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Flocculation of starch-coated solidified emulsion droplets and calcium carbonate particles

Agatha Poraj-Kozminski [a], Reghan J. Hill [a], Theo G.M. van de Ven [b,*]

[a] *Department of Chemical Engineering, Pulp and Paper Research Centre, McGill University, Montreal, Quebec H3A 2A7, Canada*
[b] *Department of Chemistry, Pulp and Paper Research Centre, McGill University, Montreal, Quebec H3A 2A7, Canada*

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Abstract

In papermaking, many colloidal particles are added to a pulp fiber suspension to improve paper properties. Given the right conditions, these different colloids can interact and flocculate. Examples of papermaking colloids are fillers and internal sizing agents, which improve opacity and hydrophobicity of paper, respectively. Internal sizing agents (added at the wet end of a paper machine) are commonly solidified emulsion droplets, stabilized by cationic starch and other stabilizers. We studied the interaction of a common internal sizing agent, alkyl ketene dimer (AKD), with calcium carbonate fillers. AKD is a liquid above 50–65 °C (depending on alkyl chain length), which can be emulsified above its melting point in the presence of a stabilizer, resulting, after cooling, in solid colloidal particles close to 1 μm in size. We investigated the interaction of AKD particles, stabilized by cationic starch, with precipitated calcium carbonate (PCC) particles. Pure PCC particles are positively charged, but they become negative in process waters. Flocculation experiments with positively charged AKD and negatively charged PCC were performed using a photometric dispersion analyzer. Instead of the expected heteroflocculation between AKD and PCC, we observed PCC homoflocculation and AKD homoflocculation, results confirmed by SEM. The results are explained by the transfer of starch from AKD to PCC, resulting in PCC flocculation by starch and AKD destabilization due to depletion of the stabilizer.

Keywords: Homoflocculation; Heteroflocculation; Internal sizing agents; Alkyl ketene dimer; Fillers; Precipitated calcium carbonate; Cationic starch; Starch transfer

1. Introduction

Alkyl ketene dimer (AKD) and precipitated calcium carbonate (PCC) interactions in wet-end papermaking have received the attention of various researchers. It is found that PCC causes AKD hydrolysis, leading to a loss of sizing and also causing size reversion after drying [1–3]. The chemical interactions that occur at the wet end of a paper machine depend on the order in which they are added, as well as their residence time in the papermaking line, prior to the formation of paper. Typically, PCC is added before AKD [4]. Thus, AKD is most likely to interact with the PCC–fiber suspension. An additional ingredient is a retention aid, such as cationic polyacrylamide (cPAM), required to retain the PCC particles in paper, and usually added last. There are several theories to suggest what will occur upon AKD addition to a papermaking suspension [5–8]. The retention of AKD on a paper machine is rather low (typically around 40%), which implies that a large fraction is returned to the paper machine via the short circulation loop. In this loop AKD can interact with other nonretained particles, such as PCC. AKD interactions with PCC may affect the retention in a subsequent pass through the machine, as it could lead to AKD–PCC heteroflocculation, or one component could induce the flocculation of the other. These aggregates will be better retained in a forming sheet than individual particles, but may affect paper properties differently. The objective of this study is to better understand the interactions between AKD and PCC, which might lead to more efficient use of these additives in papermaking.

* Corresponding author.
E-mail address: theo.vandeven@mcgill.ca (T.G.M. van de Ven).

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2. Emulsification of AKD stabilized with cationic starch

In most large-scale AKD emulsion preparations, besides starch, additional components, such as surfactants, polymers, stabilizers, and alcohols, are added. However, details of commercial formulations are usually not disclosed. Therefore, it is difficult to know if interactions of an emulsion are due to AKD or other chemicals within the emulsion. To solve this problem, we developed a method for creating a simple but stable AKD emulsion in our laboratory. The emulsion consisted of only AKD and a stabilizer (cationic starch). AKD is a waxy ester with two fatty chains, typically ranging in length from 14 to 18 carbon atoms, joined by a lactone group. It is extremely hydrophobic and insoluble in water, and thus it needs to be emulsified. Upon addition to fibers, the AKD may react with cellulose to form a β-ester covalent bond. However, this is a slow reaction, and sizing only begins in the drying section of a paper machine, continuing throughout the drying and curing process for about a week afterward [9].

For AKD to remain in emulsion, a stabilizer must be added to prevent the AKD droplets from coalescing during emulsification. Since AKD has a melting temperature of about 50 °C (depending on chain length), the emulsification is done at a higher temperature so that the AKD is in its molten phase. Immediately after emulsification, the solution must be quenched below room temperature for the AKD to revert to a more stable solid. Various methods for AKD emulsification were researched [10,11].

Alkyl ketene dimer (from Raisio Roe Lee) was obtained in pellet form. A 10-g sample was melted to 60 °C in preparation for sonication. A cationic (quaternary amine-substituted) starch, CATO-237, was received from National Starch in powder form. According to the manufacturer, this chemical has an N_2 % of 0.36–0.44. This value can be converted to a degree of substitution of 0.043–0.053%. The starch was dispersed in deionized water, obtaining solutions of 1%, 2%, or 4% starch. The starch was cooked for 40 min in a 93 °C water bath, as suggested by the manufacturer. This hot starch solution was added to a 100-ml beaker containing the melted AKD.

A sonicator (Vibracell VCF-1500, Sonics & Materials, Inc.) was used for all emulsifications. This apparatus operates at a frequency of 20 kHz. The tip of the sonicator, which is 1 inch in diameter and composed of a titanium alloy, was inserted an inch into the liquid. The sample was then sonicated for three cycles of 3 min each to ensure proper homogenization. Following sonication, the solution was quickly quenched in a beaker containing 100 ml cold deionized water. Hydrochloric acid (1 M) was added to reduce the pH to approximately 4. Samples were kept refrigerated until further testing.

3. Emulsion analysis

3.1. Particle size

A Malvern Mastersizer2000 (Malvern Instruments, UK) was used to measure the AKD particle-size distribution. This technology relies on static light scattering, using the Mie theory

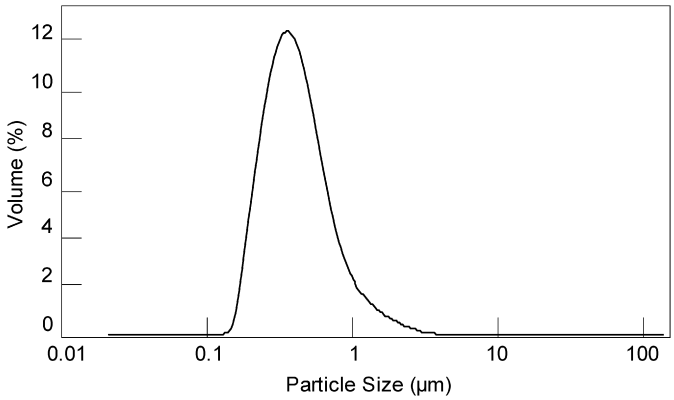

Fig. 1. Particle-size distribution of AKD emulsion (measured with Malvern Mastersizer).

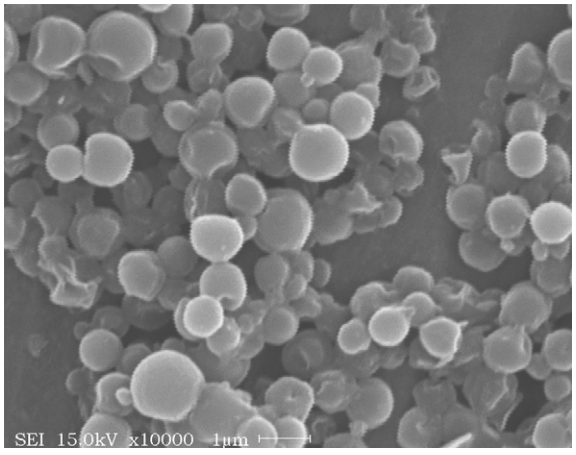

Fig. 2. SEM image of AKD emulsion at 10,000× magnification (bar scale indicates 1 μm).

to determine the particle-size distribution. The intensity of the scattered light is measured by multiple photosensitive detectors. The refractive index of AKD was taken as 1.485 (a typical value of a wax) in water with a refractive index of 1.33. Results of a typical AKD emulsion are shown in Fig. 1. The particle diameter ranges from approximately 0.2–4 μm. The calculated median value (by % volume) of the samples was used as the average particle diameter.

Periodical testing revealed that the emulsion was stable in the refrigerator for at least 2 wk. After approximately 4 wk, the two phases (waxy AKD and water) began to separate. Since AKD has a lower density than water, it begins to cream [10]. AKD stabilized with starch with the highest DS was found to be most stable.

In addition to particle size analysis, photographs were taken by scanning electron microscopy (SEM). Samples were prepared by diluting the emulsion and applying a drop onto an SEM pin. When the droplet had dried, it was sputter-coated with a gold film. Pictures were taken at 5000× and 10,000× magnification. As seen in Fig. 2, these photographs reveal a rather homogeneous sampling of AKD droplets that are just under a micrometer in diameter. Note that although most particles are similar in size, there also appear several outlying drops that have likely coalesced. Interestingly, the particles are not per-