# CORRELATING RETENTION AND DRAINAGE IN PAPERMAKING WITH FLOCCULATION: EFFECT OF POLYELECTROLYTE BRANCHING

*E. Antunes, F. A. P. Garcia, P. Ferreira and M.G. Rasteiro**

*Research Centre for Chemical Processes Engineering and Forest Products,*
*Chemical Engineering Department, Coimbra University, Pólo II, Pinhal de*
*Marrocos, 3030-290 Coimbra, Portugal*

* Corresponding author: Tel: +351239798700; Fax: +351239798703.
E-mail: mgr@eq.uc.pt

## Abstract

The effect of the degree of polymer branching on retention and drainage performance of flocculated kraft pulp fiber suspensions containing precipitated calcium carbonate (PCC) was investigated and has been correlated with flocs properties obtained by light diffraction scattering (LDS). The results show that polymers of medium charge density are more adequate to be used as retention aids since lower drainage time and higher filler retention are obtained at low flocculant contact time and low flocculant dosage. The results also demonstrate that it is possible to correlate the flocculation process evaluated by LDS with the flocculant's performance in the drainage test.

## Introduction

In papermaking, chemical flocculation is fundamental for achieving high retention and high drainage rate simultaneously (1, 2, 3). The flocculation evaluation is of great importance to control the wet-end stage in paper production since retention, drainage and sheet formation depend on the flocculation mechanisms involved and on flocs characteristics. Additionally, flocculation mechanisms depend on several factors namely on flocculants characteristics and dosage and on contact time, among others (1). For example, flocculant overdosage, which results in large flocs, can reduce drainage rates since it can be more difficult to remove the interstitial water from large flocs (4).

The polymer structure is another parameter that affects the flocculation process. In fact, some studies have shown that the branched polymers have a significant potential as papermaking retention aids on the fast paper machine. Firstly, Nicke and co-workers (5) demonstrated that a branched copolymer, is an attractive flocculant for the paper industry. In the same way, Shin and co-workers (6, 7) have studied the potential of the highly branched polymer as a retention aid for microparticulate systems by performing flocculation, retention and formation tests. They concluded that the branched polymer exhibits better retention efficiency than the linear polyelectrolytes without affecting sheet formation. More recently, Brouillette et al. (8, 9) have also studied the performance, on retention, drainage and sheet formation but in a high turbulent environment, of a branched C-PAM of high molecular weight in a microparticle retention system. They confirmed that this retention aid system improves filler retention comparing with the conventional ones and that this improvement is particularly significant as the turbulence level increases.

We believe it is of great interest to study these new polymers in single component systems to better understand the mechanisms involved since, so far, the few fundamental investigations conducted studied retention and drainage performance of these polymers in microparticulate systems.

In this present study, the effects of the degree of polymer branching on retention and drainage performance were evaluated. Additionally, the effects of flocculant concentration, flocculant charge density and flocculant contact time were investigated. The results were correlated with flocculation kinetics and flocs structure. Several new cationic polyacrylamides (C-PAM) of high molecular weight were used to flocculate the suspension. These C-PAMs differ on their charge density and number of branches. The dynamic drainage analyser (DDA) was used to evaluate retention and drainage of a flocculated kraft pulp fiber suspension containing precipitated calcium carbonate (PCC). Flocculation kinetics were assessed by using a light diffraction scattering (LDS) technique which gives simultaneously information about the flocs size distribution and the flocs structure. The flocs structure was quantified by both the mass fractal dimension and the scattering exponent parameters (10).

## Methods and materials

A short fiber bleached kraft pulp was used in this study. The fiber suspension was prepared at a consistency of 1% in distilled water. The PCC suspension was prepared at a concentration of 1% in distilled water (11). The median size of the PCC particles evaluated by LDS was 0.5μm.

The main characteristics of the six new C-PAM emulsions of very high molecular weight, developed and supplied by AQUA+TECH used in this study are summarized in Table 1. Flocculant solutions were prepared daily with distilled water at 0.1% (w/w).

**Table 1.** Flocculant characteristics.

| Alpine Floc$^{TM}$ | Molecular Weight | Number of Branches | Charge density |
|---|---|---|---|
| E1 | $1.2\times10^7$ | linear | 50% |
| E1+ | $1.3\times10^7$ | 1 | |
| E1++++ | $1.2\times10^7$ | 4 | |
| G1 | $4.6\times10^6$ | linear | 20% |
| G1+ | $4.7\times10^6$ | 1 | |
| G1++++ | $4.4\times10^6$ | 4 | |

Drainage tests were carried out in the DDA (AB Akribi Kemikonsulter). The DDA measures drainage performance but can simultaneously give information about retention and wet sheet permeability for the same sample.

The kraft pulp fiber suspension was mixed with the PCC suspension in the equipment during two minutes before the addition of the flocculant. In the DDA, the vacuum was maintained at 30 kPa and the stirring speed in the vessel was 800 rpm. For each experiment, the flocculant contact time varied from 30 to 90 seconds and a drainage test without flocculant (blank) was performed daily.

The wet sheets obtained from the drainage tests were dried at 105ºC to calculate the total solid retention. Afterwards, the samples were burned at 600ºC during 16 hours to determine the PCC retention (12).

The Malvern Mastersizer 2000 (Malvern Instruments) was used to monitor the flocculation of the PCC particles. The flocculation kinetics and the flocs structure were studied for various flocculant concentrations as described in previous papers (11, 13). Figure 1 shows an example of the flocculation kinetics obtained by LDS for E1 and E++++ and for the corresponding optimum dosage (13). For the optimum flocculant dosage, the flocculation rate is faster and larger flocs are reached. The results obtained by LDS (Table 2) will be used in this paper to correlate the drainage time and the retention performance with the flocculation kinetics and the flocs structure.

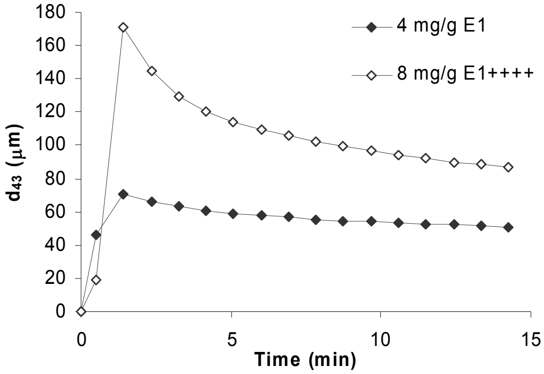

**Figure 1.** Flocculation kinetics for the optimum flocculant dosage of E1 and E1++++ (13).

**Table 2.** Main flocculation results obtained by LDS (13).

| | | | Max. kinetics curve | |
|---|---|---|---|---|
| Alpine Floc$^{TM}$ | Optimum dosage | $d_{43}$ (μm) | $d_F$ | SE |
| E1 | 4 | 46 | 1.33 | 2.36 |
| E1+ | 12 | 31 | 1.13 | 1.37 |
| E1++++ | 8 | 19 | 1.46 | 1.61 |
| G1 | 10 | 373 | 1.52 | 1.50 |
| G1+ | 30 | 436 | 1.67 | 1.51 |
| G1++++ | 30 | 345 | 1.63 | 1.34 |

## Results and Discussion

### *Drainage and retention results*

Drainage tests were performed for the optimum flocculant dosage found by LDS (Table 2) and for a common flocculant concentration, 6 mg/g. Moreover, for G1+ and G1++++, drainage tests were performed for 20 mg/g and for E1 and E1+, flocculant concentrations of 2 mg/g and 16 mg/g respectively were tested. In order to compare drainage results, the drainage times and the PCC retention are normalized relatively to the drainage time and the PCC retention of the blank test respectively. The normalized drainage times for 30 and 90 seconds of contact time are represented in Figure 2 as a function of flocculant concentration for all the flocculants tested. The average drainage time for blank experiments is 5.1 seconds (± 0.5s). In Figure 3, the normalized PCC retention is plotted for the six polymers studied. Here, the total solid retention is not presented since the change in total retention is mainly caused by filler retention (3). The average total solid retention and the average PCC retention of the unflocculated suspension are 84.3% (± 0.5%) and 11.5% (± 1%) respectively.

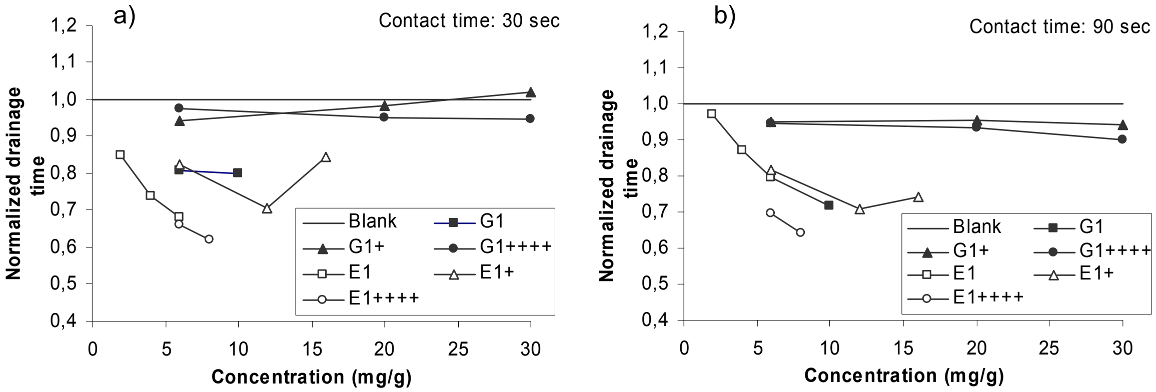

**Figure 2.** Normalized drainage time as a function of flocculant concentration for a) 30s and b) 90s of contact time.

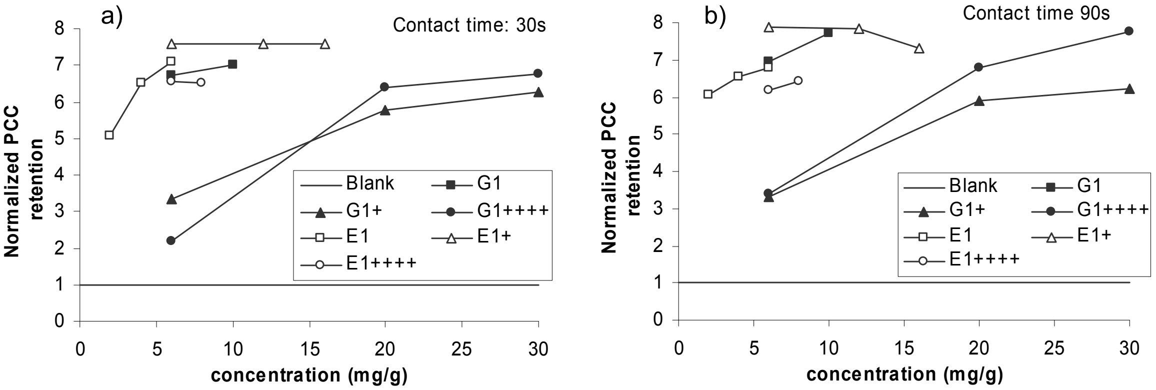

**Figure 3.** Normalized PCC retention as a function of flocculant concentration for a) 30s and b) 90s of contact time.

The addition of G1+ and G1++++ does not improve the drainage time relatively to the blank. For the high flocculant concentrations for which G1+ and G1++++ reach the optimum flocculant dosage, the amount of flocculant is too high leading to an increase of the suspending medium viscosity. Thus, the increase of the medium viscosity which makes water flow more difficult can explain the increase of the drainage time for these two flocculants. At the lowest flocculant concentration, G1+ and G1++++ not only impair drainage but also present the worst results for PCC retention. A poor flocculation results in a low drainage rate and in a low PCC retention because the flocculated suspension behavior is close to the one observed for the unflocculated suspension. At higher dosages, the PCC retention is similar to the ones observed for the other polymers.

For the other polymers, all the flocculated suspensions exhibit a better drainage time than the unflocculated suspension. As the flocculant concentration is close to the optimum dosage, a lower drainage time is obtained. In addition, PCC retention is, in general, maximum for the optimum dosage. Hence, despite the flocculation results being related only with the flocculation of the PCC and the operating conditions being different in the DDA and in the LDS, it is possible to see a good agreement between flocculation tests and drainage tests. This can be explained by the fact that in a composite furnish containing refined fibers, fines and filler, polymer preferentially flocculates the filler (2). Thus LDS and DDA tests can be complementary techniques to pre-screen flocculants performance in papermaking.

Results obtained for E1+ indicate that if the flocculant concentration increases too much, the drainage time increases again. When the flocculant is in excess, flocculation progresses at a lower rate (13) and, thus, for the flocculant contact time used in these studies the flocs are still too small (poor flocculation) and the sheet structure is relatively closer to the blank and so is the drainage time. In general, as flocculant concentration increases further retention tends to reach a plateau. Hence, it is possible to find a flocculant dosage range where a low drainage time and a high PCC retention can be achieved simultaneously. In this case, this range is 5-10 mg/g for all the polymers except the G1+ and G1++++ for the reasons explained previously.

For the E1 series the increase in the contact time results in an increase in the drainage time and PCC retention while for the G1 series the increase in the contact time results in a decrease in the drainage time. However, the highest drainage time variations with contact time are observed for the linear polymers E1 and G1. The trend of the drainage time with flocculant contact time observed for the E1 series agrees with the work of Forsberg and Ström (14). However, when the polymer E1+ is in excess (16 mg/g), the drainage time decreases as the contact time increases: for such dosage the flocculation degree is higher at 90s than at 30s resulting in the improvement of the drainage time. Nevertheless, the G1 series does not follow this behavior.

These trends can be explained by the LDS results. These results have shown that flocs produced with the G1 series are much larger than those produced with E1 series due to the lower charge density, therefore resulting in overflocculation and producing too large flocs that reduce the drainage performance. In this case, the decrease of the flocs size with flocculation time due to polymer reconformation and degradation (15) reduces the effect of the overflocculation and thus results in drainage time decrease with flocculant contact time increase. Moreover, the same effect of the flocculant contact time was observed with the PCC retention (Figure 3). Thus, for the E1s series, better drainage times and PCC retention are obtained for lower flocculant contact times while for the G1s series, the opposite happens.

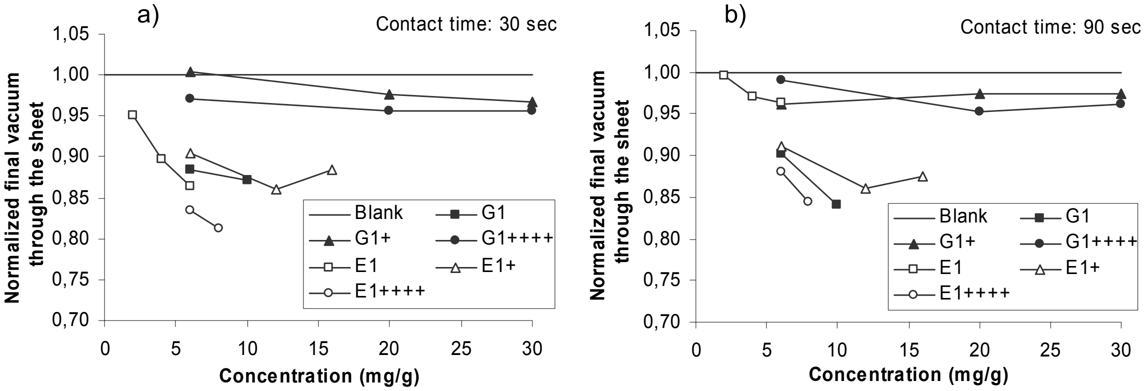

**Figure 4.** Normalized final vacuum as a function of flocculant concentration for a) 30s and b) 90s of contact time.

Figure 4 summarizes the final vacuum normalized relatively to the final vacuum of the blank test, through the sheet as a function of the flocculant concentration. A low final vacuum corresponds to high sheet permeability, i.e., to high sheet porosity. The final vacuum average through the sheet for the unflocculated suspension is 16.8 kPa (±0.6 kPa). The same trend observed for the drainage time is verified for the sheet permeability when the flocculant dosage varies. In fact, lower drainage times correspond to higher sheet permeability, i.e., higher sheet porosity. Figure 5 confirms the linear correlation between the drainage time and the sheet porosity.

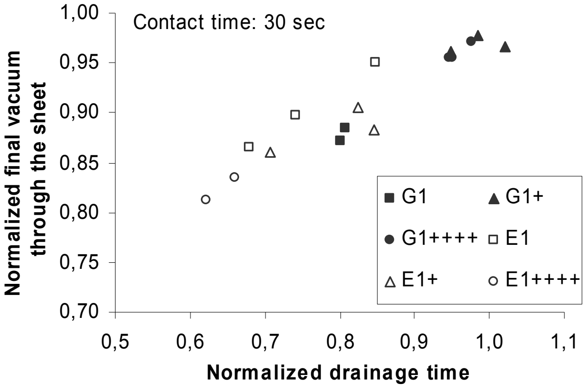

**Figure 5.** Normalized final vacuum as a function of normalized drainage time for 30s of contact time.

### *Correlation with flocs properties*

The effect of flocs size and flocs structure on the drainage time is investigated for the optimum flocculant dosage obtained by LDS.

In Figure 6a, the normalized drainage time for the optimum flocculant dosage is represented as a function of the mean flocs size. For the E1 series, the results correspond to a flocculation time of 30 seconds while for the G1 series, results refer to a flocculation time of 90 seconds for which both drainage and retention give best results. The drainage time decreases with the decrease in the flocs size and the E1 series produce the smallest flocs. Additionally, E1++++ is the flocculant that produces the smallest flocs and gives the lowest drainage time. Thus, it is possible to have fast dewatering and high filler retention with small flocs. Larger flocs reduce drainage rate as confirmed for the G1 series. This happens because flocs that are too large and have much more interstitial water which is difficult to remove. So, overflocculation (very large flocs) results in low drainage despite retention being not affected.

In Figure 6b, the drainage time is related with the flocs structure quantified by the mass fractal dimension and by the scattering exponent for the optimum flocculant dosage. The mass fractal dimension gives indication about the structure of the primary flocs while the scattering exponent gives information about the structure of secondary flocs that result from the aggregation of the primary ones. The mass fractal dimension and the scattering exponent are calculated for the maximum in the flocculation kinetic curve observed in the previous study as shown, for instance, in Figure 1 for the E1 and E1++++ polymers (13). Primary flocs produced with E1 are open (small $d_F$) while the secondary flocs are compact (high SE). Both primary and secondary flocs produced with E1+ are open (small $d_F$ and SE) when comparing with E1 flocs. The configuration of flocs produced with E1++++ seems to be the most adequate to remove easily the water from the flocs. Primary flocs are slightly more compact while secondary flocs are open comparing with E1 and E1+. This contributes to a lower drainage time as shown in Figure 6b.

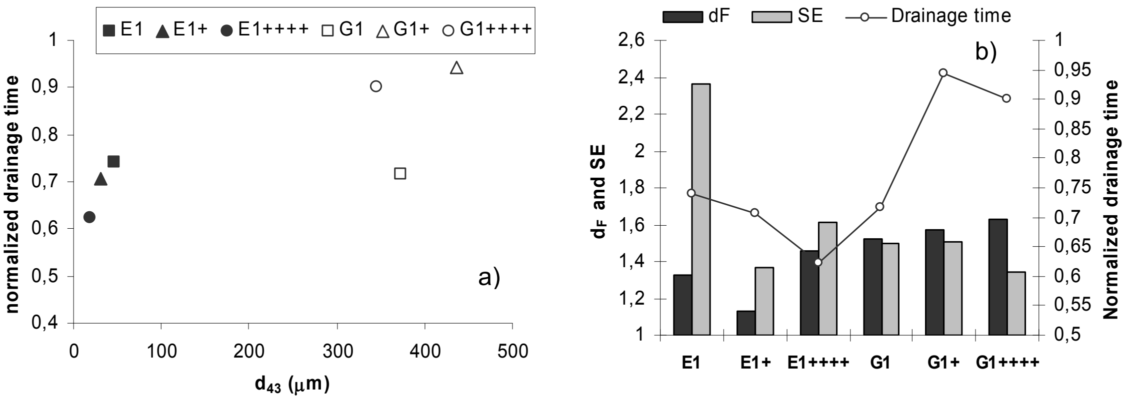

**Figure 6.** Normalized drainage time as function of a) mean floc size and b) flocs structure for the optimum flocculant dosage.

However, the structure of the flocs produced with the G1 polymers is similar to the structure of the E1++++ flocs but drainage time is much higher. In this case, the drainage time is mainly affected by the larger floc size (overflocculation).

## Conclusions

The correlation between retention and drainage results and flocculation behavior (namely the flocs properties) is fundamental to understand how the flocculant characteristics affect the retention and drainage performance in papermaking.

The retention and drainage performance is enhanced, in general, close to the optimum flocculant dosage found by the flocculation results. A low flocculation degree also results in low drainage rate but in poor filler retention.

Flocculants of low charge density do not improve drainage times compared to the unflocculated suspension but offer very high filler retention. An increase of the flocculant contact time can slightly decrease the drainage time and increase filler retention.

On the other hand, flocculants of medium charge density offer simultaneously low drainage times and very high filler retentions at low flocculant dosage and at low flocculant contact time. When a branched structure of these flocculants is used it improves significantly the drainage rate and the filler retention comparing with the linear ones.

Moreover, it was shown that for the branched polymers of medium charge density, the improvement in the drainage time is due to the formation of small flocs sizes with an open structure, mainly at the secondary aggregate level. The increase of the drainage time for the linear polymer is due to the more compact structure of the small flocs formed.

Polymers of medium charge density are more suitable to be used as retention aid because low drainage time and very high filler retention are obtained simultaneously at low flocculant contact time and low flocculant dosage. Moreover, highly branched polymers can be considered an adequate choice because the balance between flocculant dosage, drainage time and filler retention is the best. Thus, these polymers represent a promising additive for papermaking.

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## References

1. Norell, M.; Johansson, K.; Persson, M. (1999), “Retention and Drainage. Book 4: Papermaking Chemistry”, Papermaking Science and Technology, TAPPI PRESS, Finland.

2. Whipple, W.L.; Maltesh, C. (2002), “Adsorption of cationic flocculants to paper slurries”, *J. Colloid Interf. Sci.*, 256, 33-40.

3. Cadotte, M.; Tellier, M.E.; Blanco, A.; Fuente, E.; van de Ven, T.G.M.; Paris, J. (2007), “Flocculation, retention and drainage in papermaking: a comparative study of polymeric additives”, *Can. J. Chem. Eng.*, 85, 240-248.
4. Hubbe, M.A.; Heitmann, J.A. (2007), “Review of factors affecting the release of water from cellulosic fibers during paper manufacture”, *Water release*, *papermaking. BioResources*, 2(3), 500-533.
5. Nicke, R.; Pensold, S.; Hartmann, H-J.; Tappe, M. (1992), “Polydiallyldimethylammonium chloride as a flocculating agent”, *Wochenbl. Papierfabr.*, 120(14), 559-564.
6. Shin., J-H.; Han, S.H.; Sohn, C.; Ow, S.K.; Mah, S. (1997), “Highly branched cationic polyelectrolytes: filler flocculation”, *Tappi J.*, 80(11), 179-185.
7. Shin., J-H.; Han, S.H.; Sohn, C.; Ow, S.K.; Mah, S. (1997), “ Highly branched cationic polyelectrolytes: fines retention”, *Tappi J.*, 80(10), 185-189.
8. Brouillette, F.; Morneau, D.; Chabot, B.; Daneault, C. (2005), “A new microparticulate system to improve retention/drainage in fine paper manufacturing”, *Appita J.*, 58(1), 47-51.
9. Brouillette, F.; Morneau, D.; Chabot, B.; Daneault, C. (2004), “Paper formation improvement through the use of new structured polymers and microparticle technology”, *Pulp Paper Can.*, 105(5), 108-112.
10. Biggs, S.; Habgood, M.; Jameson, G.J.; Yao-de-Yan (2000), “Aggregate structures formed via a bridging flocculation mechanism”, *Chem. Eng. J.*, 80, 13-22.
11. Rasteiro, M.G.; Garcia, F.A.P.; Ferreira, P.; Blanco, A.; Negro, C.; Antunes, E. (2008), “The use of LDS as a tool to evaluate flocculation mechanisms”, *Chem. Eng. Proc.*, 47, 1329-1338.
12. Ferreira, P.; Velho, J.; Figueiredo, M.; Mendes, A. (2005), “Effect of thermal treatment on the structure of PCC particles”, *Tappi J.*, 4(11), 18-22.
13. Antunes, E.; Garcia, F.A.P.; Ferreira, P.; Blanco, A.; Negro, C.; Rasteiro, M.G. (2008), “Effect of water cationic content on flocculation, flocs resistance and reflocculation capacity of PCC induced by polyelectrolytes”, *Ind. Eng. Chem. Res.*, 47, 6006-6013.
14. Forsberg, S.; Ström, G. (1994), “The effect of contact time between cationic polymers and furnish on retention and drainage”, *J. Pulp Paper Sci.*, 20(3), 71-76.
15. Rasteiro, M.G.; Antunes, E.; Garcia, F.A.P; Ferreira, P.; Wandrey, C.; Hunkeler, D. (2008), “Flocculation by polyelectrolytes: correlating the flocculation process with polymer characteristics”, Polyelectrolytes 2008, Coimbra, Portugal.