Stickies Control with Pectinase for Improving Behavior of Cationic Polymers in a Mixture of Chemithermo-mechanical Pulp and Deinked Pulp

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In this work, a pressure-sensitive adhesive (PSA) was used as the model substance for secondary stickies. The dissolved and colloidal substances (DCS) prepared from bleached chemithermomechanical pulp (BCTMP) and the effects of pectinase treatment on the stickies deposition were evaluated. The results showed that the addition of DCS lowered the efficiency of cationic polymers and aggravated the deposition of stickies. As a major component of anionic DCS, polygalacturonic acids can be effectively degraded during pectinase treatment. Therefore, the efficiency of cationic polymers improved, and subsequently they were able to fix the destabilized sticky particles on the fibers, which led to the decrease of stickies deposition. However, the pectinase treatment of DCS insignificantly affected stickies deposition in absence of cationic polymers when the stickies deposition was caused by calcium ions.

Keywords: Pectinase; BCTMP; Dissolved and colloidal substances; Polygalacturonic acids

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INTRODUCTION

Stickies remains one of the major obstacles in paper mills, not only negatively affecting the operation of the paper machine, but also harming the quality of the final products. While using recovered papers as raw materials for papermaking, they can build up on the forming wire, the pressing felt, in the dryer section, and in the calender section (Douek *et al.* 2003; Hubbe *et al.* 2006). Compared to using one type of pulp, the problems caused by stickies are even more critical for a production line that utilizes a mixture of several pulps, such as mechanical pulp, deinked pulp, *etc.* (Allen 2002; Lenes *et al.* 2001; Dechandt *et al.* 2004). The sticky substances existing in different pulps increase the complexity of stickies problems when they are blended together (Dechandt *et al.* 2004; Haynes 2008).

Generally, the primary stickies can be efficiently removed using technological approaches, *e.g.*, the cleaning process, the screening process, and pre-flotation and post-flotation operations. However, the secondary stickies are difficult to remove from the pulps. Therefore, other strategies, *e.g.*, physico-chemical approaches such as dispersion, detackification, fixation, and retention onto pulp fibers should be considered to further control the troublesome stickies, especially the sticky substances in the form of dissolved and colloidal substances (Doshi 1992; Hubbe *et al.* 2006; Dechandt *et al.* 2004; Hamann *et al.* 2004; Gribble *et al.* 2010). Enzymes are also effective agents being used to control stickies. The ester bonds within sticky substances are broken by esterase-type enzymes, their size is reduced, and subsequently smaller compounds are formed (Jones 2005; Patrick 2004; Jones *et al.* 2010).

Cationic polymers, such as cationic polyacrylamide and polyethylene-imine, are widely used as retention aids in the wet end of a paper system. In addition to retaining the fillers and fines, they can also affix some sticky particles onto the pulp fibers, therefore reducing the deposition of stickies. However, the negatively charged dissolved and colloidal substances (DCS) that are released during the pulping and bleaching processes deteriorate the efficiency of cationic polymers. The polygalacturonic acids dissolved during the bleaching stage of mechanical pulping are considered a main source of anionic DCS (Reid and Ricard 2000; Liu *et al.* 2010), and these are responsible for the deposition of sticky substances in subsequent papermaking processes (Li *et al.* 2006a). Additionally, the polygalacturonic acids in mechanical pulp can be degraded by pectinase, which inhibits the problems caused by DCS and improves the behavior of cationic polymers (Ricard *et al.* 2004; Thornton 1994; Pruszynski *et al*. 2011).

Bleached chemithermomechanical pulp is used extensively in producing fine paper grades, due to its unique properties such as high bulk, high opacity, good ink absorption, and low production cost (Connell and Cockram 2000; Zhou 2004; Hu *et al.* 2004). DCS formed and released during the pulping processes of CTMP are negatively charged, and these detrimental substances, especially polygalacturonic acids, will affect the efficiency of cationic polymers in the wet end stage of a papermaking system (Li *et al.* 2006b; Zhang *et al.* 2011). As a bio-chemical approach for DCS treatment, pectinase has demonstrated the ability to degrade the polygalacturonic acids in DCS and subsequently improve the effectiveness of cationic polymers (Li *et al.* 2006b; Ricard *et al.* 2004). The treatment of whitewater from papermaking by using a combination of pectinase and lipase was an effective method for the reduction of cationic demand of whitewater and pitch deposition (Liu *et al*. 2012).

In this study, a polyacrylate pressure-sensitive adhesive (PSA) was used as a model substance of secondary stickies in DIP. The effectiveness of pectinase treatment on the DCS and its control of the deposition of sticky substances are evaluated and discussed.

EXPERIMENTAL

Materials and Chemicals

The bleached chemithermomechanical pulp (BCTMP) and bleached hardwood kraft pulp (BHKP) were obtained from the Huatai Group Co. Ltd. in China. In the deposition test using polyacrylate pressure-sensitive adhesive (PSA), BHKP was used instead of DIP to avoid the potential influence of other contaminants in DIP. The cationic polyacrylamide (CPAM) and polyethylene-imine (PEI) were obtained from the same mill. They were used as the fixing agent and the retention aid, respectively, in the newsprint production line. Pectinase (Novozym 863) was provided by Novozymes (China). In addition to pectinase, it consisted of traces of cellulase, xylanase, mannanase, galactanase, and amylase. Polyacrylate pressure-sensitive adhesive (PSA) was purchased from the Beijing Comens New Materials Co. Ltd. (China). When the PSA was dispersed in the water, its particle size measured with a Mastersizer 2000 particle size analyzer was in a range of 0.2 to 40 μm at a pH of 7.5.

Preparation of DCS from BCTMP

To investigate how the pectinase acts on DCS, a DCS sample was prepared from BCTMP in the laboratory. The pulp was firstly diluted with deionized water (60°C) to 2% consistency, stirred at 100 rpm for 1 hour, and then filtrated with a 200-mesh wire. The filtrate was left to stand for 24 h, and then filtrated with a G3 filtering crucible to acquire the DCS sample.

Analysis of DCS and PSA

The DCS sample was extracted with methyl tert-butyl ether (MTBE), according to the method by Örså and Holmbom (1994). The total dissolved and colloidal substances (TDCS) in the DCS sample were determined by the gravimetric method (Zhang 2000). The degraded carbohydrates present in DCS samples were determined by gas chromatography (GC) after methanolysis treatment, according to the method described by Sundberg *et al.* (1996). The cationic demand (CD) of DCS and the negative charge density of PSA was determined with a Mütek PCD 03 particle charge detector, and poly-(dimethyldiallylammonium chloride) was used as a standard cationic substance (Ben *et al.* 2003). The CD of the prepared DCS and the negative charge density of PSA at a pH of 7.5 were 210 μeq/L and 0.25 meq/g, respectively.

Application of Pectinase to DCS Sample

To examine the degradation of polygalacturonic acids in DCS samples, the pectinase treatment conditions were as follows: the dosage of the enzyme was 150 APSU/L, enzymatic treatment was carried out at 55°C, at a pH of 5.0, for 180 min. After the pectinase treatment, the cationic demand of the DCS sample was examined. For comparison, the DCS sample was also treated with deactivated pectinase and underwent enzymatic treatment under the same conditions.

Examination of Deposition of Sticky Substances

To evaluate the effectiveness of pectinase in controlling stickies, the deposition of sticky substances was examined using a method found in the literature (Li *et al.* 2005). The device consisted of a Plexiglas container with a removable polythene cylinder that was placed in the container by a holder. Holes with a diameter of 0.4 cm were distributed along the wall of the cylinder, and the effective area of the cylinder was about 500 cm^2. During the deposition test, the pre-weighed cylinder was placed in the device, into which 800 mL of DCS sample and 1200 mL hot deionized water were added. The pulp sample and the PSA latex (or DCS sample or pectinase-treated DCS, if applicable) were then added, and the experiment was started at an agitation speed of 750 rpm. The rotator was also pre-weighed. According to the scheme, the cationic polymers or calcium ions were added into the suspension, and the pH value was adjusted if/when needed. After running for 60 min, the polythene cylinder and the rotator were removed from the device and rinsed with water, then dried at 105°C for 15 min to acquire the weight of the deposited substances. An average of duplicate measurements was recorded as the result, and their difference was less than 10%. Additionally, the suspension after the deposition test was centrifuged, and the turbidity of the supernatant was used for turbidity determination.

In the deposition test for PSA + DCS and PSA + P-DCS (pectinase-treated DCS) systems, 800 mL of controlled DCS water or pectinase-treated DCS water were added to deionized water. The total volume of solution in the device was 2000 mL. Except where specially noted, the conditions for all deposition tests were a PSA concentration of 0.4

g/L, pulp consistency of 0.4%, temperature of 50°C, pH of 7.5, and a deposition time of 60 min.

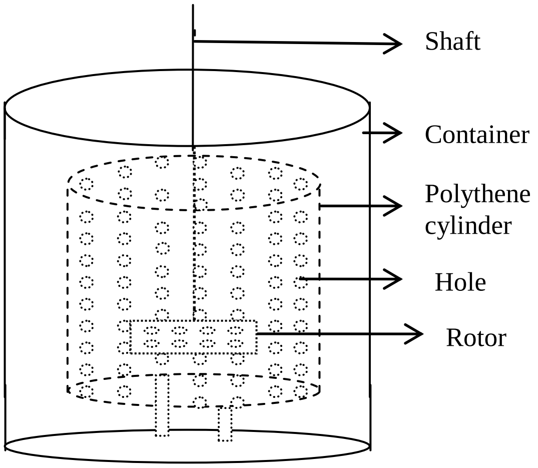


Fig. 1. Diagram of the stickies deposition tester

Microscopic Observation of Stickies on Fibers

In the deposition test, to observe the sticky substances attached to pulp fibers, after 1 minute of adding cationic polymers, the pulp fibers were observed and imaged with a BK2000/3000 light microscope (Chongqing Photoelectric Instrument Co. Ltd., China).

RESULTS AND DISCUSSION

Composition of DCS from BCTMP

The composition of DCS from BCTMP was instrumentally analyzed, and the results are shown in Table 1.

Table 1. The Composition of DCS from BCTMP

Component	Concentration (mg/L)
TDCS	800
MTBE extractives	142
Carbohydrates	287
Rhamnose	13
Arabinose	11
Galactose	12
Glucose	11
Mannose	5
Xylose	142
Galacturonic acid	55
4-*O*-methylglucuronic acid	34
Glucuronic acid	4

It can be seen that the total DCS was about 800 mg/L, and the degraded components from carbohydrates remained the major components in the DCS sample. The xylose accounted for 142 mg/L, while other monosugars were only in the range of 11 to 13 mg/L. In addition to monosugars, galacturonic acid and 4-*O*-methylglucuronic acid were predominant components in the DCS sample. These degraded carbohydrates should be released during the pulping and bleaching processes of BCTMP and DIP.

Effect of Pectinase Treatment on DCS in the Presence of Cationic Polymers

The negatively charged DCS in pulps significantly affected the efficiency of cationic polymers when applied to the papermaking system for the retention of fillers and fine fibers. In order to examine the effectiveness of pectinase treatment on DCS in the mixture of BCTMP and DIP, the stability of secondary stickies and the stickies deposition was examined in the presence of CPAM and PEI. The results are shown in Figs. 2 to 5.

It was reported that the residual turbidity could be an indicator of the destabilization of the colloidal system when cationic polymers are added (Huo *et al.* 2001). Compared to the individual colloidal PSA system, Figs. 2 and 3 show that with addition of DCS, more cationic polymers were required for flocculating the PSA, which means that the effectiveness of cationic polymers was negatively affected in the presence of DCS.

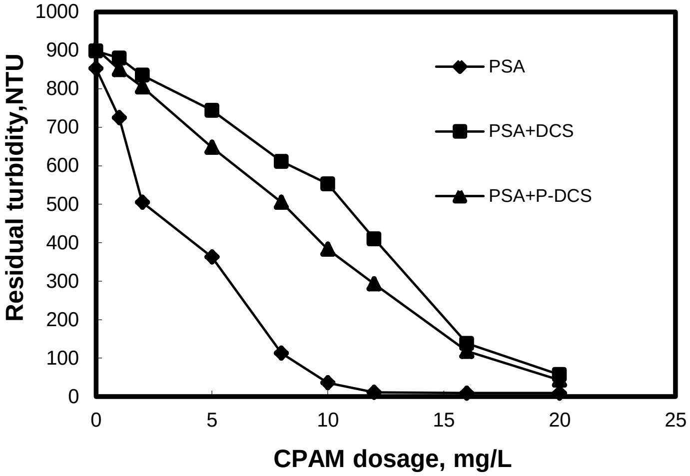


Fig. 2. Effect of CPAM on the stability of colloidal system

Compared to the DCS sample, less of the cationic polymer was needed to flocculate the colloidal substances in the pectinase-treated PSA + P-DCS system than the pectinase-treated PSA + DCS system. Based on the information provided by the manufacturer, the pectinase Novozym 863 is an enzyme mixture. In addition to pectinase, it consisted of cellulase, xylanase, mannanase, amylase, and others. As reported in the literature (Ricard and Reid 2004), it has a positive effect on improving the efficiency of cationic polymers.

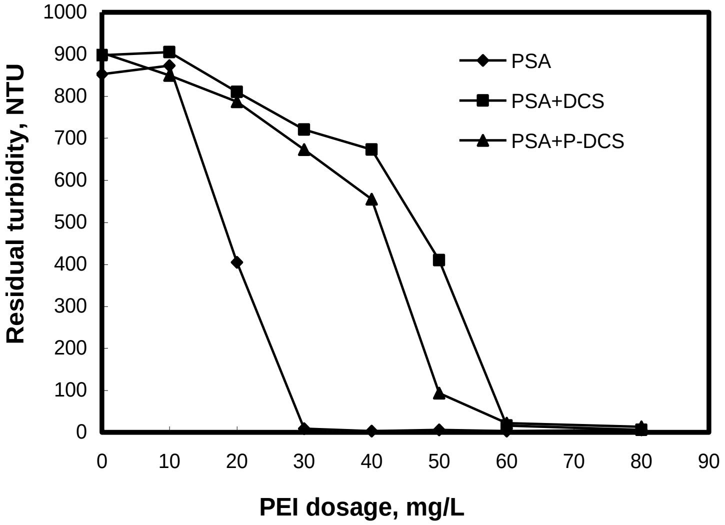


Fig. 3. Effect of PEI on the stability of colloidal system

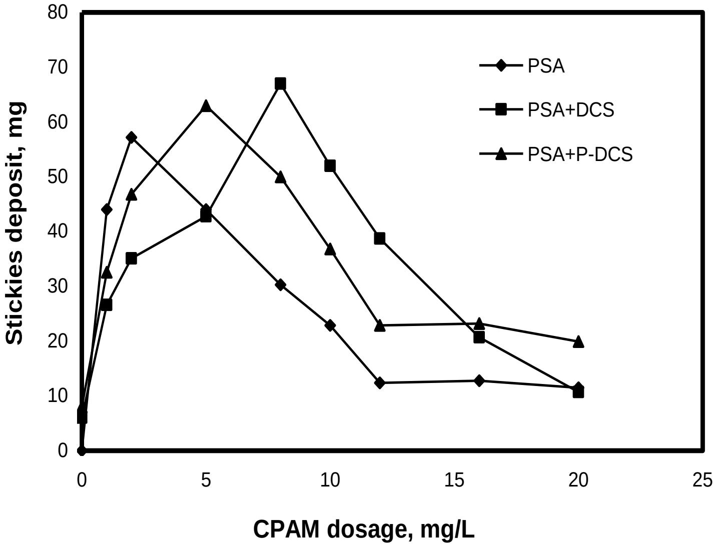


Fig. 4. Effect of CPAM on stickies deposition of colloidal system

As shown in Figs. 4 and 5, for the PSA colloidal system, cationic polymers addition caused the stickies deposition, and the stickies deposit reached the maximum value at addition of 2 mg/L CPAM and 20 mg/L PEI, respectively. Apparently, the cationic polymers resulted in the destabilization of the PSA colloidal system, and subsequently the destabilized sticky particles were deposited even when the dosage of cationic polymer was low. It can also be seen in the figures that the amount of deposited stickies decreased with an increase of cationic polymers. A possible explanation is that a portion of destabilized sticky particles was adsorbed on the pulp fibers with a high addition level of cationic polymers.

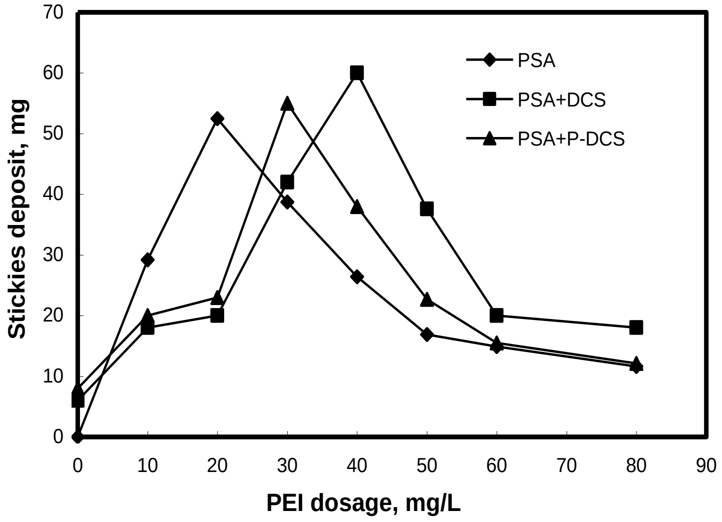


Fig. 5. Effect of PEI on stickies deposition of colloidal system

The stickies deposited from the PSA + DCS system were less than that from the PSA system, even at a low dosage of cationic polymers. The negatively charged DCS was helpful in stabilizing the PSA colloidal particles in the presence of cationic polymers. However, the sticky particles were not easily removed from the system with a low level of cationic polymers. To control sticky problems, the level of cationic polymers should be higher than the point that led to the maximum deposition of stickies. To reduce the sticky deposits to a similar level, more cationic polymers were required for the PSA + DCS system than for the PSA system, because the negatively charged DCS deteriorates the effectiveness of cationic polymers.

Compared to the PSA + DCS system, for the pectinase-treated sample, the deposited stickies decreased at the same dosage of cationic polymers, and lower amounts of cationic polymers were required to decrease the sticky deposition to a similar level. For example, to reduce the sticky deposition to about 20 mg, the necessary amount of CPAM was 16 mg/L and 12 mg/L, respectively, for the PSA + DCS and PSA + P-DCS systems.

In summary, the anionic trash in dissolved and colloidal substances decreased after the pectinase treatment, so that the efficiency of cationic polymers improved, *i.e.*, pectinase treatment benefited stickies control.

Effect of Pectinase Treatment on DCS in the Presence of Calcium Ions

Calcium ions are one of the metal ions that commonly exist in pulp suspension and process water in newsprint mills. They can cause the destabilization of secondary stickies and lead to deposition of stickies.

In order to investigate the influence of calcium ions on the stickies deposition during pectinase treatment, the stability of DCS was examined with the addition of calcium ions into the PSA and PSA + P-DCS samples. The results are shown in Fig. 6 and 7.

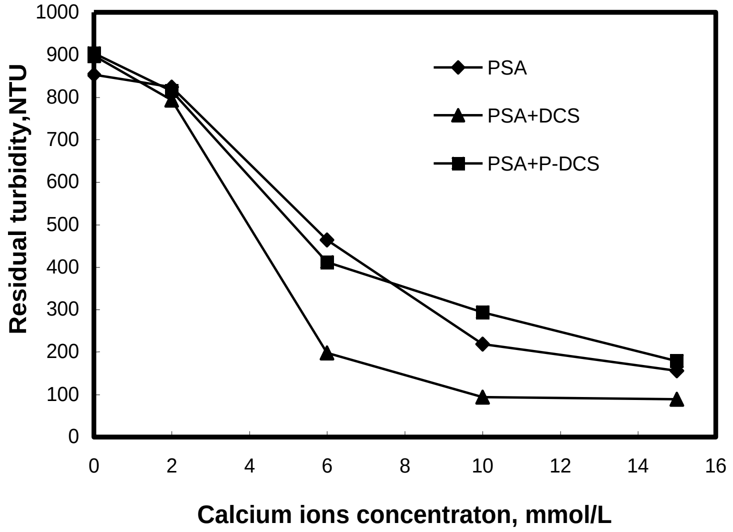


Fig. 6. Effect of calcium ions on the stability of colloidal systems

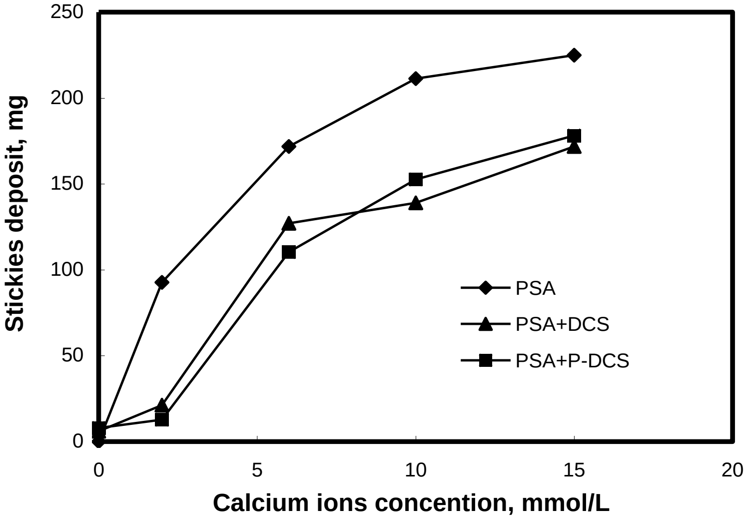


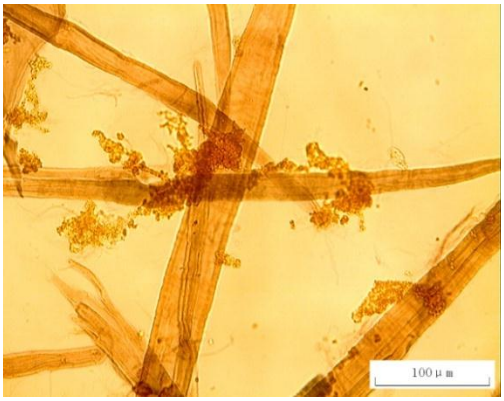
Fig. 7. Effect of calcium ions on the stickies deposition

Figure 6 shows that, compared to the PSA system and the PSA + P-DCS system, it was easier to destabilize the PSA + DCS system by adding calcium ions. This can be explained by the formation of a complex between polygalacturonic acids and calcium ions, which may absorb and flocculate the colloidal particles and destabilize the latter. Meanwhile, in the presence of calcium ions, the polygalacturonic acids were hydrolyzed by pectinase, and their effect on the stability of the colloidal system was eliminated.

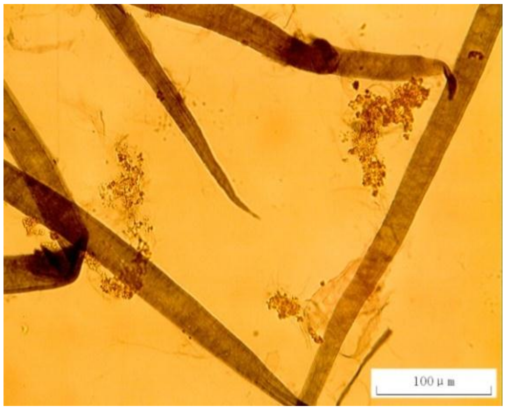
As shown in Fig. 7, with the same addition of calcium ions, the deposition of stickies decreased due to a decrease of the DCS or the pectinase-treated DCS in the PSA system. A possible reason is that the complex formed from calcium ions and components in DCS, such as polygalacturonic acids and fatty acids, were less tacky than those from calcium ions and PSA. In addition, compared to the PSA + DCS system, pectinase-treated DCS did not result in a decrease of sticky deposits caused by calcium ions in absence of cationic polymers.

Microscopic Observation of Stickies Adsorbed on Fibers

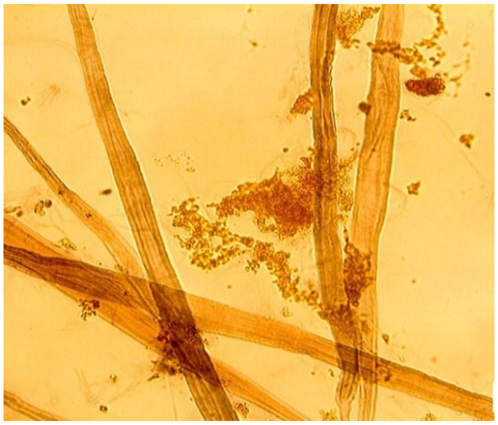
It can be seen from Fig. 8(a) that, in presence of 40 mg/L PEI, many sticky floccules were adsorbed on the fibers in the PSA system and did not tend to be deposited.



(a) PEI 40 mg/L, PSA system



(b) PEI 40 mg/L, PSA+DCS system



(c) PEI 40 mg/L, PSA+P-DCS system

Fig. 8. Adsorption of sticky particles on fibers

At the same addition of PEI, fewer sticky floccules on the fibers, *i.e.*, some free floccules, were observed after adding prepared DCS, as shown in Fig. 8(b). Due to the DCS's negative effect on the efficiency of cationic polymers, it may be suggested that the destabilized sticky floccules could not be adsorbed on the fibers because of cationic polymers. The free destabilized sticky particles were more easily deposited because they were not adsorbed on the fibers. After treating the DCS with pectinase, fewer free sticky floccules were observed, while more sticky floccules were absorbed on the fibers, as shown in Fig. 8(c), which led to a decrease of stickies deposition.

CONCLUSIONS

1. In the presence of cationic polymers, the DCS prepared from BCTMP deteriorated the deposition behavior of sticky substances. The anionic components in the DCS negatively affected the efficiency of cationic polymers, so the destabilized sticky particles could not be adsorbed on the fibers effectively and tended to deposit.
2. Polygalacturonic acids, a major component in anionic DCS, were degraded by the pectinase treatment, and the efficiency of cationic polymers was improved. Subsequently, more destabilized stickies were adsorbed on the fibers, and stickies deposition was reduced. Therefore, the pectinase treatment could be used as a potential approach for stickies control of a mixture of high yield pulp and DIP, as well as their whitewater treatment. However, the pectinase treatment of DCS was not effective for the reduction of stickies deposition caused by calcium ions in absence of cationic polymers.

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