EFFECT OF POLYMERS AND METAL IONS ON THE BEHAVIOR OF PITCH FROM A SPRUCE TMP-BASED SPECIALTY PAPER MILL BASED ON DSC AND CONFOCAL LSM ANALYSIS

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The appropriate pitch control is critical in many pulp and paper operations. One of the important approaches for pitch control is to use synthetic polymers. In this paper, we provide evidence from differential scanning calorimetry (DSC) analysis that the pitch deposits formed with polymers, such as polyDADMAC and CPAM, had better thermal stability than those without these polymers. Metal cations also affected the thermal stability of deposited pitch, depending on their valencies. The confocal laser scanning microscope (CLSM) was used to determine the distribution of pitch in the handsheets, and the results showed that polymers can aggregate pitch particles, which facilitates the retention of pitch on the paper sheet.

Keywords: Pitch control; TMP; Polymers; DSC; CLSM

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INTRODUCTION

In a number of pulping and paper making processes, extractives from wood chips, which may be comprised of fatty acids, resin acids, and triacylglycerols, can be released from different pulp and paper operations, such as pulping and bleaching (Ni et al. 1999b). They have many negative effects on the product quality and processes and are known as the "pitch problem" (Laubach and Greer 1991; Hubbe et al. 2006). Irving Paper in Eastern Canada experienced significant pitch-related deposit formation at the super-calendering roll, which resulted in negative impact on the operation and product quality. In the literature (Hubbe et al. 2006), various approaches for pitch control have been suggested, including the use of adsorbents, multivalent inorganic cations, polyelectro-lytes, non-ionic polymers, dispersants, surfactants, solvents, enzymes, and even mechanical treatment. One of the most common ways would be to use polymers, such as poly-(diallyldimethylammonium chloride) (polyDADMAC) or a cationic copolymer of acrylamide (CPAM). The mechanisms of various polymers for this purpose are somewhat different, depending on their chemistry/ properties. For the high molecular weight polymers, the so-called bridging mechanism may be dominant, whereas for highly-charged cationic polymers, the attraction between oppositely-charged pitch and polymers can be the driving force, and the polymers function as coagulants (Hubbe et al. 2006; Leroux et al. 1997). At Irving Paper, the polyDADMAC/CPAM chemistry was shown to be effective in decreasing the pitch deposit formation in the supercalendering roll (Dai, et al. 2011). Therefore, one objective of this paper was to gain further understanding of the pitch/ polymer interactions, in particular, in relation to the deposit formation in the supercalendering roll.

Pitch particles, suspended in process water, may be spherical in shape with diameters in the range of 0.2 to 2μm (Allen 1975). It was reported that the addition of cationic polymers can increase the diameter of pitch agglomerates up to 10 μm (Shetty et al. 1994). Different combinations of polymers have been investigated for the purpose of controlling the pitch-related deposit formation. By using a dynamic drainage jar, it was shown that for a 100% thermomechanical pulp (TMP) furnish, treatment with PEO, using a conventional phenol formaldehyde cofactor, offered the best results under the condition of low shear force, while PEO with a modified phenol formaldehyde cofactor was the best under the condition of high shear force (Allen and Lapointe 2005a,b). It was also found that the dual polymer system, consisting of polyDADMAC and CPAM, was effective in a pulp furnish made of 70% TMP and 30% DIP (Allen and Lapointe 2006).

Various metal ions, such as ferric (Fe^{3+}), aluminum (Al^{3+}), calcium (Ca^{2+}), manganese (Mn^{2+}), and magnesium (Mg^{2+}), may be present in a paper mill (Ni et al. 1997, 1999a). These metal ions can originate from wood and/or process water. Chemicals used in the process, for example, magnesium hydroxide in the bleaching process (Li et al. 2005), may also increase the magnesium concentration in the mill process water. Their presence can bring about negative impacts on the product quality, for example, paper brightness (Hua and Laleg 2008; Ni et al. 1997; Ghosh and Ni 1998; Mao and Ni 2008), and on the operations, including the formation of pitch-related deposits (Dai et al. 2011). We have shown (Dai and Ni 2010) that the presence of metal ions in the pitch dispersion can have great impact on the thermal stability of pitch deposits formed. For example, pitch deposit material formed from trivalent metal ions, such as Fe^{3+} or Al^{3+}, were more stable than those formed from divalent metal ions, such as Ca^{2+} or Mg^{2+}, when they were subjected to a heating treatment. However, in a real papermaking process, not only metal ions are present but also various polymers such as polyDADMAC and CPAM, are also present in the process. Therefore, another objective of this study was to investigate the impact of using polymers on improving the thermal stability of the pitch with or without the presence of metal cations.

In this study, we also determined the pitch distribution in paper sheets with or without the addition of various polymers. This was done by using confocal laser scanning microscopy (CLSM) (Willfor et al. 1997) after staining the pulp fibers.

MATERIALS AND METHODS

The pitch deposit sample was obtained from the supercalender stack of a TMP-based paper mill in Eastern Canada. The sample was then dissolved with acetone to extract acetone-dissolvable substances, followed by centrifugation at 3000 rpm for 30 min to separate the suspended solids. The thus obtained supernatant was added into deionized water drop by drop with magnetic agitation, and then the pitch material was prepared by dialysis in deionized water to remove acetone (Sundberg et al. 1996). The samples thus obtained were dried in a vacuum desiccator before the DSC analysis.

Various polymers were used in this study and their physical properties are listed in Table 1. All of them were at a 0.5% solution concentration for storage and were diluted to 0.05% before use.

Mill results showed that the acetone extractives content in the TMP going to the paper machine was around 1% (Dai et al. 2011). A typical dosage of polymer for the deposit control purpose was in the range of 1 to 3kg/t pulp (Allen and Lapointe 2005a,b). In this study, the total dosage of polymers to pitch was fixed at 0.1% (mass); for the dual-polymer system, where the ratio between polyDADMAC and CPAM was set at 2:1.

Table 1. Properties of Polymers Used in this Study

Polymer	Molecular Weight (Da)	Charge Density (meq/g)
Highly cationic polyacrylamide (HCPAM)	7.0×10^6	+1.1
Medium cationic polyacrylamide (MCPAM)	5.0×10^6	+1.5
Poly-diallyldimethylammonium (PolyDADMAC)	200,000	+3.7
Polyethylene oxide (PEO)	800	N/A

The metal ion solutions were prepared by dissolving their salts ($CaCl_2$, $MgSO_4$, $FeCl_3$, and $AlCl_3$) in de-ionized water. The concentrations, for Ca^{2+} and Mg^{2+}, were 1 mol/L, while it was 0.1 mol/L for Fe^{3+} and 1g/L for Al^{3+}.

A differential scanning calorimeter (DSC) was used to determine the thermal stability of pitch deposits when they were subjected to a heat treatment. This was carried out on a computer-controlled DSC Model 2100 (TA Instruments). The method consisted of an equilibration at 25 °C for 5 minutes, a ramp of 2 °C/min, and an equilibration at the final temperature of 200 °C for 2 minutes.

A confocal laser scanning microscope (LEICA TCS-SP2) was used to determine the distribution of pitch particles in the paper handsheets. We followed the procedures established in the literature for this purpose (Willfor et al. 1997).

RESULTS AND DISCUSSION

The thermal transition profiles are shown in Fig. 1. It was noted that the presence of polymers had almost no impact on the pitch thermal performances at a low temperature (around 40 °C). At a high temperature (at 120 °C), the auto-polymerization of pitch was observed. With the addition of polymers, this auto-polymerization behavior was decreased, and the thermal stability of pitch deposits was improved. Therefore, it can be concluded that the presence of polymers not only decreases the pitch deposition (Dai et al. 2011), but also decreases the pitch tackiness within a temperature range of 100 to 200 °C, which is of practical interest for decreasing the pitch-related deposit formation at the calendaring roll of the spruce TMP based specialty paper manufacturing process (Dai and Ni 2010).

By comparing the results from different polymer systems (Fig. 1), one can find that the dual-polymer systems were more effective than the single-polymer system in improving the thermal stability. The system of high charge density CPAM and polyDADMAC was the most effective.

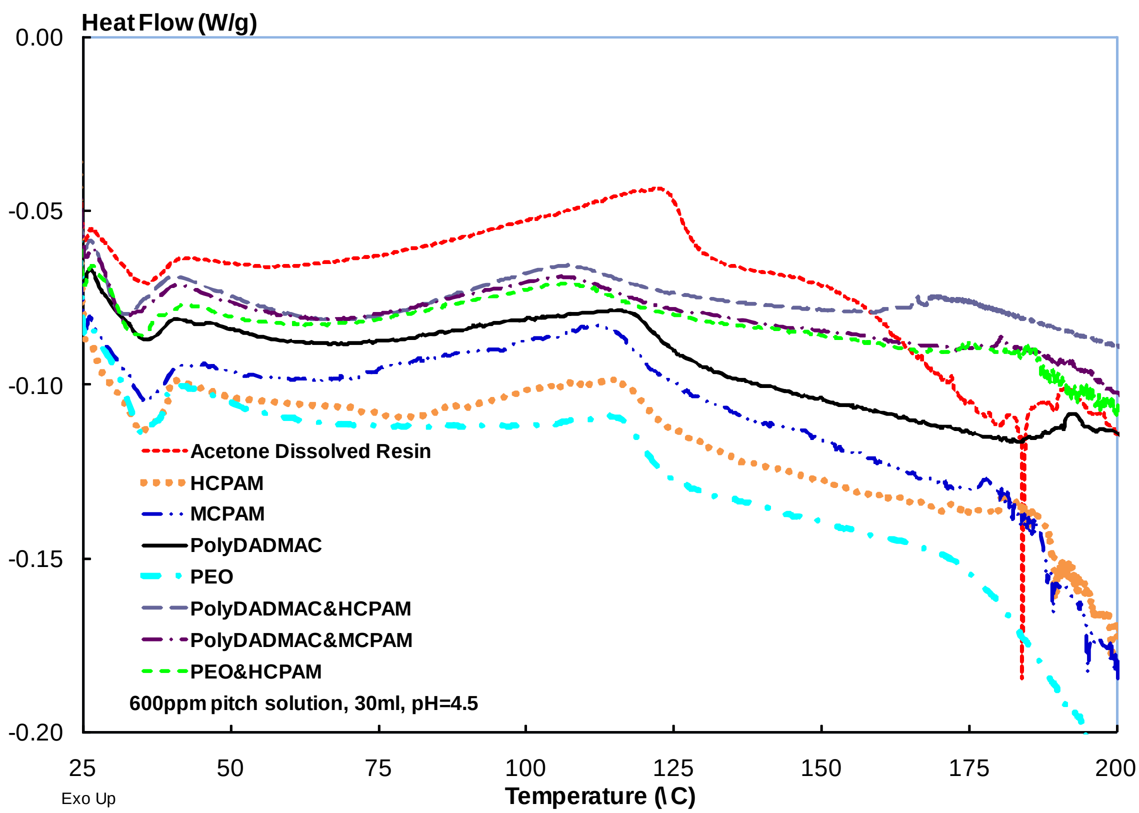

Fig. 1. Effect of different polymer systems on the pitch thermal properties

When applying polymers to pitch dispersion, a homogeneous pitch suspension was formed with polyDADMAC, while the addition of CPAM or PEO led to the formation of pitch agglomerates, indicating that the high molecular weight polymers were more effective than the high charge density polymers on agglomerating the pitch particles.

In the polyDADMAC/CPAM dual-polymer system, the combined effect from charge neutralization and bridging flocculation can result in the formation of larger pitch particles. This explains why the pitch deposits were isolated much more easily when the dual polymers were added to the dispersion. Subsequently, after centrifugation, the pitch dispersion with dual-polymer was much clearer than that from the single-polymer system. It was reported that the combination of charge neutralization and bridging flocculation is effective in controlling pitch in a TMP-based newsprint manufacturing process (Leroux et al. 1997).

Interaction of Polymers and Metal Cations

Metal ions can be important factors in determining the thermal stability of pitch dispersions (Dai and Ni 2010). Calcium, ferric, magnesium, aluminum, and others are present in the pitch deposits during the production of hemp pulp (Gutierres and Del Rio

2005). The authors have found that large amounts of metal ions (e. g. Ca^{2+} of up to 2000 ppm, Mg^{2+} of up to 300 ppm) were in the deposit samples from a TMP-based specialty paper mill (Dai et al. 2011).

To simulate the effect of polymers/metal ions on the thermal stability of a pitch-containing system, poly-DADMAC was added first, followed by the addition of metal ion, and then HCPAM. The results are shown in Fig. 2. It should be noted that the metal concentrations were chosen based on their typical profile in the mill deposit samples (Dai et al. 2011). It can be found that Ca^{2+} and Mg^{2+} can cause significant thermal instability of pitch deposits, whereas the thermal performances of deposits were more stable for Al^{3+} and Fe^{3+}, implying that the presence of Ca^{2+} or Mg^{2+} may cause more trouble in potentially forming pitch-related deposits than Al^{3+} or Fe^{3+}. Likely, the aggregates formed, such as resin and fatty acid salts, would be more sticky, and undergo more thermal transformation for divalent metals, like, Ca^{2+} and Mg^{2+}, upon heating.

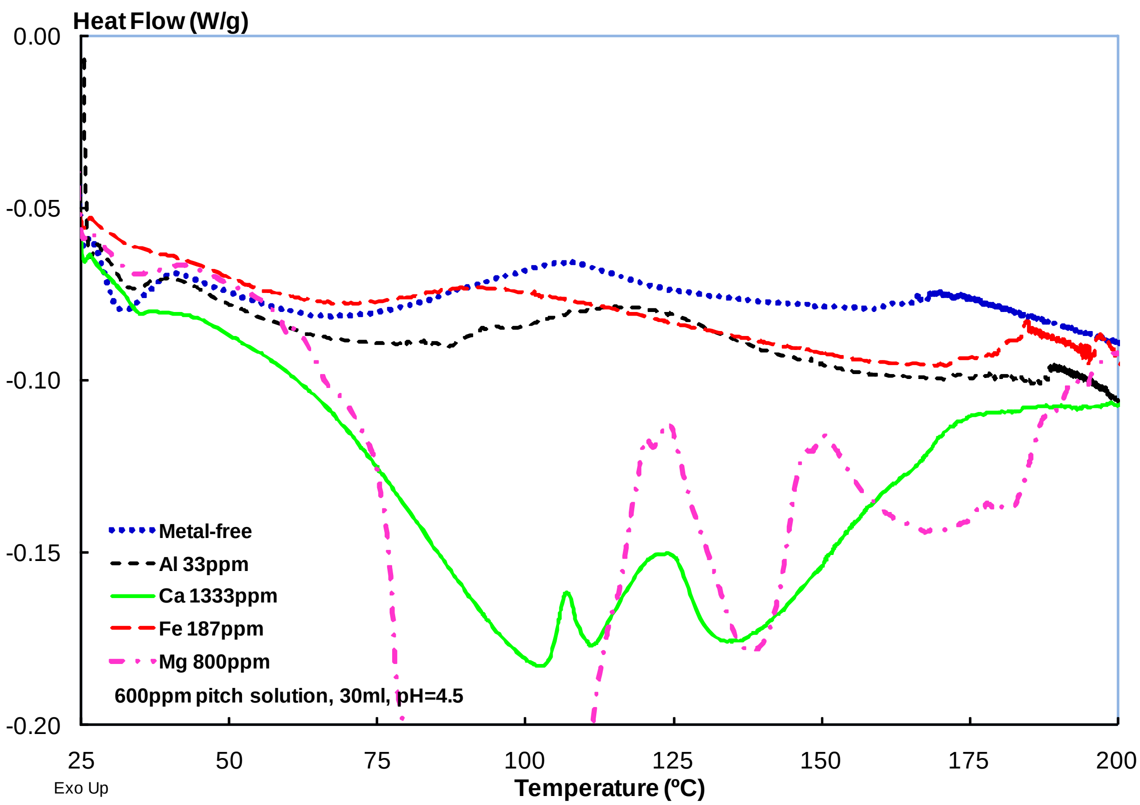

Fig. 2. Thermal stability of pitch/metal cation systems in the presence of polyDADMAC-HCPAM

Shown in Fig. 3 are the results in the presence of multi metal ions. Without Ca^{2+} and Mg^{2+}, the pitch deposit had reasonable thermal stability. Furthermore, it appears that there were two melting zones for the Ca^{2+}- and Mg^{2+}-containing systems. The presence of Mg^{2+} shifted the melting behavior to a lower temperature than that of Ca^{2+}. These results indicated that the presence of Ca^{2+} and Mg^{2+} may lead to more pitch-induced deposit formation.

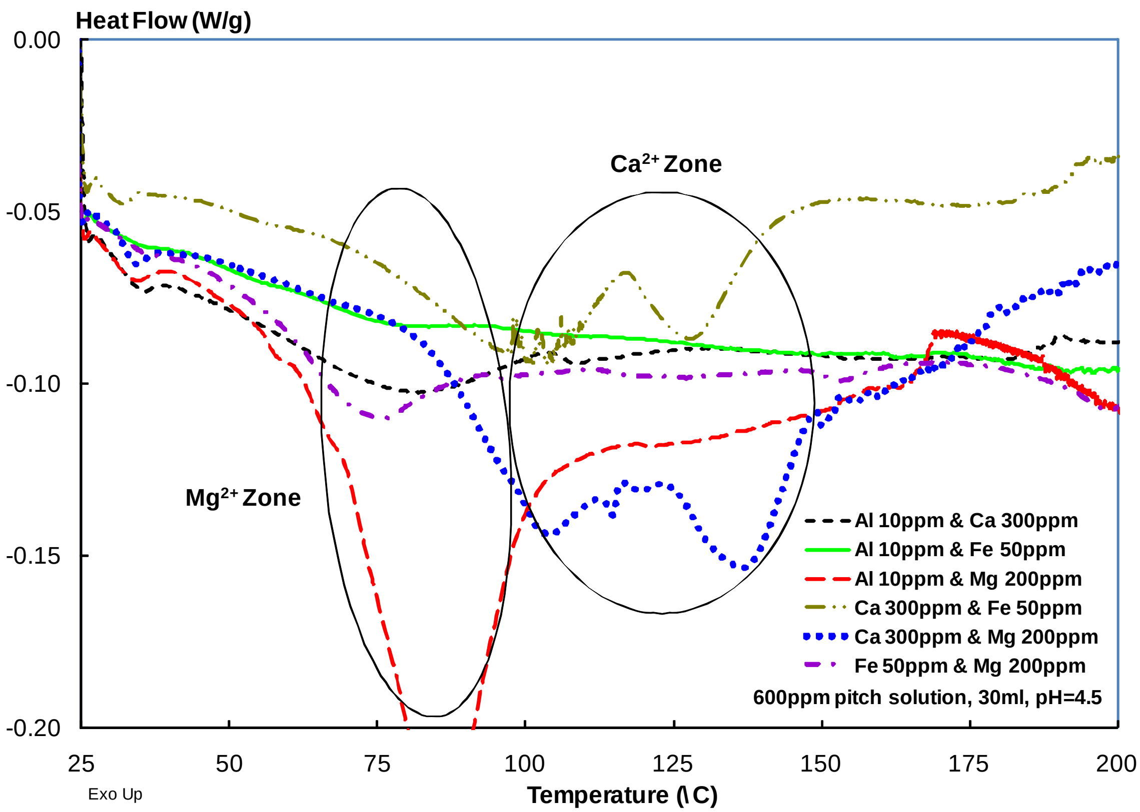

Fig. 3. Thermal stability of pitch/multi metal cation systems in the presence of polyDADMAC and HCPAM

Retention of Pitch

An extractive-free TMP was used in this set of experiments, and the same amount of pitch (0.6%) was added to the system with different polymer additives for the purpose of retaining the added pitch on pulp fibers.

Without the addition of any polymers, the pitch retention in the handsheet was 0.3% under the conditions studied; with the addition of polyDADMAC/MCPAM, the retention of pitch was the highest (0.55%). The presence of Ca^{2+} or Mg^{2+} had a negative impact on the retention of pitch particles onto the handsheets, and the pitch retention decreased to 0.42% at the addition of 50 ppm Ca^{2+} or Mg^{2+}.

By using the dye, the pitch particles were observed as colored balls under CLSM, as shown in Fig. 4. Without the addition of polymers, pitch particles were barely visible in the handsheets. With the retention chemistry, the pitch particles in handsheets became much bigger, therefore more visible, which is certainly due to the pitch agglomeration. The increase in the particle size also facilitates the capturing of pitch particles in the fiber network.

In the presence of Ca^{2+} or Mg^{2+}, the pitch aggregates were actually decreased, resulting in a less pitch retention in the handsheets.

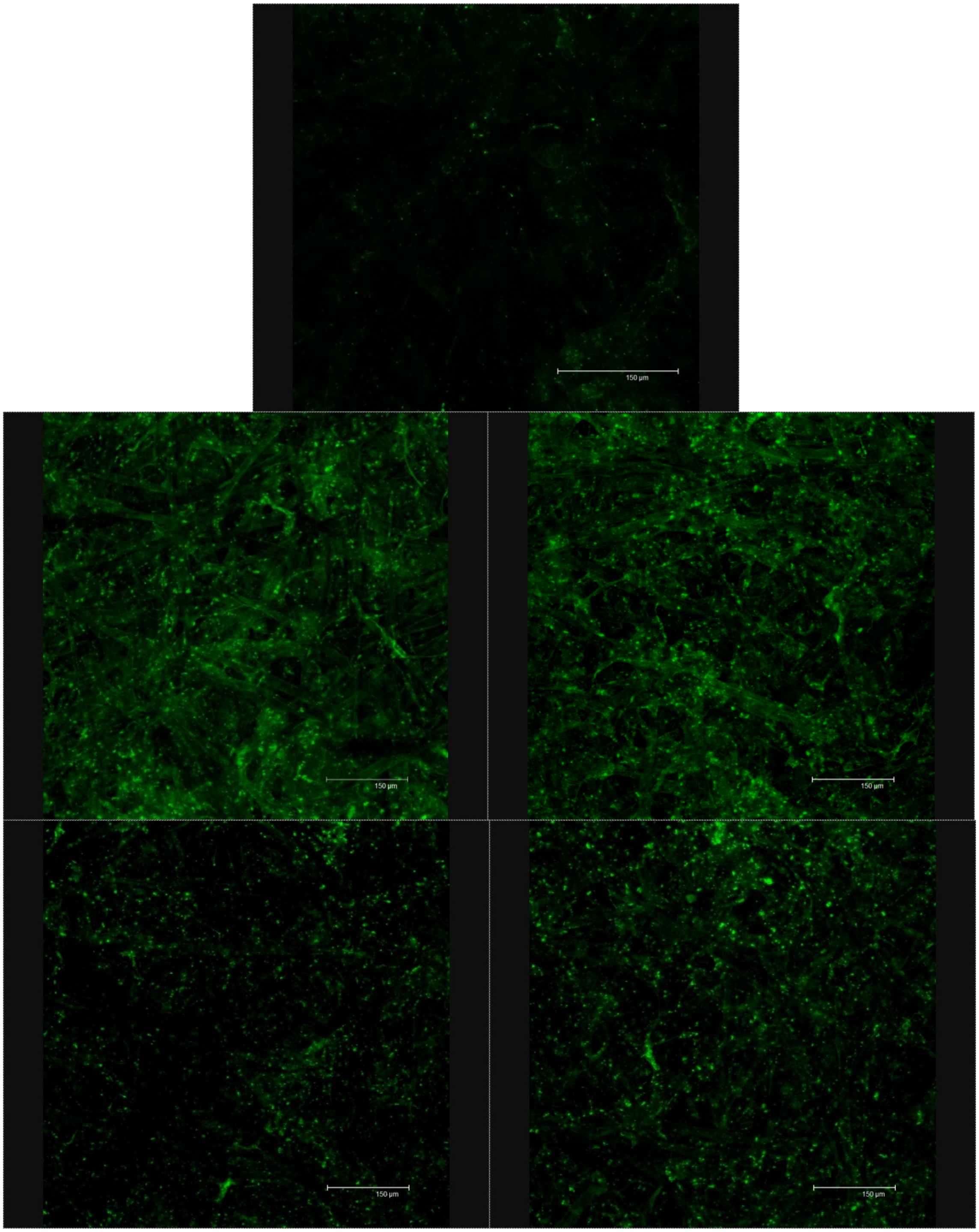

Fig. 4. Pitch distribution in handsheets from CLSM analysis (Top: Control sample without polymers, its pitch retention was 0.30%; mid-left: 0.1% polyDADMAC, its pitch retention was 0.50%; mid-right: 0. 1% polyDADMAC, 0.05% MCPAM, its pitch retention was 0. 55%; bottom-left: 0.1% polyDADMAC, 50ppmCa^{2+}, 0.05%MCPAM, its pitch retention was 0.42%; bottom-right: 0.1% polyDADMAC, 50 ppm Mg^{2+}, 0.05% MCPAM, its pitch retention was 0.42%).

CONCLUSIONS

The evidence from the present investigation further supported the notion that using cationic polymers can improve the thermal stability of the pitch dispersion, therefore, decreasing the pitch-related deposit formation. The DSC results showed that the addition of polymers to the pitch system resulted in more stable thermal behavior when the sample was subjected to heating treatment, in comparison to the untreated pitch. A dual-polymer system consisting of polyDADMAC and CPAMs showed the best results in improving the thermal stability of pitch deposit, under the conditions studied. Divalent metal cations, such as Ca^{2+} or Mg^{2+}, destabilized the pitch deposits. Deposits formed with Mg^{2+} melted at a lower temperature than those with Ca^{2+}. Trivalent cations, such as Al^{3+} or Fe^{3+}, had negligible impact on the deposit stabilization. When multi-metal cations were present, the deposit formed in the presence of Mg^{2+} started melting at a lower temperature than that with Ca^{2+}. The confocal LSM results supported the conclusion that treatments using polymers can retain more pitch onto the fiber network, while metal cations decreased the pitch retention. The function of polymers was to aggregate the pitch particles.

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