SODIUM TITANATE NANOBELT AS A MICROPARTICLE TO INDUCE CLAY FLOCCULATION WITH CPAM

Xuyan Zhang and Wenxia Liu*

Sodium titanate nanobelt was synthesized by treating titanium dioxide hydrothermally in concentrated sodium hydroxide solution. The product was characterized by SEM analysis and zeta potential measurements. It served as a microparticle to constitute a microparticle retention system with cationic polyacrylamide (CPAM), while the microparticle system was employed to induce the flocculation of kaolin clay. The flocculation behavior of kaolin clay in such a system was investigated by using a photometric dispersion analyzer connected with a dynamic drainage jar. It was found that the sodium titanate nanobelt carried negative charges and had a more negative zeta potential at higher pH. It gave a large synergistic flocculation effect with CPAM at a very low dosage, and showed higher flocculation effect with CPAM under neutral and weak alkaline conditions. A suitably high shear level was helpful for the re-flocculation of clay by sodium titanate nanobelt. The clay flocculation induced by the CPAM/titanate nanobelt system demonstrated high shear resistance and also generated dense flocs.

Keywords: Flocculation; Sodium titanate nanobelt; CPAM; Microparticle retention system; Clay

*Contact information: Key Laboratory of Paper Science and Technology of Ministry of Education, Shandong Institute of Light Industry, Jinan 250353, China. *Corresponding author: liuwenxia@sdili.edu.cn*

INTRODUCTION

Microparticle retention systems have been extensively used in the papermaking process. An anionic microparticle retention system is composed of a cationic polymer and an anionic microparticle. The cationic polymer is often added first, commencing a bridging flocculation of fibers, fines, and fillers. Shortly after the initial flocs are broken down by shear, the anionic microparticle is added to re-flocculate/consolidate the dispersed flocs by bridge formation/charge neutralization (Moberg and Georgia 1989; Gill 1991; Swerin and Ödberg 1996). The particle size and shape of the microparticle plays key roles in retention improvement and/or drainage promotion (Swerin et al. 1993; Main and Simonson 1999; Asselman and Garnier 2000a; Hubbe 2005). Microparticles with larger size or higher aspect ratio, such as montmorillonite and structured silica, have superior bridging ability (Andersson and Lindgren 1996; Hubbe 2005), while microparticles with higher charge density and smaller particle size, such as colloidal silica, work more by charge-neutralization (Gill 1991; Main and Simonson 1999). Therefore, a microparticle with a high aspect ratio may have high retention efficiency due to its high bridging ability. It has been shown that highly aggregated structured silica gives higher fines retention when the cationic polymer is linear cationic polyacrylamide (Main and Simonson 1999). Delaminated montmorillonite as the second component of an anionic microparticle retention system is more effective for the deposition of PCC filler on fibers than untreated montmorillonite (Vanerek et al. 2006). Micropolymer with a three-dimensional solid-like structure and flexible polymer strands, tails, and loops of anionic charges can provide better retention and drainage than montmorillonite when it collaborates with cationic high mass acrylamide copolymer (Honig et al. 1993). Negatively charged spherical polyelectrolyte brushes such as polystyrene nanoparticle grafted with anionic poly(styrene sulfonate) chains not only provide a higher maximum retention value but also reach the maximum retention value at a lower dose level than montmorillonite (Mei et al. 2006).

Nanobelts are a new class of one-dimensional materials that have been attracting a great deal of research interest because of their superior electrical, optical, mechanical, and thermal properties (Wang 2004; Wang et al. 2005; Liu et al. 2007). Titanate nanobelt and its derivatives are easily synthesized by a simple hydrothermal process in concentrated sodium hydroxide aqueous solution, since titanate has a layered structure with an anisotropic growth rate in different crystallographic directions (Wang et al. 2008). The length of the nanobelts are from several micrometers to several millimeters, and their typical widths and thicknesses are from tens to hundreds of nanometers and several to tens of nanometers, respectively (Meng et al. 2004; Wang and Zhang 2005; Wang et al. 2008). The extremely high aspect ratio, nanometer thickness and width, as well as the negatively charged nature as a titanate may impart titanate nanobelt a high bridging ability, as it constitutes a microparticle retention system with a cationic polymer.

In this study, sodium titanate nanobelt was prepared by an alkaline hydrothermal process using titanium dioxide powder as precursor. It was characterized by SEM and zeta potential, and employed as a microparticle component to investigate its reflocculation behavior on kaolin suspension after treatment with cationic polymer and agitation. The purpose was to investigate the feasibility and reflocculation characteristics of using nanobelt as a microparticle component.

EXPERIMENTAL

Materials

Titanium dioxide used in the study was a commercial TiO_2 nanopowder supplied under a trade name Aeroxide® TiO_2 P25 by Evonik Degussa GmbH. The TiO_2 powder has an average primary particle size of 21 nm and a specific surface area of 50±15 m^2/g. Cationic polyacrylamide (CPAM) was supplied by Ciba Specialty Chemicals Ltd. under the trademark Percol® 292. It is a cationic acrylamide copolymer with average molecular mass of approximately $5\sim8 \times 10^6$ and a degree of substitution of 20~25%. Kaolin clay was a chemical pure reagent ($Al_2O_3•SiO_2•2H_2O$) with the average particle size of 6.5 μm from Sinopharm Chemical Reagent Co. Ltd. The other chemicals used were analytical pure reagents.

Synthesis and Characterization of Sodium Titanate Nanobelt

Sodium titanate nanobelt was synthesized by an alkaline hydrothermal process similar to that described by Wang and Zhang (2005) and Wang (2009). In a typical process, 0.1 g TiO_2 nanopowder was mixed with 20 mL of 10 mol/L NaOH aqueous solution followed by the hydrothermal treatment at 180 ^oC in a Teflon-lined autoclave of 25 mL capacity for 24 hours. After the autoclave was naturally cooled to room temperature, the obtained sample was washed thoroughly with deionized water until the filtrate pH was lower than 7. Then the sample was further washed with anhydrous ethanol three times and dispersed in distilled water to form 0.2 g/L titanate nanobelt dispersion. The morphology of the obtained nanobelt was observed with a Hitachi S-4800 scanning electron microscope (SEM). The zeta potential of the nanobelt was measured with a PALS Zeta Potential Analyzer.

Flocculation Experiment and Characterization

A photometric dispersion analyzer (PDA, PDA 2000, Rank Brothers, UK), which was connected with a dynamic drainage jar (DDJ), was used to detect the flocculation of the kaolin clay suspension. The degree of flocculation, which was represented by a relative turbidity τ_f/τ_i, was estimated from the variation of direct current voltage signals (Xiao et al. 1995, 1999).

In typical flocculation experiment, 500 mL of tap water was first poured into the DDJ with no mesh fitted, and the tap water was circulated from the DDJ to the PDA for several minutes to reach a steady flow. Then, an amount of 8 mL of 100 g/L kaolin clay suspension was added at a stirring speed of 500 rpm. The contents in the DDJ were circulated through the PDA in a plastic tube at a flow rate of 20 mL/min with a peristaltic pump. The initial base voltage (V_0) was reduced to the unflocculated suspension voltage (V_i). 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 to1500 rpm and held out for 30 s to break down the initial flocculation, then the stirring speed lowered to 500 rpm and the titanate nanobelt was added to reflocculate the kaolin clay. A relatively stable reading of the final suspension voltage V_f was recorded 90 s or 30 s after the titanate nanobelt addition. The detailed procedure and the calculation of the relative turbidity have been published elsewhere (Xiao et al. 1999). The morphology of kaolin flocculation was viewed with a H-800 transmission electron microscope (TEM).

RESULTS AND DISCUSSION

Characterization of Sodium Titanate Nanobelt

Sodium titanate nanobelt is formed by a process of dissolution of TiO_2 and crystallization of $Na_2Ti_3O_7$ in concentrated NaOH aqueous solution (Wang et al. 2008). The formation of the nanobelt is similar to that of nanowire and nanotube materials in the alkaline-hydrothermal process. Higher reaction temperature and longer duration time promote the formation of sodium titanate nanobelt (Wu et al. 2006). Therefore, the TiO_2 powder was hydrothermally treated for 24 h in 10 mol/L NaOH aqueous solution at 180 ^oC. The morphology of the product is shown in Fig. 1.

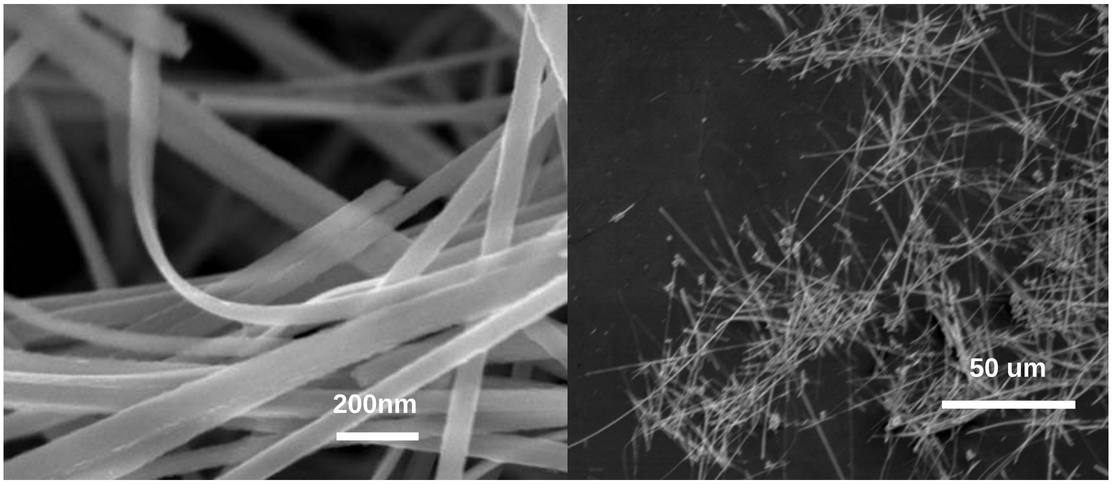


Fig. 1. SEM image of sodium titanate nanobelt

As shown in Fig. 1, the sodium titanate product was a typical nanobelt with good flexibility. The sodium titanate nanobelt had typical widths of from 20 to 200 nm, yet from 50 to 100 nm represented a large proportion. The length of the nanobelt reached up to several hundred micrometers, as observed from a low-magnification image.

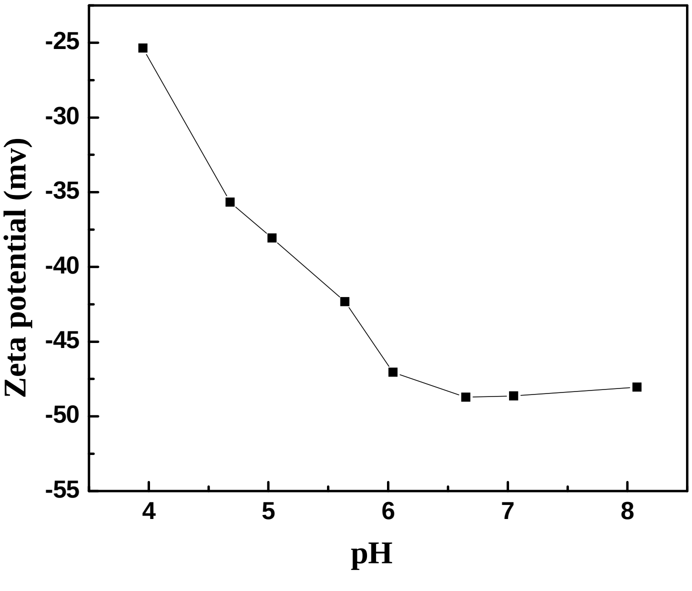


Fig. 2. Zeta potential of sodium titanate nanobelt at different pH

Sodium titanate ($Na_2Ti_3O_7$) has a layered structure composed of [TiO_6] octahedra with shared edges and vertices. The Na^+ is located between the [TiO_6] layers and can be exchanged by other cations (Wang et al. 2008). Therefore, the sodium nanobelt should carry negative charges. Figure 2 shows the variation of the zeta potential of the sodium titanate nanobelt with pH in aqueous dispersion. It can be seen from Fig. 2 that the titanate nanobelt carries negative charges from pH 4 to pH 8. The zeta potential became more negative with the increase of pH from 4 to 6, while it did not change significantly from pH 6 to pH 8.

Flocculation of Kaolin Clay by CPAM / Sodium Titanate Nanobelt

The flocculation of kaolin clay induced by the CPAM/sodium titanate nanobelt system was investigated and compared with those induced separately by sodium titanate nanobelt and by CPAM. Figure 3 shows the relative turbidity of kaolin clay suspension as a function of sodium titanate nanobelt dosage at different CPAM addition levels. The relative turbidity was calculated by the reading of flocculated clay suspension voltage V_f recorded 90 s after titanate nanobelt or CPAM addition, as the clay flocculation was induced by CPAM/titanate nanobelt or CPAM alone, respectively. The percentages of CPAM and sodium titanate nanobelt in Fig. 3 are mass fractions based on kaolin clay. Lower relative turbidity implies better flocculation. Apparently, the negatively charged sodium titanate nanobelt can induce a weak flocculation of the same negatively charged kaolin clay even at a dosage as low as 0.025% without CPAM, which is just like anionic high molecular mass polyacrylamide (Liu et al. 2003), suggesting the formation of polymer bridges between clay particles.

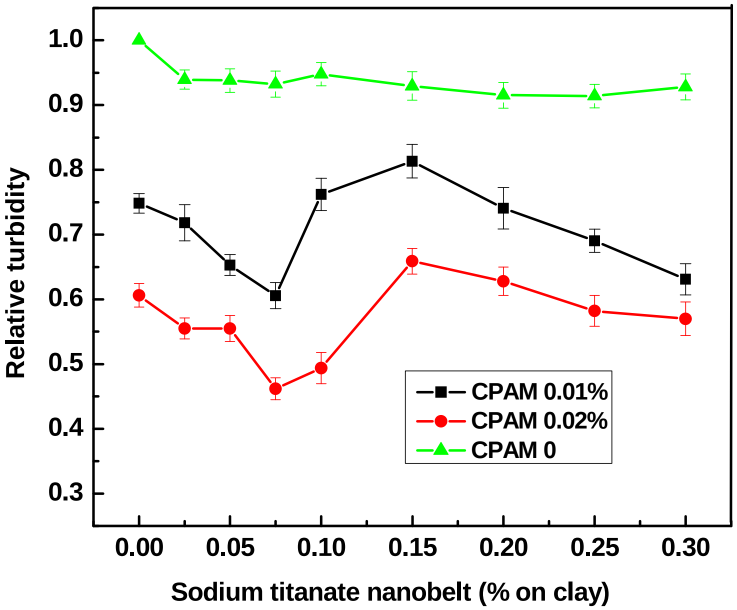


Fig. 3. Effect of sodium titanate nanobelt dosage on relative turbidity of clay suspension

When the CPAM was added to constitute a dual retention system with the negatively charged nanobelt, the flocculation of the clay was greatly improved. A higher CPAM addition level induced a higher level of clay flocculation either alone or together with the titanate nanobelt. The relative turbidities of the clay suspensions that were flocculated by the CPAM/sodium titanate nanobelt system at the two CPAM addition levels of 0.01% and 0.02% initially declined with the increase of the titanate nanobelt dosage from 0 to 0.075%, then started to increase as the nanobelt dosage was increased from 0.075% to 0.15%. After that, the relative turbidities declined again with the further increase of the nanobelt dosage. Based on turbidity, the maximum flocculation of the clay appeared at the nanobelt dosage of 0.075% as the CPAM addition levels were fixed at 0.01% and 0.02% while the nanobelt dosage was less than 0.3%. The minimum flocculation occurred at the nanobelt dosage of 0.15%, at which the relative turbidities were even larger than those of clay suspension which is flocculated just by CPAM.

In the initial decline of the relative turbidity of the clay suspension with the increase of the nanobelt, the bridging effect of the nanobelt among the clay particles with adsorbed CPAM must have played an important role, since the optimal dosage of the nanobelt to reach the maximum flocculation was much less than the conventional charge level of microparticles. The second decline with the nanobelt is tentatively ascribed to the charge neutralization of the nanobelt with chains of CPAM adsorbed on clay. According to the research of Asselman and Garnier (2000 b), and Cho et al. (2009), when CPAM-induced clay flocs were broken down by shear force, the redistribution of CPAM may create fresh CPAM-covered surfaces (which would be surfaces covered with extended CPAM chains with tails and loops able to form bridges), depleted CPAM-covered surfaces (depleted CPAM would be chains whose conformation has changed towards a flat conformation or damaged chains), and bare surfaces. At lower addition levels, titanate nanobelt interacted with the CPAM chains adsorbed on clay particles, especially with the chains with extended conformation. The clay particles with extended chains may also interact with bare clay particles. Both induce the reflocculation of clay, resulting in a decrease in turbidity. As the addition level of titanate nanobelt was higher than 0.075%, most of the fresh CPAM-covered surfaces were gradually covered by the nanobelt, causing the deterioration of clay flocculation. The relative turbidity was reduced and achieved the maximum value at addition level of 0.15%. Since clay particles covered by a depleted CPAM layer do not flocculate with the other clay particles (Asselman and Garnier 2000 b), the relative turbidity was even larger than that flocculated by CPAM alone. As in the case of montmorillonite platelet (Asselman and Garnier 2000 a), titanate nanobelt bears high charge density. The further increase of titanate nanobelt led to the adsorption of nanobelt onto depleted CPAM layers, triggering the clay flocculation by means of its high charge. Once again, the relative turbidity started to decline with nanobelt addition.

Figure 4 shows the effect of CPAM dosage on the flocculation of kaolin clay at the three titanate nanobelt dosages of zero, 0.075%, and 0.15%, respectively. The relative turbidity was calculated by the reading of final clay suspension voltage V_f recorded 30 s after final retention component addition. It is clear that without the titanate nanobelt, CPAM can induce a strong flocculation of the kaolin, clay as reported by Krogerus (1993). With the increase of CPAM dosage, the relative turbidity initially decreased sharply. After the CPAM dosage reached 0.015%, the relative turbidity remained at a constant level. Adding 0.075% of the sodium titanate nanobelt as the second retention component further reduced the relative turbidity as the CPAM dosage exceeded 0.005%, which is same as shown in Fig. 3. Moreover, the induction of clay flocculation by the CPAM/sodium titanate nanobelt system was continuously enhanced with the increase of the CPAM dosage even when it was larger than 0.015%, suggesting the inclusion of microparticle-based charge neutralization mechanism in the reflocculation process by the titanate nanobelt (Wågberg et al. 1996). However, adding 0.15% of the titanate nanobelt increased the relative turbidity of the clay suspension, which also coincides with the results shown in Fig. 3.

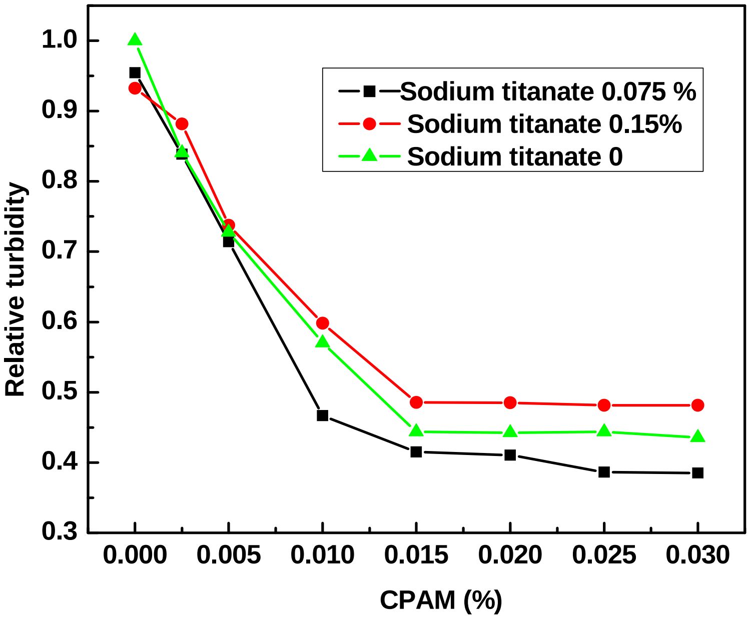


Fig. 4. Effect of CPAM dosage on relative turbidity of clay suspension

Effect of pH on Clay Flocculation

Since pH influences the zeta potential of the titanate nanobelt and kaolin clay, it may affect the charge neutralization and interactions between adsorbed CPAM and the nanobelt as well as the adsorption of CPAM on clay particles. Therefore, the influence of pH on the clay flocculation induced by CPAM/sodium titanate nanobelt system was investigated. Figure 5 shows the variation of the relative turbidity of clay suspension with pH at two nanobelt addition levels of 0.075% and 0.15%, at which the maximum and minimum clay flocculation were obtained, respectively, within the range of the titanate nanobelt addition levels used in this research. The CPAM addition level was 0.02%. The reading of final clay suspension voltage V_f was recorded 30 s after nanobelt addition.

As shown in Fig. 5, the relative turbidities of the clay suspensions at the titanate nanobelt addition levels of 0.075% and 0.15% declined remarkably with the increase of pH when the pH was lower than 6, while it decreased slowly with pH as the pH was higher than 6. Comparing Fig. 5 with Fig. 2, it is not difficult to find that the variation tendency of the relative turbidity of the clay suspension with pH followed the same pattern with that of the zeta potential of the nanobelt with pH. This suggests that the attraction force between the nanobelt and pre-adsorbed CPAM plays a key role in the flocculation of clay even when CPAM-induced clay flocculation is worsened by the unsuitable amount of titanate nanobelt.

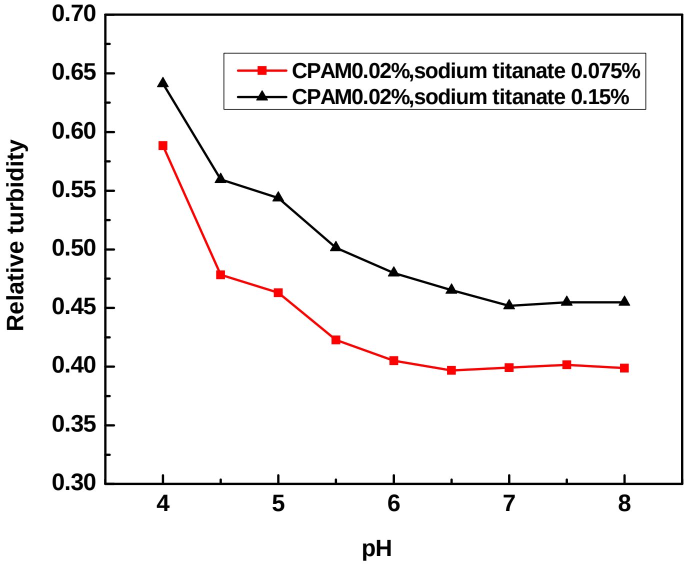


Fig. 5. Influence of pH on relative turbidity of clay suspension

Effect of Shear after CPAM Addition on Clay Flocculation

In a typical microparticle retention process, hydrodynamic shear is generally applied to the paper furnish that is initially flocculated by cationic polymer before the addition of anionic microparticle. The hydrodynamic shear breaks down the fiber-to-fiber flocs to provide good formation and drainage (Hubbe 2005), and to provide more adsorption sites for microparticle bridging (Swerin et al. 1993). Here, we use the stirring of the DDJ propeller to imitate the shear in the papermaking process. Figure 6 shows the effect of stirring rate before the addition of titanate nanobelt on the relative turbidity of clay suspension at two titanate nanobelt addition levels of 0.075% and 0.15%. The addition level of CPAM was fixed at 0.01%. The stirring time was kept at 30s. The reading V_f was recorded 30 s after nanobelt addition.

It is evident from Fig. 6 that the relative turbidity of the clay suspension was initially decreased as the stirring rate was increased, and then it started to increase with further increase of the stirring rate. The greatest flocculation of the clay suspension at 0.075% and 0.15% titanate nanobelt were obtained at the stirring rates of 1500 rpm and 1250 rpm, respectively. The results suggest that a moderate increase in stirring rate increased the collision rate and therefore enhanced the reflocculation rate, and furthermore it increased breakage kinetics in such way that the amount of adsorbed CPAM chains with extended conformation able to interact with nanobelts increased. As a result the relative turbidity decreased with moderate increases of stirring rate. However, too high a shear level damaged CPAM chains, increasing the degree of depletion of CPAM-covered surface and reducing the reflocculation ability, resulting in the reduction of clay flocculation at the end of process. At the nanobelt addition level of 0.075%, the maximum flocculation was attained at a wider shear level interval since the saturation of the extended adsorbed CPAM chains (i.e. the coverage of all the extended CPAM chains by the nanobelts, causing a decrease in reflocculation ability) was less probable.

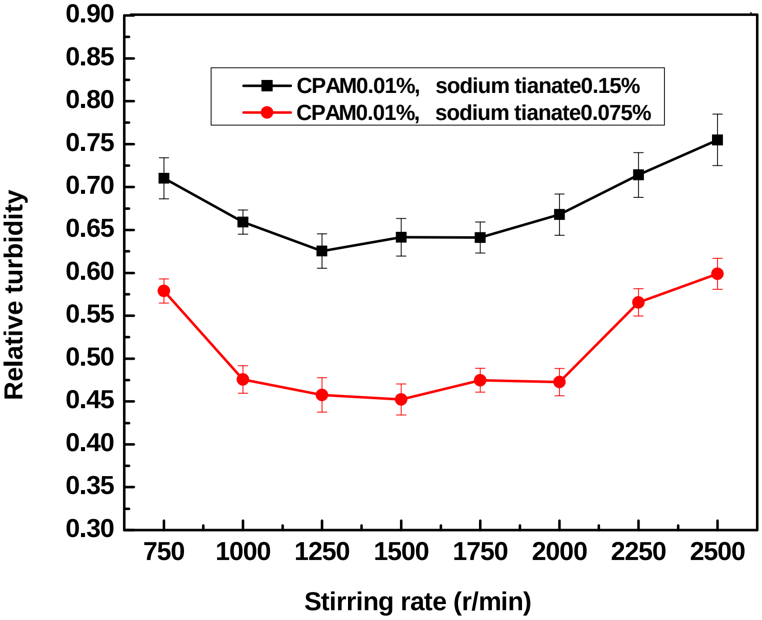


Fig. 6. Influence of stirring rate after CPAM addition on relative turbidity of clay suspension

Shear Resistance of Clay Flocculation

Microparticle retention systems generally induce flocculation with stronger shear resistance than conventional bridging polymers due to the bridge formation of microparticles between adsorbed cationic polymers (Swerin et al.1996; Clémencon and Gerli 1999). It is of interest to know that whether the sodium titanate nanobelt as a microparticle with extremely large aspect ratio can induce the clay flocculation with a high shear resistance when it is employed to constitute a microparticle retention system with CPAM. The shear resistance of the CPAM/titanate nanobelt system induced clay flocculation was judged by the variation of final clay flocculation with the stirring rate after the titanate nanobelt was added at a fixed stirring time of 30 s. Figure 7 shows the shear resistances of the CPAM/titanate nanobelt system induced clay flocculation at two titanate nanobelt addition levels of 0.075% and 0.15%. The addition level of CPAM was fixed at 0.01%. The stirring rate for imitating the high shear after CPAM addition was 1500 rpm. The relative turbidity was calculated by the reading V_f after 30 s nanobelt addition.

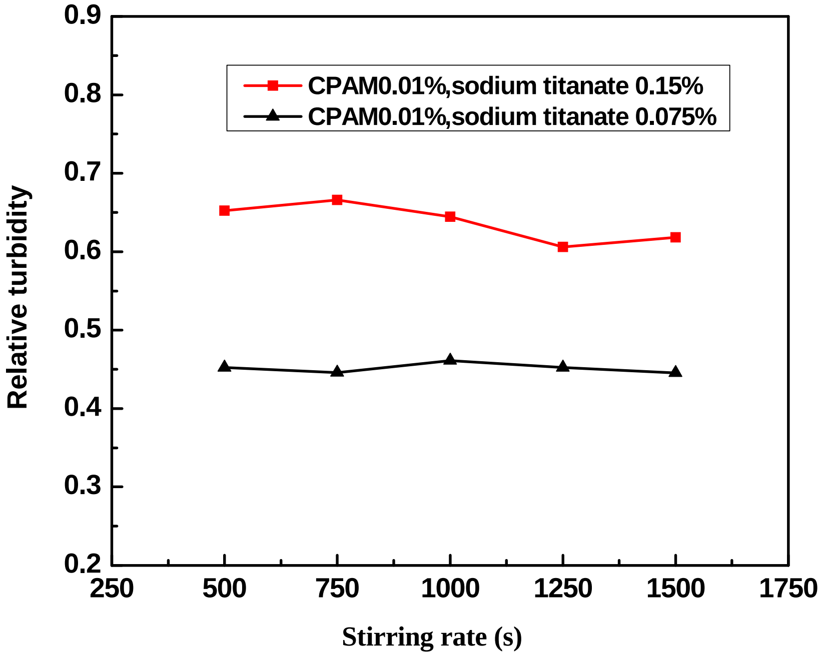


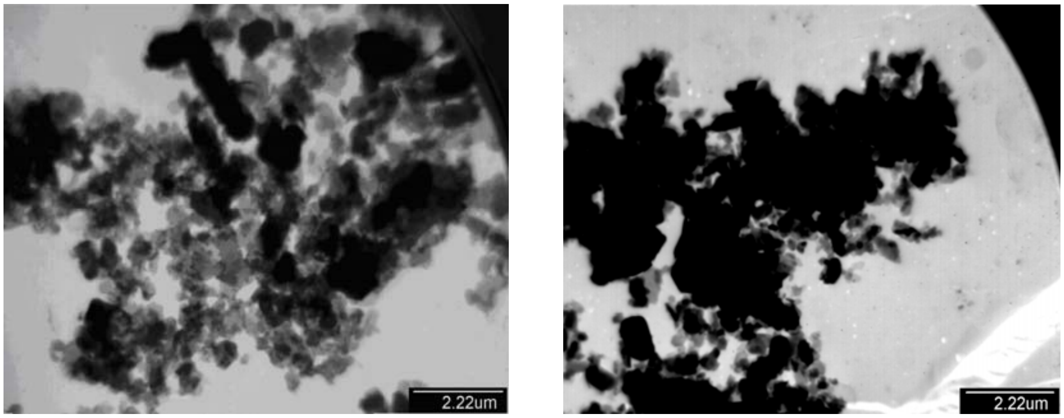
Fig. 7. Influence of stirring rate after titanate nanobelt addition on relative turbidity of clay suspension

Apparently, the relative turbidity of the clay suspension flocculated by 0.01% CPAM and 0.075% titanate nanobelt was almost constant as the final stirring rate was increased from 500 rpm to 1500 rpm, while that of a suspension flocculated by 0.01% CPAM and 0.15% titanate nanobelt even showed an observable reduction. Thus, it can be concluded that the clay flocculation induced by CPAM/sodium titanate microparticle system has a high shear resistance. This may be attributed to the large bridging capacity of titanate nanobelt among clay particles covered by CPAM, and strong interaction with the CPAM.

Morphologies of Clay Flocs

The morphologies of the clay flocs induced by bridging polymer CPAM and CPAM/titanate nanobelt system were observed with a transmission electron microscope (TEM). Figure 8 shows the TEM image of clay flocs (a) induced by 0.02% CPAM and (b) induced by 0.02% CPAM/0.075% nanobelt.

It can be seen from Fig. 8 that the clay flocs induced by CPAM alone were large flocs consisting of loosely connected clay particles, while the clay flocs induced by the CPAM/titanate microparticle system were denser, implying that sodium titanate nanobelt can also compress the CPAM-induced clay flocs through charge neutralization mechanism when it bridges through CPAM that adsorbed on clay particles.



(a) Induced by CPAM (b) Induced by CPAM/titanate nanobelt

Fig. 8. TEM image of clay flocs

CONCLUSIONS

1. Sodium titanate nanobelt with a typical width of 20 to 200 nm and a length of up to several hundreds micrometers was prepared. It carries negative charges and has an increasingly negative zeta potential at higher pHs.
2. Sodium titanate nanobelt gives its largest synergistic flocculation effect with CPAM at a very low dosage, and has a better performance under neutral and weak alkaline conditions than under acidic conditions.
3. A suitably higher shear level is helpful for the reflocculation of clay by sodium titanate nanobelt. The clay flocculation induced by CPAM/titanate nanobelt yields a high shear resistance and denser flocs.

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