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Research paper

## Development of a clay-polymer compatibility approach for nanocomposite applications

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## ABSTRACT

Na-montmorillonite (Na-Mt) from Reşadiye Region of Turkey was modified by three different cationic and two different nonionic surfactants. The raw Na-Mt was purified before modification in order to remove mineral impurities other than Mt. The intercalation ability of surfactants into Na-Mt interlayer was investigated by X-ray diffractometry (XRD). Interaction of surfactant with Na-Mt surface was examined by various techniques involving Fourier Transform Infrared Spectroscopy (FTIR), thermal stability by Thermal Gravimetric Analysis (TGA), and the clay-polymer compatibility using surface energy and solubility parameters approaches. The present study was mainly focused on the evaluation of clay-polymer compatibility due to the lack of knowledge in this research field. It was found that different type of surfactants required different methodologies to evaluate the clay-polymer compatibility. It is proposed that the surface energy approach is very suitable for cationic surfactants used in this study due to their hydrophobic nature, however, such approach is not suitable for relatively less hydrophobic nonionic surfactants. The possibility of using the surface energy approach for cationic surfactants and that of solubility parameter for nonionic surfactants is discussed in the light of experimental data and theoretical considerations.

## 1. Introduction

Montmorillonite (Mt) is found throughout the world in small quantities in its natural geological state. In the large deposits where the mineral is found in concentrations > 50%, it is admixed with a variety of other minerals including quartz, feldspar, calcite, opal crystalite/trydimite (Opal-CT), illite and mica which are classified as impurities (Karmena, 2005; Boylu et al., 2012).

Mt with a general formula of  $\{Si_4[Al_{1.67}Mg_{0.33}]O_{10}(OH)_2 \times nH_2O \times X_{0.33} = Na, K \text{ or } Ca\}$  has a layered structure, with 1 nm thickness and several hundred nm in length, where the octahedral  $Al(OH)_3$  or  $Mg(OH)_2$  sheets are sandwiched between  $SiO_4$  tetrahedral sheets. As the isomorphous substitution of tetrahedral  $Si^{4+}$  atoms with  $Al^{3+}$  or  $Mg^{2+}$  in octahedral sheet changes the layer charge to negative, the Mt is also called cationic clay mineral. The negative charge generated by isomorphous substitution is usually compensated by the exchangeable cations such as  $Li^+$ ,  $Na^+$ ,  $K^+$  and  $Ca^{2+}$  and depending on the interlayer cations, they are called Na-Mt, Ca-Mt, Li-Mt or K-Mt (Ray and Okamoto, 2003; Uddin, 2008).

In the last past decade, Mt was a major raw material for nanoclay mainly used as a filler for polymer nanocomposites to reinforce their

physical, thermal, barrier, flame retardant properties (Alexandre and Dubois, 2000). Among different kinds of Mt, Na-Mt is usually selected as raw material for nanoclay applications. However, the hydrophilic nature of Na-Mt is compatible only with hydrophilic polymers. In order to monitor the compatibility of hydrophobic polymers, Na-Mt modified with cationic surfactants such as quaternary ammonium, primary ammonium, phosphonium, pyridinium, imidazolium and stibonium surfactants is utilized (Ray and Okamoto, 2003; Ha and Xanthos, 2009). Nonionic surfactants are also used to modify Na-Mt surfaces to make them compatible for hydrophobic polymers (Zamporia et al., 2012). However, the modification alone is not enough to promote the homogeneous dispersion and exfoliation of modified Na-Mt in polymer matrix. Some studies in the literature have attempted to predict the clay-polymer compatibility using surface energy approach and solubility parameters (Vaia and Giannelis, 1997; Jang et al., 2005).

In this study, Na-Mt from Reşadiye Region of Turkey was systematically modified with three different cationic surfactants and two nonionic surfactants to investigate their intercalation, thermal, and clay-polymer compatibility properties. It is proposed that while surface energy approach can be conveniently used for cationic surfactants, the solubility parameter method can be used for nonionic surfactants.

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## 2. Experimental

### 2.1. Materials

Raw Na-Mt with a particle size below 75  $\mu\text{m}$  and with cation exchange capacity (CEC) of 75 meq/100 g was supplied from Karakaya Bentonit Company from Tokat-Reşadiye Region of Turkey. Reşadiye Na-Mt assays 57.09%  $\text{SiO}_2$ , 16.73%  $\text{Al}_2\text{O}_3$ , 2.51%  $\text{Na}_2\text{O}$ , 3.18%  $\text{CaO}$ , and 3.24%  $\text{Fe}_2\text{O}_3$  in its chemical structure with loss on ignition (LOI) value of 13.40% (Boylu et al., 2012). Water soluble, PVP (Polyvinylpyrrolidone) coded K-30 with an average molar mass of 40,000 g/mol and PEG (Polyethyleneglycol) with molar mass of 1500 g/mol were used as modification agents for nonionic compounds. Hexadecyltriphenyl phosphonium bromide (HDTPH) with molar mass of 567.62 g/mol, cetylpyridinium bromide (CPB) with molar mass of 384.44 g/mol and coco alkylbis (hydroxyethyl) methyl ethoxylated chlorides also called as Ethoquad C12 with 320 g/mol average molar mass were used as cationic modification compounds. All cationic surfactants were supplied from the manufacturers as analytical grade.

### 2.2. Purification and modification of Na-Mt by cationic compounds

The modification of Na-Mt was accomplished in a pilot plant. The mixing was performed in a reactor of 500 L capacity equipped with baffle operating at 300 rpm. A dispersion of 250 L consisting of 2% raw Na-Mt was conditioned for 3 h and then transferred to an industrial centrifuge where it was centrifuged in a three successive stages until a desired level of purification was achieved. Small amounts of test samples were taken in each stage to assess the product quality and characterization. The remaining dispersion was modified with cationic compounds in a high shear mixer at 1800 rpm for 10 min. The modified dispersion was filtered with a vacuum disc filter equipped with 100 L reservoir and washed three times by fresh water. The removal of all organic compounds which did not adhere to the Mt surfaces was analyzed by simple  $\text{AgNO}_3$  test, where the presence of Br and Cl anions was monitored at each washing step. The modified Mt was dried for two days at 60  $^\circ\text{C}$  temperature. The amount of cationic compound was calculated as 80% of the total CEC of purified Na-Mt; this value was chosen because the purified Na-Mt yielded higher CEC.

### 2.3. Modification by non-ionic compounds

A different methodology was utilized for non-ionic compounds. In the first step, the raw Na-Mt dispersion with 6% solids content was prepared using high shear mixing equipment at 1800 rpm, and in the second step, the non-ionic compounds were added at 50% by weight to the dispersion and then mixed 10 min in high shear mixer at 1800 rpm. A total of 30 L dispersion was prepared and centrifuged twice. The purified dispersion was dried followed by grinding for characterization studies. Thus, purification and modification were simultaneously accomplished in a single step. Unlike the cationic compounds no washing/rinsing was required and very little water was consumed compared to the modification of cationic compound.

### 2.4. Characterization

The CEC measurement was conducted by ASTM C837 standard (Boylu et al., 2012). The X-ray diffraction patterns (XRD) of the raw and modified Mt were obtained by Shimadzu XRD-6000 diffractometer employing  $\text{Cu-K}\alpha$  radiation with 1.5405  $\text{\AA}$  wave lengths under operating condition of 40 kV and 30 mA. The thermal stability of modified Mt was performed by Seiko Exstar SII 6300 together with simultaneously TGA/differential thermal analysis (DTA) instruments under constant nitrogen flow of 30 mL/min. The TGA experiments were performed with sample weight in the range of 15–20 mg and at 10  $^\circ\text{C}/\text{min}$  heating rate, from room temperature to 1000  $^\circ\text{C}$ .

The self-supported film from purified Mt was prepared for the contact angle measurements as described by Norris et al. (1992). Here it is essential to remove particles higher than 2  $\mu\text{m}$  and then evenly spread them onto glass slides kept in petri dishes. After drying a very smooth self-supporting film was produced on glass slide surface.

## 3. Results and discussions

### 3.1. Purification

In previous study (Boylu et al., 2012) conducted under laboratory conditions, it was demonstrated that purification of Na-Mt in the centrifuge subsequently improved CEC values by preferentially removing impurities of low CEC values. The CEC value of the purified Na-Mt reached 130 meq/100 g. The particle size of purified dispersion was tested by passing it through 2  $\mu\text{m}$  filter; this procedure in the present case assured the highest level of purification that could be reached. The purified dispersion had approximately 1% Na-Mt with a particle size lower than 2  $\mu\text{m}$ . The 50% of the raw Na-Mt was removed from the dispersion and other impurities with a small amount of Mt of higher particle size were also removed. The XRD patterns of raw and purified Reşadiye Na-Mt are shown in Fig. 1. Raw Reşadiye Na-Mt consists of considerable impurities like quartz, mica, illite, calcite, feldspar, cristobalite e.g., which were removed upon the purification process. However, some very fine impurities like cristobalite (opal-CT) could not be removed by simple physical purification methods such as sedimentation, hydrocyclone and centrifugation (Onal et al., 2003; Boylu et al., 2010). The Tributh and Lagaly (Steudel, 2008) method, which is very time consuming and not suitable for commercial purposes is usually used for removing most impurities.

### 3.2. XRD characterization of modified Mt

#### 3.2.1. Cationic surfactant modification

As the measured CEC of the purified Na-Mt is 130 meq/100 g and rather high, in this study, only 80% of the total Na-Mt CEC was modified. In most cases, 80% CEC surfactant loading was enough for the modification, where  $d_{001}$  value did not change much with further increase in concentration (Xie et al., 2001; Lee and Kim, 2003; Osman et al., 2003). The XRD patterns of the modified Mt are shown in Fig. 2. The Mt modified with CPB, HDTPH and Ethoquad C-12 is abbreviated as CPB-Mt, HDTPH-Mt, and Etho-Mt, respectively. All the three modified Mt exhibited  $d_{001}$  values near 19  $\text{\AA}$ , which was explained with the successful intercalation of the cationic surfactants. The 001 reflection for HDTPH-Mt and Etho-Mt are very sharp, which were attributed to the

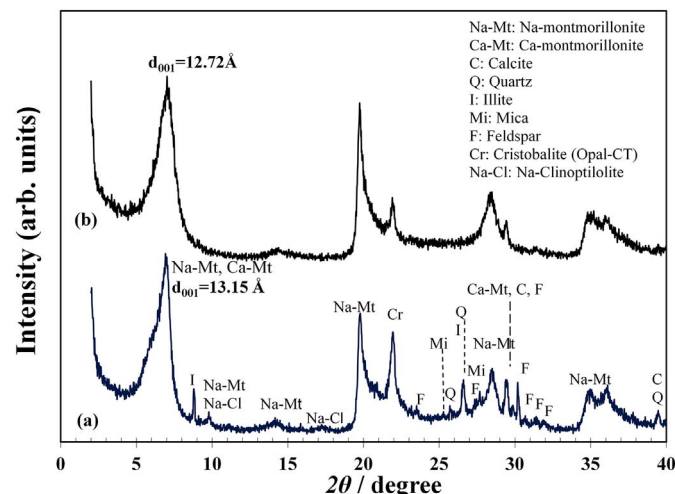


Fig. 1. XRD pattern of Reşadiye Na-Mt before (a) and after (b) purification.

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