



EFFECTS OF THE THREE TYPES OF SURFACTANTS ON THE STRUCTURE OF ORGANO-MODIFIED BENTONITE

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ABSTRACT

A new surface modification for sodium bentonite clay (Na-Bent) was analyzed and the organo-modified bentonite clays were obtained with the sequential mixture of cationic surfactants; these were namely long chained (cetyltrimethylammonium bromide-CTAB), short chained (tetraethylammonium bromide-TEAB) and ringed (benzyltriethylammonium bromide-BTEAB) surfactants. These modified organoclays were characterised by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectrometry, Scanning Electron Microscopy (SEM) and zeta potential analysis. It was seen that the highest basal spacing of the organoclay was obtained by (CTAB+BTEAB) surfactants. The synergistic effect of the surfactants on the interlayer space of the organoclay in terms of developing novel clay based nanocomposites was investigated.

Keywords: Surfactant, Organo-bentonite, Surface characterization.

1. INTRODUCTION

Bentonite mainly constituted by montmorillonite and also varying small amounts of minerals like (SiO₂) and calcium and sodium feldspar hydrous silicate of aluminum, is a hydrophilic clay-mineral. With its three-phase crystalline structure, two tetrahedral layers of silicon oxide (SiO₄)⁴⁻ and one octahedral layer formed by aluminum, magnesium or iron oxide, typically bentonites have two types; which are Na-bentonite and Ca-bentonite [1-2]. Bentonite clays used in many different industrial applications such as in ceramics, as adhesives and catalysts, adsorbent of heavy metals, cosmetics and pharmaceutical uses and as a barrier material for biopolymer films [3-5]. These fields and also new clay-based application areas can be found with their ability of the degree of exfoliation with the medium and for this reason they should be dispersed in organic phases and have an organophilic structure. Exfoliation is a method used for the modification of clays in the presence of surfactants to enhance the interaction of the clay with the medium [1]. Organoclays can be obtained as a result of the reaction of the clay mineral with an alkyl ammonium salt, under suitable conditions. The surfactants used may be ammonium salts of different structures.

Therefore in our study it was proposed to obtain the organo-modified bentonite clay with the sequential mixture of three cationic surfactants (CTAB, TEAB and BTEAB). The modified organoclays were characterised and the synergistic effect of the surfactants on the interlayer space of the organoclays in terms of developing novel clay based nanocomposites were examined.

2. MATERIALS AND METHOD

2.1. Experimental

The clay used was Sodium Bentonite (Na-Bent), gently supplied by Karben Kimya Enerji Madencilik Sanayi ve Ticaret A.Ş., Ankara, Turkey. The bentonite is grey and consists mainly of sodium montmorillonite with minor illite, kaolinite and quartz. The raw bentonite was soaked in distilled water for 24h for the impurities to settle down. After 24h, the supernatant was decanted and the sedimentation

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process was repeated. The collected supernatants (twice) were centrifuged for 15 minutes at 15 000 rpm and dried at 60 °C for 24h [6]. This purification step is repeated twice and afterwards a bentonite clay with a cation exchange capacity (CEC) of 101.70 meq/100 g clay was determined by the method of adsorption of methylene blue.

2.2. Synthesis of Organo-Modified Bentonites

Purified clay used in the synthesis was dried at 80 °C for 48 h before the experiments. The amount of surfactant to be added to the reaction medium varied depending on the type of surfactant. The calculations were made according to the CEC value of the clay. Table 1 shows the amount of surfactant to react with 1 g of clay.

Table 1. The amount of surfactant to react with 1 g of clay

Surfactant	Amount of surfactant (mg)
CTAB	370.65
BTEAB	276.85
TEAB	213.73

For each modification system, 5 g Na-Mt and 400 ml of water were first mixed and stirred for 0.5h at room temperature. After addition of the surfactant solutions to the mixture, the stirring continued for an additional 2h at 60 °C. The sequence of surfactant addition followed by cationic surfactants by CTAB (1.0 CEC), BTEAB (1.0 CEC) and TEAB (1.0 CEC).

2. RESULTS AND DISCUSSION

2.1. XRD Analyses

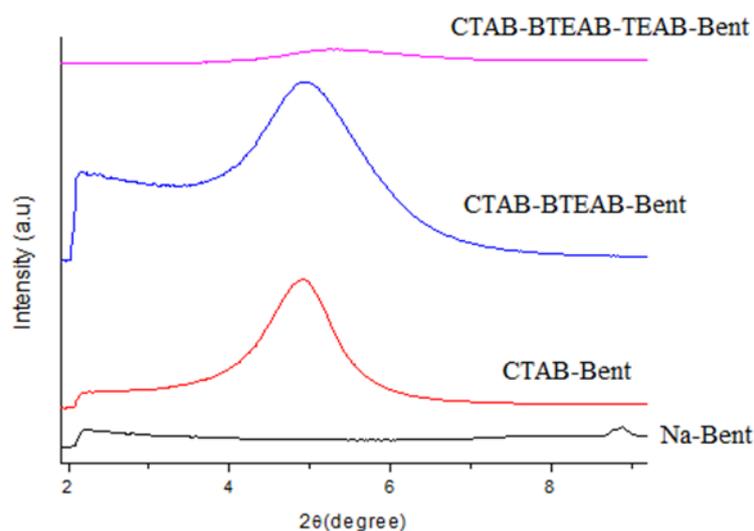


Figure 1. XRD patterns of the Bentonite samples

From Figure 1 it is seen that the basal spacing for purified Bentonite was 1.12 nm and after the modification by CTAB it shifted to 1.76 nm with the expansion of 0.64 nm. After the addition of BTEAB, the basal spacing was given 1.78 nm, and it declined to 1.68 nm after the addition of TEAB. The expansion in bentonite interlayer was obtained with the addition of CTAB and BTEAB helped to further expansion the interlayer. On the other hand, this difference is thought to result from the fact that

an extra benzene ring is attached to the BTEAB surfactant compared to the TEAB surfactant. Besides to these with the TEAB surfactant, the structure of the bentonite became more stable and ordered [7-8].

2.2. FTIR Analyses

From Figure 2, the peaks at ~ 2920 and 1470 cm^{-1} attributed to C-H and C-C stretching vibrations. The sharp peak at $\sim 1034\text{ cm}^{-1}$ was observed for Si-O stretching frequency [9]. The fundamental bands at $\sim 3430\text{ cm}^{-1}$ corresponding to O-H stretching of water, that were decreased by the addition of each surfactants sequentially, suggesting that the intercalation of surfactants removed the excess water from the interlayer of bentonite and obtaining an increased hydrophobicity [1,8].

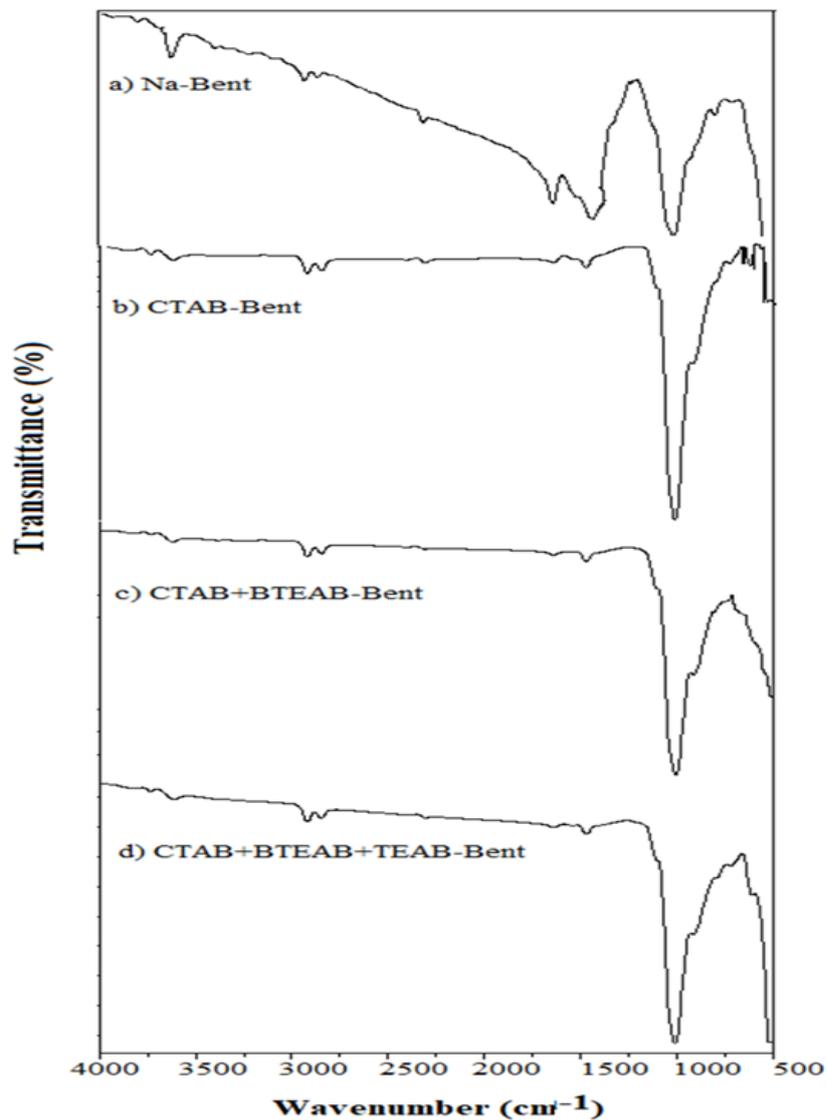


Figure 2. FTIR spectra of bentonite samples before and after surfactant intercalation

2.3. Zeta Potential

Figure 3 shows the zeta potential result of Na-Bent and organo-modified bentonites. As shown in graph, the zeta potential value of 0.5 wt% Na-Bent was -34.5 mV [9], on the other hand for CTAB-Bent, CTAB+BTEAB-Bent and CTAB+BTEAB+TEAB-Bent they were 38.6, 29.24 and 33.72 mV, respectively. The negative potential of Na-Bent showed the negative surface charges of the natural bentonite. The positive charges of organo-modified bentonites indicate that they were organophilic because of the adsorption of cationic surfactants onto the negatively charged Na-Bent particles [1, 9]. In general it is known that zeta potential values of clays greater than +30 mV or lower than -30 mV are accepted as stable suspensions. Therefore, all of the prepared organo-bentonites can be considered to establish more stable connections with the space in a uniform and non-aggregated way [1].

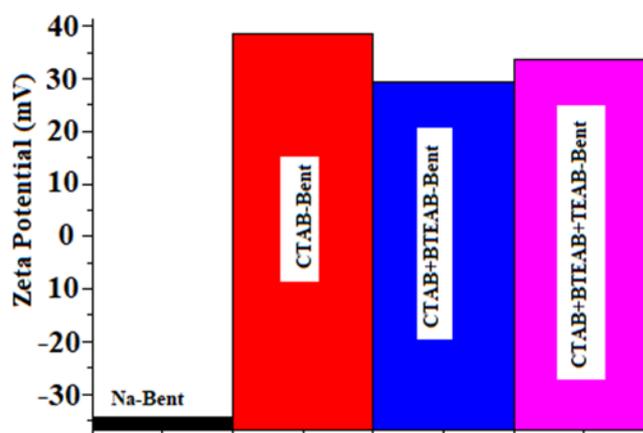


Figure 3. Zeta potential values of Na-bentonite and organo bentonite samples

2.4. Scanning Electron Microscopy

SEM images of all prepared organo-bentonites and Na-Bent were given in Figure 4. Figure 4 (a) shows that Na-Bent had stacked silicate layers with lamellar surface. After the purification step, the lamellar surface of the bentonites were enlarged for intercalating the surfactants. The disaggregated particles were the indicative of the intercalation of CTAB between the silicate layers (Figure 4b) [1]. With the addition of BTEAB surfactant to the medium, the stacked silicate layers were dispersed with the help of intercalated functional groups (Figure 4c). The dispersed silicate layers in Figure 4c, were again stacked after the addition of TEAB surfactant. This result is also consistent with the XRD results, that showed a decrement in the basal spacing of the prepared organo-bentonites (Figure4d).

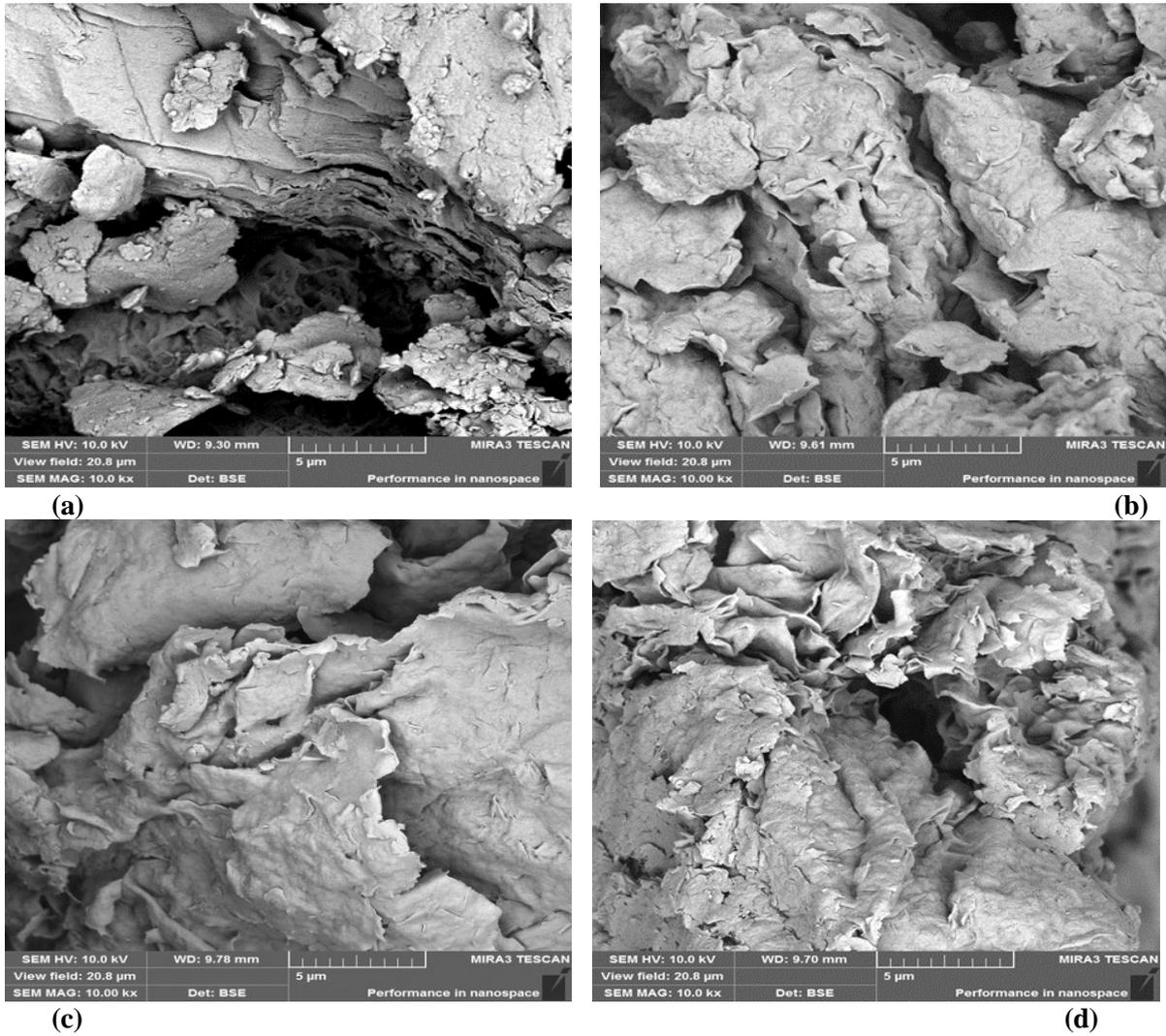


Figure 4. Scanning electron microscopy, (a) Na-Bent, (b) CTAB-Bent, (c) CTAB+BTEAB-Bent, (d) CTAB+BTEAB+TEAB-Bent. Magnitude: 10.00kx

3. CONCLUSION

In this study, from the three cationic surfactants sequential modifications were made and organo-modified bentonites were obtained. Among these cationic surfactants TEAB with the synergistic effect of CTAB surfactant (CTAB+BTEAB) was appeared as the best one for reinforcement material in nanocomposites, because of the higher basal spacing that observed from XRD analyses. SEM micrographics also showed that the stacked silicate layers in CTAB surfactant were dispersed with the help of intercalated functional groups from the structure of BTEAB surfactant; and indicated that the uniformicity with the tendency of stabilizing.

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