Zn-Al LAYERED DOUBLE HYDROXIDE AS HOST MATERIAL FOR SUNSCREEN COMPOUND OF *p*-AMINOBENZOIC ACID

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ABSTRACT

Zn-Al layered double hydroxide can be used as host material for UV active compound p-aminobenzoic acid (PABA), which is having capability to block UV light of sunlight. The formation of Zn-Al-PABA was best developed in which the nucleation process was done at room temperature and followed by hydrothermal treatment at 100 ^{o}C. To make a better product, the molar ratio of Zn to Al to PABA was adjusted to 3:1:1. From the elemental analysis and the content of PABA, it was observed that the product has structural formula of $Zn_{0,745}Al_{0.254}(OH)_{1.650}(PABA)_{0.349}.0.684H_2O$. The particle size of the powder as estimated using SEM was in the range 100-200 nm. FTIR and XRD proved that the p-amino benzoate ion occupied the interlayer space. This material is expected to have high sun protection factor (SPF).

Keywords: *layered double hydroxide, sunscreen, p-amino benzoic acid, nanoparticle*.

INTRODUCTION

Layered double hydroxides (LDHs), also known as hydrotalcites and anionic clays, consist of $M^{II}(OH)_6$ and $M^{III}(OH)_6$ edge-sharing octahedrons forming sheets similar to those of brucite [1]. The net positive charges on the sheets are balanced by exchangeable anions occupied the interlayer space [2-5]. For instance, the mineral known as hydrotalcite is a Mg-Al LDH in which CO_3^{2-} is charge balancing anions in the interlayer space so that it is formulated as $Mg_6Al_2(OH)_{16}\cdot CO_3\cdot 4H_2O$ [6,7]. LDHs have been studied extensively for many possible applications such as anion exchangers, acid scavengers, polymer additives, battery cathodes, catalysts, catalyst supports, electrode modifiers, etc. [5-12].

In the recent years, layered double hydroxides have been studied extensively for possible application in drug delivery system, organic-inorganic composite materials, and so on [1]. In this work, an organic-inorganic sunscreen will be prepared from Zn-Al-Cl LDH. Food and Drug Administration (FDA) has issued a list of chemicals in sunscreens in which TiO_2 and ZnO can comprise up to 20% of total weight and PABA up to 15%. Most organic sunscreens consist of benzene ring as main chromophoric subunit and other substituents such as carbonyl. The combination of them produces sun screening effect since in the UV range, where the compound will absorb the light at low wavelength and then release those high wavelengths. LDHs have net positive charge layer that must be balanced with the interlayer anion. If the sunscreen compound bearing negative subunit such as sulphonate and carboxylate, they can occupy the interlayer space the way charge balancing ions do, creating organic-inorganic composite of sunscreen. Organic-inorganic sunscreen is not only safe but also reduce the amount of the UV active compounds. The LDH can act as physical blocking and UV active compound will provide chemical blocking. Further, the product is also expected to have small particle size in the range of 50-200 nm. In this paper, we wish to report the preparation, characterization, and morphology of Zn-Al-PABA prepared from corresponding zinc chloride, aluminium chloride and *p*-amino benzoic acid. Since ZnO and Al_2O_3 have been found extensively in various topical drugs, the Zn-Al-PABA is also expected to have high biocompatibility.

EXPERIMENTAL SECTION

Zinc and aluminium salts were obtained from Merck and are of analytical grade chemicals. *P*-benzoic acid (PABA) was also a pure chemical and other chemicals obtained from Merck used as received.

Zn-Al-Cl LDH was prepared according procedure in the literature [11]. Synthesis of the Zn-Al-PABA from zinc and aluminium chlorides was performed in a three-necked round flask. A 25.0 mL aqueous solution of 0.60 M (15.0 mmol) was mixed with 25.0 mL aqueous solution of 0.20 M (5.0 mmol) aluminium chloride and stirred quickly at about 1000 rpm using a magnetic stirrer. To this mixture, a 50.0 mL solution containing 10.0-mmol sodium *p*-amino benzoate (Na-PABA) was added using a funnel and stirred quickly. Na-PABA was prepared prior to the mixing by stoichiometric reaction of PABA with NaOH. It took about 2 minutes to complete the addition of Na-PABA.

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Then, the slurry was hydrothermally heated in a PTFE bottle at 100°C for 15 hours. The product was separated using centrifuge and repeatedly washed three times using double distilled water. The collected solid was dried in an oven at 70 °C for 48 h. After being dried, its layered structure was confirmed using X-ray Diffraction (XRD) on Shimadzu 6000 series. The metal contents were determined using atomic absorption spectrometry (AAS) using appropriate standard solution. The amount of water is determined gravimetrically using porcelain crucible container after the sample was heated at 180 °C for 3 h. The PABA in the interlayer space was recovered by reacting the solid with dilute nitric acid. PABA was separated to become solid since other metal components were dissolved. The results of the elemental analysis were used to determine the structural formula of the product [6].

The morphology of the solid was scanned using scanning electron microscope (SEM).

RESULT AND DISCUSSION

From the results of elemental analysis, the structural formula of synthesized Zn-Al-PABA is $Zn_{0.745}Al_{0.254}(OH)_{1.650}$ $(PABA)_{0.349}.0.684H_2O$. Note that the water content was determined gravimetrically after heating at 180°C for 3 h. Metal were determined using atomic absorption spectrometry (AAS). The formulae are fit to the general structure of layered double hydroxide of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{-}_{z1}A^{2-}_{z2}\cdot mH_2O]$. From this structure, it is expected the structural formula is very close to the ideal structure of hydrotalcite.

The PABA content was slightly higher, however, meaning that some of PABA may be included in the interlayer space and form ionic bonding between PABA and zinc or aluminium. For ideal structure, aluminium should have equal molar to the anion. In the structure, the charge balance should be maintained in which zinc, aluminium, hydroxide, and PABA are contributing. This product shows that it is confirmed to the layered doubled hydroxide structure.

Fig 1 shows the XRD pattern of the Zn-Al-PABA prepared from the salts of zinc chloride and aluminium chloride. The d_{003} of the product was 11.77 Å (corresponding to $2\theta = 7.5^o$). For comparison purposes, the d_{003} of the Zn-Al-Cl where no organic compound are present is 7.80 Å [11]. The net increase of nearly 7.40 Å is attributed to the replacement of small anion of chloride with *p*-amino benzoate.

The scanning electron microscopy (SEM) image of the product is shown in Fig 2 and Fig 3.

The particle size can be estimated from the image which is about 100-200 nm. Besides having nano size, the powder also shows uniform particle size. No

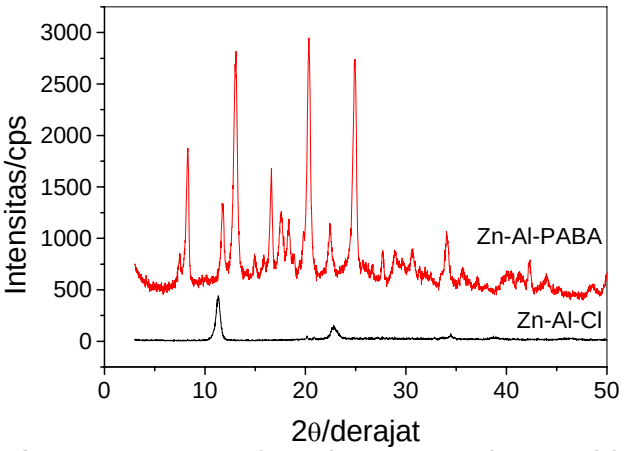

Fig 1. XRD pattern of Zn-Al-PABA LDH (prepared from zinc chloride and aluminium chloride) (top) and Zn-Al-Cl (bottom).

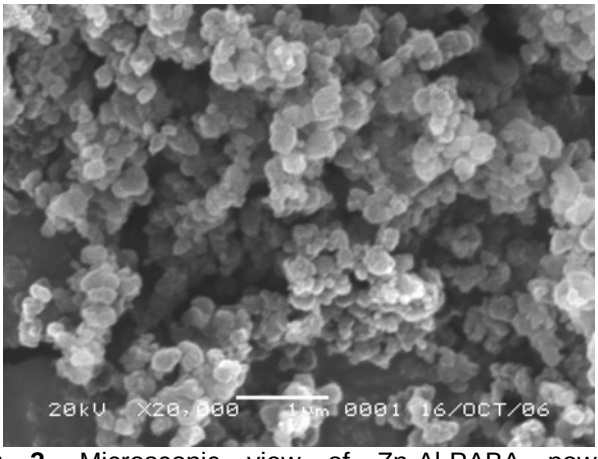

Fig 2. Microscopic view of Zn-Al-PABA powder (prepared from zinc chloride and aluminium chloride) recorded using SEM at magnification of 20,000 X. As seen in the image the diameter of the particle approximately 100-200 nm.

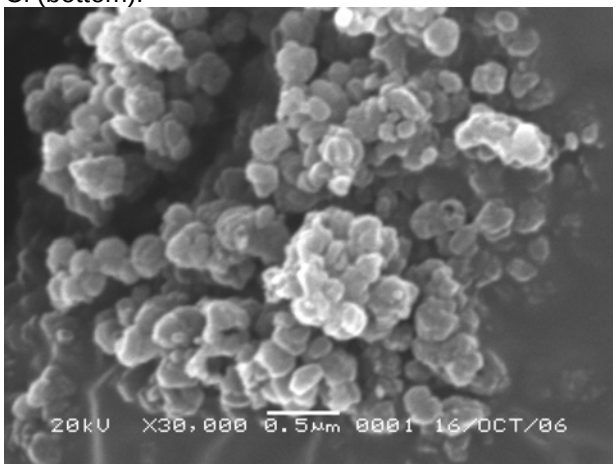

Fig 3. Microscopic view of Zn-Al-PABA powder (prepared from zinc chloride and aluminium chloride) recorded using SEM at magnification of 30,000 X. As seen in the image the diameter of the particle approximately 100-200 nm.

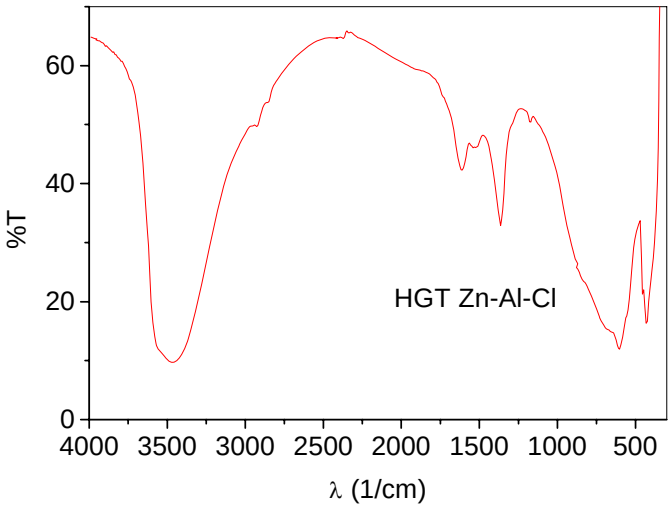

Fig 4. FTIR spectra of Zn-Al-Cl layered double hydroxide, without organic compound.

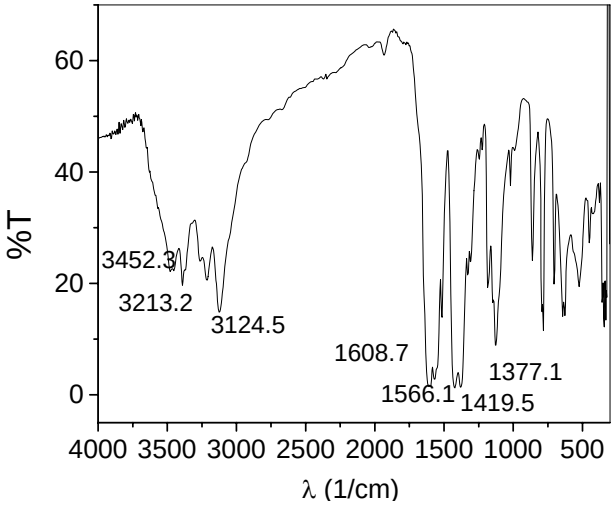

Fig 5. FTIR spectra of Zn-Al-PABA layered double hydroxide (prepared using chloride salts).

particle size larger than 200 nm or smaller than 100 nm was observed, indicating that the product is quite homogeneous in size.

Xu *et al.* have reported that small particle size can be achieved by hydrothermal treatment of the layered double hydroxide slurry after the nucleation process was completed [12-13]. They had successfully prepared plain Zn-Al and Mg-Al LDH with the particle size around 50 nm. Their LDHs do not have organic compound inside the interlayer space. In this work, with PABA in the interlayer space we can manage to prepare LDH with the particle size about 100-200 nm, reasonably low. Note, however, that our method of LDH preparation is very simple. The Zn-Al-PABA can be produced by adjusting the concentration of Zn^{2+}, Al^{3+}, and PABA. pH adjustment during the synthesis was not necessary, since the product can be achieved easily. Adjusting the solution pH during the preparation is usually difficult and time consuming.

Figure 4 shows FTIR spectra of native Zn-Al-Cl layered double hydroxide without p-aminobenzoic acid. As expected, the vibration mode of O-H stretching is seen at 3500 cm^{-1}. The corresponding vibration mode of O-H bending is observed at 1630 cm^{-1}. The presence of trace carbonate ion in the interlayer space is also detected at near 1360 cm^{-1}. Zn-Al-Cl layered double hydroxide is formed by mixing zinc chloride and aluminium chloride with NaOH. Atmospheric CO_2 reacts with the mixture to produce the impurity.

After *p*-aminobenzoic acid was inserted into the interlayer space of Zn-Al-Cl layered double hydroxide, the FTIR spectra of the product was, once again, recorded. Figure 5 shows FTIR spectra of Zn-Al-PABA layered double hydroxide. A band of O-H stretching is seen at 3452 cm^{-1}, in which related O-H bending is not observed at 1630 cm^{-1}, probably overlaid by other bands. The N-H stretching is very close to O-H stretching, which is observed at 3213 cm^{-1}. Further, C-H stretching of the aromatic ring can be confirmed with the band at 3124 cm^{-1}. The C=C vibration of the aromatic ring (benzene) is also supported by the vibration at 1419 $cm^{-1}$and 1566 cm^{-1}, respectively. The band near 1608 cm^{-1} correspond to the C=O vibration mode. In addition, the C-H bending of aromatic ring is also clearly recorded at 710 cm^{-1}.

From the XRD, elemental analysis, and FTIR it is convincing that the product is Zn-Al-PABA. The nanosize particle as recorded using SEM proved that the product has a narrow particle size between 100-200 nm, confirming that nanosize Zn-Al-PABA can be prepared at very mild condition. Unlike what was reported before the hydrothermal treatment [12] and rigorous mixing using colloid mill [14] were not necessary to prepare nanosize Zn-Al-PABA.

CONCLUSION

Zn-Al-PABA can be prepared by reaction of zinc chloride and aluminium chloride with sodium *p*-amino benzoate. The product shows to have homogenous particle size between 100 to 200 nm. XRD pattern reveals that this nanoparticle has basal spacing of 15.22 Å. Meanwhile, Zn-Al-Cl has a lower of about 7.80 Å. The increase in basal spacing is attributed to the replacement of chloride with *p*-amino benzoate. The presence of PABA in the interlayer space of Zn-Al-Cl LDH is proven using FTIR. This material is subjected to the measurement of sun protection factor (SPF) by both *in vitro* and *in vivo* before it is used as suncreen.

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