

DEPTH PROFILE OF PAPER ADDITIVES WITHIN A PULP FIBRE

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ABSTRACT

Paper sheets containing polyacrylamide (PAM) as a paper chemical additive have been analysed by attenuated total reflectance Fourier transform infrared (ATR/FT-IR) spectroscopy. Absorbance ratios of the selected band of PAM to that of cellulose were used to determine PAM content. In order to determine the distribution of the additive in the radial direction of pulp fibre, ATR/FT-IR analysis was carried out after successive etching of the paper sheet. From the relationship between etching time and the thickness of removed surface layer it is possible to follow the partial concentration profiles of the additive as a function of distance from the original surface. The obtained profiles are found to be consistent with those of variable-angle ATR/FT-IR depth profiling method qualitatively. Being distributed from fibre surface toward the centre of fibre wall, PAM exists, on the whole, close to fibre surface. Addition level does not affect the distribution curve, i.e. the concentration at every depth

level is roughly proportional to the addition level. In the case of a paper sheet from heavily beaten pulp, this tendency is not so clear i.e. PAM shows broad distribution at near surface layer. PAM whose molecular weight is low is distributed widely toward the inner side of the fibre wall.

INTRODUCTION

A wide range of chemicals is utilised in papermaking stock furnish to impart or enhance specific properties or to serve other necessary purposes. Alum, sizing agents, starches, water soluble polymers and dyes are common chemicals as paper additive chemicals. Although the content of the chemicals is very small, they are located on fibre surface or are distributed within a pulp fibre to fulfil the specific function. Quantitative determination of the chemical retained in the fibres is not easy due to its small amount. Furthermore, it has been almost impossible to measure its concentration/depth profile within a fibre wall because of the lack of a suitable method and its small amount. The depth profile might affect the mechanism of the additives to develop the specific function.

In the previous paper (1), attenuated total reflectance (ATR) infrared spectroscopy was applied to paper sheets containing a polyacrylamide (PAM) dry-strength additive. The results show that the difference spectra between those of the sheets with and without PAM give spectra of the PAM retained in the sheets and that the absorbance of a PAM characterising band linearly increases with PAM content. These findings are based on the measuring condition of ATR/FT-IR spectroscopy, fibre wall thickness and the distribution of PAM in thickness. That is, IR beam penetrates to ca. 1.2 μm thickness under the condition we used (correctly depending on the variation of ATR element and wavelength), whereas ATR analysis is a surface analysis. On the other hand fibre wall thickness

is 1–3 μm and the depth profile from surface side may be the same as that from lumen side, and moreover, PAM tends to be located on the surface. Therefore, the ATR/IR analysis can be regarded as a bulk analysis in the case of paper fibres (2), and was proposed for determining PAM content in paper sheets (1).

On the basis of these findings a novel method, which is carried out in combination with sputter etching and ATR/FT-IR spectroscopy, was proposed for determination of the radial distribution (depth profile) of a paper additive chemical within a paper fibre (3). In this paper the proposed depth profiling is briefly described and the obtained depth profiles of PAM within a paper fibre are discussed in relation to the addition level, molecular weight of PAM, pulp beating, and paper-recycling.

DEPTH PROFILING BY THE USE OF ATR/FT-IR SPECTROSCOPY

ATR/IR spectroscopy has been widely used as a common surface characterising method due to its practical advantages in terms of ease of application and sample preparation. In particular, depth profiling with ATR spectroscopy has been investigated by the use of a variation of the penetration depth, d_p (4). Variation of d_p with refractive index of ATR element, n_1 , and the angle of beam incidence, θ , at the given wave number (1670cm^{-1} : stretching of amide group in PAM) is shown in Table 1. Taking the range of d_p into consideration, depth profiling with ATR/IR spectroscopy should be limited to coarse profiling in μm order. Furthermore, the change of ATR/IR spectrum intensity with d_p does not provide quantitative profile but a qualitative information of the profile (5). Several ATR/IR studies have been done assuming a function form for unknown depth profile (4), and in some other studies ATR intensity (absorbance) was inversely Laplace transformed in order to obtain a quantitative depth

profile without an assumed function (6). Such an approach, however, is not easy because of the difficulty of numerical inversion of Laplace transformation. Eventually the depth profiling with ATR spectroscopy has so far been regarded as a qualitative determination.

ATR element	n_1	θ (deg.)	d_p at 1670 cm^{-1} (μm)
Ge	4.0	45	0.40
KRS-5	2.4	60	0.67
KRS-5	2.4	45	1.2

Table 1: ATR conditions and penetration depths, d_p .

For depth profiling in small scale under μm a surface etching and the subsequent chemical analysis becomes the most direct and common technique (7). ATR/IR analysis in combination with etching technique, however, has been used only to study the spectral changes associated with polymer morphology and the corresponding crystallinity feature (8, 9).

The Proposed Depth Profiling with ATR/IR Spectroscopy in Combination with Sputter Etching (3)

In the previous study (3) a sputter etching treatment was introduced to handsheets containing PAM for depth profiling: after etching successively, the surface PAM content was determined by ATR/IR spectroscopy. Figure 1 is an example showing the relationship between the surface PAM content (C_{PAM}) and etching time. C_{PAM} can be obtained from the absorbance ratio of a PAM characterising peak, ΔA_{PAM} , to a characteristic cellulose peak, A_{cell} , in an ATR/IR spectrum. As suggested above, the surface PAM content is almost same as the bulk PAM content. The decrease of the PAM content

must be caused by surface layer removal from the original surface by sputter etching. The curved plots in Figure 1 do not indicate actual depth profile, however, the difference of measured PAM content after t minutes etching over original PAM content ($1 - [C_{\text{PAM}}]_t / [C_{\text{PAM}}]_0$) means the contribution of the PAM content in the removed surface layer to the total PAM content. The contribution is plotted against the etching time t in Figure 2. The abscissa is also plotted with the distance from original surface, z_t , assuming that the removed surface layer thickness z_t proportionally increases with the etching time t (the exchange rate from t to z_t was given by the separate etching of some polymer films). Thus, Figure 2 can be considered to be the depth profile of PAM within a fibre wall as a cumulative distribution form. A differential distribution form of the depth profile in Figure 2 is shown in Figure 3. The ordinate was changed to PAM content in each layer (wt%) by multiplying the contribution by the total PAM content and the thickness ratio of each layer to the fibre wall (supposing $2 \mu\text{m}$ in this study). It clearly shows that PAM content in the surface layer is very high.

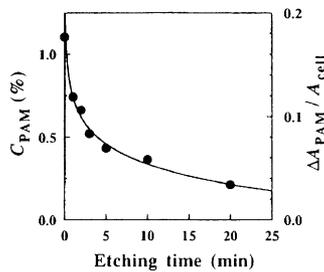


Figure 1: Dependence of the determined PAM content (C_{PAM}) on etching time for lightly beaten pulp (PAM addition level of 1%).

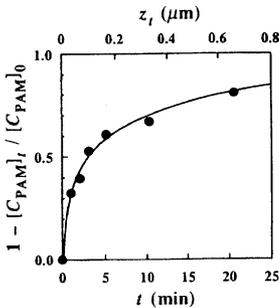


Figure 2

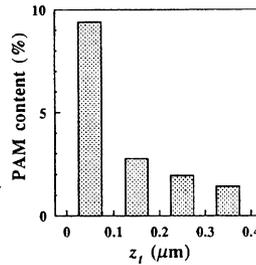


Figure 3

Figure 2: Dependence of the contribution $(1 - [C_{\text{PAM}}]_t / [C_{\text{PAM}}]_0)$ on the etching time (t), which can be converted to the distance from the surface (z_t) if these are proportional.

Figure 3: Depth profiles of PAM within a pulp fibre: Based on the contribution curves in Figure 2.

A similar result was qualitatively obtained by the non-destructive ATR/IR depth profiling. PAM content of the sample without sputter etching was determined by ATR/IR analysis with three different penetration depths shown in Table 1. The PAM content determined by ATR/IR analysis, C_{PAM} , was plotted against that determined by nitrogen analysis (1) in Figure 4. The closed relationship between the PAM content with $d_p = 1.2 \mu\text{m}$ and the broken line indicating bulk PAM content means that the PAM content measured with $d_p = 1.2 \mu\text{m}$ can be experimentally regarded as the bulk PAM content. This relation is reasonable as mentioned above, taking into consideration that d_p is comparable to the half of the fibre wall thickness and/or the biased distribution of PAM at the fibre surface.

The PAM content by ATR/IR analysis linearly increases with the amount of PAM retained in the sheet in spite of different d_p . An increase of the slopes of the linear relationship with decreasing d_p indicates that PAM is distributed at the surface. This tendency is more clearly illustrated in Figure 5 by plotting the PAM content, C_{PAM} , as a function of d_p at the PAM retained levels of 0.75 and 1.5%. Whereas these curves are not simply related to the depth profile curves across each fibre wall, they show the similar result from the depth profiling by the use of sputter etching (Figure 3). The higher PAM content at smaller d_p implies that PAM widely exists within a fibre wall but mainly exists at the surface. The tendency is clearer at higher addition level.

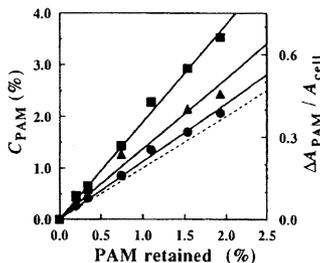


Figure 4: PAM content determined by the spectroscopy (C_{PAM}) vs. PAM content determined by nitrogen analysis, which shows the amount of PAM retained in the paper sheet. Solid lines show the variation of (C_{PAM}) with different penetration depths, d_p μm : 0.40 (■), 0.67 (▲); 1.2 (●), and broken line shows the bulk PAM content.

Although no information on the depth profile of PAM has been reported, Tanaka *et al.* (10) have mentioned the possibility of PAM migration or penetration through the micro pores by their adsorption

experiments. Their results may be generally interpreted as “polymer diffusion based on the repeated adsorption and desorption”. Other explanation for the results may be considerable, e.g. PAM adsorption on external fibrils of fibres in wet condition and the following collapse of fibrils on drying may lead similar results as shown in Figure 6 (11).

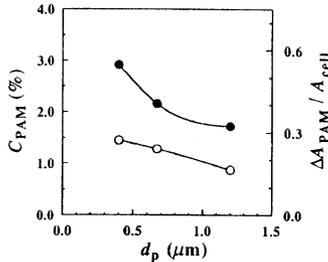


Figure 5: Variation in PAM content (C_{PAM}) with some penetration depths (d_p). PAM addition level %: 0.75(○); 1.5 (●).

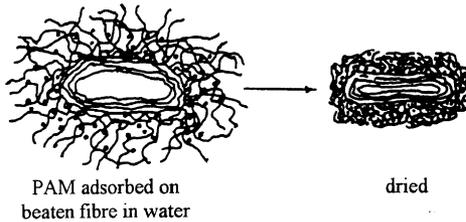


Figure 6: Drying a single beaten fibre with PAM (This figure was originally used to describe filler location within a beaten fibre (11)). PAM shown as dark spots adsorbed on a beaten fibre in water.

REMOVAL OF SURFACE LAYER BY SPUTTER ETCHING

Sputter etching is well known as an etching method causing less chemical modification (12). Etching rate was determined by measuring the weight loss of samples before and after etching. Assuming uniform removal of surface layer, the thickness of etched surface layer ΔT is given by

$$\Delta T = \frac{W - W'}{W} T \quad (1)$$

where W and W' are the weight of a sample before and after sputter etching respectively, and T is the thickness of the sample before etching.

Polyethylene terephthalate (PET) film and cellulose film (cellophane) were used for determination of the etching rate instead of paper samples. The thickness ΔT linearly increased with etching time for both films up to 10 min as shown in Figure 7 and the calculated etching rate was 33 nm/min for both films and probably for the paper fibres too.

The etched surface was observed by a scanning electron microscope (SEM) to check uniform etching. Figure 8 shows the typical surface structure of the etched sample. Whereas no detectable structural change was found in the samples treated for 2 min (Figure 8-A), many rather homogenous microcraters were found faintly through the entire fibre surface etched for 5 min (Figure 8-B), and the craters were found to become large by further treatment (Figure 8-C: etched for 20min).

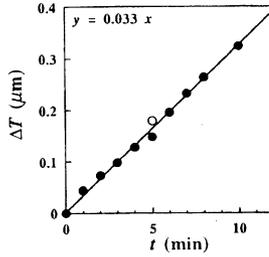


Figure 7: Experimental relationship between etching time (t) and thickness of the etched layer determined by mass decrease (ΔT): PET (●); cellophane (○). Each spot is an average of 2-4 times measurement.

The micro-structure may affect the depth profiling of PAM within a paper fibre. Thus, a double-layered film, polystyrene (PS) cast coated PET film, was etched stepwise and was measured by ATR/FT-IR in order to examine proportional etching. The original thickness of the coated PS film (T) was obtained by (13)

$$T = -\frac{d_p}{2} \ln \left[\frac{A_{\text{PET}}(T)}{A_{\text{PET}}(0)} \right] \quad (2)$$

where $A_{\text{PET}}(T)$ is the absorbance of a peak of PET which is covered with PS layer of T thickness; thus, $A_{\text{PET}}(0)$ is the absorbance of uncovered PET. The thickness obtained was $0.39 \mu\text{m}$.

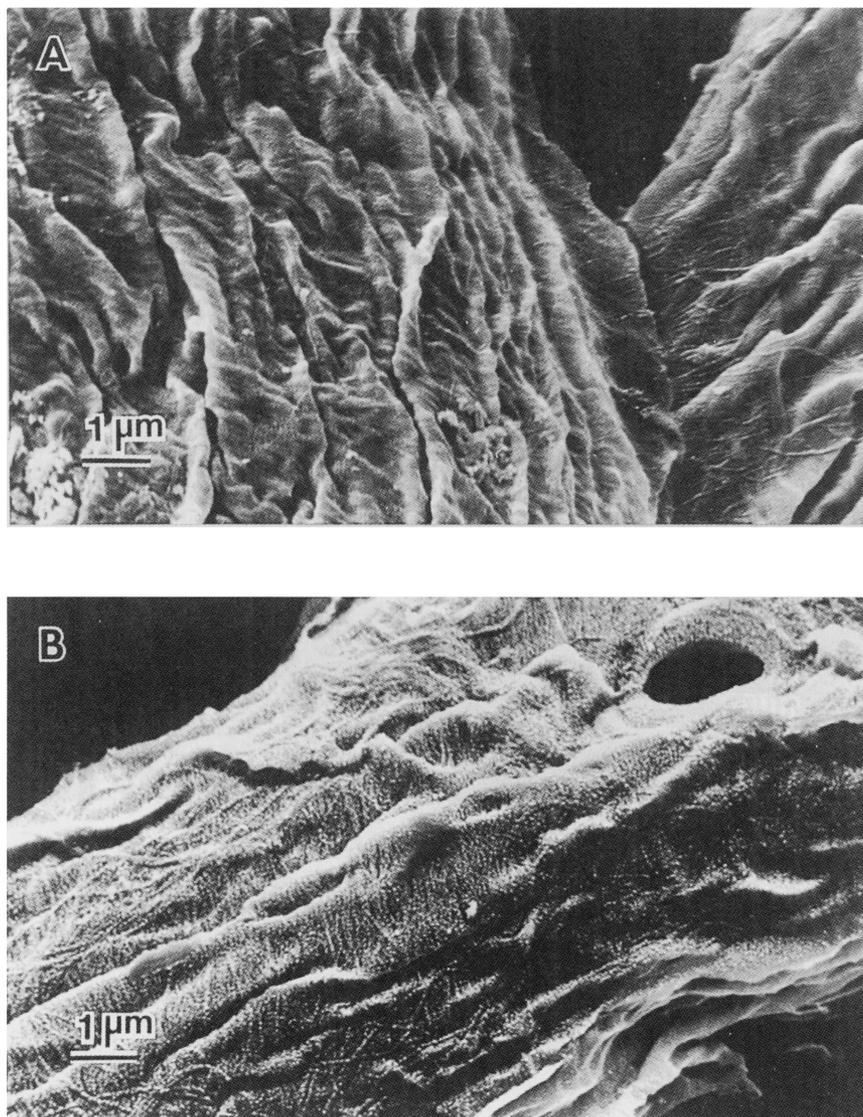


Figure 8: SEM images of etched paper surface: (A) 2min, (B) 5min of etching

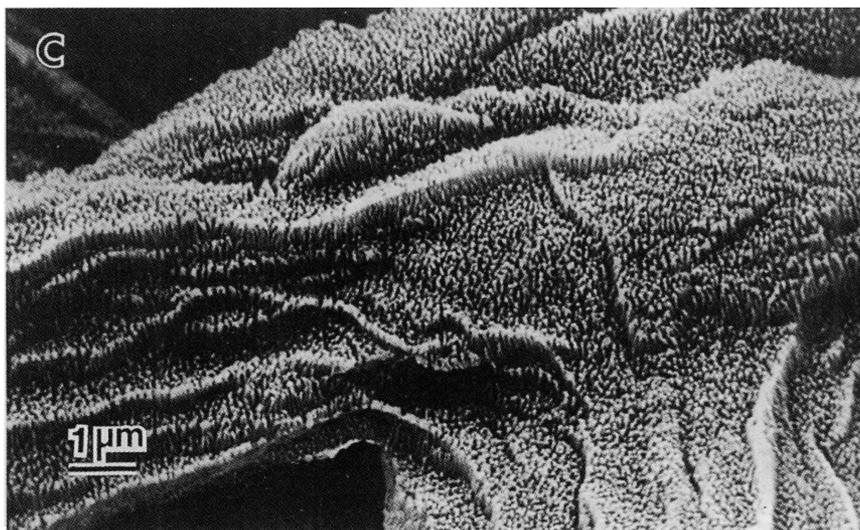


Figure 8 (continued): SEM images of etched paper surface: (C) 20min of etching

An absorbance ratio of the polymer characterising peak of ATR/IR spectrum ($\Delta A_{PS} / A_{PET}$) was plotted against etching period in Figure 9, including the calculated thickness of etched layer (ΔT). The broken line shows an assumed absorbance ratio if the sputter etching homogeneously removes PS layer with etching rate of 33nm/min. The absorbance ratio under homogeneous etching condition should linearly decrease with etching time and diminish at 12.5 min etching (i.e., $\Delta T = 0.39 \mu\text{m}$) as shown by the broken line. The observed absorbance ratio $\Delta A_{PS} / A_{PET}$ decreased along the assumed straight line with the etching time at the first half, and then the decreasing rate is gradually reduced with the etching time at the second half.

These results from Figure 7–9 prove that the etching until 5 min is homogeneous and proportional to obtain the precise depth profile and further suggest that depth profiling from 0.2 up to 0.4 μm needs some correction.

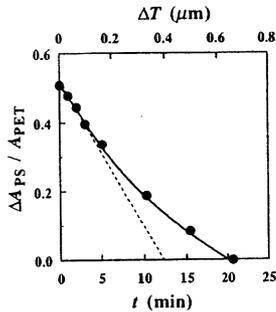


Figure 9: Absorbance ratio of PS coated PET film as a function of etching time (t). Broken line shows proportional relation between absorbance ratio and thickness of the etched layer (ΔT).

EXPERIMENTAL

Materials

The pulp used for handsheet making was a commercial bleached kraft pulp prepared from mixed hardwoods. The pulp was previously classified by a classifier with a 100 mesh screen in order to remove fines derived from parenchyma cells. This is because they can adsorb PAM more easily than fibres (14) and should affect the reproducibility of the experiment.

The PAM used in the present study was a commercially available (molecular weight: 2×10^6 and the charge density: 0.6 meq/g) and some laboratory made cationic PAM of varying molecular weight: acrylamide and *N,N*-dimethylaminopropylacrylamide were polymerised in 17% aqueous solution with ammonium persulfate (APS)–sodium pyrosulfite (SPS) redox initiator under a nitrogen atmosphere at 55 °C for 2h. The amounts of the initiator are given in Table 2, which includes some physical properties of the PAM obtained. The charge density of the PAM was determined by polyelectrolyte titration (15), in which an anionic polymer, potassium polyvinylsulfate, was used together with a cationic indicator, *ortho*-toluidine blue. The molecular weight of the PAM was determined by a Tosoh GPC-LS system. Unless otherwise noted, the commercially available PAM was used.

The fines-free pulp was beaten with a PFI mill to CSF 585 ml except the one used for the experiment to evaluate the effect of beating. Aliquots of the pulp slurry were diluted with tap water and then an aqueous solution of the PAM adjusted to 0.75% concentration was added to the pulp slurry in the range of 0.5–3.0%, based on dry pulp. No other additives such as alum were added to the slurry to simplify the experiment. After the addition of the PAM, the slurry was allowed to stand at room temperature for 25 min before sheet

making. Handsheets (ca. 60 g/m²) were made according to Tappi Test Methods (T205). The pH of the slurry was about 8 during the whole process. Before measuring, all sheets were thoroughly conditioned at 23 °C, 50% relative humidity.

The bulk PAM content of the sample sheets was determined by nitrogen analysis as described in the previous paper (1). Some basic properties of the sheets are given in Table 3.

	A	B*	C	D**
APS (g)	0.210	0.403	0.350	1.050
SPS (g)	0.044	0.084	0.147	0.440
Charge density (meq/g)	0.55	0.60	0.59	0.59
\bar{M}_w ($\times 10^6$)	3.3	2.0	1.2	0.4
\bar{M}_w / \bar{M}_n	1.7	1.9	2.0	2.0

*High MW PAM in the text (almost as same as “the commercially available PAM”).

**Low MW PAM in the text.

Table 2: Physical properties of laboratory made PAMs.

PAM* addition level (%)	CSF (ml)	Sheet density (kg/m ³)	Tensile index (kNm/kg)	Light scatter. coeff. (m ² /kg)
None	585	595	38.1	39.3
0.5	630	616	46.2	34.7
1.0	625	610	63.1	34.9
1.5	625	599	72.7	35.6
2.0	555	607	84.0	35.5
3.0	530	649	85.1	31.7

*Commercially available PAM.

Table 3: Basic properties of the handsheets.

Recycling Process

Many experimental factors are required to reproduce paper recycling, the following conditions were adopted as a simplified recycling experiment in the present study. First a fines-free commercial hardwood kraft pulp was beaten to 520 ml CSF with a PFI mill. The commercial PAM was added to the pulp furnish at the addition level of 1%. The sheets were heated at 80 °C for 24 h and were soaked in water for 24 h. After defibrillation with a standard disintegrator and a homogenising mixer, the furnish was again sheeted. These processes were regarded as a one cycle and further two cycles were carried out without further addition of PAM. Further addition of PAM was also carried out after one recycling. Table 4 shows the tensile indices and PAM retention of these sample sheets.

Number of recycling	Tensile index (kNm/kg)	Retention ^a (%)
0	62.2	100
1	43.5	89.7
1 ^b	54.1	---
2	38.3	80.5
3	34.6	70.9

^aThe value of "Recycle 0" to be 100.

^bFurther addition of PAM (1%) after 1 time recycling.

Table 4: Tensile indices and PAM retention of the recycled papers.

Sputter Etching

The sample sheet cut in a rectangle of 14 × 40 mm was dried in vacuum for 24 h before etching. The sample on the electrode was sputter etched stepwise from 1 to 20 min in a radio frequency sputtering equipment Shinku Kiko RFS-200 under the following

conditions: an electric power of 3 W and an Argon gas pressure of 10 Pa. As describe above, the etching rate was 33 nm/min till 5 min etching. For the etching over 5 min, the etching rate was corrected using the observed relationship between the absorbance ratio and etching time in Figure 9: ΔT of 20 min etching sample was assumed to be the same as that of PS surface layer (0.39 μm).

Infrared Spectroscopy

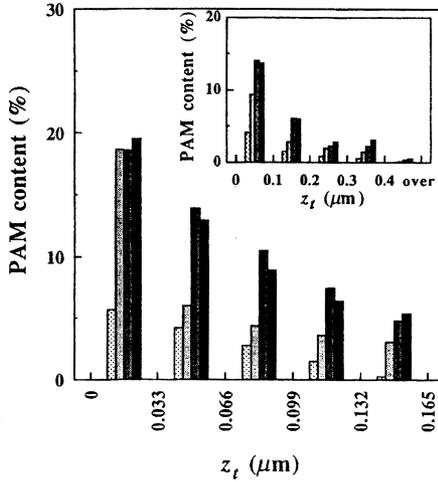
ATR/FT-IR spectra were collected on a Shimadzu FTIR-8200PC spectrophotometer equipped with an ATR accessory with a KRS-5 internal reflection element (IRE) at a fixed incident angle (θ) of 45°, unless otherwise noted. After conditioning in the standard atmosphere, two pieces of the paper sample (14 × 40 mm) were placed on each side of the IRE. The FT-IR data were collected over 100 single-beam scans with a resolution of 4 cm^{-1} .

In order to isolate the selected band of PAM (1670 cm^{-1} : stretching of amide group), difference spectra were obtained by spectral subtraction with a spectrum of a blank paper sheet. The blank sheet was also etched for the same time as the sample sheet. For internal normalisation, the absorbance of the PAM characterising band in a difference spectrum (ΔA_{PAM}) was divided by that of a characteristic cellulose band (A_{cell}), and the absorbance ratio was converted to the apparent surface PAM content (C_{PAM}). The details of the analysis, including the correction for sample-IRE contact, have been described in the previous papers (1, 3).

RESULTS AND DISCUSSION

The Effect of Addition Level

In commercial papermaking PAM addition level is about 0.5%. More addition of PAM makes the sheet stronger, while the strength increment gradually decreases (Table 3). The effect of addition level on the depth profile is shown in Figure 10 for the lightly beaten pulp sheet.



PAM addition levels %: 0.5 (□); 1 (▨); 2 (■); 3 (■).

Figure 10: Effect of addition level on the depth profile of PAM in lightly beaten pulp.

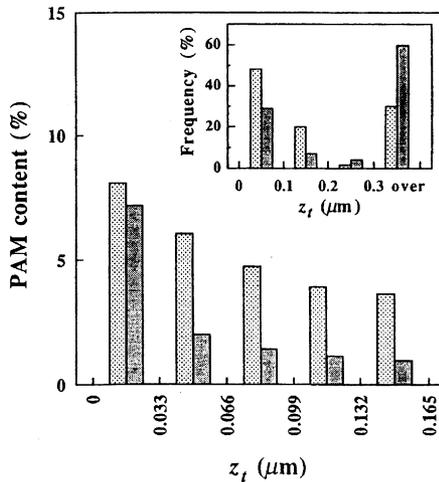
Generally the most PAM is distributed at the surface and the content decreases toward inner side regardless of addition level. In the layer closest to the surface (≤ 33 nm), over 1% addition brings about hi-level PAM content ca. 20 wt%, which might suggest that the PAM highly covers on the surface and that the adsorption site at the surface is almost saturated. The PAM content in each layer from 33 to 165 nm increases with an increase of addition level from 0.5 to 1 and 2 %, however 3% addition shows almost the same distribution as 2% addition sample, which agrees with a decrease of PAM retention rate from 72 to 60%.

The distribution, which has a distinguishing peak at the surface and is tailing toward the inside, is to a greater or lesser degree common for all sheets tested as described below. Assuming the additional bonding between fibre surfaces as the strengthen mechanism (16), the observed depth profile of PAM showed that the most part of the PAM retained may not contribute to the increase of the strength. However, it is hard to imagine that almost all of the PAM within a fibre wall might not participate in the strength enhancement. The PAM in the fibre wall might play some roles in the strength enhancement such as a partial fibre reinforcement.

The Effect of Molecular Weight of PAM

If the observed depth profile of PAM arises from its migration in a wet fibre wall, the depth profile may vary with its molecular weight (MW) and/or the time period of wet condition i.e. the soaking time after PAM addition till sheet drying. In the present study, a series of PAMs different in MW was synthesised. The depth profiles of the PAMs of high and low MW (B and D in Table 2, respectively) at addition level of 1% are shown in Figure 11.

PAM of low MW has wider profile toward inner side i.e. the content in each layer of the surface side is lower than that of high MW. This tendency is clearly illustrated in the upper figure, whose ordinate represents the frequency of PAM existence. More than the half of the low MW PAM exists in the depth over $0.3 \mu\text{m}$. On the other hand the soaking time (10 days) after PAM addition has little effect on the PAM distribution. These results suggest that the low MW PAM can penetrate into finer pores of wet fibre wall in the adsorption stage.

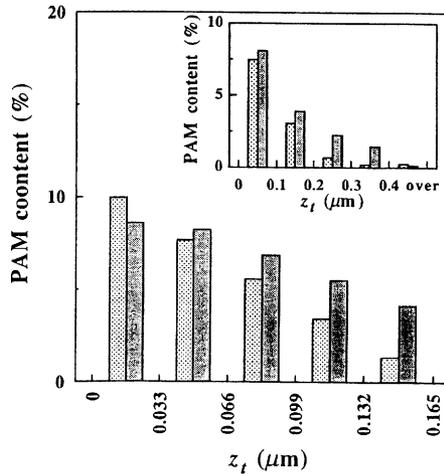


Molecular weight of PAM: high (□); low (▨).

Figure 11: Effect of molecular weight of PAM on the depth profile in lightly beaten pulp.

The Effect of Refining

Paper strength increases by addition of dry strength resin, PAM. The extent of strength improvement, however, depends on beating degree of the pulp. The depth profiles of PAM in beaten and unbeaten pulps are shown in Figure 12 at the addition level of 1%. The PAM distribution differs between unbeaten and beaten pulps. In the unbeaten pulp the PAM is remarkably distributed at the surface and the PAM content gradually decreases toward inner side.



Beating degree of pulp: unbeaten (\square), heavily beaten (\boxtimes).

Figure 12: Effect of beating on the depth profile at the PAM addition level of 1%.

On the other hand in the well beaten pulp (PFI mill 2000 rev, 375 ml CSF), the PAM content is almost the same level from the surface to at least 66 nm thickness from the surface. Furthermore, the PAM content in beaten pulp is higher than that in unbeaten pulp up to 0.4 μm thickness from the surface.

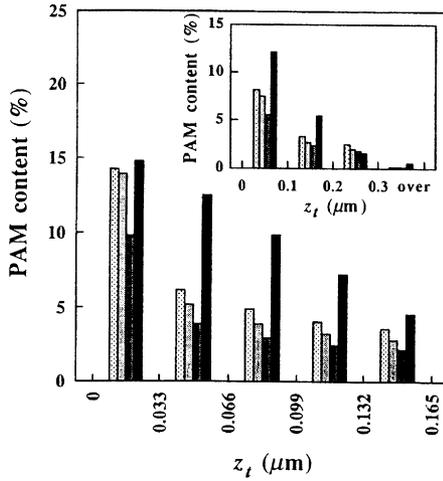
The difference of the depth profile of PAM between unbeaten and beaten pulp may suggest that the obtained distribution is at least partly attributed to the PAM adsorption on external fibrils and the following collapse of the fibrils on drying (Figure 6).

The Effect of Recycling

The rate of paper recycling has been increasing from ecological and economical view points and an use of the dry strength additives eventually follows, since the recycling causes a loss of the strength. The recycled fibres, therefore, include the dry strength additives within a fibre wall and the amount may increase with recycle number if the additive is further used at every sheetmaking stage. In order to use the recycled fibres more effectively, it is important to know the remaining ratio of dry strength additives and the depth profile after the recycling processes. In the present study, a recycle treatment including an accelerated ageing was carried out several times to the handsheets with PAM. The depth profile of these sheets was shown in Figure 13.

In our experimental conditions recycling causes the PAM content to decrease by ca. 10% after passing one recycle process (Table 4) and recycling generally does not affect the pattern of depth profile. The reason is not clear at the present time, however, a rubbing out of the surface layer during defibrillation process may cause these distribution changes.

The PAM added after recycling generally exists on the surface side but is not distributed on the first surface layer. It is well known that further addition of PAM is not much effective for strength enhancement. The higher concentration of electrolytes in stock and the adsorption on fines have been considered as the reasons (16). Not being distributed on the first surface layer may be another plausible reason.



Number of recycling: 0 (□); 1 (▨); 3 (■) and further addition of PAM after 1 time recycling (■).

Figure 13: Effect of recycling on the depth profile.

CONCLUSIONS

ATR/FT-IR spectroscopy in combination with sputter etching has been found to be useful for depth profiling of paper chemical additives within a fibre wall.

The PAM is on the whole located at the surface, but some is broadly distributed toward the inside of fibre wall. The use of low molecular weight PAM makes the distribution wider toward the inner side of the fibre wall. In the case of beaten pulp PAM is broadly distributed at near surface layer. The majority of the PAM retained in the sheets may not contribute to the strength enhancement. Further investigations are needed to clarify the depth profile in relation to the mechanism of sheet strengthening.

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Transcription of Discussion

Depth Profile of Paper Additives within a Pulp Fibre

Tatsuo Yamauchi, Lecturer, Kyoto University, Japan

Gil Garnier, Research Engineer, Paprican/McGill, Canada

You presented a graph in which you compared the different concentration profiles of polyacrylamide versus AKD. I saw with great pleasure that the AKD molecules diffused much further inside the fibres than those of the polyacrylamide. How could you explain such a phenomenon?

Tatsuo Yamauchi

It is the AKD that we studied. It was just an initial study with one set of conditions and I am not sure how it is different. Generally on the slides it shows that the AKD and the PAM is not much different.

Gil Garnier

Knowing that AKD is usually added as a colloidal suspension with an average diameter of 0.5 and 5.0 microns - it is impossible that the suspension diffuse inside the fibre. But the results, if they are true, they really support that hypothesis. On the other hand in our lab we showed that AKD vapours control the sizing mechanism. Would it be possible that what you compared is the diffusion of AKD vapours versus the diffusion of macro molecules of PAM?

Tatsuo Yamauchi

The method we developed is useful for other additives, these graphs just apply to the AKD.

Gil Garnier

Have you done a study between the diffusivity as a function of the molecular weight of the polymer?

Tatsuo Yamauchi

I think there is some migration or penetration mechanism possibly. Our results show that there is a some difference between the low molecular and high molecular weight .But this is variable. With long soaking time there is no difference and I am still wondering what the different penetration mechanisms are.

William Scott, Chair, Miami University, USA

Did you look at the lumen to see if you could find polymer?

Tatsuo Yamauchi

I did not check the lumen side but generally speaking I think the lumen side and the fibre side is the same.

Lars Ödberg, Vice President, Basic Research, STFI, Sweden

Concerning the AKD results, can it be that at least some of the AKD is still present as a patch on the fibre surface and what you are doing is just spattering away part of the AKD without the AKD ever penetrating into the fibres?

Professor John Roberts, UMIST, UK

I also noticed that there were 1% AKD additions which I think are quite high in comparison to normal use .

Tatsuo Yamauchi

This is a comparison with PAM at some level of addition. In this study the mechanisms have not been determined yet. I have tried to study the relation between dry strength mechanism and its profile within the fibre wall. I have much knowledge about strength measurements eg. fracture toughness - I have not expanded into the sizing study. AKD data is just the application of this method.

Theo van de Ven, Director, Paprican/McGill, Canada

My question relates to recycled fibres - I thought it puzzling that if you do the experiment with recycled fibres that more seems to go inside. You would expect that some of the pores have been filled with PAM from the previously treatment. How do you account for that?

Tatsuo Yamauchi

The distribution regime during the recycling is dependent on the conditions, so in my case the defibrations we have used are a strong defibration system. So this is one reason there is a similar pattern even after one or two passes, probably rubbing out from the surfaces occurred. I am just speculating.

Rasik Somaiya, R & D Chemist, Sonoco Products Co, USA.

Over the years it has been noticed that due to molecular weight distribution the FTIR response varies a lot. So if you are looking at one set of molecular distribution and comparing against a different molecular distribution set then the response factor will be greatly different. Secondly you mentioned that on the surface of the paper you are looking for AKD by using FTIR and ATR techniques after you have etched it. What frequency band are you using and what was your detection limit?

Tatsuo Yamauchi

Firstly, basically I can't say anything until I have checked the report. So far no change of band peak was observed, and the effect could be negligible in this study. Secondly, I have not checked the detectable smallest amount using this method, probably depending on the characterising band absorbance. As to the frequency, I have referred to the IR spectra of AKD reported in TAPPI Journal some years ago. Sorry I can't remember the frequency number which is characterising AKD.