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Modified physical properties of kaolin by intercalation and exfoliation method

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Abstract. The intercalation method and combination of the intercalation-exfoliation method were applied to modify kaolin. The intercalation process was prepared using urea 60 % as an intercalated agent and the exfoliation process was carried out by ultrasonication. The samples were characterized by X-ray diffraction (XRD), X-Ray Fluorescence (XRF), scanning electron microscope (SEM), and particle size analysis (PSA). Experimental results showed that the physical properties of kaolin significantly improved after modification. This was indicated by the increasing interlayer spacing of modified kaolin, which was confirmed by SEM and XRD analysis. Based on XRF analysis, the loss on ignition value increased after kaolin modification, suggesting that the urea had successfully intercalated into the kaolin interlayer. Kaolin modification with intercalation method produced the most significant physical properties improvement, which increased surface area from 2508.607 to 27297.990 cm²/g and decreased particle size average from 41.535 to 13.836 μ m and had surface area close to illite clay.

1. Introduction

In the last four years (2016-2019), the growth of clay consumption for construction industry materials in Indonesia has increased [1,2,3,4]. In 2019, the import of clay for the construction industry in Indonesia has reached 57,000 tons per year, with a transaction value more than \$38 million [4]. Some of the applications clay in the construction industry are for reinforcing filler and fire-resistant material. Illite is one of clay mineral that is widely imported for the construction industry material in Indonesia, such as the fiber cement board industry. The cement board factory with a 36,000 tons/year capacity is estimated to require illite more than 1000 tons/year. The development of the construction industry in Indonesia will increase the import of illite clay for industry materials. Therefore, the development of alternative materials for substitute illite clay in the construction industry is very potential to be studied in Indonesia to reduce dependence on imported materials.

Illite is a clay mineral mica which has a layer structure 2:1. Illite is composed of two silica tetrahedral sheets with one aluminum octahedral sheet, in which the interlayer cation is potassium [5]. Illite has a wide range of physical properties, thus making them applicable to many different construction industry products. The physical properties of illite that are important for the construction



industry are high plasticity, fine in particle size, high surface area, good in green and dray strength, good in fire color, and fire strength.

In contrast to illite, kaolin is less reactive when incorporated into the most industrial formulations because it has low surface area, low ion exchange, and particle shape. Illite has a higher surface area than kaolin (i.e., 30 compare 10 m²/g) and has a smaller particle size than kaolin (i.e., 5.8 compared to 7.3 μm) [6]. This property makes illite very good to be applied as a filler construction material to increase product strength and fire resistance. On the other hand, kaolin is a potential clay mineral in Indonesia with potential reserves of more than 723.56 million tons [7]. Kaolin has some physical properties that are potential for application in construction industry products such as plasticity, green and dray strength, good in fire color and fire strength [5]. Depending upon the application, kaolin must be modified from its natural state by physical or chemical treatments to improve the surface area and reduce particle size.

Kaolin is a clay mineral that has layer structure 1:1 that is combined from a single silica tetrahedral sheet and a single alumina octahedral sheet [5]. Unlike illite, kaolin has no cation interlayer which holds the individual layer in the structure. The layers are held together by hydrogen bonds between hydroxyl groups on the silica in the tetrahedral sheet and the aluminium in the octahedral sheet [8]. because of its structure, kaolin relatively has a low surface area and non-expandable mineral, while only a limited number of polar organic compounds can be directly intercalated [9].

Thus, to improve the physical properties of kaolin, some methods for modification of surface area can be achieved either by the use of acid activation [10], base activation [11], microwave treatment [11], calcination [12], intercalation of organic compounds [13] and exfoliation using ultrasonic wave treatment [14]. Intercalation and exfoliation is a common method used to improve physical properties of organic and inorganic materials. Recently, more studies have used this method for the improvement of kaolinite properties. Zou et al. [8] increase the aspect ratio of kaolin with a combination of the Intercalation method using sodium dodecyl sulfate and ultrasonic exfoliation method for rubber/layered silicate nanocomposites. Zhang et al. [14] using the intercalation-exfoliation method at high temperatures to improve sodium adsorption capacity in kaolin. Experimental results showed that the diameter and pore volume were expanded after modification, which was beneficial to improve adsorption capacity. Guessoum et al. [15] has modified the surface of kaolin by intercalation method using urea then with an ammonium salt and a surface treatment with a silane coupling agent. Then modified and unmodified kaolin were applied as inorganic fillers that are used to improve polypropylene (PP) properties. Experimental results showed that the application of intercalated kaolin as PP filler slightly increased the thermal stability of the composites.

It demonstrated that the intercalation and exfoliation method was able to improve the physical properties of kaolin, especially the surface area. However, there is little literature with study of physical properties modification of kaolin through this method as substitution material for reinforcing filler in the construction industry in Indonesia. Based on the issues in the construction industry described above, the present work aims to study the intercalation method and combination of the intercalation-exfoliation method for improving the physical properties of kaolin as reinforcing filler in the construction industry. The intercalation process was prepared using urea 60 % as an intercalated agent and the exfoliation process was carried out by ultrasonic wave treatment. Afterwards, the properties of modified kaolin are compared with illite clay to determine the potential of modified kaolin as reinforcing filler in the construction industry.

2. Materials and methods

2.1. Materials

The kaolin used in this study with a particle size 325 mesh, moisture content 1.6 %, white color, was manufactured by Aneka Kaolin Utama Ltd., Bangka Belitung, Indonesia. Urea (NH₂CONH₂) as an intercalated agent used in this study that is urea fertilizer with nitrogen content 46 % manufactured by Pupuk Kaltim Ltd. Illite clay was provided by Sinar Nusantara Industries Ltd. (one of the particle

cement board industries in Indonesia). It was imported from Taiwan, having particle size 325 mesh, moisture content of 2.2 %, and cream color.

2.2. Kaolinite treatments

The experimental method for intercalation and exfoliation of kaolin was prepared according to the previous reports [14, 16] with some modified method. In the first experiment, the kaolin modification was prepared by intercalation processes with urea 60 % (KI). 10 g of kaolin was dissolved in 66 mL urea 60 % aqueous solutions, and then the mixture solutions were stirred by Scilogex magnetic stirrer type MS-PA at a speed rate of 1000 rpm, the temperature of 80° C, for 24 h. After 24 h, the mixture solutions were centrifuged by Ohaus centrifuge type FC5707 at a speed rate of 2500 rpm for five minutes and the suspending system was filtrated and washed with aquades to remove residual urea in kaolin. Then, KI was dried in the oven at a temperature rate of 100°C and mashed again up to 325 mesh sizes. In the second experiment, the kaolin modification was prepared by a combination of the intercalation-exfoliation process (KIE). First, Intercalated kaolin was prepared with the same method in the first experiment. Then, 10 g KI was dissolved in 100 ml aquades to form a KI suspension. Furthermore, the KI suspension was exfoliated by ultrasonic treatment with SIBATA ultrasonic cleaner type SU-3THE, at the temperature of 50° C, for 30 minutes. After ultrasonic treatment, the suspension KIE was centrifuged and kaolin filtrated, then dried in the oven at a temperature rate of 100°C and mashed up to 325 mesh sizes.

2.3. Characterization

A series of characterizations were carried out to investigate the effect of intercalation and exfoliation modification on the physical properties of kaolin, i.e., X-ray diffraction patterns (XRD), X-ray fluorescence (XRF), scanning electron microscope (SEM), particle size distribution and surface area. The XRD patterns and XRF of the samples were collected by an ARL 9900 series of X-ray spectrometers. The SEM was analyzed with a JEOL JSM-6360LA scanning electron microscope. The particle size distribution and surface area of the samples were measured with laser particle size analyzer LLPA-C10. A series of this characterization was also carried out to determine the physical properties of illite clay.

3. Results and discussion

3.1. XRD analysis

Figure 1 shows the XRD patterns of unmodified kaolin, modified kaolin dan illite clay. Pattern (a) in figure 1 displays the 001 reflections of unmodified kaolin at major peak (2θ) 12.32° dan 24.85° with the basal spacing of 7.17 and 3.58 Å, respectively. After kaolin being intercalated with urea (KI), a new reflection appeared at peak (2θ) 8.20° with the basal spacing of 10.76 Å (pattern b), this corresponded to a typical 2θ distance of intercalated kaolin with urea as described before [13]. Intercalation kaolin with urea also decreased the peak of kaolin pattern at (2θ) 12.32°, from 1200 to 800 cps (figure 1, pattern a & b).

The new (2θ) reflections and the expansion of XRD patterns indicated that the intercalation of urea was able to deform hydrogen bonds of the hydroxyl group in the lattice structure of kaolin, and provide a new hydrogen bond structures from Amina group which expanded the basal spacing of intercalated kaolin and make the characteristic of kaolin more swellable [16]. It as described before [15], the basal spacing of the crystal lattice layer of kaolin has been increased by urea intercalation, this formation allowed to provide the expanded basal spacing for cation exchange in the interlayer of kaolin.

Figure 1(c) shows the XRD pattern of modified kaolin with the intercalation and exfoliation process (KIE). After the modification process, a new 001 reflection with significant peak intensity appeared at (2θ) 8.28° with the basal spacing of 10.66 Å. The obtained results suggested that the combination of intercalation and ultrasonic exfoliation process was deformed the lattice structure and

expanded the basal spacing of kaolin. Pattern c also shows that the peak intensity of KIE at around (2θ) 12° had decreased significantly compared to the peak intensity of unmodified kaolin at around (2θ) 12° (pattern a).

Based on the expanded results of peak intensity in XRD patterns of kaolin (figure 1) shows the modification of kaolin with a combination of intercalation and exfoliation method (KIE) had a higher peak intensity at (2θ) around 8° than modification with intercalation method (KI). The obtained results suggested that a combination of intercalation and exfoliation methods was more significant to expand the basal spacing of kaolin than only using the intercalation method. The previous study [14] reported that the exfoliation process by ultrasonic treatment supported to break hydrogen bonds and reduced the amount of hydroxyl group in the interlayer of kaolin, which could provide more sites for cation exchange in interlayer kaolin.

Figure 1 shows the XRD pattern of illite clay with the 001 reflections was observed at (2θ) 9.07° with the basal spacing of 9.74 \AA . The illite clay had the basal spacing about 10 \AA , which the interlayer cation is potassium (K^+). This interlayer cation gives the structure of illite had basal spacing more expanded than kaolin and correlated with higher surface properties of illite clay [5]. Analysis results in figure 1 also show that after the modification process, kaolin had XRD patterns and basal spacings close to illite (figures 1 b, c, and d).

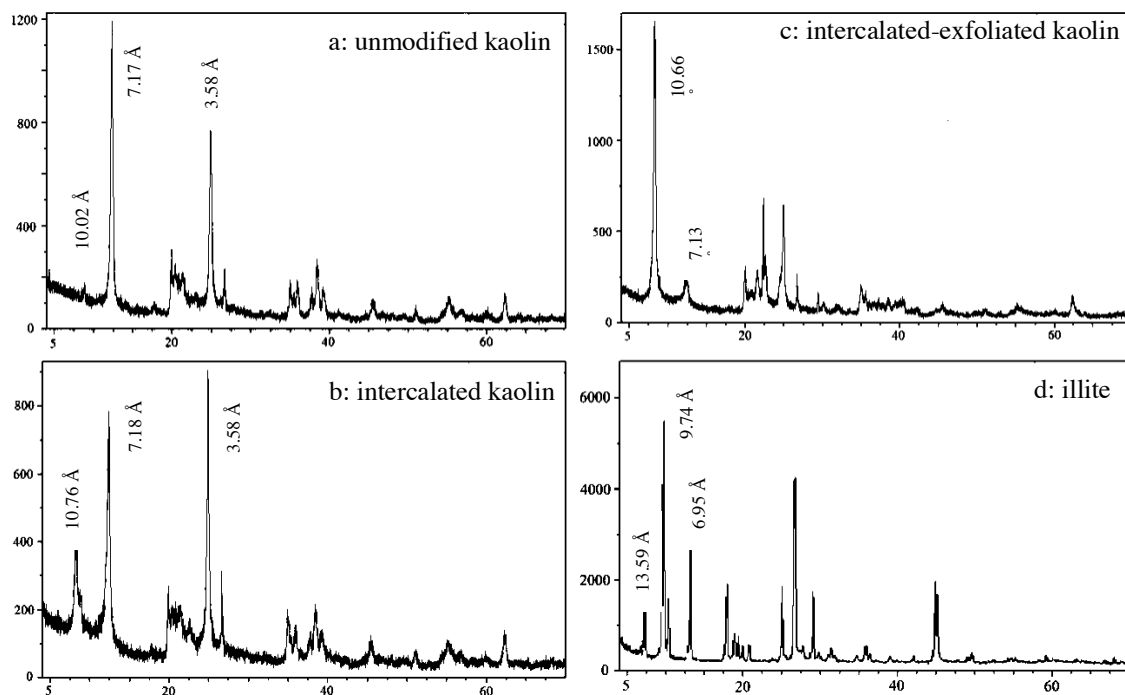


Figure 1. XRD pattern of kaolin, modified kaolin and illite.

3.2. XRF analysis

XRF analysis was performed to analyze the compositions of the clay minerals that were present in table 1. The XRF results showed that the compositions of silica (SiO_2) and alumina (Al_2O_3) in kaolin decreased after the modification process. The compositions of silica decreased from 50.02 to 44.95 (KI) and 39.53 % (KIE), while the compositions of alumina decreased from 32.01 to 27.87 (KI) and 22.86 % (KIE), respectively. The intercalation and exfoliation process were contributed to discharge a number of silica and alumina layers in kaolin. As reported before by Aroke and El-Nafaty [17], the intercalation of kaolin with cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) was decreased silica content from 56.29 to 48.42 % and increased Br content up to 6.33%.

On the other hand, the mass of loss on ignition (LOI) of kaolin was gradually increased from 15.29% (K0) to 20.43% (KI) and 35.09 % (KIE) after a modification process. LOI can describe the estimated content of organic matter, inorganic matter and moisture contents in properties of clay [18]. Based on the XRF results, the increase of LOI in modified kaolin indicated the successful intercalation of organic urea in the kaolin.

Table 1. Chemical composition of the unmodified kaolin, modified kaolin and illite.

Chemical compositions (%)	K0	KI	KIE	Illite
SiO ₂	50.02	44.95	39.53	54.63
Al ₂ O ₃	32.01	27.87	22.86	28.20
Fe ₂ O ₃	0.75	0.75	0.78	3.64
MgO	0.18	0.15	0.12	0.99
CaO	0.02	0.02	0.02	0.37
P ₂ O ₅	0.03	0.02	0.02	0.03
K ₂ O	0.95	0.92	0.90	4.64
TiO ₂	0.31	0.31	0.31	0.57
LOI	15.29	20.43	35.09	4.90

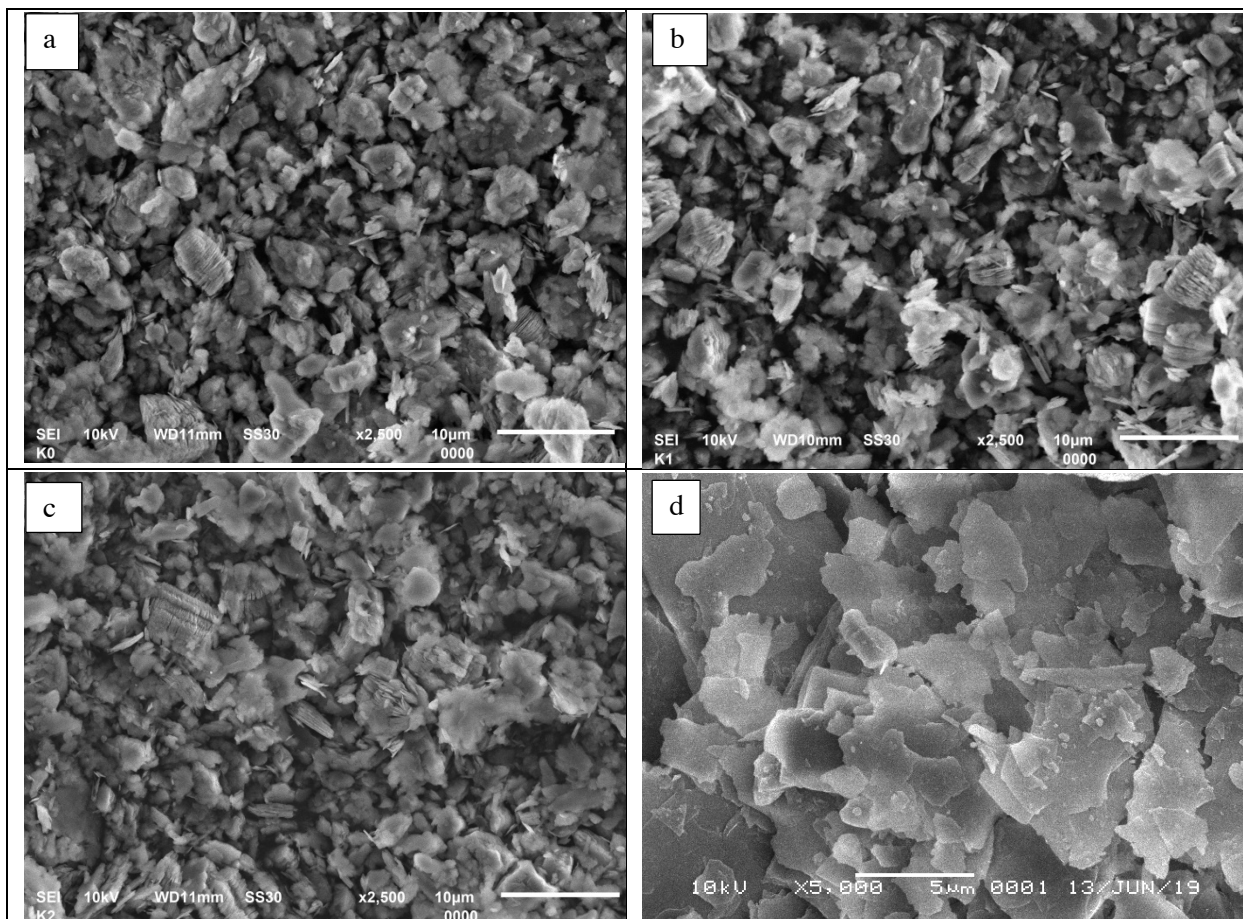


Figure 2. SEM image of (a) unmodified kaolin, (b) intercalated kaolin, (c) intercalated-exfoliated kaolin and (d) illite.

3.3. SEM analysis

Figure 2 shows the morphologies of unmodified kaolin, modified kaolin and illite clay. The unmodified kaolin was mainly composed of typical stacks of tetrahedral and pseudo-hexagonal (figure 2a). Compared with unmodified kaolin, the morphology images of intercalated kaolin by urea (figure 2b) showed no significant changes. However, the space among of kaolin particle stacks observed slightly distant after the intercalation process.

Figure 2c displays the morphology of intercalated-exfoliated kaolin, which exfoliation process was treated by ultrasonication. Compared with unmodified kaolin and intercalated kaolin, the morphology images of intercalated-exfoliated kaolin also showed nearly no changes. However, the type of particle stacks with smaller sizes was more observed than morphology of kaolin particle without ultrasonic treatment.

Previous studies also reported the effect of intercalation and exfoliation process on the SEM morphology of kaolin. Yuan et al. [18] reported that the kaolin particles were mostly transformed to nanorolls after intercalation with cetyltrimethylammonium chloride (CTMACl) in the modified kaolin prepared at 80° C. Zuo et al. [8] reported that a few kaolin particles would transform into nanoscrolls after intercalated with dimethyl sulfoxide (DMSO) and exfoliation treated by ultrasonication.

Figure 2d displays the morphology of illite clay with structure composed of tetrahedral and pseudo-hexagonal particle types, like the kaolin structure. In comparison with unmodified and modified kaolin, the SEM images of illite particle have the sheet forms which the type of layer stacks saw thinner than kaolin. This structure was influenced by the potassium interlayer cation (K⁺) in illite that gives the basal spacing structure more expanded than kaolin [5].

3.4. Particle size analysis

The results of particle size analysis (PSA) are shown in figure 3 and table 2. After kaolin intercalated with urea and exfoliated with ultrasonication, the particle size distribution peaks shifted to a small size (figures 3 a,b,c) and the mean particle diameter (D₅₀) decreased from 41.535 to 13.836 (KI) and 13.672 μm (KIE) (table 2). These results also showed that the decreased of particle size from KI to KIE has no significant change. These indicated that the exfoliation process in KIE was less significant in changing the particle size of kaolin after the intercalation process.

Compared with unmodified kaolin, the average particle size of modified kaolin decreased nearly three times and their size was closer to the illite clay particle. Moreover, modified kaolin produced the average particle size that was slightly smaller than illite. Figure 3 also showed that the particle size distribution peaks in modified kaolin formed a distribution curve nearly the same as illite.

The smaller of kaolin particle size formed, the higher surface area of kaolin produced. The improved of the surface area of modified kaolin has been confirmed in PSA results, which increased from 2508.607 to 27297.990 (KI) and 24912.340 cm²/g (KIE). Compared with the surface area of modified kaolin, illite clay has surface area 29664.200 cm²/g. These results showed that the modification of kaolin via intercalation and combination intercalation-exfoliation process was produced a surface area of kaolin closer to illite clay.

Table 2. The particle size of kaolin, modified kaolin (KI dan KIE) dan illite.

Sampel	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	D _{average} (μm)
Kaolin	12.183	31.520	81.562	41.535
KI	0.970	5.518	31.375	13.836
KIE	1.061	5.741	31.061	13.672
Illite	0.897	5.430	32.874	14.551

D₁₀, D₅₀, D₉₀ indicate the diameters at 10%, 50% and 90% of the cumulative volume distribution.

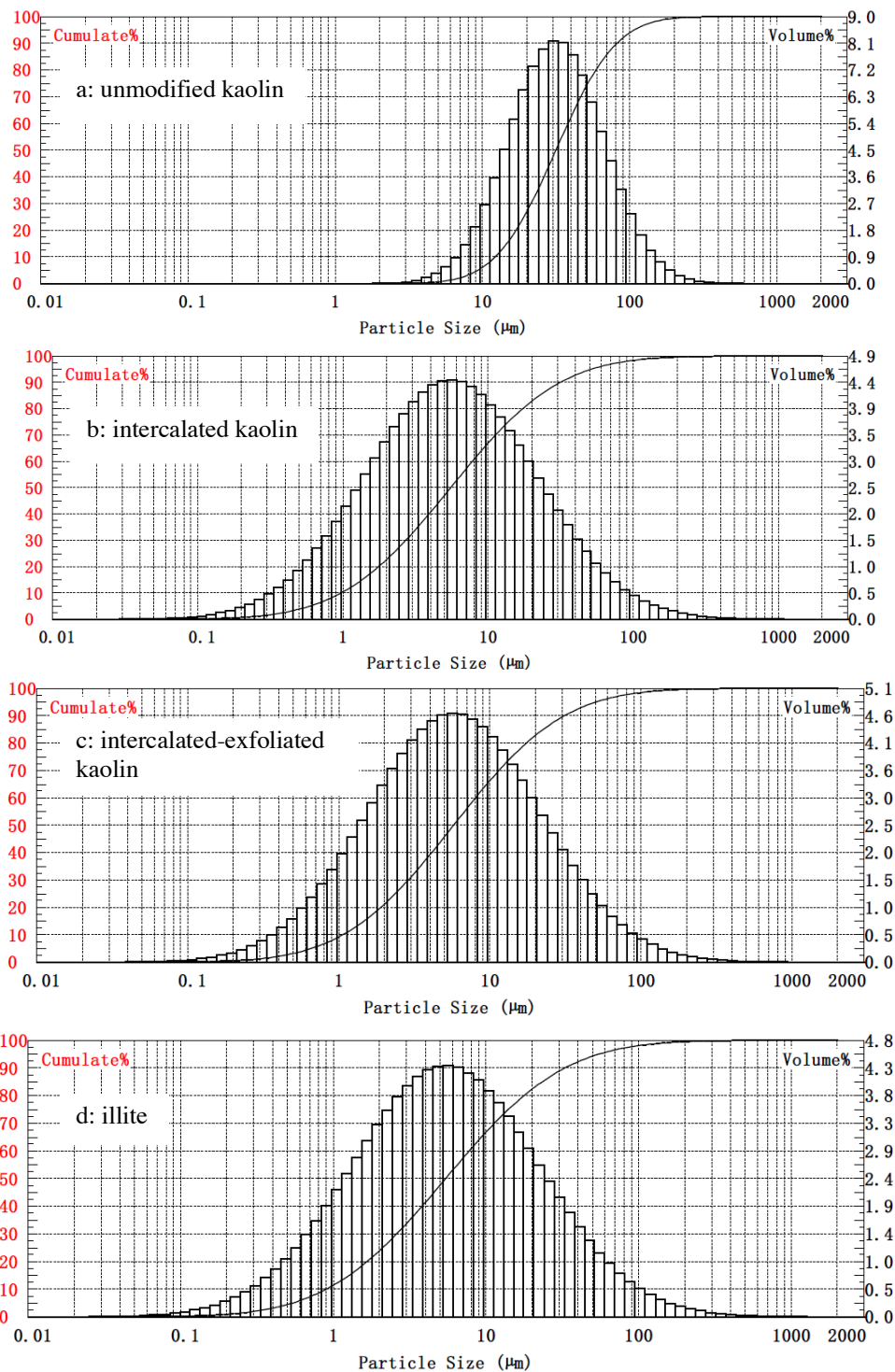


Figure 3. Particle size distribution curve of unmodified kaolin, modified kaolin and illite.

4. Conclusion

Modified physical properties of kaolin for reinforcing filler in the construction industry have been successfully prepared by the intercalation method and combination of the intercalation-exfoliation method. The XRD analysis indicated that the basal spacing of kaolin expanded from 7.17 to 10.76 (KI) and 10.66 Å (KIE) after modification. Based on XRF analyses, it was found that the loss on

ignition value increased from 15.29 to 20.43 (KI) and 35.09 % (KIE), which implies successful intercalation of the urea in the interlayer of kaolin. The SEM analysis showed that kaolin has particle stacks that were slightly distantly spaced and few kaolin particles were transformed into smaller sizes after the modification process. The average particle size of kaolin decreased significantly from 41.535 to 13.836 (KI) and 13.672 μm (KIE), and surface area of kaolin increased greatly from 2508.607 to 27297.990 (KI) and 24912.340 cm^2/g (KIE). Based on the XRD pattern, particle size, and surface area analysis showed that the modified kaolin produced physical properties close to illite clay.

Based on the results of this study, the intercalation method with urea 60 % more recommended for prepare kaolin as reinforcing filler than combination intercalation and ultrasonic method. Because the addition of ultrasonic treatment after the intercalation process was not significantly increase the physical properties of kaolin, so the addition of ultrasonic treatment considered less efficient from the aspect of production costs.

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