Location and composition of silicon derivatives in rice straw pulp obtained by organic acid pulping

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SUMMARY

Cooking of rice straw in a mixture of formic acid / acetic acid / water, results in the retention of silicon derivatives in the pulp. Study of the various morphological fractions of the pulp by Scanning Electron Microscopy equipped with Energy Dispersive Spectrometry, shows that the silicon derivatives are essentially localised in epidermic cells where they occur as silica and calcium silicate.

Keywords
Rice straw, crude pulp, silica, silicate, epidermic cells, scanning electron microscopy

Numerous studies (*1-3*) concerning the chemical structure of the silicon derivatives present in cereal straw show that they are in the form of silica or dehydrated silicic acid.

During cooking in alkaline media, an important part of the silicon derivatives of cereal straw is solubilised as silicates. This causes an increase in black liquor viscosity and leads to deposit of these silicates in the evaporation units (*4,5*) during chemical recovery.

We showed previously (*6,7*) that, during the cooking of the rice straw in formic acid/acetic acid / water media, approximately 93% of the silicon derivatives were retained in the crude pulp and constituted 95% of the ash.

In this study, we clarify, by Scanning Electron Microscopy equipped with Energy Dispersive Spectrometry, that the silicon derivatives are present in epidermic cells and that they are in the form of silica and calcium silicate.

MATERIALS AND METHODS

Pulping raw material

The raw material used was rice straw from Vietnam (*Oryza sativa*). This straw contained 9% moisture. Its chemical composition was 37.0% cellulose, 18.3% lignin, 22.0% pentosans, 14.6% ash and 7.0% silica based on dry straw.

Cooking

Cooking (*7*) was carried out in a one-litre glass reactor at atmospheric pressure. The rice straw (40g o.d.), cut into fragments of an average length of 3.0 cm, was first impregnated with the cooking liquor at 50°C for 30 min. The rise to temperature was set at 30 min. After impregnation, cooking was carried out under various conditions.

The pulp so obtained was filtered, pressed and washed twice with a formic acid / acetic acid / water mixture, then with water. It was finally dried and analysed.

Ash and silica analysis

The quantities of ash and silica of the crude pulp were determined according to the Chinese standard G.B 2677.3-81. The sample was heated at 600C for 3 hours in an oven and the ash amount and ratio weight of ash/weight of the dried material were calculated. The ash was treated with hydrochloric acid; the resultant solution was concentrated, and then heated at 900C for one hour. The residue was determined as silica.

Analysis of the chemical elements present in the crude pulp, as well as those present in the various morphological fractions of the pulp, was made by Scanning Electron Microscopy equipped with Energy Dispersive Spectrometry (SEM-EDS).

RESULTS AND DISCUSSION

Figure 1 shows the image of a typical pulp sample used to study the location of silicon derivatives in the rice straw pulp.

It is seen from this image that the pulp obtained by rice straw cooking in organic acid media consists of three main fractions:

- cellulosic fibres
- epidermic cells
- parenchyma cells

Global analysis by SEM-EDS was undertaken to determine the chemical composition of these different fractions and the results are reported in Figure 2.

It is clearly seen that the silicon derivatives are essentially localised in epidermic cells attached to the fibres or released during the cooking. The presence

Fig. 1 SEM photomicrograph of a crude pulp sample obtained by rice straw cooking in organic acid media.

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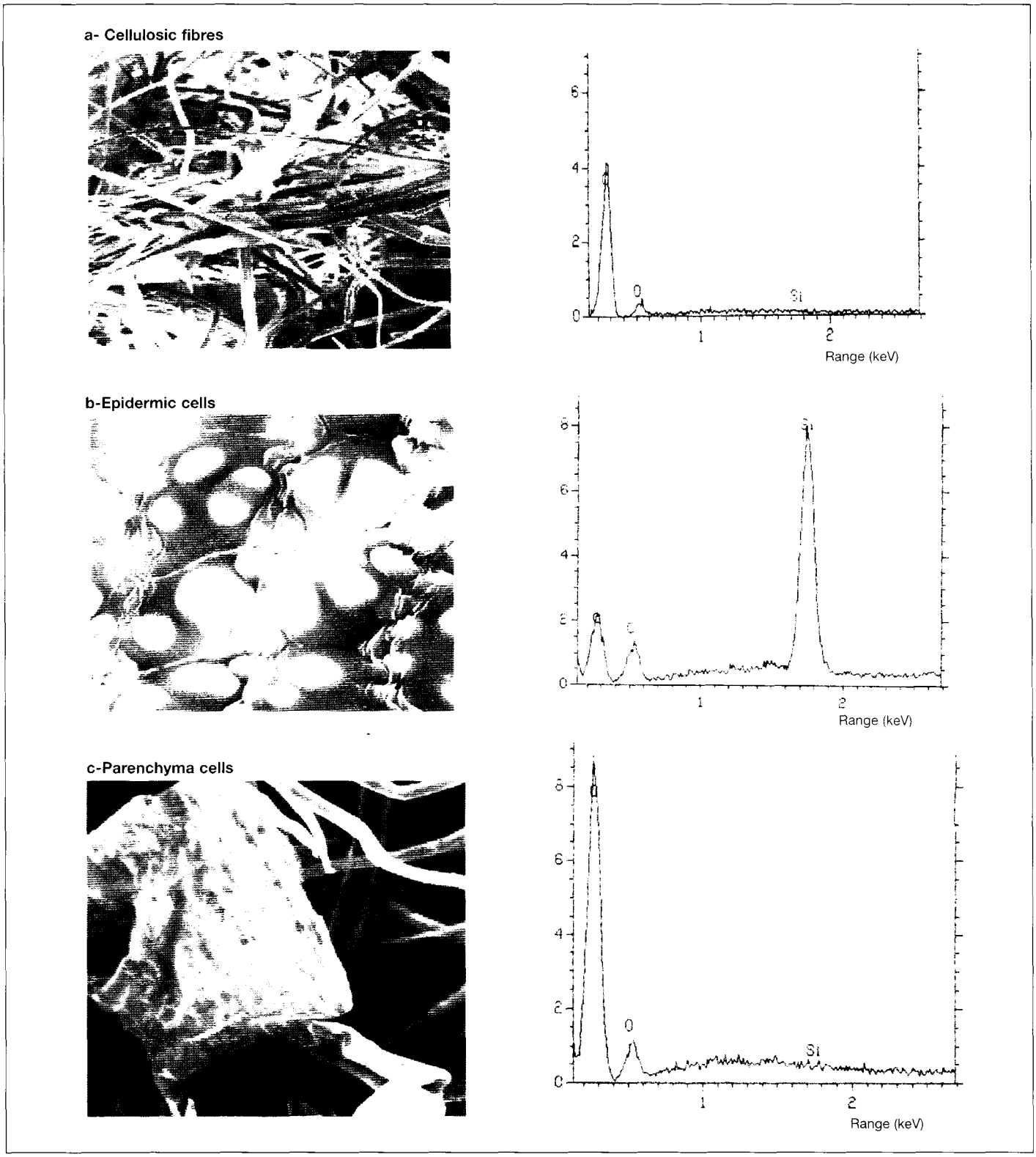

Fig. 2 Analysis of the chemical composition of the various fractions of pulp.

of silicon derivatives in fibres and in parenchyma cells was not observed. It can also be seen (Fig. 2b) that the epidermic cell surface is irregular with a 'tooth like' appearance. These 'teeth' would be covered with a membrane of wax and hemicelluloses, according to Juliano (*8*).

A more precise analysis of the chemical elements present in epidermic cells of pulp (Fig. 3) gives very interesting information: The 'teeth' (Fig. 3b) contain silicon and calcium while the other parts of these cells contain silicon, but very little calcium.

These results show that the silicon derivatives can, according to the place where they are in epidermic cells, exist as various chemical structures. So, in teeth, these compounds are very probably in the form of calcium silicate; in fact calcium silicate is very weakly soluble in acid media, except in hydrochloric acid and fluorhydric acid. Around the teeth, the silicon would be present in the form of silica.

The simultaneous presence in epidermic cells of silicon derivatives in two different structures explains why Parry et al. (*1*) and Kaufman et al. (*2,3*) thought that these compounds exist essentially in the

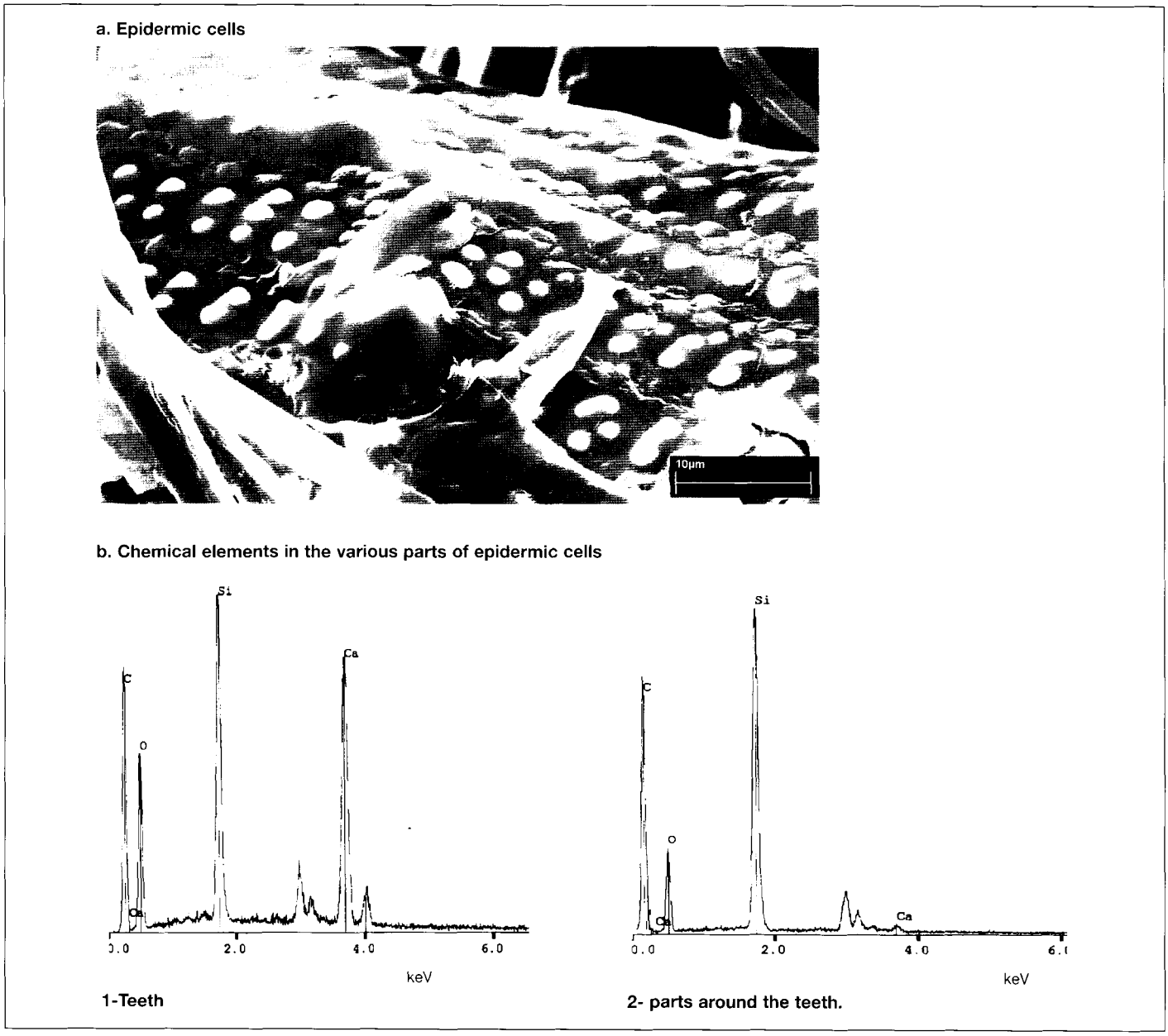

Fig. 2 A wetting force loop of a sized and cured glass cover slip.

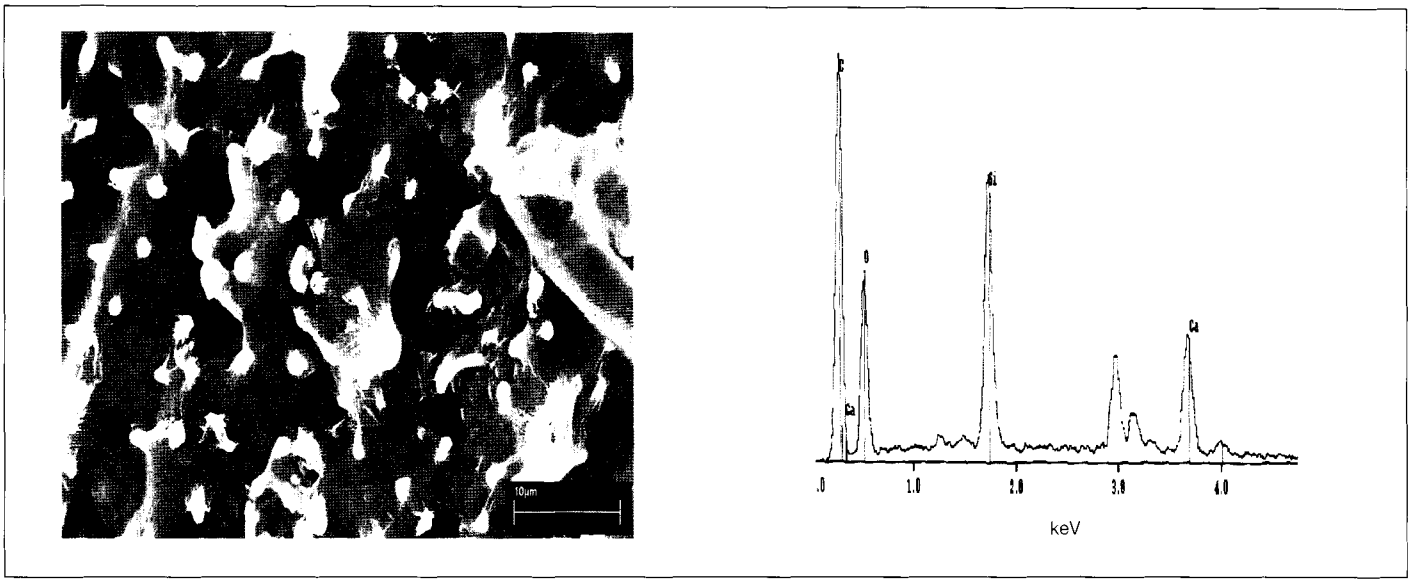

Fig. 4 Epidermic cells of rice straw pulp, post-treated with NaOH (30%).

form of silica (SiO_2), while Seisto et al. (9) suggested that they exist mainly in the form of sodium and potassium silicate.

The analysis of epidermic cells of the same crude pulp treated with a solution of sodium hydroxide (30% NaOH on o.d. pulp) (Fig. 4) shows that the silicate stays partially in teeth, while the silicon derivatives, which contain calcium in their structure, were solubilised. This phenomenon is confirmed by:

- The low ash content of this pulp (0.8%)
- The total absence of silicon in the part of cells around the teeth.

CONCLUSIONS

Cooking rice straw in organic acid media (formic acid / acetic acid / water) allows the retention of silicon derivatives in the crude pulp. These compounds are predominantly found in epidermic cells of the resultant pulp. Analysis of the chemical elements present in the various parts of epidermic cells shows that the silicon derivatives can, according to the place where they are (teeth or around the teeth), exist under various chemical structures. These observations confirm that the organic acid process is perfectly adapted to fibrous plants having a high content of silicon derivatives, such as rice straw.

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REFERENCES

(1) Parry, D.W. and Smithson, F. – Opaline silica in the inflorescence of some British grasses and cereals, *Annals of Botany* **30**:525 (1996).

(2) Kaufman, P.B., Bigelow, W.C., Soni, S.L., Lacroix, J.D. and Rosen, J.S. – Electrophobe microanalysis of silicon in the epidermis of rice (*Oriza sativa*) internodes, *Planta* **104**:10 (1972).

(3) Soni, S.L., Kaufman, P.B. and Bigelow, W.C. – Electromicrophobe analysis of the silicon and others elements in the leaf epidermal cells of rice plants (*Oriza sativa*), *Am J. Bot.* **59**:38 (1972).

(4) Lengyel, P. – Investigation and technical experiences in the recovery of straw black liquor, *Proc. Symposium on Recovery of Pulping Chemicals, Helsinki*, p.563 (1968).

(5) Chou, B.C. – Alkaline recovery system for rice and wheat straw based black liquor, *Proc. International Non-wood Fiber Pulping and Papermaking Conference, Beijing, China*, p.839 (1988).

(6) Hoang, Q.L. – **Séparation sélective de la cellulose, des hémicelluloses et des lignines par le système catalyseur / solvant : acide formique / acide acétique, de matières végétales à teneur variable en silicium**, Ph. D. Thesis, INP. Toulouse (2000).

(7) Delmas, M., Hoang, Q.L., Le Bigot, Y. and Avignon, G. – A new non-wood pulping process for high silicon content raw materials. Application to rice straw, *Appita J.* **56**(2):102 (2003).

(8) Juliano, B.O. – **Rice: Chemistry and Technologies**, The Am. Assoc. of Cereal Chem. Inc., St. Paul, Minnesota, USA, p.689 (1985).

(9) Seisto, A., Poppius-Levlin, K. and Jousima, J. – Peroxyformic acid pulping of non-wood plants by the Milox method, *TAPPI J.* **80**(10):235 (1997).

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REFERENCES

(1) Seth, R.S. and Page, D.H. – Fracture resistance: a failure criterion for paper, *Tappi J.* **58**(9):112 (1975).

(2) Yuhara, T. and Kortschot, M.T. – The J-integral as a parameter for characterizing the fracture toughness of paper. *Trans. 10th Fundamental Research Symposium*, Oxford, p.783 (1993).

(3) Fellers, C. – Fracture toughness a new paper property, L&W Handbook, **Paper Testing and Process Optimization**, Lorentzen & Wettre, Sweden, p.100 (1995).

(4) Casey, J.P. – **Pulp & Paper**, 3rd edn, Vol. III, John-Wiley & Sons, New York (1981).

(5) Seth, R.S. and Page, D.H. – Fiber properties and tearing resistance, *Tappi J.* **71**(2):103 (1988).

(6) Seth, R.S. – Implications of the single-ply Elmendorf tear strength test for characterizing pulps, *Tappi J.* **74**(8):109 (1991).

(7) Yan, N. and Kortschot, M. – Modelling of out-of-plane tear energy absorption of paper, *Appita J.* **49**(3):176 (1996).

(8) Tanaka, A., Otsuka Y. and Yamauchi, T. – In-plane fracture toughness testing of paper using thermography, *Tappi J.* **80**(5):222 (1997).

(9) Yamauchi, T. and Tanaka, A. – Tearing test for paper using a tensile tester. J. Wood Sci. **48**(6):532 (2002).

(10) Yamauchi, T., Okumura, S. and Noguchi, M. – Application of thermography to the deforming process of paper materials. *J. Mater. Sci.* **28**(17):4549 (1993).

(11) Ebeling, K.I. – Distribution of energy consumption during straining of paper, *Trans. 5th Fundamental Research Symposium*, Cambridge, p.304 (1976).

(12) Dumbleton, D.P., Kringstad, K.P. and Soremark, C. – Temperature profiles in paper during straining, Svensk Papperstidn. **76**(14):521 (1973).

(13) Yamauchi, T. and Murakami, K. – Amplitude distribution analysis of acoustic emission signals from the tensile testing of paper, *Jpn. Tappi J.* **46**(3):84 (1992).

(14) Tanaka, A., Matsumoto, T. and Yamauchi, T. – Calculative correction of the essential work of fracture method for paper, *Sen'i Gakkaishi* **54**(12):685 (1998).

(15) Welch, L.V. and Kerekes, R.J. – Characterization of the PFI mill by the C-factor, *Appita J.* **47**(5):387 (1994).

(16) El Maâchi, A., Sapieha, S. and Yelon, A. – Angle-dependent delamination of paper. Part II: Determination of deformation and detachment work in paper peeling, *J. Pulp Paper Sci.* **21**(12):401 (1995).

(17) Irwin, G.R. – Analysis of stresses and strains near the end of a crack traversing a plate, *J. Applied Mech.* **24**:361 (1957).

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