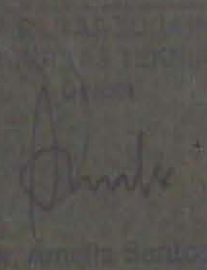


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Effect of the Surfactant Molecule as Intercalating Agent toward Natural Bentonite Structure

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Abstract

Synthesis of organo-clay from natural bentonite with several surfactants using sol-gel methods has been conducted. The objective of this work is to modify the surface properties of the natural bentonite using several surfactants molecule. The modified materials can be further applied as composite materials, adsorbent and catalyst. The kind of surfactants which used on this work is HDTMA-Br (Hexadecyl Trimethyl Ammonium Bromide), TMA-Cl (Tetra methyl Ammonium Chloride) and PVA (Poly Vinyl Alcohol). The temperature for material synthesis was 80°C and it was agitated with hotplate magnetic stirrer for 5 hours. In order to characterize the structure of organo-clay that has been synthesized, X-ray diffraction and nitrogen adsorption with BET methods were performed. The XRD data showed that surfactant cause increasing of inter layer d-spacing of bentonite. The organo-clay that synthesized by intercalation bentonite using HDTMA-Br 0.75% showed the highest inter layer d-spacing, while intercalated bentonite using PVA and TMA-Cl described similar inter layer d-spacing. The pore size distribution of organo-clay was at micropore range, which was widest surface area and biggest pore volume showed by intercalated bentonite using TMA-Cl 0.75 %.

Keywords : bentonite, organoclay, intercalation, sol-gel methods

Introduction

Bentonite is abundant material in Indonesia. The total production of bentonite in Indonesia in last 5 years is shown in table 1^[1]. Bentonite is mainly utilized as drilling mud, as bleaching earth in palm oil industries, and as additive substance on ceramic industries. Because of the major end-uses for bentonite, especially in Indonesia, are in

relatively low-technology applications, it should be improved to be more valuable material, so that it has high-specification and high-value applications.

Table 1. Indonesia production of natural bentonite mining per-year from 2000 to 2004

Year	Production (m ³ ton)
2000	70.000
2001	80.000
2002	80.000
2003	80.000
2004	80.000

The modification of bentonite and its study for some uses has attracted much interest in recent year. Bentonite able to growth its pore size based on its surrounding. It cause the bentonite has low adsorption and catalytic selectivity. To increase its selectivity, some modifications of bentonite have been done. One of the modifications is clay intercalation using organic molecules such as octadecylamine (ODA)^[2] and hexadecyl trimethyl ammonium-bromide (HDTMA-Br)^[3] as intercalating agent in interlayer vermiculite structure. The others surfactant materials have also been used as intercalating agent in smectite structure^[4,5] H-herite structure^[6] and bentonite structure^[7].

The thermal stability of organoclay which was prepared from montmorillonite and N,N-dimethyl-N,N-dioctadecyl quaternary ammonium (DMDODA) as intercalating agent has also been studied^[8]. The other researcher focuses on study the conformation of surfactant molecule on interlayer of montmorillonite^[9].

This paper demonstrates the preparation and characterization of modified bentonite by intercalation and pillarisation using sol-gel method.

Experiment

The starting clay was a natural Pacitan bentonite, extracted from Pacitan region, East Java, Indonesia. The particle size of bentonite was 140 meshes. The intercalating agents were hexadecyl trimethyl ammonium-bromide (HDTMA-Br, Merck), polyvinyl alcohol (PVA, Merck), and tetramethyl ammonium chloride (TMA-Cl, Merck). The methods of pillarisation referred to sol-gel method that has been carried out before^[7,10]. Pillarisation and intercalation process of the clay was carried out by mixing bentonite and intercalating agent solution with ratio [gram bentonite/ volume of solution] = 1 gram/50 mL. The mixture was agitated at 80°C. After 5 hours, the mixture was cooled and washed with aquadest. The obtained solid was dried at 100°C. All the materials were systematically characterized by *Fourier Transform Infra Red* (FTIR, Bruker Tensor 27, Germany) and powder X-ray diffraction (Shimadzu XRD-1000). Nitrogen adsorption was determined with an ASAP 2010 Adsorption Analyzer from Micrometrics. The specific surface areas were obtained from the BET method.

Result and Discussion

The materials obtained from pillarisation of bentonite were encoded below (see table 2).

Tabel 2. Catalyst materials code

Code	Material
Fresh bentonite	Natural bentonite unmodified
Bent.-HDTMA-Br	Intercalated bentonite using HDTMA-Br 0.75%
Bent.-PVA	Intercalated bentonite using PVA 0.75%
Bent.-TMA	Intercalated bentonite using TMA-Cl 0.75%

Figure 1 shows the comparison between fresh bentonite, intercalated bentonite. It shows that there are difference pattern absorption peak in the wave number region of $500 - 2000 \text{ cm}^{-1}$.

The band at $500 - 600 \text{ cm}^{-1}$ corresponds to the pore character of the intercalated bentonite. The sharp peak in the fresh bentonite reflects that in natural there is the pore structure in the fresh bentonite, but it does not stable because of its swelling properties. The similar band at around this wavenumber for Bent.-TMA Cl and Bent.-PVA were sharper and slightly shift. This indicates their pores structure relatively more stable since the sharper peak reflects that the tetrahedral silica structure is formed between two bentonite layers. Phenomenon of pores structure formation is supported by the presence of band at the region of $1040-1200 \text{ cm}^{-1}$ which is known to be assignable to O-Si-O and O-Al-O species^[7,10-11]. The wider and the shifted band to the higher wavenumber in this region indicate that intercalation process of the surfactant TMA-Cl and PVA is successful. These processes cause the increment of the external stretching energy of O-Si-O and O-Al-O bonding. These indicate that the surfactants molecules have been adsorbed into interlayer of natural bentonite and created interaction with bentonite layers. In the case of HDTMA-Br as intercalating agent, it shows that the band at $500 - 700 \text{ cm}^{-1}$ is similar with that of fresh bentonite. This phenomenon is also supported by the band at $1040 - 1200 \text{ cm}^{-1}$ which is sharper than that of fresh bentonite. It indicates that HDTMA-Br molecules may not be absorbed optimally by bentonite. It might be because of the size of HDTMA-Br micelle is bigger than that of TMA-Cl and PVA.

Beside the FT-IR spectra, the easiest way to determine whether intercalation is successful is to record the X-ray diffraction pattern of intercalated bentonite. The main diffraction peak of fresh bentonite was detected at $2\theta = 5.8^\circ$ (as crystallite surface 001). Figure 2 shows that the diffraction peaks of intercalated bentonite using HDTMA-Br, TMA-Cl and PVA, were slightly shifted to the lower 2θ values. Shifting of 2θ values clearly suggests expansion of bentonite layer during intercalation process.

Figure 3 describes the pore distribution and pore volume of natural bentonite and intercalated bentonite. It shows that bent.-TMACl has bigger pore volume compare to that of natural bentonite and other intercalated bentonite. Although all the organoclays

show that the pore distribution is still in micropores region, this figure describes that TM-Cl molecules may intercalate better than the other surfactants.

Nanostructuring is verified by microscopic inspection allowing studying locally the relevance of the intercalating agents for improvement of bentonite structure using SEM techniques. The SEM images of intercalated bentonite in figure 4 show that the porous structure of bentonite is improved by intercalation process using TMA-Cl and HDTMA-Br. SEM images of natural bentonite as shown in this figure reveal non-porous structure. On the other hand SEM images of bent.-TMACl reveal better porous structure than that of bent.-HDTMABr. It indicates that TMA molecules may introduce inside the bentonite layer easier than that of HDTMA-Br.

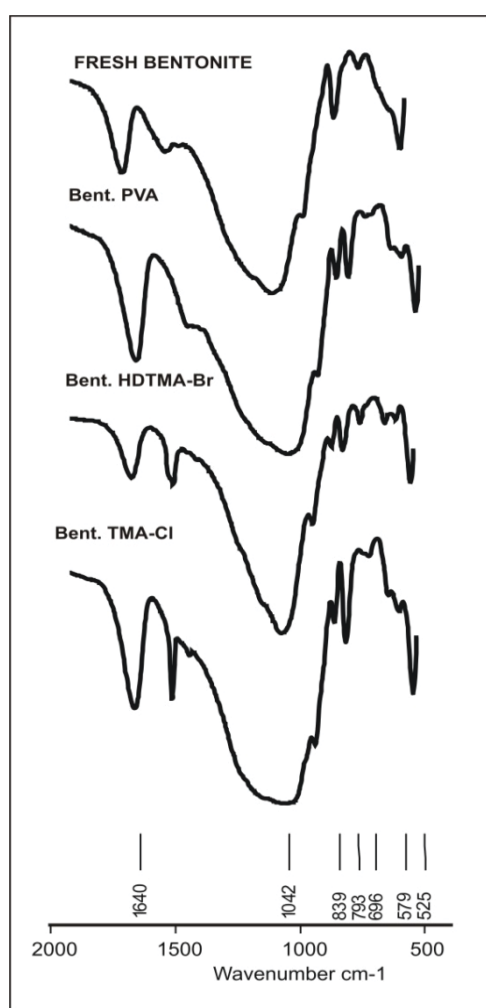


Figure 1. FTIR spectra of fresh bentonite and intercalated bentonite using PVA 0.75%, HDTMA-Br 0.75% and TMA-Cl 0.75%

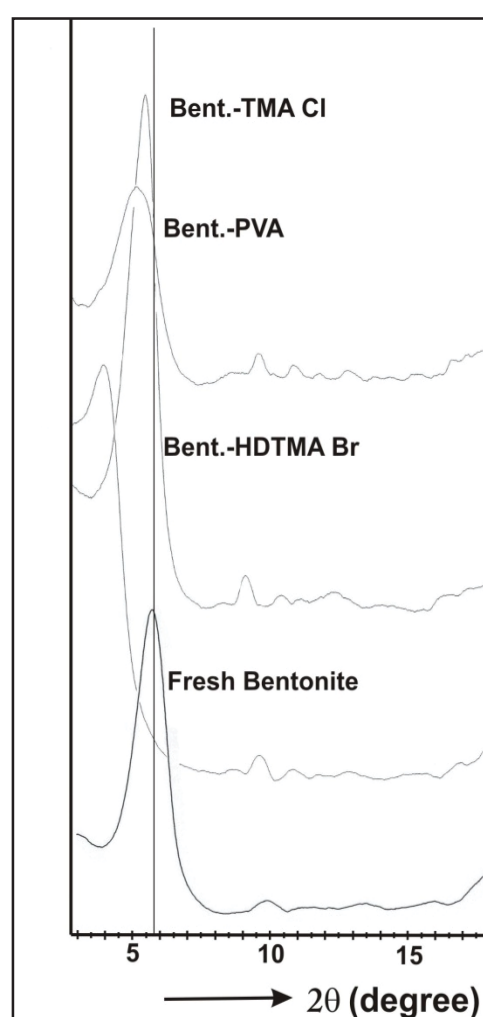


Figure 2. The powder X-ray diffraction patterns of the fresh bentonite, intercalated bentonite using PVA 0.75%, HDTMA-Br 0.75% and TMA-Cl 0.75%

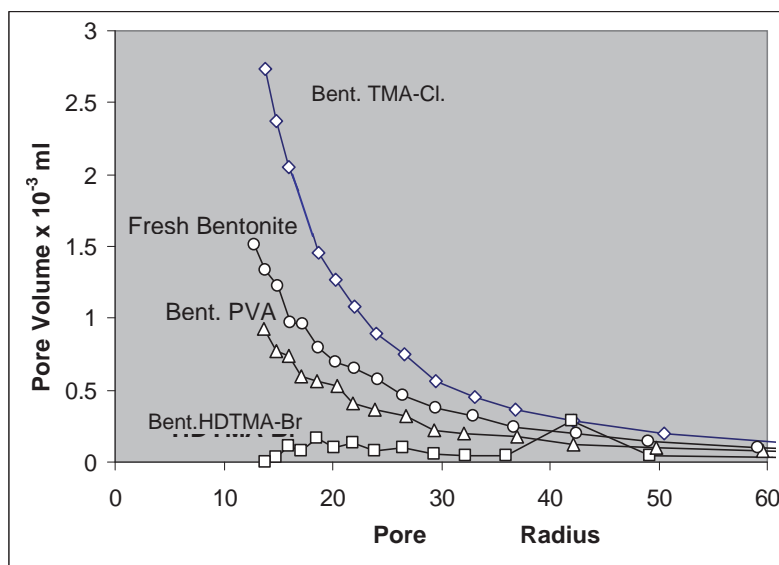


Figure 3. The pore distribution and pore volume of fresh bentonite and intercalated bentonite using PVA 0.75%, HDTMA-Br 0.75% and TMA-Cl 0.75%

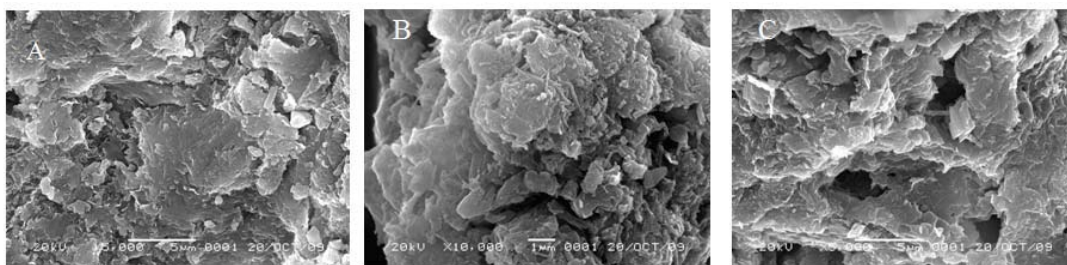


Figure 4. SEM images of fresh bentonite (A), and intercalated bentonite using TMA-Cl (B) and HDTMA-Br (C)

4. Conclusion

Study of the used of TMA-Cl, HDTMA-Br and PVA as intercalating agent for bentonite modification is successfully done. An interesting observation made during these experiments is that the results show effectively modified in bentonite. TMA-Cl shows the most effective surfactant as intercalating agent compare to that of PVA and HDTMA-Br. Further investigation of the application of the intercalated bentonite need to be carries out (such as it performance as composite materials, catalyst or adsorbent).

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