Effect of polyethylene oxide and kraft lignin on the stability of clay and its deposition on fibers

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ABSTRACT

The mechanism by which PEO (polyethylene oxide) operates in the retention of clay was investigated. Two potential mechanisms were considered: (a) flocculation of suspended clay particles, with the resultant flocs captured in the forming web of fibers; (b) direct deposition of clay particles on fibers. Neither PEO alone nor in combination with a cofactor (sulfonated kraft lignin, SKL) flocculated clay in the absence of salt ($CaCl_2$). Indeed, the cofactor SKL acted as a dispersant, stabilizing the clay suspension. Thus floc capture is an unlikely mechanism for clay retention. However, when PEO alone was added to mixtures of fiber and clay, deposition of clay onto fibers was observed. This action was enhanced by the presence of SKL. Asymmetric polymer bridging is proposed as the mechanism for deposition and retention of clay on fibers. The bridge, however, is transient without the presence of a cofactor, implying that the cofactor strengthens the polymer bridge.

Application:

This paper describes the mechanism of polyethylene oxide-assisted retention of clay.

EVER SINCE THE INTRODUCTION OF nonionic polyethylene oxide (PEO) as a retention aid in mechanical pulp furnishes, opinions have differed as to its efficiency and the mechanisms by which it operates. A cofactor, also called an enhancer or adjuvant, is deemed necessary for PEO to be effective. The rationale for using a neutral polymer in a system contaminated with anionic soluble and colloidal substances is simple. Unlike a cationic polymer, which is consumed by anionics and thus made ineffective, the performance of a nonionic polymer should not be affected. There is, however, the question of how to explain its performance.

In the case of a conventional cationic retention aid, three possible mechanisms can be considered:

1. Surface-charge modification of components (fibers, fines, fillers) by cationic polymer adsorption, which results in a mutual electrostatic attraction and, consequently, deposition of fine particles on fibers
2. Simultaneous adsorption of a large macromolecule on fibers and fine particles, which results in polymeric bridging, thus keeping fiber and fine particles together
3. Flocculation of fine particles alone, resulting in capture of the flocs in the forming sheet by mechanical entrapment.

When dealing with nonionic and neutral polyelectrolytes, the first mechanism, based on electrostatic interaction, is improbable. The second mechanism appears to be doubtful because it has been reported that PEO does not adsorb on either bleached chemical pulps or mechanical pulps *(1)*. That leaves the third mechanism, the flocculation of fines and their entrapment in an assembly of fibers. If none of the mentioned mechanisms is applicable, then there is a need to find another explanation as to how PEO operates.

The intention here, therefore, is to investigate the possibility of either mechanism by observing the behavior of clay suspensions in the presence of PEO and a cofactor. Sulfonated kraft lignin (REAX 85, Westvaco) was used as the cofactor because of its effectiveness in groundwood furnishes *(2)*. Two aspects are of interest:

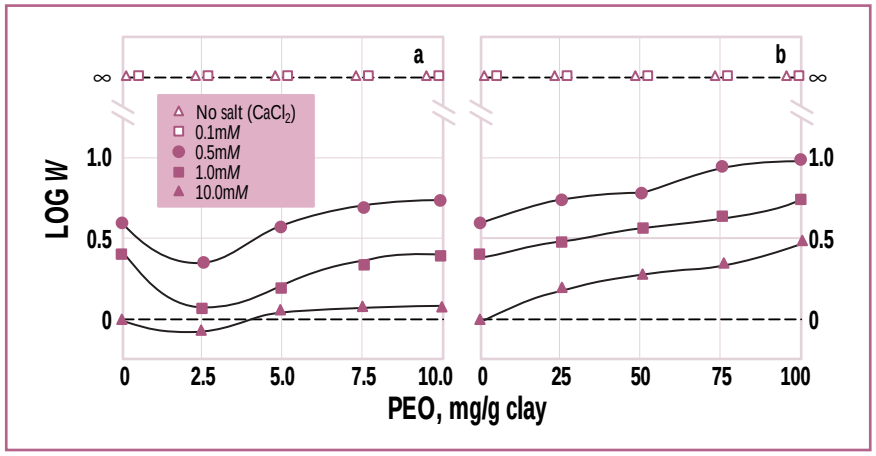
1. The flocculation of clay dispersions
2. The interaction of clay with fibers suspended in water.

The flocculation of clay in the presence of PEO, but in the absence of a cofactor, has already been described by us *(3)*. The deposition of clay on fibers, also in the absence of a cofactor, was discussed and explained by the mechanism of heteroflocculation by asymmetric polymer bridging *(4)*.

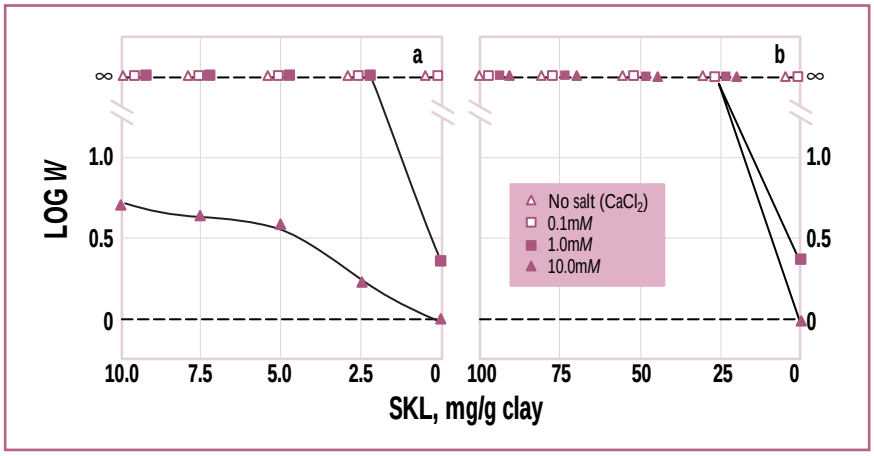
STABILITY OF CLAY SUSPENSIONS

The clay used in this study was a water-processed kaolin (Hydrite UF, Georgia Kaolin) with an average equivalent spherical diameter of 0.2 µm. The clay was dispersed in distilled water and continuously stirred by a paddle at 80 rpm during the experiments.

The response of dispersed clay suspensions to a given condition is given by the "stability ratio" W. This ratio is obtained by comparing the rate of change in the state of dispersion (i.e., destabilization) at a given condition with the maximum rate of destabilization. This means that at $W = 1$ ($\log W = 0$), the process of destabilization, i.e., coagulation or flocculation, proceeds at the fastest rate. On the other hand, when $W = \infty$, the state of dispersion does not change,



1. Stability ratio of a clay suspension (200 ppm) as a function of PEO addition at different salt ($CaCl_2$) concentrations. Fast aggregation occurs at log W = 0. Clay remains dispersed over a period of 1 hour at log W = ∞.



2. Stability ratio of a clay suspension (200 ppm) as a function of SKL addition at different salt ($CaCl_2$) concentrations

and the system is stable or, more realistically, the system remains dispersed over a long period of time. As W decreases, the system becomes more unstable.

The rate of destabilization of colloidal suspensions can be monitored by measuring the change of light transmittance (or turbidity), which is a function of the state of the dispersion. The procedure is described elsewhere *(5)*. In determining W, the time over which the transmittance keeps changing is divided by the time required for the fastest change.

When dealing with PEO, a few comments are in order. In general, PEO is claimed to be a good flocculant for clay *(6, 7)*, which is contrary to our observation when using this particular clay without salt ($CaCl_2$). This is because in the absence of salt, the electrical double layer is thicker than the adsorbed polymer layer, and electrostatic repulsion dominates. In the presence of salt, the double layer is compressed and PEO readily flocculates the clay *(3)*. Furthermore, the use of high-molar-mass PEO presents a problem. A dramatic change in appearance and behavior was observed during preparation of a stock solution (0.01%). After an apparently complete dissolution, which took 15–20 min at moderate stirring, the clear solution appears as a thick honey-like liquid when being poured, but it becomes watery with prolonged stirring. However, the change in viscosity is not very pronounced, dropping from 1.35 mPa·s after 5 min of stirring down to 1.19 mPa·s after one day of stirring *(8)*.

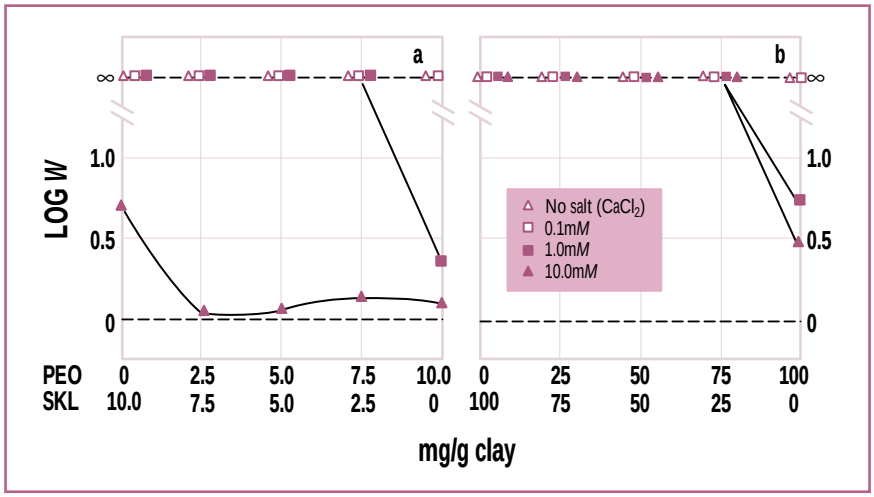
What is of considerable interest is the change in flocculating ability. When freshly prepared PEO is introduced into the clay suspension in the absence of salt, the system flocculates even faster than with salt alone ($W < 1$). However, when the solution is subjected to prolonged stirring prior to its addition, PEO loses the ability to destabilize clay *(8)*. This phenomenon deserves comment. On the basis of previous studies *(9)*, it is believed that even when the freshly prepared solution becomes clear, the PEO macromolecules are not fully dissolved but remain entangled. With prolonged stirring, PEO eventually becomes fully dissolved. Therefore, when PEO is present in the form of entangled macromolecules, it can extend beyond the electrical double layer and flocculate clay via the bridging mechanism. In contrast, the individual macromolecules apparently cannot initiate bridging because they are buried within the double layer. This transformation process, which takes place during preparation of the stock solution, could be the reason for the sometimes erratic performance of PEO on a paper machine. However, we should emphasize that in the experiments reported here, the PEO was well dissolved and had lost its ability to flocculate clay in the absence of salt.

The concentration of the investigated clay suspension was 200 ppm, and the pH was adjusted to 8 to encourage clay dispersion. The fastest rate of destabilization was established by introducing salt, $CaCl_2$, in increasing amounts until no further change of the rate occurred, indicating that the maximum rate was achieved. Subsequently, the rate

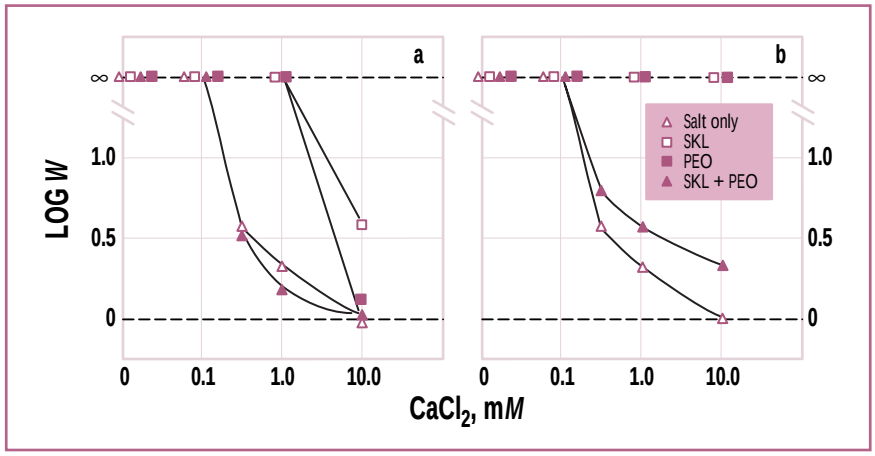
of destabilization was determined in the presence of PEO and kraft lignin separately, as well as in combination. The results, expressed as the stability ratio *W*, are presented in **Figs. 1–3**.

Figure 1 shows the response of clay suspensions to the addition of PEO at 0–10 mg/g clay (Fig. 1a) and up to 100 mg/g clay (Fig. 1b) in the presence of 0–10m*M* $CaCl_2$. The flocculation behavior of clay in the presence of salt and PEO can be readily explained by the classical theories of electrostatic repulsion, polymer bridging, and steric stability. When the distance over which electrostatic repulsion is acting, δ_{el}, is larger than the thickness, δ_{pol}, of the polymer layer adsorbed on clay particles, electrostatic repulsion dominates and the clay suspension is stable. This is the case in the absence of salt or at low salt concentrations (0.1m*M* $CaCl_2$). At higher salt concentrations, when $\delta_{pol} > \delta_{el}$, polymer bridging occurs when the fractional coverage of PEO on clay is low (around 2.5 mg PEO/g clay). At higher PEO concentrations (≥5 mg PEO/g clay), the surface coverage of clay by PEO increases, and steric repulsion starts to dominate.

The effect of the cofactor sulfonated kraft lignin (SKL) in the absence of PEO is shown in Fig. 2. For easier visualization, when comparing the combined addition of PEO/cofactor later on in Fig. 3, *W* is plotted as a function of decreasing addition per gram of clay. The results clearly show that the cofactor acts as a stabilizer. The rate of destabilization slows down with increasing addition of kraft lignin, even in the presence of 10m*M* $CaCl_2$, and at 1m*M* $CaCl_2$ the system remains completely stable. Figure 2b shows that increasing the addition of cofactor prevents destabilization even in the presence of 10m*M* $CaCl_2$. It is clear from these observations that SKL adsorbs onto clay and increases the charge density of the clay (i.e., the clay becomes more negatively charged). This results in a larger repulsion between the clay particles (i.e., an increase in δ_{el}) and thus an increased stability.



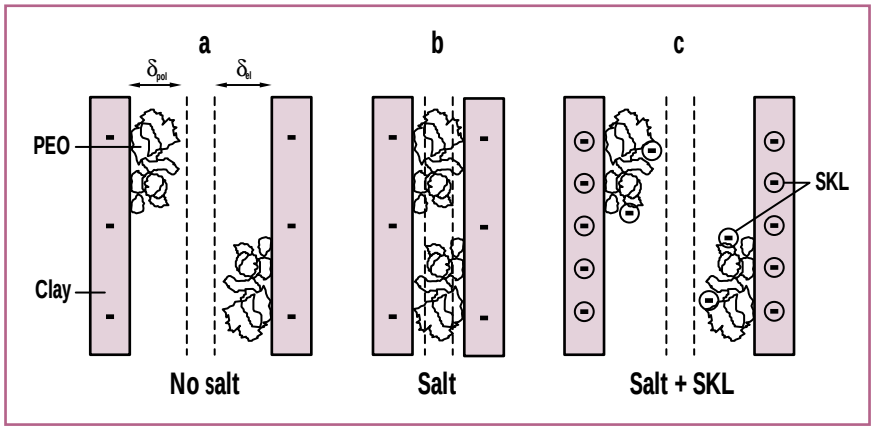
3. Stability ratio of a clay suspension (200 ppm) as a function of combined PEO and SKL addition at different salt ($CaCl_2$) concentrations



4. Stability ratio of a clay suspension (200 ppm) as a function of a salt ($CaCl_2$) concentration in the presence of PEO, SKL, and their combination added in the amount of (a)

The combined effects of PEO and a cofactor are shown in Fig. 3. Comparison with Fig. 2 reveals that the presence of PEO does not affect the behavior of the clay, which apparently is dominated by the kraft lignin. The only indication that PEO plays a role is observed at the highest salt concentration (10m*M*) in Fig. 3a, where the destabilization proceeds faster than with kraft lignin alone (Fig. 2a), probably because at 10m*M*, the thickness of the polymer layer δ_{pol} exceeds the distance δ_{el} over which electrostatic repulsion is felt.

These results are shown in a more conventional way in **Fig. 4**, where the stability ratio *W* is plotted against salt concentrations for selected values of PEO, cofactor SKL, and their combination (5 mg/g clay in Fig. 4a and 50 mg/g clay in Fig. 4b). It is apparent that at 5 mg PEO addition, the response is about the same as for salt alone. At 50 mg PEO addition, the rate of destabilization decreases somewhat in comparison with salt alone because of the increased steric stability caused by PEO adsorption. The addition of SKL alone, or in combination with PEO, makes the system stable up to 1m*M* $CaCl_2$ at the lower additions (5 mg) and up to 10m*M* $CaCl_2$ at the higher additions (50 mg).



5. Clay behavior in the presence of PEO with and without salt and SKL. (a) In the absence of salt, the thickness of the electrical double layer δ_{el} is larger than the polymer thickness δ_{pol}. Clay remains stable because of electrostatic repulsion. (b) In the presence of salt, δ_{el} is compressed and the polymer can form a bridge (provided that the clay particles are not fully coated with PEO), and the clay flocculates. (c) When SKL adsorbs on clay (and also interacts with PEO), the increased surface charge results in larger δ_{el} and thus the clay remains stable. It will flocculate only at higher salt concentrations.

The behavior of clay particles in the presence of PEO, SKL, and salt is shown schematically in **Fig. 5**. At zero or low salt concentrations, the electrostatic interaction distance δ_{el} is larger than the polymer thickness δ_{pol}, and electrostatic repulsion between negatively charged clay particles keeps them apart (Fig. 5a). At sufficiently high salt concentrations, δ_{pol} exceeds δ_{el}, and polymer bridging occurs provided that the clay particles are not fully coated by PEO (Fig. 5b). In the presence of SKL, SKL adsorbs onto the clay and increases the surface charge, thus increasing the electrostatic interaction distance δ_{el} (as compared with the case in Fig. 5b). As a result, the system again becomes stable (Fig. 5c). Under such conditions, a higher salt concentration is required to flocculate the clay.

The general conclusion is that in the absence of salt, the clay suspension remains stable within the range of PEO and kraft lignin addition (0–100 mg/g clay). In the presence of salt, the clay becomes more stable with PEO–SKL addition, apparently because of the adsorption of kraft lignin, which then acts as a dispersant. The relevance of these observations will become apparent in the following discussion of the interaction of clay with fibers.

KEYWORDS
Alkali lignins, polyethylene oxide, clay, deposition, retention, flocculation, fibers, dispersions, stability, cross linking, particles.

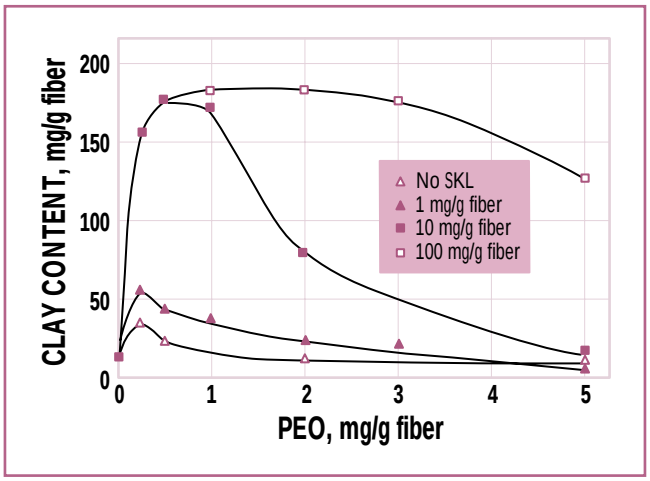
CLAY–FIBER INTERACTIONS

Of the three possible mechanisms for filler retention, electrostatic interaction has been ruled out simply because, in the presence of PEO and kraft lignin, both the fiber and the filler particles remain negatively charged *(3, 8, 10)*. The mechanism of filler flocculation and subsequent capture of flocs in the forming sheet also appears to be unrealistic in view of the preceding observations. Finally, the mechanism of bridging is questionable if PEO does not adsorb on fiber.

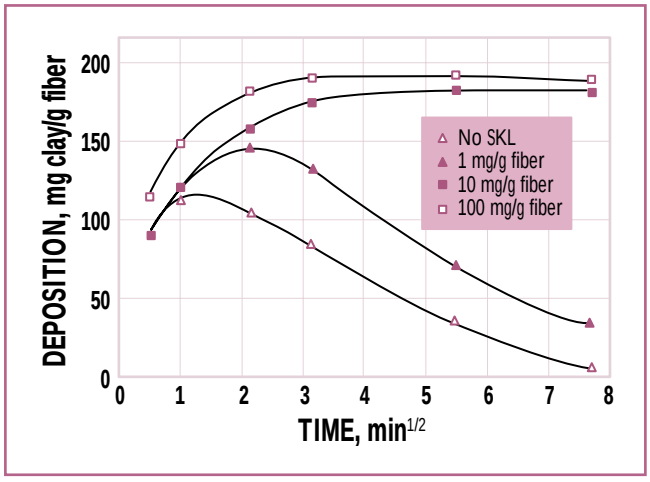
Yet the retention of clay can be very effective, as shown in **Fig. 6**. For handsheets made from a mixture of unbeaten bleached kraft fibers and clay (added in the amount of 200 mg/g fiber) in the presence of PEO (0–5 mg/g fiber) and kraft lignin (0–100 mg/g fiber) using deionized water, almost all the clay was retained with 0.5–1 mg PEO addition and 10–100 mg kraft lignin addition.

The handsheets were formed from a mixture that had been slowly stirred with a paddle (80 rpm) for 60 min. At the end of the mixing period, the supernatant was sampled to determine the electrophoretic mobility of the clay particles. It was found that the added PEO and SKL has practically no effect on the negative charge of clay particles. There is a small decrease with increasing amounts of PEO, and at the highest addition of SKL (100 mg/g fiber) the charge becomes more pronounced. However, in all cases the clay is negatively charged, and the charge is sufficient to keep the clay particles dispersed. Similarly, in all cases there is an electrostatic repulsion between the clay particles and the fibers.

Although the flocculation of clay and the subsequent capture of flocs was deemed improbable, it could not be dismissed without proof that clay particles become attached to the suspended fibers, despite their mutual electrostatic repulsion. The deposition of clay on fibers suspended in water has been reported by us before *(4)*, and this is reconfirmed by the data in **Fig. 7**. In a system composed of one gram of unbeaten bleached kraft fibers and 0.2 g clay dispersed in 500 mL deionized water, the deposition of clay on fibers was monitored as a function of time. The mixture was stirred continuously at low speed (80 rpm) with a paddle, and different amounts of kraft lignin were added, followed by the addition of 1 mg PEO. (Essentially the same behavior was observed with a lesser charge of 0.5 mg PEO.) It is of considerable interest to note that an initial deposition of clay takes place even in the absence of a cofactor. This provides support for the suggestion that the



6. Clay content of handsheets formed from a mixture of unbeaten bleached kraft fibers (2 g/L) and clay (0.4 g/L) in the presence of PEO (0–5 mg/g fiber) and SKL (0–100 mg/g fiber) after continuous paddle stirring for 60 min at 80 rpm



7. Deposition of clay on fibers suspended in water (2 g fiber, 0.4 g clay in 1 L deionized water) as a function of time in the presence of PEO (1 mg/g fiber) and SKL (0–100 mg/g fiber). The mixture was kept under constant slow paddle stirring (80 rpm).

mechanism of retention is indeed mediated by the polymer, causing interaction between clay and fibers.

In order to explain the performance of PEO, two possible mechanisms were proposed. It has been reported that PEO can indeed adsorb on fibers in the presence of a variety of phenolic-type cofactors, including sulfonated kraft lignin *(11)*. Therefore it was suggested that bridging is possible if the cofactor introduces "active sites" by adsorbing on fibers and then interacting with PEO *(10, 11)*. There is a problem, however, because the often used cofactor, phenol formaldehyde, was found not to adsorb on cellulosic fibers in the absence of salt *(12)*. Moreover, as already mentioned, in the absence of a cofactor, PEO induces a transient deposition of clay on fibers.

Another explanation is based on a polymer network mechanism *(13, 14)*. PEO and a cofactor are assumed to interact and form a three-dimensional polymer network in which colloidal particles are captured. When this network is stirred in the presence of fibers, it collapses (for some unknown reason) on the fibers together with the enmeshed particles. The problems with this mechanism have been discussed before *(15)*. Also, the network mechanism cannot explain the behavior shown in Fig. 7, i.e., an initial clay deposition on fiber in the absence of a cofactor.

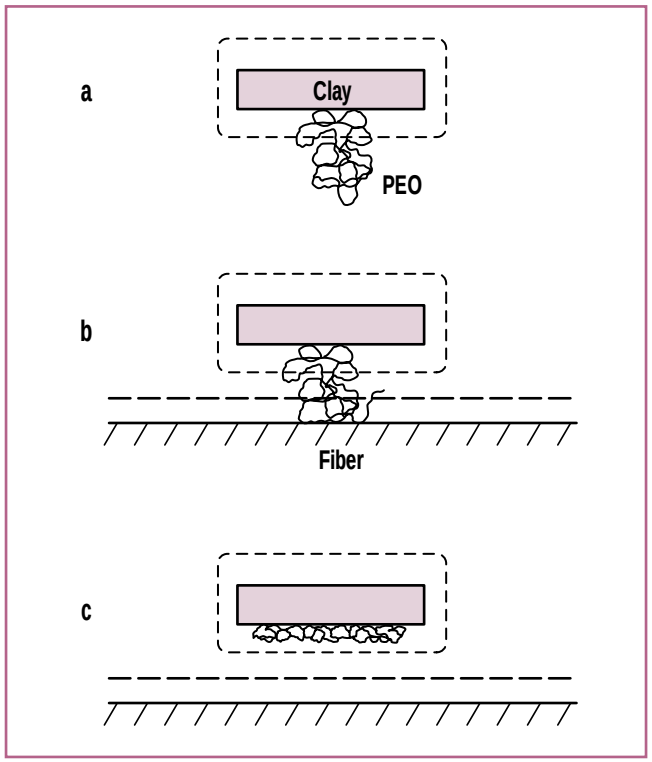
When PEO alone is introduced into a mixture of fibers and clay, the clay initially deposits and later departs from the fiber. This indicates that, in the early stage, polymer bridging takes place. An explanation was found in a proposed mechanism described as "heteroflocculation by asymmetric polymer bridging" *(4)*. This mechanism can operate in a system composed of two solid components. The polymer adsorbs on one component (in this case clay) but not on the other (i.e., fibers) when added to solutions containing only a single component. However when the polymer is added to a mixture of the two components, it adsorbs on the clay particles and undergoes a change in its conformation and entropy. With this modified conformation, the polymer can acquire the ability to adsorb on the fiber. This results in bridging and, consequently, attachment of clay to the fibers.

If bridging is to occur, the polymer must be large enough to extend beyond the thickness of the electrical double layer, which is in the order of 100 nm at very low ionic strength. However, the attachment is only temporary, as documented by the gradual detachment of clay. This happens because the adsorbed polymer flattens with time, thus reducing the distance between the clay and the fiber surface. Consequently, the electrostatic repulsion between clay and fiber increases until it becomes dominant, forcing a break in the polymeric bond with one of the surfaces (likely the fiber surface). The process is shown schematically in **Fig. 8**.

A simple experiment provides support for the suggested mechanism. When PEO is added to the fibers first (no SKL) and the suspension is mixed for different periods of time before the clay is added, the deposition proceeds similarly, as shown in Fig. 7 (curve for no added SKL), thus confirming two points:

1. PEO does not interact with fibers.
2. Clay is needed to trigger the action.

When PEO is added to the clay only and the suspension is immediately introduced to the fibers, clay deposition proceeds as shown (curve for no added SKL). However, when the PEO and clay are allowed to interact for a prolonged period of time before being introduced to the fibers, no deposition takes place. This means that the PEO that adsorbed on clay had time to flatten on the surface and became buried within the electrical double layer.



8. PEO behavior on clay and fiber. (a) PEO adsorbs on clay particles and extends beyond the electrical double layer surrounding the clay. (b) Upon adsorption on clay, the PEO acquires the ability to adsorb on fibers, thus forming a bridge. (c) With time, PEO flattens onto the clay surface, and electrical double layers on clay and on fibers repel each other.

The other curves in Fig. 7 represent the behavior when PEO and a cofactor are used together. When 10 mg or 100 mg of SKL and 1 mg of PEO are present per gram of fiber, the clay deposits but no detachment takes place. This suggests that SKL inhibits the flattening of the PEO molecules adsorbed on clay. Thus, in the presence of SKL, the thickness of the polymer layer is larger than the thickness of the electrical double layer, i.e., $\delta_{pol} > \delta_{el}$. In the absence of SKL, δ_{pol} is also initially greater than δ_{el}, but with time δ_{pol} gradually becomes smaller than δ_{el}. Since PEO adsorbs onto the fibers in the presence of excess SKL [a process called association-induced polymer adsorption *(15)*], at high SKL concentration, clay deposits on fibers by the mechanism of polymer bridging. The mechanism by which SKL reinforces the PEO bridge is also observed in a system composed of latex particles linked to a glass surface by a PEO–SKL complex *(16)*.

CONCLUSIONS

In an attempt to understand the mechanism by which polyethylene oxide (PEO) operates in retaining clay, the stability of a dispersed clay suspension was established in the presence of PEO and sulfonated kraft lignin (SKL). In the absence of salt, no destabilization of clay was observed within a broad range of PEO and SKL concentration (0–100 mg/g clay). The stability of the clay under these conditions ruled out the possibility of floc entrapment in the forming sheet as a mechanism for clay retention.

The actual mechanism is based on polymer bridging between clay particles and fibers, despite the fact that PEO by itself does not adsorb on fibers. However, the initial adsorption of PEO on clay produces conformational and entropic changes in the PEO. The altered PEO forms a transient bridge between fibers and clay particles. Permanent bridging is accomplished when PEO and a cofactor form a complex capable of adsorbing on both the fiber and clay particles. The complex strengthens the bridge by inhibiting the flattening of PEO.

The performance of PEO can be affected by its state of dissolution. Initially, the macromolecules are entangled, and these entangled molecules are capable of flocculating clay. However, after prolonged mixing, the clusters disintegrate into single macromolecules that do not cause flocculation at low salt concentrations because their size becomes smaller than the electrostatic interaction distance. **TJ**

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LITERATURE CITED

1. Lindström, T. and Glad-Nordmark, G., *J. Colloid Interface Sci.* 94(2): 404(1983).
2. Pelton, R. H., Allen, L. H., and Nugent, H. M., *Tappi* 64(11): 89(1981).
3. Lapcik, L., Alince, B., and van de Ven, T. G. M., *J. Pulp Paper Sci.* 21(1): J19(1995).
4. Van de Ven, T. G. M. and Alince, B., *J. Colloid Surface Sci.* 181: 73(1996).
5. Alince, B. and van de Ven, T. G. M., *J. Colloid Interface Sci.* 155: 465(1993).
6. Rubio, J., *Colloids Surfaces* 3: 79(1981).
7. Braun, D. B. and Ehms, D. A., *Tappi J.* 67(9): 110(1984).
8. Kratochvil, D., unpublished results.
9. Polverari, M., Ph.D. thesis, McGill University, Montreal, 1994.
10. Stack, K. R., Dunn, L. A., and Roberts, N. K., *Appita* 43(2): 125(1990).
11. Leung, P. S. and Goddard, F. D., *Tappi J.* 70(7): 115(1987).
12. Stack, K., Dunn, L., and Roberts, N., *Colloids Surfaces, A: Physicochem. Eng. Aspects* 70(1): 23(1993).
13. Lindström, T. and Glad-Nordmark, G., *J. Colloid Interface Sci.* 97(1): 62(1984).
14. Lindström, T. and Glad-Nordmark, G., *Colloids Surfaces* 8(4): 337(1984).
15. Van de Ven, T. G. M. and Alince, B., *J. Pulp Paper Sci.* 22(7): J257(1996).
16. Takase, H. and van de Ven, T. G. M., *Colloids Surfaces, A: Physicochem. Eng. Aspects* 118: 115(1996).