Thermal properties of Bentonite Modified with 3-aminopropyltrimethoxysilane

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Abstract. Chemical modifications of Bentonite (BNT) clay have been carried out by using 3-aminopropytrimethoxysilane (APS) in various solvent media. The degradation properties of products (BNTAPS) were characterized by thermogravimetric analysis (TGA). Samples were heated at 30 to 700 °C with a heating rate 10 deg/min, and the total silane-grafted amount was determined by calculating the weight loss at 200 – 600 °C. The thermogram of TGA showed that there were three main decomposition regions which are attributed to the elimination of physically adsorbed water, decomposition of silane and dehydroxylation of Bentonite. High weight loss attributed to the thermal decomposition of silane was observed between 200 to 550 °C. Quantitative analysis of grafted silane results high silane loaded using a solvent with high surface energy, which indicates the type of solvent affected interaction and adsorption of APS in BNT platelets.

1. Introduction
Clay is cheap and an abundant inorganic material resource on Earth. In Indonesia, Ca-Mg bentonite (BNT) is dominant type of clays which is contained in soil and generally used for purification [1]. BNT consists of monmorillonite-MMT as the largest component and other oxides such as Fe2O3 in its structure. The BNT structure was covered by two tetrahedral sheets of silica and octahedrons of alumina sheets with exchangeable cations such as Mg2+, Ca2+, Na+ in the interlayer space. The ions are strongly hydrated in the presence of water, resulting in a hydrophilic environment of BNT [2].

BNT and several clays are widely applied as adsorbent and inorganic components in polymer composites [3-6]. Clay is naturally has polar properties and easily agglomerate due to strong interaction between clay particles compared to clays with polymers [7]. It is necessary for clay mineral to be modified to improve the surface and clay interlayer properties so that the polymer can be intercalated. Clay modification with quaternary ammonium salts compounds have been previously reported to improve interlayer spacing [8]. Another clays modification to improve thermal stability at high temperature, modification with organosilane such as 3-aminopropyltrimethoxysilane has been previously reported [9, 10]. The reaction between the clay with modifier can occur on the surface and interlayers of the clay, and it was influenced by the type of solvent. Modification of clays with
organosilane changes both chemical properties and physical properties of clays such as the thermal stability [11].

In this paper, we studied a chemical modification of BNT with 3-aminopropyltrimethoxysilane (APS) and thermal properties of modified materials. In order to understand the effect of a dispersion medium, Water, Ethylene glycol and the combination of solvent was used. The modified BNTs (BNTAPS) were characterized with Thermogravimetric analysis (TGA).

2. Experimental

2.1 Materials

Bentonite (BNT) 180 mesh supplied by a local industry in Indonesia. 3-Aminopropyltrimethoxysilane (APS) was obtained from Aldrich Chemical Company, Ethanol (Merck) and Ethylene glycol (Merck) solvents were used without further purification.

2.1.1 Aminosilane functionalization of BNT.

Five gram of BNT was dispersed in 250 mL of solvent and stirred at room temperature for an hour. Five gram of APS dissolved in 250 mL of solvent was added to the BNT dispersion and stirring was continued for an hour. The product was then filtered and dried at 40 °C for 24 hours. The products were designated by BNTAPS_x_y, where x and y represent the solvents. Distilled water (W), Ethylene glycol (EG), Ethanol (Et) were used as solvents.

2.1.2 Thermal Analysis.

Thermogravimetric analyses were carried out using Simultaneous Thermal Analyzer (STA) LITSEIS PT1600 in the temperature range from 30 to 700 °C at heating rate 20 °Cmin⁻¹ with air atmosphere. Using TGA data, silane loaded amount was calculated using equation 1, where \( W_{200-600} \) is percentages of weight between 200 °C and 600 °C [10, 12].

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\text{Silane load amount (\%) = } \frac{100 \times W_{200-600}}{100 - W_{200-600}}
\]  

(1)

3. Results and Discussion

To analyse interaction of BNT with APS and total grafted silane, thermal analysis was conducted. Thermogram TGA and differential thermal gravimetric (DTG) of BNT and BNTAPS were shown in Figure 1 and Figure 2. BNT thermogram shows two major stages of degradation process, that are in the below 100 °C and about 500 °C which is attributed to dehydration and dehydroxylation alumnosilicate [13]. Weight loss at temperatures below 100 C is attributed to evaporation of water molecules that physically interact on the BNT surface and obtain a total degradation about 11%. At a temperature range of 150-450 °C BNT is slowly degraded and the high weight loss observed at 450-550 °C. The degradation peak around 450-550 °C is attributed to the dehydroxylation of aluminosilicate layers.

Table 1 shows mass loss percentages of BNT and BNTAPS. Modified materials showed higher mass loss at 150-450 °C than BNT. BNTAPS modified in water media showed highest mass loss which is about 9.57%, while the lowest mass loss about 6.81% was observed in BNTAPS modified in mixture solution of ethylene glycol and ethanol. At a temperature of 550-700 °C, the degradation is obtained for BNTAPS in various solvents; on the other hand, this is not obtained for BNT. BNTAPS
modified in water and mixture of water and ethanol showed higher mass loss, 2.83% and 3.56% respectively. The lowest mass loss about 1.34% was observed in BNTAPS_Eg.

Figure 1. Thermogram TGA of BNT and BNTAPS in any solvents.
Figure 2. Thermogram DTG BNT and BNTAPS

Table 1. Mass loss characteristics of BNT and BNTAPS obtained from TGA analysis

| Sample       | 40-125 °C | 150-450 °C | 450-550 °C | 550-700 °C |
|--------------|-----------|------------|------------|------------|
| BNT          | 11.8      | 4.10       | 3.07       | -          |
| BNTAPS_W     | 6.8       | 9.57       | 4.65       | 2.83       |
| BNTAPS_EG    | 8.8       | 9.18       | 4.17       | 1.34       |
| BNTAPS_Wet   | 6.5       | 8.72       | 5.15       | 3.56       |
| BNTAPS_EG_Et | 7.2       | 6.81       | 3.77       | 2.18       |

The usage of different types of solvents produces different degradation patterns at 150-450 °C. Water and mixtures of water and ethanol as dispersing medium resulted in degradation at 100-150 °C which is attributed to evaporation of physisorbed water molecules and hydration water of exchangeable cations [9, 11]. The next degradation peaks are obtained at a temperature of about 150-
450 °C and this degradation is also produced on the use of EG and mixtures of EG and Et. The degradation around 150-450 °C is related to the decomposition of absorbed and intercalated APS. In this study, the modification of APS in BNT resulted in degradation peak at 550-700 °C area for all dispersing media, while that degradation did not occur in BNT. Peaks at 550-700 °C are related to the degradation of cross-linked APS on the inter-clay layer BNT and followed by the dehydroxylation of aminosilicate layers.

Previous studies reported that clay modification with amimosilane is influenced by surface energy or surface tension of the solvent [9]. Solvents with lower surface tension or similar to the BNT surface tension (γ-MMT 44 ± 2 mJ / m²) can wet the BNT and facilitate the APS to react with BNT on the surface. While solvents with higher surface tension can increase basal spacing of BNT so that APS can be intercalated or form a crosslink in the basal spacing of BNT. Figure 3 shows the effect solvent surface tension on the silane load, which calculated using equation 1. The using of solvents with low surface energy produce lower total silane load than higher surface energy solvents, and these result agree with previous study [9]. The use of mixed EG solvent with ethanol produced the lowest silane load which is about 11.5%, meanwhile the usage of EG (γ 52.4 mJ / m²) and water (γ 72 mJ / m²) were obtained 14.77% and 16.7%, respectively. The modification using high surface energy such as water not only facilitates the APS reaction on the BNT surface, but also intercalates and interacts with the -OH groups in the basal spacing of BNT and it is produced higher thermal degradation [9, 11].

![Graph showing the effect of solvent surface tension on silane load](image)

**Figure 3.** Effect of solvent surface tension on silane load

4. **Conclusion**

Chemical modifications of bentonite have been prepared with APS under various solvents. Thermal analysis was performed to determine the interaction and total grafted silane on BNT. The TGA and DTG data of BNTAPS shows degradation below 150 °C, 150-450 °C, 450-550 °C, and above 550 °C due to releasing water molecules, degradation of absorbed and intercalated APS, bonded APS in the clay interlayers, and degradation of aluminosilicate layers. The percentage of grafted silane on the BNT, calculated using TGA, showed a higher grafted silane for high surface tension solvent. The usage of water as solvent produces a large grafted silane with a percentage 16.7%.
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References
[1] Koswojo R, Utomo R P, Ju Y H, Ayucitra A, Soetaredjo F E, Sunarso J and Ismadji S 2010 Appl. Clay Sci. 48 81-86
[2] Özcan A S and Özcan A 2004 J. Colloid Interf. Sci. 276 39–46
[3] Othman N, Ismail H and Mariatti M 2006 Polym. Degrad. Stabil. 91 1761-1774
[4] Tahir S S and Rauf N 2006 Chemosphere 63 1842 - 1848
[5] Wang P, Ma J, Wang Z, Shi F and Liu Q 2012 Langmuir 28 4776 - 4786
[6] Bergaya F and Lagaly G 2001 Appl. Clay Sci. 19 1-3
[7] Zulfiqar S, Kausar A, Rizwan M and Sarwar M I 2008 Appl. Surf. Sci. 255 2080-2086
[8] Paiva L B, Morales A R and Diaz F R V 2008 Appl. Clay Sci. 42 8-24
[9] Shanmugharaj A M, Rhee K Y and Ryu S H 2006 J. Colloid Interf. Sci. 298 854–859
[10] Piscitelli F, Posocco P, Toth R, Fermeglia M, Priel S, Mensitieri G and Lavorgna M 2010 J. Colloid Interf. Sci. 351 108–115
[11] Bertuoli P T, Piazza D, Scienza L C and Zattera A J 2014 Appl. Clay Sci. 87 46 – 51
[12] Herrera N N, Letoffe J M, Putaux J L, David L and Bourgeat-Lami E 2004 Langmuir 20 1564-1571
[13] Holtzer M, Bobrowski A and Zymankowska-Kumon S 2011 J. Mol. Struct. 1004 102–108