

Aggregation Process and Mechanism of Pitch Deposits with Ca²⁺ in Papermaking White Water

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The lipophilic colloidal substances (CS) in papermaking white water mainly originate from sizing agents applied during paper manufacturing operations and wood extractives, such as resin acids and fatty acids. In this study, the aqueous dispersions of sodium resinate and sodium stearate were used to simulate the colloidal substances concentrated in white water. The aggregation process and mechanism of pitch deposits developed from soluble colloidal particles were investigated by the determination of turbidity and zeta potential of colloidal substances simulacra dispersions as a function of Ca²⁺ concentration, as well as through morphological observation, structural characterization, and contact angle measurement of calcium-induced pitch deposits. The results showed that the micelles with hydrophilic groups extending in the water could be formed when the colloidal substances accumulated to a certain concentration. The Ca²⁺ can exchange Na⁺ of colloidal substance micelles, and hydrophobic pitch deposits can then be produced by either particle-particle collision or “layer by layer” adsorption with addition of Ca²⁺, or by both of the mechanisms mentioned above. The complete destabilization of the colloidal substance simulacra occurred when the Ca²⁺ concentration reached 5 mmol/L. The initial contact angles of water on the surfaces of calcium resinate and calcium stearate discs were 90.2° and 96.0°, respectively.

Keywords: Colloidal substances; Ca²⁺; Pitch deposits; Aggregation process and mechanism

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INTRODUCTION

Within the pulp and paper industry, the recycling of white water to reduce fresh water consumption and effluent discharge leads to an accumulation of dissolved and colloidal substances (DCS). Such accumulated DCS can interact with electrolytes, especially Ca²⁺, thus adversely affecting papermaking efficiency or product quality. The negatively charged dissolved and colloidal substances in papermaking white water are also called “anionic trash”, because most components of DCS commonly contain carboxylic acid groups that will dissociate to their negatively charged carboxylate forms (Hubbe *et al.* 2012). The complex components of DCS mainly originate from wood extractives and chemical additives consumed during paper manufacturing operations (Wang *et al.* 2013a; Chen *et al.* 2014b, 2015b). The DCS are generally stably dispersed in the pulp suspension or white water, while easily gathering together and forming non-ionic and sticky interfering substances when operating conditions change or react with multivalent metal ions (Allen 1979a,b; McLean *et al.* 2005). Due to the increasing use of CaCO₃ as fillers and the use of hard water, Ca²⁺ is the most common multivalent metal ion accumulated in the white water circuit (Lee *et al.* 2012a; Yuan *et al.* 2012). Charge-neutralized pitch deposits will be

produced when colloidal substances (CS), such as resin acids and fatty acids, react with Ca^{2+} (Nurmi *et al.* 2004; Wang *et al.* 2004; Ye *et al.* 2009b; Wei *et al.* 2014). These insoluble materials can interfere with papermaking by deteriorating the wet-end environment and degrading paper machine runnability (Francis and Ouchi 2001; Whipple and Maltesh 2002; Zhang *et al.* 2007; Yuan *et al.* 2011a; Chowdhury and Wikman *et al.* 2014).

There is a growing concern for water resources protection. Thus, the pulp and paper industry has been moving toward more intensive recycling of white water to reduce fresh water consumption and effluent discharge that leads to colloidal destabilization and pitch problems because of the accumulation of CS and inorganic electrolytes in white water. Most of the studies investigated the stability of CS under different conditions (Nylund *et al.* 2007; Lee *et al.* 2012b; Stack *et al.* 2014; Li *et al.* 2015) and the control of them (Miao *et al.* 2013; Wang *et al.* 2013b; Xiao *et al.* 2015). However, little is understood about the aggregation process and mechanism of pitch deposits developed from soluble colloidal particles. Once the soluble CS have been converted to charge-neutralized pitch deposits and have lost their electronegativity, they could not be fixed onto fibers and then removed from process water, even using fixatives with a high cationic charge density (Miao *et al.* 2013). Such a chain of events implies that problems with pitch deposits may remain as prevalent as ever. Hence, it is desirable to understand the formation characteristics and corresponding mechanism of pitch deposits in each stage of the aggregation process, so that a specific strategy can be used to control or remove them in the appropriate stage, thus solving the problems resulting from them. For example, the concentration of dissolved multivalent metal ions, such as Ca^{2+} , could be controlled within a certain range by a modified natural macromolecular substance called anionized cationic starch (ACS) (Ye *et al.* 2009a), so that the destabilization probability of CS, as well as the content of the pitch deposits can be reduced. In addition, some anionic components of CS can be fixed onto fibers and removed from the process water together with the wet sheet when using fixatives with relatively low molecular mass and high cationic charge density before CS reacts with Ca^{2+} .

According to the conclusion conducted from the previous study on the composition of white water in a fine paper of UPM (Changshu, China), the results showed that the white water contains a lot of fibers fine and fillers (such as titanium dioxide, calcium carbonate and talc, *etc.*) and the DCS mainly originated from latex, paper additives, and their ineffective products such as defoaming agent, dispersant, surface sizing agent, and brightening agent (Chen *et al.* 2015a). Furthermore, the sizing agents (alkyl ketene dimer sizing and rosin sizing) accounted for a large proportion of the DCS. Therefore, the present study used the aqueous dispersions of sodium resinate and sodium stearate to simulate sodium resinate (originated from resin acid or rosin sizing agents) and sodium fatty acids (originated from fatty acid or alkyl ketene dimer sizing agents), respectively (Chen *et al.* 2014b, 2015a,b). The aggregation process of pitch deposits was investigated by the measurement of turbidity, zeta potential, average particle size, and morphological observation of CS simulacra with a various addition of Ca^{2+} . The aggregation mechanism of pitch deposits was analyzed by characterization of their structure and hydrophobicity. The present study aims to provide a theoretical foundation for the application of pitch control, thus making it possible for the pulp and paper industry to reduce fresh water consumption and effluent discharge by more intensive recycling of white water, and to ultimately realize clean production.

EXPERIMENTAL

Materials

The rosin acid was supplied by Fengkai Forest Chemical, Guangdong, China. The acid value was 165.79 mg/g, and the softening point was 80.50 °C. The stearic acid (Lingfeng, Shanghai, China) was of an analytical reagent grade, the acid value was 196.09 mg/g, and the melting point was 80.50 °C. The hydrochloric acid, sodium hydroxide, and calcium chloride were all of analytical reagent grade.

The aqueous dispersions of sodium resinate and sodium stearate were prepared by dissolving 0.400 g of rosin or stearic acid in 1 L of distilled water containing the given amounts of NaOH in a round flask at certain temperatures (sodium resinate: 85 °C, sodium stearate: 75 °C). Then, the dispersions were stirred at 250 rpm for 4 h, such that the final dispersions were 0.4 g/L concentration. Yuan *et al.* (2011b) previously reported this method.

Methods

Stability experiments

The CaCl₂ was dissolved in distilled water as stock solutions with various concentrations.

For each test, a given amount of distilled water was added into 200 mL of dispersions of sodium resinate or sodium stearate, and the pH of the resultants was adjusted to 7.5 by adding minimal quantities of NaOH/HCl. Then, constant volumes of CaCl₂ solutions with various concentrations were added to the above dispersions, such that all the concentrations of final dispersions of CS simulacra with a total volume of 400 mL were the same as 0.2 g/L. The final dispersions of CS simulacra were then put into a constant temperature shaker bath (SHA-C, Guohua, Changzhou, China) at 45 °C and agitated at 250 rpm for 1 h. After the agitation, partial dispersions were removed and the zeta potential was measured immediately with a Zetasizer Nano ZS instrument (Malvern, UK). Another part of the dispersions were removed and centrifuged at 3000 rpm for 20 min, then the resulting upper supernatants were pipetted off and the turbidity (considered as residual turbidity) was measured with a turbidimeter (2100P, Hach, Colorado Springs, CO, USA) in Nephelometric Turbidity Units (NTU).

Observation of the aggregation process of pitch deposits

The volume of 20 mL dispersions of CS simulacra with various additions of Ca²⁺ after agitation that were prepared in stability experiments were used in this experiment to observe the aggregation process of pitch deposits. The turbidity was measured using a turbidimeter (2100P, Hach, Colorado Springs, CO, USA), the average particle size was determined by a laser particle size analyzer (Topsizer, OMEC, Zhuhai, China), and the aggregation morphology of CS simulacra at varying Ca²⁺ concentrations was observed with an optical microscope (U-TV1X-2 Olympus, Tokyo, Japan).

Structural characterization of CS simulacra and pitch deposits

The weight of 10 g rosin and stearic acid were vacuum-dried at 40 °C. The volume of 10 mL dispersions of sodium resinate and sodium stearate were oven-dried at 120 °C and further vacuum-dried at 40 °C. Pitch deposits were prepared as previously mentioned, and the final dispersions of CS simulacra with a Ca²⁺ concentration of 5 mM after agitation were filtrated in a Buchner funnel equipped with a microfiltration membrane with an

average pore size of 0.22 μm . The filter cakes were then collected to be vacuum-dried at 40 $^{\circ}\text{C}$, and the solid samples finally obtained were calcium resinate and calcium stearate.

The vacuum-dried solid samples, including rosin, sodium resinate, calcium resinate, stearic acid, sodium stearate, and calcium stearate, were ground to powders, and then characterized by employing an Attenuated Total internal Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) apparatus (FTIR-650, Gangdong, Tianjin, China) of pressed KBr pellets (200 mg of KBr and 3 mg of sample).

Contact angle measurements of pitch deposits

The vacuum-dried solid samples, including calcium resinate and calcium stearate, were ground to powders and then pressed into discs with a homogeneous diameter and thickness using a tablet machine (DF-4, Gangdong, Tianjin, China). A contact angle meter (JC2000D Powereach, Shanghai, China) in conjunction with measurement software (Newjc2000, Zhongchen, Shanghai, China) was used to calculate the static contact angle (CA) of distilled water on the surfaces of the above discs at room temperature.

RESULTS AND DISCUSSION

Characterization of Basic Properties of CS Simulacra

Particle size analysis of CS simulacra

It is well known that colloidal particles refer to the substances with a particle size of 1 μm to 10 μm (Chen *et al.* 2015a). The concentration of the dispersions of CS simulacra in this experiment was adjusted to 0.2 g/L, and their particle sizes at different pH values were measured. The results are shown in Fig. 1. Sodium carboxylate groups of both the sodium resinate and sodium stearate can be ionized to a carboxylate group ($-\text{COO}^-$) and Na^+ in aqueous dispersion, and the pH value affects the ionization (McLean *et al.* 2005). The protonation of CS simulacra increased with decreased pH value, and the colloidal particles collapsed into aggregation with larger size more easily due to the decreased electrostatic repulsive force. In contrast, the colloidal particles dispersed to smaller ones when the pH value increased, due to the increased negative surface charge of colloidal particles caused by dissociation of carboxylic acid groups, which led to an increase in the electrostatic repulsive force between the particles.

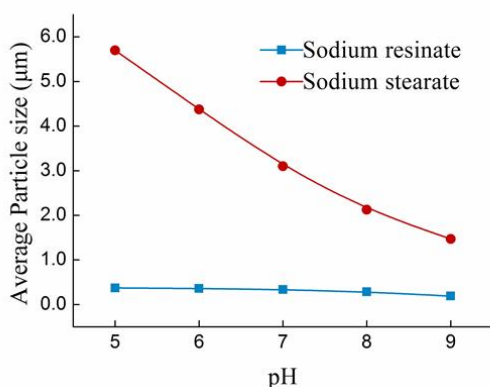


Fig. 1. Average particle size of CS simulacra at different pH value

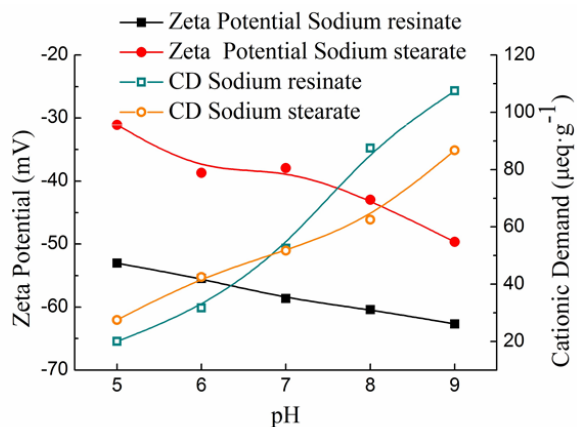


Fig. 2. Charge characteristics of CS at different pH value

As shown in Fig. 1, the average particle size of sodium resinate decreased from 0.370 μm to 0.189 μm as the pH value increased, and the particle size of sodium stearate decreased from 5.700 μm to 1.467 μm , which was still within the range of colloidal particle size.

Charge properties of CS simulacra

The zeta potential and cationic demand can be used to characterize the charge properties of CS simulacra (Nylund *et al.* 2007). The zeta potential reflects the surface charge of particles, which were closely related to the colloidal stability, while the cationic demand reflects the amount of negative charges of dissolved substance in the system. The two parameters mentioned above of CS simulacra dispersions under different pH values are shown in Fig. 2. As shown in the figure, the zeta potential and cationic demand of CS simulacra constantly increased as the pH value increased, which indicated the increased surface negative charges of CS simulacra. The amount of negative charges on the surface of sodium resinate was more than that of sodium stearate at the same pH value.

Aggregation Process and Mechanism of Pitch Deposits

To be close to the practical situation, CaCl_2 was used to simulate the Ca^{2+} (Yuan *et al.* 2011a) in the white water system. The concentration of CS simulacra was adjusted to 0.2 g/L, the pH value was 7.5, and the reaction temperature was 45 °C. The residual turbidity and zeta potential of CS simulacra dispersions as a function of Ca^{2+} concentration were measured to characterize the stability of the CS simulacra. The turbidity, average particle size, and morphological observation of CS simulacra were also detected to analyze the aggregation process and mechanism of pitch deposits developed from soluble colloidal particles with the addition of Ca^{2+} .

Effect of Ca^{2+} on the stability of the CS simulacra

The turbidity of CS dispersions has a high correlation with their concentration (Sundberg *et al.* 1993). In this experiment, the dispersions of CS simulacra were centrifuged after the reaction with Ca^{2+} , and the residual turbidity of the upper supernatant was measured to reflect the concentration of the remaining stable CS simulacra. The lower residual turbidity represented higher amounts of unstable CS simulacra. Most of the dissociated CS was dispersed as negatively charged colloids in white water, and the suspension was stable due to the repulsive force between particles. While the concentration and valency of inorganic electrolytes strongly influences the repulsive force, thus affecting the colloidal stability (Lee *et al.* 2012). The stability of CS simulacra as function of Ca^{2+} concentration is shown in Figs. 3 and 4.

As shown in Fig. 3, the residual turbidity of CS simulacra dispersions decreased dramatically with increased Ca^{2+} concentrations, and then reached plateaus. The dispersion of sodium resinate lost stability completely with residual turbidity close to 22.7 NTU at a Ca^{2+} concentration of 5 mmol/L. However, the residual turbidity of the dispersion of sodium stearate decreased tremendously at even lower Ca^{2+} concentrations, which agreed with the conclusion in a previous study that the combination between fatty acid and Ca^{2+} shows better stability than that between resin acid and Ca^{2+} (Kamijo *et al.* 2000). Furthermore, according to the DLVO theory (Lee *et al.* 2012b), the dissociated CS has an electric double layer when dispersed in a solution, and the addition of positively charged inorganic metal ions (Ca^{2+}) compressed the thickness of the diffusion layer by shoving the counter ions (Na^+) into the adsorption layer. This weakened the repulsive force between

colloidal particles and made the CS particles closer to each other and aggregated. The influence above strengthened with increased concentration of inorganic metal ions (Johnsen *et al.* 2004).

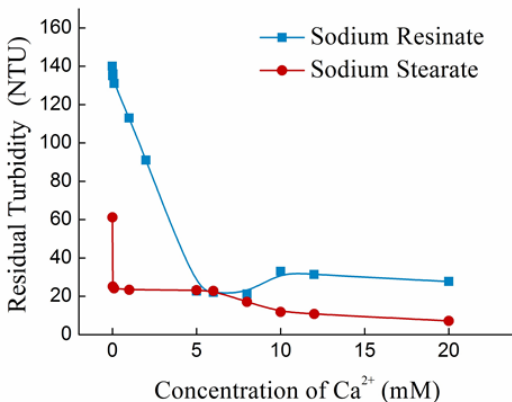


Fig. 3. Effect of Ca²⁺ on residual turbidity of CS simulacra dispersion

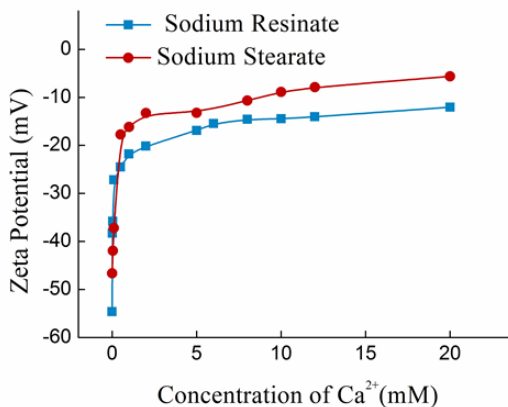


Fig. 4. Effect of Ca²⁺ on zeta potential of CS simulacra

Meanwhile, the compression of the electric double layer of colloidal particles resulted in a reduction of the absolute value of zeta potential (Brouwer 1991). In general, the transformation of zeta potential to 0 mV implies an increase in the aggregation potential of colloidal particles (Lee *et al.* 2012b). As shown in Fig. 4, the zeta potential of CS simulacra decreased remarkably with increased Ca²⁺ concentration, reached a plateau at a Ca²⁺ concentration above 5 mmol/L, and the stability of sodium resinate was better than that of sodium stearate.

Aggregation process of pitch deposits developed from soluble CS

The effect of Ca²⁺ on the turbidity of the dispersions of CS simulacra is shown in Fig. 5. The turbidity of the dispersions of CS simulacra increased as the Ca²⁺ concentration increased, and gently increased at a Ca²⁺ concentration above 5 mmol/L.

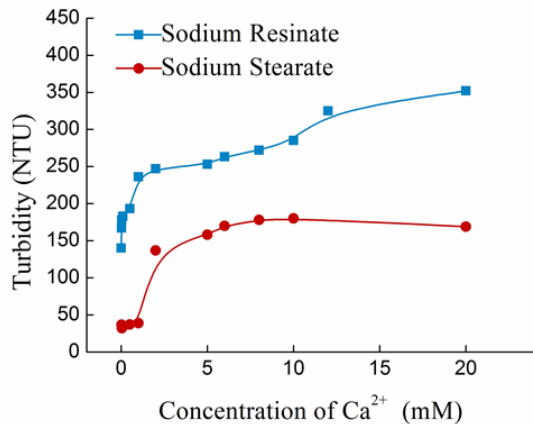


Fig. 5. Effect of Ca²⁺ on turbidity on CS simulacra dispersion

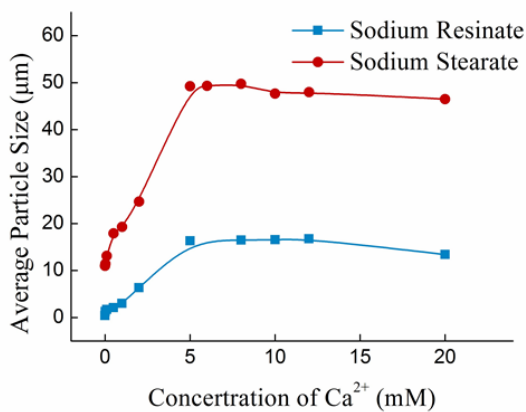


Fig. 6. Effect of Ca²⁺ on average particle of CS simulacra

The effects shown in Fig. 5 were explained by the fact that the CS simulacra existed as soluble colloidal particles when there was no Ca^{2+} in the system, so that the turbidity was low. When adding Ca^{2+} , the Na^+ of sodium resinate and sodium stearate was exchanged, resulting in insoluble calcium resinate and calcium stearate. This increased the characteristic size of the suspended matter to the range of about 0.2 to 5 μm , such that the scattering of light was high, giving an increase of the turbidity. The higher the Ca^{2+} concentration, the more pitch deposits and higher turbidity there will be (Wang *et al.* 2016). The change of turbidity tended to be gentle after a complete reaction of CS simulacra and Ca^{2+} .

The change of particle size distribution of colloidal substance under different conditions clearly reflected the aggregation of colloidal particles. The aggregation and instability of CS caused the increase of particle size. As shown in Fig. 6, the addition of Ca^{2+} caused a clear aggregation of CS simulacra. The average particle size of CS simulacra tended to be stable and slightly decreased at a Ca^{2+} concentration above 5 mmol/L. This is because that the concentration of CS simulacra in this experiment was fixed, and their reaction with Ca^{2+} was completed at a Ca^{2+} concentration of 5 mmol/L. Some loose aggregation caused by electrostatic attraction re-dispersed, and the average particle size of pitch deposits ultimately became gentle and slightly decreased.

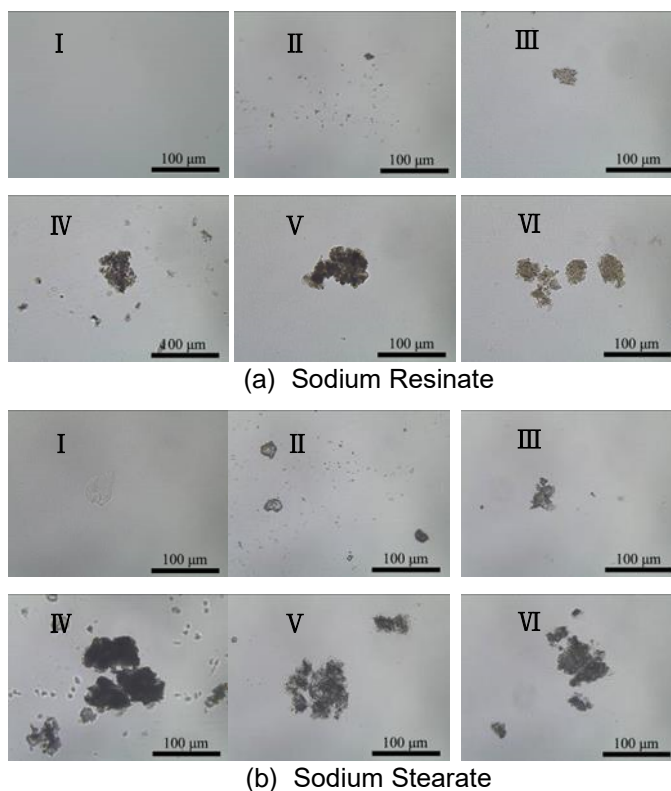


Fig. 7. Aggregation process of CS simulacra at different Ca^{2+} concentration; a) sodium resinate and b) sodium stearate; I to VI stand for Ca^{2+} concentrations of 0 mmol/L, 0.1 mmol/L, 1 mmol/L, 5 mmol/L, 12 mmol/L, and 20 mmol/L, respectively

The aggregation process of CS simulacra at different Ca^{2+} concentrations is shown in Fig. 7. As shown in Fig. 7, initially the sodium resinate and sodium stearate existed as soluble colloids in dispersion, and presented as a clear, transparent liquid by microscopic

observation. While with the constant addition of Ca^{2+} , the CS simulacra reacted with Ca^{2+} and then produced insoluble pitch deposits. As the Ca^{2+} concentration increased, the radial size of insoluble deposits gradually increased. The pitch deposits can continue to combine with other colloidal particles or pitch deposits due to its high viscosity (Clas *et al.* 1993), and further gathered to larger loose aggregations. The size of pitch deposits tended to be gentle or even slightly decreased at a Ca^{2+} concentration above 5 mmol/L.

Structure and hydrophobic characteristics of pitch deposits

Based on the results mentioned above, it can be concluded that the reaction between CS simulacra and Ca^{2+} was almost completed when the Ca^{2+} concentration increased to 5 mmol/L. Combined with the actual Ca^{2+} concentration in papermaking white water, the Ca^{2+} concentration in this experiment was adjusted to 5 mmol/L, the structure of pitch deposits (including calcium resinate and calcium stearate) were then analyzed under this condition. The structure of rosin acid, sodium resinate, stearic acid, and sodium stearate were also analyzed to compare the structural changes during the reaction process with the addition of Ca^{2+} . The IR spectra are shown in Fig. 8.

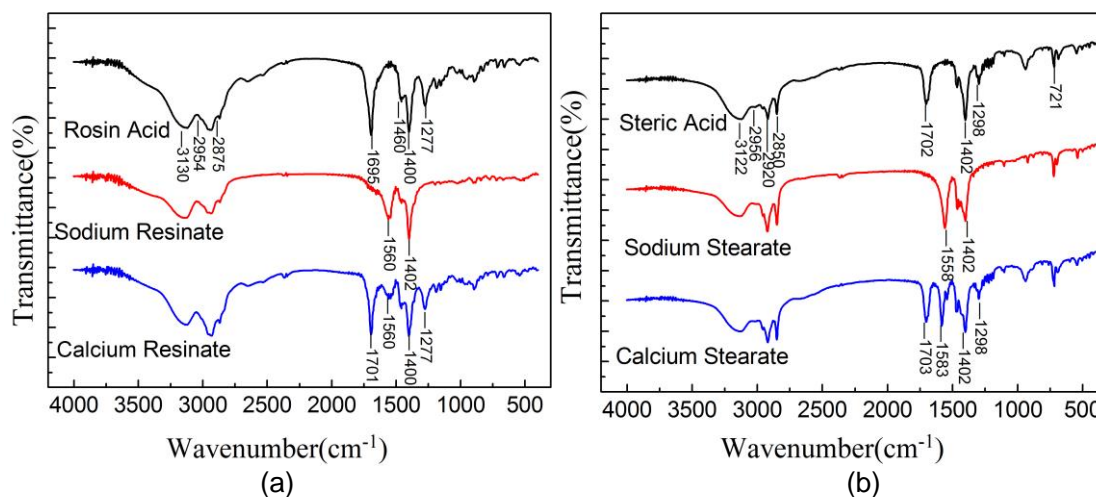


Fig. 8. IR spectra of (a) rosin acid, sodium resinate, and calcium resinate; (b) stearic acid, sodium stearate, and calcium stearate

As shown in Fig. 8a, the IR peaks of the stretching and bending vibration of O—H bonds (around 3130 cm^{-1} and 1400 cm^{-1}), and the stretching vibration of C=O bonds (1695 cm^{-1}) suggested the presence of —COOH groups in the rosin acid (Chen *et al.* 2014; Ren *et al.* 2014). The peak at 3130 cm^{-1} was also ascribed to the stretching vibration of =C—H bonds in the ring structure of rosin acid, which covered the stretching vibration peak of O—H bonds. The peaks at 2954 cm^{-1} , 2875 cm^{-1} , and 1460 cm^{-1} corresponded to the asymmetric stretching vibration, the symmetric stretching vibration and bending vibration of C—H bonds in — CH_3 group, respectively. All of the above-mentioned peaks agreed with the functional groups of the chemical structure of rosin acid (Fig. 9a). When developed to sodium resinate (Fig. 9b) from rosin acid, the peaks at 1695 cm^{-1} and 1277 cm^{-1} disappeared, while two new peaks appeared between the intervals, which resulted from the homogenization between C=O and C—O bonds in a — COO^- group. This caused the generation of two C=O bonds (Silverstein *et al.* 1998), whose bond strength was

between the range of C=O and C—O bonds. The vibration frequency of these two C—O bonds that were linked to the same carbon atom and had strong coupled vibration, were nearly the same, thus it induced the asymmetric and symmetric stretching vibration of —COO⁻ (around 1402 cm⁻¹ and 1560 cm⁻¹) (Hui *et al.* 2001; Li *et al.* 2002; Alvarez-Puebla and Garrido 2005). In addition, the O—H bonds did not exist in the carboxylate groups in sodium resinate due to the replacement of H⁺ in the carboxylic acid group of rosin acid by Na⁺. When developed to calcium resinate from sodium resinate with the addition of Ca²⁺, the stretching vibration of C=O (1277 cm⁻¹) and C—O (1701 cm⁻¹) reappeared, which indicated its possible charge-neutralized structure (Fig. 10a). While the peaks ascribed to the stretching vibration of —COO⁻ groups (around 1560 cm⁻¹ and 1400 cm⁻¹) still existed, and represented the —COO⁻ structure in calcium resinate that may have resulted from the remaining unreacted sodium resinate, or indicated the ionized structure of calcium resinate shown in Fig. 10b.

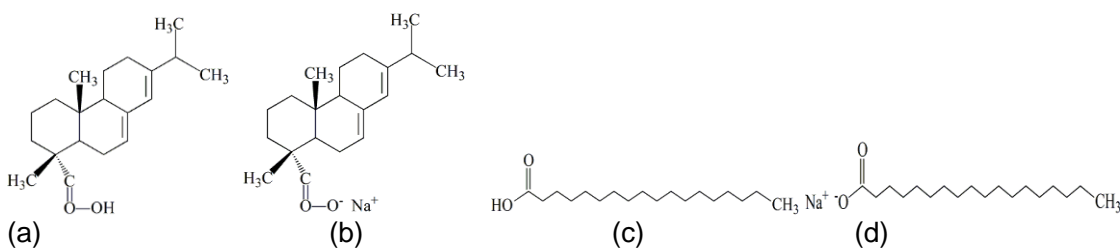


Fig. 9. Chemical structural formula of (a) rosin acid, (b) sodium resinate, (c) stearic acid, and (d) sodium stearate

The IR spectra of stearic acid, sodium stearate, and calcium stearate during the reaction process is shown in Fig. 8b. The stretching and bending vibration of O—H bonds (1402 cm⁻¹ and 3122 cm⁻¹), the stretching vibration of C=O bonds (1702 cm⁻¹) (Zhang *et al.* 2014), and the stretching vibration of C—O bonds (1298 cm⁻¹) suggested the existence of —COOH groups in the chemical structure of stearic acid (Fig. 9c). The peak at 2956 cm⁻¹ ascribed to the asymmetric stretching vibration of C—H bonds in —CH₃ groups, and the peaks at 2850 cm⁻¹ and 2920 cm⁻¹ ascribed to the asymmetric and symmetric stretching vibration of C—H bonds in —CH₂ groups. The peaks around 721 cm⁻¹ corresponded to the bending vibration of long chains (CH₂)_n of stearic acid (Luo *et al.* 2007). The changing regulation of IR spectra during the reaction process from stearic acid to sodium stearate (Fig. 9d) and then to calcium stearate was similar to that of Fig. 8a, which indicated the possible chemical structure of calcium stearate in Fig. 10.

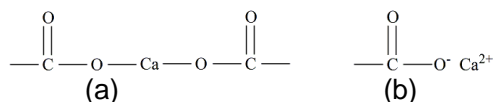


Fig. 10. Possible chemical structural formula of calcium carboxylate of stickies

The vacuum-dried solid samples of calcium resinate and calcium stearates were ground into powders and then pressed to discs with homogeneous diameters and thicknesses. Then the initial static contact angle (θ_s CA) of distilled water on the surfaces of the discs above was calculated to determine the hydrophobicity of pitch deposits. The

results are shown in Fig. 11. The 0 s CA of calcium resinate and calcium stearate discs were 90.2° and 96.0° , respectively, which indicated the hydrophobic characteristic of the pitch deposits (Qin *et al.* 2003). Therefore, this kind of substance was easy to adhere to the solid surfaces of the paper machine, such as the polymeric surfaces of forming fabrics, felts, rolls, *etc.*; thus it affected the paper machine's runnability.

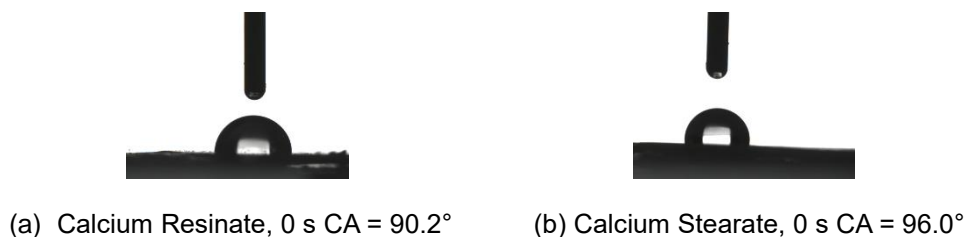


Fig. 11. CA images of (a) calcium resinate and (b) calcium stearate at 0 s; the concentration of calcium ions is 5 mmol/L

Mechanism of pitch deposits developed from soluble CS

In light of the aggregation process and structural characteristics of pitch deposits developed from CS simulacra as a function of Ca^{2+} concentration, three possible mechanisms were proposed for the formation process of colloidal pitch deposits in papermaking white water: “particle-particle collision” model, “layer by layer adsorption” model, and “hybrid collision-adsorption” model. The mechanisms are shown in Fig. 12.

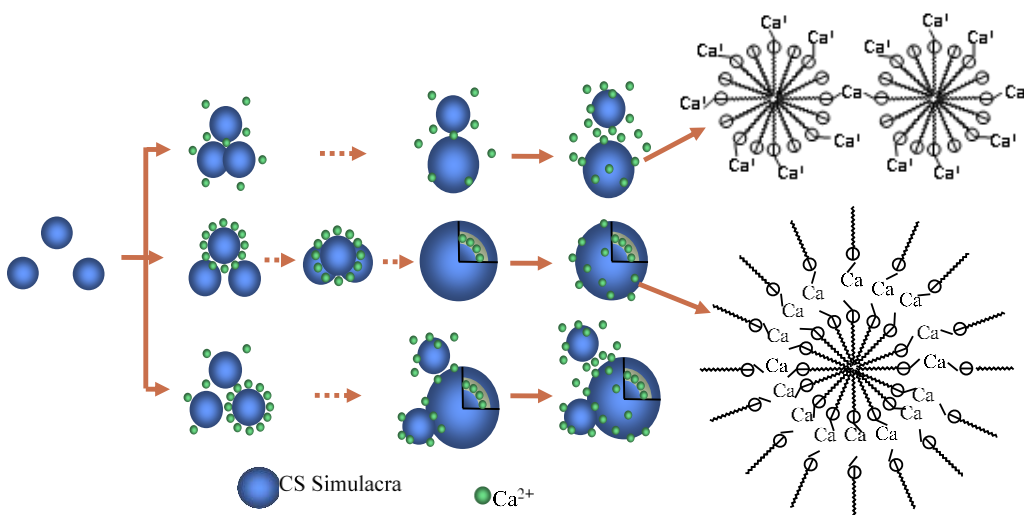


Fig. 12. Schematic drawing of formation process and mechanism of colloidal pitch deposits in presence of Ca^{2+}

Sodium resinate and sodium stearate belong to the category of anionic surfactants. These types of CS have both hydrophilic and hydrophobic structures. When they accumulate to a certain concentration in white water, the micelles with hydrophobic groups in the core and hydrophilic groups in the sheath can be formed (Hubbe *et al.* 2012). The non-ionic pitch deposits were produced when micelles reacted with Ca^{2+} , and according to the DLVO theory, the repulsive force between colloidal particles will be reduced due to the compression of an electric double layer with addition of Ca^{2+} , which makes it easier for

particles to agglomerate and form larger particles. The above-mentioned process is consistent with the “particle-particle collision” model. Moreover, the micelles could also react with hydrophilic groups of other soluble colloids after their reaction with Ca^{2+} , form larger micelle aggregations with hydrophobic groups extending in the water, and then adsorb other hydrophobic groups of soluble colloids due to similar polarity; therefore they produced insoluble and large sticky pitch deposits by the “layer by layer adsorption” model. In actual white water systems, the aggregation process of pitch deposits develop from CS with Ca^{2+} and could be carried out by both of the mechanisms above, *i.e.* the “hybrid collision-adsorption” model.

CONCLUSIONS

1. The Ca^{2+} ion was easily able to exchange with the Na^+ of CS species such as sodium resinate and sodium stearate in aqueous dispersions. The interaction resulted in sticky and hydrophobic pitch deposits with high agglomerating tendency.
2. The micelles with hydrophobic groups in the core and hydrophilic groups in the sheath were formed when CS accumulated to a certain concentration in white water. The insoluble pitch deposits were produced after micelles reacted with Ca^{2+} , followed by particle-particle collisions. Moreover, the micelles also reacted with hydrophilic groups of other soluble colloids after their reaction with Ca^{2+} and formed a larger micelle aggregation with hydrophobic groups extending in the water. They also then adsorbed other hydrophobic groups of soluble colloids due to similar polarity, and thus produced pitch deposits with larger size *via* a “layer by layer” adsorption. In addition, both of the mechanisms above could also contribute to the aggregation process of pitch deposits.

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REFERENCES CITED

- Allen, L. H. (1979a). “The importance of pH in controlling metal-soap deposition,” *TAPPI Journal* 71(1), 61-64.
- Allen, L. H. (1979b). “Characterization of colloidal wood resin in newsprint pulps,” *Colloid and Polymer Science* 257(5), 533-538.
- Alvarez-Puebla, R. A., and Garrido, J. J. (2005). “Effect of pH on the aggregation of a gray humic acid in colloidal and solid states,” *Chemosphere* 59(5), 659-667. DOI: 10.1016/j.chemosphere.2004.10.021
- Brouwer, P. H. (1991). “The relationship between zeta potential and ionic demand and how it affects wet-end retention,” *TAPPI Journal* 74(1), 170-179.
- Chen, C., Xu, H., Su, W., and Dai, H. (2014a). “Separation and characterization of dissolved and colloidal substances from white water and study on their stability,”

- Transaction of China Pulp and Paper* 29(4), 23-29. DOI: 10.11981/j.issn.1000-6842.2014.04.23
- Chen, W., Li, Q., Wang, Y., Yi, X., Zeng, J., Yu, H., Liu, Y., and Li, J. (2014b). "Comparative study of aerogels obtained from differently prepared nanocellulose fibers," *Chemoschem* 7(1), 154-161.
- Chen, C., Wang, J., Mao, S., Su W., and Dai, H. (2015a) "Origin analysis and characterization of dissolved and colloidal substances from white water in fine paper mill," *Journal of Nanjing Forestry University (Natural Science Edition)* 39(3), 106-112. DOI: 10.3969/j.issn.1000-2006.2015.03.020
- Chen, C., Mao, S., Wang, J., Bao, J., Xu, H., Su, W., Dai, H. (2015b). "Application of ultrafiltration in a paper mill: Process water reuse and membrane fouling analysis," *BioResources* 10(2), 2376-2391. DOI: 10.15376/biores.10.2.2376-2391
- Chowdhury, D. A., and Wikman, B. (2014). "Colloidal stability in pulp and paper industry process waters," *European Scientific Journal* 10(12), 100-116.
- Clas, S. D., Koller, E., and Allen, L. H. (1993). "Characterization of the effect of hemicellulose on the deposition of calcium soaps of tall oil using factorial design analysis," *Journal of Pulp and Paper Science* 19(5), 177-180.
- Francis, D. W., and Ouchi, M. D. (2001). "Effect of dissolved and colloidal solids on newsprint properties," *Journal of Pulp and Paper Science* 27(9), 289-295.
- Hubbe, M. A., Sundberg, A., Mocchiutti, P., Ni, Y., and Pelton, R. (2012). "Dissolved and colloidal substances (DCS) and the charge demand of papermaking process waters and suspensions: A review," *BioResources* 7(4), 6109-6193. DOI: 10.15376/biores.7.4.6109-6193
- Hui, R., Guan, C., and Hou, D. (2001). "Study on IR characteristics of carboxylic acid and their salts," *Journal of Anshan Teachers College* 3(1), 95-98. DOI: 10.3969/j.issn.1008-2441.2001.01.027
- Johnsen, I. A., Lenes, M., and Magnusson, L. (2004). "Stabilization of colloidal wood resin by dissolved material from TMP and DIP," *Nordic Pulp and Paper Research Journal* 19(1), 22-28.
- Kamijo, Y., Ono, H., and Miyanishi, T. (2000). "Adsorption of anionic dissolved and colloidal substances on the calcium carbonate," *Cornell Law Review* 97(4), 693-751.
- Lee, R., Stack, K., and Richardson, D. (2012a). "Effect of shear, temperature and pH on the dynamics of salt induced coagulation of wood resin colloids," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 396(7), 106-114. DOI: 10.1016/j.colsurfa.2011.12.049
- Lee, R., Stack, K., Richardson, D., Lewis, T., and Garnier, G. (2012b). "Multi-salt coagulation of soft pitch colloids," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 409(17), 74. DOI: 10.1016/j.colsurfa.2012.06.005
- Li, B., Zhang, C., Fu, S., and Liu, Y. (2015). "Stabilization of potentially sticky substances in pulp mill process water with polysaccharides," *BioResources* 10(3), 4922-4932. DOI: 10.15376/biores.10.3.4922-4932
- Li, X., Hu, K., and Huang, Y. (2002), "IR spectra of dicarboxylate of alkali-earth metal," *Spectroscopy and Special Analysis* 2(3), 392-395.
- Luo, M., Guan, P., and Liu, H. (2007). "The identification of several saturated fatty acids and their salts by means of infrared spectrometry," *Spectroscopy and Special Analysis* 27(2), 250-253.

- McLean, D. S., Stack, K. R., and Richardson, D. E. (2005). "The effect of wood extractives composition, pH and temperature on pitch deposition," *Appita Journal* 58(1), 52.
- Miao, Q., Huang, L., and Chen, L. (2013). "Advances in the control of dissolved and colloidal substances present in papermaking processes: A brief review," *BioResources* 8(1), 1431-1455. DOI: 10.15376/biores.8.1.1431-1455
- Nurmi, M., Westerholm, M., and Eklund, D. (2004). "Factors influencing flocculation of dissolved and colloidal substances in a thermomechanical pulp water," *Journal of Pulp and Paper Science* 30(2), 41-44.
- Nylund, J., Sundberg, A., and Sundberg, K. (2007). "Dissolved and colloidal substances from a mechanical pulp suspension—interactions influencing the sterical stability," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 301(1-3), 335-340. DOI: 10.1016/j.colsurfa.2006.12.068
- Qin, M., Hannuksela, T., and Holmbom, B. (2003). "Physico-chemical characterisation of tmp resin and related model mixtures," *Colloids & Surfaces A: Physicochemical and Engineering Aspects* 221(1-3), 243-254. DOI: 10.1016/S0927-7757(03)00146-8
- Ren, P., Yu, C., and Wang, X. (2014). "Study on esterification of rosin and glycidyl methacrylate," *Chemical Research and Application* 26(3), 427-431. DOI: 10.3969/j.issn.1004-1656.2014.03.020
- Silverstein, R. M., Webster, F. X., Kiemle, D. J., and Bryce, D. L. (1998). *Spectrometric Identification of Organic Compounds*, 8th Edition, John Wiley & Sons, New York, USA, pp. 94.
- Stack, K., Lee, R., Richardson, D., Lewis, T., and Garnier, G. (2014). "Complex formation and stability of colloidal wood resin pitch suspensions with hemicellulose polymers," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 441(3), 101-108. DOI: 10.1016/j.colsurfa.2013.08.057
- Sundberg, A., Ekman, R., Holmbom, B., Sundberg, K., and Thornton, J. (1993). "Interactions between dissolved and colloidal substances and a cationic fixing agent in mechanical pulp suspensions," *Nordic Pulp and Paper Research Journal* 8(2), 226-231.
- Wang, C., Chen, C., Ren, H., Yang, Y., and Dai, H. (2016) "Polyethyleneimine addition for control of dissolved and colloidal substances: Effects on wet-end chemistry," *BioResources* 11(4), 9756-9770. DOI: 10.15376/biores.11.4.9756-9700
- Wang, J., Mao, S., Su, W., *et al.* (2013a). "The origin and analysis methods of DCS in papermaking wet-end system," *Transaction of China Pulp and Paper* 28(3), 59-62. DOI: 10.11981/j.issn.1000-6842.2013.03.59
- Wang, L., Li, G., Zhang, Y., and Xiao, H. (2013b). "Synthesis and evaluation of p(am-b-dadmac) as fixative for dissolved and colloidal substances," *Journal of Applied Polymer Science* 130(6), 4040-4046.
- Wang, X., Zhan, H., and Chen, G. (2004). "Effects of pH value on resin deposition with the presence of calcium ion," *Journal of South China University of Technology* 32(2), 10-13. DOI: 10.3321/j.issn:1000-565X.2004.02.003
- Wei, L., Song, H., Xu, N., Hou, Q., and Xu, L. (2014). "Effects of magnesium-based alkali on the dissolved and colloidal substances in the alkaline peroxide bleaching of poplar ctmp," *Industrial & Engineering Chemistry Research* 53(8), 2897-2902. DOI: 10.1021/ie4037752

- Whipple, W. L., and Maltesh, C. (2002). "Adsorption of cationic flocculants to paper slurries," *Journal of Colloid & Interface Science* 256(1), 33-40. DOI: 10.1006/jcis.2001.7867
- Xiao, H., He, B., Qian, L., and Li, J. (2015). "Cationic polystyrene spheres for removal of anionic contaminants in white water of papermaking," *Journal of Applied Polymer Science* 132(5), 41379
- Ye, C., Dai, H., and Wang, S. (2009a). "Study on the ACS as adsorbent of calcium ions," *Transactions of China Pulp and Paper* 24(1), 85-90. DOI: 10.3321/j.issn:1000-6842.2009.01.019
- Ye, C., Dai, H., and Wang, S. (2009b). "The formation of calcium resinate and its affecting factors," *Transactions of China Pulp and Paper* 24(1), 91-94. DOI: 10.3321/j.issn:1000-6842.2009.01.020
- Yuan, G., Dai, H., Ye, C., and Zhang, Y. (2011a). "Adsorption of Ca(II) from aqueous solution onto cellulosic fibers and its impact on the papermaking process," *BioResources* 6(3), 2790-2804. DOI: 10.15376/biores.6.3.2790-2804
- Yuan, G., Dai, H., and Zhang, Y. (2011b). "The influence of closed white water recycle on flocculation system," *China Pulp and Paper Industry* 32(10), 40-43.
- Yuan, G., Dai, H., and Zhang, Y. (2012). "Mathematical analysis of calcium ions controlling by ACS," *Transactions of China Pulp and Paper* 27(1), 1-8. DOI: 10.3969/j.issn.1000-6842.2012.01.001
- Zhang, H., He, Z., Ni, Y., Hu, H., and Zhou, Y. (2007). "Characteristics of dissolved and colloidal substances in high yield pulp and their impact in filler retention," *Appita Journal* 60(5), 390-395.
- Zhang, W., Liu, W., Li, H., Hubbe, M. A., Yu, D., Li, G., and Wang, H. (2014). "Improving stability and sizing performance of alkenylsuccinic anhydride (ASA) emulsion by using melamine-modified laponite particles as emulsion stabilizer," *Industrial and Engineering Chemistry Research* 53(53), 12330-12338. DOI: 10.1021/ie501381a

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