Influence of impulse drying on the retention and sizing of paper with alkyl ketene dimer

PAULA MENDES, HUINING XIAO, CARLOS A. V. COSTA, MOHAMED NACEUR BELGACEM, AND JOHN C. ROBERTS

ABSTRACT: An increase in pressing temperature had a detrimental effect on impulse-pressed handsheets in terms of alkyl ketene dimer (AKD) retention and the degree of sizing. The mechanisms of dewatering in the impulse drying technique are thought to be responsible for the negative effect. The longer pressing times also reduced paper sizing by lowering the total amount of AKD retained and the amounts of reacted AKD. However, the addition of polyamide epichlorohydrin resin (PAE) or polyethyleneimine (PEI) had a positive effect on AKD retention under conventional pressing conditions.

Application: Impulse drying has a negative effect on AKD retention and sizing, but PAE and PEI may offer a solution.

In the paper machine press section, impulse drying enhances paper web dewatering through intense temperature and pressure [1]. Pressing at high temperatures decreases the water viscosity and surface tension and makes the fibers more flexible, making it easier for the fiber web to release water and become consolidated [2]. In theory, the improvement in dewatering efficiency at high roll temperatures is also partially attributable to the formation of a steam pressure gradient inside the web. The steam pressure gradient has been reported to be effective in expelling the liquid water from the web and into the backing felt [3, 4].

Alkyl ketene dimer (AKD) is one of the most commonly used internal sizing agents in the paper industry [5]. Solid AKD made from saturated fatty acids has a melting point between 40°C and 60°C [5]. AKDs, which are liquid at room temperature, can be formed by using either unsaturated fatty acids or branched fatty acids [6]. Liquid AKDs have been developed to improve machine cleanliness and to minimize the detrimental effect that AKDs of high melting point have on the frictional properties of paper [6, 7].

The retention of the stabilized AKD on fibers is believed to take place as a result of the coagulation of the positively charged AKD colloids over the negatively charged fiber surfaces [5]. For effective sizing, the AKD must be distributed evenly over the fiber surface and anchored to the cellulose fibers [8]. AKD is retained as large particles which spread and melt over the fiber surface during heat treatment [9]. AKD must spread onto the surface of fibers before any esterification takes place [10]. AKD reacts chemically with cellulose hydroxyl groups to form β-ketoesters [6], but AKD can also react with water and form the unstable β-keto acid, which decarboxylates to form a ketone. The hydrolysis of AKD leads to less sizing and in certain situations can lead to a complete loss in sizing [11]. In addition, the hydrolysis of the reactive size is a competitive reaction with the reaction through which esters are formed.

The AKD sizing reaction is very slow, but the alkalinity increases the rate of esterification [5, 12, 13]. Bicarbonate ions (HCO_3^-) are the most effective sizing accelerators of these systems [5]. Polymers that contain amine groups, such as polyamide epichlorohydrin (PAE) and polyethyleneimine (PEI), are also important catalysts [14–16]. They can be added to the AKD emulsion or used in the stock as accelerators and retention aids [5].

In this study, we determined the extent of sizing, the extent of AKD retention, and the amount of reacted AKD on papers submitted to impulse drying. Papers from bleached kraft pulp of *Eucalyptus globulus* were impulse dried, and Hercules sizing tests and solvent extractions were performed. To better understand the effect of pressing and drying on AKD retention and sizing, we pressed AKD papers in the wet state and dried them under different conditions.

Apart from the effects of pressing and drying conditions, we also studied the effects of PAE and PEI on AKD sizing and retention with Portuguese pulp.

EXPERIMENTAL

Materials

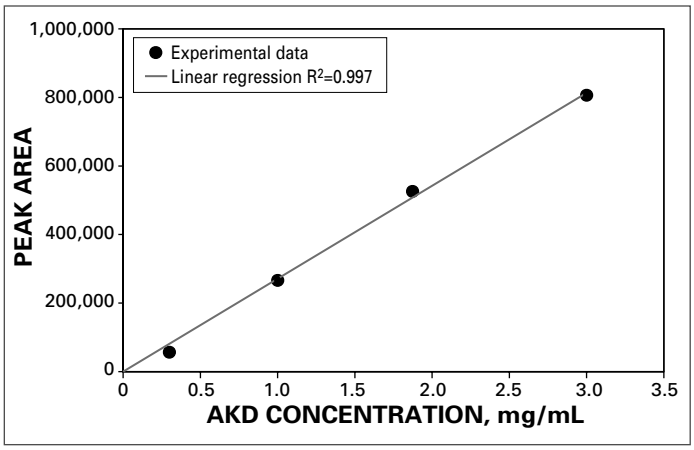
A bleached kraft pulp from *E. globulus* was beaten to 25°SR and 40°SR with a Valley beater. The pulp refined to 25°SR had 6.7% fines, and the 40°SR furnish had 9.4% fines. The fines content was determined using a dynamic drainage jar and a 200-mesh screen.

The AKD emulsion and raw AKD used to prepare the GC calibration curve were provided by Raisio Chemicals. The AKD used was synthesized from branched fatty acids and had a melting point close to room temperature. The AKD emulsion was constituted by 13.35 wt% AKD and 5.15 wt% emulsifier–stabilizer, mostly cationic starch. Sodium bicarbonate ($NaHCO_3$) was used to achieve high alkalinity. PAE provided by Raisio Chemicals was used as a wet-strength agent, and a high-molecular-weight PEI obtained from BASF was used as a retention aid.

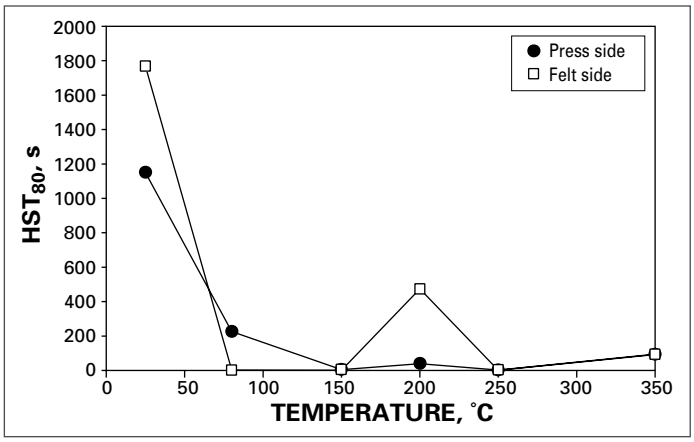
Sheet preparation

In a typical procedure, we added 0.5 g of $NaHCO_3$ (3×10^{-3} mol/L) to 2000 mL of pulp with a consistency of 8 g/L. The contact time between $NaHCO_3$ and pulp was 10 min. The AKD emulsion was diluted (1:100) with deionized water immediately prior to use. We prepared the AKD-sized handsheets by adding 0.15% AKD (wt/wt with respect to oven-dry pulps) to the fiber suspension and stirring the mixture for 5 min. Handsheets with a basis weight of 80 g/m^2 were prepared. In one set of experiments, the consistency was changed to 23 g/L.

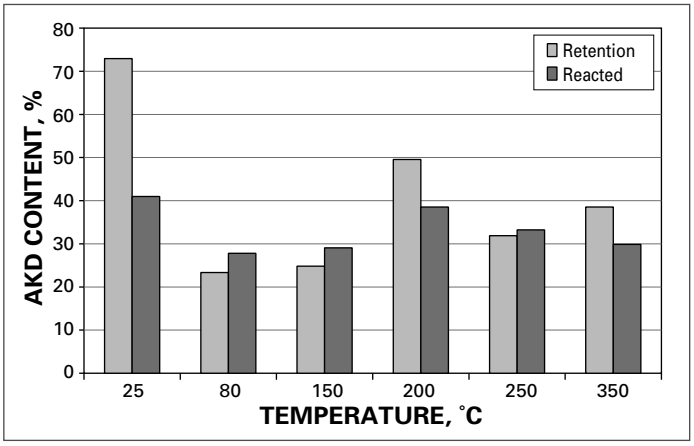
The same procedure was used in the preparation of handsheets with PAE and PEI. We added 0.15% (wt. on dry fibers) of AKD to a fiber suspension of 0.8% consistency and mixed it for 5 min. We added PAE or PEI to the stock and stirred the suspension for 5 min more before making the handsheets. We used two dosing lev-



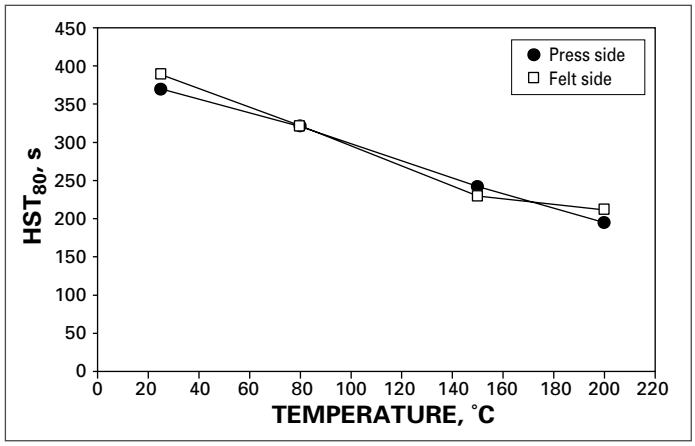
1. AKD calibration curve.



2. Sizing level for both paper sides vs. pressing temperature (25°SR, Method I).



3. The effect of pressing temperature on the amount of AKD retained and reacted on the handsheets (25°SR, Method I).



4. Sizing level for both paper sides vs. pressing temperature (40°SR, Method I).

PULP CONSISTENCY, g/L	BEATING LEVEL, °SR	AKD RETENTION, %	REACTED AKD, % OF AKD RETAINED	HST_{80}, s
8	25	56.7	49.5	1799.5
8	40	60.9	51.8	653.7
23	25	38.9	50.2	47.4
23	40	45.8	54.9	392.5

I. The effects of pulp consistency on AKD-retention, reacted AKD, and HST (Method II).

els of PAE or PEI—0.05% and 0.1% (wt. on dry fibers).

Pressing and drying methods

After the paper samples were formed, they were submitted to one of three different methods of pressing and drying.

Method I. Handsheets samples in a small size (7.5 × 7.5 cm^2) were pressed by impulse drying on a laboratory-scale platen press. The sheet is pressed between a smooth heated plate and a felt in which moisture is controlled (15%). The wet paper webs, with an initial dryness of 30%–40%, were pressed at 6 MPa for 50 ms. The pressing temperatures were set at 25°C, 80°C, 150°C, 200°C, 250°C, and 350°C. The sheets were dried for 10 min at 105ºC in an oven and were put in the conditioned room for three weeks to ensure a complete sizing development of AKD.

Method II. After being pressed for 7 min at a pressure of 345 kPa (conventional method), the handsheets were put in the conditioned room at 23ºC and 50% relative humidity (RH). After 24 h, the samples were cured at 105ºC for 30 min.

Method III. After being pressed for 30 s or 7 min at a pressure of 345 kPa, the handsheets were put in the oven at 105ºC or 180ºC for 5 min and then in the conditioned room at 23ºC and 50% RH. After 24 h, the samples were cured at 105ºC for 30 min.

Sizing characterization

Sizing efficiency was measured using the Hercules size test (HST), representing an average of four tests. The acid ink used contained basacid dye and 0.75% formic acid. The HST was set for 80% reflectance for all measurements.

AKD analysis

AKD content in handsheets was determined by gas chromatography (GC) with a Perkin Elmer 1022 GC Plus instrument. To obtain the gas chromatographic response factors, we made the GC calibration curve using four concentrations of pure AKD—0.3, 1.0, 1.9, and 3.0 mg/mL in toluene.

We used a solution containing 0.3 g of *n*-decane in 1000 mL of toluene as an internal standard (IS). We transferred 0.5 mL of IS and 0.5 mL of AKD solution at each of the four concentrations mentioned to a sample vial and injected 2 µL of this mixture into the gas chromatograph. The peak areas of AKD and IS were identified and quantified.

Extraction procedure

Handsheets containing AKD were subjected to solvent extraction of unreacted AKD followed by the extraction of reacted AKD.

The unreacted AKD was extracted by means of a soxhlet extraction with dichloromethane. This extraction was performed for about 24 h. The extracted component (AKD) was isolated by evaporation in a rotary evaporator. The residue was washed with 0.5 mL of toluene and 0.5 mL of IS. We injected 2 µL of the washed solution into the gas chromatograph and determined the peak areas of AKD and IS.

After the unreacted AKD was extracted, the sheet was boiled with a 0.4*M* alcoholic solution of potassium hydroxide for about 3 h. After the solution cooled, hydrochloric acid was added to reach a pH of less than 4.0. The solution was transferred to a separating funnel and was washed several times with toluene. The solution containing the extracted toluene portions (top layer) was removed by rotary evaporation, and the residue was treated the same way the unreacted AKD residue had been treated. Each handsheet extraction was replicated twice.

RESULTS AND DISCUSSION

The AKD emulsion was a mixture of several ketene dimers with different chain lengths of the hydrocarbon groups. This mixture led to chromatographs with a broad peak configuration between retention times of 10 and 32 min.

Control sample and GC calibration

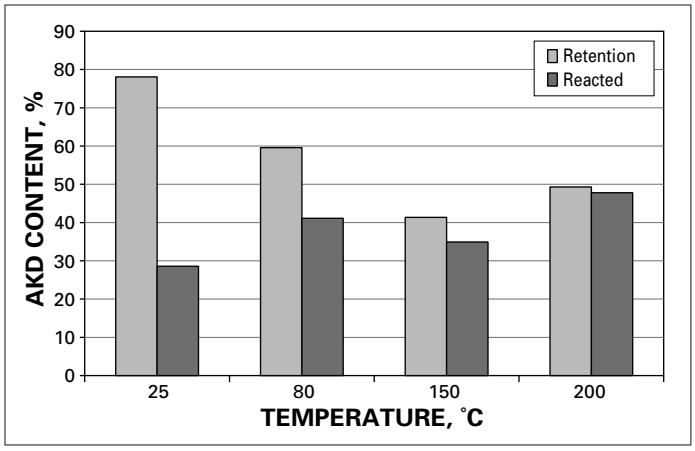
To determine if any other organic chemical compounds are also being extracted from pulp in the extraction of unreacted and reacted AKD, we followed the same procedure to extract an additive-free handsheet as a control sample. Without the addition of AKD, some chemical compounds were indeed extracted from the paper samples. In fact, the peaks of chemical compounds extracted from pure pulp overlapped some peaks of AKD compounds.

Consequently, we could not construct a calibration curve using the integrated area between 10 and 32 min. However, two peaks at a retention time of about 30 min were not complicated by overlapping peaks from other compounds, and these two peaks were assigned as the characteristic peaks for GC calibration. The GC calibration curve in **Fig. 1** shows good linear correlation.

Pulp consistency

In our initial work, we examined the effects of pulp consistency on AKD retention and sizing performance. As the results in **Table I** show, a pulp consistency of 23 g/L is detrimental to AKD retention and sizing. In this table, retained AKD pertains to all AKD-related compounds on the handsheets, or the total amount of AKD obtained by extracting unreacted and reacted AKD. (Reacted AKD was calculated from the retained AKD based on mass balance).

At a consistency of 23 g/L, mechanical entanglement induces shearing on fiber surfaces, which probably removes some of the AKD particles deposited [15]. In contrast, pulps at a consistency of 8 g/L undergo much less shearing. Therefore, in the subsequent experiments, we mainly focused on the pulp at a consistency of 8 g/L.



5. The effect of pressing temperature on the amount of AKD retained and reacted on the handsheets (40°SR, Method I).

For both consistencies, AKD retention correlated well with the degree of sizing. As expected, higher retention led to more efficient sizing on AKD handsheets. However, for the consistency of 8 g/L, the pulps refined at 25°SR and 40°SR displayed similar values for retained and reacted AKD, but the less refined pulp had better sizing.

This result is in accordance with the studies of Ramamurthy *et al*. [17], in which the presence of fines was found to be detrimental to paper sizing. Cationic AKD emulsion particles are predominantly adsorbed onto fines of beaten pulp [14]. Hence, fines retention is expected to be important. However, Cooper *et al*. [16] have shown that no strong correlation exists between fines retention and AKD sizing. In fact, the main reason for less sizing in the presence of greater amounts of fines is that increased fines increases the total surface area in the sheet, leading to less AKD per unit area and thus to less efficient sizing.

Influence of pressing temperature

Figure 2 shows the sizing obtained for handsheets refined at 25°SR when impulse pressed at different temperatures. AKD sizing was decreased dramatically at elevated pressing temperatures. This negative effect was verified on the press side of the paper as well as on the felt side. The lower values of retention at higher temperatures, as illustrated in **Fig. 3**, are the main reason for decreased sizing on impulse-pressed papers refined at 25°SR.

A likely explanation for the considerable decrease in retention in this set of papers is to be found in the mechanisms of dewatering in impulse drying. The high temperatures and pressures allow large amounts of water be squeezed out of the paper web in the space of a few milliseconds. The water flow is enhanced because the viscosity of the water and surface tension decrease and the compressibility of the paper web is improved with higher temperatures. These effects, in concert with a possible steam pressure gradient, create a large flow of water through the paper web, which can be responsible for dragging some AKD particles out from the sheet and into the backing felt or transferring them to the platen press.

PRESSING TIME AT 345 kPa, min	MOISTURE CONTENT OF PAPER BEFORE DRYING, %	OVEN DRY TEMP.,°C	AKD RETENTION, %	REACTED AKD, % OF AKD RETAINED	HST_{80}, s
0.5	71	105	65.9	53.2	1209.7
0.5	71	180	66.5	54.8	1333.0
7*	54	105	60.2	46.5	630.0
7*	54	180	62.1	50.0	760.8

* Standard pressing

II. The effects of wet pressing on AKD-retention, reacted AKD, and HST (40°SR, Method III).

RETENTION AID	POLYMER ADDITION, %	AKD RETENTION, %	REACTED AKD, % OF AKD RETAINED	HST_{80}, s
PAE	0.05	100	50.8	802.4
PAE	0.1	87.8	47.0	1215.5
Polymin SK	0.05	95.2	38.9	922.1
Polymin SK	0.1	66.2	45.7	1002.9

III. The effects of PAE and PEI addition on AKD-retention, reacted AKD, and HST (40°SR, Method II).

Moreover, the attractive forces in the AKD retention mechanism are not very strong because the emulsion particles are relatively large (0.2–2.0 μm) and the cationic stabilizer is not necessarily tightly attached to the surface of the particle [8]. When AKD particles are removed from the paper web, cationic starch stabilizer has probably been left on the fiber surfaces.

For more highly refined handsheets (40ºSR), AKD sizing also decreased with increasing pressing temperature, as illustrated in **Fig. 4**. These results agreed well with the lower retention obtained in these handsheets for higher temperatures, as illustrated in **Fig. 5**. However, the retention values in this set of papers (40ºSR) are better than those observed in handsheets refined at 25ºSR (Figs. 3 and 5). As in conventional pressing, paper sheet permeability is an important factor in determining the water removal ability. Water flows according to the pore structure and thickness of the sheet. In more highly refined sheets, the hydraulic flow resistance across the web thickness is more significant in reducing the removal of water and in reducing the tendency of the water to drag AKD particles out of paper web.

Although the sizing of papers sheets beaten at 40ºSR decreases with increasing pressing temperature (Fig. 4), the amount of reacted AKD is improved, as Fig. 5 shows. This outcome could arise from incomplete extraction of unreacted AKD in the first extraction procedure. In fact, the increased pressing temperatures could trap some of the AKD in the fiber structure, which would constitute AKD that was not easily accessible to the solvent extraction (i.e., extraction of unreacted AKD). However, AKD trapped in this way could be extracted in the second extraction stage (i.e., extraction of reacted AKD) because the alkali swells the fiber structure whereas the solvent does not. Therefore, it is probable that the amount of reacted AKD is actually decreasing with temperature, but because there is trapped, unreacted AKD, this amount is being measured as reacted AKD and is giving a falsely elevated result.

Influence of pressing time

We also performed experiments using the wet pressing process, at 30 s and at 7 min, to determine the effects of pressing time on AKD retention and sizing. After having been wet-pressed, the handsheets were dried at 105ºC or 180ºC for 5 min. After 24 h, these handsheets were cured at 105ºC for 30 min (Method III).

As **Table II** shows, the handsheets exposed to pressing for a short period (30 s) were better in both AKD retention and sizing efficiency that those handsheets pressed for a long period (7 min.). Apparently, the improved sizing achieved in the short pressing period results from high AKD retention as well as an increase in the amount of reacted AKD. The effect of pressing time on sizing performance could be related to the bonding areas alternated by pressing. In previous work, it has been proven that AKD particles located in the fiber bonding areas may not be available to an esterification reaction, with the consequent loss of valuable sizing [10]. A longer pressing period increases bonding areas, making less AKD available for reacting with cellulose fibers.

Results in Table II also show the positive effect of high oven drying temperature on both sizing performance and AKD reactivity. Even if hydrolysis is accelerated at high temperature, it seems not to compete significantly with the esterification reaction.

Effect of PAE or PEI on AKD retention and sizing

To further enhance the AKD retention, we used two conventional cationic polymers, PAE or PEI, in conjunction with AKD. Despite the surface of the AKD particles having been modified with cationic starches, PAE and PEI may still have a significant impact on AKD retention. Our results, shown in **Table III**, indicate the remarkable improvement in AKD retention with the addition of either PAE or PEI. In other words, AKD emulsion particles can be reinforced in pulp suspension by cationic polymer PAE or PEI, which provides an alternative solution for achieving high AKD retention levels during impulse drying.

PAE, used as a wet-strength agent, appears to be slightly more effective than PEI, which is a conventional retention aid, with respect to improving AKD retention. With the addition of 0.05% PAE, a retention of 100% AKD was reached. However, when these polymers were added at a high level of 0.1%, the AKD retention decreased. The addition level at 0.1% likely exceeds the optimal dosage for flocculation, leading to a re-dispersion of flocs, particularly if polymer adsorption is assisted by the shear-induced destruction of flocs [12].

In addition, the high AKD retention of 100% does not necessarily give better sizing. As Table III shows, sizing efficiencies with high AKD retention achieved by both PAE and PEI at 0.05% are not as good as the sizing efficiencies achieved with low AKD retention. There are two possible explanations. First, the high AKD

retention results from the formation of AKD flocs induced by PAE or PEI via a conventional bridging mechanism. However, those flocs could allow AKD to disperse in pulp in a patch form instead of a uniform layer, consequently reducing the sizing efficiency. The second possible explanation is that at 0.05% polymer addition, the fines retention was also increased, which is detrimental to sizing, as already explained.

CONCLUSIONS

Increasing pressing temperature resulted in lower degrees of sizing and poor AKD retention. The dewatering effect during impulse drying is responsible for driving AKD particles out of the fiber network.

Experiments performed using the wet pressing process demonstrated that pressing time influences AKD sizing. The improved AKD sizing efficiency obtained with short pressing periods is attributed to high AKD retention and an increase in the total amount of reacted AKD.

The presence of PAE or PEI was effective in promoting AKD retention and sizing performance. This result suggests that cationic polymers can be added to improve AKD retention during impulse drying processes. **TJ**

LITERATURE CITED

1. Sprague, C. H., *Tappi J.* 70(4): 79(1987).
2. Back, E. L, *Tappi J.* 74(3): 135(1991).
3. Wahren, D., U. S. pat. 4,324,613 (April 13, 1982).
4. Arenander, S., and Wahren, D., *Tappi J.* 66(9): 123(1983).
5. Eklund, D., and Lindström, T., *Paper Chemistry: An Introduction*, DT Paper Science Publications, Grankulla, Finland, 1991.
6. Roberts, J. C., "A Review of Advances in Internal Sizing of Paper," 11th Fund. Res. Symp., Cambridge, 1997, Vol. 1, p. 209.
7. Hoyland, R. W., and Neill, M. P., "The Effect of AKD on Paper Friction," 11th Fund. Res. Symp., Cambridge, 1997, Vol. 2, p. 1617.
8. Dumas, D. H., *Tappi* 64 (1): 43(1981).
9. Isogai, A., *J. Pulp Paper Sci.* 25(7): 251(1999).
10. Lindström, T., and O'Brian, H., *Nordic Pulp Paper Res. J.* 1(1): 34(1986).
11. Marton, J., *Tappi J.* 73(11): 139(1990).
12. Roberts, J. C., *Paper Chemistry*, 2nd edn., Chapman & Hall, United Kingdom, 1996.
13. Crouse, B. W., and Wimer, D. G., *Tappi J.* 74(7): 152(1991).
14. Lindström, T., and Söderberg, G., *Nordic Pulp Paper Res. J.*, 1(2): 39(1986).
15. Lindström, T., and Söderberg, G., *Nordic Pulp Paper Res. J.*, 1(2), 31(1986).
16. Cooper, C., Dart, P., Nicholass, J., and Thorn, I., *Paper Tech.* 36(4): 30(1995).
17. Ramamurthy, P., Vanerek, A., and Van De Ven, T., *J. Pulp Paper Sci.* 26(2): 72(2000).

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INSIGHTS FROM THE AUTHORS

Impulse drying has been tested on additive-free papers, but only a limited range of paper properties can be achieved in paper made from wood fibers exclusively. To the best of our knowledge, there is no report dealing with the combination of impulse drying and the presence of a wet-end additive. To investigate both, we studied the effect of impulse drying on paper containing AKD as an internal sizing agent.

The most difficult aspect of our research was to establish the gas chromatograph calibration curve for the branched liquid AKD. The most surprising finding for us was that the impulse drying technique unfortunately tends to drive AKD particles out of the fiber network, decreasing AKD retention. In further research, we will focus on other wet-end additives.

The introduction of impulse drying in paper mills is expected to result in major energy savings, more efficient use of raw materials, and a considerable reduction in the capital costs of new paper machines. The purpose of our research is to increase the understanding of impulse drying technology, not only to further its development but also to help in the future implementation of impulse drying in mills.

Mendes and Costa are with LEPAE – Dept. of Chemical Engineering, Faculty of Engineering, University of Porto, Portugal; Xiao is with the Dept. of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 5A3, Canada; Belgacem is with École Française de Papeterie et des Industrie Graphiques, INPG, Laboratoire de Génie des Procédés Papetiers, Grenoble, France; and Roberts is with the Dept. of Paper Science, UMIST, Manchester, England; email Xiao at hxiao@unb.ca.


Mendes


Xiao


Costa


Belgacem


Roberts