Research Article

Bentonite-Based Nano Organic Clay Using Chalcone and Azo Dye as Organophilic Reagents

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Abstract

Organclays (OBNTs) were prepared using two new organic surfactants including 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-on (CH) synthesized from a Claisen–Schmidt condensation reaction between p-aminoacetophenone and p-chlorobenzaldehyde; and 4-((4-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl) (AZ) prepared from reaction of sulfadiazine and p-nitoaniline. Organclays OBNTs were characterized by Fourier transform infrared spectroscopy (FTIR) to evaluate the incorporation of 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 organoclays. The FTIR and XRD results showed that the OBNTs were successfully incorporated in the layers of 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 a promising polymer nanocomposite.

Keywords: Sodium bentonite; Modification; Surfactants; Organic cations

Introduction

Bentonite, which is predominantly amontmorillonitic clay, is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay. This charge imbalance is offset by exchangeable cations typically Na^+ and Ca^{2+} at the clay surface. The layered structure of the clay allows expansion after wetting. Na^+ and Ca^{2+} are strongly hydrate in the presence of water, resulting in ahydrophilic 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 wetttability 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].

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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 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]. Melt processed nylon 6-clay nanocomposites have been prepared using organoclay [6]. It was reported that, based on X-ray diffraction analysis, various arrangement of alkyl chains in organoclays had proposed. Novel organomontmorillonites 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-nitrophenyl)diazenyl)-N-(pyrimidin-2- yl)(AZ) were used to modify the compatibility of bentonite clay. These organoclays can be used in both medical and industrial applications specially in both promising polymer and biopolymer nanocomposites.

Experimental
Material

Hydrochloric acid from J. T. Baker, USA. Sodium hydroxide was obtain from merck, British. p-aminoacetophenone and p-chlorobenzaldehyde were obtained from Fluka, Germany.

Characterization
XRD analysis

The 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.

FTIR spectroscopy

The fourier transform infrared spectroscopy (FTIR) spectra of the blends samples were recorded by the FTIR spectrophotometer (Perkin Elmer FTIR-Spectrum BX, USA) using KBr disc technique.

NMR techniques

^{1}H-NMR (nuclear magnetic resonance) and ^{13}C-NMR spectra were obtained with Bruker, Ultra Shield 300 MHz and 75 MHz, using dimethyl sulfoxide (DMSO) as solvent and transcranial magnetic stimulation (TMS) as an interanal standard.

TGA analysis

Thermogravimetric analysis (TGA) was recorded by thermal gravimetric analyzer, STA PT-1000 linseis TGA, Germany.
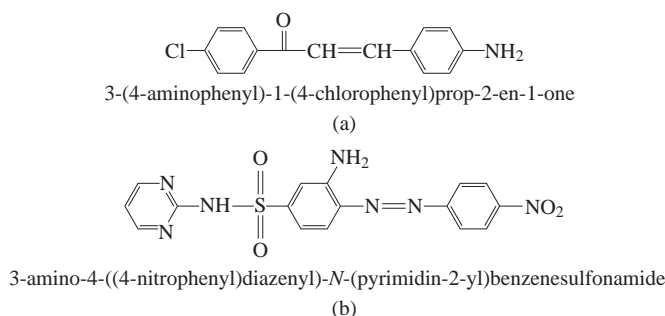
Preparation of chalcone [9]

0.5 g (0.002 mol) p-aminoacetophenone and 1 mmol p-chlorobenzaldehyde, were mixed with aqueous solution 10% NaOH. 0.5 mL of 99% EtOH was then added to the mixture. The resulting mixture was stirred at room temperature for 4hrs, and then poured in to ice water. After that, 10% HCl solution was added to the product. The solid formed was filtered then washed with ethanol and water at a ratio of 10:5. Recrystallization from 99% ethanol afforded produced pure chalcone (67% yield, yellow solid, m.p. 160-165 °C).

Preparation of azo [10]

2 gm (0.0145 mol) of 4-nitro aniline was dissolved in 3 mL of concentrated hydrochloric acid and 15 mL of distilled water. The mixture was cooled at 0-5 °C in ice-water bath, then 0.9 g (0.0145 mole) of a solution of sodium nitrite was dissolved in 5 mL of distilled water and then cooled at 0-5 °C. This solution was added a drop wise to the mixture with stirring at the same temperature. Design amount of diazonum salt solution was added portion wise to solution of 3.62 g (0.0145 mol) sulfadiazine in distilled water with 1.5 g of sodium hydroxide dissolved in 100 mL distilled water. The pH was maintained with 6-7 and temperature at 0-5 °C. The mixture was stirred for 30 min and then left over night. The product was precipitated and filtered, washed well with sodium bicarbonate and distilled water under-crystallized from ethanol (yield 72% , brown solid, m.p. 193-198 °C).

Preparation of organoclays (OBNT) [11]

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, 4.50 g of both CH and AZ, which had been dissolved in 400 mL of hot water and 16.00 mL concentrated hydrochloric acid was 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 mol silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay was ground until the particle size was 100 μm [12-13]. Scheme 1 shows the structures of CH and AZ

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3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-one

(a)

3-amino-4-((4-nitrophenyl)diazenyl)-*N*-(pyrimidin-2-yl)benzenesulfonamide

(b)

Scheme 1 The structures of **(a)** CH; and **(b)** AZ.

used to prepare organoclays.

Results and Discussion
XRD analysis

The alkyl ammonium cation exchange enables the conversion of the hydrophilic interior clay surface into the hydrophobic surface and consequently increase the layer distance aswell [14]. In this study, Na-BNT was surface treated with CH and 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 organoclays prepared in this work, 3-(4-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1on-BNT (CH-BNT) and 4-((4-nitrophenyl)diazenyl)-N-(pyrimidin-2-yl)-BNT (AZ-BNT), were investigated using XRD measurements in the 2Θ ranges from 2-10°. 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 [16]. After the ion exchange reaction, the basal spacing (d001 value) increases from 1.25 (Na-BNT) to 1.76 and 1.77 for CH-BNT and AZ-BNT, respectively (Fig. 1).
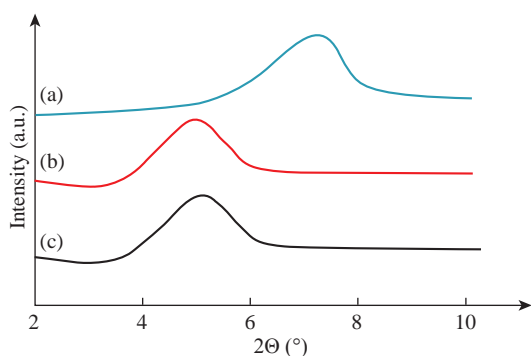
Table 1 Diffraction angle and basal spacing of bebtonite and its modification with different organic cations

Sample	Exchanged cation	2Θ (°)	d(001) spacing (nm)
Bentonite	Na^+	7.08	1.25
CH	$C_{15}H_9ClO\ NH_3^+\ CH^+$	4.99	1.77
AZ	$C_{16}H_9N_5O_4SNH_3^+\ AZ^+$	5.01	1.76

Diffraction angle and basal spacing of bebtonite and its modification with different organic cations suggested that CH and AZ have been intercalated into the Na-BNT galleries. The results were summarized in Table 1.

FTIR spectroscopy

FTIR is a useful technique to verify the presence of CH and AZ in the clay. Fig. 2 shows the FTIR spectra of Na-BNT, CH and CH-BNT and Fig. 3 shows the FTIR spectra of Na-BNT, AZ and AZ-BNT. In Fig. 3, FTIR of the Na-BNT shows two peaks, which correspond to Si—O stretching at 1047 cm^{-1} and interlayer water deformation vibration at 1645 cm^{-1} [17, 18]. The peak at 3628 cm^{-1} was from the O—H stretching vibration. The peaks at 2850-2920 cm^{-1} and 2872-2939 cm^{-1}
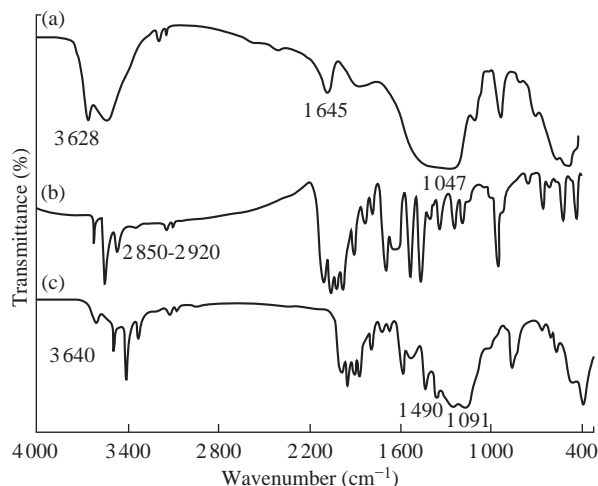

Fig. 1 The XRD patterns of **(a)** Na-BNT; **(b)** CH-BNT; and **(c)** AZ-BNT.

Fig. 2 FTIR Spectra of **(a)** Na-BNT; **(b)** CH; and **(c)** CH-BNT.

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correspond to the presence of the C—H asymmetric and symmetric stretching vibration for CH-BNT and AZ-BNT, respectively.

In the spectra of CH-BNT and AZ-BNT, the absorption bands at 3626 and 3640 cm^{-1} indicate the presence of free O—H stretching and at 1091 and 1109 cm^{-1} correspound to C—N stretching [19, 20]. In addition to the bands of the original Na-BNT, the band at 1490 and 1438 cm^{-1} suggests the existence of the ammonium ion. Therefore, these results indicate that of CH and AZ were successfully intercalated in the silicate layers.

NMR technique

Fig. 4 shows ^{1}H-NMR spectra of CH and AZ, while ^{13}C-NMR spectra of CH and AZ are shown in Fig. 5. ^{1}H-NMR (300 MHz, DMSO) appearance of multiple signals at the site 6.3-7.8 ppm corresponded to the
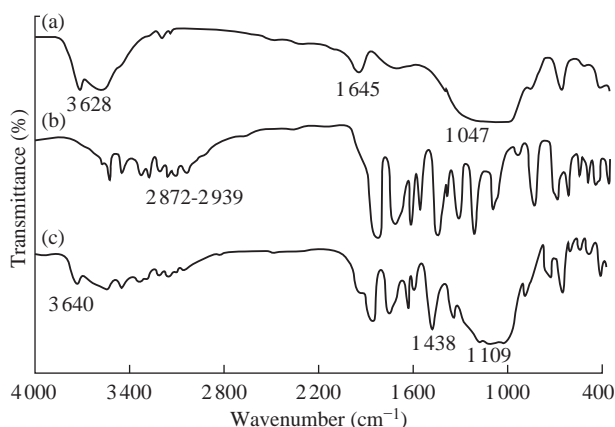

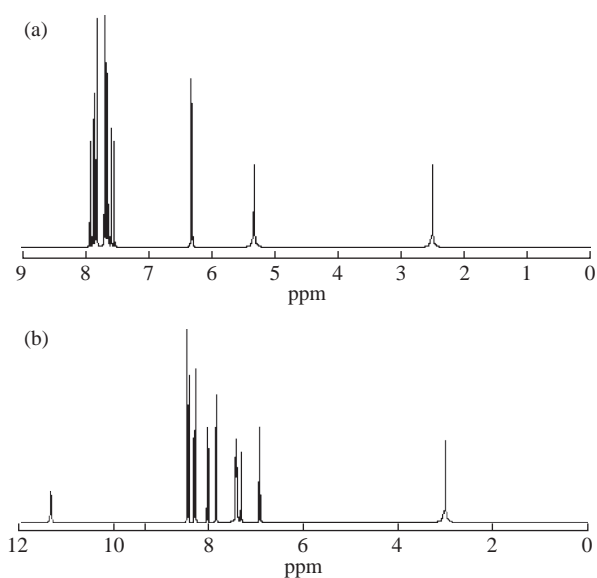**Fig. 3** FTIR Spectra of **(a)** Na-BNT; **(b)** AZ; and **(c)** AZ-BNT.

Fig. 4 ^{1}H-NMR spectra of **(a)** CH; and **(b)** AZ.
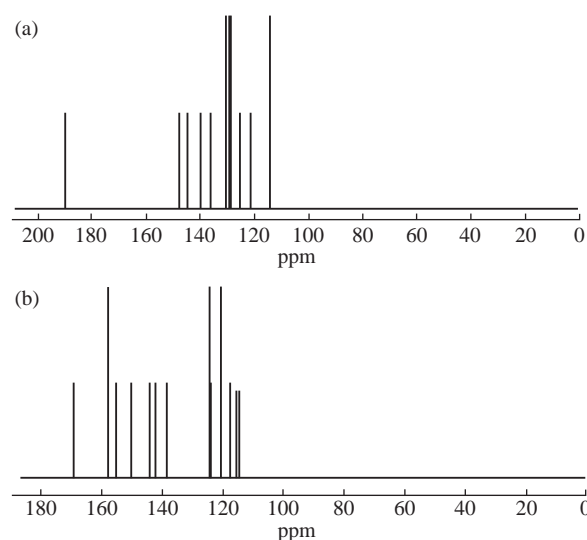

Fig. 5 ^{13}C-NMR spectra of pure **(a)** pure CH; and **(b)** pure AZ.

protons of benzene rings. The peak at the site 5.3 ppm referred to the protons of NH$_2$, and the appearance of signals at the site 7.5-7.9 ppm corresponded to the protons of CH ═ CH. ^{1}H-NMR spectra revealed the appearance of multiple signals of AZ at the site 7.6-8.5 ppm, which was due to the protons of benzene rings. The peak at 6.5 ppm corresponded to the protons of NH$_2$, and the appearance of signals at the site 11-32 ppm was due to the protons of NH in sulfadiazine. The ^{13}C-NMR (75 MHz, DMSO) (Fig. 3(a)) appearance of multiple signals at the site 114.0-130.6 ppm was due to the carbons of benzene rings. The peak at 189.7 ppm referred to the carbons of C ═ O, and the appearances of signals at the site 145.2-121.3 ppm corresponded to the carbons of CH ═ CH. The peak at around 2.5 ppm corresponded to DMSO as a solvent.

^{13}C-NMR spectra of AZ (Fig. 3(b)) shows multiple signals at the site 114.3-169.3 ppm, which were due to the carbons of benzene rings.

TGA analysis

TGA graph shows the curves of weight loss for increasing temperatures of Na-BNT, CH-BNT and AZ-BNT (Fig. 6).

The TGA curves gave information on the structure of the intercalating molecules by the weight loss steps. Thermal degradation of BNT was shown to be before 200 °C because of the volatilization of water adsorbed on the external surfaces of the BNT and water inside the interlayer space. The BNT contained water due to the hydrated sodium Na$^+$ cations intercalated inside the clay layers. The presence of alkylammonium groups within the BNT interlayer spacing lowered the surface
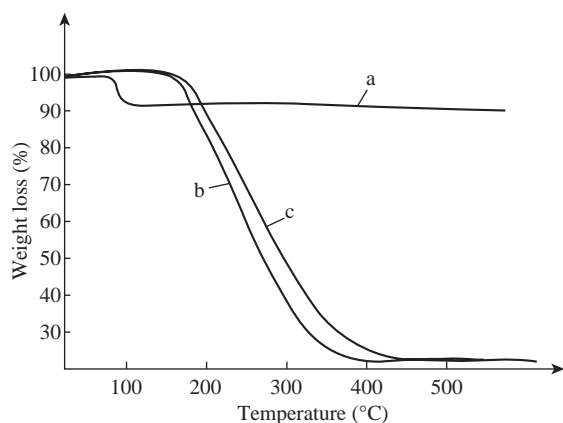
Fig. 6 TGA graph of **(a)** Na-BNT; **(b)** CH-BNT; and **(c)** AZ-BNT.

energy of the inorganic structure and would transform organophobic materials to organophilic materials ones.

The major difference between the thermogram of the unmodified clay and that of the organoclay was that the organic constituents in the organoclay decompose were in the range from 180 to 500 °C.

Conclusions

Based on the results of this study, we concluded that the ammonium cations from CH and AZ ccould be successfully incorporated in the bentonite clay, and that the basal spacing of the bentonite clay increased as a result of incorporating CH and AZ. We also found that the new organoclay could be susceptible to produce polymer nanocomposites, and that the thermal stability was enhanced by incorporation of clay into CH and AZ.

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