



## THE EFFECTS OF TYPE AND AMOUNT OF QUATERNARY SALTS ON MODIFICATION OF ÇANAKKALE BENTONITE

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Received: 23.10.2017, Accepted: 11.12.2017

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doi: 10.22531/muglajsci.357263

### Abstract

The improved dispersion of clay minerals has an essential role for polymer clay nanocomposite manufacturing. In this regard, different organomodifications of clay have been attempted to obtain intercalated/exfoliated structures of composites. In present study, Çanakkale bentonite was organically modified by four different quaternary ammonium salts: tetramethylammonium chloride (TMAC), hexadecylpyridinium chloride (HDPC), hexadecyltrimethylammonium bromide (HDAB), phenyltrimethylammonium chloride (PMAC). Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis and thermogravimetric analysis (TGA) were performed to characterize the organobentonites. The results revealed that there is an increment of basal spacing of bentonite with HDAB and HDPC salts from 14.9 Å to 20.7 Å and 21.4 Å, respectively. However, other modifiers cannot lead to significant changes in d-spacings.

**Keywords:** Polymer clay nanocomposite, organomodification, bentonite

## KUVATERNER TUZLARININ TÜRÜ VE MİKTARININ ÇANAKKALE BENTONİTİNİN MODİFİKASYONU ÜZERİNE ETKİLERİ

### Öz

Kil minerallerinin düzgün dağılımı, polimer kil nanokompozit üretiminde önemli bir role sahiptir. Bu bakımdan, kompozitlerin interkale/eksfoliyeli yapılarını elde etmek için kilin farklı organomodifikasyon yöntemleri denenmiştir. Bu çalışmada, Çanakkale bentonitinin tetrametilamonyum klorür (TMAC), hekzadesilpiridinyum klorür (HDPC), hekzadesiltrimetilamonyum bromür (HDAB), feniltrimetilamonyum klorür (PMAC) olmak üzere dört farklı kuvaterner amonyum tuzu ile organomodifikasyonu incelenmiştir. Organobentonitler Fourier transform infrared spektroskopisi (FTIR), X-ışını kırınımı (XRD) analizi ve termogravimetrik analiz (TGA) ile karakterize edilmiştir. HDAB ve HDPC tuzları kullanılarak bentonitin bazal aralığı 14.9 Å'dan sırasıyla 20.7 Å'a ve 21.4 Å'a kadar artırılmıştır. Bununla birlikte, diğer modifiye edici tuzlar d-aralıklarında önemli değişikliklere neden olamamışlardır.

**Anahtar kelimeler:** Polimer kil nanokompozit, organomodifikasyon, bentonit

### 1. Introduction

The natural bentonite has been used widely to refer the clay rich deposits of volcanic origin and is associated with aqueous smectitic horizons [1]. Furthermore, the most commonly used definition was that "bentonites are the product of early diagenetic alteration of vitric fallout ash by [2-4]. The dominant component of bentonites is the most expandable clays, smectites. Many recent studies have focused on polymer bentonite nanocomposites for different applications. Nanocomposites have been used as adsorbents and decoloration agents to remove heavy metals, phenols and other micro pollutants from water [5]. They are utilized as thickeners in paints and in oil drilling fluids [6,7]. They have better mechanical strength, dimensional stability, thermal stability, barrier and rheological properties compared with either polymer or clay alone [8,9]. Polymer clay nanocomposites involving organically modified montmorillonite also improved the ionic conductivity of the solid polymer electrolytes [10]. The abovementioned improved properties of nanocomposites can only be achieved by the intercalated and/or exfoliated morphologies of layered silicates. The reason clay agglomerates in the hydrophobic polymer matrix is that the hydrophilic nature of the clay minerals. In order to obtain nanoscale

dispersion in polymer, hydrophilic clay layers should be converted lipophilic character and its surface energy should be lowered [11, 12]. In general, chemical modifications such as grafting functional groups on to the clay surface or ion exchange with quaternary or tertiary alkyl ammonium / phosphonium based surfactants were employed [13]. The increment in the basal spacing of clay by modification with long alkyl chains results in a good compatibility with polymers. Modification may also lead to better diffusion of polymer chains into the galleries and delamination of silicate layers. Organomodification is based on ion exchange reaction between the interlayer cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, etc.) with the cations of organomodifiers.

Filho et. al. investigated organo modification of bentonite by cetyl trimethyl ammonium bromide and prepared nanocomposites with isotactic polypropylene by melt intercalation technique. They evaluated the effect of an organophilic bentonite on the thermal degradation of polypropylene and found that the modified bentonite had higher thermal stability than the natural clay [14]. Seyidoglu et. al. modified montmorillonite rich local bentonite with four different quaternary ammonium and phosphonium salts. Organoclays were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and x-

ray diffraction (XRD) analysis. The increased basal spacings of the bentonite after modification indicates intercalation and mechanical properties of PP have been enhanced by incorporating organoclay (modification and characterization of bentonite) [15]. High exfoliation level in organo-montmorillonite/polyurethane nanocomposites resulted in higher tensile modulus, stress at break and lower deformability (elongation at break) [16].

In the present work, the modification of Çanakkale bentonite was investigated for potential use in polymer clay nanocomposite production. Four different quaternary alkyl ammonium salts were examined and the effects of the concentrations and alkyl chain length of salts on modification of bentonite were evaluated. The chemical structures and d-spacings of organobentonites were determined by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis. Thermal stabilities of organobentonites were also investigated by thermogravimetric analysis (TGA).

## 2. Experimental

### 2.1. Materials

Na-hexametaphosphate (96%, Sigma), methylene blue (Merck), tetramethylammonium chloride (98%, Sigma), hexadecylpyridinium chloride (99%, Sigma), hexadecyltrimethylammonium bromide (98%, Sigma), phenyltrimethylammonium chloride (99%, Merck) were used as received. The chemical structures of ammonium salts were given in Table1.

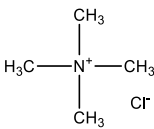
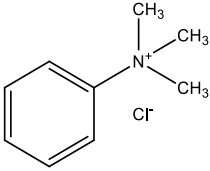
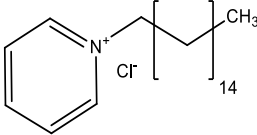
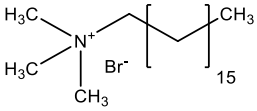
### 2.2. Separation of fine fraction

Separation of clay size fraction was an essential component of purification of bentonite. Sample preparation was completed in Clay Mineralogy Laboratory of Mugla Sıtkı Kocman University following the combined methods of [17-20]. The bulk sample was disaggregated gently with agate pestle and mortar. Then, the disaggregated samples were placed in a 600 ml beaker, filled with distilled water. Then, it was mixed with a magnetic stirrer for two minutes by adding 3 mg of Na-hexametaphosphate to avoid the flocculation. Then, the slurry was left for approximately 22 hours (room temperature 22 °C according to Stoke's Law). The supernate of fine fraction was then siphoned into a 250 ml beaker. The supernate was finally poured off into six falcon tubes and centrifuged for 10 minutes at 10 000 rpm. At the end of the run, the clean water and clay was separated. The clay fraction was collected in a smaller beaker and dried out in the oven at 60 °C overnight.

### 2.3. Determination of Cation Exchange Capacity

The method of [21] was followed in Methylene Blue (MB) solution preparation and in determination of cation exchange capacity of the fine fraction of the bentonite sample. 3gr of methylene blue is weighed and mixed with 300 cc distilled water by magnetic stirrer for 3 minutes. At the same time, the fine fraction of the bentonite sample was powdered by agate paste and mortar and then weighed as 7.5 g, mixed with 50 cc distilled water by magnetic stirrer.

**Table1.** Structure of ammonium salts and abbreviations of organobentonites

Ammonium Salts	Chemical Structures of Salts	Abbr.
Tetramethyl ammonium chloride		TMAC
Phenyltrimethyl ammonium chloride		PMAC
Hexadecyl pyridinium chloride		HDPC
Hexadecyltrimethyl ammonium bromide		HDAB

Methylene blue solution was placed in a brute that was fixed at vertical position over the beaker containing clay-water mixture. 1cc methylene blue was added to the bentonite-water mixture and mixed continuously by magnetic stirrer for 1 minute. A droplet was taken from the MB added bentonite-water mixture with the help of a glass pipette and placed on a filter paper. This procedure continued till the white halo around the dark blue droplet became light blue colored which shows that the substitution of the cations between the methylene blue and montmorillonite was completed. Cation Exchange Capacity (CEC) of the fine fraction of bentonite was calculated with the provided formula (1) [22].

$$(C. E. C.) = 100/f * V_{cc} * NMB = (\text{meq}/100\text{gr}) (1)f(x) \quad (1)$$

where f stands for dry weight of clay sample (7.5 gr), Vcc is the amount of methylene blue diluted added to clay sample, NMB is the normality of the MB solution (standard =0.028).

### 2.4. Modification

Typically, 1 g raw bentonite was dispersed in 100 mL deionized water and the mixture was stirred for 24 h by magnetic stirrer at ambient temperature. The bentonite/water suspension was poured into a 3-necked flask with condenser, thermocouple and dropping funnel. Then the flask was heated to 65°C in oil bath. 0.7xCEC of the ammonium salt was dissolved in 100 mL deionized water and added slowly to the bentonite/water suspension by dropping funnel. Separately, 1.4xCEC and 2.1xCEC of ammonium salts were also examined to understand the effect of the amount of salts on basal spacing increment. The cation exchange reaction was maintained at 65°C for 4 hours by a magnetic stirrer and then the flask was cooled to ambient temperature. The solution was centrifuged at 4000 rpm for 15 min. and the modified bentonite was then washed with deionized water for four times by centrifuge. The product was dried at 55°C in a vacuum oven and stored in a desiccator.

## 2.5. Characterization

FTIR spectra of the raw bentonite and organomodified bentonites were acquired on Thermo Scientific Nicolet is 50 with a number of scan 32 and resolution  $16\text{ cm}^{-1}$  within  $4000\text{--}400\text{ cm}^{-1}$  range. For characterization of the natural bentonite, mineralogical analysis was first conducted by the x-ray diffractometer. The powder mounts of the bulk dried bentonite sample was ground gently, placed in a sample holder and scanned using Panalytical Expert Pro diffractometer with a Cu tube at 40kV voltage and 30mA current. The diffractogram was plotted between  $4^{\circ}\text{--}70^{\circ} 2\theta$  with a scanning rate of  $2^{\circ}/\text{min}$ . Qualitative determinations of the minerals were based on [23, 19]. The minerals in the clay size fraction were determined by operating Rigaku Diffractometer equipped with a Cu tube at 40kV voltage and 30 mA current. The diffractograms of the clay-size sample were plotted between  $2^{\circ}\text{--}82^{\circ} 2\theta$  with a scanning rate of  $2^{\circ}/\text{min}$ . Thermal stabilities and decomposition temperatures of samples were determined by Perkin Elmer TGA 4000 analyzer within  $35^{\circ}\text{--}850^{\circ}\text{C}$  under nitrogen atmosphere. 5-10 mg samples were heated with  $10^{\circ}\text{C}/\text{min}$  rate and % weight losses vs. temperature thermograms were obtained.

## 3. Results and Discussion

The CEC of raw bentonite was found as 45.5 meg/100g. Four different quaternary salts were used in various percentages of CEC (0.7, 1.4 and 2.1) and then, modified bentonites were characterized by different methods.

### 3.1. FTIR Analysis

FTIR spectrum of raw bentonite revealed the characteristics bands and given in Figure 1. The peak at  $3620\text{ cm}^{-1}$  is associated with  $\text{--OH}$  stretching and the band at  $1634\text{ cm}^{-1}$  is attributed to  $\text{--OH}$  bending. The strong peak at  $1014\text{ cm}^{-1}$  shows Si-O stretching and Al-OH deformation and AlFe-OH vibrations can be seen clearly at  $912\text{ cm}^{-1}$  and  $792\text{ cm}^{-1}$ , respectively. After the organomodification of bentonite with hexadecyltrimethyl ammonium bromide (HDAB) a pair of bands between  $2921$  and  $2845\text{ cm}^{-1}$ , which result from asymmetric and symmetric C-H stretching of the  $\text{CH}_3$  and  $\text{CH}_2$  groups appeared newly in Figure 1. FTIR spectra of HDAB modified bentonite also depict a peak at  $1469\text{ cm}^{-1}$  which can be assigned as flexural vibrations of  $\text{CH}_3$  (Fig. 1a) [24].

Figure 1b and 1c represent the FTIR spectra of modified bentonite with phenyltrimethylammonium chloride (PMAC) and tetramethylammonium chloride (TMAC), respectively. Comparison of the spectra shows the presence of the same peaks in all samples, indicates that the structure of the bentonite samples was maintained after PMAC and TMAC treatment. Hence, the salt molecules cannot be incorporated into the galleries of bentonites.

Figure 1d displays the FTIR spectra of organobentonites modified with hexadecylpyridinium chloride (HDPC) and both clay and modifier related peaks can be identified. The bands at  $2926$  and  $2846\text{ cm}^{-1}$  represent the symmetric and asymmetric C-H stretching of  $\text{CH}_2$  groups. Also the peak at  $1481\text{ cm}^{-1}$  corresponds to the C-H bending of long alkyl groups. These results indicate the intercalation of HDPC within the bentonite layers and this effect can be seen as more intense peak in FTIR spectra of modified bentonites from  $0.7\times\text{CEC}$  to  $2.1\times\text{CEC}$  modifier ratios.

### 3.2. XRD Analysis

The  $<2\mu\text{m}$  size fraction includes montmorillonite, illite, cristobalite and calcite (Fig. 2). Montmorillonite shows the highest peak of  $14.91\text{ \AA}$  at  $5.92^{\circ} 2\theta$ . Very weak reflection of illite  $d(001)$  at  $10\text{ \AA}$  and relatively intense  $d(002)$  at  $5\text{ \AA}$  were observed. Intense cristobalite peak ( $4.04\text{ \AA}$ ) and weak calcite peak ( $3.03\text{ \AA}$ ) were seen in the clay fraction.

XRD data of raw bentonite and organobentonite were given in Table 2. XRD of organically modified bentonite with 0.7 HDAB shows that the montmorillonite peak shifted to smaller two theta angle and the d spacing value increased up to  $15.18\text{ \AA}$ . The nonclays remain at the same angles with the same reflections. The increment of salt as 1.4 HDAB resulted in increased d-spacing of montmorillonite to  $20.58\text{ \AA}$  at  $4.29^{\circ} 2\theta$ . When the concentration of salt was 2.1 HDAB, bentonite sample did not create significant difference from 1.4HDAB modification (Fig. 2).

The second and third modifiers were PMAC and TMAC, respectively (Table 2). Both, PMAC and TMAC organomodification did not cause expansion in basal spacing of bentonite (Fig. 2). For TMAC modifier, short alkyl chain length is not enough to increase the d-spacing, therefore the incorporation of the salt into the gallery of the bentonite did not occur.

The final organomodification was tried by HDPC (Table 2). The maximum unit thickness values were observed by 1.4 and 2.1 HDPC ratios as  $20.39\text{ \AA}$  at  $4.34^{\circ} 2\theta$  and as  $21.43\text{ \AA}$  at  $4.12^{\circ} 2\theta$ , respectively (Fig. 2). XRD characterizations show that the organomodification of bentonite was successful just for HDAB and HDPC ammonium salts.

### 3.3. TGA Study

Thermal stabilities of the raw bentonite and modified bentonites were determined by thermogravimetric analysis (TGA) (Fig. 3-6). The decomposition temperatures and char yields of the samples were tabulated in Table 2. TGA data revealed that the initial weight loss (T1) at around  $90^{\circ}\text{C}$  can be attributed to evaporation of adsorbed water. The second weight loss (T3) was observed at  $657^{\circ}\text{C}$  and is reflected with the equivalent endothermic peak due to dehydroxylation of bentonite [25]. Raw bentonite was thermooxidatively stable up to  $850^{\circ}\text{C}$  and only 15% of weight of raw bentonite was lost at this temperature (Fig. 3-6). For organomodified bentonites one or two degradation stages were added due to the decomposition of intercalated alkyl tails of the salts in the range of  $323\text{--}454^{\circ}\text{C}$  (Fig. 3-6). It was also found that organically modified bentonites have lower percent char yield than that of raw bentonite and the value decreases with increasing salt content in modification. This effect can be clearly seen in organobentonites which modified with HDAB and HDPC salts (Fig. 3 and 6). Besides, TGA analysis showed that PMAC and TMAC salts modified bentonites have less residual char which indicates less organic content present in the organobentonites (Fig. 4 and 5).

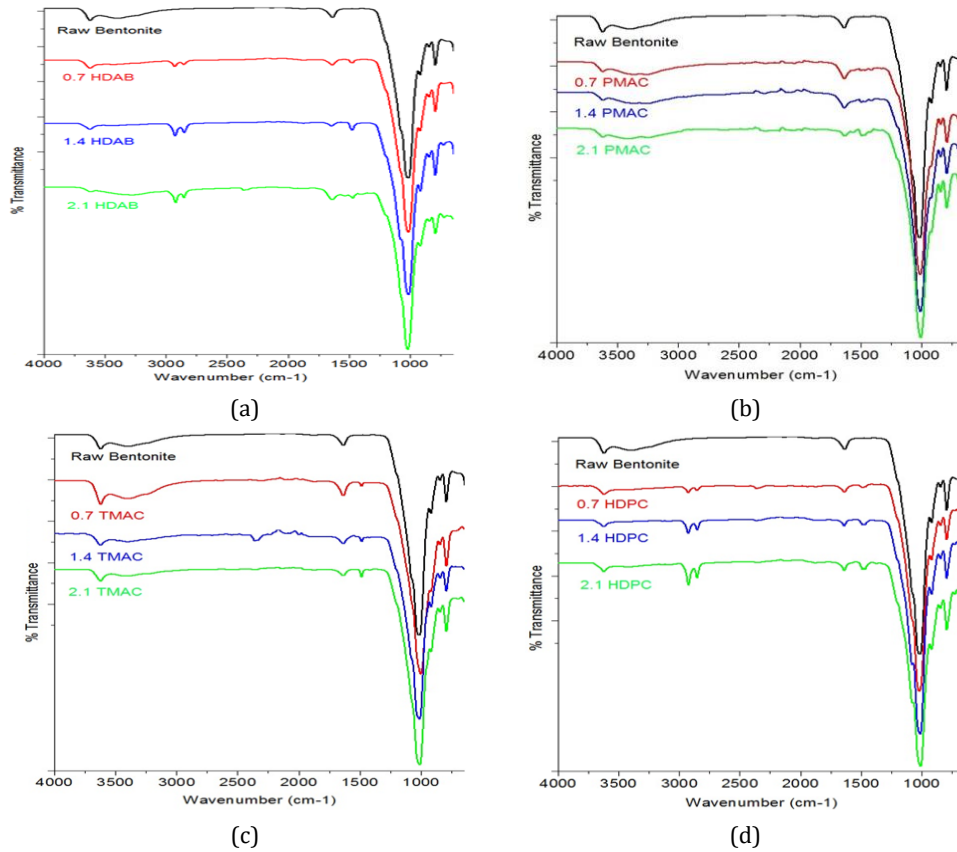


Figure 1. FTIR spectra of raw bentonite and organobentonites modified with a) hexadecyltrimethyl ammonium bromide (HDAB); b) phenyltrimethylammonium chloride (PMAC); c) tetramethylammonium chloride (TMAC); d) hexadecylpyridinium chloride (HDPC)

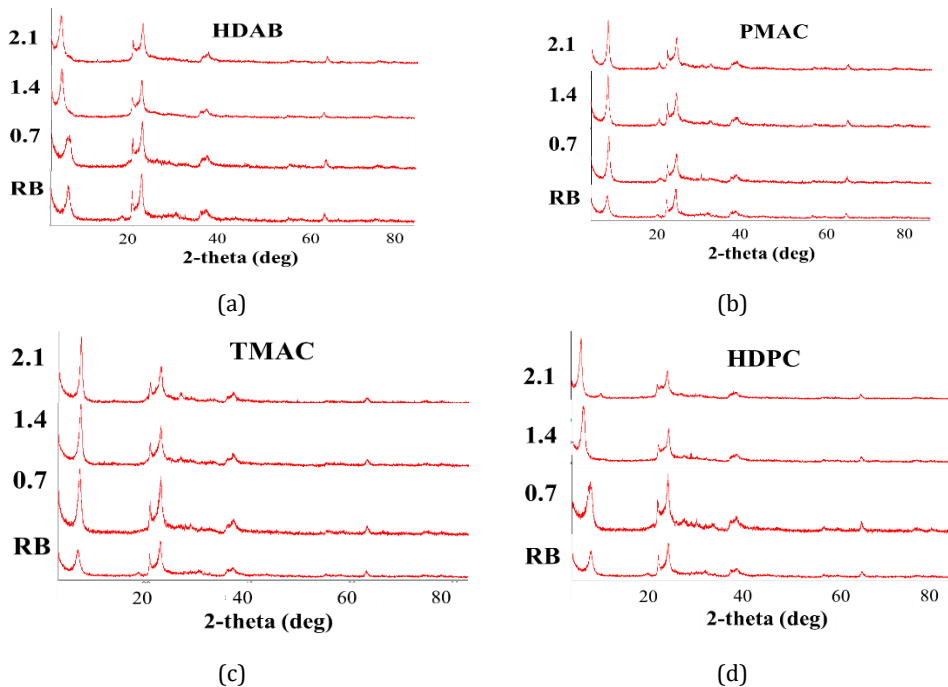
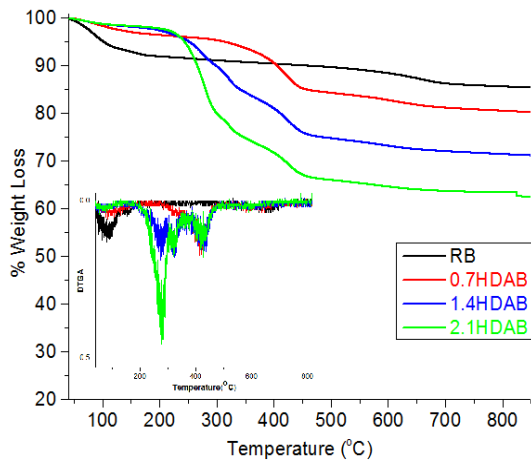
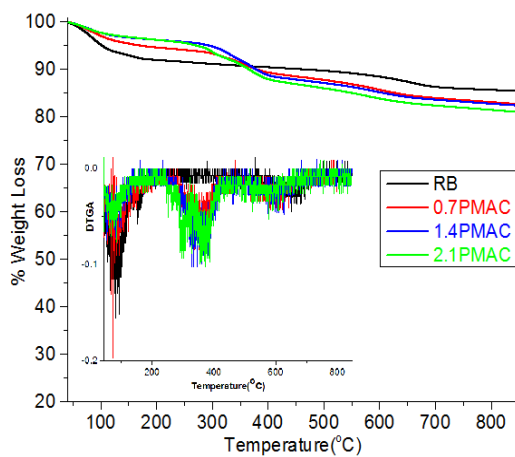


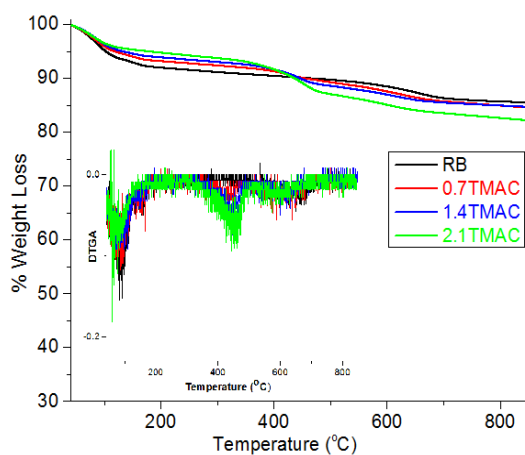
Figure 2. X-ray diffractograms of fine fraction bentonite (RB) and organomodified bentonites



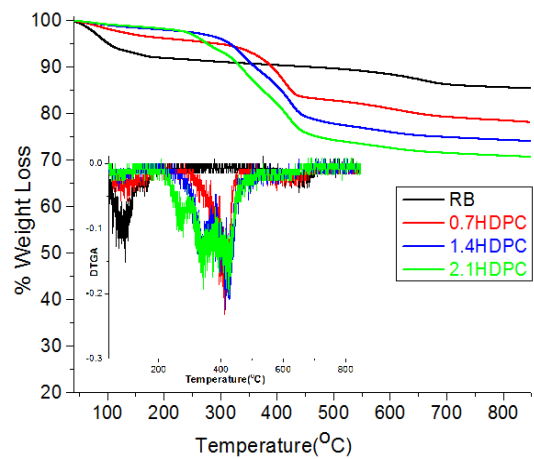
**Figure 3.** TGA and DTGA thermograms of raw bentonite and organobentonites modified with hexadecyltrimethyl ammonium bromide



**Figure 4.** TGA and DTGA thermograms of raw bentonite and organobentonites modified with phenyltrimethyl ammonium chloride



**Figure 5.** TGA and DTGA thermograms of raw bentonite and organobentonites modified with tetramethylammonium chloride



**Figure 6.** TGA and DTGA thermograms of raw bentonite and organobentonites modified with hexadecylpyridinium chloride

#### 4. Conclusion

The effect of different ammonium salts on the intercalation with the bentonite sample was evaluated by XRD, FTIR and TGA analyses. XRD results clearly present the increment in the basal spacings of bentonite by HDAB and HDPC salts. FTIR analyses also confirm the intercalation with the same salts in that new absorption bands appear after modification. Furthermore, new degradation stages of bentonite on TGA showed the decomposition of the intercalated alkyl tails of HDAB and HDPC salts. Consequently, it can be concluded that HDAB and HDPC salts modified the bentonite sample to be used in further polymer clay nanocomposites, whereas, PMAC and TMAC salts were determined insufficient for the intercalation.

**Table 2.** TGA Data for raw bentonite and organobentonites

Sample Code	T <sub>1</sub> (°C)	T <sub>2</sub> (°C)	T <sub>3</sub> (°C)	Char yield at 850°C	d (Å)	2θ
Raw Bent	92	-	657	85.4	14.91	5.92
0.7HDAB	97	423	635	80.2	15.18	5.82
1.4HDAB	-	323	601	71.2	20.58	4.29
2.1HDAB	-	323	600	62.5	20.72	4.26
0.7PMAC	89	356	602	82.6	14.41	6.12
1.4PMAC	87	379	601	82.3	14.88	5.93
2.1PMAC	79	373	590	80.9	14.95	5.90
0.7TMAC	92	431	626	84.5	14.36	6.14
1.4TMAC	86	447	620	84.6	13.81	6.39
2.1TMAC	80	454	611	82.1	14.02	6.30
0.7HDPC	90	414	624	78.2	14.92	5.91
1.4HDPC	84	339	615	74.1	20.34	4.31
2.1HDPC	83	345	607	70.7	21.43	4.11

## 5. Acknowledgment

This study was financially supported by Mugla Sıtkı Kocman University with BAP 17/011 project number. Part of this study was presented in 17th National Clay Symposium, 2017.

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