

# Preparation of new nano-organoclays from Hexadecylamine, Tetradecylamine and Chalcone with Montmorillonite using ion exchange processes

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## Abstract

This study reports the effect of three new organic cations including hexadecylamine (HDA), tetradecylamine (TDA) and 1-(4-aminophenyl)-3-(4-chlorophenyl)prop-2-en-1-one, chalcone (CH) on the basal spacing of the montmorillonite clay to MMT modification. Fourier Transform infrared spectroscopy (FTIR) was used to evaluate the incorporation of these cations in the MMT. X-ray diffraction technique was utilized to indicate the basal spacing of the treated clay as a measure of susceptibility of new organoclays. The FTIR and XRD results shown that the three new organic cations were successfully incorporated in the montmorillonite clay.

Keywords: sodium montmorillonite, modification, surfactant, organic cation

Kulcsszavak: nátrium montmorillonit, modifikálás, felületaktív anyag, szerves kation

## 1. Introduction

Sodium montmorillonite (MMT) is a naturally occurring clay mineral characterized by relatively low negative charge of its aluminosilicate layers as a result of octahedral substitutions of Al by Mg (II), Fe (II) or other divalent metal ions in a central octahedral sheet (Meleshyn, Bunnenberg, 2006). This negative charge is compensated by inorganic cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> in the interlayer space while these inorganic cations can be exchanged by other cations (Chen *et al.*, 2008). However, cation-exchange reaction have been traditionally exploited as an effective method to replace these inorganic ions with organic cationic surfactant molecules, which intercalate into the clay gallery, resulting in expansion of the interlayer spacing and leading to an increase in the basal spacing. These organic cations render the surface of the clay mineral hydrophobic, leading to the increase of the clay wettability and providing favourable interactions with organic molecules. Both organic-modified and unmodified clays have been used for different industrial applications such as rheological additives, thickeners in coating products glues, plastisols, drilling fluids and cosmetics (Jaynes, Boyd, 1991). Recently, clays were used in the field of materials science such as solid phase polymeric nanocomposites. In the 1990's, the use of organically modified clays in polymer-clay nanocomposites has attracted researchers into this area of materials science and technology (Zhang, Wilkie, 2003). The organic modification of clay minerals leads to a decrease in surface energy making clays compatible with polymers. The surface energy of clay minerals and polymer can be determined from contact angle measurements (Maiti, Bhowmick, 2005; Stretz *et al.*, 2005). Studies reported that melt processed nylon 6-clay nanocomposites was prepared

using organoclay. Based on X-ray diffraction analysis, various arrangement of alkyl chains in organoclays HDA proposed by Lagaly (1986). Novel organo-montmorillonites have been synthesized and characterized using different ammonium compounds (Rajkrian *et al.*, 2008; Arroyo *et al.*, 2003). Series of anion-cation surfactants modified organoclays were prepared by incorporating of cationic surfactant hexadecyltrimethyl ammonium bromide and anionic surfactant, sodium dodecylsulfonate to montmorillonite (Chen *et al.*, 2008; Rathanawan *et al.*, 2001). In this study, three different ammonium; HDA, TDA and CH were used to modify the compatibility of montmorillonite clay with polymer. These organo-montmorillonites can be used in both medical and industrial applications as polymer nanocomposite.

## 2. Experimental

### 2.1. Materials

Sodium montmorillonite, Hexadecylamine and Tetradecylamine obtained from Sigma Aldrich, Germany were used. Hydrochloric acid was obtained from J.T. Baker, USA. p-aminoacetophenone and p-chlorobenzaldehyde were obtained from Fluka. Sodium hydroxide was obtained from B.D.H.

### 2.2. Preparation of CH (Sadiq *et al.*, 2015)

0.5 g (1 mmol) of p-aminoacetophenone with 1 mmol p-chlorobenzaldehyde were mixed, then 0.5 mL of 10% NaOH aqueous solution and 5 mL of 99% ethanol were added to the mixture. The mixture was stirred at room temperature for 4 hrs. The crude mixture was poured in to ice water and then

acidified the product with 10% HCl solution. The solid formed was filtered then washed with ethanol and water at a ratio of 10:5 mL. Recrystallization from 99% ethanol afforded (67% yield, yellow solid, m.p 160–165 °C).

### 2.3. Preparation of organoclays (OMMTs)

Organoclay was prepared with a cationic exchange process, where Na in the MMT was exchanged with the alkylammonium ion, which was prepared applying the procedure reported by Al-Mulla *et al.* (2011) in an aqueous solution. Sodium montmorillonite (Na-MMT) 4.00 g was stirred vigorously in 600 mL of hot distilled water for 1 h to form a clay suspension. 4.50 g of HDA, TDA and CH, which HDA been dissolved separately in 400 mL of hot water with 16.00 mL of concentrated hydrochloric acid were added into the clay suspension. After being stirred vigorously for 1 h at 80 °C, the organoclay suspension was filtered and washed with distilled water until no chloride was detected with a 1.0 M silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay was ground until the particle size was 100µm (Al-Mulla *et al.*, 2010a; 2010b). Structure of HDA, TDA and CH is shown in Fig. 1.

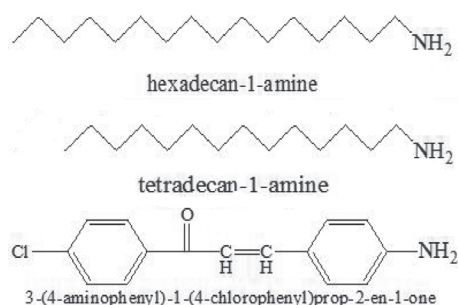


Fig. 1. Structures of the three organic cations  
1. ábra A három szerves kation szerkezete

### 2.4. Characterization

Organoclays were characterized using two different techniques including X-ray diffraction and Fourier Transform Infrared Spectroscopy.

#### 2.4.1. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) study was carried out using a Shimadzu XRD 6000 diffractometer with Cu K radiation ( $k = 0.15406$  nm). The diffractogram was scanned in the ranges from 2° to 10° at a scan rate of 1°/min.

#### 2.4.2. Fourier Transform Infrared (FTIR) spectroscopy

The FTIR spectra of the blend samples were recorded by the FTIR spectrophotometer (Perkin Elmer FT-IR-Spectrum BX, USA) using KBr disc technique.

## 3. Results and discussion

### 3.1. XRD analysis

The alkyl ammonium cation exchange enable the conversion of the hydrophilic interior clay surface into the hydrophobic surface and consequently increase the layer distance as well

(Phua *et al.*, 2013). Na-MMT was surface treated with HDA, TDA and CH as intercalation agents through cation exchange process. The cationic head groups of the intercalation agent molecule would preferentially reside at the layer surface and the tail of the compound will radiate away from the surface. The presence of these chains in the galleries makes the originally hydrophilic silicate to organophilic and thus, increase the layer-to-layer spacing of Na-MMT (Al-Mulla *et al.*, 2009). The obtained HDA-MMT, TDA-MMT and CH-MMT were studied using XRD measurements in the  $2\Theta$  ranges from 2° to 10°. Na-MMT shows a d001 diffraction peak at  $2\Theta = 6.91^\circ$  which, assigns to the interlayer distance of the natural montmorillonite with a basal spacing of 1.27 nm (Agag, Takeichi, 2001). Fig. 2 reveals XRD the basal spacing (d001 value) increase from 1.27, 1.51, 1.57 and 1.78 nm for Na-MMT, HDA-MMT, TDA-MMT and CH-MMT, respectively.

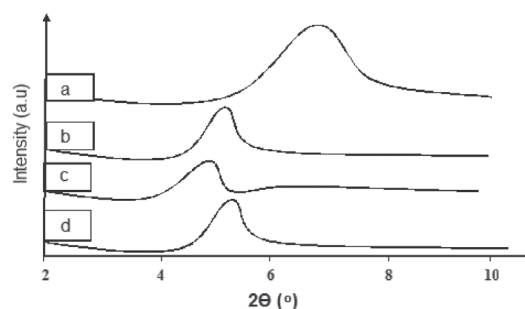


Fig. 2. The XRD patterns of (a) Na-MMT, (b) HDA-MMT, (c) TDA-MMT and (d) CH-MMT  
2. ábra Röntgendiffraktogramok; (a) Na-MMT, (b) HDA-MMT, (c) TDA-MMT és (d) CH-MMT

HDA, TDA, CH have been incorporated into the Na-MMT galleries to products organoclays. The basal spacings and angles of these organoclays were shown Table 1. Thus, XRD result indicate that organoclays are successfully intercalated into the silicate layer.

Sample	Exchanged cation	$2\Theta$ (°)	d(001) spacing (nm)
Montmorillonite	Na <sup>+</sup>	6.91	1.27
HDA	C <sub>16</sub> H <sub>32</sub> NH <sub>3</sub> <sup>+</sup> (HDA <sup>+</sup> )	5.64	1.57
TDA	C <sub>14</sub> H <sub>28</sub> NH <sub>3</sub> <sup>+</sup> (TDA <sup>+</sup> )	4.96	1.78
CH	C <sub>15</sub> H <sub>9</sub> ClO NH <sub>3</sub> <sup>+</sup> (CH <sup>+</sup> )	5.86	1.51

Table 1. Diffraction angle and basal spacing of montmorillonite and modified montmorillonite with different organic cations  
1. táblázat Diffrakciós szög és rácscik távolság; montmorillonit és különböző szerves kationokkal modifikált montmorillonit

### 3.2. FTIR spectroscopy

FTIR spectra are a useful technique to verify the presence of HDA<sup>+</sup>, TDA<sup>+</sup> and CH<sup>+</sup> in the clay. Fig. 3 shows the FTIR spectra of Na-MMT, pure HDA and HDA-MMT, Fig. 4 shows the FTIR spectra of Na-MMT, pure TDA and TDA-MMT, Fig. 5 shows the FTIR spectra of Na-MMT, pure CH and CH-MMT. The infrared spectrum of the Na-MMT shows two peaks, which correspond to Si-O stretching at 1033 cm<sup>-1</sup> and interlayer water deformation vibration at 1632 cm<sup>-1</sup> (Guo *et al.*, 2006). The band at 3625 cm<sup>-1</sup> results from the O-H

stretching vibration and the band at  $3043\text{ cm}^{-1}$  results from the CH= stretching vibration back to compound CH. The peaks observed at  $2924\text{--}2854\text{ cm}^{-1}$ ,  $2926\text{--}2852\text{ cm}^{-1}$  and  $2850\text{--}2920\text{ cm}^{-1}$  correspond to the presence of the C-H asymmetric and symmetric stretching vibration for HDA-MMT, TDA-MMT and CH-MMT, respectively. The IR spectrum reveals a weak incorporate of the compound CH in the clay (Fig. 5.c).

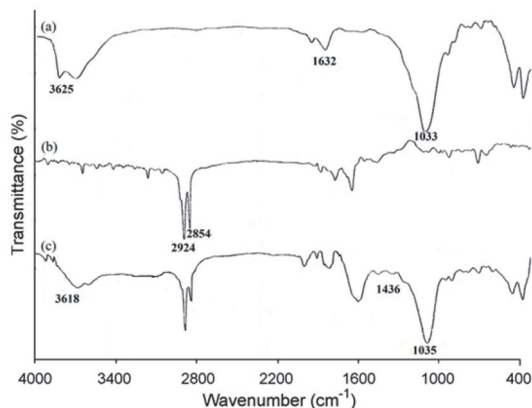


Fig. 3. FTIR spectra of (a) Na-MMT, (b) pure HDA and (c) HDA-MMT  
3. ábra FTIR spektrumok; (a) Na-MMT, (b) tiszta HDA és (c) HDA-MMT

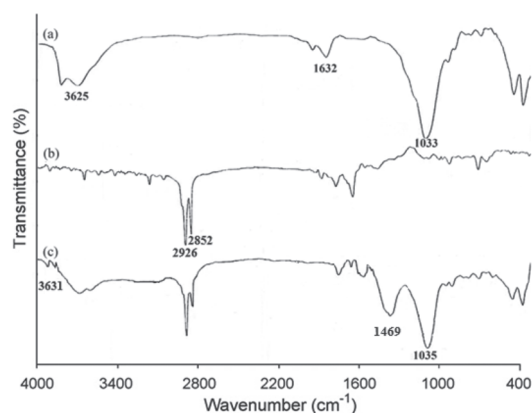


Fig. 4. FTIR spectra of (a) Na-MMT, (b) pure TDA and (c) TDA-MMT  
4. ábra FTIR spektrumok; (a) Na-MMT, (b) tiszta TDA és (c) TDA-MMT

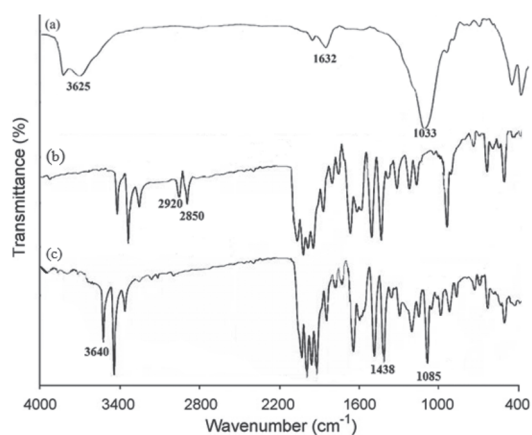


Fig. 5. FTIR spectra of (a) Na-MMT, (b) pure CH and (c) CH-MMT  
5. ábra FTIR spektrumok; (a) Na-MMT, (b) tiszta CH és (c) CH-MMT

In the spectra of HDA-MMT, TDA-MMT and CH-MMT, the absorption bands  $3618$ ,  $3631$  and  $3640\text{ cm}^{-1}$  indicate the

presence of free O-H stretching and at  $1035$ ,  $1033$  and  $1085\text{ cm}^{-1}$  correspond to C-N stretching, respectively (Ramachandran *et al.*, 2007). In addition to the bands of the original Na-MMT the band at  $1436$ ,  $1469$  and  $1438\text{ cm}^{-1}$  suggest the existence of the ammonium ion. Therefore, these indicate that HDA<sup>+</sup>, TDA<sup>+</sup> and CH<sup>+</sup> were intercalated in the silicate layers. This suggests that HDA, TDA and CH are sorbed into the silicate layers of Na-MMT.

## 4. Conclusions

Three new ammonium cations including HDA, TDA and CH were used to modify montmorillonite clay in an attempt to create susceptible clay to polymers. The organoclays were characterized using FTIR and XRD based on results of this study. Based on results of this study, the following conclusions can be drawn:

- These ammonium cations can be successfully incorporated in the montmorillonite clay.
- The basal spacing of the montmorillonite clay increases as a result of incorporating HDA, TDA and CH.
- The IR spectrum showed that there is a weak incorporate of the compound CH in the clay.
- The new organoclay can be used to produce polymer nanocomposites.

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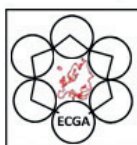
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