The facile synthesis of a nanoscale composite from fly ash and lime stone

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Abstract. Here we report the synthesis of a nanocomposite SiO2/CaCO3 by extraction of SiO2 from fly ash and CaCO3 from limestone via the sol-gel method followed by ultrasonication. The preliminary analysis of SEM has been used to characterize the nanocomposite. Results showed that the synthesized material has a nanoscale structures and a typical similarity of composition compared to quartz, vaterite, and calcite respectively. Size distribution of nanocomposite was better than PCC, a conventional paper filler used in paper industry. The application of nanocomposite as paper filler would promise the better physical properties improvement. In terms of efficiency, the estimation of production cost by using nanocomposite would be lower than the conventional filler such as PCC. The utilization of hazardous waste from coal combustion would be also important to develop a green framework of pulp & paper industry.

1. Introduction

The use of Precipitated Calcium Carbonate (PCC) as high paper filler contents, 20% – 25% ash content in average, has contributed to several technical problems in paper production. Loss of physical properties related to low paper bulky and poor retention as well as paper dusting has raising concern at industrial scale. Consequently PCC will also increase the use of sizing agent and cause environmental issues.

The use of nanocomposite (SiO2/CaCO3) is an alternate way to overcome those actual problems caused by PCC. Its applicable promise as paper filler could enhance quality of paper products based on physical-optical properties such as parameters of bursting, tearing, tensile, brightness and whiteness indexes.

The use of 1% paper filler would contribute to cost efficiency about USD 3.7/ton paper if compared to PCC price about USD 1.2/ton based on the following table:

| Item                | Unit   | Ash | 19.5% Quantity | Unit Price | Amount | Ash | 20.5% Quantity | Unit Price | Amount | Est. Saving |
|---------------------|--------|-----|-----------------|------------|--------|-----|-----------------|------------|--------|-------------|
| P                   |Ton     |     | 0.0009          | 0.46       | 0.0009 | 0.46 |
| U                   |Ton     |     | -               | -          | -      | -   |
| L                   |Ton     |     | 0.8197          | 261.47     | 0.8097 | 357.98 |
| P                   |Ton     |     | -               | -          | -      | -   |
| Sub Total           |        |     | 0.8206          | 361.94     | 0.8166 | 357.54 | 4.40 |
| C                   |Kg      |     | 86.95           | 6.09       | 96.95 | 6.79 | (0.70) |
|                     |        |     |                 |            |        |      | 3.70           |
The use of nanocomposite (SiO2/CaCO3) is also promising a green industrial concept on utilization of hazardous waste from coal combustion which will decrease air pollution. The current amount of fly ash powder at Power Plant PT. IKPP Perawang-Riau is about 32 tons/month.

The extraction of SiO2 from fly ash powder by using NaOH, followed by reaction with Ca(OH)2 to produce CaSiO3. The Ca(OH)2 was previously obtained from calcinated limestone (CaO). As reported that fly ash containing 40 to 60% of SiO2 [1] and limestone containing about 52% CaO [2].

The nanocomposite (SiO2/CaCO3) has been synthesized from rice straw ash [3]. A micrometer scale of SiO2/CaCO3 composite has been synthesized from fly ash [4] and applied to paper products with high brightness 91% ISO, low bulk density 0.31g/cm3 and high surface area 121 m2/g [5]. Zhang also reported that co-flocculation of cellulose fibers with SiO2/CaCO3 composite could enhance bulk and tensile strength. The last research was reported by Papynov [6] that wollastonite (CaSiO3) with dimension of 160 nm synthesized by sol-gel method combined with spark plasma sintering (SPS) with immobilization of Au-nanoparticles.

2. Methods

To synthesize the fly ash-based composite at nano scale, the sonochemical reaction was encouraged [7,8] through nucleation of nanoparticles initiated by ultrasound probe 10 mm 20 W at variation of times [9, 10]. Furthermore the reaction time of carbonation process will be faster due to high surface area after nucleation process [11].

Fly ash was calcinated at 600°C for 2h to remove hydrocarbon and forming colloid with NaOH. A 100 mesh filtration applied to obtain homogenous particle size. Before extraction process, fly ash was immersed with hot distilled water for 2h to reduce Kalium and Natrium ions. In order to extract SiO2, 120 g NaOH 5M added to 20 g fly ash then being heated at 130°C, 500 rpm, 2h. The Na2SiO3 added with H2SO4 carefully to get silica gel, and then washed with distilled water. Silica sol will be formed after drying silica gel in the oven.

Limestone was treated in a ball milling and filtered to obtain particle size about 150 μm. After furnace at 900°C for 1h, about 0.8 g of calcinated CaO was dissolved in 1000 ml distilled water and then mixed at 700 rpm for 15 min to form Ca(OH)2. The CO2 (g) has been applied into reaction system and silica sol being added at variation of concentrations 0.25 M to 1.5 M. Nucleation process and morphology of nanocomposite has been controlled by ultrasound probe 10 mm 20 W at variation of times.
3. Results and Discussion

The finite structure of composite was found as the finest size of particle which synthesized from fly ash and lime stone via sol-gel method [12]. SEM images below have showed a needle-like structure with the dimension range from 10 to 20 nm widths and 0.1 to 1 μm lengths. The electron microscopic images confirmed that the synthesized composite belong to a nanoscale composite material. The morphology of nanocomposite has slight similarity with PCC and GCC in despite of previously reported Fly Ash based Calcium Silicate (FACS) or modified GCC [5, 13].

![Figure 2](image_url)

**Figure 2.** Morphology of needle-like structure of nanocomposite was observed by SEM.

The nanometer size particles are also tend to be aggregated and attached strongly between each other in order to minimize their surface energy and resulting the low detachment rate during the washing and papermaking process [14].

The mechanism in the traditional filling method, some fillers exist on the surface of fibers and disturb the fiber-fiber hydrogen bonding. In contrast, in the co-flocculation filling method, FACS are enfolded and entwined by fines, which decrease the direct contact between fillers and fibers. Fines bridge the interaction between fibers and fillers and bring fibers closer together, which increases paper strength and decreases bulk. However, the formed composites have a larger particle size than FACS flocs, which compensates for the decrease in bulk to some extent [15].
4. Conclusion

Nanocomposite SiO$_2$ / CaCO$_3$ has been successfully synthesized from fly ash and limestone by sol-gel method through a nucleation process with ultrasound probes. Based on literature, the needle-like structure with the dimension range from 10 to 20 nm widths and 0.1 to 1 μm lengths is proposed to be the finest SiO$_2$ / CaCO$_3$ particle which has been synthesized from fly ash and limestone via sol-gel method. The composite material has a typical similarity of composition compared to quartz, vaterite, and calcite respectively with better distribution compared to PCC. The nanocomposite is expected to be a solution for some technical problems due to the use of PCC filler, more economical, more environmentally friendly and can improve the physical properties of paper products.

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