

EXTRACTED WOOD POLYMERS AND COLLOIDAL PITCH STABILITY UNDER HIGH IONIC STRENGTH.

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Abstract

Pitch deposits have plagued papermakers for many decades. Little is understood, however about the stability of pitch in the presence of extracted wood polymers especially under the high ionic strength conditions typical of system closure. This paper explores the effect of extracted wood polymers released by the pulp fibres on the stability of pitch colloids.

The effect of extracted wood polymers on pitch colloidal stability was found to vary depending on how the wood polymers were added. Coagulation and aggregation of the wood polymers were to occur under high ionic strength. Further, the pitch colloids were found to undergo two states of destabilisation due to the addition of extracted wood polymers to the colloid. The stabilisation of the colloids is affected by both the ionic strength and the time allowed for colloidal reorganisation.

Introduction

The formation of pitch deposits has plagued papermakers for many decades. The problem increases as paper mills close the water system to reduce water consumption, a national priority in Australia. Considerable research has been undertaken to understand the factors behind the formation of these deposits. One successful strategy adopted in most mills is to use polymeric fixatives which reduce both deposits and the accumulation of wood resins in the process water. It is believed that the wood resin colloids either adsorb onto individual fibres or heterocoagulate into the fibre web. Organic wood extracts released from the pulp have also been found to stabilise the wood resins and reduce pitch deposition. However, little is understood about the stability of pitch in the presence of extracted wood polymers and fixative polymers, especially under the high ionic strength conditions typical of system closure [1-7].

This paper investigates, under the conditions critical to papermaking, pitch colloid stability using a Photometric Dispersion Analyser PDA 2000. Turbidity variations of a moving colloidal suspension were determined. This allows the colloid stability to be quantified by the stability ratio W [8, 9] defined as:

$$W = \frac{\text{Number of collisions between particles}}{\text{Number of collisions that result in coagulation}}$$

W is a function of any property of a dispersion that affects the strength of the interparticle forces and the energy barrier that slows down coagulation. The stability ratio W is a measure of the effectiveness of the potential barrier in preventing the particles from coagulating in the presence of electrolyte and with variation in organic wood extracts or polymer additives.

This study firstly investigates the reorganization behaviour of wood polymers extracts which consist mostly of galactoglucomannans when submitted to shocks in ionic strength. In the second part, the effect of these extracted wood polymers on colloidal pitch stability is studied in conjunction with high ionic strength. Lastly, the stability of pitch/wood extract complexes formed in different ways is analysed.

Experimental

Pulp

Thermo-mechanical pulp (TMP) from *Pinus radiata* was collected from the primary refiners at Norske Skog's Boyer mill in Tasmania. The pulp was freeze dried and then Soxhlet extracted with hexane to remove wood resin extractives.

Wood Resin Colloidal Solutions

The methods developed by both Sundberg *et al* [4] and Stack *et al* [10] were used to prepare dispersions of colloidal wood resins. Dispersions were made by dissolving extracted wood resin in acetone (99.5% purity) and adding to distilled water with a concentration of 1 mM KNO₃, and pH adjusted to 5.5. This dispersion was dialysed for 24 hours to remove the acetone. Dialysis was conducted using a cellulose membrane tubing (Sigma D-9402, 76mm wide, >12,000 MW). Wood resin extractives concentration was 100 mg /L pre-dialysis.

Preparation of extracted wood polymers

Extracted wood polymers were obtained using the soxhlet extracted pulp from *Pinus Radiata* TMP following the procedure of Johnsen I. [11] The pulp was disintegrated in water to 2% consistency at 60°C for 3 hours, and then repeating this process up to 5 times after filtering out the wet wood fibre. The solution was then concentrated. This dispersion was dialysed for 24 hours in 1mM KCl and pH adjusted to 5.5 to remove unwanted material. Dialysis was conducted using a cellulose membrane tubing (Sigma D-9402, 76mm wide, >12,000 MW).

PDA Wood Resin aggregation Analysis

A Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, Cambridge, UK) was used to monitor changes in aggregation of colloidal wood resin dispersions. A Cole Palmer Masterflex L/S peristaltic pump and 3 mm tubing were used to circulate the suspension. The instrument was initially calibrated with distilled water and the DC gain control was adjusted to give a DC value of 10 V as suggested in the operating manual [12] and Hopkins, C. and J. Ducoste [13]. Shear conditions stirrer rate was set at 500 rpm for all tests, and flow through the PDA was set at 70mL/min.

Particle Size Analysis

The particle size distribution of the polystyrene beads was measured with a Micrometrics Saturn 5200 Laser Particle Size Analyser. The instrument background was taken with distilled water.

Results and Discussion

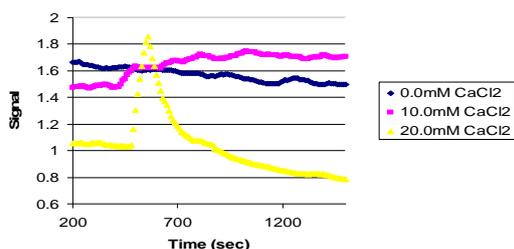


Figure 1: Effect of CaCl₂ on the dynamics of extracted wood polymers destabilisation and rearrangement. Extracted wood polymer concentration = 360 mg/L.

The effect of CaCl₂ on the dynamics of extracted wood polymers reorganisation is shown on Figure 1. In the absence of CaCl₂ the PDA signal is relatively flat indicating no aggregation is occurring and that the extracted wood polymers are stable under the shear conditions imposed. On addition of 10mM CaCl₂ a small increase in the PDA signal occurs. This response represents an aggregation or

reorganisation of the wood polymers. The addition of 20mM CaCl₂ resulted in a significant increase in the PDA signal reaching a maximum then decreasing. This shape in the PDA signal represents floc aggregation followed by floc break up [13]. This behaviour is typical of electrolyte induced precipitation/coagulation.

The addition of extracted wood polymers to polystyrene beads functionalised by carboxylic groups was studied in order to determine if absorption of extracted wood polymers onto the surface of the pitch colloids was occurring. The carboxylated polystyrene beads were chosen to model the pitch colloid.

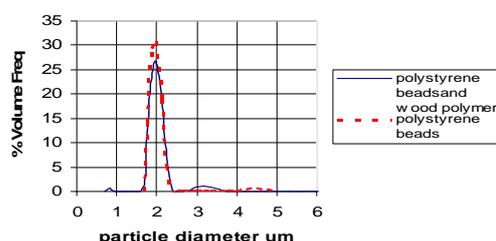


Figure 2: carboxylated polystyrene beads and the effect of addition of extracted wood polymers.

It can be seen, in Figure 2, which upon addition of the extracted wood polymers to the polystyrene beads there is a growth in the particle size. The average particle size was found to increase from 2.0 microns to 2.2 microns. The particle size distribution in Figure 2 shows the appearance of larger particles and also a slight shift in the main peak due to polymer adsorption resulting in an increase in the particle size.

The effect of extracted wood polymers concentration on pitch colloidal stability is represented on Figure 3. This graph is a graph of the stability factor *W*. obtained from a series of PDA response curves at different additions of the wood polymers to a dispersion of the pitch colloids. The slope of the initial part of the PDA signal is used to measure the rate of aggregation. When a series of curves of different conditions are obtained the ratio of the slope of the curve of interest to the fastest rate is calculated to determine *W*, the stability factor [9, 13] When $-\log W$ is equal to 0 the colloidal system to classified as being completely destabilised. Extracted wood polymers induce pitch coagulation with the fastest rate achieved at (10 mg/L)]. The addition of extracted wood polymers above this concentration was found to increase colloidal stability as evident by the positive increase in the slope of the curve.

The maximum pitch stability was achieved at the highest extracted wood polymers dosage of 40 mg/L. This curve is typical of colloidal steric stabilisation by polymer adsorption. Only low stability ratio was reached as the fastest rate of coagulation is only 10 times faster the slowest in the PDA response curves.

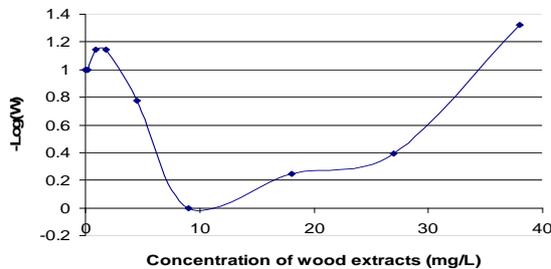


Figure 3: Effect of extracted wood polymers concentration on colloidal pitch stability – low concentration regime

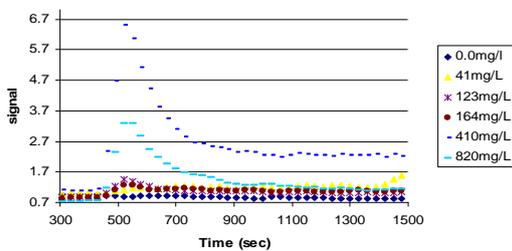


Figure 4: Effect of extracted wood polymers concentration on the dynamics of colloidal pitch coagulation. - high extracted wood polymers concentration regime. Pitch concentration = 100 mg/L

Figure 4 depicts the effect of extracted wood polymers on the dynamics of colloidal pitch coagulation at a higher concentration regime of wood polymer. High coagulation rates are reached at the high extracted wood polymers concentration as represented by the high slope and PDA signal level reached upon extracted wood polymers addition in Figure 4. The stability curve of colloidal pitch as a function of extracted wood polymers concentration is presented in Figure 5 for this high concentration regime. Maximum pitch stability is reached at around 50 mg/L extracted wood polymers and maximum flocculation rate is achieved at 400 mg/L extracted wood polymers. The peak at around 50 mg/L of extracted wood polymers seen in figure 5 very likely represents the point of steric stabilisation of the pitch colloids achieved by full polymer coverage.

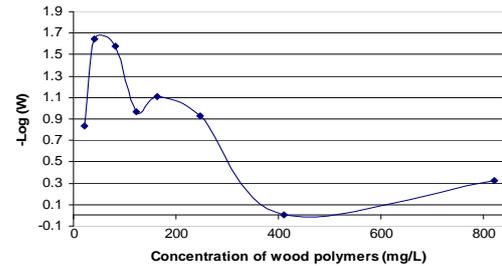


Figure 5: Effect of extracted wood polymers concentration on colloidal pitch stability – high concentration regime.

There are a number of variables controlling the size and structure of the colloids formed between pitch and soluble wood polymers. These include the manner in which the colloids are made, the time that the colloids are allowed to rest and reorganise in solution before addition of electrolytes, the concentration of the extracted wood polymers in solution compared to the pitch colloids and the ionic strength of the final solution after addition of electrolyte.

Figure 6 shows the effect of extracted wood polymers concentration on the dynamic stability of preformed pitch and extracted wood polymer complexes upon addition of 10mM CaCl_2 . The preformed complexes were made prior to dialysis and were allowed to reorganise for 24hr. Figure 7 represents the stability curve.

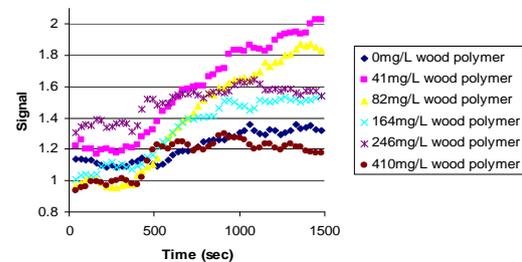


Figure 6: Effect of the extracted wood polymers concentration on the dynamics of preformed pitch/extracted wood polymers complex stability upon addition of 10mM CaCl_2 .

At low wood polymers concentrations, the colloidal complexes are destabilised upon addition of electrolyte as shown by the decrease in $-\log W$ to 0 at approximately 50mg/L. This destabilization effect is reduced and even disappears as the extracted wood polymers concentration increased.

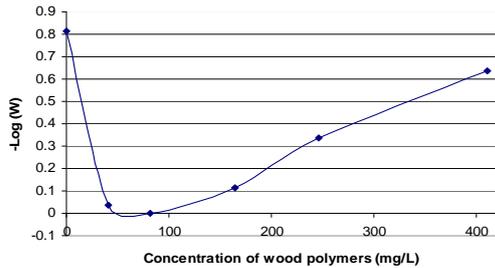


Figure 7: Effect of extracted wood polymers concentration on the stability preformed pitch/ extracted wood polymers complexes upon 10mM CaCl₂ addition (above pitch CCC).

Very high salt concentrations are expected for modern papermaking under increased system closure. The stabilising effect of extracted wood polymers on pitch stability was therefore also quantified upon addition of 50mM CaCl₂. This salt concentration is above the pitch critical coagulation concentration (CCC) of 6.6 mM [14]

The results in Figure 8, shows the extracted wood polymers did not restabilise pitch at 50mM CaCl₂. In this experiment the wood polymers were added just prior to dialysis of the colloid. The trend in Figure 8 differs from the trend at 10 mM CaCl₂. Comparison with Figure 7 reveals that it takes 4 times more polymer to reach the maximum coagulation rate at 50 mM CaCl₂ than it does at 10mM CaCl₂. This suggests that the wood polymer coils adopt a tighter configuration under high ionic strength.

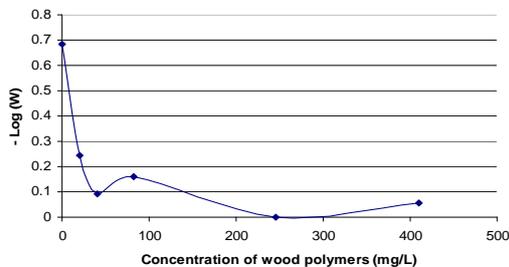


Figure 8: Effect of extracted wood polymers concentration on the stability of preformed pitch/ extracted wood polymers complexes upon 50mM CaCl₂ addition (above pitch CCC).

The stability curve of newly formed pitch/wood polymer complexes submitted to a shock in salt concentration (CaCl₂ 50 mM) is presented as a function of polymer concentration in Figure 9. Comparison with Figure 8, in which the wood polymers were allowed to reach their equilibrium conformation on the pitch colloids, reveals that it takes four times more wood polymer to reach maximum flocculation with newly formed pitch/ wood polymer complexes.

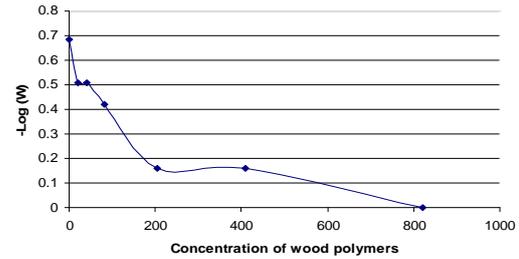


Figure 9: Effect of extracted wood polymers concentration on the stability of newly formed pitch/ extracted wood polymers complexes under high ionic strength. (50mM CaCl₂ addition -above pitch CCC).

The polymer coils adopting a tighter configuration under high ionic strength, has a follow on affect in that we don't see the restabilisation of the pitch by the extracted wood polymers. As seen in figure 8 and 9 the increase in the extracted wood polymers addition has a negative impact on the colloidal stability.

Conclusions

- Dissolved wood polymers released from Pinus radiata TMP pulp, consisting mostly of large oligomers of galactoglucomannans coagulate or assemble upon addition of CaCl₂.
- Dissolved wood polymers can influence pitch colloidal stability under dynamic conditions. Low concentrations of wood polymer destabilise pitch while at higher wood polymer concentration, the pitch colloid is completely stabilized. This is an indication of steric stabilization through polymer adsorption. At even higher wood polymer concentration, the pitch colloids coagulate again, very likely by depletion coagulation.
- Dissolved wood polymers can flocculate pitch at salt concentrations below and above CCC of CaCl₂. However, steric stabilization was achieved at high wood polymer concentration only for salt concentrations below the CCC.
- Wood Polymer adsorption on pitch is affected by both ionic strength and time. Wood polymers adsorb/reorganise into more compact coils at high ionic strength and lower rearrangement time.

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