Temperature-Dependent Behavior of Polyethylene Oxide in Papermaking Suspensions

Kh. Kh. Khoultchaev, R. J. Kerekes, and P. Englezos
Pulp and Paper Centre and Dept. of Chemical Engineering, The University of British Columbia,
Vancouver, BC V6T 1Z4, Canada

The adsorption of polyethylene oxide (PEO) on chemi-thermo-mechanical pulp (CTMP), clay, and chalk suspensions was investigated at 303 and 343 K. These conditions corresponded to points below and above the critical solution temperature (CST) of a 0.005 mass % polyethylene oxide solution in the presence of 2 mol/L of KCl. The PEO adsorption on CTMP and clay particles was also studied at different initial PEO concentrations up to 50 mg/L. PEO adsorbed onto papermaking furnish particles at both temperatures, but the adsorbed amount was found to be larger above the CST in all systems. At 303 K it increased with the increase in PEO added to the system until it reached a plateau, but at 343 K it increased with the increase in PEO added in all the range of PEO concentrations up to 50 mg/L. The state of aggregation of PEO-clay and PEO-chalk suspensions was also studied by monitoring fluctuations in the intensity of light transmitted through the suspension. These measurements indicated a strongly temperature-dependent aggregation. It was concluded that the entropically driven phase separation leads to enhanced aggregation, which in turn favors the retention of fiber fines and clay filler.

Introduction

Pelton et al. (1980) demonstrated that polyethylene oxide (PEO) with a molecular mass exceeding 4.0×10^6 can be used as a flocculating agent in some mechanical pulp containing papermaking suspensions. It is customary in papermaking to call the flocculants retention aids. Those pulps were unwashed and hence contained materials which were found to activate the action of PEO. The motivation to use PEO instead of cationic polymeric flocculating agents in mechanical pulp suspensions is the high content of dissolved and colloidal substances (DCS) in these pulps. The presence of DCS reduces substantially the efficiency of cationic retention aids and renders them expensive to use. Further work by Pelton's group (Pelton et al., 1981) revealed that a few parts per million (ppm) of kraft lignin when added to the papermaking suspension render PEO an effective retention aid. Thus, lignin-type chemicals were considered to be the PEO activators. The chemicals which act in a synergistic manner with the PEO are commonly known as cofactors or activators. Phenol-formaldehyde resin (PFR) is one of the most effective cofactors used in industry. Rahman and Tay (1986) reported that a significant improvement in first pass retention is achieved by using PEO and PFR. This was a laboratory study with samples from newsprint paper mills. In a mill study, Barnes et al. (1989) reported an increase from 33 to 47% in the first pass retention by adding a commercial PEO-PFR system to a newsprint furnish.

Pelton and co-workers also pursued the novel idea of preparing copolymers which would combine the advantages of PEO without its disadvantages (Xia et al., 1995a). The sensitivity of PEO to high shear stress, its tendency to chemical degradation and the high cost of PEO with suitable molecular mass, that is, greater than 4.0×10^6 Da are cited as the disadvantages (Xia et al., 1996a). Copolymers of acrylamide and polyethylene glycol in conjunction with PFR were found to improve the retention of fines. It is noteworthy that even though the molar mass of PEO must exceed 4.0×10^6 Da in order to be an effective flocculant, the PEO pendant chains in the copolymer were short, that is, as low as nine monomers. The copolymers were also found to exhibit improved aging resistance compared to PEO and to form complexes with PFR (Xia et al., 1995a, b).

Correspondence concerning this article should be addressed to P. Englezos.

Recently, the state-of-the-art on the use of PEO as a retention aid was presented (van de Ven, 1996). Retention with a PEO-PFR aid was attributed to heteroflocculation with the PEO and the cofactor (van de Ven and Alince, 1996a). This heteroflocculation was named *association-induced polymer bridging* because polymer bridging is facilitated by adsorption of a cofactor-PEO association complex or linkage of PEO to a fiber or filler surface via the adsorbed cofactor. Central to this mechanism is the phenomenon of stiffening of the PEO polymer chain caused by its association with the cofactor. The cofactor stiffens the chain much the same way charged groups make polyelectrolytes stiffer than neutral molecules. The authors explained the retention in the PEO-kraft lignin-clay and PEO-kraft lignin-precipitated calcium carbonate systems in terms of the *association-induced polymer bridging* mechanism. Van de Ven and Alince (1996b) also explained the flocculation behavior of PEO in the fiber/clay system without the presence of a cofactor. The proposed mechanism, heteroflocculation by *asymmetric polymer bridging* refers to a situation where even though the dissolved polymer, that is, PEO does not adsorb on one surface (fiber), flocculation takes place. Polymer bridging occurs when $\kappa\delta > 1$ where (δ) is the polymer layer thickness and (κ^{-1}) is the thickness of the double layer (Lapcik et al., 1995).

A mechanism called *complex bridging* was also proposed by Pelton's group to explain the retention behavior of the PEO-PFR and the Copolymer-PFR retention aids (Xia et al., 1995b, 1996a,b). Central to this mechanism is the complex formation between the cofactor (PFR) with the PEO or the copolymer. In a latex or pulp-filler suspension, PFR is added first and part of it adsorbs on the suspended particle surface while the remainder is dissolved in the water. When the PEO or the copolymers are added into the suspension, they form association complexes with the dissolved PFR. This is followed by heteroflocculation of the latex or fines, and the complex and the formation of aggregates. These aggregates are then deposited on the fibers.

The modification of PEO is the central idea underlying all the discussed mechanisms. Cofactors modify PEO by aggregating it or forming a complex with it or by providing a surface on which PEO can adsorb (van de Ven, 1996). However, modification of the PEO can also be brought about in the absence of cofactor by a temperature change (Bailey et al., 1958; Bailey and Koleske, 1976; Kjellander and Florin, 1981). In particular, the PEO-water system undergoes an entropically driven liquid-liquid phase separation into a PEO-rich and a PEO-lean phase (Kjellander and Florin, 1981). The boundary separating the two phases on a temperature-composition phase diagram is called cloud point temperature or critical solution temperature (CST). It is also known that the CST can change significantly in the presence of electrolytes (Bailey and Koleske, 1976; Florin et al., 1984) and under the effect of a hydrodynamic flow field (James and Saringer, 1982; Tirrel, 1986; Klenin et al., 1993).

Khoultchaev et al. (1997) were the first to take the phase separation into account and were able to link the solution behavior of the PEO-water system with the level of fines and filler retention. It was found that by using a PEO with a molecular mass of 5×10^6 Da the fines retention at a temperature above the CST was 82.2%, whereas below the CST it was 55.0%. The corresponding clay retentions were found to be 71.9 and 31.7%. It is conceivable that, in a real papermaking suspension, the electrolyte content as well as the level of shear may bring the CST near papermaking conditions and this could affect the retention. It is thus possible that some of the observed variability in the performance could be attributed to phase separation.

It is noted that there is a large body of work on the impact of temperature on the stability of colloidal dispersions (Napper, 1983). However, no one considered the role of temperature in the retention capability of PEO. Most of the work was centered around the correlation between the θ-temperature and the critical flocculation temperature (CFT). It is noted that at the limit of infinite polymer molecular weight, the critical solution temperature corresponds to the θ-temperature (Napper, 1983). Pelton (1988) was the first to report that the CFT corresponds to the cloud point temperature of the stabilizing polymer. In our opinion, it is more appropriate to link CFT with the cloud point rather than the θ-temperature because the cloud point clearly defines a phase boundary separating two regions of a completely different solution structure.

Some other aspects of the PEO-water solution were also examined. Polverari and van de Ven (1996) reported that PEO molecules associate and form clusters which exist in equilibrium with free polymer coils. The diameter of these clusters was found to be independent of molar mass and to decrease from 0.90 to 0.45 μm with time. The clusters were found to decrease the calculated hydrodynamic layer thickness of PEO adsorbed on latex particles (Polverari and van de Ven, 1994). Klenin et al. (1993) have also reported the formation of particles in aqueous solutions of PEO in laminar and turbulent flow.

The objective of this work was to investigate the role of the PEO-water solution behavior on the adsorption of PEO on chemic-thermo-mechanical pulp and clay or chalk surfaces as well as the state of aggregation in PEO-filler suspensions. It is an extension of our previous work which established the temperature-dependent retention behavior of PEO. Adsorption experiments were carried out at the same shear rates and PEO concentrations with those in the retention study. The state of aggregation of PEO-filler suspensions was studied by monitoring the fluctuations in the intensity of transmitted light through the suspension. This work does not involve cofactors.

Experimental Studies

Materials

Chemi-thermo-mechanical pulp (CTMP) from a mill in British Columbia was used. Dry pulp was suspended in hot, distilled water (~ 353 K) to 1% consistency and left overnight. For each experiment, a fresh sample of pulp suspension was disintegrated in the British Pulp Evaluation Apparatus (Mavis Engineering Ltd., UK) for 35 min. The fines fraction of the pulp was 16%. PEO with an average molar mass of 5×10^6 Da was received from Aldrich Chemical Company (Milwaukee, WI). Potassium chloride of analytical grade and Tannic acid (TAN) used in the experiments were received from Fisher Scientific Inc. (Ottawa, Ont.). A clay sample WP from ECC International (Sandersville, GA) was received from MacMillan Bloedel Research as a 70 mass % suspension. The particle-size distribution and the electrophoretic mobility of clay samples were measured by using the Malvern Zetasizer 3 (Malvern Instruments Inc., Malvern, U.K.) at room temperature (295 K). The average particle size (equivalent hydrodynamic spherical diameter) was found to be 490 nm. Based on the electrophoretic mobility measurements, the zeta potential was calculated and found to be equal to -40 mV at pH $= 5.5$. A sample of chalk, Faxe Chalk 86 from Faxe Kalk (Stevens, Denmark), was received from MacMillan Bloedel Research. The specific surface area of the Faxe Chalk 86 was 2.2 m^2/g, and the equivalent spherical diameter of particles corresponding to the 50% of the cumulative mass of the particle-size distribution was 2 μm.

Adsorption Experiments

Adsorption of PEO on the papermaking furnish particles was studied at 303 and 343 K which correspond to points above and below the cloud point of the PEO-water system in the presence of 2 mol/L of KCl. Potassium chloride was added in order to lower the CST to papermaking conditions. The experiments were conducted by following the depletion method. Each adsorption measurement was repeated four times and the mean value was reported.

In the case of the pulp + clay mixture, a 1 L beaker with 420 g of a CTMP pulp suspension at 1% consistency, 1.43 g of clay suspension and 74.5 g of KCl was heated using the VWR Scientific water bath to maintain the temperature at 303 or 343 K. The mixture was agitated with a magnetic stirrer during heating. When the desired temperature was reached, the preheated amount of the PEO solution (for instance, 26 mL of 0.1 mass % concentration to maintain the overall PEO concentration of 0.005 mass %) was added to the clay + pulp suspension and stirred for 30 s. Subsequently, the resulting suspension was transferred to the preheated with a hot water Drainage Jar and stirred 1 min before starting the collection of samples. The volume of the samples was approximately 100 mL. The samples were filtered under pressure through a Millipore membrane filter with 0.22 μm diameter holes on the preheated high-pressure filtration column (Millipore Canada Ltd., Nepean, Ont.). Filtered samples were cooled down to the room temperature before the determination of their PEO concentration by the modified nephelometric method of Attia and Rubio (1975).

The experiments on PEO adsorption by pulp in the absence of clay were performed as described above, but clay was not added. In the experiments on PEO adsorption on clay alone, the amount of pulp suspension was replaced by an equal amount of distilled water. In the case of PEO adsorption on chalk, 1 g of oven dried chalk was ground in the mortar prior to the addition to 420 g of water. Then, the chalk water suspension was ultrasonicated in the Branson 5200 (Branson Co., Shelton, CT) ultrasonic bath for 15 min and 74.5 g of KCl was added to it. In the adsorption experiments with chalk, the addition of tannic acid to the filtrate caused the formation of large and small flocs. The sedimentation of the large flocs resulted in an error in the PEO concentration, which is as high 25%. The error is even higher at 303 K.

Aggregation experiments

In order to monitor the changes in the state of aggregation of the filler dispersions, the light transmittance of flowing suspensions was measured using the Photometric Dispersion Analyzer (PDA, Rank Brothers Ltd., Cambridge, England). The 0.2 mass % filler suspension was prepared in a beaker and was circulated through the PDA cell using a peristaltic pump. The flow rate was maintained at 50 mL/min. The PDA monitors the fluctuations in intensity of light transmitted through the suspension. The changes in the degree of particle aggregation are reflected as changes in the root mean square of the fluctuations in voltage (V_{rms}). The ratio of V_{rms} to the mean transmitted light intensity (DC) was measured. It is not possible to measure the actual size of the aggregates, but the V_{rms}/DC ratio is used as an indication of the relative size. The theoretical background and the technical details of the PDA are given elsewhere (Gregory, 1985; Gregory and Nelson, 1986).

Results and Discussion

The results on PEO adsorption on clay and pulp are shown in Figures 1 and 2. There is clearly an enhancement in the adsorption of PEO above the CST of the PEO-water system.

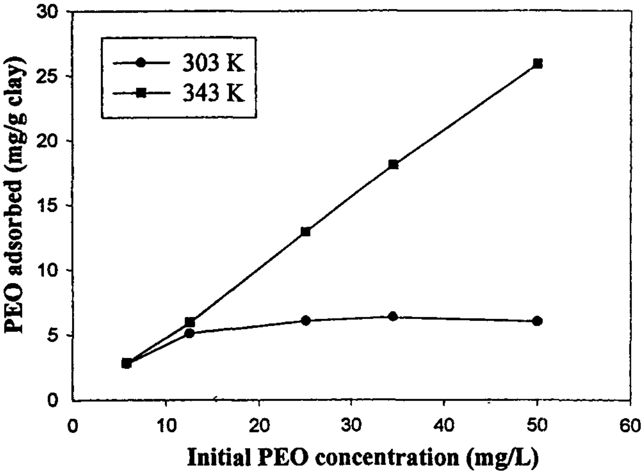

Figure 1. Amount of PEO adsorbed on clay vs. initial PEO concentration.

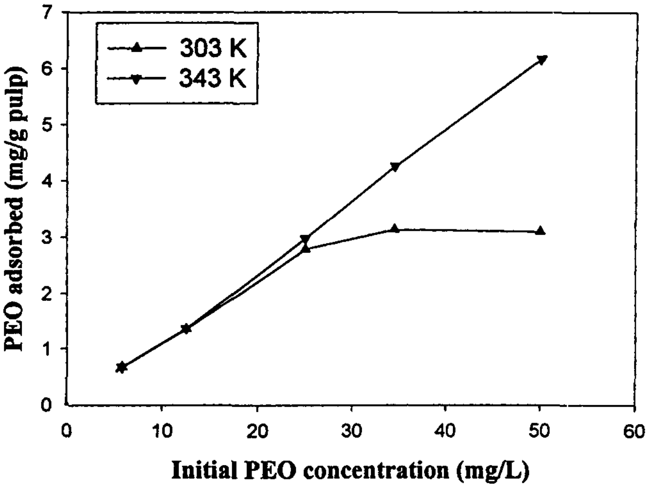

Figure 2. Amount of PEO adsorbed on pulp vs. initial PEO concentration.

As seen from the figures, the adsorption curves at 303 K (point below the CST) reach a saturation level. However, at 343 K (point above the CST) the dependence is linear in the range of the studied PEO concentrations. This indicates that all the PEO introduced into the system remained with the furnish. Lapcik et al. (1995) reported that the maximum adsorption of PEO on clay was 6–7 mg PEO/g clay and did not practically change in the presence of salt. This number compares well with our results on PEO adsorption on clay at 303 K (6.0 mg PEO/g clay). In the experiments with chalk at an initial PEO concentration equal to 50 mg/L, the amount of PEO adsorbed on chalk was found to be 15.6 and 23.3 mg/g below and above the CST respectively. As discussed earlier, due to the sedimentation of a PEO-tannic acid complex, the amount of PEO adsorbed is overestimated especially at 303 K.

Picaro and van de Ven (1995) estimated the adsorption capacity of PEO on the unbleached pulp fibers as 0.7 mg PEO/g fiber. Lindstrom and Glad-Nordmark (1983) measured PEO adsorption on unbleached kraft pulp fibers (1.5 mg PEO/g pulp) and concluded that the adsorption sites were the phenolic lignin residues in the pulp. There was no evidence of PEO adsorption on mechanical pulp fibers and unbleached kraft pulps with blocked phenolic groups. PEO adsorption was observed in our work with CTMP and the uptake was 3.1 mg PEO/g pulp. It is noted, however, that there is 2 mol/L of KCl in our system and the fines were not removed from the pulp.

The response of the photometric dispersion analyzer (PDA) to the addition of PEO and KCl to the 0.2 mass % clay suspensions are presented in Figure 3. The addition of PEO to the clay suspension in the absence of KCl did not change the value of the $V_{\rm rms}$/DC ratio. However, the addition of PEO in a suspension containing KCl had a noticeable effect on the PDA readings which indicated the formation of aggregates above as well as below the CST. The value of the $V_{\rm rms}$/DC ratio was much higher above the CST indicating a higher degree of aggregation (or flocculation) of clay particles. It can also be seen in Figure 3 that there is a reduction in the $V_{\rm rms}$/DC ratio after reaching the highest level. It is due to the formation of aggregates larger than the diameter of the tube carrying the suspension to the PDA cell. These aggregates were not accounted for in the light transmittance which caused the decline in the $V_{\rm rms}$/DC values. Figure 4 shows that the aggregation behavior of the PEO-chalk system below and above the CST is similar to that for a clay.

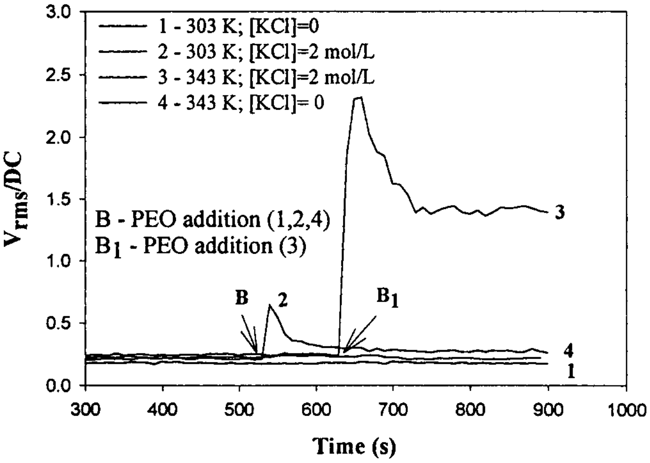

Figure 3. Response of photometric dispersion analyzer to the addition of KCl and PEO to clay suspensions at different temperatures.

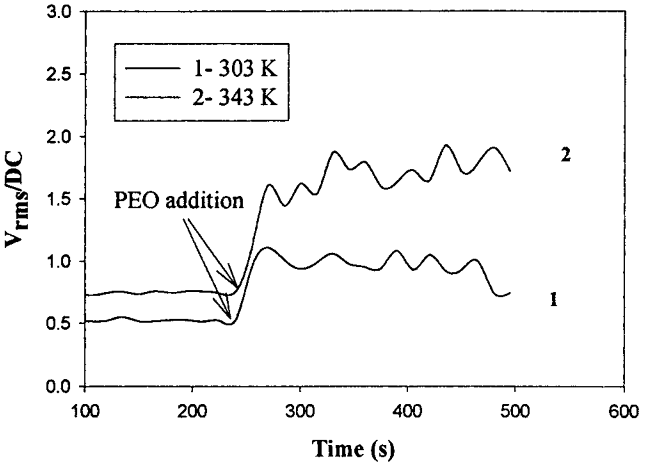

Figure 4. Response of the photometric dispersion analyzer to the addition of PEO to the chalk suspension at different temperatures.

The above experimental findings clearly demonstrate increased adsorption and aggregation above the CST. The PEO molecules do not simply aggregate among themselves but clearly facilitate flocculation. Otherwise, the retention would not follow the same trend. Increased flocculation and adsorption of polymers above the CST was reported in several cases but not in connection with retention in papermaking (Deng et al., 1996; Miura et al., 1994; Zhao and Brown, 1995). The main driving force for the greater adsorption with increased temperature corresponds to a decrease in solubility.

How does the phase separation enhance adsorption and aggregation? The phase separation proceeds either via spinodal decomposition or nucleation (Galina et al., 1986; Fuzita, 1990). Phase separation is foreshadowed by substantial concentration fluctuations. Whether these fluctuations are followed by one or the other mechanism to lead to the two separate phases depends on where exactly the concentration of the initial solution lies in the phase diagram. If it lies within the unstable region, spinodal decomposition occurs. In this case, the phase separated system may be viewed as consisting of vaguely separated submicroscopic domains whose composition is either polymer rich or lean (almost polymer-free). If the initial concentration corresponds to a point between the cloud point curve (binodal) and the spinodal curve, that is, within the metastable region, then nucleation occurs. In this case, the concentration fluctuations are so large that the nucleus concentration is either polymer-rich or polymer-lean when the concentration of the original system is on the left or the right of the concentration corresponding to the critical point, respectively.

The binodal curve for the PEO-water system has been determined (Khoultchaev et al., 1997), but the spinodal is not known. A technique for its determination is pulse induced critical scattering (Galina et al., 1986), but results for the PEO-water system are not available, In any case, however, a common characteristic of both phase separation mechanisms is the fact that the water phase is not a "desirable environment" for PEO to reside when the temperature is above the CST. Furthermore, phase separated PEO molecules have a smaller entropy barrier to overcome in order for adsorption to occur. It is possible then that heteroflocculation by asymmetric polymer bridging (van de Ven and Alince, 1996b) also occurs above the CST with an even smaller entropy barrier for adsorption. This explains the observed enhanced adsorption, aggregation and retention. It is also possible that the complex bridging mechanism (Xiao et al., 1996a,b) took place simultaneously as an aggregation of the fines and subsequent deposition on the fibers.

It is interesting to point out the role of the quality of the solvent or suspension medium on the nature of forces between colloidal particles having adsorbed layers of macromolecules. Klein (1980) and Klein and Luckham (1982) have reported measurements of forces between particles immersed in bad and good solvents. There was no evidence of attraction between PEO adsorbed on mica surfaces in water at conditions in which water is a good solvent. However, a strong attraction was noticed when mica surfaces bearing layers of absorbed polystyrene in cyclohexane approached closer than three radii of gyration of the polymer. The solvent at the experimental conditions was worse than a θ-solvent. Napper (1983) suggested that the idea of segmental attraction was responsible for the flocculation of colloidal systems stabilized with grafted polymers. It was suggested that although the van der Waals attraction between the core particles covered with polymer is not sufficient to cause the instability, the interaction between the segments of the stabilizing polymer becomes attractive in slightly worse than θ-conditions inducing the flocculation.

It is reasonable to conclude from our experimental findings as well as the relevant discussion of the literature data that the enhanced adsorption and flocculation above the CST is a consequence of the fact that the phase separation of the PEO-water system leads to a modification in the state of the PEO. The modification reduces the entropic barrier for adsorption since the PEO has already paid an entropic penalty to phase separate. A cofactor also modifies the state of PEO. Even though the modified state due to a cofactor is different than that from a phase separation, a similarity between the two systems is apparent. In both cases, the water becomes a less desirable place for the PEO to reside. Hence, the PEO is forced to adsorb on the surface of the suspended materials and cause flocculation in the system by bridging.

Summary and Conclusions

Adsorption experiments of polyethylene oxide (PEO) on chemi-thermo-mechanical pulp (CTMP) and filler (clay and chalk) particles as well as aggregation of PEO-filler suspensions indicated a temperature-dependent interaction between PEO and the fibers or the filler. In particular, it was found that the amount of adsorbed PEO and the level of aggregation were much higher above the CST of the PEO-water system. It was concluded that the entropically driven liquid-liquid phase separation in the PEO-water system results into a modified PEO state in the solution. This then leads to an enhanced adsorption, possibly due to a reduced entropy barrier. The flocculation is then facilitated, which manifested as increased retention of fines and fillers.

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