Bentonite-based organoclays using chalcone and azo dye as organophilic reagents

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Abstract
Organoclays (OBNTs) was prepared using two new organic surfactants including 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-on (CH) synthesized from a Claissen–Schmidt condensation reaction between p-aminocetophenone and p-chloro benzaldehyde; and 4-(4-(4-nitrophenyl) diazenyl)-N-(pyrimidin-2-yl) (AZ) prepared from reaction sulfadiazine and p-nitroaniline. OBNTs were characterized by Fourier Transform infrared spectroscopy (FTIR) to evaluate the incorporation above surfactants in bentonite. The X-ray diffraction (XRD) technique was utilized to indicate the basal spacing of the treated clay as a measure of susceptibility of new organo clays. The FTIR and XRD results show that the OBNTs were successfully incorporated in the bentonite clay. Thermogravimetric analysis (TGA) was also used to determine thermal stability. An enhancement in stability was observed in OBNTs compare to pure bentonite. OBNTs prepared in this study can be used to produce disposable packaging polymer nanocomposite.
Keywords: sodium bentonite, modification, surfactants, organic cations

1. Introduction
Bentonite, which is predominantly ammontmorillonite clay, is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets. The isomorphous substitution of Al⁴⁺ for Si⁴⁺ in the tetrahedral layer and Mg²⁺ for Al³⁺ in the octahedral layer results in a netnegative surface charge on the clay. This charge imbalance is offset by exchangeable cations typically Na⁺ and Ca²⁺ at the clay surface. The layered structure of the clay allows expansion after wetting. Na⁺ and Ca²⁺ are strongly hydrate the presence of water, resulting in hydrophilic environment at the clay surface [1]. 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 [2,3]. Recently, clays were used in the field of materials science such as solid phase polymeric nanocomposites. In the 1990s, the use of organically modified clays in the polymer-clay nanocomposites has attracted researchers into this area of materials science and technology [4]. 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 [5,6] reported that melt processed nylon 6-clay nanocomposites was prepared using organoclay. Based on X-ray diffraction analysis, various arrangement of alky chains in organoclay had proposed by Lagaly (1986). Novel organo montmorillonites have been synthesized and characterized using different ammonium compounds [7,8]. In this study, two new different ammonium compounds 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-on (CH) and 4-(4-(4-nitrophenyl) diazenyl)-N-(pyrimidin-2-yl) (AZ) were used to modify the compatibility of bentonite clay. These organo-bentonites can be used in various research and industrial application specially polymer nanocomposites.

2. Experimental
2.1. Materials
Hydrochloric acid from J.T. Baker,USA, p-amino acetophenone were obtained from Fluka and chlorobenzaldehyde were obtained from Fluka sodium hydride were obtain from B.D.H.

2.2. Characterization
Organoclay were characterized using two different techniques including X-Ray Diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR).

2.2.1. 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.
2.2.2. Fourier-transform infrared (FT-IR) spectroscopy

The FTIR spectra of the blends samples were recorded by the FTIR spectrophotometer (Perkin Elmer FTIR-Spectrum BX, USA) using KBr disc technique. Measurements were made at the faculty of Pharmacy, University of Kufa.

2.2.3. Nuclear magnetic resonance (NMR)

The 1H- NMR and 13C-NMR spectra were obtained with Bruker, Ultra Shield 300 MHZ, using DMSO as solvent and TMS as an internal standard.

2.2.4. Thermogravimetric analysis (TGA)

TGA was recorded by thermal gravimetric analyser, STA PT-1000 linseis TGA, Germany, Measurements were made at the College of Education for Sciences Ibn Al-Haitham, University of Baghdad.

2.2.5. Preparation of organoclays (OBNT)

Organoclay was prepared in an aqueous solution. Sodium Bentonite (Na-BNT) 4.00 g was stirred vigorously in 600 mL of hot distilled water for 1 h to form a clay suspension. Subsequently, 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-** on** (CH) and 4-(4-nitrophenyl) diazenyl)-N-(pyrimidin-2-yl) (AZ) 4.50 g, which had been dissolved in 400 mL of hot water and concentrated hydrochloric acid 16.00 mL was added into the clay suspension of. 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 [11]. The dried organoclay was ground until the particle size was 100 μm before the preparation of the nanocomposite [12,13].

Table 1 shows the structures of two organoclays.

| 3-amino-4-(4-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)|benczenenfórsüveg|

3. Results and discussion

3.1 X-ray diffraction (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 [14]. In this study, Na-BNT was surface treated with 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-** on** (CH) and 4-(4-nitrophenyl) diazenyl)-N-(pyrimidin-2-yl) (AZ) as intercalation agent 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 a ways 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-BNT [15]. The obtained 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-** on**-BNT and 4-(4-nitrophenyl) diazenyl)-N-(pyrimidin-2-yl)-BNT were studied by using X-ray diffraction measurements in the 2Θ range from 2Θ-10Θ. Na-BNT shows diffraction peak at 2Θ = 7.0762 which assigns to the interlayer distance of the natural Bentonite with a basal spacing of 1.25 nm as known in Fig. 1 [16]. After the ion exchange reaction, the basal spacing (d001value) increase from 1.25-1.77 for 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-** on**-BNT and 4-(4-nitrophenyl) diazenyl)-N-(pyrimidin-2-yl)-BNT respectively, suggesting that CH+ , AZ- have been intercalated into the Na-BNT galleries. These results are summarized in Table 2. Thus, X-ray diffraction results indicate that are successfully intercalated into the silicate layer.

![Fig. 1. XRD patterns of (a) Na-BNT; (b) CH-BNT; (c) AZ-BNT](image)

Table 1. Structure of the two organoclays

| Sample | Structure |
|--------|-----------|
| Na-BNT | 3-amino-4-(4-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)|benczenenfórsüveg|
| CH-BNT | 4-(4-nitrophenyl) diazenyl)-N-(pyrimidin-2-yl)|benczenenfórsüveg|
| AZ-BNT | 3-amino-4-(4-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)|benczenenfórsüveg|

1. ábra Röntgendiffrazkogram (a) Na-BNT; (b) CH-BNT; (c) AZ-BNT
Table 2. Diffraction angle and basal spacing of montmorillonite and modified montmorillonite with different organic cations

| Sample          | exchange change | θ (°) | d spacing (nm) |
|-----------------|-----------------|------|----------------|
| Bentonite       | Na⁺             | 7.08 | 1.25           |
| CH-modified     | C₆H₅NO₂⁺       | 4.99 | 1.77           |
| AZ-modified     | C₆H₅N₃O₄SNH⁺   | 5.01 | 1.76           |

3.2 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is a useful technique to verify the presence of CH⁺ and AZ⁺ in the clay, respectively. Fig. 2 shows the FTIR spectra of Na-BNT, pure CH and CH-BNT. Fig. 3 shows the FTIR spectra of Na-BNT, pure AZ and AZ-BNT. The infrared spectrum of the Na-BNT shows two peaks, which correspond to Si-O stretching at 1047 Cm⁻¹ and interlayer water deformation vibrational 1645 Cm⁻¹ [17]. 3628 Cm⁻¹ result from the O-H stretching vibration. The peaks observed in the CH-BNT (2850-2920 Cm⁻¹) and AZ-BNT (2872-2939 Cm⁻¹) infrared spectra correspond to the presence of the C-H asymmetric and symmetric stretching vibration, respectively.

3.3 Nuclear magnetic resonance

Nuclear magnetic spectroscopy is a useful technique to verify the presence of the ¹H-NMR spectra of CH pure and AZ pure (Fig. 4), and the ¹³C-NMR spectra of CH pure and AZ pure (Fig. 5). The nuclear magnetic spectrum of CH, which ¹H-NMR (300 MHz, DMSO) appearance of multiple signals at the site 6.6-7.8 ppm date back to protons benzene rings, also showed referring at the site 5.3 ppm back to protons (NH₂), and appearance signals at the site 7.5-7.9 ppm back to protons (CH = CH). ¹H-NMR spectra of AZ appearance of multiple signals at the site 7.6-8.5 ppm date back to protons benzene rings, also showed referring at the site 6.5 ppm back to protons (NH₂) and...
appearance signals at the site 11.32 ppm back to protons (NH) in sulfadiazine. The nuclear magnetic spectrum of CH, which $^{13}$C-NMR (300 MHz, DMSO) appearance of multiple signals at the site 113.2-130.6 ppm date back to carbons benzene rings, also showed referring at the site 186.2 ppm back to carbon (C=O) and appearance signals at the site 145.2-123.6 ppm back to carbon (CH=CH). $^{13}$C-NMR spectra of AZ appearance of multiple signals at the site 115.9 -165.134 ppm date back to carbon benzene rings.

3.4 Thermogravmetric analysis (TGA)

Fig. 6 shows the weight loss curves for increasing temperatures of Na-BNT, CH-BNT, AZ-BNT. Thermogravimetric analysis (TGA) gives information on the structure of the intercalating molecules by the weight loss steps. Thermal degradation of BNT shows before 200 °C because of the volatilization of water adsorbed on the external surfaces of the BNT and water inside the interlayer space.
The thermal degradation of the modified BNT can be explained occurs at below 200 °C due to the vaporization of water.

The weight loss curves (TGA) of the BNT, CH-BNT and AZ-BNT were illustrated in Fig. 6. BNT contains water due to hydrated sodium (Na\(^+\)) cations intercalated inside the clay layers. The presence of alkyl ammonium groups within the BNT interlayer spacing lowers the surface energy of the inorganic structure and will transform organophobic to organophilic materials.

Fig. 5. H-NMR Spectra of (a) CH; (b) AZ
5. áb. H-NMR spektrumok (a) CH; (b) AZ
The major difference between the thermogram of the unmodified clay and that of the organoclay is that the organic constituents in the organoclay decompose in the range from 180 to 500 °C, as the organic constituent in the organoclay decomposes in this range.

4. Conclusions

Two new ammonium cations CH and AZ were used to modify bentonite clay in an attempt to create susceptible clay to polymers. The organoclays were characterized using FTIR, XRD, ¹HNMR, ¹³CNMR and TGA. Based on result of this study, the following conclusion can be drawn:

- These ammonium cations can be successfully incorporated in the bentonite clay;
- The basal spacing of the bentonite clay increases as a result of incorporating CH and AZ.
- The new organoclay can be susceptible to polymers.
- Thermal stability was enhanced by incorporation of clay into CH and AZ.

References

[1] Yun-Hwei S. (2001): Preparations of organobentonite using nonionic surfactants. Chemosphere, Vol. 44, No. 5, pp. 989-995. https://doi.org/10.1016/S0045-6535(00)00564-6

[2] Motawie, A. M. – Madany, M. M. – El-Dakrory, A. Z. – Osman, H. M. – Imaiel, E. A. – Badr, M. M. – El-Komy, D. A. – Abulyazied, D. E. (2014): Physico-chemical characteristics of nano-organo-bentonite prepared using different organo-modifiers. *Egyptian Journal of Petroleum*, Vol. 23, No. 3, pp. 331-338. https://doi.org/10.1016/j.ejpe.2014.08.009

[3] Jaynes, W. F. – Boyd S. A. (1991): Clay mineral type and organic compound sorption by hexadecyltrimethyl ammonium exchanged clays. *Soil Science Society of America Journal*, Vol. 55, No. 1, pp. 43-48.

[4] Zhang, J. – Wilkie, C. A. (2003): Preparation and flammability properties of polyethylene-clay nanocomposites. *Polymer Degradation and Stability*. Vol. 80, No. 1, pp. 163-169. https://doi.org/10.1016/S0141-3910(02)00398-1

[5] Matti, M. – Bhowmick, A. K. (2005): Structure and properties of some novel fluorolastomer/clay nanocomposites with special reference to their interaction. *Journal of Polymer Science*, Part B, Polymer Physics, Vol. 44, No. 1, pp. 162-176. https://doi.org/10.1002/polb.20680

[6] Dutta, A. – Singh, N. (2015): Surfactant-modified bentonite clays: preparation, characterization, and atrazine removal. *Environmental Science and Pollution Research*, Vol. 22, No. 5, pp. 3876–3885. https://doi.org/10.1007/s11356-014-3656-3

[7] Motawie, A. M. – Ahmed, N. M. – El Mesllamy, S. M. – Sadek, E. M. – Kandile, N. G. (2014): Unsaturated Polymers / Layered Silicate Nanocomposites: Synthesis and Characterization. *IOSR Journal of Applied Chemistry (IOSR-JAC)*, Vol. 7, No. 10, pp. 34-43.

[8] Khazaal, M. S. – Tomma, J. H. (2011): Synthesis and Characterization of Novel Schiff Bases Containing Isoxazoline or Pyrazoline. *Ibn Al-Haitham Journal for Pure & Applied Sciences*, Vol. 24, No. 2, pp. 1-14.

[9] Salaman, F. W. – Radhi, S. W. – Jodh, A. M. (2015): Preparation and study antibacterial activity of a new polymer. *Journal of Babylon University, Pure and Applied Sciences*, Vol. 23, No. 2, pp. 620-626. https://doi.org/10.1007/s11814-010-0373-6

[10] Al-Mulla, E. A. J. – Yunus, W. M. Z. – Ibrahim, N. A. (2010): Enzymatic synthesis of fatty amides from palm olein. *Journal of Oleo Science*, Vol. 59, pp. 59–64.

[11] Yunus, W. M. Z. – Ibrahim, N. A. – Mohm, Z. A. (2011): Epoxidized palm oil plasticized polyfolic acid/fatty nitrogen compound modified clay nanocomposites: preparation and characterization. *Korean Journal of Chemical Engineering*, Vol. 28, No. 2, pp. 620–626. https://doi.org/10.1007/s11814-011-0351-6

[12] Yunus, W. M. Z. – Ibrahim, N. A. – Zaki, A. (2010): Difatty acyl urea from corn oil: synthesis and characterization. *Journal of Oleo Science*, Vol. 59, pp. 157–160.

[13] Phua, Y. J. – Chow, W. S. – Mohd Ishak, Z. A. (2013): Organomodification of Montmorillonite and Its Effects on the Properties of Poly(butylene succinate) Nanocomposites. *Polymer Engineering and Science*, Vol. 53, No. 9, pp. 1947–1957. https://doi.org/10.1002/pen.23460

[14] Mansor, B. A. – Wisam, H. H. – Nor Azowa B. I. – Emad, A. J. A. (2009): Modification of Montmorillonite by new surfactants. *Journal of Engineering and Applied Science*, Vol. 4, No. 3, pp. 184-188.

[15] Khalaf, A. I. – Hegazy, M. A. – El-Nashar, D. E. (2015): Synthesis and Characterization of Cationic Gemini Surfactant Modified Na–Bentonite and Its Applications for Rubber Nanocomposites. *Polymer composites*, Vol. 38, No. 2, pp. 396–403. https://doi.org/10.1002/pc.23598

[16] Guo, L. – Wu, S. – Zeng, F. – Zhao, J. (2006): Synthesis and Fluorescence property of terbium complex with novel Schiff-base macromolecular legend, *European Polymer Journal*, Vol. 42, pp. 1670-1675. https://doi.org/10.1016/j.europolymj.2006.01.025

[17] Ramachandranl, E. – Baskaran, K. – Natarajan, S. (2007): XRD, Thermal, FTIR and SEM studies on gel grown glyicine crystals. *Crystal Research and Technology*, Vol. 42, No. 1, pp. 73-77. https://doi.org/10.1002/crat.200610774

Bentonit alapú szerves agyagok szintézise kalkon és azovegyület szerves reagensekkel

A cikk szerves reagensekkel szintetizált szerves agyagok előállítását és jellemzőit mutatja be. Az előállított vegyületek struktúráját és a bentonit alapanyaghoz kapcsolódásának mértékét Fourier transzformációs infravörös spektroszkópiával (FTIR) és röntgendifrakcióval (XRD) vizsgálták. Az FTIR és XRD vizsgálatok igazolták, hogy a szerves komponensek sikeresen megkötődtek a bentonit agyagon. Termoanalitikai (TGA) vizsgálatokkal vizsgálták a vegyületek stabilitását. A TGA vizsgálatok ráműtattak, hogy a szerves agyagok stabilitása jobb a tiszta bentoniténél. A szintetizált szerves agyagok alkalmazása sikeres lehet eldobható, lebomló nano-kompozit csomagolóanyagok előállítása során.

Külösevők: nátrium bentonit, modifikálás, felületaktív anyagok, szerves katonok