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Cooling as the key parameter in formation of kaolinite-ammonium acetate and halloysite-ammonium acetate complexes using homogenization method

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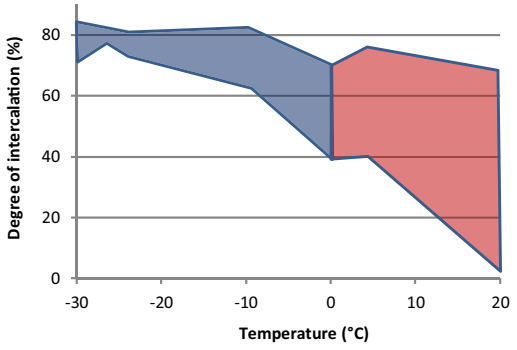
HIGHLIGHTS

- Experiments were performed to enhance the efficiency of ammonium acetate intercalation.
- Cooling below 0 °C was proved to be the key parameter for this intercalation.
- Cooling helps to significantly accelerate and increase the intercalation of ammonium acetate.
- Cooling decreases the influence of kaolinite crystallinity on this intercalation.
- To achieve high degree of intercalation, the use of closed sample holder was essential.

GRAPHICAL ABSTRACT

Changes in the degree of intercalation of different kaolin minerals after aging.



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ABSTRACT

Although the one-step homogenization method has proved to be the simplest and cost-efficient way to intercalate ammonium acetate into kaolinite, the effectiveness of this method is not high enough for potential industrial applications in the area of nanocomposites. To enhance its efficiency we performed systematic experiments to analyze the influence of the intercalation parameters (kaolin mineral content, ammonium acetate to water mass ratio, type of sample holder, temperature, crystallinity and type of kaolin minerals).

Instead of keeping the samples at room temperature or slightly above (60–80 °C), which is generally preferred in intercalation methods, cooling below 0 °C was proved to be the key parameter for direct intercalation of ammonium acetate by the homogenization method. Even after 8 weeks of aging at room temperature with optimal additional intercalation parameters, not more than 57% degree of intercalation was achieved, while only 1 week of cooling at −10 °C resulted in about 80% degree of intercalation (using the same additional parameters). The most applicable intercalation procedure was obtained by using 2.1:1. AAc to water mass ratio with 48 wt% kaolin mineral content and keeping the samples at −24 °C (where the influence of kaolin mineral type can become negligible) for 1 week in closed sample holder.

1. Introduction

Kaolin minerals are dioctahedral 1:1 phyllosilicates formed by superposition of kaolin layers which contains one tetrahedral and one octahedral sheet [1]. The kaolin minerals including kaolinite, dickite, nacrite, and halloysite can directly intercalate various

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organic and inorganic compounds such as formamide, dimethyl sulfoxide, urea, potassium acetate, and ammonium acetate [2–29]. Kaolin mineral–organic intercalations are used to identify types and reactivity of these minerals, as well as to modify their structure, morphology, and property for possible industrial applications (e.g. plastic, paper, ceramic, and pharmaceutical industry) [7,18,29].

During intercalation reactions the guest molecules enter the interlayer space and break the hydrogen bonds between kaolin layers [6,18,29]. The displacement reactions of these directly intercalated molecules are suitable to prepare a wide variety of intercalation compounds. There are such displacement reactions which can be applied to transform platy kaolinite structure into tubular one [29–31]. In this way, it is possible to produce kaolinite nanocomposites or nanohybrids with unique properties [16,18,23,27,29]. The intercalation reactions are influenced by several parameters (e.g. type of guest molecules, temperature, concentration, as well as the type and particle size of kaolin minerals) [16,29,32]. Ammonium acetate (AAc) [3,6,16,29] is an eco-friendly intercalation compound, therefore, its industrial applications should be preferred. Direct intercalation of AAc with kaolinite can be performed by solution and homogenization techniques [3,6,25,29]. As compared to the solution method, the homogenization one is simple and effective, but unfortunately, it was rarely applied over the last decades [16,32]. To our knowledge, the first homogenization intercalation of kaolinite with AAc was performed by Hauser-Fuhlberg [16], and the highest degree of intercalation (85%) was achieved by mixing 60 wt% kaolinite with 30 wt% AAc and 10 wt% distilled water and aging it for 1.6 weeks. In our previous research [32], a detailed experimental and molecular simulations characterization of the 1.7-nm and 1.4-nm kaolinite-AAc intercalation complexes was performed. We prepared three different mixtures: 48 wt% kaolinite with 35 wt% AAc and 17 wt% water (M48); 65 wt% kaolinite with 22.5 wt% AAc and 12.5 wt% water; 75 wt% kaolinite with 15 wt% AAc and 10 wt% water. The mixtures were aged for 0.14–7 weeks at room temperature and 1–45% intercalation was achieved. The highest degree (45%) of intercalation was achieved with the M48 sample aged for 7 weeks, which was obtained by using two orders of magnitude lower amount of reagents than in the case of the solution method. As a continuation of this study [32], we systematically investigated the effect of other factors (kaolin mineral content, ammonium acetate to water mass ratio, type of sample holder/open/closed/, temperature, crystallinity, and type of kaolin minerals) affecting the formation of intercalation complexes. We are primarily concerned to draw attention to the effectiveness of cooling during the homogenization intercalation, which was not used before. In this paper, a detailed experimental analysis of the influencing factors is presented in order to support the efficiency enhancement of the homogenization intercalation method, which is essential for potential industrial use of kaolinite-AAc intercalates as precursors of nanocomposites and nanohybrids.

2. Materials and methods

2.1. Samples and preparation procedure

Four clays containing kaolin minerals were used in this study: the Zettlitz kaolin (Z) from the Czech Republic, the Királyhegy kaolin (K) from Hungary, the Szegi kaolin (S) from Hungary, and the New-Zealand halloysite (N) from New-Zealand. The chemical compositions of studied clays are shown in Table 1. Mass ratios of kaolinite to halloysite-7 Å were determined by the method of Churchman et al. [7]. The major mineral component of Zettlitz kaolin is medium-defect kaolinite (91 wt%) with a Hinckley index of around 0.8 [32–34]. Minor amounts of quartz (2 wt%) and muscovite (7 wt%) are also present. The Királyhegy kaolin contains around 30 wt% of low-defect kaolinite with a Hinckley index of around 1.4. This kaolin contains around 70 wt% quartz. The Szegi and New Zealand clays contain mixtures of kaolinite and halloysite-7 Å. The Szegi kaolin (in 95 wt%) consists of kaolinite and halloysite-7 Å mixture with a Hinckley index of around 0.3. The mass ratio of kaolinite to halloysite-7 Å is 48:52 [7]. The New Zealand halloysite contains 85 wt% of halloysite-7 Å and kaolinite with 89:11 mass ratio [7]. Minor amounts of quartz (7 wt%) and cristobalite (4 wt%) are also present. These clays were selected for this experiment because of their different kaolinite crystallinity and kaolinite to halloysite-7 Å mass ratios. As a guest compound, analytical grade ammonium acetate (AAc) was used from Reanal (Budapest, Hungary).

Table 1
The chemical compositions of the investigated kaolins and halloysites.

	Kaolin and halloysite			
Oxide elements(wt%)	K	S	Z	N
SiO_2	81.59	46.89	46.97	49.65
Al_2O_3	12.1	33.51	36.32	33.57
K_2O	0.05	0.35	1.21	0.84
Na_2O	0.16	0.16	–	0.37
CaO	0.35	0.53	0.54	0.48
MgO	0.51	0.71	0.26	0.41
Fe_2O_3	0.07	3.1	0.37	0.78
TiO_2	0.001	0.06	0.05	0.15
Loss on ignition	5.09	14.33	12.85	13.76

The homogenization intercalation procedure was performed according to our previous study [32] by wetting the clays with mixtures of solid AAc and distilled water in an agate mortar at room temperature. (In all cases raw clays were used for the homogenization intercalation.) Afterwards the mixtures were aged for different period of time in closed or open sample holder at various temperatures.

Considering that in our previous study [32] the M48 sample was found to be the optimal one for intercalation, now Z samples with 43, 48, 53, and 60 wt% kaolin mineral contents (close to that of the M48 sample) were mixed with AAc and water using a constant 2.1:1 AAc to water mass ratio in each case. These samples were aged in closed sample holder (C), at room temperature (RT) for 8 weeks. In the followings, these samples (with constant AAc to water mass ratio) will be denoted as Z_43_2.1_C, Z_48_2.1_C, Z_53_2.1_C, and Z_60_2.1_C.

We prepared additional Z samples at a constant 48 wt% kaolin mineral content with 1:1, 1.5:1, 2.5:1, and 4:1. AAc to water mass ratio, which have not been studied previously [16,32]. These samples (with constant kaolin mineral content) were also aged in closed sample holder (C) at RT for 8 weeks (Z_48_1_C, Z_48_1.5_C, Z_48_2.1_C, Z_48_2.5_C, and Z_4_2.1_C samples).

To study the effect of the type of sample holder, the Z_48_2.1 samples aged at RT up to 8 weeks were examined in closed (Z_48_2.1_C) and open (Z_48_2.1_O) sample holders.

The effect of temperature was studied in the case of Z_48_2.1_C sample, which was aged for 1 week at RT, 30, 4, 0, −10, −24, and −30 °C, in closed sample holder. The Tenney Junior Compact Temperature Test Chamber was used for keeping the temperature below 0 °C. The intercalation progress was systematically characterized at −24 °C and RT, aging the samples up to 8 weeks.

The Z_48_2.1_C, K_48_2.1_C, S_48_2.1_C, and N_48_2.1_C samples were applied to investigate the effect of crystallinity and type of kaolin mineral content. These samples were aged for 1 week at 30, 20, 4, 0, −10, −24, and −30 °C.