การศึกษาความเข้มข้นของโพแทสเซียมอะซิเทตต่อโครงสร้างดินเหนียว
A study of potassium acetate concentration on clay structure

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บทคัดย่อ

การศึกษานี้มีวัตถุประสงค์เพื่อศึกษาความเข้มข้นของสารละลายโพแทสเซียมอะซิเทตในการขยายชั้นดินเหนียวเคโอลินโดยกระบวนการแทรกชั้นดิน (intercalation) และการให้ความร้อนโดยใช้โพแทสเซียมอะซิเทต ความเข้มข้น (3 4 5 6 7 และ 8 โมล่าร์) การแช่ดินในสารละลายช่วยทำให้เกิดคอมเพล็กซ์ของดินเหนียวและอะซิเทต จากการวิเคราะห์ด้วยเครื่องเอกซ์เรย์ดิฟแฟรกโตมิเตอร์ (X-ray diffractometer: XRD) พบว่าเมื่อใช้โพแทสเซียมอะซิเทตความเข้มข้นมากขึ้นทำให้สัดส่วนการเกิดการแทรกชั้นดินเพิ่มขึ้นด้วย อย่างไรก็ตามการศึกษานี้เลือกใช้โพแทสเซียมอะซิเทตความเข้มข้น 5 โมล่าร์เพื่อรักษาสิ่งแวดล้อม การเกิดคอมเพล็กซ์ของดินเหนียวและอะซิเทต อย่างสมบูรณ์ที่อุณหภูมิห้องใช้เวลา 3 วัน โดยคอมเพล็กซ์ดินจะขยายตัวและถูกแยกชั้นเมื่อโดนความร้อน ผลวิเคราะห์จากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกวาด (Scanning electron microscopy: SEM) และ XRD พบว่าโพแทสเซียมอะซิเทตมีผลต่อโครงสร้างของดินเหนียว เคโอลินด้วยการทำให้ชั้นดินเหนียวแยกตัวออกจากกัน

Abstract

This research study aims to study the potassium acetate concentrations on the increase of kaolin interlayers through intercalation and heat treatment processes. The effect of six different concentrations of potassium acetate : KAc (3, 4, 5, 6, 7, and 8 M) were used. The soaking process was applied on clay to form clay-acetate complex. X-ray diffraction (XRD) results indicated that the higher KAc concentration caused the higher intercalation ratio. However, a concentration of 5 M KAc was chosen to gain an optimum intercalation ratio if green chemistry was taken into account. The clay-intercalating complex was carried out completely at room temperature for 3 days. The complex was heat treated to delaminate the expanded layer. SEM and XRD confirmed that KAc especially influence on kaolin structure by expanding the kaolin layer.

คำสำคัญ : การแทรกชั้นดิน, โพแทสเซียมอะซิเทต, การขยายชั้นดิน
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1.Introduction

Kaolin is a crucial raw material for ceramic, paint, plastics, paper, rubber, ink, cements, pesticides, pharmaceuticals and cosmetics industries [1-2]. Its properties are hydrophylic, fine in particle size, platy in shape, low in surface area, and chemically inert [1]. Microstructure of kaolin ($Al_2[Si_2O5](OH)_4$) consists of a silicon tetrahedral sheets and aluminum octahedral sheets in a 1:1 stoichiometric ratio. Each layer adheres together by van der Waals forces and hydrogen bonds from AlOH prohibiting the reaction on AlOH group [2].

Recently, kaolin can be modified for the unique application by intercalation and heat treatment process [2]. One of the interesting applications of a kaolin intercalation is the ion exchange capacity. The ion exchange capacity can be used in embedding cations such as Ag into the kaolin layers to increase the disinfection properties in ceramic glaze. The intercalation is to insert organic compound into the interlamella of stacking kaolin, causing the expanded layer. Potassium acetate (KAc) is a chosen intercalating compound because its strong dipole interactions with the silicate layer induce the layer expansion [3]. Heat treatment will be subsequently applied to eliminate the intercalating compound. These processes activate aluminol group (Al-OH) to be ion exchanger with organic compounds [2]. The previous investigation [4-11] almost focused on the intercalation on high purity of kaolin. However, the natural kaolin from the northern Thailand usually contains quartz and muscovite [12]. A layer of muscovite ($KAl(Al_2Si_3O_{10})(OH)_2$) possesses 2 tetrahedral sheets :1 octahedral sheet arranges in a form of sandwich. K^+ is an interlayer balancing the strong negative charge due to Si for Al tetrahedral substitution. Therefore, muscovite is a chemical inertness[7]. This study try to emphasize the effect of KAc concentration on natural-muscovite containing kaolin.

2.Experimental

2.1 Materials and reagents

2.1.1 Lanna white® clay (LW) from Compound Clay Co., Ltd.

2.1.2 Potassium acetate (CH3COO-K) 99% from Fluka Analysis

2.2 Preparation of intercalation and modified clay

The modified clay was prepared by intercalation method and heat treatment on a commercial kaolin LW clay. The LW clay was chosen because of its highest cation exchange capacity. The intercalation clay was prepared by using 50 g of LW clay soaked in 3, 4, 5, 6, 7, and 8 M of KAc solution of 100 ml for 3 days. All suspensions were filtrated using vacuum filtration and dried at 100°C. The modified clay was prepared by heating the intercalation clay at 350°C for 1 hr.

2.3 Characterizations

A wavelength dispersive X-ray fluorescence (WDXRF; Bruker, S8 Tiger) was performed on as received LW clay. The crystalline structure of intercalated clay was investigated using a Bruker X-ray diffraction (XRD, D8 advance). XRD equipped with Ni filtered Cu K radiation, λ = 0.1541 nm, using a voltage of 40 kV and a generator current of 40 mA. The scan was recorded cover a range of 5-80° with a step size of 0.02° and a step time of 6 s/step. The degree of intercalation was calculated according to the following equation (Eq.1) [4]

$$\text{Intercalation ratio} = \frac{I_{Intercalation}}{I_{Intercalation} + I_{Kaolin}} \quad \text{(Eq.1)}$$

where I_{Kaolin} is the basal d_{001} peak intensity of the unexpanded kaolin and $I_{Intercalation}$ is the peak intensity of the expanded kaolin.

Particle morphology of as-received clay, intercalated clay, and modified clay were studied by scanning electron microscope (SEM, Philips, XL30). SEM was operated at 13 kV on back-scattered mode. The modified clay samples were placed on a sample stub lined with a carbon tape. The samples were gold-sputtered coated for good electron conduction before putting in the microscope.

3.Results and Discussion

The chemical composition of as-received LW clay is shown in Table 1. The major composition consists of SiO_2 and Al_2O_3. The XRD pattern (Fig.2) shows that LW clay composed of kaolinite ($Al_2Si_2O_5$), muscovite ($KAl(Al_2Si_3O_{10})(OH)_2$), albite ($NaAlSi_3O_8$), mica(K-Mg-Fe-Al-Si-O-$H_2O$) and quartz ($SiO_2$).

Table 1 Chemical composition of LW clay

XRF (% wt)	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Na_2O	K_2O	CaO	MgO
LW Clay	50.94	34.19	0.05	0.71	0.94	4.28	0.09	0.28

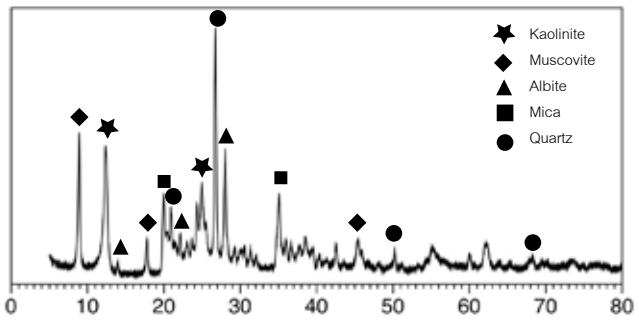


Fig. 1 XRD pattern of LW clay

Figure 2 shows the XRD pattern of LW clay (Fig 2a) and 6 different KAc concentrations (fig 2b – 2g). Notice that in Fig 2a there is no peak at d-spacing = 1.4 nm (2θ = 6.2). Upon adding Kac, the extra peak at 2θ = 6.2 gradually appears. The higher KAc concentration, the higher the peak at 6.2 degree. The XRD patterns of LW clay and intercalated clays shows that the basal d-spacing $d_{(001)}$ of kaolinite expands from 0.7 nm (2θ = 13) to 1.4 nm (2θ = 6.2) (increasing 0.7 nm) as shown in Table 2. This expansion is related to the insertion of KAc in the interlayer of stacking kaolin. Moreover, the higher KAc concentrations, the lower intensity of (001) and (002) planes. This can be concluded that KAc could disorder the crystalline structure of kaolin especially on 00l plane. The basal $d_{(002)}$ of muscovite becomes broad peak when the concentration of KAc is higher. This indicated that KAc can disorder well-crystallized muscovite. However, the expanded muscovite reflection is found at the higher concentration of KAc (6-8M) only (Table 2).

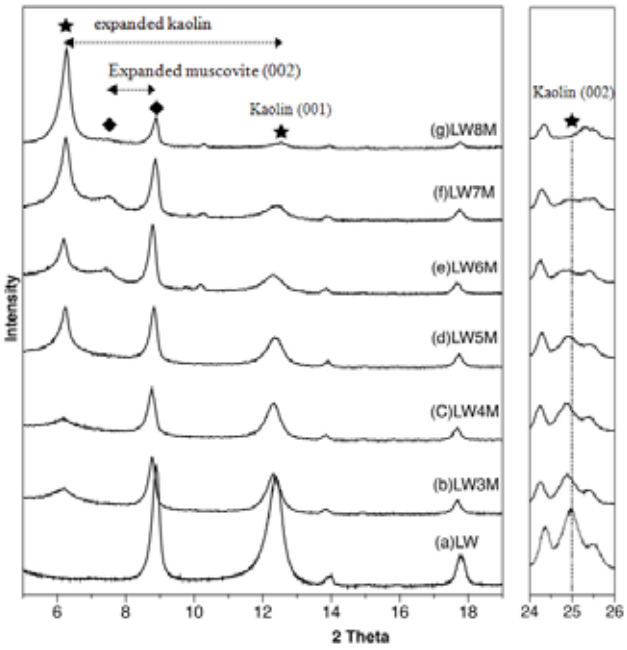
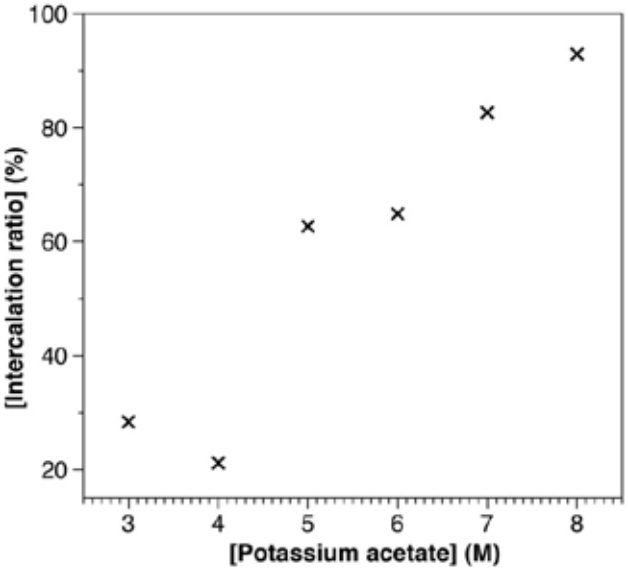


Fig. 2 XRD patterns of (a) LW clay and intercalated with 6 different KAc concentrations of (b)3M, (c)4M, (d)5M, (e)6M, (f)7M, and (g)8M

Table 2 d-Values of normal and expanded (00l) planes from kaolin and muscovite



The intercalation ratio was calculated using Eq.1. The intercalation ratio increases with increasing KAc concentration (Fig 3). The higher KAc concentration caused easier intercalation for kaolinite. Noted that if the KAc concentration was increased from 4 M to 5 M, the intercalation ratio was increased by almost 70%. However, if the KAc concentration was increased from 5 M to 6 M, the intercalation ratio was increased only by 22%. Although the higher intercalation ratio was desirable, green chemistry must be taken into consideration. The 50-60% ratio was

satisfied for cation exchange purpose. Therefore, the 5M KAc concentration was chosen in this study.

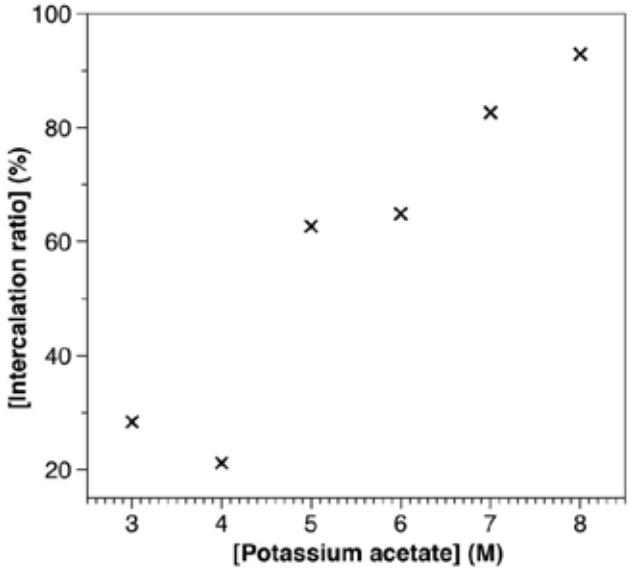


Fig. 3 The intercalation ratio curve of clay-KAc complexes

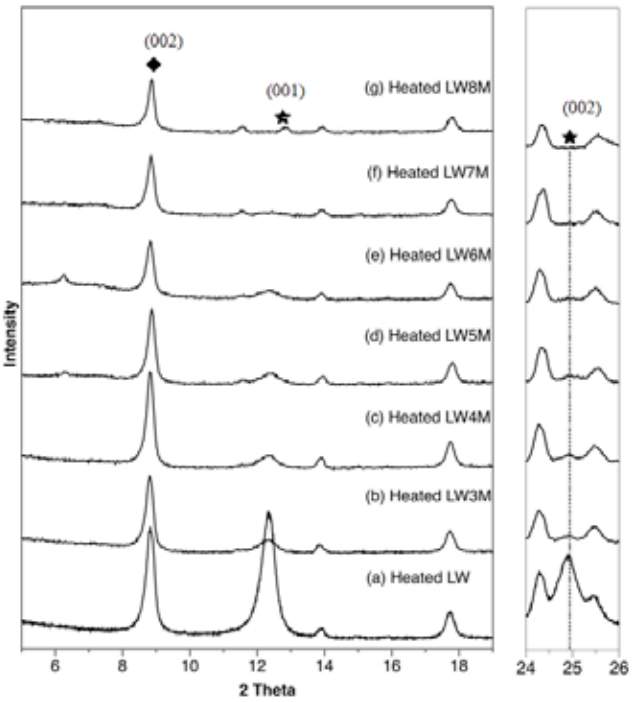


Fig. 4 XRD patterns of (a) heat treatment LW at 350 ºC (b) LW3M, (c) LW4M, (d) LW5M, (e) LW6M, (f) LW7M, and (g) LW8M

Fig. 4 shows the XRD patterns of LW clay and KAc-intercalated clay after heat treatment at 350 ºC for 1 hr. The intensity of kaolin-expanded peak (2θ = 6.2) and expanded muscovite peak (2θ = 7.5) disappear. (Fig 4b – 4g) because heat treatment accelerated the split of extended kaolin and muscovite layer [1-2,5-6]. The disappearing of kaolin peaks confirms that the kaolin structure is destroyed due to delamination of kaolin layers. Notice that the XRD pattern of heated LW (Fig 4a) is unchanged compared to the pattern before heating (Fig 2a). The structure of kaolin and muscovite in LW clay remains stable after heating because there is no interference from KAc.

The morphology of a modified kaolin particles was investigated by scanning electron microscope (SEM). A large number of KAc intercalating molecules rapidly penetrate inter lamella resulting in open structure of kaolin layers (Fig.5). In addition, the morphology of modified kaolin indicates the mechanism of the intercalation begins from the edge along one site and moves forward to the opposite site [3]. A modified particle is still agglomerated but the plates are not separated. It could result from the shorten length of heat-treated time.

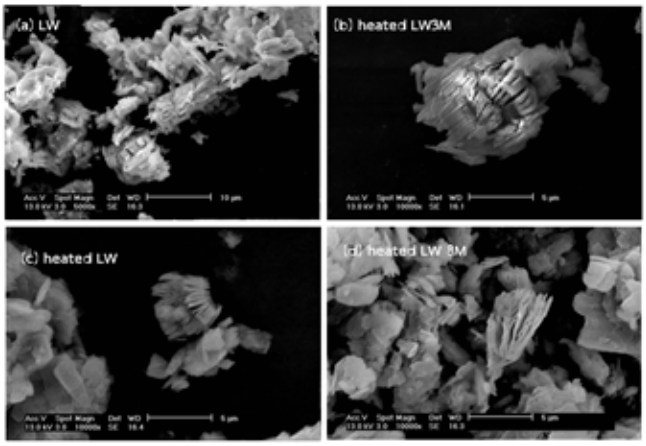


Fig. 5 Modified kaolin particles of (a) LW, (b) heated LW3M, (c) heated LW5M, and(d) heated LW8M.

4. Conclusion

Potassium acetate solution was used to intercalate inter lamella of natural kaolin. KAc had influenced on kaolinite and muscovite structure. Preparation of kaolin and muscovite for the specific application has exploited intercalation and heat treatment process on natural kaolin. Different concentrations have influenced on degree of relating directly to the particle size of modified kaolin particle. The 5M of potassium acetate concentrations satisfied enough intercalation ratio. Heat treatment method was applied on intercalated complex to eradicate the intercalating compound.

5. Acknowledgement

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