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Colloids and Surfaces A: Physicochem. Eng. Aspects 297 (2007) 79–83

COLLOIDS AND SURFACES A

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The effect of calcium ions on the efficiency of polyethylene oxide–cofactor retention aid systems

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Received 5 July 2006; received in revised form 7 September 2006; accepted 9 October 2006
Available online 13 October 2006

Abstract

Polyethylene oxide (PEO)–cofactor retention aid systems are used in papermaking to improve fines retention in mechanical grade papers and in the control of pitch in process waters. Mill experience has shown that these retention aid systems work less well in furnishes containing a large amount of deinked pulps. Various dissolved and colloidal substances could possibly interfere with the PEO–cofactor complex and make it less effective. One of the compounds that could negatively affect the PEO–cofactor retention aid system is calcium, since deinked pulps can contain calcium carbonate fillers, which dissolve at neutral pH, thus increasing the calcium ion concentration in the whitewater. In this study the effects of calcium ions on fines deposition on fibers and on fines flocculation are examined. It is found that calcium ions can form colloidal-like complexes with the cofactor, which decrease the flocculation efficiency of PEO. The effects can be minimized by adding the cofactor just before the PEO addition.

Keywords: Fines flocculation; Deposition; Pulp fibers; Polyethylene oxide; Calcium ions; Cofactors; Retention aids

1. Introduction

The use of recycled paper in paper making may have undesirable side effects. Deinked pulps contain dissolved and colloidal substances (DCS), which might interfere with wet-end papermaking chemicals. Also, progress towards mill closure leads to a higher amount of suspended solids in the mill water [1–7]. Mills usually remove suspended solids from the whitewater by using filtration and clarification techniques [8]. However, even with the use of polymer based cationic fixation agents, DCS are difficult to remove from the whitewater [9]. A neutral polymer such as polyethylene oxide (PEO) is expected to be less affected by anionic compounds in the DCS than a cationic polyelectrolyte [10]. Therefore, the recycling of whitewater from recycled pulps is not expected to have such a detrimental effect on the efficiency with which PEO retains fines.

However, mill experience shows that the efficiency of PEO diminishes when the content of deinked pulp in a furnish is too large. The decrease in PEO efficiency has also been seen in dynamic drainage jar experiments in which residual deinking chemicals were introduced [11]. Although the problem can be solved with the addition of bentonite [12–15], it would be of interest to know what causes the problem. Model experiments on fines deposition on fibers have shown that various compounds did not affect the deposition efficiency and thus cannot account for the detrimental effect of DCS in deinked pulps [16]. Compounds that were tested and found to have no effect are: oleates (a common fatty acid), silicates and DTPA (a chelating agent). Compounds that affected the PEO efficiency negatively were all of colloidal nature: oleate soaps, rosin particles (abietic acid), clay and fines. Their effect appeared to be related to surface area: PEO adsorption on colloidal material reduces the amount of PEO available for polymer bridging between fines and fibers. On a paper machine, PEO is usually added very close to the headbox, and little PEO adsorption on colloidal particles is expected, since the time scale of polymer adsorption on fibers is much shorter than that of PEO adsorption on colloids [17]. Thus, also colloidal

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doi:10.1016/j.colsurfa.2006.10.026

material is unlikely to have a large effect on the fines retention. Another candidate for interfering with PEO is calcium. In studying the performance of various PEO–cofactor systems, it was found that a high ionic strength of the whitewater was detrimental to the PEO flocculation efficiency [18]. Calcium ions are present at high concentrations in whitewater from deinked pulp containing calcium carbonate fillers. Their effects on a PEO–cofactor retention aid system are the topic of this paper.

2. Experimental set-up

Two types of experiments were performed to measure the PEO efficiency: fines deposition on fibers and fines flocculation. Each type of experiment was performed in a beaker, to which water and fibers and/or fines were added. The suspension was stirred by a paddle, rotating at 200 rpm. Some of the suspension was circulated as a bypass stream flowing from the beaker through a detector back to the beaker. In case fibers were used, a 200 mesh screen prevented the fibers to enter the bypass. A brush mounted on a stirring paddle was used to prevent the accumulation of fibers on the screen. No screen was used when the vessel contained only fines. As a detector we used either a UV–vis spectrophotometer (for fines deposition experiments), or a photometric dispersion analyzer (PDA) (for fines flocculation experiments). For fines deposition experiments we used a thermomechanical pulp (TMP) (Donahue, Matane), whereas for the fines flocculation experiments we used fines separated from a mixture of pulps of an actual mill (Papiers Masson, Masson-Angers, Quebec). The sizes of fines vary from a few to about 75 μm and the shapes vary from chunky to fibrillar.

As a retention aid system we used PEO (Floc 999) of molecular weight 6 million and cofactor (Interac 1323), a mixture of modified phenolic resins and sulfonated kraft lignin, the structure of which is discussed elsewhere [19] and in a study comparing various cofactors [18] was found to be the best performing in retaining fines and clay in mechanical furnishes. Both the PEO and the cofactor were provided by EQUIP Inc. (now Kemira) PEO was dissolved for 24 h prior to use and a stock solution of 0.1% was prepared. A stock solution of the cofactor of 0.1% was prepared as well. All experiments were performed at room temperature.

3. Results and discussion

3.1. Fines deposition on fibers

In a typical experiment the transmittance or absorbance of the suspension passing through the spectrophotometer was measured. Since fibers could not pass the screen, the suspension contains fines only. First the cofactor was added, followed 2 min later by the addition of PEO. A typical result is shown in Fig. 1. It can be seen that the cofactor has no effect, but the PEO causes a sudden drastic drop in absorbance, followed by a slow change back towards the initial absorbance. Also, a little spike is present prior to the sudden drop. The drop in absorbance is due to a lower concentration of fines in the bypass stream, caused by fines deposition on fibers. Probably most fines deposit as aggregates, since for the low shear conditions used here, fines are already in a flocculated state, even in the absence of retention aids [20]. Retention aids increase the level of flocculation. Extensive fines flocculation results in fines flocs too large to pass through the holes in the screen [20], but this is unlikely to happen in the early stages of flocculation. Fines deposition on fibers has also been studied with cationic polyacrylamide as a retention aid [21]. It was shown that the initial deposition process is fast and approximately follows Smoluchowski kinetics. In our experiments shear conditions are similar and fines deposition occurs equally fast.

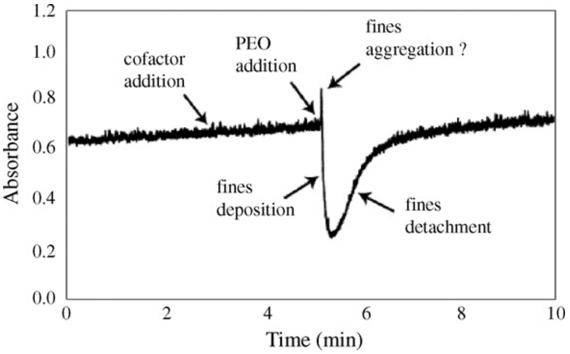

Fig. 1. Absorbance vs. time during fines deposition on fibers. [TMP] = 0.2%, [PEO] = 0.5 mg/g, [cofactor] = 2 mg/g.

The initial spike, which was seen in all experiments in which fines deposition occurred, is most likely due to fines flocculation, which occurs on the same time scale. According to Mie light scattering theory, the amount of light scattered, and thus the observed absorbance, can go up or down with flocculation, depending on particle size (and wavelength of light). For fines the same could apply, although here the situation is complicated by a large polydispersity in size and shape. The increase in absorbance following the rapid drop after PEO addition is due to fines detachment. For the PEO system used here, the most likely cause of this is the flattening of PEO on the fiber and fines surfaces. Flat PEO adsorption layers are ineffective in polymer bridging, since the polymer layer thickness is less than the distance over which electrostatic repulsion forces act. The same flattening has been observed on clay particles [22].

Fig. 2 shows the effect of whitewater on the fines deposition on fibers. The whitewater, obtained from deinked pulp, was filtered through a 0.2 μm millipore filter, to eliminate most of the colloidal material. It can be seen that the whitewater reduces the

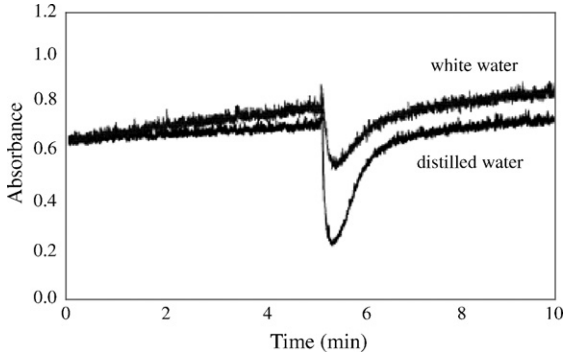

Fig. 2. Comparison of fines deposition on fibers in distilled and whitewater.