Polymer conformation effect on the fibre retention process — Study of blocking agent systems

By O. Oulanti, B. Chabot, F. Brouillette, and C. Daneault

Abstract: Bridging polymer conformation effect on retention was investigated by a sequential addition of two cationic polymers using a blocking agent system. The linear non-bridging polymers improved the bridging polymer retention efficiency at certain pre-adsorbed polymer dosages. Maximum retention levels corresponded to an optimum surface neutralization. The pre-adsorbed polymers promote an expanded bridging polymer conformation improving the retention process. Increasing the pre-adsorbed polymer dosage strongly disturbed the system and decreased the bridging polymer retention efficiency. The pre-adsorption of a branched non-bridging polymer presents a similar trend to linear polymers.

The bridging flocculation mechanism is a common process in many industrial applications such as papermaking or water treatment. This mechanism is based on the ability of a polymer to create bridges between different components of a suspension and to flocculate them [1]. Molecular characteristics of polymers, such as molecular weight and charge density, or many factors like charge surface or electrolyte concentration have an important influence on the flocculation efficiency of polymers. In papermaking, the interfibre bridging efficiency of a polymer depends strongly on the polymer conformation at interfaces [2]. The general polymer adsorption concept consists of a polymer adsorption at surface in the form of a train, loop, or tail [3]. It has already been proposed that the most suitable polymer conformation to improve flocculation is achieved when large numbers of extended loops and tails are present [4]. Previous research has shown that polymer retention efficiency decreased with time after polymer addition. This reduction was due to polymer relaxation at fibre/water interfaces [5]. Variation of polymer conformation, from an extended loop and tails to a flattened conformation decreased the presence of polymer segments in solution which can improve retention [6]. Development of polymer retention efficiency with time depended on polymer molecular characteristics. For two polymers of similar molecular weights or charge densities, the higher charge density or higher molecular weight polymer presented the highest retention efficiency with time [7]. Polymers with high charge densities or high molecular weights could induce strong molecular interactions between macromolecules at interfaces which promoted a faster limitation of their relaxation amplitude.

The study of polymer conformation at interfaces is of high importance for the interpretation of the bridging flocculation efficiency. Different techniques, such as scanning probe microscopy, ellipsometry, and small angle neutron scattering have been used to characterize experimentally the polymer conformation at interfaces [8-10]. The concept of site blocking agents is commonly used to improve the flocculation efficiency inducing an extended conformation of post-adsorbed flocculants [11]. Generally, the site blocking agent is a non-bridging polymer or nanoparticle having a charge density similar to the polymer used for the flocculation [12,13]. Swerin et al. [14] have studied the blocking effect obtained by the sequential addition of two polymers. First, a low molecular weight (LMW) and high charge density (HCD) polymer was added to neutralise some of the fibre and filler anionic sites, reducing the number of available sites for post-adsorbed polymer. Then, the adsorption of a high molecular weight (HMW) polymer with less attachment to the surface resulted in a loops and tails polymer conformation increasing the flocculation efficiency. It was suggested that the sequential addition of two cationic polymers could induce a thicker polymer layer than a single HMW polymer [15]. Stemme et al. [9] have shown that the combination of two polymers is an efficient flocculation system. This gives a thick and recharged layer even when a reduced amount of HMW polymer is adsorbed. Study of the site blocking effect on the conformation of adsorbed C-PAM (Cationic polyacrylamide) using scanning probe microscopy have shown a decrease of polymer attachment number with site blocking agent addition [16]. Moreover,
the increase of the hydrodynamic diameter of adsorbed polymer with site blocking agents is induced by an increase in the polymer tails portion.

In the present paper, we have studied the polymer retention process using blocking agent systems. Linear and branched polymers were used as blocking agents to determine their influence on the bridging polymer retention efficiency. We were also interested in determining the effect of polymer conformation on the fibre retention process. For this purpose, two retention processes were studied: direct and indirect retention.

EXPERIMENTAL
Pulp furnish
A thermomechanical pulp (TMP) was provided by a local pulp and paper mill. It was sampled after the second refiner stage before the bleaching stage. Pulp freeness was approximately 320 ml CSF. The pulp was first disintegrated in a British Disintegrator in 50°C water for 5 minutes. The consistency was adjusted to 1% with deionised water for retention trials.

Polymers
Polymer used as flocculants in this investigation were linear cationic polyacrylamides (C-PAM or copolymers of acrylamide and acryloxyethyltrimethylammonium chloride) having a high molecular weight (HMW) and high charge density (HCD). Various coagulants of linear and branched structures characterized by a higher charge density and various molecular weights have been used as blocking agents. Linear polymers consisted of poly(diallyldimethylammonium chloride) (P-DADMAC) and polyamine (PA). The branched polymers were branched polyamines (B-PA). They were kindly provided by Ciba Specialty Chemicals. Table I presents the chemical characteristics of these polymers. To avoid hydrolysis, fresh polymer solutions were prepared daily from concentrated chemicals using distilled water at a concentration of 1 mg/ml, without any pH adjustment.

METHODS
Retention measurements
The retention level was determined using a retention/drainage apparatus (Mütek DFR 04 + RET-20 Lab Module), according to Tappi Standard Method T 261 cm-94.

Table I. Polymer characteristics.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Charge density (meq/g)</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPAM</td>
<td>3.07</td>
<td>HMW</td>
</tr>
<tr>
<td>P-DADMAC 1</td>
<td>5.5</td>
<td>LMW</td>
</tr>
<tr>
<td>P-DADMAC 2</td>
<td>5.5</td>
<td>HMW</td>
</tr>
<tr>
<td>PA 1</td>
<td>7</td>
<td>LMW</td>
</tr>
<tr>
<td>PA 2</td>
<td>7</td>
<td>HMW</td>
</tr>
<tr>
<td>B-PA 1</td>
<td>7.7</td>
<td>LMW</td>
</tr>
<tr>
<td>B-PA 2</td>
<td>7.7</td>
<td>HMW</td>
</tr>
</tbody>
</table>

This procedure was applied to assess the tendency of fines and fillers to flocculate or to be lost in the filtrate with the aqueous phase. The suspension was continuously stirred during filtration to simulate the shearing conditions of a paper machine. Total, fines, and filler retentions were determined from the solid contents of pulp and filtrate samples. Applying the Peak Method, which is based on light diffusion, the equipment transmitter determines the fibre content in the filtrate, for subsequent automatic calculation of total retention [17].

Direct retention
Pulp fibre direct retention was studied by a sequential addition of two cationic polymers (blocking agent system) directly to the pulp suspension. Polymers adsorbed onto fibre surfaces of opposite charge induced the flocculation process. The polymer residence time in the suspension before retention measurements was 30 seconds for pre-adsorbed polymer (coagulant) and 15 seconds for subsequent flocculants.

Indirect retention
For these experiments, untreated fibres were mixed with fibres that had already been pre-treated with polymers using the direct retention procedure. Experimentally, we first determined the retention after polymer addition on fibres (direct retention). Then, pre-treated fibres were recovered and mixed at 1:1 weight ratio with untreated fibres (without any new addition of polymer). The indirect retention level was determined after 15 seconds of mixing. During both direct and indirect retention measurements, the pulp suspension was agitated at 500 rpm which corresponded to a shear level of approximately 2000 s⁻¹ [18].

RESULTS
In this investigation, we first studied the effect of the pre-adsorbed polymer on the retention process. For this purpose, we have studied the retention level according to polymer dosage for all pre-adsorbed polymers used in our investigation (P-DADMAC, PA, B-PA). Experiments were carried out by direct addition of pre-adsorbed polymer in the pulp suspension at several dosages. Variations in fibre surface charge with polymer dosage were also measured indirectly by means of zeta potential measurements (Mütek SZP-06 system). Figure 1 presents the effect of pre-adsorbed polymer dosage on retention levels for polymers characterized by different molecular structures, charge densities and molecular weights. Similar polymer behaviour was observed for all pre-adsorbed polymers used. We obtained a plateau retention level which remained constant against pre-adsorbed polymer dosage. Charge surface variation according to polymer dosage curves are shown in Fig. 2. P-DADMAC, which is characterized by a lower charge density compared to PA or B-PA, presented the largest gradient of fibre charge surface against polymer dosage. We also noted the increase of the gradient variation of fibre surface charge with molecular weight for similar polymers.

Blocking agent system
In this second part, we were interested in determining the effect of blocking agent systems on the retention process. The investigation was realized by a sequential addition of two cationic polymers to the pulp suspension and a subsequent measurement of retention. Linear and branched polymers were used as blocking agents to determine their effect on the post-adsorbed bridging polymer (C-PAM) retention efficiency.

Linear polymer
Linear polymers used in this study were a P-DADMAC and a PA characterized by different molecular weights. Figs. 3 and 4 present the relative retention level for the
direct retention process with a sequential addition of P-DADMAC or PA at several dosages and C-PAM at fixed dosage of 0.50 mg/g. \( R(Q) \) is the retention level at added amount \( Q \) of pre-adsorbed polymer followed by C-PAM addition at constant dosage. \( R(0) \) is the retention level without any polymer pre-adsorption.

The shape of all retention curves shown in Figs. 3 and 4 is similar. In the first part of the curve, the retention level increased against pre-adsorbed polymer dosage reaching a maximum value. A significant reduction of retention was observed thereafter for all systems studied. We obtained the same maximum retention level for similar pre-adsorbed polymers. However, this maximum was obtained at different added amount of pre-adsorbed polymers. For pre-adsorbed P-DADMAC, the maximum retention level corresponded to 5.50 and 2.75 \( \mu \text{eq/g} \) of added P-DADMAC 1 and 2 respectively, while for pre-adsorbed PA 1 and 2, maximum retentions were obtained at 17.5 or 14.0 \( \mu \text{eq/g} \) respectively.

The next step consisted of the investigation of the effect of the bridging polymer dosage. Figure 5 presents the sequential addition of PA 1 at several dosages and C-PAM at 0.50 and 0.75 mg/g. The relative retention level \( [R(Q) / R(0)] \) improves with C-PAM dosage. The maximum retention was obtained at the same added amount of pre-adsorbed polymer for both C-PAM dosages.

Figures 6 and 7 present the relative retention level for a sequential addition of PA 2 or P-DADMAC 1 followed by C-PAM at 0.50 mg/g using the indirect...
retention process. The shape of each curve was similar to those obtained with the direct retention process. In both direct and indirect retention processes, the maximum retention level was obtained at the same pre-adsorbed added amount for all linear polymers studied.

Branched polymer
In this last part of our study, branched polymers B-PA 1 and 2, characterised by different molecular weights, were used. Curves obtained for the sequential addition of B-PA and C-PAM presented a similar behaviour to those obtained for linear pre-adsorbed polymers (Fig. 8).

The maximum retention levels for pre-adsorbed branched polymers were obtained at 3.85 and 1.92 µeq/g of added pre-adsorbed amount of PA-1 and PA-2 respectively. Results for the sequential addition of B-PA and C-PAM showed that the maximum retention was not obtained at the same pre-adsorbed added amount with direct and indirect retention processes (Figs. 9 and 10).

DISCUSSION
The addition of pre-adsorbed linear or branched polymers to the pulp suspension gave a plateau retention level which remained constant against polymer dosages. This result indicated that pre-adsorbed polymers were in these cases non-bridging polymers unable to flocculate fibres. Behl et al. [12] have shown that site blocking additives must not be able to flocculate particles without the presence of polymeric flocculants. Measures of fibre surface charge have shown that polymer structure...
Retention curves corresponding to the sequential addition of linear or branched pre-adsorbed polymers followed by C-PAM using the direct retention procedure presented a similar behaviour for all systems studied. The retention increase was only attributed to the bridging polymer efficiency. Improvement of retention level was probably relative to the polymer conformation at interfaces (Fig. 11a). The pre-adsorbed polymer neutralized some adsorption sites on fibre surfaces leaving fewer attachment points for the bridging polymer. In consequence, the extended polymer conformation was promoted for the bridging polymer (Fig. 11b). The maximum retention level obtained probably corresponded to the more extended polymer conformation at interfaces.

Similar maximum polymer retention levels were obtained for similar pre-adsorbed linear or branched polymers. Those results showed that the molecular weight of the linear or branched pre-adsorbed polymers have no influence on post-adsorbed polymer retention efficiency. The maximum polymer retention efficiency achieved depended strongly on the pre-adsorbed polymer. The added amount of pre-adsorbed polymer required to reach this maximum (Qm) decreases when the gradient of fibre surface charge increased for similar pre-adsorbed polymers. Then, after this maximum, adding more pre-adsorbed polymer disturbed the system and deteriorated the retention efficiency of the bridging polymer. This decrease is more important when the gradient of the fibre surface charge increased for similar pre-adsorbed polymers (see Fig. 2). This result indicated that the decrease of polymer retention efficiency depended strongly on the fibre charge neutralisation state after pre-adsorbed polymer. In a paper mill, we usually observe that the blocking agent system improves the retention process for some furnish, whereas the same process deteriorates the retention process for another furnish compared to individual polymer addition. The difference in blocking agent system efficiency between these two cases depends on the initially available adsorption sites. The study of blocking agent systems by varying the polymer dosage has shown that the maximum retention was obtained at the same pre-adsorbed added amount (Qm) for both dosages studied. This result proves that the Qm corresponded to an optimum neutralization of adsorption sites promoting the polymer adsorption in an extended conformation. Moreover, we note the increase of the relative polymer retention level [R(Q)/R(0)] with polymer dosage. This increase is probably induced by the fact that the increase of polymer dosage added at the same available adsorption site promotes the extension of polymer conformation at interfaces.

In order to determine if the polymer conformation was indeed responsible for the retention level improvement, we studied the indirect retention process. The interpretation of this process was based on the presence of pre-adsorbed bridging polymers in solution to improve indirect retention. The indirect retention curves present a similar trend to those obtained for direct retention process. Moreover, the results have shown that the maximum retention level for the direct and indirect retention process was obtained at the same Qm for similar linear pre-adsorbed polymers. This indicates that in this case for direct retention process, at the maximum retention level, the polymer has the more extended conformation which induces a maximum retention level for indirect retention. On the other hand, the maximum retention level in the direct and indirect retention process was obtained at different Qm for branched pre-adsorbed polymers. This indicates that in this case for direct retention process, at the maximum retention level, the polymer has the more extended conformation which induces a maximum retention level for indirect retention. On the other hand, the maximum retention level in the direct and indirect retention process was obtained at different Qm for branched pre-adsorbed polymers. The improvement of polymer retention efficiency in the blocking agent systems is relative to polymer conformation at interfaces enhanced by pre-adsorbed polymer. This investigation put in evidence the importance of polymer conformation at interfaces in the retention process.

CONCLUSIONS
The application of blocking agent systems to pulp suspensions has shown an improvement of the retention process efficiency. However, this improvement was limited to certain pre-adsorbed polymer dosages or fibre surface charge neutralisa-
tion states. The enhancement of polymer retention efficiency is induced by an increase of the extension of polymer conformation at interfaces. This result showed the importance of polymer conformation in the retention process. The maximum retention level obtained corresponded to an optimum surface charge neutralization which in turn depended strongly on the pre-adsorbed polymer. Then, after this maximum, increasing the amount of pre-adsorbed polymer affected the retention process negatively.

**LITERATURE**


Résumé: L’étude de l’influence de la conformation du polymère sur la rétention a été réalisée par une addition séquentielle de deux polymères cationiques en utilisant le principe d’agent de blocage. Les polymères linéaires améliorent l’efficacité de la rétention du floculant à un certain dosage de polymère pré-adsorbé. Le niveau maximum de rétention obtenu correspond à un optimum de neutralisation de surface. Le polymère pré-adsorbé favorise l’extension de la conformation du floculant améliorant le processus de la rétention. L’augmentation du dosage du polymère pré-adsorbé perturbe fortement le système et diminue l’efficacité de rétention du polymère. La pré-adsorption d’un polymère branché sur le floculant est similaire à celui des polymères linéaires.


**Keywords:** FIBRE RETENTION PROCESS, RETENTION AGENT, BLOCKING AGENT SYSTEM, PAPER FORMATION, POLYMER INTERFACIAL CONFORMATION, SITE BLOCKING AGENT, POLYMER RETENTION EFFICIENCY