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Use of New Branched Cationic Polyacrylamides to Improve Retention and Drainage in Papermaking

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Cationic polyacrylamides of very high molecular weight and with different charge densities and degrees of branching have been investigated as retention aids for papermaking. The effects of polymer charge density and polymer branching on drainage and retention of a suspension containing fibers and precipitated calcium carbonate have been correlated with flocs properties. Additionally, the effects of flocculant dosage and contact time with the furnish were investigated. 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 short contact time and low flocculant dosage. The branched polymers exhibited better performance than the linear polymers: drainage performance is significantly improved because highly branched polymers produce small flocs with a more open structure.

Introduction

During papermaking, mechanical entrapment is the most dominant retention mechanism for fines and fillers in the absence of retention aids.[1] However, since the holes in the wire are larger than these particles, significant mechanical retention of the small particles on the wire cannot be achieved.[1,2] Additionally, the unflocculated fine and filler fraction of the stock suspension can increase drainage resistance.[1] Chemical flocculation is therefore fundamental for achieving both a high retention and a high drainage rate simultaneously.[1,3−5] However, the choice of the retention aid systems has to be made with caution since retention, drainage, and sheet formation depend mainly on the flocculation mechanisms involved, and the balance between retention and drainage is essential for good sheet formation. Moreover, flocculation mechanisms depend on several factors namely on flocculant characteristics and dosage or residence time, among others.[6−10] In fact, flocculant overdosage can be a problem in papermaking due to its significant negative effect on dewatering.[11] A high degree of flocculation, resulting in large flocs, reduces drainage because it is difficult to remove the interstitial water from these types of flocs.[12] Hence, flocs characteristics are of great importance to improve dewatering. The contact time between the furnish and the chemical additives must be also taken into account for the choice of the retention system. Indeed, long contact times can drastically reduce the effect of the flocculant and thus the process efficiency.[1]

The polymer structure is another parameter that affects the flocculation performance and thus the wet-end efficiency. Few studies have been conducted to analyze the polymer conformation at the particle surface using branched polymers instead of the traditional linear ones. Nicke and co-workers demonstrated that a branched copolymer is an attractive flocculant for the paper industry.[13] Shin and co-workers compared flocculation of ground calcium carbonate induced by highly branched cationic polyacrylamides (C-PAMs) of low molecular weight and low cationic charge with conventional linear C-PAMs of high molecular weight.[14] They concluded that the highly branched polymer produces small flocs with great shear resistance and, when associated with microparticles, the flocs' size increases. The same authors have studied the potential of the highly branched polymer as a retention aid for microparticulate systems by performing retention tests.[15] The results showed that the branched polymer exhibits better retention efficiency than the linear polyelectrolytes. Handsheets formation tests also allowed the authors to conclude that the microparticle system used with the highly branched polymer produces sheets with good formation even if the amount of filler in the sheet is higher. More recently, Brouillette and co-workers have also studied the performance of branched C-PAM of high molecular weight in conjunction with a microparticle system on retention, drainage, and sheet formation but under high turbulence levels.[16,17] As in earlier studies, they found that this retention aid system improves filler retention comparing with the conventional ones and that sheet formation is not affected by the increase of the filler content. Nevertheless, this improvement is particularly significant as the turbulence level increases. The branched polymers are less affected by shearing and thus give the best efficiency. In addition, the polymer dosage required to obtain a good retention decreases with the increase of the shearing for the branched polymer, while it increases for the linear one. This polymer dosage reduction could result in savings on chemical costs.

As a result of these studies, the branched polymers are expected to exhibit better performance than the linear ones on fast paper machines and thus have a significant potential as papermaking retention aids. However, the few studies presented so far have been based on the retention and drainage performance of these polymers in microparticulate systems. It is however also of great interest to study these new polymers in a single component system in order to better understand the mechanisms involved.

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Table 1. Flocculant Characteristics

Alpine floc	molecular weight[a]	charge density[b]	number of branches
E1	1.2×10^7	50%	linear
E1+	1.3×10^7		1
E1++++	1.2×10^7		4
G1	4.6×10^6	20%	linear
G1+	4.7×10^6		1
G1++++	4.4×10^6		4

[a] Calculated from intrinsic viscosity. [b] Calculated by titration.

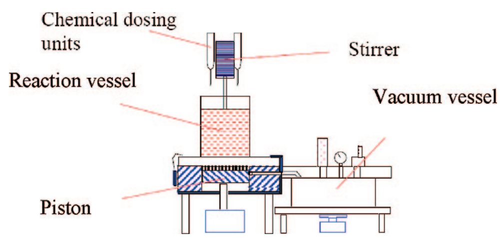

Figure 1. Schematic illustration of a DDA.[20]

In this context, the objective of this study was to evaluate the effect of the degree of polymer branching on retention and drainage performance and simultaneously to correlate the results with flocculation kinetics and flocs structure, making use of the flocculation tests previously performed.[18−20] Additionally, the effects of flocculant concentration, flocculant charge density and flocculant contact time were investigated. A dynamic drainage analyzer (DDA) was used to evaluate retention and drainage of a flocculated fiber suspension containing precipitated calcium carbonate (PCC). Six new C-PAMs of high molecular weight were used to flocculate the suspension. These C-PAMs differ on the charge density and on the number of branches. Flocculation results were obtained by using a light diffraction scattering (LDS) technique which gives information about flocculation kinetics, flocs size, and flocs structure.[18] The flocs structure was quantified by the mass fractal dimension and the scattering exponent calculated based on the scattering matrix provided by LDS.[9,21]

Experimental Details

Materials. In all experiments, a eucalyptus bleached kraft pulp was used. The length weight of the fibers was 0.582 mm. The pulp suspension, refined to 32° SR, was diluted to a consistency of 1% in distilled water. A scalenohedral PCC supplied by the industry, was used as filler and a suspension with a concentration of 1% in distilled water was prepared.[18] The median size of the PCC particles, measured by LDS, was 0.5 μm.

Six new C-PAM emulsions of very high molecular weight, developed and supplied by AQUA+TECH, were used in this study. The main characteristics of these C-PAMs are summarized in Table 1. The cationic monomer in all the polymers is dimethylamino-ethyl-acrylate. Flocculant solutions were prepared daily with distilled water at 0.1% (w/w).

Methods. Drainage Evaluation. Drainage tests were carried out using the Dynamic Drainage Analyzer (DDA, AB Akribi Kemikonsulter) (Figure 1). This equipment measures drainage and simultaneously gives information about retention and wet sheet permeability. It consists of a drainage unit and a microprocessor with control for the vacuum, the shear and the chemical addition during the test.[22,23] During the experiment the vacuum and the time are recorded and stored by the microprocessor. Figure 2 illustrates a typical drainage curve obtained with the DDA.[24] The sharp drop in vacuum, starting at zero time, is associated with the initial rapid flow of white water through the forming wire. The point “A” on the curve refers to the point where the wire effectively has become covered with a layer of suspension. The increase in vacuum from point A to point B corresponds to the increase in flow resistance due to the formation of the fiber mat. Point B is related with the “dry line”, just before breakthrough of air. The final vacuum value of the curve (point C) can be used as a measure of the permeability to air of the wet sheet. The permeability to air expressed in pressure units (bars) is related with the sheet porosity. Forsberg and Bengtsson showed that a more porous sheet gives a higher drainage rate.[22] Moreover, the sheet permeability is an indication of the degree of flocculation of the formed wet web. A low permeability, i.e., low porosity, indicates an undesirable high degree of flocculation, resulting in large flocs that would not easily allow removal of the interstitial water. A low permeability could also result in poor sheet formation. As a result, a low drainage time in combination with a high sheet permeability is the desired response to have good dewatering without poor formation.

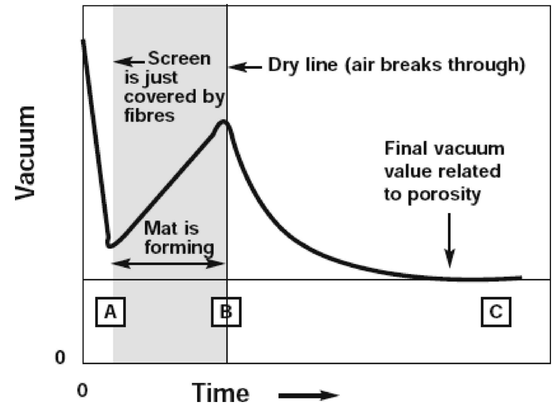

Figure 2. Typical vacuum curve obtained with the DDA.[21]

Pulp suspension was prepared by mixing 500 mL of the fiber suspension and 100 mL of the PCC suspension corresponding to 0.83% (w/w) of fiber, 0.17% (w/w) of PCC, and 99% (w/w) of water. The mixture was added to the DDA vessel equipped with a 350 μm square openings wire. In this way, a solids concentration (PCC + fiber) of 10 g/L was reached. The vacuum was maintained at 30 kPa, and the stirring speed in the vessel was 800 rpm. The suspension of fiber and PCC was stirred during 2 min before the addition of the flocculant in an adequate concentration. For each experiment, the flocculant contact time varied from 30 to 90 s and a drainage test without flocculant (blank) was performed daily.

Determination of Retention. The wet sheets obtained from the drainage tests in the DDA were used to determine fines and filler retention. The residues collected were dried at 105 °C to calculate the total solid retention. Afterward, the samples were burned at 600 °C during 16 h to determine the PCC retention degree.[25]

Flocculation Tests. The flocculation of the PCC particles was monitored by measuring the size of the aggregates by LDS in a Malvern Mastersizer 2000. The methodology adopted to evaluate the flocculation kinetics and the flocs structure for various flocculant concentrations has been described in previous papers.[18,20] The influence of flocculant concentration and of flocculant branching on flocculation kinetics and on flocs structure was previously studied for the polymers E1, E1+, and E1++++.[20] The main results, summarized in Table 2, will be used in this paper to correlate the drainage time and the retention

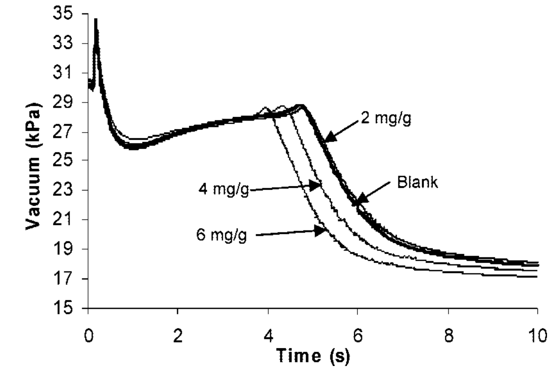

Figure 3. Drainage curves obtained for several E1 dosages and for 90 s of contact time.

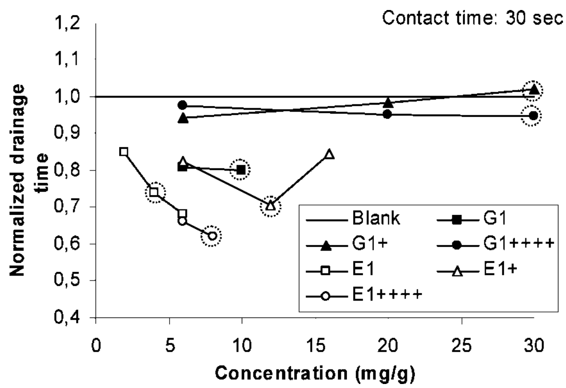

Figure 4. Normalized drainage time as function of flocculant concentration for 30 s of contact time: (○) dosage for maximum flocculation.

Table 2. Main Flocculation Results Obtained by LDS[20]

Alpine floc	dosage for maximum flocculation (mg/g)	d_{43} (μm)	maximum in the kinetic curve	
			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

performance with the flocculation kinetics and the flocs structure. The dosage of flocculant is expressed in the text as milligrams per gram which means milligrams of flocculant per gram of PCC.

Results and Discussion

Drainage Results. Drainage tests were performed for the flocculant dosage corresponding to maximum flocculation at the end of the flocculation process, as determined by LDS (Table 2), and also for a common flocculant dosage of 6 mg/g for all the flocculants used. Additionally, drainage tests were performed with 20 mg/g for G1+ and G1++++, and with 2 and 16 mg/g for E1 and E1+, respectively. As an example, Figure 3 shows the drainage curves for E1 with a flocculant contact time of 90 s.

In order to compare drainage results, the normalized drainage times were calculated relatively to the drainage time of the blank test. The normalized drainage times for 30 and 90 s of contact time are represented in Figures 4 and 5 against the flocculant dosage for all the flocculants tested. The average drainage time for the blank experiments was 5.1 s ($\pm$0.5 s).

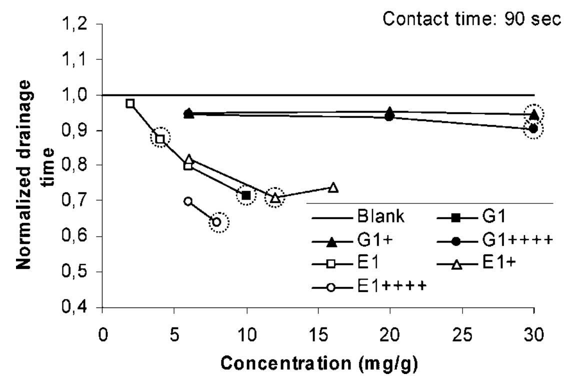

Figure 5. Normalized drainage time as function of flocculant concentration for 90 s of contact time: (○) dosage for maximum flocculation.

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 flocculant dosage corresponding to maximum flocculation, the amount of flocculant is too high, leading to an increase of the suspending medium viscosity, and, thus, to an increase of the drainage time. On the contrary, when dosed at a lower level of 6 mg/g the degree of flocculation is low, far from the optimum (30 mg/g), resulting in a drainage time close to the one observed for the blank unflocculated suspension.

For the other polymers, all the flocculated suspensions exhibit a lower drainage time than the unflocculated suspension. As the flocculant dosage becomes close to the optimum for the flocculation, lower drainage times are observed. Hence, despite the flocculation results being related only with the flocculation of PCC suspension and the operating conditions being different in the DDA and in the LDS, it is possible to observe a good correlation between the flocculation tests (performed in the LDS) and the drainage tests performed in the DDA. In fact, it is observed that a lower drainage time corresponds to the flocculant dosage for maximum flocculation. This can be explained by the fact that in a composite furnish containing refined fibers, fines, and filler particles, the polymer adsorbs preferentially on the filler and flocculates it.[3] Thus, LDS and DDA tests can be regarded as complementary techniques to prescreen flocculants for use in papermaking.

In the case of E1+, if the flocculant concentration increases too much, the drainage time increases again. When the flocculant is in excess, the flocculation progresses at a lower rate as shown by LDS and,[20] thus, for the flocculant contact time used in these studies the flocs are still too small (low flocculation) and the sheet structure is relatively closer to the blank and so is the drainage time.

The flocculant contact time is also an important parameter. For the E1 series the increase in the contact time results in an increase in the drainage time 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 the 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.[1] They demonstrated that the increase of the drainage time with the contact time is due to the polymer configuration at the particle surface. At the first stage of the flocculation process the polymer has an extended conformation at the particle surface but as the time increases the flocs becomes smaller and more compact due to polymer reconformation and degradation. In this case, it becomes more difficult to remove the interstitial water from this type of flocs and thus the drainage time

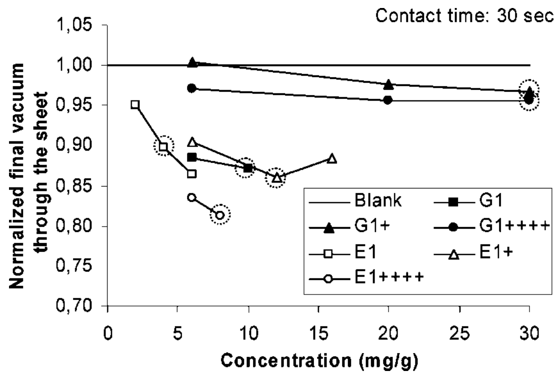

Figure 6. Normalized final vacuum as function of flocculant concentration for 30 s of contact time: (○) dosage for maximum flocculation.

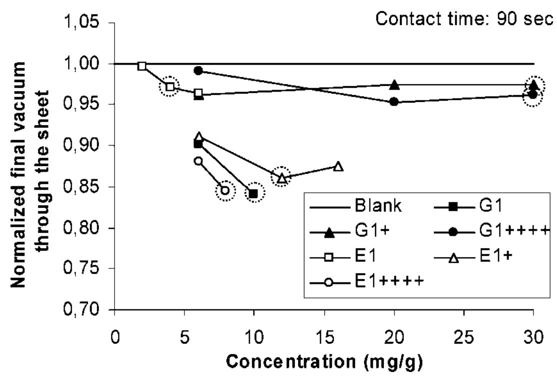

Figure 7. Normalized final vacuum as function of flocculant concentration for 90 s of contact time: (○) dosage for maximum flocculation.

increases. 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 90 s than at 30 s resulting in the improvement of the drainage time.

Nevertheless, the G1 series do not follow this behavior. LDS 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[26] reduces the effect of the overflocculation and thus results in drainage time decrease with flocculant contact increase.

Figures 6 and 7 summarize the final vacuum normalized relatively to the final vacuum obtained in the blank tests, through the formed sheet, as a function of the flocculant concentration. A low final vacuum corresponds to high sheet permeability. 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 that corresponds to lower final vacuum through the sheet.[22] Figure 8 confirms the linear correlation between the drainage time and the sheet porosity. A similar trend was observed for 90 s of flocculant contact time.

From these results, it is possible to conclude that the polymers of the E1 series (medium charge densities) are the most adequate since fast paper machines require good dewaterability with low contact time. Moreover, for this series of polymers, a significant improvement of the drainage time can be achieved with the low flocculant dosage. The highly branched polymer, E1++++,

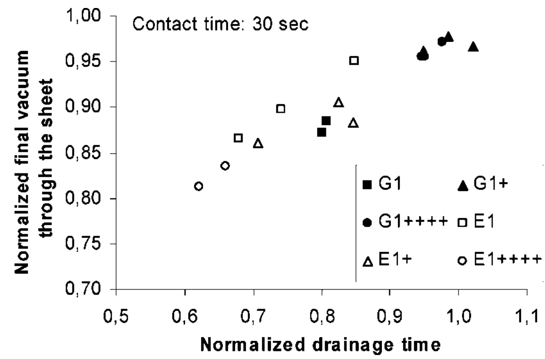

Figure 8. Normalized final vacuum as function of normalized drainage time.

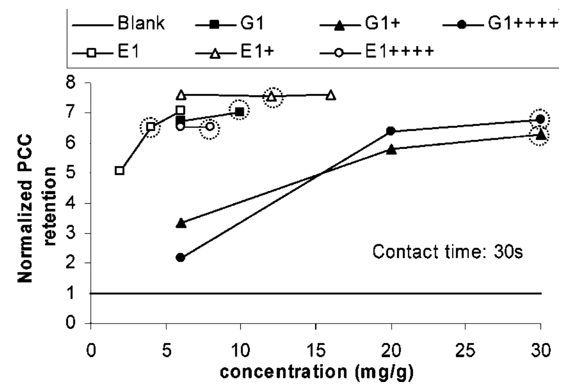

Figure 9. Normalized PCC retention as function of flocculant concentration for 30 s of contact time: (○) dosage for maximum flocculation.

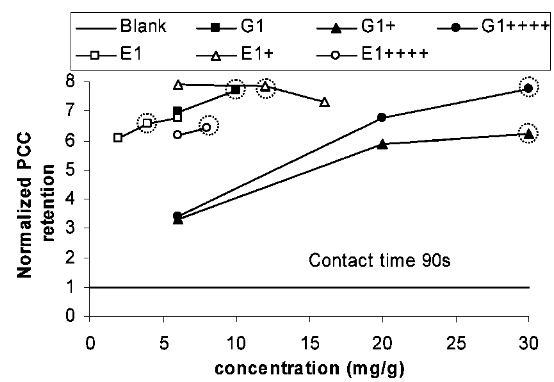

Figure 10. Normalized PCC retention as function of flocculant concentration for 90 s of contact time: (○) dosage for maximum flocculation.

exhibits the best result in a compromise between the flocculant dosage and the drainage time.

Retention Results. The PCC retentions, normalized relatively to the PCC retention obtained for the blank tests, are plotted for the six polymers against the polymer dosage in Figures 9 and 10. The total solid retention is not presented since the change in total retention is mainly caused by filler retention as referred by Cadotte et al.[5] This fact confirms also that the polymer flocculates the fillers preferentially. The average total solid retention and the average PCC retention of the unflocculated suspension are 84.3% (±0.5%) and 11.5% (±1%), respectively. At the lowest flocculant concentration, G1+ and G1++++ not only impair drainage but also present the worst results for PCC retention. Low flocculation results in a low drainage rate and in a low PCC retention because the poorly flocculated suspension behavior is close to the one observed for the unflocculated

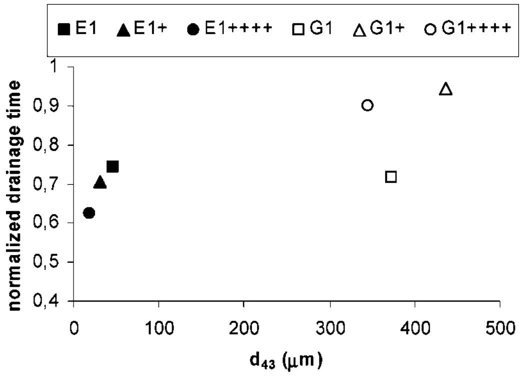

Figure 11. Normalized drainage time as function of mean floc size for the flocculant dosage corresponding to maximum flocculation.

suspension. At higher dosages of G1+ and G1++++, the PCC retention is similar to the one observed for the other polymers.

In general, for all the polymers tested, the maximum in the PCC retention corresponds to the flocculant dosage corresponding to maximum flocculation. However, as the flocculant dosage increases 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 study, the range is 5−10 mg/g for all the polymers except G1+ and G1++++, according to the previous explanations. In this range, E1+ offers the best PCC retention and E1++++ the lowest PCC retention. As for drainage, the increase in the contact time impairs the PCC retention for the E1s series as opposed to the G1s series that improves retention, though the differences, as far as retention is considered, are small. As a consequence, the E1s polymers are more adequate as retention aids for papermaking.

Drainage and retention results have shown that branched flocculants of medium charge density give the best results as retention and drainage agents. However, it is important to stress that E1++++ is probably the most adequate polymer to improve retention and drainage simultaneously. Indeed, with this polymer the retention degree is high despite of being slightly smaller than with E1+ and, most important, the drainage times are the lowest with a low flocculant dosage. Moreover, a previous study showed that this polymer is less affected by the changes in the cationic content of the suspending medium due to its branched configuration.[20] Hence, highly branched polymers have a significant potential as retention aids in papermaking due to the improvement of retention and drainage of pulp fiber suspensions.

Correlation with Floc Properties. Since the best results for both retention and drainage are obtained close to or for the flocculant dosage corresponding to maximum flocculation, the effect of flocs size and flocs structure on the drainage time was investigated for the flocculant dosage leading to maximum flocculation obtained by LDS (Figures 11 and 12).[20]

The normalized drainage time corresponding to the optimum flocculant dosage is represented in Figure 11 as a function of the average flocs size. The results correspond to a flocculation time of 30 and 90 s, for the E1s and the G1s polymers respectively, for which both drainage and retention give best results. The E1 set produces smaller flocs and within the series, 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, since they retain much more interstitial water that is difficult to remove.

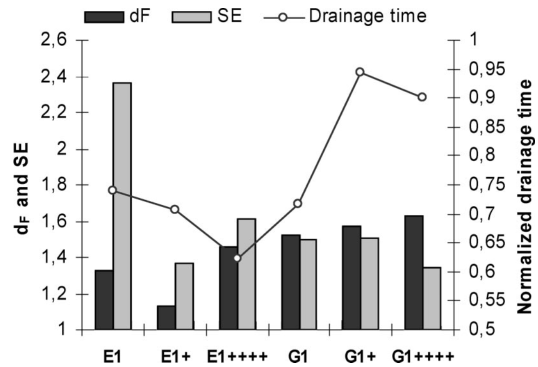

Figure 12. Flocs structure and normalized drainage time for flocculant dosage corresponding to maximum flocculation.

Table 3. Effect of the Polymer Charge Density and Branching on Drainage and Retention

charge density	branching	drainage time	PCC retention	sheet permeability
50%	↑	⇊	↓	⇈
20%	↑	⇈	↓	⇊

So, overflocculation (very large flocs) results in low drainage despite retention being not significantly affected.

The drainage time is plotted as a function of the flocs structure, quantified by the mass fractal dimension and by the scattering exponent, for the flocculant dosage corresponding to maximum flocculation, in Figure 12. The mass fractal dimension, d_F, gives indication about the structure of the primary flocs while the scattering exponent, SE, gives information about the structure of secondary flocs that result from the aggregation of the primary ones.[9,21] The mass fractal dimension and the scattering exponent were calculated for the maximum in the flocculation kinetic curve as reported in a previous study.[20] Primary flocs produced with E1 have an open structure (small d_F) while the secondary flocs are compact (high SE). As for the primary and secondary flocs produced with E1+, they are open (small d_F and SE) when compared to the E1 flocs. Besides, the configuration of the flocs produced with E1++++ seems to be the most adequate to easily remove the water, since the primary flocs are slightly more compact while secondary flocs are open compared to E1 and E1+.

However, the flocs structure of those flocs produced with the G1s polymers is similar to the structure of the E1++++ flocs. In this case, the drainage time is mainly affected by the larger floc size (overflocculation).

The effects of the polymer charge density and degree of branching on drainage time, PCC retention, and sheet permeability, when the flocculant concentration corresponding to maximum flocculation are used, are summarized in Table 3.

Conclusions

As expected, the polymer characteristics namely the charge density and the number of branches per molecule affect the drainage and the retention performance in papermaking.

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.

Polymers with medium charge density offer simultaneously low drainage times and very high filler retentions at low flocculant dosage and at low flocculant contact time.

The lowest drainage times are obtained for the flocculant dosage corresponding to maximum flocculation, at the end of the flocculation process, determined previously. A low flocculation degree also results in low drainage rate and in poor filler retention.

Polymers of medium charge density and with a branched structure improve significantly the drainage rate and filler retention in comparison with the linear ones. In this case, 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.

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. However, it is necessary to investigate the effect of these flocculants on paper sheet formation to complement this study since good paper sheet formation is also essential to achieve product quality and process efficiency. Moreover, it is important, in the future, to extend this study to other systems, that is to different types of furnish and fibers; namely considering the differences in the anionic charge level.

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Literature Cited

(1) Forsberg, S.; Ström, G. The effect of contact time between cationic polymers and furnish on retention and drainage. *J. Pulp Paper Sci.* **1994**, *20* (3), 71–76.

(2) Norell, M. ; Johansson, K. ; Persson, M. Retention and Drainage. *Papermaking Science and Technology, Book 4: Papermaking Chemistry*; Neimo, L., Ed.; TAPPI PRESS: Finland, 1999.

(3) Whipple, W. L.; Maltesh, C. Adsorption of cationic flocculants to paper slurries. *J. Colloid Interface Sci.* **2002**, *256*, 33–40.

(4) Blanco, A.; Negro, C.; Fuente, E.; Tijero, J. Effect of shearing forces and flocculant overdose on filler flocculation mechanisms and flocs properties. *Ind. Eng. Chem. Res.* **2005**, *44*, 9105–9112.

(5) Cadotte, M.; Tellier, M. E.; Blanco, A.; Fuente, E.; van de Ven, T. G. M.; Paris, J. Flocculation, retention and drainage in papermaking: a comparative study of polymeric additives. *Can. J. Chem. Eng.* **2007**, *85*, 240–248.

(6) Yu, X.; Somasundaran, P. Kinetics of polymer conformation changes and its role in flocculation. *J. Colloid Interface Sci.* **1996**, *178*, 770–774.

(7) van de Ven, T. G. M.; Alince, B. Heteroflocculation by asymmetric polymer bridging. *J. Colloid Interface Sci.* **1996**, *181*, 73–78.

(8) Bremmell, K. E.; Jameson, G. J.; Biggs, S. Kinetic Polyelectrolyte adsorption at the solid/liquid interface interaction forces and stability. *Colloids Surf.* **1998**, *139*, 199–211.

(9) Biggs, S.; Habgood, M.; Jameson, G. J. Yao-de-Yan, Aggregate structures formed via a bridging flocculation mechanism. *Chem. Eng. J.* **2000**, *80*, 13–22.

(10) Blanco, A.; Fuente, E.; Negro, C.; Tijero, J. Flocculation monitoring: focused beam reflectance measurement as a measurement tool. *Can. J. Chem. Eng.* **2002**, *80*, 734–740.

(11) Hubbe, M. A.; Heitmann, J. A. Review of factors affecting the release of water from cellulosic fibers during paper manufacture. *BioResources* **2007**, *2* (3), 500–533.

(12) Unbehend, J. E. Wet end chemistry of retention, drainage and formation aids. *Pulp and Paper Manufacture*, 3rd ed.; Hagemeyer, R. V., Ed.; TAPPI PRESS: Atlanta, 1992; Vol. 6.

(13) Nicke, R.; Pensold, S.; Hartmann, H.-J.; Tappe, M. Polydiallyldimethylammonium chloride as a flocculating agent. *Wochenbl. Papierfabr.* **1992**, *120* (14), 559–564.

(14) Shin, J.-H.; Han, S. H.; Sohn, C.; Ow, S. K.; Mah, S. Highly branched cationic polyelectrolytes: filler flocculation. *Tappi J.* **1997**, *80* (11), 179–185.

(15) Shin, J.-H.; Han, S. H.; Sohn, C.; Ow, S. K.; Mah, S. Highly branched cationic polyelectrolytes: fines retention. *Tappi J.* **1997b**, *80* (10), 185–189.

(16) Brouillette, F.; Morneau, D.; Chabot, B.; Daneault, C. A new microparticulate system to improve retention/drainage in fine paper manufacturing. *Appita J.* **2005**, *58* (1), 47–51.

(17) Brouillette, F.; Morneau, D.; Chabot, B.; Daneault, C. Paper formation improvement through the use of new structured polymers and microparticle technology. *Pulp Paper Can.* **2004**, *105* (5), 108–112.

(18) Rasteiro, M. G.; Garcia, F. A. P.; Ferreira, P.; Blanco, A.; Negro, C.; Antunes, E. The use of LDS as a tool to evaluate flocculation mechanisms. *Chem. Eng. Process.* **2008**, *47*, 1329–1338.

(19) Rasteiro, M. G.; Garcia, F. A. P.; Ferreira, P.; Blanco, A.; Negro, C.; Antunes, E. Evaluation of flocs resistance and reflocculation capacity using the LDS technique. *Powder Tech.* **2008**, *183*, 231–238.

(20) Antunes, E.; Garcia, F. A. P.; Ferreira, P.; Blanco, A.; Negro, C.; Rasteiro, M. G. Effect of water cationic content on flocculation, flocs resistance and reflocculation capacity of PCC induced by polyelectrolytes. *Ind. Eng. Chem. Res.* **2008**, *47*, 6006–6013.

(21) Liao, J. Y. H.; Selomulya, C.; Bushell, G.; Bickert, G.; Amal, R. On different approaches to estimate the mass fractal dimension of coal aggregates. *Part. Part. Syst. Charact.* **2005**, *22*, 299–309.

(22) Forsberg, S. ; Bengtsson, M. The dynamic drainage analyzer (DDA). *Tappi 1990 Papermakers Conference Proceedings*; Tappi Press: Atlanta, 1990.

(23) *The Dynamic Drainage Analyser Manual*; AB Akribi Kemikonsulter: Sweden, 2001.

(24) Hubbe, M. A. Selecting laboratory tests to predict effectiveness of retention and drainage aid programmes. *Proceedings of Filler & Pigments for Papermakers, Pira Conference*, Barcelona, October 2003.

(25) Ferreira, P.; Velho, J.; Figueiredo, M.; Mendes, A. Effect of thermal treatment on the structure of PCC particles. *Tappi J.* **2005**, *4* (11), 18–22.

(26) Rasteiro, M. G.; Antunes, E.; Garcia, F. A. P.; Ferreira, P.; Wandrey, C.; Hunkeler, D. Flocculation by polyelectrolytes: correlating the flocculation process with polymer characteristics. *Polyelectrolytes 2008*, Coimbra, Portugal, June 2008.

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