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Hydrophobically Associating Polyethylenimine for Controlling Dissolved and Colloidal Substances of Alkaline Peroxide Mechanical Pulp

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In a paper mill's water circuit, normal runnability of the paper machine is often disturbed due to buildup of hydrophobic dissolved and colloidal substances (DCS), such as wood pitch, white pitch, and stickies. General cationic fixing agents such as hydrophilic polymers do not always work to minimize these problems. In the present study, two kinds of novel hydrophobically associating polyethylenimine (PEI) coagulants grafted by acetic anhydride and 1,2-epoxydodecane, named PEI-Ac and PEI-Ed, respectively, were synthesized to remove hydrophobic DCS. The performances of the modified PEI samples were evaluated using a model suspension containing alkaline peroxide mechanical pulp (APMP) and styrene-butadiene latex. The results showed that the modified PEI was more inclined to interact with hydrophobic substances than was non-modified PEI. The relationship between DCS removal and non-modified or modified PEI content was not linear, but there was a maximum. The turbidity and particle counts of model suspensions decreased 30% and 80%, respectively, when the dosage of PEI-Ed(a) was 0.025%. Compared with the 72.8% decrease in the case of non-modified PEI, cationic demand decreased by 67.7% when the PEI-Ed(a) concentration was 0.2%. It was also found that PEI-Ed had a better affinity for DCS than PEI-Ac, which may be because the PEI-Ed had a long hydrophobic chain.

Keywords: PEI; DCS; Alkaline peroxide mechanical pulp; Fixing agent

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INTRODUCTION

Dissolved and colloidal substances (DCS) in a papermaking system continuously accumulate with increases in the usage of waste paper pulp, high-yield pulp, and whitewater closure. These build-ups lead to many serious problems, such as poor runnability of the paper machine, inefficiency of chemicals, and poor physical properties of the paper produced (Habets *et al*. 1997; Rundlof *et al*. 2002; Francis and Ouchi 2001; Whipple and Maltesh 2002). Because of their ability to fix and bind DCS onto fibers, fixing agents are widely used to remove DCS from the system for cleaner production (Wågberg *et al*. 2007; Mclean *et al*. 2010). Traditional fixing agents are hydrophilic polymers with high charge density and low molecular weight, which will cause self-agglomeration of colloidal particles. The agglomerates are easily precipitated from the whitewater system and lead to more deposition on the surface of the paper machine (Maher *et al*. 2007). An even more serious issue is that completely hydrophilic polymers can be relatively ineffective for control DCS containing large amounts of hydrophobic substances (such as styrene-butadiene latex, polyacrylate, fatty acids, or resin acids), in comparison to hydrophobic polymers (Murata *et al*. 2012; Hlivka and Wai 1998).

Fixing agents with partially hydrophobic character might be a way to achieve favorable solubility characteristics between polyelectrolytes and tacky materials, ensuring sufficient adsorption onto tacky materials (Hubbe *et al*. 2006). Currently, hydrophobic polymers have been gradually applied to control DCS in the papermaking process. Petzold *et al*. (2012) found that benzyl starch and chitosan with a high charge density could decrease turbidity and TOC by charge neutralization and that benzyl starch and chitosan with a low charge density could remove stickies significantly with hydrophobic action. Sakai invented an effective coagulant by changing the charge density, molecular weight, and hydrophobicity. This kind of multifunctional organic polymer could reduce free pitch particles in the process by fixing micro-pitch onto fibers before growing into a large-size pitch (Sakai *et al*. 2007).

Polyethylenimine (PEI) is widely used as an effective fixing agent because of its high charge density and adjustable molecular weight (Baumann *et al*. 2002; Gill 1996). However, hydrophobically associating PEI has not received much attention for its ability to remove DCS and avoid particle self-agglomeration. In this study, two kinds of novel hydrophobically associating PEI, which involved grafting with acetic anhydride and 1,2-epoxydodecane, were synthesized to reduce issues associated with pitch. Interactions between model suspensions with modified PEI were characterized by measuring characteristics such as turbidity, cationic demand, surface tension, and particle size.

EXPERIMENTAL

Acylation of Polyethylenimine

PEI (70 kDa) was purchased from Aladdin Industrial Inc. and purified by freeze-drying before use. The synthesis procedures for PEI-Ac were adopted from previously published methods (Nimesh *et al*. 2007). Briefly, PEI (2 g) was suspended in 25 mL of dry methanol, followed by drop-wise addition of acetic anhydride with continuous stirring at 60 °C. The reaction solution was stirred at 60 °C for 12 h and quenched by the addition of 5 mL of double distilled water. The reaction mixture was re-dissolved in distilled H_2O (20 mL) and dialyzed against 5% aqueous sodium bicarbonate solution for three days; the product was then dried by freeze-drying for 24 h (Fig. 1, route A).

Synthesis of Alkyl-Grafted PEI

1,2-epoxydodecane as an alkylating agent was also purchased from Aladdin Industrial Inc. and was used without further purification. The synthesis procedure followed a previously described procedure (Chen *et al*. 2007). Two grams of PEI was suspended in dry methanol (25 mL), followed by the drop-wise addition of 1,2-epoxydodecane with continuous stirring under a nitrogen atmosphere at 60 °C for 12 h. After the solvent was removed by a rotary evaporator, the viscous solution was poured into hexane to precipitate the polymer. Finally, the product was dried at 60 °C for 48 h in a vacuum oven (Fig. 1, route B).

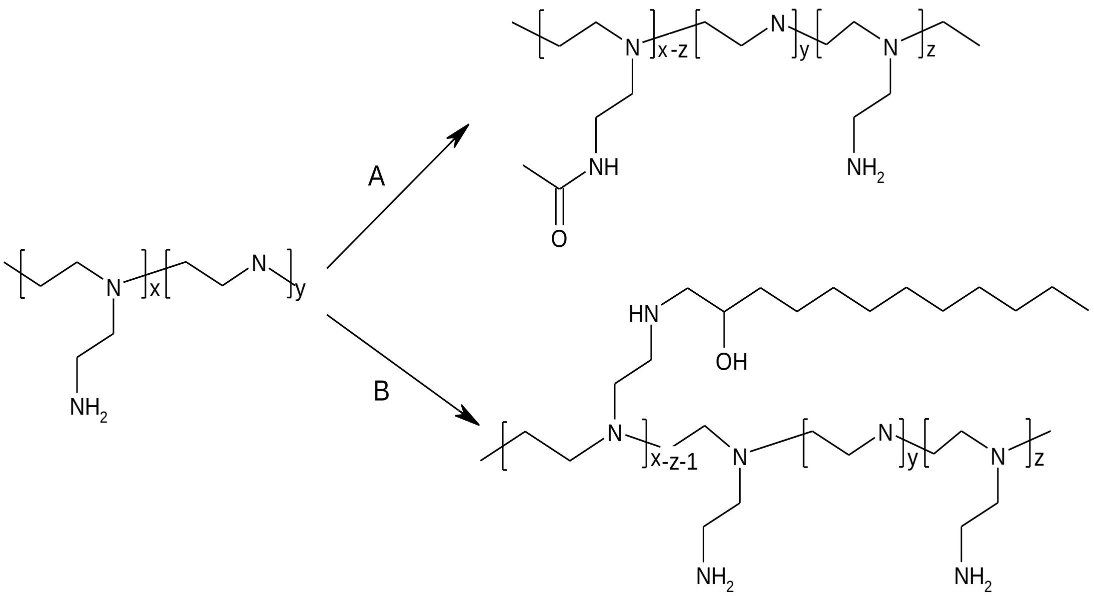


Fig. 1. Modification reaction of PEI with acetic anhydride (A) and 1,2-epoxydodecane (B)

Preparation and Characterization of Model Suspension

Seventy grams of dry APMP was first dispersed by stirring in water to form a 2% suspension solution at 60 °C. Seven grams of commercial styrene-butadiene latex (50% solid content) was added, and the mixture was then diluted to 1% after stirring at 60 °C for 1 h. After cooling to room temperature, a certain mount of PEI was added and mixed for 1 min at 400 rpm in a DSC75 DDJ (Paper Research Materials Inc., USA). Finally, the suspension was diluted to 0.5%, dispersed at 750 rpm for 1 min, and filtrated with a 200-mesh filter screen to collect white water and wet fibers.

The turbidity of the collected white water was tested using a 2100P turbidity instrument (Hach, USA). The surface tension of white water was measured with a DCAT21 surface and interface measurement instrument (Sartorius, Germany). Particle size and distribution were characterized by focused beam reflectance measurement using a D600L (Mettler-Toledo, USA) device.

White water was centrifuged at 2000 rpm for 20 min to obtain DCS samples. The charge densities of different PEI and the cationic demand of the DCS samples were examined using a particle charge detector, PCD-04 (Mütek, Germany) with a standard 0.001 N PES-Na and a standard 0.001 N poly-DADMAC.

Substitution degree of hydrophobic groups were tested by Aplus-400 (Brucker, Germany) for ^{1}H NMR.

Molecular weight of different PEI were measured by DAWN HELEOS-Optilab rEX (Wyatt, USA) equipped with a HPLC pump (Waters, USA). The eluent was 0.5 M acetic acid and 0.5 M sodium acetate solution. The flow rate was 0.6 mL/min, and the operating temperature was 40 °C.

Finally, the fiber with the agglomeration of DCS after freeze-drying (including styrene-butadiene latex) was observed using an SEM, EVO18 (ZEISS, Germany).

RESULTS AND DISCUSSION

Preparation and Characterization of Modified PEI

The active primary amine of PEI could be grafted with hydrophobic groups using nucleophilic addition reaction with a micro-molecular modification method. The charge density of PEI modified with either acetic anhydride or 1,2-epoxydodecane is shown in Table 1. It is clear that the charge density of PEI decreased after the hydrophobic substituent groups substituted their side chain amino groups, and it was further reduced when the degree of substitution increased. Molecular weight of PEI increased after graft modification, and it was increased with increasing degree of substitution. However, the effect on PEI charge density of the two hydrophobic groups with the same substitution degree was almost the same.

Table 1. Properties of Non-modified PEI and Modified PEI

	Amount of hydrophobic reactants	**Substitution degree of hydrophobic groups**	**Charge density (meq/g)**	**Molecular weight (Mw)**
Unmodified PEI	-	-	12.2	70000
PEI-Ac a	5%	3.4%	10.2	70980
PEI-Ac b	20%	15.8%	8.8	77050
PEI-Ed a	5%	4.4%	10.0	72700
PEI-Ed b	20%	18.1%	8.2	83700

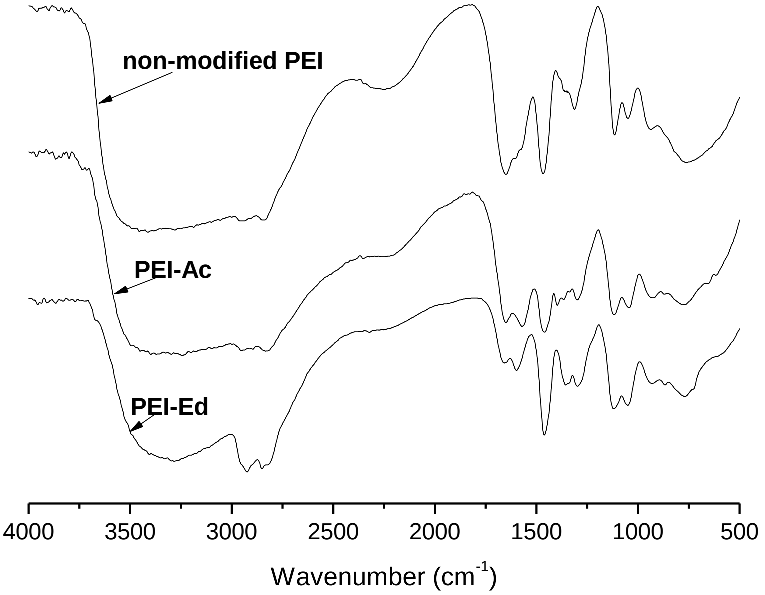


Fig. 2. FT-IR spectra of non-modified PEI, PEI-Ac, and PEI-Ed

Figure 2 shows the FT-IR spectra of non-modified PEI, PEI-Ac, and PEI-Ed. Wavenumbers 3300 to 3500 cm^{-1} show a characteristic stretching vibration peak of an N-H bond of a primary amine, and wavenumbers 2833 to 2958 cm^{-1} show a characteristic stretching vibration peak of a C-H bond of methylene. The methylene peak of PEI-Ed is more noticeable than that of the other materials. The peak at 1650 cm^{-1} is representative of a deformation vibration of an N-H bond and it is split into two peaks and shifted to a long wavelength because of the substitution reaction of a primary amine. The C-H deformation vibration adsorption peak of methyl appeared at 1365 cm^{-1} (Nimesh *et al*. 2007; Chen *et al*. 2007).

Figure 3 shows the ^{1}H NMR spectra of non-modified PEI, PEI-Ac, and PEI-Ed in CD_3OD. The signal at δ 2.62 to 2.74 ppm was assigned to ($-N-CH_2-CH_2-N-$), and the signal of ($-NH_2$) was generated at δ 4.85 ppm. δ 1.84 ppm in the PEI-Ac ^{1}HNMR was assigned to ($CH_3C=O$), while δ 1.33 ppm and δ 0.91 to 0.93 ppm in the PEI-Ed ^{1}HNMR spectra were assigned to ($-CH_2-$) and ($-CH_3$), respectively.

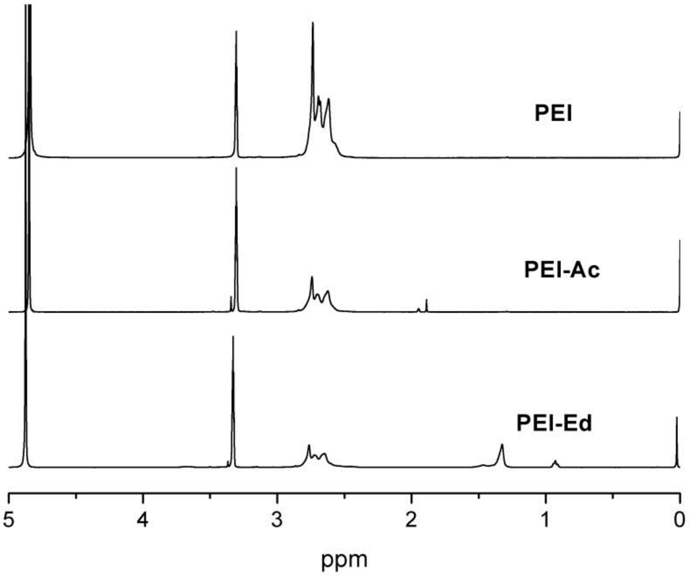


Fig. 3. ^{1}H NMR spectra of non-modified PEI and modified PEI in CD_3OD

DCS Treatment with Non-modified PEI and Modified PEI

When fixing agents interact with DCS, some colloidal substances will coagulate and easily fix to fibers to decrease the turbidity of white water; other dissolved substances will agglomerate and easily precipitate out of solution to increase the turbidity of white water (Dunham *et al*. 2002). Figure 4 shows the effects of non-modified PEI and modified PEI on the turbidity of the solution. The turbidity of the solution decreased with increasing various PEI dosage, and PEI-Ed(a) was the best at removing DCS. When the non-modified PEI dosage was 0.025%, the turbidity of the solution showed only a 3% reduction, while modified PEI decreased the turbidity by more than 30%. That means the interaction of modified PEI with hydrophobic substances (styrene-butadiene latex) was greater than that of non-modified PEI. When the additive amount exceeded 0.05%, the effects of various PEI solution turbidities were nearly the same. Although non-modified

PEI showed no affinity toward hydrophobic DCS, the strong charge neutralizing capacity offsets its deficiencies with higher amounts of additives.

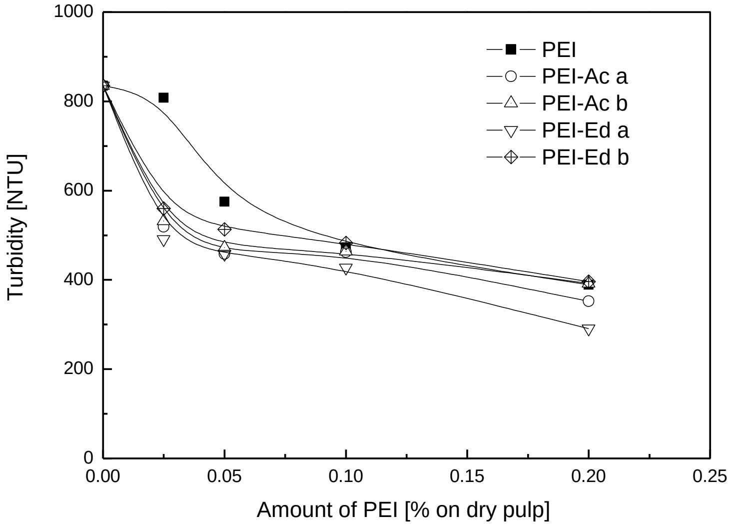


Fig. 4. Effect of various PEI content on the turbidity of solutions

The DCS removal capability of various PEI samples improved with their hydrophobic character. However, when adding excess modified PEI, the force between modified PEI and DCS is greater than that between fibers and modified PEI, which results in self-agglomeration of DCS (Esser *et al.* 2005). As a result, the turbidity of the model suspension would not decline remarkably.

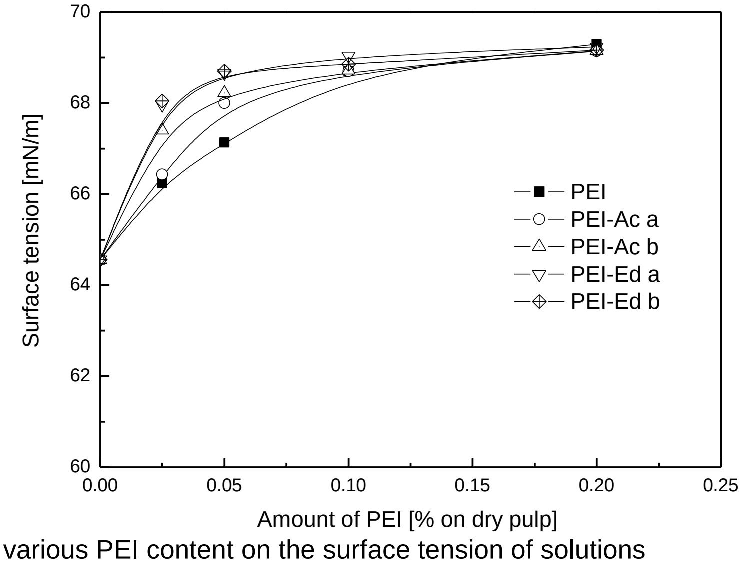


Fig. 5. Effect of various PEI content on the surface tension of solutions

The surface tension curves of solutions with different PEI contents are compared in Fig. 5. When adding a small dosage of various PEI samples, the surface tension of the suspension with modified PEI increased more than did that with the unmodified PEI solution. While the amount of various PEI added exceeded 0.1%, the solution surface tension with various PEI additives tended to be the same, similar to the variation of turbidity described previously. The highest surface tension was about 69 mN/m. It is obvious that the surface tension of PEI-Ed(b) was the highest at the same ratio. PEI-Ed(b) therefore showed the highest capacity for DCS removal. It could be inferred that the surface tension of the suspension primarily depended on hydrophobic action, rather than charge neutralization.

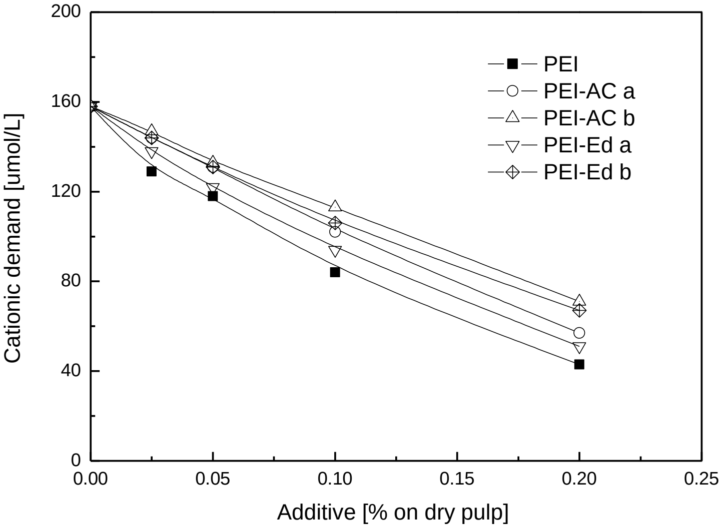
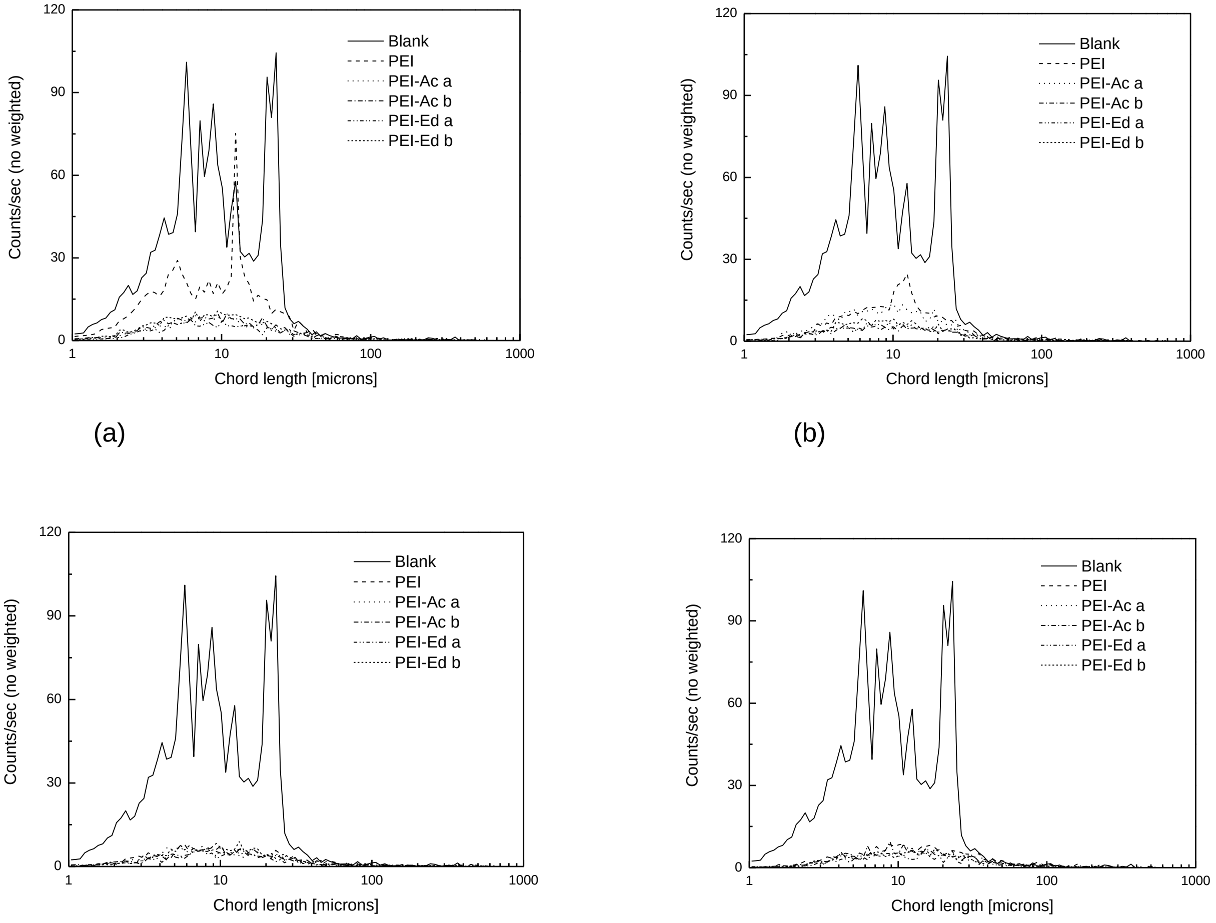


Fig. 6. Effect of various PEI content on the cationic demand of solutions

The cationic demand was determined by standard polymer solutions of poly-DADMAC (cationic) and PES-Na (anionic). As shown in Fig. 6, the cationic demand of solutions decreased with the addition of various PEI. When the dosage was 0.2%, the cationic demand of the solution was reduced by 72.8%, 63.9%, and 67.7% with non-modified PEI, PEI-Ac(a), and PEI-Ed(a), respectively, while the cationic demand with PEI-Ac(b) and PEI-Ed(b) decreased by only 55.1% and 57.6%, respectively. The decrease in cationic demand was consistent with the increase in various PEI amounts, which was different from the results for turbidity and surface tension and may indicate that modified PEI is more efficient than non-modified PEI for fixing hydrophobic DCS on fibers and that the situation is directly opposite for neutralized strongly anionic DCS.

Focused beam reflectance measurement (FBRM) was used to investigate the continuous particle size distribution of DCS (Saarimaa *et al*. 2006 A; Blanco *et al*. 2002; Saarimaa *et al*. 2006 B). The effects of various PEI content on the particle size distribution of the suspension filtrate are shown in Figs. 7 and 8. From Fig. 7, it can be observed that the DCS of the suspension was greatly reduced after the addition of various PEI; moreover, the distribution curves were basically the same after 0.05% addition, which implies that DCS was well fixed on fibers by various PEI. Figure 7 (a and b) also shows that the particle size of various PEI in the filtrate increased, which might come from the agglomeration of DCS.

From Fig. 8, the DCS was primarily composed of particles with sizes below 10 μm and from 10 to 50 μm. When the dosage was 0.025%, about 60% of DCS particles were removed by non-modified PEI, and more than 80% were removed by modified PEI. The removal performance of various PEI improved with the increase in various PEI content; after various PEI content exceeded 0.1%, the residual DCS was less than 10% for both modified and unmodified PEI.



(a) (b)

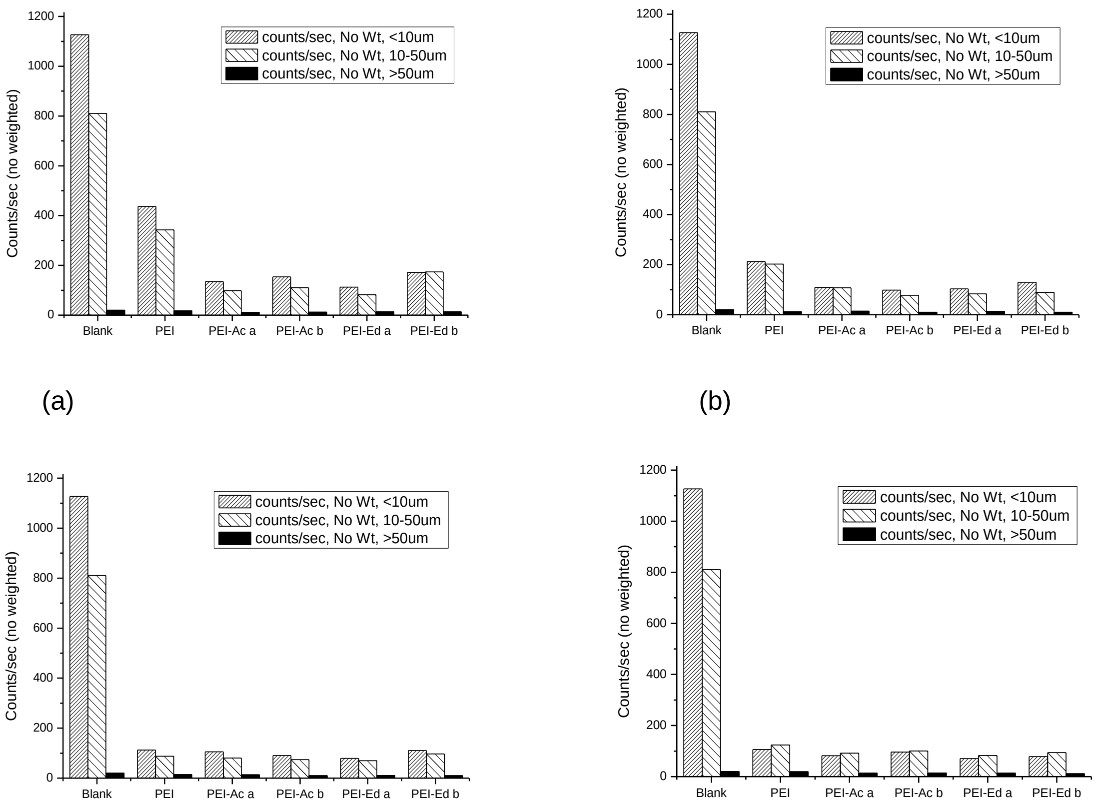
(c) (d)

Fig. 7. Effect of various PEI content on the particle size distribution of the suspension filtrate (a: 0.025% odp, b: 0.05% odp, c: 0.1% odp, d: 0.2% odp)

When various PEI amount reached up to 0.2%, the number of DCS particles in the 10 to 50 μm range was greater than the number of particles in the range below 10 μm. An overdose of various PEI could cause destabilization of DCS, and eventually the collision between destabilized particles might lead to even larger aggregates.

SEM images of DCS agglomeration with various PEI on fiber surfaces are shown in Fig. 9. Styrene-butadiene latex was rarely adsorbed on the fiber surfaces, and there were no polyelectrolyte-DCS complexes visible on the fibers (image A). Polymer-DCS complexes appeared on the fiber surfaces after the addition of various PEI, as can be seen from images B and C.

When the dosage of various PEI was up to 0.2%, more complexes were adsorbed on the fiber surfaces. Much more polymer-DCS complexes and styrene-butadiene latex were fixed onto the surface of fibers with modified PEI, compared to non-modified PEI, as seen in images D and E.



(a) (b)

(c) (d)

Fig. 8. Effect of various PEI content on the number of particles in the suspension filtrate (a: 0.025% odp, b: 0.05% odp, c: 0.1% odp, d: 0.2% odp)

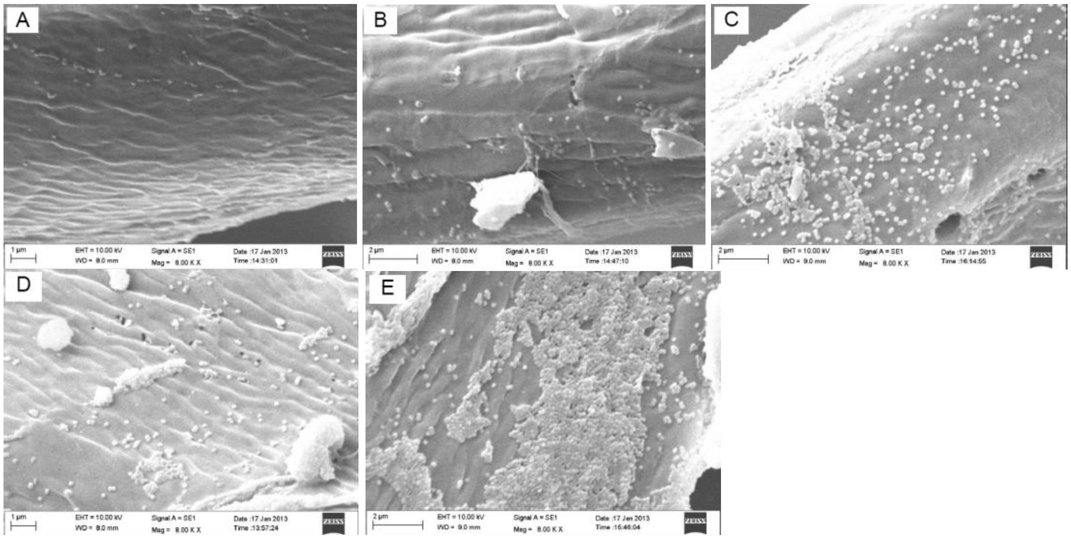


Fig. 9. SEM images of DCS agglomeration (A: blank, B: 0.025% non-modified PEI, C: 0.2% non-modified PEI, D: 0.025%PEI-Ed (a), E: 0.2%PEI-Ed (a))

CONCLUSIONS

1. The interaction between modified PEI and APMP with styrene-butadiene latex led to a significant decrease in turbidity, cationic demand, and particle size distribution of the suspension, but there was an increase in surface tension. PEI-Ed(a) may be the most effective for removing DCS in suspension.

2. The difference between non-modified PEI and modified PEI was attributed to the suitable hydrophobicity and charge density of the modified PEI. Modified PEI had a higher hydrophobicity than non-modified PEI, though its capacity to neutralize strong anionic DCS was lower than that of non-modified PEI. Modified PEI with long hydrophobic side chains had a greater affinity for hydrophobic DCS than that with short hydrophobic side chains.

3. Non-modified PEI fixed DCS onto fibers primarily by charge neutralization and a patch mechanism, but the behavior of fixation of DCS by modified PEI was a combined effect of hydrophobic interactions, charge neutralization, and the patch mechanism.

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