Colloids and Surfaces A: Physicochem. Eng. Aspects 414 (2012) 9–16

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Delaminated sodium titanate nanobelts in synergy with cationic polyacrylamide to induce flocculation on kaolin clay

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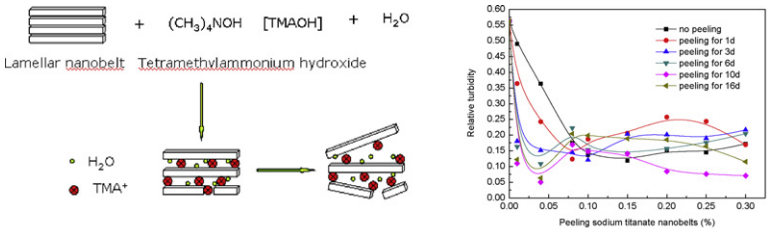
HIGHLIGHTS

- Peeling reduced both the length and the width of sodium titanate nanobelt.
- Peeled nanobelts offered the maximum synergistic flocculating effect with CPAM at a very low dosage.
- CPAM/peeled nanobelt induced larger and denser flocs of kaolin clay than CPAM alone.
- Prolong the peeling time resulted in forming even denser but smaller flocs.

GRAPHICAL ABSTRACT



Peeled nanobelts showed their largest synergistic flocculation effect with CPAM at a very low dosage

ARTICLE INFO

Article history:
Received 14 May 2012
Received in revised form 10 August 2012
Accepted 13 August 2012
Available online 23 August 2012

Keywords:
Flocculation
Delamination
Sodium titanate nanobelt
CPAM
Microparticle retention system
Kaolin clay

ABSTRACT

Nanoparticle with higher aspect ratio and greater surface area renders higher micro-bridging ability in flocculating paper furnishes adsorbed with cationic polymers. Sodium titanate nanobelt is a typical one-dimensional nano-material with extremely high aspect ratios. In this paper, the nanobelt was synthesized hydrothermally and successfully peeled with tetramethylammonium hydroxide (TMAOH). The peeled nanobelt was characterized by XRD, TEM, BET surface area and surface charge measurement, and employed as a microparticle component partnered with cationic polyacrylamide (CPAM) to constitute a retention system. The flocculation behavior of kaolin clay by CPAM/nanobelt system was investigated using a photometric dispersion analyzer connected with a dynamic drainage jar. The morphology of flocculated kaolin was characterized by TEM and optical microscope. The results showed that the peeling treatment reduced both the length and the width of nanobelt, increased the charge density and sorption capacity to CPAM but did not significantly alter its structure and zeta potential in aqueous dispersion. The peeled nanobelts partnered with CPAM offered the biggest synergistic flocculating effect at a very low dosage, especially the ones that were peeled for 6–10 days. The kaolin flocs induced by CPAM/peeled nanobelt were larger and denser than those induced by CPAM alone, and become even denser but smaller with increased peeling time.

1. Introduction

In papermaking processes, retention aids are often used to improve the retention of fines or filler [1,2]. Microparticle retention systems, also known as nanoparticle retention systems, have been extensively used in high speed paper machine. An anionic

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http://dx.doi.org/10.1016/j.colsurfa.2012.08.024

microparticle retention system is typically composed of a cationic polymer and an anionic microparticle. The cationic polymer is added first to papermaking furnish, adsorbed on fibers, fines and fillers and to set off formation of flocs via bridging flocculation mechanism. Not soon after the initial flocs are broken down by shear, the anionic microparticle is introduced to re-flocculate/consolidate the dispersed flocs by bridging to and/or charge neutralization of the previously adsorbed cationic polymers [3–5]. Generally speaking, microparticles with larger sizes or higher aspect ratios, such as montmorillonite and structured silica, have higher bridging ability than those with smaller particle size or lower aspect ratios, such as colloidal silica [6–8], conferring better retention effect on fines and fillers. The delaminated montmorillonite is usually a more effective anionic microparticle retention aid for precipitated calcium carbonate (PCC) filler to deposit on fibers than untreated montmorillonite [9].

Recently, one-dimensional nanostructured titanate, including nanobelts [10–13], nanotubes [14–17], nanorods [18–20], nanowires [21] and nanofibers [22], has received more attention because of its diversity of applications and relatively simple preparation procedures. Particularly the nanobelts have been drawing a great research interest due to their extremely high aspect ratio, nanometric thickness and width [23,24]. Zhang and Liu [23] synthesized a sodium titanate nanobelt with a very high length-to-width ratio, which induces clay flocculation efficiently at a very low dosage when used as the second retention component introduced after cationic polyacrylamide (CPAM). This indicates that the negatively charged nanobelt may act in a similar way as polymers by bridging particles through previously adsorbed CPAM. However, the synthesized nanobelt is usually composed of a few stacked titanate layers [13]. If the nanobelts are delaminated into single-layer belts, the surface area and adsorption capacity would be further improved, consequently the particle flocculation efficiency is bettered when used along with cationic polymers.

Delamination is usually carried out through interlaminar ion exchange or embedded reaction, and often applied for preparing low dimensional nano-materials, such as zero-dimensional nanoparticles, one-dimensional nanofibers and nanotubes and as well two-dimensional nanoplates. It has been a new topic of nanometer materials [25,26]. However, the strong attraction force among nanobelt layers makes the delamination rather time-consuming [27–29]. In this paper, we introduced a method to delaminate sodium titanate nanobelts by using tetramethylammonium hydroxide. The delaminated nanobelts with different dimensions were first characterized by TEM, XRD and zeta potential and were employed as microparticle component. The re-flocculation behavior of delaminated nanobelts on kaolin clay suspension was investigated.

2. Experimental

2.1. Materials

Titanium dioxide, Aeroxide® TiO_2 P25, was commercial TiO_2 powder from Evonik Degussa GmbH. According to the supplier, the TiO_2 nanopowder has an average primary particle size of 21 nm, and a specific surface area of $50 \pm 15\ m^2/g$, which is identical with the value of $52.64\ m^2/g$ measured via nitrogen adsorption using SSA-4300 pore size and specific surface area analyzer (Beijing Biaode Instrument Co., Ltd). Cationic polyacrylamide (CPAM), Percol 292, was from Ciba Specialty Chemicals Ltd. The relative molecular mass is approximately $5–8 \times 10^6$ and the degree of substitution 20–25%. Kaolin clay purchased from Sinopharm Chemical Reagent Co., Ltd was chemical pure reagent ($Al_2O_3 \cdot SiO_2 \cdot 2H_2O$) with an average particle size of 6.5 μm. Tetramethylammonium hydroxide was supplied by Sinopharm Chemical Reagent Co., Ltd. All the other chemicals were analytically pure reagents.

2.2. Synthesis and peeling of sodium titanate nanobelt

Sodium titanate nanobelt was synthesized through alkaline hydrothermal method [11,14]. 0.1 g TiO_2 nanopowder was mixed with 20 mL of 10 M NaOH aqueous solution, followed by the hydrothermal treatment at 180 °C in a 25-mL Teflon-lined autoclave for 24 h. After the autoclave cooled off naturally to room temperature, the content was washed thoroughly with deionized water till the pH of filtrate was less than 7. The sample was then further washed with anhydrous ethanol three times, dried at 65 °C and milled. The obtained sodium titanate nanobelt was mixed with 0.2 M tetramethylammonium hydroxide (TMAOH) aqueous solution, and the slurry was stirred for a preset time. At the termination of reaction, the sample was washed thoroughly with deionized water till the pH of filtrate was less than 7. Thus obtained peeled sodium titanate nanobelt was further washed with anhydrous ethanol three times, freezing dried and milled.

The morphology of both peeled and unpeeled nanobelts was analyzed with a JEM-100CXII transmission electron microscope (TEM). The variation of nanobelt surface area with pealing time was detected by BET method using SSA-4300 pore size and specific surface area analyzer (Beijing Biao De Instrument Co., Ltd). The structure of the nanobelts was characterized by X-ray powder diffraction (XRD), the instrument used was Bruke D8 Advance Diffractometer, with Cu Kα ($\lambda = 0.15406$ nm). The charge properties were characterized by zeta potential and surface charge density, which were measured by a PALS Zeta Potential Analyzer and polyelectrolyte titration using Mütek™ PCD-03 particle charge detector combined with Mütek™ PCD-T3 automatic titrator, respectively. The average nanobelt length and width and as well size distribution of both were analyzed by using a microscopic image analysis software.

2.3. Adsorption of CPAM onto sodium titanate nanobelt

The adsorption isotherm of CPAM onto the peeled or unpeeled sodium titanate nanobelt was determined by charge titration using Mütek™ PCD-03 particle charge detector combined with Mütek™ PCD-T3 automatic titrator [30,31]. A series of 0–3.5 mL of CPAM at the concentration of 1000 mg/L was mixed with 3.5–0 mL of 2 g/L sodium titanate nanobelt and diluted to 5 mL with deionized water. The mixture was left overnight at ambient temperature and then centrifuged at 5000 rpm for 15 min. The nonadsorbed CPAM in the supernatant was titrated with 0.1 mmol/L sodium polyvinyl sulfate (Na-PVS).

2.4. Flocculation experiment of kaolin clay

A photometric dispersion analyzer (PDA, PDA 2000, Rank Brothers, UK), which was connected to a dynamic drainage jar (DDJ) [30,31], was used to examine kaolin clay flocculation induced by CPAM and peeled titanate nanobelt. Typically 500 mL tap water was first poured into the DDJ without fitted mesh, and started to circulate from DDJ to PDA for several minutes to reach a steady flow. Then, 8 mL of 100 g/L kaolin clay suspension was added while stirring at 500 rpm. By using a peristaltic pump, the content from DDJ was circulated through PDA in a conduit of plastic tube at a flow rate of 20 mL/min. After 200 s, the stirring speed was increased to 750 rpm and CPAM was added to induce the flocculation of kaolin clay. After 30 s, the stirring speed was further increased to 1500 rpm and maintained for another 30 s, during which the initially formed flocculation was broken down. Finally, the stirring speed was lowered to 500 rpm and the titanate nanobelt was added