Novel retention aids for mechanical pulps

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ABSTRACT

Acrylamide and poly(ethylene glycol) macromonomer copolymers, in conjunction with phenolic formaldehyde resin (PFR),were evaluated as novel retention aids for newsprint pulps. The first-pass retention of the pulp fines was increased from 37% without polymer to nearly 90% with copolymer addition.This retention performance was similar to that of the high molecular weight poly(ethylene oxide) (PEO)/phenolic resin dual-polymer systems. However, the copolymers exhibited improved aging resistance and produced a higher fines retention than PEO (MW = 8 million) under high shear stress.The retention performance of the copolymers was very sensitive to the molecular weight. A new retention mechanism called complex bridging was proposed to explain the retention effects.

Application:

This work deals with a new copolymer that newsprint producers may be able to use to improve first-pass retention.

THE FIRST-PASS RETENTIONO pulp fines in a modern newsprint machine is often less than 50%. In spite of poor retention,the newsprint industry has had only an intermittent interest in the use of retention aid technology. However, the increasing use of fillers and deinked pulp has forced many manufacturers to use polymeric retention aids. Sophisticated cationic polymers, which are effective in fine paper furnishes, are usually not cost effective in mechanical pulps because of the presence of large quantities of dissolved and colloidal substances (DCS) originating from wood. The negatively charged DCS molecules form inactive polymer/polymer complexes with cationic retention aids causing excessive consumption of polymers.

Pelton and co-workers were the first to report that very high molecular weight poly (ethylene oxide) (PEO) was an effective retention aid in some mechanical pulp *(1)*. Instead of being harmed by the DCS fraction it was discovered that some pulps had a crucial component of the DCS which was required to make PEO function.In recent years, the second component required for the PEO flocculation system has been called a cofactor. For pulps without an indigenous cofactor in the DCS fraction,phenolic resins *(2)* or kraft lignin *(3)* are effective cofactors. Of these PEO/phenolic resins dual-polymer retention systems have been the most widely used *(4–6)*.

There have been problems preventing the universal acceptance of PEO retention aids. These include the following:(a) PEO is susceptible to high shear stress which dictates careful handling in the makeup system *(7)*; (b) PEO readily undergoes chemical degradation particularly in the presence of iron salts, which means that polymer solutions must be continuously freshly made *(8, 9)*; and (c) compared with polyacrylamide-based polymers, very high molecular weight PEO is expensive. For effective retention PEO must have a very high molecular weight so a small degree of hydrodynamic or chemical degradation can completely eliminate polymer-induced retention.

In this work, we describe laboratory retention results with a new copolymer which has the advantages of PEO but is not so sensitive to hydrodynamic or chemical degradation. The copolymers have a long polyacrylamide (PAM) backbone supporting short PEO pendant chains (see **Fig. 1**) *(10)*. The polyacrylamide forms a robust and inexpensive backbone,whereas the short PEO pendant chains provide the associating sites for interaction with cofactor. Such structures are called comb copolymers where the very short PEO chains form the teeth of the comb.Like a comb,the functionality of the copolymer should not be significantly damaged if a few teeth are oxidatively cleaved. By contrast, the rupture of one bond in a PEO homopolymer lowers the molecular weight resulting in a loss of flocculation efficiency.

The new copolymers were prepared by copolymerization of acrylamide and PEO (meth)acrylate macromonomers. The macromonomers had PEO pendant chains with 5–40 ether repeat units and a vinyl reactive end group. Details on preparation of the copolymer have been presented elsewhere *(10)*.

The objectives of this work were:(a) to correlate the copolymer structures such as pendant PEO chain lengths, copolymer composition and molecular weight to their performances as retention aids for newsprint pulps;(b) to compare the copolymer retention performance under high shear stress with that of conventional high molecular weight PEO homopolymer; and (c) to compare newsprint fines retention with flocculation of polystyrene latex which is a model colloid used in studying flocculation mechanisms.

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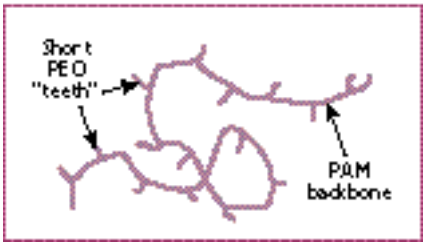
EXPERIMENTAL

The macromonomers used in the syntheses were supplied by Poly-Sciences Inc. and Monomer-Polymer Inc. Chemical structures of the macromonomers are given in **Fig. 2**. The acrylate-based PEO macromonomers are designated herein as A-n,where n is the number of repeat units of the PEO pendant chain which was 10, 20, and 40. Similarly, MA-n is used to denote the methacrylate PEO macromonomers with n of 5,9,and 23.

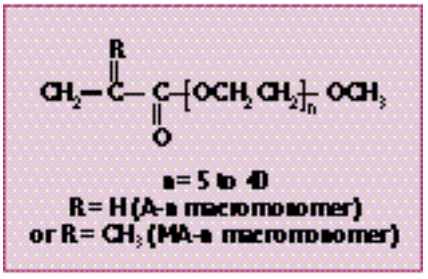
Phenol formaldehyde resin, Cascophen C271 (40% wt solids content in aqueous solution), was supplied by Borden Chemicals. High molecular weight poly(ethylene oxide) samples were obtained from Union Carbide Corp. PEO-301 (Polyox 301) had a weight average molecular weight of 4 million, and PEO-309 (Polyox 309) had a molecular weight of 8 million.

The newsprint pulp (Abitibi Price Co., Iroquois Falls) was based on 65% stone groundwood and 35% high yield sulfite pulps (70% yield, acid sulfite). The pulps were made from a mixture of mostly black spruce plus a few percent jack pine and white spruce.The fines content of the pulp,defined as total fine particles capable of passing through the perforated stainless steel plate (76 µm diameter holes) was 58% (wt).

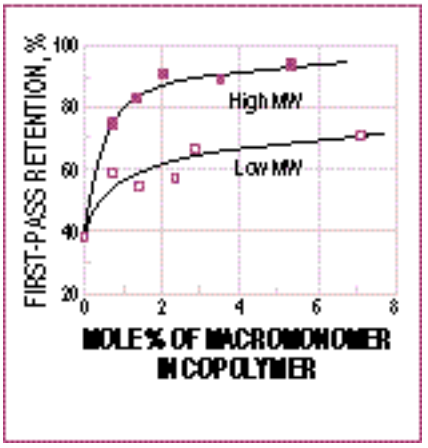
Evaluation of the copolymers as retention aids was carried out in a Dynamic Drainage Jar (Paper Research Materials Inc.) which was fitted with a perforated stainless steel plate containing 0.6-mm holes. The first-pass retention was measured at 50°C with the propeller speed ranging from 250 to 1000 rpm. Detailed operating procedures were the same as those described by Pelton *et al.(11).* The standard deviation of retention values was 5–8% of the mean values based on 4 duplicates.



1. Schematic of comb copolymer.The long, linear polyacrylamide backbone supports very short PEO chains about 1 in every 100 backbone repeat units.



2.Structures of PEG-(meth)acrylate macromonomers



3. Effect of copolymer structure on first-pass retention of newsprint in the dynamic drainage jar. Lower molecular weight copolymers were obtained at 40°C with mole feed ratios of A-10 to AM from 1.0 to 10%. High molecular weight copolymers were obtained at 25°C with mole feed ratios of MA-23 to AM from 1.0 to 7.0%. The propeller speed was 250 rpm for both samples.

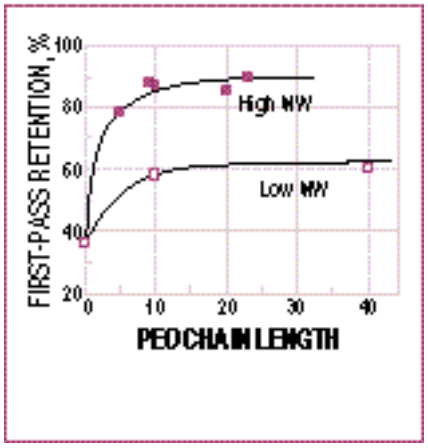
To prepare retention samples, 250 mL of newsprint pulps (about 1.0% consistency) were diluted to 500 mL with water and heated up to 50°C. The pH of the pulp was adjusted to 5 by adding 1.0 mL 0.02 *N* HCl solution; 4.0 mL (0.025% wt) phenol formaldehyde resin C271 was then added. Finally, 2.0 to 10.0 mL of PEO or the copolymer (0.025% wt in aqueous solution) was added.Collection of the first 100 mL whitewater was initiated 2 min after PEO or copolymer addition.

Flocculation of the polystyrene latex particles was conducted by addition of small quantities (1.0–4.0 mg/L) of phenolic resin and PEO or copolymer in the presence of bleached fiber. Thirty-five milliliters of Milli-Q treated distilled water and 10 mL bleached kraft pulp of 0.5% consistency were added to a 50 mL test tube, followed by 1 mL 0.25% (wt.) of PS latex.The pH of the solution was adjusted to about 5 by adding 0.1 mL 0.02 *N* HCl. Subsequently, 0.1 mL 1 *N* NaCl was also added to maintain the electrolyte at a concentration of 2 x 10^{-3} *M*. The transmittance for the control was measured by using a UV spectrophotometer (Hewlett Packard) at a wavelength of 500 nm after 0.4 mL 0.025% (wt.) phenolic resin had been added. Finally, copolymer or PEO aqueous solution at a concentration of 0.025– 0.05% was added with water to give a total volume of 50 mL and the mixture was vigorously shaken for 3 to 5 s.After 1 h of sedimentation time, the supernatant was collected and filtered with a 200 mesh steel plate to separate suspended fiber fragments.

The supernatant transmittance was measured and relative turbidity was calculated by:

$$t_R = \log(100/T_s)/\log(100/T_c) \quad (1)$$

where T_c and T_s were percent transmittances of the control and the sample, respectively. In the analysis of the data,it was assumed that the relative turbidity represented the frac-



4. Effects of pendant PEO chain lengths on fines retention.Lower molecular weight copolymers were obtained at 40°C. High molecular weight copolymers were obtained at 25°C. The measurements were conducted at 50°C with propeller speed 250 rpm.

Polymer	Types of macro-monomer	Mw of polymers 10^{-6}	Composition, mol % of (M)A-n	First-pass retention, %
56-108	MA-9	4.6	0.69	90.6
43-129	MA-23	3.7	0.65	81.5
56-110	MA-23	3.7	1.40	87.5
23-145	A-40	1.1	2.84	61.3
23-157	A-10	1.3	0.71	58.7
23-149	A-10	0.7	1.42	40.5
PEO-309	—-	8.0	—-	83.7
PEO-301	—-	4.0	—-	70.0

I. Effect of molecular weight of copolymers on the fines retention;propeller speed at 250 rpm and at 50°C

tion of latex not removed by flocculants.

RESULTS

A series of copolymers were prepared and characterized in our laboratories. **Table I** summarizes the key copolymer properties.Also shown in Table I are the Dynamic Drainage Jar, DDJ, first-pass retention values for newsprint pulp in the copolymers. Data for two commercial very high molecular weight PEO homopolymers are included for comparison. Phenolic resin Casophen C271,PFR, was added as a cofactor to all pulps before all measurements. More than 80% of fines retention was achieved by addition of the copolymers with a molecular weight higher than 3.5 million.PEO 309,the highest molecular weight PEO homopolymer, produced similar fines retention.By contrast, the retention without polymer addition was 37%. The copolymer with a molecular weight of about 1 million gave limited retention improvement, whereas copolymers with molecular weight lower than 1 million (such as sample 23-149) showed almost no improvement even though this sample contained more macromonomer A-10 (1.42% mole). Thus, flocculation appeared to be more sensitive to the molecular weight of copolymers than to the content of pendant PEO chains.

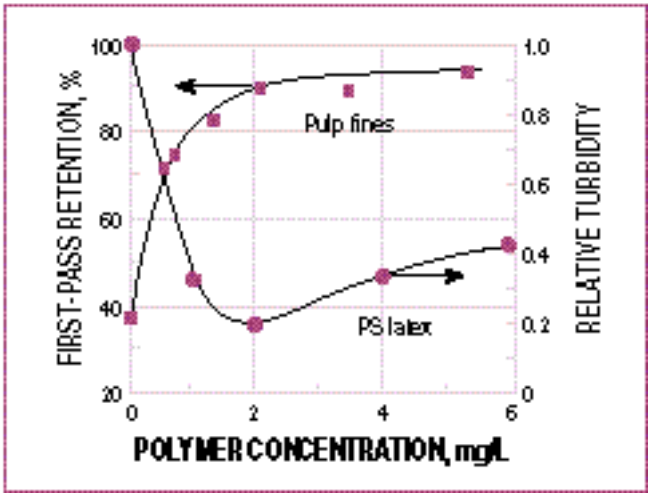
First-pass retention values for PEO homopolymers also showed a strong dependence on polymer molecular weight. First-pass retention for PEO-301,which had a molecular weight of 4 million, was 70%.When the molecular weight of PEO was doubled,the retention was increased to 83.7%. This result has been reported by many other workers. For example, Pelton *et al. (4)* reported the effects of PEO molecular weight ranging from 1000 to 5 million on the pulp fines retention. The results indicated that only PEO with a molecular weight of 5 million increased fines retention.

Effects of the copolymer structure on retention

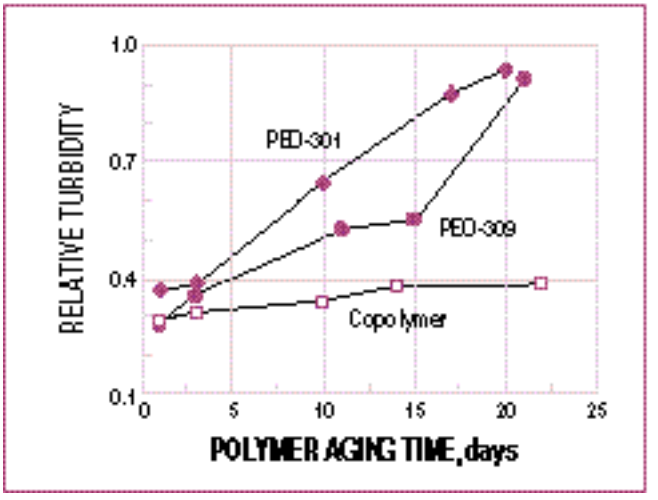
Figure 3 shows the first-pass retention as a function of the density of PEO pendant chains expressed as a mole fraction of macromonomer in the copolymer. The two curves in Fig. 3 represent results from two series of copolymers with different macromonomers. The curve labeled "low MW" in Fig. 3 was obtained using a series of copolymers from copolymerization of macromonomer A-10 and AM to give a molecular weight of approximately 1 million. When as little as 0.8% (mole) A-10 macromonomer was incorporated into the copolymer, a significant enhancement in retention was achieved. Further increasing the A-10 amount in the copolymers did not substantially increase fines retention.

The curve labeled "high MW" in Fig.3 was obtained using a series of copolymers based on MA-23 and AM to give a molecular weight of approximately 4 million. The retention increased to 75% when only 0.8% (mole) macromonomer was incorporated into the copolymer. From 0.8% (mole) to 2.0% (mole), retention increased linearly up to 90% as the composition of MA-23 in the copolymer increased.No further significant improvement was observed for composition above 2.0% (mole) and up to 5.0% (mole). The scatter in the data points reflects the difficulty in preparing a series of copolymers of varying composition but constant molecular weight.

The influence of PEO pendant chain length on fines retention is shown in **Fig. 4** for two molecular weight series. It is remarkable that significantly increased retention was observed with a copolymer containing PEO chains with only 5 ether repeat units and located on average every 65 repeat units along the PAM backbone. By contrast, with linear



5. Comparison of Dynamic Drainage Jar fines retention measurements with latex flocculation experiments both conducted as a function of copolymer concentration. First-pass retention of newsprint fines and latex relative turbidity (t_R) as functions of copolymer 56-108 concentration with a fixed PFR concentration of 2 mg/L.



6. The extent of polystyrene latex flocculation as a function of the time during which copolymer 43-129 was aged in water at room temperature. Corresponding data for commercial PEO homopolymer are also shown.

PEO homopolymer about 10^5 ether repeat units are required for good retention. Further increasing the PEO pendant chain length from 20 to 40 gave only limited improvement in the first-pass retention. The data point for zero chain length was for a polyacrylamide (PAM) homopolymer. As was shown years ago, high molecular weight PAM is not an effective retention aid for newsprint pulps *(1)*.

Influence of polymer concentration

Figure 5 describes the influence of copolymer concentrations on first-pass retention for newsprint pulps at constant phenolic resin concentration (= 2.0 mg/L). The copolymer used was 56-108 which contained approximately 0.69% (mole) MA-9 PEO pendant chains and a molecular weight of 4.6 million. Fines retention increased with copolymer concentration to a maximum of 90% at a concentration of 2.0 mg/L. Beyond 2.0 mg/L,there was little increase in retention.

Polymer degradation in aqueous solution

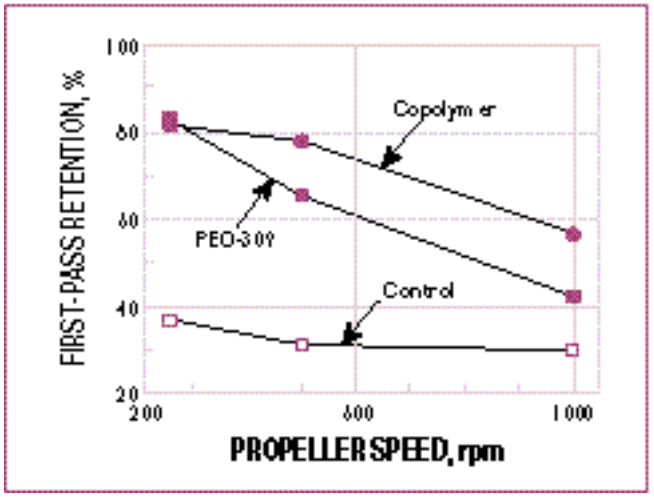
One of the major disadvantages of PEO homopolymer is that molecular weight decreases with storage time in water. **Figure 6** compares the ability of PEO and copolymer to flocculate latex as a function of aging time. The copolymer showed no change in flocculation performance,whereas the PEO homopolymer gave poorer flocculation (i.e., higher t_R) with longer storage time. Indeed,after having been stored for about 20 days, the PEO almost totally lost its ability to induce latex flocculation.Chemical changes associated with PEO aging have been described elsewhere *(12)*. The durability of the copolymer is attributed to the fact that cleavage of a few pendant PEO chains should not affect the performance of the molecule in the same way that a hair comb can lose a few teeth and still function. By contrast, one broken link in a PEO chain renders it ineffective as a retention aid.

Effects of hydrodynamic forces on retention

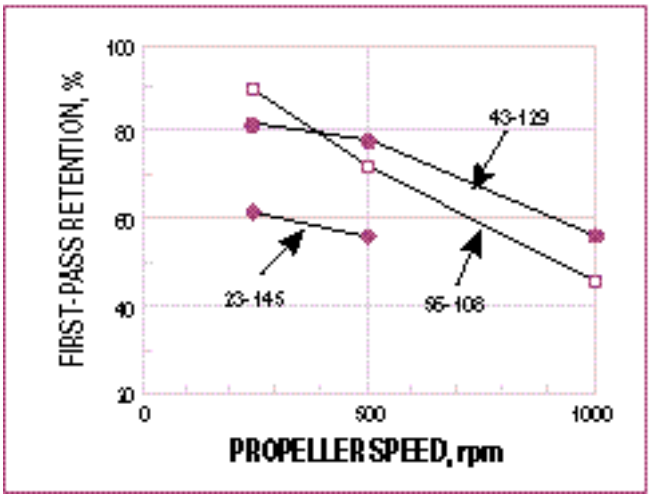
There are several variables which affect fines retention in the dynamic drainage jar (DDJ). These include propeller speed, screen hole size, pulp consistency, and temperature. Generally, a low propeller speed, small screen hole size,and high temperature result in higher first-pass retention for either the control or the samples with polymer addition *(13)*. Of these factors, propeller speed and stirring time are the most important. These factors influence the extent to which polymer flocs are irreversibly destroyed by hydrodynamic forces.

Figure 7 shows the effects of DDJ propeller speed on fines retention. Both copolymer 43-199 and PEO gave lower retentions at higher propeller speeds. However, the copolymer seemed to be less sensitive to hydrodynamic forces than PEO homopolymer.

The hydrodynamic sensitivity of retention with three copolymers is compared in **Fig. 8**. Copolymer 56-108 with the highest molecular



7. Influence of Dynamic Drainage Jar propeller speed on newsprint fines retention with PEO and copolymer 43-129. The control was without polymer.



8. The effect of DDJ stirring speed on fines retention with three copolymers. See Table I for polymer structures.

weight (4.6 million) gave the best retention at low rpm but showed the largest decrease at high rpm. This behavior was similar to PEO-309. Sample 23-145,which had the lowest molecular weight (1.1 million) among the three samples, exhibited no significant decrease in retention efficiency under higher shear rate compared with sample 56-108.

Hydrodynamic forces can fracture both polymer chains in solution and flocs formed with polymer *(14, 15)*. When very high molecular weight polymer solutions are exposed to hydrodynamic forces the molecules partially break down to a critical molecular weight M_c. Abdel-Alim and Hamielec *(16)* proposed an empirical correlation for the critical molecular weight as a function of degrading shear stress for polyacrylamide with the formula:

$$M_c = 3.59 \times 10^8/t^{0.41} \qquad (2)$$

where M_c, the critical molecular weight, is the maximum molecular weight present at the specified shearing condition and t is the applied shear stress in dynes/cm^2. Tam Doo *et al.* estimated that the maximum shear stress at a fiber wall in the DDJ at 1000 rpm is 10^3 Pa *(17)*. Thus, according to the above equation, the $M_c \approx 8 \times 10^6$ which, in turn, indicates that our copolymers may survive the DDJ at 1000 rpm.On the other hand, when a flocculant molecule bridges two fines particles to give a dumbbell structure, the polymer will be much more susceptible to shear-induced rupture.

Comparing newsprint fines retention with polystyrene latex flocculation

Fundamental studies on retention mechanism have been done in our laboratories *(18)* and others' *(19)* using polystyrene latex and bleached kraft pulps as model systems. This system has the advantage of being well defined and giving reproducible results.In a typical experiment,a suspension of latex particles and bleached kraft fibers is exposed to flocculant. After the fibers and latex flocs are allowed to settle, the concentration of latex is measured turbidimetrically; the lower the relative turbidity, the more latex particles have been flocculated.

Latex flocculation results are compared with newsprint fines retention results in Fig. 5. In both cases, optimal flocculation was obtained at 2 mg/L. Correlation between fines retention and latex flocculation is further illustrated by the results in **Table II**, which compares DDJ fines retention data with relative turbidity values for six polymers. First-pass retention and relative turbidity were linearly related with a correlation coefficient of 0.995. This observation permits us to extend mechanistic conclusions based on model studies to pulp flocculation.

DISCUSSION

Our laboratory retention tests indicate that the comb copolymers consisting of long polyacrylamide backbone supporting very short pendant PEO chains are as effective as the leading commercial very high molecular weight PEO homopolymers. Furthermore, the new copolymers offer potential practical advantages which include:

1. The copolymers can be stored for long times as aqueous solutions with little loss in performance.Indeed,they may be manufactured and supplied as water-based emulsion products. This is in contrast to high mole-

KEYWORDS
Acrylamide, copolymers, fines, mechanical pulps, monomers, newsprint, polyethylene glycol, polyethylene oxide, polyphenolics, retention aids.

cular weight PEO which must be dissolved very carefully and used immediately.
2. The DDJ experiments conducted at different stirring speeds indicate that the copolymer may be less sensitive than PEO to hydrodynamic forces in the paper machine. This could be important with some high-speed newsprint paper machines where the hydrodynamic forces can be great.
3. The copolymers could be manufactured by many companies with expertise in polyacrylamide manufacture. This is in contrast to very high molecular weight PEO which is only manufactured by a very few companies.

It was shown that for both newsprint fines and flocculation experiments in our model colloidal system (polystyrene latex + bleached kraft pulp), the effects of copolymer molecular weight, pH, and polymer concentration were the same. This suggests that many of the mechanistic conclusions generated by the model studies can be applied to this work. The highlights of our mechanistic studies which are published elsewhere are *(18)*:

- The polyether oxygens in PEO pendant copolymers, like those in high molecular weight PEO homopolymer, form hydrogen bonding complexes with the phenol hydroxyl groups on PFR *(20, 21)*.

Sample	Relative turbidity, t_R	First-pass retention, %
56-108	0.25	90.6
43-129	0.29	81.5
23-145	0.42	61.3
23-157	0.44	58.7
PEO-309	0.27	83.7
PEO-301	0.37	70.0

11. Correlation between PS latex flocculation and pulp fines retention. Propeller speed was maintained at 250 rpm in the retention measurement. First-pass retention % = 129.5 - 161.3 x t_R

- The copolymers and PEO homopolymers which give the best flocculation also form precipitates when added directly to PFR. Furthermore, if PFR and PEO (or copolymer) are mixed and the resulting suspension of precipitates is then added to the test latex, little latex flocculation is observed. We concluded that the precipitation of PEO/PFR complex competes with fines or latex flocculation.
- Adsorption of PFR or the complex onto the colloids and fibers is required. This is in contrast to Lindström's network flocculation model which postulates that PEO forms a network structure with cofactor which mechanically traps colloids *(22)*.

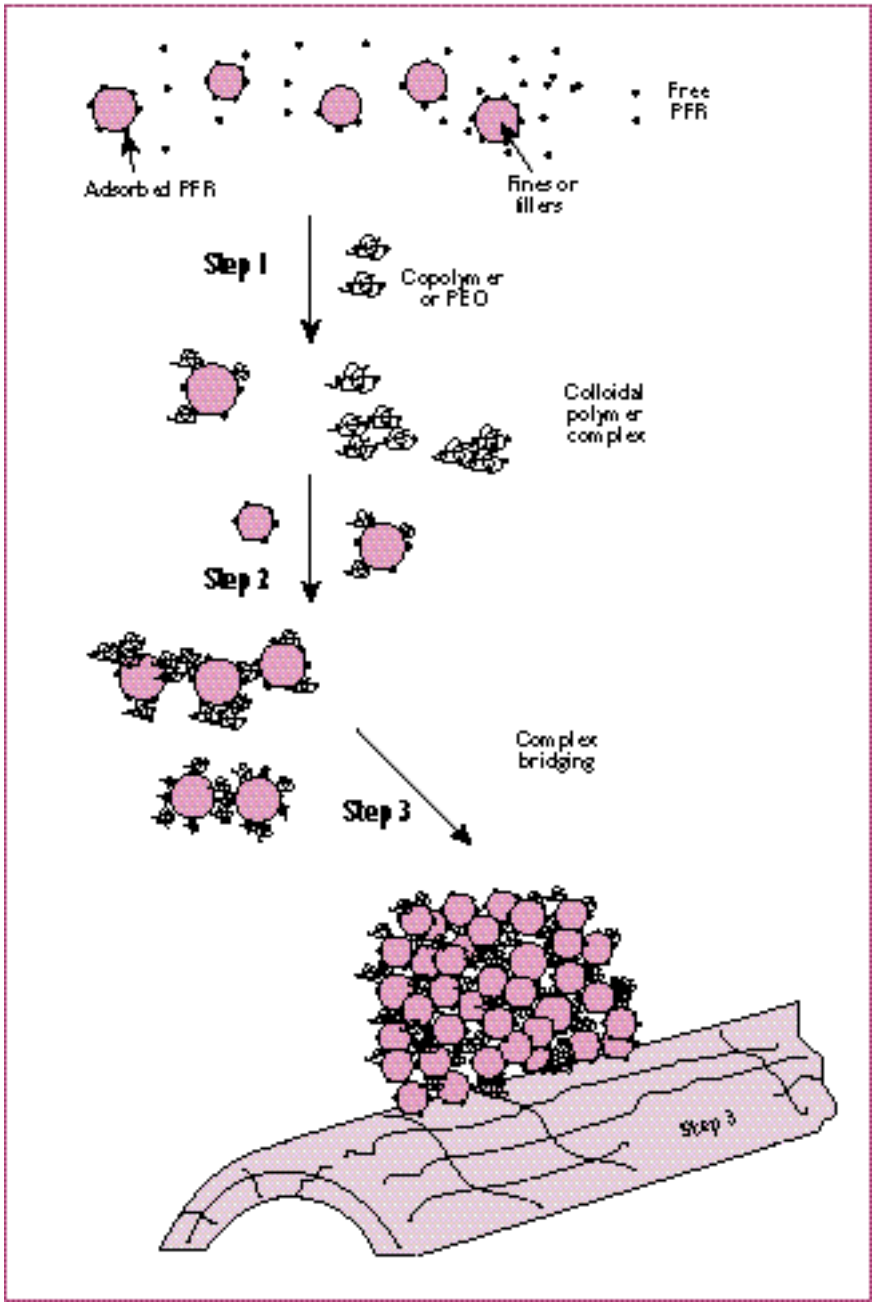
We have proposed a model for the PEO/PFR and copolymer/PFR flocculant systems which we call complex bridging *(18)*. The key features of our mechanism are illustrated in **Fig. 9**. In conventional experiments, PFR is added first and adsorbs to cover the latex and fiber surfaces leaving excess PFR in solution. Upon addition of PEO or copolymer (Step 1), the high molecular weight polyethers form colloidally unstable complexes with dissolved PFR. The suspension (Step 2) undergoes heteroflocculation of colloidally unstable PEO/PFR complex with the other colloids (latex or fines) to give large aggregates. The colloidally unstable aggregates (Step 3) deposit onto fiber surfaces.

A detailed mechanistic discussion should account for the requirement for high PEO or copolymer molecular weight as well as other possible events not shown in Fig. 9. This has been discussed elsewhere *(18)*.

CONCLUSIONS

The main conclusions of this work are:

1. Comb copolymers consisting of long polyacrylamide backbones bearing very short pendant PEO chains are novel and effective retention aids for mechanical pulps.
2. The optimum polymer structure had a molecular weight ≥3 x 10^6 and contained 1–2 mole percent macromonomer which, in turn, has between 9 and 23 ether oxygens. Of these parameters, the total molecular weight is the most important.
3. Compared with conventional high molecular weight PEO, the copolymers had far superior aging resistance and possibly better shear resistance. **TJ**



9. A schematic diagram of the complex bridging mechanism.

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This work was supported by the Mechanical and Chemimechanical Wood-pulps Network of the Canadian Network of Centers of Excellence pro - gram. We thank Borden Chemicals and Union Car - bide for kindly supplying polymers and Abitibi Price for the newsprint pulp.

Received for review April 4,1995.

Accepted Dec. 5,1995.

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