
Di Linh Clay-pillared by Cetyltrimethyl Ammonium Bromide Used as an Antifouling Paint Additive

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Abstract: Di Linh (Lam Dong Province, Vietnam) clay was chemically treated and pillared by cetyltrimethyl ammonium bromide (CTAB) surfactant under different preparation conditions. The synthesized organoclays were characterized by XRD, FT-IR, SEM, TEM, BET... techniques. The insertion of CTAB into the treated Di Linh clay leads to a significantly increased basal spacing. These pillared clays were further used as a paint additive. The preliminary results indicated that the presence of such an additive has a significant improvement of the mechanical properties of the organoclay-added paint.

Keywords: Clay, Organoclay, Additive, Antifouling Paint

1. Introduction

The surfactant intercalated montmorillonite known as organoclays, has paid much attention owing to their academic and industrial applications [1–3]. For example, these organoclay have used in rheological controlling of paints [1], sorption of organic compounds [2, 3] and as precursors in the synthesis of polymer intercalated nanocomposites [4], template for the fabrication of porous carbon material [5]. Properties of organoclays are controlled by their structural characteristics and the amount of intercalated surfactant. The insertion of surfactant into clay galleries was known as a “self-assembly” process [6]. With increasing loading amount, surfactants are first adsorbed as cation by ion exchange with the natural inorganic cations in the clay gallery, and then adsorbed as molecular species by hydrophobic interaction between the surfactant alkyl chains and the clay interlayer surface. Thereby, the organoclay may possess the characteristics of both surfactant guest and clay host [2, 6, 7].

The objective of the present study is to investigate the influence of both loading amount of surfactant and characteristics of clay host on the clay material structure, and tested these materials as additives for antifouling paint.

2. Experimental

The clay mineral was distributed by Drilling Mud Joint Stock Corporation, Vietnam. Firstly, 15 grams of the clay were added to HCl 0.5 M solution with continuous stirring for 24 h. The suspension was filtered, washed with deionized water, and dried in an oven. Metal cationic ions are removed by treatment with 0.5 M sodium chloride solution at room temperature for 24 h. The resultant was filtered, washed and then dried at 100°C. Secondly, pillaring is performed on the pretreated clay. CTAB–montmorillonite was synthesized as follows: quantity of 5.0 grams of montmorillonite was dispersed in 200 mL of distilled water, and then a desired amount of CTAB (10–150 wt.% of the original montmorillonite) was added to the suspension. The suspension was stirred at 40°C for 2 h and then aged at 60°C for 24 h. The products were washed with distilled water five times and dried at 80°C for about 24 h. The final products were named as Bent.DL-*i* in which *i* batch number.

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK_α radiation ($\lambda = 1.59 \text{ \AA}$). Fourier transform infrared (FT-IR) spectrum was obtained in 4000 – 400 cm⁻¹ range on a FT/IR spectrometer (DX-Perkin Elmer, USA). The elemental composition of catalyst was also

measured using an AA-6800 atomic absorption spectrophotometer (Shimadzu, Japan). TEM images were collected on a Japan Jeol. Jem. 1010. Scanning Electron Microscopy (FESEM) Hitachi S-4500 (Japan) with the magnification of 600,000 times. The nitrogen physisorption was measured at 77 K on an Autochem II 2920 (USA). The element analysis of samples was characterized by Energy-Dispersive X-ray (EDX) spectroscopy on EDX ISIS 300 apparatus.

The desired amount of antifouling paint (provided by Hai Phong Paint Company, Vietnam), ethanol solvent and organoclay were mixed together. The detailed procedure may be found in elsewhere [8]. In a typical procedure, 12.5 grams of modified clay was added into 15 grams of solvent and aged for 12 hours. Then, 250 grams of paint were added to the suspension and ground in a mortar for a period of time. Then, the antifouling paint and certain amount of ferric oxide was added in order to prepare the paint having 5 wt. % of organoclay in the final product.

Testing paint properties were followed the Vietnamese

Standard Protocols [9]. The modified paints were tested for viscosity (Protocol-2092-2005), adhesion (Protocol-2097-1993), T-bent (Protocol- 2099-2007), impact resistance (Protocol-2100-2007).

3. Results and Discussion

3.1. X-ray Diffraction

Five organoclay samples were prepared with different loadings of CTAB in the range of 23.1 - 52.4 wt. %. XRD was used to investigate the influence of cetyltrimethyl ammonium bromide surfactant loading amount on the interlayer spacings of organoclay particles. Figure 1 presents a set of XRD patterns for all modified samples. It is noted that all X-ray diffraction patterns show general features of montmorillonite phase such as weak signals at low angles (Fig. 1A), and strong lines at high 2-theta values in the range of 5-70° (Fig. 1B) [10].

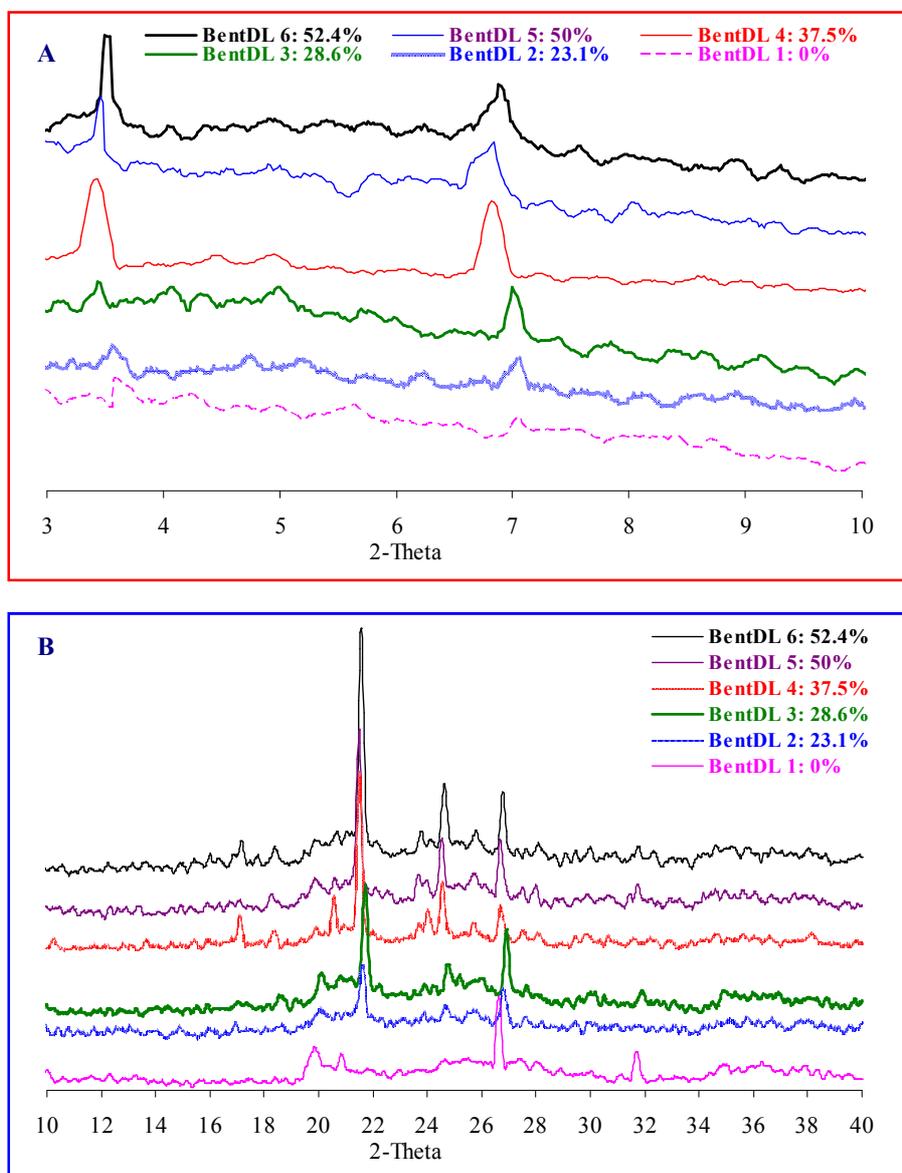


Figure 1. XRD patterns at 2-theta of 2-10° (A) and 10-40° (B).

Indeed, typical XRD reflection of Bent-Na related to the basal spacing between the clay platelets appeared at 2-theta of 5.8-6.3° indexed to 100 plane [11]. A decrease of 2-theta values reflects increased basal spacing values owing to the successful intercalation of the surfactant molecules in clay

platelets (Fig. 1A). These basal spacing significantly increases with CTAB loadings from 0-37.5 wt.% (Table 1), suggesting the existence of quaternary amine pillars within interlayer spaces [11-13]. The changes in basal spacings are collected in Table 1.

Table 1. Influence of CTAB amount on the basal spacings of clays.

Batch	Organoclays	CTAB loadings, wt. %	d_{001} , spacings Å	$\Delta = (d_{001} - 9.6^a)$, Å
1	Bent.DL - 1	0	15.53	5.93
2	Bent.DL - 2	23.1	16.94	7.34
3	Bent.DL - 3	28.6	18.64	9.04
4	Bent.DL - 4	37.5	25.03	15.43
5	Bent.DL - 5	50.0	25.61	16.01
6	Bent.DL - 6	52.4	25.12	15.52

^a: 9.6 Å is the length of aluminum silicate layer consisting of two tetrahedral SiO₄ sheets and octahedral AlO₄⁻ sheet [13].

At a higher CTAB content (> 37.5 wt.%), the d_{100} -spacing values are almost unchanged. This may be explained by the fact that the material was saturated and/or the extra-amount of quaternary amines may posit on the clay surface instead of intercalating between interlayers [2, 14]. The analysis of nitrogen physic sorption corroborates this observation. The specific surface area decreases from 68.9 m²/g (Batch No. 1) to 33.8 m²/g (Batch No. 4).

3.2. Infrared Spectra (FT-IR)

In order to confirm the presence of CTAB surfactant between interlayer spaces, we have collected FT-IR spectra of organoclays. Figure 2 displays two representative IR spectra for BentDL-1 (Bent-Na) and BentDL-4 (37.5 wt.% CTAB) samples.

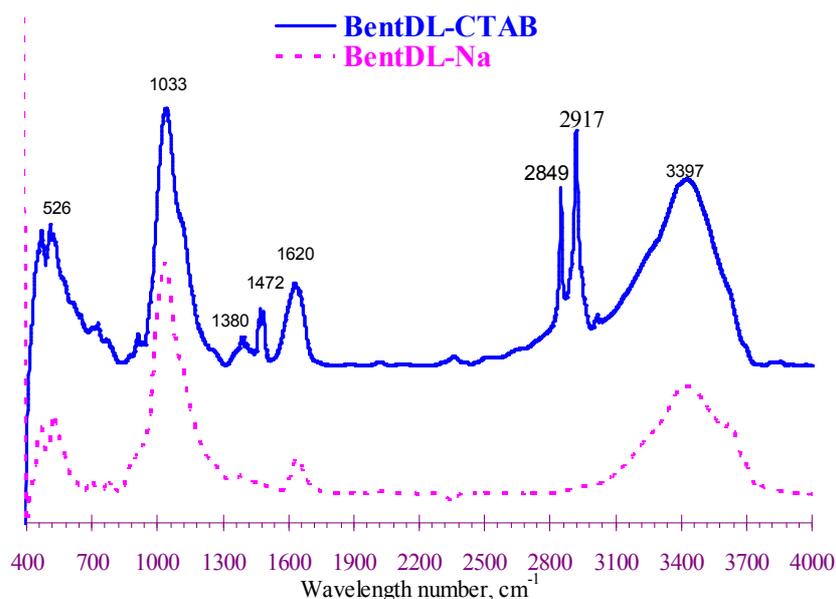


Figure 2. FT-IR spectra of Bent.DL-1 and Bent.DL-4 with 37.5 wt.% CTAB surfactant.

For both samples, FT-IR spectra show the appearance of a strong, broad absorption band at 3400-3500 cm⁻¹, firmly assigned to the OH stretching mode of hydroxyl groups from the interlayer absorbed water molecules and hydroxyls in the layers [12]. The bending vibration of H-O-H appears at 1620 cm⁻¹ [14]. In the case of Bent.DL-CTAB, the appearance of the new peaks at 2917 and 2849 cm⁻¹ characterizes to CH₂ asymmetric and symmetric stretching vibrations, respectively [2, 13]. These stretching vibrations are influenced by the conformation of the intercalated organic chains. It was well known that the frequency shift of CH₂ stretching vibrations can be used to determine the molecular environment of the

surfactant molecules in the organoclay interlayers. The higher frequencies exhibit a liquid-like environment of surfactant while the lower frequencies represent a solid-like environment of the surfactant within the montmorillonite layers, meanwhile these bands slightly shift to lower wave numbers (Fig. 2), suggesting the less ordered conformation of the alkyl chains as compared to the pure CTAB [2, 14, 15]. The peaks of scissoring vibrations of -CH₂- was observed at 1472 cm⁻¹. The band at 1033 cm⁻¹ is assigned to the characteristic vibrations of the tetrahedral sheets (for Si-O stretching vibrations). Si-O-Al and Si-O-Si bending modes are characterized by the band at 526 cm⁻¹ and a shoulder around 474 cm⁻¹ [12, 14].

3.3. Transmission Electron Microscopy (TEM)

Microscopic characteristics of clay samples are investigated using TEM technique and obtained in Figure 3. The TEM analysis strongly demonstrates the findings from XRD and

FT-IR results. For Bent.DL-1 and Bent.DL-4 (CTAB pillared-samples), TEM images reveals the features of multilayered silicate platelets having aligned as ordered, parallel and straight lines [13, 14]

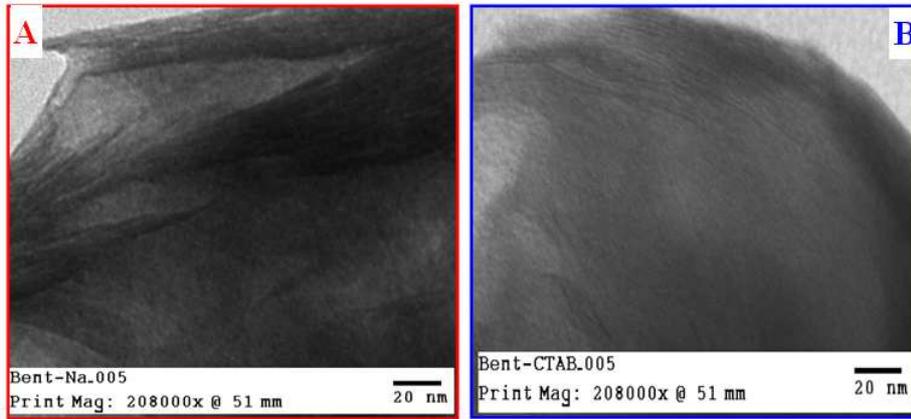


Figure 3. TEM images of Bent-Na (A) and Bent-CTAB (Bent.DL 4) (B).

Under the same magnification levels, TEM image of Bent.DL-4 is brighter and the layered structure is probably observable while Bent.DL-1 specimen shows evidence of semi-regular layered structures along with several enhanced contrast regions. The appearance of the darker regions in the TEM image of Bent.DL-1 infers a higher clay density due to the absence of the intercalated organic molecules in the mineral [14]. This is in good agreement with the change in basal spacing values conducted from XRD analysis.

3.4. Scanning Electron Microscopy (SEM)

The SEM results also provide useful information about the clay morphology. The SEM photograph of Bent.DL-1 in Fig. 5A illustrates the distinct sphere-like grains of the clay mineral with slightly wavy lattice fringes. The surface morphology of the clay particles is very close to what is observed for the montmorillonite structure [13]. The thin platelets tend to form thick and large agglomerates and show the typical swelling-related features, especially curled edges and folds [15].

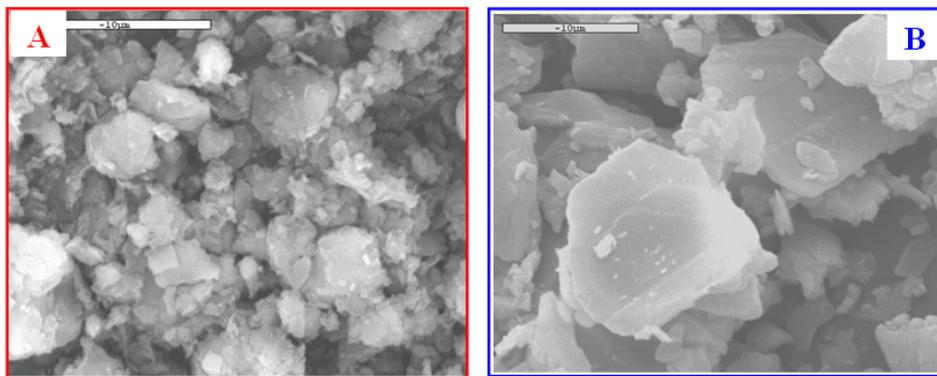


Figure 4. SEM photographs of Bent-Na (A) and Bent-CTAB (Bent.DL 4) (B).

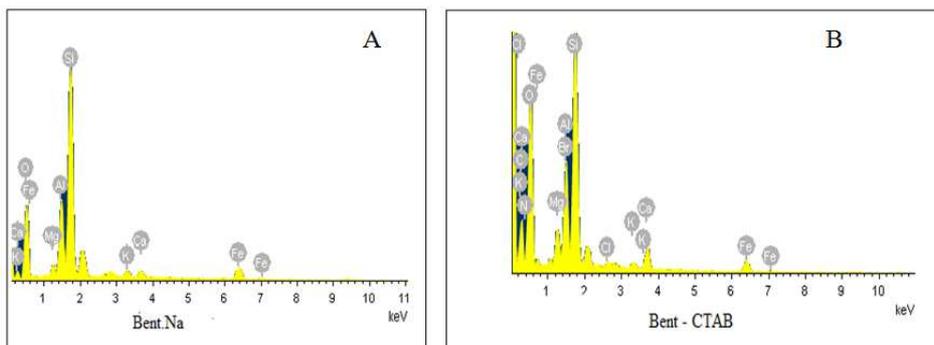


Figure 5. EDX spectra Bent.DL-1 (A) and Bent-CTAB (Bent.DL- 4) (B).

Meantime, Figure 5B shows that the physical appearance of the clay particles changed significantly. The sphere-like seeds changed to the flake-shaped particles. The clay platelets were stacked together in a disordered pattern to form several agglomerates in some parts, and small and well-separated particles were also observed. In various parts of the SEM photographs of Bent.DL-4, the grain boundaries steadily vanished. These changes in the morphologies and particle sizes are associated with the intercalation and adsorption of surfactant molecules [16]. In order to shed light on the microscopic structure of clay mineral, SEM coupled with an EDX provides a semi-quantitative elemental analysis of the solid surface. The major surface elements of montmorillonite are Si, O, and Al on the Bent-Na sample (Fig. 5A). In the EDX spectrum of Bent-CTAB (Fig. 5B) N and Br signals are clearly observed in addition to the presence of Si, Al, O, Mg, Ca, Fe, K, C elements. It is noted that C is not apart of the montmorillonite structure; it is related to the coating material sputtered on the sample. The impregnation of CTAB does change the chemical composition and expands the interlayer distance of the mineral. A higher content of N, Br in the Bent-CTAB demonstrates the existence of CTAB pillars. Fe, Ca, K have found to be normally present in most of the clays since they were not completely leached out during the pretreatment step [15].

3.5. Mechanical Properties of Antifouling Paint-Added Organoclays

5 wt.% of the synthesized organoclays was added into the antifouling paint as additives. The influence of the organoclay structure on the antifouling paint characteristics was studied. Apart from Batch 1, the others were prepared with the mass ratio of paint to organoclays of 95/5. Firstly, the viscosity of the organoclay-paint was recorded. Table 2 presents the viscosity obtained on six samples.

Table 2. Viscosity of the antifouling paint added organoclay additive.

Batch	Additives	Viscosity (s)
1	None	14.0
2	Bent.DL. Na	14.0
3	Bent.DL – CTAB, 23.1 wt%	15.2
4	Bent.DL – CTAB, 28.6 wt%	16.0
5	Bent.DL – CTAB, 37.5 wt%	19.0
6	Bent.DL – CTAB, 50.0 wt%	25.0

Table 2 shows an observable change in viscosity with the nature of organoclay additives [16]. No difference in viscosity between the parent paint (Batch 1) and Bent.DL-1 (Na) added antifouling paint (Batch No. 2) was observed (Table 2). The viscosity gradually increases with increasing the amount of CTAB in the montmorillonite layers [14, 16]. This is explained by the possibility that the organoclay pillared by surfactant molecules with a long alkyl chain has enhanced an interaction between clay embodiment and the paint-polymer structure. In other words, the presence of long alkyl chains in montmorillonite layers makes the organoclays become more compatible with the polymer molecules [17]. Therefore, an

introduction of organoclay additives into antifouling paint has some significant effects on the mechanical properties of the parent paint [16, 17].

Adhesion of the organoclay-paint was tested according to No. 2097-1993 standard protocol [9]. The paint was swept on the steel plate surface and dried for 48 h prior to the adhesion test. The adhesion results are reported in Table 3.

Table 3. Mechanical properties of antifouling paint modified organoclays.

Additives	Adhesion	T-Bend (mm)	Impact test, (kg.cm)
None	2	20	30
Bent.DL-1	2	18	50
Bent.DL-4 (CTAB, 37.5 wt.%)	2	10	50

Adhesion of the organoclay-modified paints was found to be independent of the montmorillonites content and the nature of organoclays (Table 3). The adhesion is about 2 points for all tests: unmodified paint, Bent-Na modified paint and Bent-CTAB-added paint.

The T-bent resistance was tested according to No. 2099 – 2007 standard protocol [9]. The test results show no significant difference in T-bent between the parent paint (20 mm) and anti-fouling sample added Bent.DL-1 additive (18 mm), but the T-bent value drastically decreases as Bent.DL-4 was introduced into the paint. This is attributed to the swelling property and the interaction ability between paint polymers and the organic molecules in clays [18-20]. The surfactant has facilitated the ability to dissolve the clay minerals in paint solvent.

Impact test was carried out according to the TCVN 2100 – 2007 protocol [9]. In contrast to T-bent results, the impact test result for the parent paint is much different from the value for the paint added Bent-Na. Meanwhile, there is no observable difference in impact test result between the Bent-Na and Bent-CTAB adding paints (Table 3), but the presence of organoclays in the paint promotes the impact resistance value. The silicate component has known as good impact resistance agent [14, 18, 19].

4. Conclusions

A set of clays pillared cetyl trimethyl ammonium bromide has been successfully prepared. The intercalation of CTAB has a significant effect on the d-spacing interlayers of bentonite. The interlayer distance is dependant on the amount of CTAB and preparation conditions. The basal spacings increases as the amount of CTAB varies from 10 to 40 wt.%. The intercalation of CTAB into the montmorillonite interlayers has also led to the modification of clay structure and morphology. Thus, the synthesized organoclays are further used as an additive for antifouling paint. The organo-paint was found to have some good paint testing properties. The preliminary results indicate the montmorillonite pillared by CTAB surfactant may be a promising additive for the antifouling paint.

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