the bounding water in the raw bentonite; another peak at 112°C in the purified bentonite is related to the physically adsorbed water. The different temperature value is related to the percentage of hydration water present in the interlayer.

The TG-DTG traces of organobentonites show two peaks in the temperature range of 50–300°C, typically; the first corresponds to the dehydration of adsorbed

water and interlayer water. This first water loss follows the trend B-[MPrPPI] > B-[MPrPI] > B-[BMIM] > B-[BrPrMIM] due to their hydrophobic character caused by the organomodification, and depending of intercalation efficiency observed in XDR patterns. On further heating, the second peak show that the decomposition of the ILs started at 200°C and was complete at 350°C, depending on the ionic liquid type (Figure 3). The results are in general agreement with similar behavior was observed by Awad et al.^[30] and Reinert et al^[27] where the piperidinium salts usually possess a lower thermal stability than imidazolium ones.

The TGA/DTG analyses indicated the following observations:

- B-[MPrPI] started and finished decomposing before B-[MPrPPI]; this difference could be assigned to nature and on physical-chemical feature of ionic liquids intercalated into the interlayer of bentonite.
- Whatever the cation type, and based on the results presented in literature, the thermal stability of B-[BMIM] was lower than B-[BrPrMIM] one. The fact that the butyl imidazolium starts decomposing before the propyl bromide can be explained by the presence of bromine atom linked in the propyl chain attached to nitrogen^[31].
- The piperidinium bentonites started and finished decomposing before the imidazolium bentonites; this difference could be explained by the higher stability of the imidazolium cation. These results confirm that the imidazolium salts are excellent candidates for application in nanocomposites.

From the thermo-grams of organobentonites, it was clear that the thermal stability could be arranged in the order :

B-[MPrPI] < B-[MPrPPI] < B-[BMIM] < B-[BrPrMIM].

In addition, no thermal decomposition or dehydroxylation of the structural OH units of the bentonite was detected within the operational temperature range limit from 0 to 400°C in our study.

According to DTG test, Figure 3 shows mass loss peaks for B-[MPrPI], B-[MPrPPI] at 255°C and 261°C, and for B-[BMIM], B-[BrPrMIM] at 290°C and 306°C, respectively, demonstrating that the piperidinium organo-bentonite is more readily decomposed than imidazolium organo-bentonite.

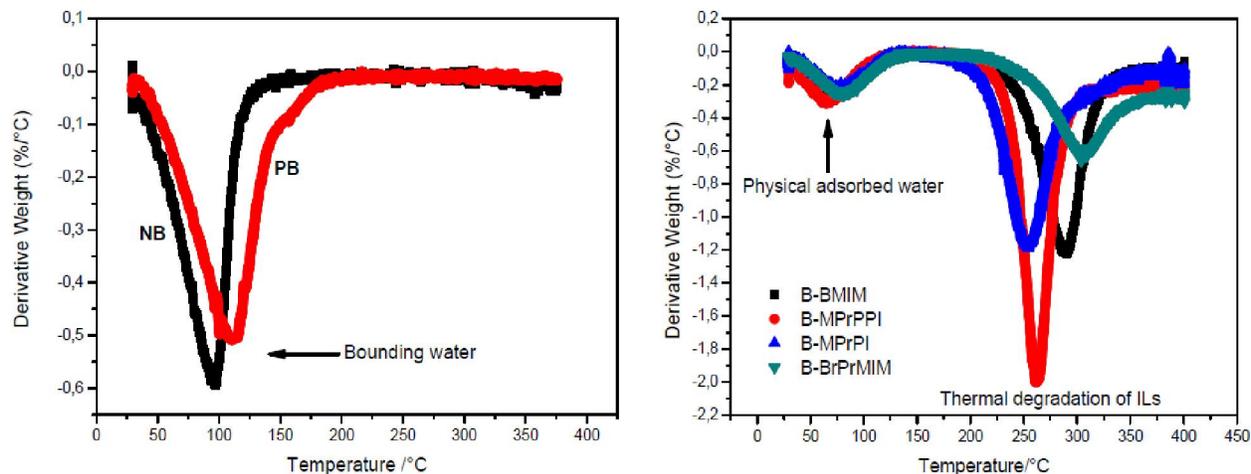


Figure 3 : DTG curves of the raw, purified and modified bentonites

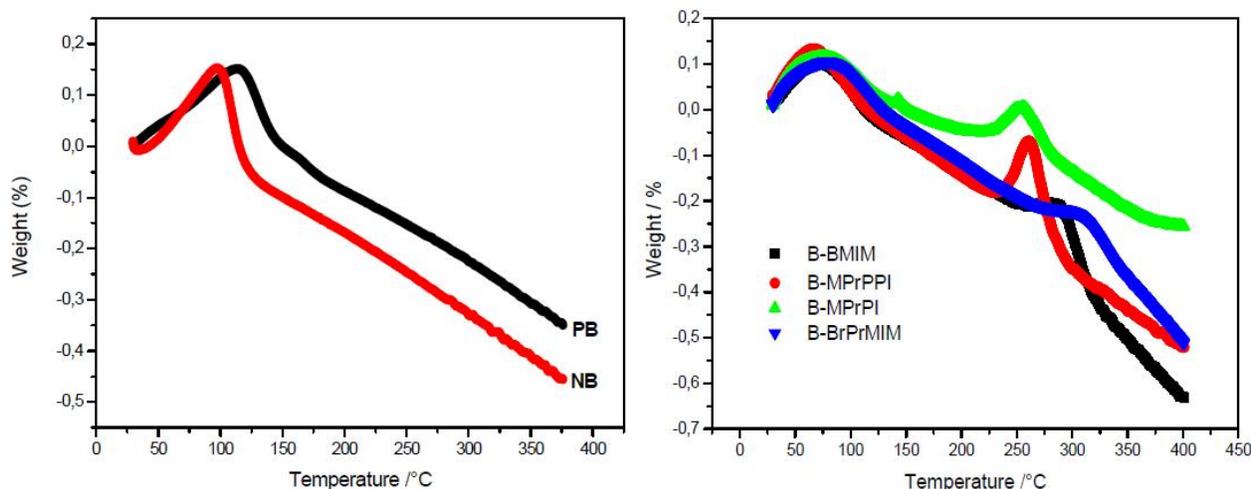


Figure 4 : DSC curves of the raw, purified and modified bentonites

DTG/DSC curves of the raw and purified bentonite shows one peak advanced that 100°C, due to the volatilization of the free water. Comparatively, modified organo-bentonites have lower mass loss at this temperature, implying less free water in the modified bentonites, A possible explanation is that the presence of ILs lowers the surface energy of the inorganic material, and converts the hydrophilic silicate surface to an organophilic one^[32-34].

As conclusion in this part, the TGA/DTG study exactly fits and confirmed the DSC study. It was also observed from TGA/DTG and DSC analysis that thermal stability depend on the mass loss of the intercalated IL.

CONCLUSION

In summary, Bentonite was organically modified using four different ILs of organo-modifiers namely; 1-methyl-1-propyl piperidinium bromide, trimethylene bis-

methyl piperidinium bromide, 1-butyl-3-methylimidazolium bromide, 1-propyl bromide-3-methylimidazolium bromide. Analysis was conducted using XRD, TGA, DTG and DSC.

The variation of the Bentonite interlayer space gallery was affected by the type of organo-modifiers used. The prepared organoclays could be arranged according to their space galleries in the order: B-[MPrPPI] > B-[MPrPI] > B-[BMIM] > B-[BrPrMIM]. Most importantly, XDR results indicated that variation of the interlayer space gallery was effected by the type of the penetrator used; the molecular weight was the dominant factor, whereas for the organoclays, the chemical structure controlled the thermal stability. Also, the arrangement of the imidazolium and piperidinium ions exchanged is mainly monolayer in the bentonite interlayer.

Furthermore, the study of the thermal behaviour of the organically modified bentonite shows a two step

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degradation process due to the overlapping of clay dehydration processes and organic modifier volatilization. The thermal stability of the prepared modified bentonites can be arranged in the order: B-[MPrPI] < B-[MPrPPI] < B-[BMIM] < B-[BrPrMIM].

To sum up, these organically modified bentonites have potential utility in the preparation of polymer nanocomposites and in other possible applications. The application of these modified montmorillonites is under investigation.

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REFERENCES

- [1] L.B.De Paiva, A.R.Morales, F.R.V.Díaz; Appl. Clay Sci., **42**, 8 (2008).
- [2] R.S.Juang, S.H.Lin, K.H.Tsao; J. Colloid Interface Sci., **269**, 46 (2004).
- [3] F.Bergaya, G.Lagaly; Appl. Clay Sci., **19**, 1 (2001).
- [4] L.Wu, L.Liao, G.Lv, F.Qin, Z.Li; Chem. Eng. J., **236**, 306 (2014).
- [5] N.H.Kim, S.V.Malhotra, M.Xanthos; Microporous Mesoporous Mater., **96**, 29 (2006).
- [6] B.Sarkar, M.Megharaj, Y.Xi, R.Naidu; Naidu, J. Hazard. Mater., **195**, 155 (2011).
- [7] A.Zazoua, I.Kazane, N.Khedimallah, C.Dernane, A.Errachid, N.Jaffrezic-Renault; Mater. Sci. Eng., C., **33**, 5084 (2013).
- [8] J.W.Gilman, W.H.Awad, R.D.Davis, J.Shields, R.H.Harris, C.Davis, H.C.DeLong; Chem. Mater., **14**, 3776 (2002).
- [9] J.U.Calderon, B.Lennox, M.R.Kamal; Appl. Clay Sci., **40**, 90 (2008).
- [10] L.I.Min, W.A.N.G.Li, J.Y.Chen, Y.L.Jiang, W.J.Wang; J Fuel Chem Technol. **42** (2014) 1266.
- [11] S.Letaief, T.A.Elbokl, C.Detellier; J. Colloid Interface Sci., **302**, 254 (2006).
- [12] S.Letaief, C.Detellier; Clays Clay Miner., **56**, 82 (2008).
- [13] Y.Y.Siao, S.M.Shau, S.H.Hu, R.H.Lee, C.H.Lin, J.Y.Wu, R.J.Jeng; Polym. J., **54**, 3850 (2013).
- [14] C.W.Chiu, T.K.Huang, Y.C.Wang, B.G.Alamani, J.J.Lin; Prog.Polym.Sci., **39**, 443 (2014).
- [15] H.Khalaf, O.Bouras, V.Perrichon; Microporous Mater., **8**, 141 (1997).
- [16] B.Makhoukhi, M.A.Didi, H.Moulessehoul, A.Azzouz, D.Villemin; Appl. Clay Sci., **50**, 354 (2010).
- [17] B.Haddad, D.Villemin, E.H.Belarbi; J. Mater. Environ. Sci., **3**, 312 (2012).
- [18] B.Haddad, D.Villemin, E.H.Belarbi, N.Bar, M.Rahmouni; Arab. J. Chem., **7**, 781 (2014).
- [19] T.Rajkumar, G.R.Rao; Mater. Chem. Phys., **112**, 853 (2008).
- [20] P.N.Tshibangu, S.N.Ndwanwe, E.D.Dikio; Int. J. Electrochem. Sci., **6**, 2201 (2011).
- [21] B.Makhoukhi, M.A.Didi, H.Moulessehoul, A.Azzouz; J. Med. Chem., **1**, 44 (2011).
- [22] T.C.Huang, H.Toraya, T.N.Blanton, Y.J.Wu; Appl. Crystallogr., **26**, 180 (1993).
- [23] B.V.Pokid'ko, I.A.Tutorskii, V.V.Bitt, N.M.Sklyarevskaya, P.L.Zhuravleva; Colloid J., **71**, 810 (2009).
- [24] C.Takahashi, T.Shirai, M.Fuji; Mater. Chem. Phys., **135**, 681 (2012).
- [25] Z.Li, W.T.Jiang, P.H.Chang, G.Lv, S.Xu; J. Hazard. Mater., **270**, 169 (2014).
- [26] Z.Gu, M.Gao, Z.Luo, L.Lu, Y.Ye, Y.Liu; Appl. Surf. Sci., **290**, 107 (2014).
- [27] L.Reinert, K.Batouche, J.M.Lévêque, F.Muller, J.M.Bény, B.Kebabi, L.Duclaux; Chem. Eng. J., **209**, 13 (2012).
- [28] W.Abdallah, U.Yilmazer; Thermochim. Acta., **525**, 129 (2011).
- [29] S.K.Goswami, S.Ghosh, L.J.Mathias; J. Colloid Interface Sci., **368**, 366 (2012).
- [30] W.H.Awad, J.W.Gilman, M.Nyden, R.H.Harris, T.E.Sutto, J.Callahan, D.M.Fox; Thermochim. Acta., **409**, 3 (2004).
- [31] Y.Hao, J.Peng, S.Hu, J.Li, M.Zhai; Thermochim. Acta., **501**, 78 (2010).
- [32] S.I.Marras, A.Tsimpliaraki, I.Zuburtikudis, C.Panayiotou; J.Colloid Interface Sci., **315**, 520 (2007).
- [33] B.Makhoukhi, M.A.Didi, D.Villemin; Mater. Lett., **62**, 2493 (2008).
- [34] R.R.Tiwari, K.C.Khilar, U.Natarajan; Appl. Clay Sci., **38**, 203 (2008).