Enhanced intercalation of organo-muscovite prepared *via* hydrothermal reaction at low temperature

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Abstract. Muscovite clay is an ideal reinforcing filler due to its high-aspect ratio. However, it does not swell in water, making it hard to be treated and intercalated. In this study, ion exchange treatment is carried out on muscovite clay using cetyltrimethylammonium bromide (CTAB) cations *via* two-step intercalation method. The intercalation steps included: inorganic–inorganic ion exchange treatment and inorganic–organic ion exchange treatment under hydrothermal conditions. The intercalation of muscovite particles was examined with various techniques to analyse the physical and chemical changes. Furthermore, the hydrothermal conditions for effective CTA⁺ ion intercalation within muscovite interlayers prepared *via* the hydrothermal process at low temperature, 180°C, under different hydrothermal reaction times and CTAB/Li-Mus mass ratio were investigated. Fourier transform infra-red (FTIR) analysis revealed that the CTA⁺ ions are diffused into the interlayers of aluminosilicate and formed a strong electrostatic bond with the clay surface. X-ray powder diffraction analysis showed that the interplanar spacing in the organo-muscovite samples is almost identical as the hydrothermal reaction time is prolonged beyond 12 h. An optimum limit of the CTAB to Li-Mus ratio is observed as the d_{002} plane spacing is increased with an increase of the mass ratio of CTAB to Li-Mus up to 1.0 C and decreased with a further increase in the mass ratio. In addition, the intercalated CTA⁺ chains are homogeneously distributed and formed a paraffin-like arrangement in the muscovite clay. Besides, the structure of aluminosilicate layers is not affected or damaged after both treatments according to FTIR analysis.

Keywords. Muscovite; intercalation; organic ion exchange treatment; layered silicates.

1. Introduction

Clay silicates have been widely employed in a variety key area of applications including absorbents, electrode modifiers, catalysts, as well as filler materials, sealants and suspending medium in many applications [1,2]. The type of layered silicates that are extensively studied and used as reinforcement phase in polymer composite are smectite, especially montmorillonite [3–5] and saponite [6,7]. The nature of swelling behaviour of both layered silicates has made them favourable in the organic cation exchange treatment [8,9]. In addition, there is another type of layered silicate mineral i.e., mica, especially muscovite that has gradually attracted the attention among researchers recently. Various studies on muscovite reinforced polymer composites had been performed [10–12]. Basically, muscovite is a potassium-rich mica [13] where each of its unit cells (composed of two silica tetrahedral sheets and an alumina octahedral sheet in the form of sandwich structure) are bonded by K⁺ ions [14,15]. Moreover, muscovite

has a higher aspect ratio than montmorillonite [10], making it more suitable as an ideal reinforcing material for polymer composites.

The properties of polymer composites are significantly influenced by the dispersion of layered silicate fillers in the polymer matrix. Generally, dispersion of neat-layered silicates in the polymer matrix is limited due to the natural surface hydrophilicity of aluminosilicate layers [16]. Hence, minimized the compatibility of layered silicates in the polymer matrix [17]. However, the incompatibility issue of silicate particles can be overcome by altering their surface nature from hydrophilic to hydrophobic *via* ion exchange treatment [11].

It is noted that ion exchange and intercalation of muscovite are not easily performed as it does not swell in water. Basically, strong electrostatic bonding is formed between the interlayer cation chains and aluminosilicate layers of muscovite due to homogeneous charge distribution on aluminosilicate layers [18]. Thus, it is difficult to intercalate the muscovite particles with organic cations

using a conventional direct ion exchange treatment method [8]. To address this issue, specific modification on the interlayer cations of muscovite particles was carried out; for instance, ion exchange treatment with other inorganic ions.

Previously, different groups of researchers [19–21] had utilized Li and other alkaline earth metals (Ba, Ca and Mg) as the inorganic cations as first-step ion exchange treatment to modify the muscovite structure. However, the muscovite structure obtained after delamination was not satisfactory. In 2005, a breakthrough was obtained by Zhao and coworkers [22], where delaminated muscovite particles with a high-specific surface area were successfully prepared using hot saturated LiNO_3 solution to treat the muscovite powder. After LiNO_3 treatment, the muscovite particles were more favourable for the organic intercalation process as their basal spacing was expanded significantly.

The aim of organic ion exchange treatment is to alter their surface property into hydrophobic. Basically, quaternary ammonium ions are the common organic cations used in organic ion exchange treatment [23]. One of the organic cations that are frequently used to modify the muscovite surface property is cetyltrimethylammonium ions (CTA^+). Muscovite particles were intercalated by Yu and coworkers [9] using cetyltrimethylammonium bromide (CTAB) as an organic surfactant *via* a hydrothermal reaction at 200°C which resulted in an increment of muscovite interlayers spacing up to $27.4 \text{ \AA}$. In a recent paper, Che Ismail *et al* [24] reported the structural changes of intercalated organo-muscovite clay prepared using different concentrations of the surfactant.

Although various studies have been carried out on the preparation of organo-muscovite with different amines, yet there is a lack of information available on the effect of the hydrothermal reaction time and the CTAB to Li-muscovite concentration ratio prepared at low temperature, 180°C . Hence, this study was conducted with the aim of altering the hydrophilic nature of muscovite particles into organo-muscovite *via* the two-step intercalation method using LiNO_3 treatment and CTAB as the organic surfactant at 180°C hydrothermal reaction. LiNO_3 treatment was chosen since the solution does not alter the structural and chemical compositions of muscovite [8,24], whereas alkylammonium cations are well known to be easily adsorbed on muscovite crystals forming stable molecules with different arrangements [9]. The chemical, morphological and structural changes of the intercalated muscovite clay were investigated. In addition, the hydrothermal conditions for the effectiveness of CTA^+ ions intercalated within muscovite interlayers at different hydrothermal reaction times and CTAB/Li-Mus mass ratios were studied and the structural changes and orientation of CTAB molecules were analysed. Based on the analyses result, the optimum intercalation of muscovite particles using an organic surfactant, i.e., CTAB could be accomplished at a certain hydrothermal reaction time and CTAB concentration.

2. Experimental

2.1 Materials

Muscovite powder, 2M_1 was obtained from Lingshou County Xinfu Mineral Co. Ltd., China. Lithium nitrate powder (LiNO_3 , purity $\geq 99\%$) was purchased from Alfa Aesar, USA and CTAB (purity $\geq 98\%$) was obtained from Merck.

2.2 Synthesis of Li-Mus and CTA-Mus powders

Li-muscovite (Li-Mus) and CTA-muscovite (CTA-Mus) were prepared based on the modified method by Yu and coworkers [9]. Muscovite powder, 2M_1 was mechanically mixed with LiNO_3 powder in a ratio of 1:17 (muscovite: LiNO_3) using ball mill for 2 h. Subsequently, the mixture was heated in a furnace at 300°C for 12 h. The product was then filtered and washed repeatedly three times using deionized water, followed by drying in an oven at 100°C for 24 h. LiNO_3 treatment was repeated for three times and the final product was named Li-Mus. Then, organo-muscovite (CTA^+ -muscovite, CTA-Mus) powder was prepared using CTAB as the cationic surfactant under hydrothermal conditions. In this study, two parameters were varied during the hydrothermal reaction, which were (1) reaction time and (2) mass ratio of CTAB to Li-Mus.

For the study of the hydrothermal reaction time, CTA-Mus particles were prepared using 0.5 mass ratio of CTAB to Li-Mus. First, 1.6 g of CTAB powder was dissolved in 400 ml deionized water. Then, 3.2 g of Li-Mus was added and mixed with aqueous CTAB solution at room temperature. Subsequently, the mixtures were placed in a hydrothermal reactor equipped with a Teflon-lined stainless-steel autoclave and reacted under hydrothermal conditions at 180°C for 12, 16, 20 and 24 h, respectively. The surfactant-muscovite product (CTA-Mus) was then filtered and washed with ethanol three times. The filtered paste was dried in an oven at 50°C for 12 h and ground using an agate mortar. The prepared samples were named CTA-Mus 12, CTA-Mus 16, CTA-Mus 20 and CTA-Mus 24.

The investigation on the CTAB to Li-Mus mass ratio was performed after the optimum hydrothermal reaction time was selected. In this study, the CTA-Mus particles with different CTAB to Li-Mus mass ratios (0.5C, 1.0C and 1.5C) were prepared under hydrothermal conditions at 180°C for 12 h. The samples prepared were labelled as CTA-Mus 0.5C, CTA-Mus 1.0C and CTA-Mus 1.5C.

2.3 Characterization of Li-Mus and CTA-Mus powders

The X-ray fluorescence (XRF) spectrometer (Rigaku Rix 3000) was used to identify the elements present in the raw and treated muscovite particles by pressing 1 g of muscovite particles into a 13 mm diameter cylindrical pellet with 2 mm thickness as the XRF sample. The amount of each element

present in the treated and untreated muscovite samples was obtained using XRF analysis.

X-ray powder diffraction (XRD) analysis was performed using a PANalytical X-ray diffractometer (X'Pert PRO MRD PW 3040/60 generator, PANalytical). The X-ray beam employed was derived from $\text{CuK}\alpha$ radiation (wavelength, $\lambda = 0.154 \text{ nm}$) in a sealed tube operated at 40 kV/35 mA. Measurements were collected at the 2θ angle range for both the wide angle (from 1 to 50°) and small angle (from 1 to 10°). Furthermore, the scan step time and step size parameter used in the XRD analysis were 2.5 s and 0.05° , respectively.

The elemental bonding present in the treated and untreated muscovite particles was examined using an Fourier transform infrared (FTIR) spectrometer (Spectrum One FTIR spectrometer, PerkinElmer). Each specimen was scanned with 32 scans over the mid-infrared frequency wavelength in the range of $550\text{--}4000 \text{ cm}^{-1}$. A KBr pellet measurement method with a resolution of 4 cm^{-1} was performed on each sample during FTIR measurement.

Morphological analysis of samples was acquired using scanning electron microscopy (SEM) (Zeiss Supra 35VP, Germany) operated at 5 kV. In addition, energy dispersive X-ray (EDX) spectroscopy analysis was also performed on the samples to identify the elements of the samples.

Samples for transmission electron microscopy (TEM) analysis were prepared by dispersing the powder in ethanol using ultrasonic for 30 min. Next, drops of the dispersed sample were placed onto a copper grid and dried in air. High-resolution TEM (HRTEM) analysis was carried out

on treated and untreated muscovite using TECNAI G² 20 S-Twin, FEI HRTEM operated at 200 kV.

3. Results and discussion

3.1 Intercalation of Li^+ ions into muscovite

Muscovite is composed of negatively-charged aluminosilicate layers and K^+ cation layers in alternate positions, parallel to the (001) plane [25]. Basically, muscovite particles do not swell like other layered silicates during interactions with water due to the existence of strong electrostatic bonding between aluminosilicate layers with K^+ cations [18]. Therefore, the cleaving process is necessary to ensure the muscovite particles are intercalated with an organic surfactant. Muscovite particles are cleaved by using the molten alkaline cations, Li^+ at 300°C [22] to allow the organic ion exchange treatment to be held easily. Figure 1 shows the intercalation procedure of muscovite particles. Raw muscovite was first treated with LiNO_3 solution to swell the interlayer spacing of the particles. The small Li cations entered the vacant sites of the octahedral layer of muscovite during LiNO_3 treatment and caused a partial release of K^+ ions between the clay layers. As a result, strong electrostatic force between layers was reduced and resulted in the interlamellar expansion [25].

Figure 2 shows the X-ray diffractograms of raw muscovite, Li-Mus after first-time and third-time LiNO_3 treatments.

Figure 1. Intercalation procedure of muscovite particles.

Figure 2. XRD patterns of samples: (a) muscovite 2M₁, (b) Li-Mus after first LiNO₃ treatment and (c) Li-Mus after third LiNO₃ treatment.

Table 1. *d*-values of diffraction (00l) for muscovite 2M₁, Li-Mus after first LiNO₃ treatment and Li-Mus after third LiNO₃ treatment.

Samples	<i>d</i> -values of diffraction (00l), Å	
	<i>d</i> ₀₀₂ [#]	<i>d</i> ₀₀₄ [°]
Muscovite 2M ₁	10	5
Li-Mus after first LiNO ₃ treatment	12.1	—
Li-Mus after third LiNO ₃ treatment	12.2	6.1

The changes occur in the *d*-spacing of aluminosilicate interlayers in the muscovite after ion exchange treatments were calculated by using the Bragg's law and are summarized in table 1.

After the first-time LiNO₃ treatment, some changes occurred on the muscovite structure as the new diffraction peak for (*d*₀₀₂) was visible around $2\theta = 7.2^\circ$ (figure 2b). The relative intensity of a new diffraction peak increased with the number of LiNO₃ treatments. Thus, the diffraction peaks of new (*d*₀₀₂) and (*d*₀₀₄) of muscovite were visibly emerged after third-time LiNO₃ treatment (figure 2c). In addition, the diffraction peak for the (004) plane (around $2\theta = 14.4^\circ$) became more visible after the third treatment compared to the first LiNO₃ treatment. Furthermore, the intensity of original muscovite peaks was reduced after third LiNO₃ treatment. Based on the results obtained, it can be concluded that three times of LiNO₃ treatment is sufficient to enlarge the basal spacing of muscovite aluminosilicate interlayers (12.2 Å). A wider spacing of muscovite aluminosilicate interlayers is preferred for the CTA⁺ cation exchange treatment.

Figure 3. XRD patterns of (a) muscovite 2M₁, (b) Li-Mus and (c) CTA-Mus.

Table 2. *d*-values of diffraction (00l) of muscovite 2M₁, Li-Mus and CTA-Mus.

Samples	<i>d</i> -values of diffraction (00l), Å	
	<i>d</i> ₀₀₂ [#]	<i>d</i> ₀₀₄ [°]
Muscovite 2M ₁	10	5
Li-Mus	12.2	6.1
CTA-Mus	28.4	13.8

3.2 Characterization of CTA-Mus powder

CTAB, acted as an organic surfactant, is an amphiphilic compound which contains hydrophilic (head) and hydrophobic (tail) parts. During the hydrothermal reaction of Li-Mus with CTAB, the CTAB molecules were intercalated within the aluminosilicate clay layers, hence, increased the basal spacing. During the intercalation process, the positive polar heads of CTA⁺ cations were attached on the hydrophilic surfaces of aluminosilicate clay layers, while strong repulsive forces arise between hydrophobic ends of CTAB molecules.

The XRD patterns of muscovite, Li-Mus and CTA-Mus are shown in figure 3. The XRD patterns of muscovite observed were identical to potassium-type mica [26]. The muscovite structure was modified as there is appearance of new diffraction peaks which include (002) and (004) planes after LiNO₃ and CTAB treatments, marked as hash (#) and circle (o) symbols, respectively. The calculated *d*-values of diffraction for each sample are summarized in table 2. It is noted that the *d*-spacing of aluminosilicate layers in muscovite increased after ion exchange treatments, as the organo-clay platelets tend to repel each other. Similar findings were also observed by other researchers [9,17,19,22].

The diffraction peak of the (002) plane of muscovite 2M₁ arises at 8.85° , where the *d*-spacing of the corresponding interlayer is around 10.0 Å. On the other hand, the (*d*₀₀₂)

peak of Li-Mus was shifted to a lower 2θ angle, around 7.2° and the gap of the interlayer had increased to $12.2 \text{ \AA}$. Similarly, the diffraction peak of (d_{002}) of CTA-Mus was shifted to a lower angle, $2\theta = 3.1^\circ$ as compared to Li-Mus and the d -spacing has widened to $28.4 \text{ \AA}$. Hence, almost 184% increment of the d -spacing between aluminosilicate layers was obtained in muscovite after both LiNO_3 and CTAB ion exchange treatments. Therefore, a new series of XRD line patterns was obtained for Li-Mus and CTA-Mus.

Besides, the calculated d -spacing for Li-Mus and CTA-Mus is in line with the relationship, $d_{002} \approx 2d_{004}$ (table 2). Moreover, the peak height intensities of muscovite include (d_{002}), (d_{004}), (d_{006}) and (d_{010}) and have reduced significantly after the LiNO_3 and CTAB treatments. Generally, the intensity of diffraction peaks could be affected by various factors, such as the atom species and its fractional coordination and the cell parameter [8]. Based on this finding, it can be concluded that the decrement in intensity of original peaks may be due to the existence of partial or full exfoliation between some muscovite clay layers [27].

The crystallite sizes of treated and untreated muscovite at the (002) plane are of major concern as the intercalation and exfoliation of the muscovite structure can be determined based on the crystallite size of the (002) plane. The crystallite size (D) of stacked aluminosilicate layers was calculated using the Scherrer equation [28]. Then, the calculated crystallite size of stacked aluminosilicate layers was collected and summarized in table 3. The crystallite size of stacked aluminosilicate layers decreased after LiNO_3 treatment and remained constant after CTAB treatment. Reduction in the crystallite size indicates that the lattice structure of muscovite clays becomes less rigid [24]. Therefore, a lower energy is required to modify the structure and surface properties of muscovite particles after LiNO_3 treatment. The number of stacked aluminosilicate layers was reduced after LiNO_3 treatment and further decreased after CTAB treatment, which indicates a significant increase in interlayer spacing of muscovite particles after ion exchange treatments.

Elemental analysis was performed on the raw muscovite, Li-Mus and CTA-Mus powders using XRF. As displayed in table 4, decrement of Na^+ and K^+ elements sited in the aluminosilicate interlayers of muscovite was observed after the third LiNO_3 treatment. This phenomenon occurs as most of the interlayer cations (potassium, K^+ ions) between

Table 4. Chemical composition of untreated and treated muscovite.

Element	Mass%		
	Muscovite	Li-Mus	CTA-Mus
Na	0.1	0	0
K	7.4	4.5	4.4
Al	16.5	16.5	16.4
Si	24.9	25.6	26.2
Mg	0.4	0.3	0.3
Fe	4	4.9	5

layered silicate were replaced with lithium, Li^+ ions during the cleavage process [8]. Thus, the aluminosilicate layers in muscovite were partially delaminated for the ease of organic ion exchange treatment.

In contrast, the ion exchange process between the alkaline earth cations, such as Li^+ and K^+ ions in the Li-Mus interlayer and CTA^+ cations occurred during CTAB treatment. Hence, this led to the reduction of K^+ ions in muscovite after CTAB treatment. Concurrently, the content of Al and Mg elements (composition of aluminosilicate layers of muscovite) was almost similar to CTA-Mus and Li-Mus. Meanwhile, the increment in the amount of Fe after LiNO_3 treatment suggests that the contamination of Li-Mus occurred during the cleaving process. Furthermore, the amount of silica in treated muscovite also increased after LiNO_3 and CTAB treatments. The increment of Si elements in treated muscovite particles was due to the effect of the grinding process which led to an increase in the amount of exposed hydroxyl bonded muscovite aluminosilicate layers. Similar observation was reported by Che Ismail and friends [24].

The effectiveness of both LiNO_3 and CTAB treatments for intercalating the muscovite particles can be examined using FTIR analysis. It can be observed that there were several overlapping and new bands appeared in muscovite after both LiNO_3 and CTAB treatments. The band, at about 1020 cm^{-1} in figure 4, is attributed to the stretching and bending vibrational motions of Si–O bonds [8] as their vibration bands were commonly observed in the range of $1100\text{--}950 \text{ cm}^{-1}$ [29]. This indicates that the backbone structure of the aluminosilicate layer for Li-Mus and CTA-Mus remains similar to muscovite 2M_1 after both LiNO_3 and CTAB treatments. In addition, the transmission band appeared at around 3624 cm^{-1} was due to the stretching motion of OH groups in muscovite particles. Meanwhile, the infrared transmission bands in region between $1300\text{--}500 \text{ cm}^{-1}$ (figure 4) correspond to the vibrations in the aluminosilicate layers [30].

Furthermore, there were transmission bands observed at around 920 , 828 , 751 and 530 cm^{-1} . The band at about 920 cm^{-1} was attributed to the OH in-plane vibration as a result of bending motion of OH groups arranged in the octahedral Al pair [8,31]. The transmission band at 828 cm^{-1} was attributed to the stretching motion of Al–O bonds [32].

Table 3. d -values of diffraction (001) of muscovite 2M_1 , Li-Mus and CTA-Mus.

Samples	d -values of (002) plane, nm	Crystalline size (D), nm	Number of stacked aluminosilicate layers (D/d values)
Muscovite 2M_1	1	88.5	88.5
Li-Mus	1.2	13.5	11.3
CTA-Mus	2.8	13.5	4.8

Figure 4. FTIR spectra of (a) muscovite 2M₁, (b) Li-Mus and (c) CTA-Mus.

Figure 5. Selected regions of FTIR spectra of (a) muscovite 2M₁, (b) Li-Mus and (c) CTA-Mus.

However, its height intensity seems to be decreased after LiNO₃ treatment due to the increment of octahedral substitution content; such as Fe ions between the aluminosilicate layers in muscovite particles [30]. Reduction of this peak intensity is in good agreement with the results obtained in XRF analysis.

The infrared transmission bands detected at 751 and 530 cm⁻¹ were corresponded to the Si–O–Al in-plane and Si–O–Al^{VI} vibrational motion, respectively. The intensity of the transmission band at 751 cm⁻¹ was affected by the amount of octahedral Al present in the aluminosilicate layers [30]. However, the intensity of this band remained constant in the spectra of Li-Mus and CTA-Mus (figure 5b and c), indicating that the amount of octahedral Al in muscovite was not affected by both LiNO₃ and CTAB treatments. Therefore, it can be concluded that the main structure of the aluminosilicate layers in muscovite was not damaged after LiNO₃ and CTAB treatments. The intensity of every transmission band in

the infrared spectra remains unchanged, except for the Al–O stretching vibration peak appearing at around 828 cm⁻¹.

The intensity of new bands at around 3435 and 1638 cm⁻¹ appeared stronger for Li-Mus after LiNO₃ treatment. This indicates that a large amount of water is absorbed onto the interlayers of aluminosilicate which leads to an increment in the *d*-spacing of aluminosilicate interlayers [8]. Both new transmission bands appear in figure 4b were attributed to the H₂O stretching and bending vibrations, respectively. Nevertheless, the intensity of both infrared transmission bands decreased after CTAB treatment (figure 4c). As the Li⁺ ions in aluminosilicate layers were replaced with CTA⁺ cations, the water content in CTA-Mus nanoclays was reduced, since the amount of strong hydroscopic Li⁺ ion content in the muscovite decreased after CTAB treatment [8].

Several new bands were present after the CTA⁺ cations exchange process as shown in figures 4c and 5c, confirming the binding of the long chain of CTA⁺ ions on the aluminosilicate nanosheet surface. New transmission bands appeared at around 2918 and 2849 cm⁻¹ were attributed to the stretching vibrations of asymmetric and symmetric CH₂. The stretching vibration of symmetric CH₂ has a lower dipole moment, thus, appearing at lower frequency [33]. Furthermore, the vibration mode of the CH₂ frequency and its peak width are affected by the presence of the gauche/trans methylene chains conformer ratio [17,18].

The transmission band at 1488 cm⁻¹ of CTA-Mus was assigned to the asymmetric bending motion of the methyl head group, suggesting the formation of the bond between methyl head groups, (CH₃)₃N⁺ and the aluminosilicate layers' surface [17]. Besides, the bands at 1473–1463 and 720 cm⁻¹ (figures 4c and 5c) were corresponded to the scissoring and rocking vibration mode of methylene, respectively. This phenomenon occurs due to the intermolecular interactions between the two adjacent hydrocarbon chains [9]. Based on the infrared spectrum exhibited in figure 4, it can be concluded that the ion exchange treatments were successfully performed on neat muscovite particles.

The morphological changes of muscovite after both treatments were observed using SEM (figure 6). In the beginning of the process, the aluminosilicate layers of muscovite particles were attached to each other (figure 6a). The high-electrostatic forces were present between layers and led to poor organic ion exchange treatment [34]. There were changes observed on the structure of muscovite particles after LiNO₃ treatment, in which some aluminosilicate layers were partially delaminated from each other (figure 6b). It justified the XRD result obtained as the spacing of aluminosilicate interlayer was increased after LiNO₃ treatment hence, allows the organic intercalation process to be performed easily. The spacing of aluminosilicate interlayers in CTA-Mus was further expanded after CTAB treatment due to the presence of the repelling effect between the organic cations present on the aluminosilicate surface layers.

Moreover, the atomic percentage of elements in untreated and treated muscovite was acquired using EDX analysis

Figure 6. SEM images of (a) muscovite 2M₁, (b) Li-Mus and (c) CTA-Mus at 5 k $\times$ magnification.

Table 5. EDX analysis of untreated and treated muscovite.

Element	Atomic%			
	Muscovite	Li-Mus		CTA-Mus
		First treatment	Third treatment	
Oxide, O	50.6	55.1	51.7	43.8
Potassium, K	6.7	4.2	2.8	2.7
Aluminium, Al	17.4	15.2	18.5	21.2
Silicon, Si	22.4	21.7	23.2	28.6
Magnesium, Mg	0.8	1.4	1.6	1.6
Iron, Fe	2.2	2.4	2.2	2.2

(table 5). The EDX analysis suggests that oxygen, O₂ contributed major elements for muscovite, Li-Mus and CTA-Mus. The amount of potassium, K element decreased significantly after LiNO₃ treatment and further decreased after CTAB treatment. On the other hand, the amounts of Si and Al elements (main composition of aluminosilicate layers) present in CTA-Mus and Li-Mus nanoclays were almost similar.

Microstructural changes of muscovite after LiNO₃ and CTAB treatments were observed using HRTEM. Figure 7 illustrates the ultrathin section of muscovite, Li-Mus and CTA-Mus samples. The (002) plane of muscovite remained in a parallel and compact interlayer spacing configuration arrangement after LiNO₃ and CTAB treatments. The aluminosilicate interlayers' spacing of raw muscovite (figure 7a) is 10 Å. This result is in agreement with the *d*-spacing of

Figure 7. HRTEM images of (a) muscovite 2M₁, (b) Li-Mus and (c) CTA-Mus samples in an ultrathin section.

the (002) plane of muscovite in XRD analysis (table 2). Furthermore, the galleries of muscovite were enlarged after LiNO₃ treatment. This phenomenon occurs due to the alkali ion exchange process that took place on the aluminosilicate layer surface, where some K⁺ and Na⁺ ions were replaced with Li⁺ ions during the cleaving process. Hence, this led to the expansion of d_{002} spacing in Li-Mus from 10 Å to about 12 Å. The interlayer spacing of (d_{002}) obtained *via* HRTEM analysis for Li-Mus is almost similar to the XRD result, which is 12.2 Å.

In addition, the d -spacing of aluminosilicate layers in muscovite was further increased *via* the organic ion exchange treatment. The HRTEM image of CTA-Mus (figure 7c) shows a spacing of 21 Å for the (002) plane. The expansion of CTA-Mus aluminosilicate interlayer spacing was attributed to the repelling effect of the organo-cation that present on the silicate layer surface [17]. A slight difference in the (002) plane spacing of CTA-Mus was observed *via* the HRTEM image as compared to the d -spacing obtained (28.4 Å) in XRD analysis. According to Lee and Kim [35], the occurrence of this

phenomenon may be due to the collapse of aluminosilicate layers when collided with the electrons during HRTEM observation.

3.3 Effect of reaction time during hydrothermal process

Diffraction peaks and d -spacing values of CTA-Mus samples treated at different hydrothermal reaction times are shown in figure 8 and table 6, respectively. The structure of all CTA-Mus samples was modified by the organic treatment as their d -values of the (002) plane diffraction peak were augmented from 12.2 Å (d -values of Li-Mus) to 28.4 Å. By varying the reaction times, the type of arrangement of organic molecules within the interlamellar spacing of clay platelets could be deduced from the increment of basal spacing. According to the literature, the organic molecules are arranged in the form of monolayer, bilayer, pseudo-trimolecular layer or paraffin complex between the clay unit layers [36,37].

Initially, the aluminosilicate interlayer spacing of the (002) plane in muscovite was calculated to be ~10.0 Å, whereas

Figure 8. XRD patterns of (a) Li-Mus, (b) CTA-Mus 12, (c) CTA-Mus 16, (d) CTA-Mus 20 and (e) CTA-Mus 24.

Table 6. *d*-values of diffraction (001) obtained from the XRD pattern of samples at different hydrothermal reaction times.

Samples	<i>d</i> -values of diffraction (001), Å	
	<i>d</i> ₀₀₂ [#]	<i>d</i> ₀₀₄ [°]
Li-Mus	12.2	6.1
CTA-Mus 12	28.4	13.8
CTA-Mus 16	28.3	13.8
CTA-Mus 20	28.3	13.9
CTA-Mus 24	28.4	13.8

the diameter of K⁺ ions is generally ~2.7 Å [38]. Thus, the thickness of aluminosilicate sheets in the muscovite is around 7.3 Å. In addition, the fully stretched CTA⁺ chain length is about 23.6 Å [39,40]. Thus, the spacing of aluminosilicate interlayers left in the half unit cell is ~21.1 Å (28.4–7.3 Å) after considering the *d*-spacing of CTA-Mus samples (table 6) and the calculated thickness of aluminosilicate sheets.

Hence, based on the *d*-spacing values obtained for all samples at different hydrothermal reaction times, the CTA⁺ cations were bonded with the respective aluminosilicate layer surface in the perpendicular or tilted arrangement (paraffin-type bilayer configuration) as spacing of aluminosilicate layers in CTA-Mus samples was almost equivalent to the length of the fully stretched CTA⁺-chain (figure 1). Paraffin arrangement of the CTA⁺-chain allows homogeneous charge distribution of the organic cation, CTA⁺ throughout aluminosilicate layers which results in higher charge density [9]. Moreover, the (002) plane diffraction peaks of CTA-Mus samples were almost similar in terms of the position and their *d*-value as the hydrothermal reaction time is prolonged to more than 12 h. An increase in the basal spacing and paraffin arrangement of CTA⁺ of treated muscovite is important for

Figure 9. FTIR spectra of (a) CTAB and CTA-Mus samples ((b) CTA-M 12, (c) CTA-M 16, (d) CTA-M 20 and (e) CTA-M 24) prepared at different hydrothermal reaction duration.

Figure 10. FTIR spectra of (a) CTAB and CTA-Mus samples ((b) CTA-M 12, (c) CTA-M 16, (d) CTA-M 20 and (e) CTA-M 24) prepared at different hydrothermal reaction duration in selected region at 1500–1440 cm⁻¹.

the interaction between the polymer matrix with muscovite as a filler during the preparation of polymer composites. The head of CTAB is attached to the muscovite surface, while the tail will interact with the polymer matrix hence, promote strong adhesion between the filler/matrix interface. This phenomenon will aid the compatibility between the filler and matrix and enhance the dispersion of filler hence, further improve the final properties of the polymer composite.

The FTIR spectra of CTA-Mus samples prepared at 12, 16, 20 and 24 h are shown in figures 9 and 10. It is observed that the intensity of the transmission bands in the spectra of all CTA-Mus samples was almost unchanged. Furthermore, the asymmetric bending vibration of the (CH₃)₃N⁺ group at around 1488 cm⁻¹ in all samples is almost similar to the crystalline CTAB (figure 10). This indicates that the head groups of CTA⁺ ions in all samples are homogeneously distributed and form bonding with the aluminosilicate layers' surface

Figure 11. XRD patterns of (a) Li-Mus, (b) CTA-Mus 0.5 C, (c) CTA-Mus 1.0 C and (d) CTA-Mus 1.5 C.

Table 7. d -values of diffraction (00l) obtained from XRD patterns of samples in different CTAB to Li-Mus mass ratios.

Samples	d -values of diffraction (00l), Å	
	$d_{002}^{\#}$	d_{004}°
Li-Mus	12.2	6.1
CTA-Mus 0.5 C	28.4	13.8
CTA-Mus 1.0 C	28.6	13.8
CTA-Mus 1.5 C	28	13.7

[9]. Therefore, the intercalation process of CTA^+ cations into muscovite particles is not significantly enhanced by further increase in the duration of the hydrothermal reaction up to 16 h and more.

3.4 Effect of CTAB concentration

XRD diffraction peaks of CTA-Mus samples with different CTAB to Li-Mus mass ratios prepared in the hydrothermal reaction at 180°C for 12 h are shown in figure 11 and the value of d_{002} is summarized in table 7. The value of d_{002} in CTA-Mus increased gradually with the CTAB to Li-Mus mass ratio. However, the d -spacing of interlayers declines beyond 1.0 mass ratio of CTAB to Li-Mus. The space available in the gallery of the interlayer seems to be fully occupied by CTA^+ ions at 1.0 as it is the threshold concentration limit.

Figure 12 illustrates the FTIR spectra of CTA-Mus samples prepared at 0.5, 1 and 1.5 mass ratios of CTAB to Li-Mus. The intensity of both asymmetric and symmetric CH_2 stretching bands was gradually increased with the CTAB to Li-Mus mass ratio. However, the intensity of these bands remained almost constant once the mass ratio of CTAB to Li-Mus is beyond the threshold concentration limit (1 C). The intensity of both CH_2 bands was similar to both CTA-M 1 C and

Figure 12. FTIR spectra of CTA-Mus samples prepared at different ratios: (a) CTA-M 0.5 C, (b) CTA-M 1.0 C and (c) CTA-M 1.5 C.

Figure 13. FTIR spectra of CTA-Mus samples prepared at different ratios in a selected region between $2950\text{--}2800\text{ cm}^{-1}$.

CTA-M 1.5 C, even the mass ratio of CTAB to Li-Mus is increased (figure 13). Hence, it can be concluded that threshold of the CTAB to Li-Mus mass ratio is limited to the amount of not more than 1 ratio.

Therefore, the information obtained on the changes of basal spacing and surfactant arrangement in the treated organoclay as a function of reaction time and CTAB concentration during the hydrothermal reaction may allow the tailor of polymer intercalation to a specific purpose.

4. Conclusion

Alkylammonium cations were successfully intercalated within the aluminosilicate layers of muscovite using a two-step intercalation method. The chemical properties as well as the morphological and structural changes of the intercalated muscovite clay were explored *via* several analytical techniques. XRD analysis showed that the d_{002} plane

spacing of muscovite clays had enlarged from 10 to 12.2 Å after LiNO₃ treatment. In addition, decrement of K⁺ and Na⁺ ions observed *via* EDX analysis after LiNO₃ treatment, suggesting the replacement with Li⁺ ions. Furthermore, CTA⁺-intercalated muscovite was obtained after ion exchange treatment between inorganic and organic cations *via* the hydrothermal process. After CTAB treatment, *d*-values of the (002) plane had increased significantly to 28.4 Å. FTIR analysis of CTA-Mus indicated that the head groups of CTA⁺ were uniformly distributed on the surface of aluminosilicate layers due to the electrostatic bond. The effect of the hydrothermal reaction time and the CTAB to Li-Mus mass ratio was investigated during CTA-Mus preparation at 180°C and several findings were observed. First, the arrangement and intercalation of CTA⁺ chains were not affected by the duration of the hydrothermal reaction, since the *d*-spacing of the (002) plane for all the samples prepared at different reaction times are almost similar, *d* ~ 28.4 Å. Besides, the CTA⁺ chain arrangement in the CTA-Mus samples appeared in a fully stretched paraffin-like structure. Hence, the optimum reaction time for CTAB treatment under hydrothermal conditions at 180°C was obtained at 12 h. Secondly, there were optimum limit observed during the preparation of CTA-Mus at different CTAB to Li-Mus ratios. The *d*-values of the (002) plane of CTA-Mus is increased with the mass ratio up to 1 and decreased with a further increase in the mass ratio. Thus, the optimum mass ratio in obtaining almost fully intercalated CTA-Mus sample is taken as 1 mass ratio with 28.6 Å basal spacing. Apart from this, FTIR analysis suggested that the structure of aluminosilicate layers was not affected and damaged after both LiNO₃ and CTAB treatments. Therefore, the surface treatments of the muscovite layers in this study allows for further exploration of their potential use as filler materials in various applications.

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