A new method for measuring deposition of microstickies using QCM-D technique

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ABSTRACT

A QCM-D (quartz crystal microbalance with dissipation monitoring) technique was employed to measure microstickies deposition. This technique enables simultaneous measurements of shifts in resonance frequency ($\Delta f$) and in energy dissipation ($\Delta D$). The amount and the viscoelastic properties of the deposits, caused by dissolved and colloidal substances (DCS) in various DIP processes, were studied.

A model experiment using fluorescence-dyed stickies showed that microstickies formed deposits on the surface of QCM-D sensor. The experiments, using mixtures of DIP and HBKP, revealed that the $\Delta f$ values of the filtrates from those slurry were proportional to the DIP content in the mixture. Therefore, it was found that this method was able to measure microstickies deposition both qualitatively and quantitatively. The data from QCM-D measurements was not always subordinate to wet-end parameters like turbidity, cationic demand, static surface tension and consistency of the filtrate. In results of the mill survey, flotation processes decreased the $\Delta f$ values of filtrate from DIP by 0-40 %, and a replacement of process water by dewatering decreased the $\Delta f$ values significantly. An enzyme treatment decomposed stickies/filler complexes and prevented the growth of secondary stickies. Thus, it was considered that this technique gave significant information concerning the deposition of microstickies.

INTRODUCTION

In recent years, the ratio of deinked pulp (DIP) in paper has been increasing in terms of lowering the manufacturing cost of paper and saving resources. Conversely, over use of DIP causes deterioration of paper quality and process runability such as, increasing dirt speckles and defects in paper, and causing deposit problems in paper machine. The quality of recovered paper has decreased enormously in recent years due to the increasing amounts of stickies in recovered paper. Especially in Japan, since the average content of DIP in newsprint is around 75 %, the problem caused by stickies is getting worse year by year. Thus, it is necessary to understand the behavior of the stickies to deal with the deposit problem, and the establishment of the evaluation method of stickies becomes important.

Stickies are generally classified as macrostickies and microstickies according to their size [1-3]. As for macrostickies, the measurement method has been standardized [4,5]. Contrastively, as for the microstickies measurement, various methods [6-8] were proposed, but there were strengths and weaknesses in each proposal. Therefore, a satisfactory method that is able to use in industry has not been established yet.

Most of proposed methods are divided into two groups, direct measurements of deposition and indirect measurements of dispersed and colloidal substances. Typical direct measurements [9-11] used adsorbents, such as low-density polyethylene (LDPE) films, stainless steel strips and paper machine wires, and measured the increase of the weight of probes after deposition testing. Those direct methods can certainly measure the deposition of stickies, however, the weight of the deposit is too small, therefore a problem remains in reproducibility and accuracy by gravimetric analysis. One solution of these deposition measurements is using image analyses to estimate the accumulation of deposits. In this case, the uniformity of adsorbed deposits film creates another difficulty for precise measurements. Castro and coworkers proposed a method [12] that could monitor the microstickies deposition by pressure drop through a collector. This method seems to be promising for microstickies measurement. However, industry needs a simple method, which can be measure microstickies, in a short time.

Conversely, indirect measurements [13-15], like solvent extraction, TOC, COD and thermogravimetric measurement methods, tend to get relatively high reproducibility of the measurements, however, it is not measure the deposition phenomenon itself, therefore a problem remains in qualitatively. It was recognized that the instrument analysis like mass spectroscopy after solvent extraction gave qualitative information. Unfortunately, this approach tends to take
long time to get a set of data. Thus, the biggest problem in microstickies measurements is extremely difficult to achieve qualitatively and quantitatively of minute materials at the same time in a short period.

The authors attempted to apply a QCM-D (quartz crystal microbalance with dissipation monitoring) technique [16] to measure a hint of microstickies deposition in a relatively short time. This apparatus was recently applied to studies in wet-end chemistry and other colloid chemistry [17-20]. In our previous report, we found that the method using QCM-D technique had potential to measure microstickies deposition both qualitatively and quantitatively [21].

The concepts of this method are as follows;
1) Only the adsorbed mass onto the hydrophobic surface is measured.
2) An extremely minute weight change is detected accurately as frequency changes in a quartz crystal microbalance.
3) As for practical and prompt measurement method, the initial stage of deposition, i.e., the film formation of hydrophobic materials containing microstickies onto the surface of fabrics such as forming wires and dryer canvases, is monitored.

The objective of this study was to establish the measurement method for the deposition of microstickies using QCM-D, and to survey the behavior of microstickies in mill processes. The measure for deposit problem was also evaluated by using this method.

EXPERIMENTAL

Materials
Polystyrene beads, polymethylmetacrylate beads, ethanol (99.5 %), toluene (99.5 %), dichloromethane (99 %), acetone (99.5 %), sodium dodecyl sulfate, Rhodamine 6G, and N/400 poly-diallyldimethylammonium chloride (poly-DADMAC) standard solution were purchased from Wako Pure Chemical Industries, Japan. Model adhesive, Saibinol AT-39, a copolymer of acrylate and vinyl acetate, was donated by Saiden Chemical Industry. Deinking agent, SA520 was donated by Lion Corporation. Enzyme, Optimize 525, as for detackify stickies, was purchased from Buckman Laboratories, Japan.

The Final DIP and the pulp from deinking processes used in this experiment were obtained from three mills in Nippon Paper Industries. Those deinking furnish were the mixture of old news print (ONP) and old magazine (OMG) as resources. Hardwood bleached kraft pulp (HBKP) was also obtained by one of the mills.

Model Experiment Using Fluorescence-dyed Stickies
Filter paper was coated with the adhesive containing 0.1 % Rhodamine 6G, and cut into small pieces (1 cm x 1 cm). A mixture of ONP and OMG (60/40 by weight), which contained 1% adhesive-coated filter paper, was disintegrated in a laboratory pulper at 3 % consistency, 40°C for 30 minutes with deinking agent (0.2% based on O.D. pulp) and sodium hydroxide 1 %. Disintegrated pulp was diluted to 1 % consistency with tap water. The pulp was filtered through a 500-mesh sieve (opening 25 µm) and used for QCM-D measurement.

Measurement Using QCM-D

QCM-D apparatus
A QCM-D300 apparatus delivered by Q-Sense, Gothenburg, Sweden was used. The techniques and methods of QCM-D measurements were described in detail elsewhere [22]. This apparatus allows the simultaneous measurements of changes or shifts of resonance frequency $f$ and energy dissipation $D$. The shift of $f$ ($\Delta f$) corresponds to a relative change in the amount of adsorbed material on the surface of the sensor, which is calculated from the Sauerbrey’s equation (1) [23]. Note that the frequency shift includes the adsorbed substance as well as water, which is strongly bounded or incorporated to the adsorbed layer. Therefore, the weight calculated from the equation (1) was including water, i.e., the value was a wet-mass.
\[
\Delta m = -C \frac{\Delta f}{n}
\]  
(1)

where \(m\) is the adsorbed mass, \(C (=17.7 \text{ ng cm}^{-2} \text{ Hz}^{-1} \text{ at } f = 5 \text{ MHz})\) is a constant, and \(n\) is the overtone number, the fundamental resonance frequency (5 MHz) and its 3rd, 5th and 7th overtones (15, 25 and 35 MHz, respectively).

The shift of energy dissipation (\(\Delta D\)) reflects viscoelastic properties of the materials adsorbed on the sensor surface. It is defined as the ratio between the energy dissipated and stored in the crystal during a single oscillation, the \(D\) value is calculated from equation (2). The change in dissipation value gives information about adsorbed layer such as film thickness, film density and shear viscosity when it comes to fit the Voigt model using software prepared in QCM-D. Since the deposition of microstickies is not homogeneous, it is difficult to apply the Voigt model. However, it is possible to obtain the information about the change in surface roughness from the \(\Delta D\) and \(\Delta f\) values.

\[
D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}
\]  
(2)

The sensor crystal used in this study was 5 MHz AT-cut quartz coated with gold electrode of approximately 100 nm in thickness (Q-Sense). All measurements were recorded at the fundamental resonance frequency (5 MHz) and its 3rd, 5th and 7th overtones (15, 25 and 35 MHz, respectively). Temperature of the QCM-D sample chamber was controlled at 25 ± 0.03°C.

**Sensor coating**

Generally, the stickies are a hydrophobic material. Ling has reported that the critical surface tension of the adhesive was 31.7 mJ/m² [24]. From the viewpoint of surface chemistry, the affinity between two materials increases when the surface free energy of these two materials is similar. Therefore, in this method, the QCM-D sensor surface was coated with polystyrene whose critical surface free energy of solid is ca. 33 mJ/m².

The QCM-D sensor crystals were spin-coated with polystyrene (PS) in the following way. First, a 0.5 % of PS in toluene was prepared. Those solutions were filtered through a 0.45 \(\mu\)m polypropylene filter (Arbor Technologies, MI, USA) to remove any contaminants and non-dissolution polystyrene beads. Then, the sensor was mounted in the spin-coater with suction, and the solution was dropped on the sensor surface. The sensor was rotated at 2000 rpm for 20 seconds. Finally, remaining toluene was evaporated by heating at 80 °C for 30 minutes.

**QCM-D measurement**

Figure 1 shows the schematics of a typical QCM-D experiment. In typical QCM-D measurements, a sensor crystal was mounted on the QCM-D sample chamber and was checked to find the resonance frequencies. The mixture of distilled water and ethanol (50/50 by weight), which was stood at least one day after mixing and then degassed by ultrasonic, was introduced to the chamber with suction to remove remaining air and to wet the sensor surface completely, and then the mixture was replaced by distilled water. Note that the air in the sample chamber must be excluded to wet the sensor surface uniformly.

The \(\Delta f\) and \(\Delta D\) values of distilled water were recorded to set a baseline. After recording the baseline, 50 ml of pulp sample was filtered through a 500-mesh sieve (25 \(\mu\)m opening), and immediately, the filtrate was injected into the T-loop of the QCM-D instrument and maintained there for 3 minutes to ensure that its temperature was 25 °C. Then the filtrate was delivered to the QCM-D sample chamber from the T-loop and the time was set to \(t_0\). The time 15 minutes after filtrate injection (\(t_0\)), the filtrate that was not deposited on the sensor surface was washed by injection of distilled water and removed any factors on the wet-end parameters such as pH and conductivity. After 3 minutes injection of distilled water, the chamber was rinsed again by distilled water in the same way. The variation of QCM-D measurements was about 10 %.
Figure 1  Schematics of adsorption measurements by QCM-D (quartz crystal microbalance with dissipation) and typical trace of resonance frequency ($\Delta f$) and energy dissipation shift ($\Delta D$). The injection of filtrate increased absolute values of $\Delta f$ and $\Delta D$.

Other Measurements

Calcium ion and turbidity
The pulp slurry was filtered through paper filter (#2, AdvanTech Toyo, Japan), and the calcium ion and turbidity of the filtrate were measured by photometer (LASA100, DR. LANGE, Germany).

Cationic demand
The pulp slurry was filtered through 200-mesh wire, and the content of anionic functional groups in filtrate was measured with a streaming current detector (PCD03, Mütek, Germany) by titration with poly-DADMAC standard solution.

Surface tension
Static surface tension of filtrate, which was obtained through a filter paper (#2, AdvanTech Toyo, Japan), was measured with CBVP-Z (Kyowa Interface Science, Japan) tensiometer based on Wilhelmy plate method. Three sets of measurements were done at 25°C.

Microscopy
The deposition of model stickies on the QCM-D sensor was observed by a fluorescent microscopy (IX-FLA, Olympus, Japan). The deposition of colloidal materials in filtrate on the sensor surface was also observed by a violet laser scanning microscope (VK-9500, Keyence, Japan).

RESULTS AND DISCUSSION

Deposition of Microstickies onto the QCM-D Sensor

First, a model experiment using fluorescence-dyed stickies was conducted to verify the deposition of microstickies onto the polystyrene-coated surface of the QCM-D sensor. The filtrate from model DIP slurry containing fluorescence-dyed stickies was injected into the QCM-D chamber. The sensor crystal after rinsing twice was produced from the chamber and dried with inert gas. Figure 2 shows pictures the optical and fluorescence image of the polystyrene-coated sensor surface after the QCM-D measurement. The red spots in fluorescence image were dyed stickies. Therefore, QCM-D measurement was able to evaluate the deposition of microstickies in the filtrate from pulp slurry.
Figure 2  Optical image (left) and fluorescence image (right) of adsorbed colloidal materials on the sensor surface after the QCM-D measurement of the filtrate from the model pulp containing fluorescence-dyed stickies. The red spots in fluorescence image were dyed stickies. The highlights in optical image were agglomerate filler particles.

Quantitative Measurement of Microstickies Deposition

The authors reported previously that QCM-D measurements gave a linear frequency change, i.e., adsorbed mass change, when the filtrate from DIP was diluted with a certain amount of water. The linear relationship was observed both static and dynamic conditions, i.e., a batch and flow measurement, as well. The correlation coefficient values of linear regression in the QCM-D measurements under those conditions were 0.98 and 0.99, respectively.

In this experiment, the frequency and dissipation change in QCM-D measurements of filtrates, which were prepared from the mixture of two pulps, HBKP and DIP, were examined. The final DIP from mill A (DIP-A) and HBKP and the blends of those pulps in 25% increments at the pulp consistency 1% were used as model samples. The filtrates of these samples were injected into the QCM-D chamber individually and the frequency changes were monitored.

Figure 3  Shifts of resonance frequency: Δf (left) and energy dissipation: ΔD (right) at the third overtone (15 MHz) as a function of time after injection of filtrate from DIP-A, HBKP and the mixture of DIP-A and HBKP (50/50 by weight). The pulp consistency was adjusted 1% by weight. The arrows indicate injection points: filtrate at a and distilled water at b.
Figure 3 shows the results of resonance frequency shift ($\Delta f$) and energy dissipation shift ($\Delta D$) as a function of time after the injection of filtrate from DIP-A, HBKP and the mixture of DIP-A and HBKP (50/50 by weight). The filtrate, which filtered through 500-mesh sieve (opening 25 µm), from DIP-A gave the largest $\Delta f$ and $\Delta D$. This meant apparent amount of deposit on the QCM-D sensor surface, which probably included hydration water molecules, was increased when the DIP-A content in the filtrate increased, and the surface of sensor became more viscous or rough.

![Graph showing $\Delta f$ and $\Delta D$ vs. DIP-A content](image)

$R^2 = 0.967$

Figure 4 shows the results of resonance frequency shift ($\Delta f$) after rinsing twice as a function of DIP-A content in the filtrate from the mixture of HBKP and DIP-A. The 100% of DIP-A content meant DIP-A itself, and 0% of that was HBKP.

![Graph showing $\Delta f$ vs. DIP-A content after rinsing](image)

Figure 4 shows the results of resonance frequency shift ($\Delta f$) after rinsing twice as a function of DIP-A content. It was clear that the frequency shifts were proportional to the DIP-A content. The correlation coefficient value of linear regression was 0.97. According to the Saurebrey’s equation, the amount of adsorbed mass including water at DIP-A 100% was estimated to ca. 1290 ng/cm².

![Graph showing $\Delta f$ vs. $\Delta D$ for different DIP-A contents](image)

Figure 5 shows the relationship between resonance frequency shift ($\Delta f$) and energy dissipation shift ($\Delta D$) of the filtrate from DIP-A, HBKP and the mixture of DIP-A and HBKP (50/50 by weight).
By plotting the $\Delta D$ value against the corresponding $\Delta f$ value, the relationship between the adsorbed mass on the sensor surface and the viscoelastic properties of the adsorbed layer can be inferred. The $\Delta D$-$\Delta f$ plots are shown in Figure 5. The results revealed that the slope of the plot of HBKP 100% was smaller than that of DIP-A 100%. The large values indicated that the adsorbed layer was more viscous or very rough.

![Figure 6](image_url)

Figure 6  The dissipation shift/frequency shift ($|\Delta D/\Delta f|$) of filtrate at t=15 as a function of DIP-A content in the filtrate from the mixture of HBKP and DIP-A

Figure 6 shows the influence of DIP-A content on the $|\Delta D/\Delta f|$ values. It was considered that the $|\Delta D/\Delta f|$ value increased with increasing the portion of DIP-A content. This implied that the properties of the adsorbed layer were different between HBKP and DIP-A, and the surface of the sensor became viscous or rough by increasing the DIP-A content. Since the filtrate obtained from DIP contained many filler particles and fragments of coating colors, the adsorbed layer of the filtrate from DIP-A on the sensor surface was not homogeneous. This could be the reason of the increasing $|\Delta D/\Delta f|$ value when the DIP-A content increased.

The other wet-end parameters were also summarized in Table 1. In these model experiments, the ash content, conductivity, cationic demand and turbidity of the samples were changed depending on the proportion of DIP-A content. It is well known that the deposits caused by secondary stickies in wet-end process is a mixture of sticky materials (acrylates, ethylene vinyl acetate, etc.), natural furnish (natural pitch), chemicals (sizing agent, coating formulations, etc.) and ash (filler, pigment). Especially, ash from DIP was coated by microstickies. Therefore, it was reasonable to obtain a high correlation between QCM-D data and the wet-end parameters in this system.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Wet-end parameters of the samples for QCM-D measurements.</th>
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<tbody>
<tr>
<td></td>
<td>T-1</td>
</tr>
<tr>
<td>DIP-A</td>
<td>%</td>
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<tr>
<td>HBKP</td>
<td>%</td>
</tr>
<tr>
<td>Consistency of slurry</td>
<td>%</td>
</tr>
<tr>
<td>Ash</td>
<td>%</td>
</tr>
<tr>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/m</td>
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<tr>
<td>Cationic demand</td>
<td>µeq/l</td>
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<tr>
<td>Turbidity</td>
<td>FTU</td>
</tr>
<tr>
<td>Consistency of filtrate</td>
<td>%</td>
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</table>
Relationship between QCM-D Measurements and Wet-end Parameters

Empirically, it is also well known that the deposition problems caused by microstickies, in many cases, are not corresponding to the wet-end parameters like cationic demand, turbidity, etc. Thus, the samples from DIP process in Mill-B were measured by QCM-D, and the relationship between wet-end parameters and QCM-D data was analyzed. There are two DIP lines, DIP-I and II, in Mill-B. In both DIP lines, three flotation cells, which were installed in different point of each line, were selected and the samples from before and after flotation were tested for QCM-D measurements. Since the consistency of these samples was quite different, the measurements were executed on both the filtrate and the twice-diluted filtrate, which was adjusted the consistency to half of original filtrate by distilled water.

Figure 7 shows that the result of the frequency shift (\( \Delta f \)) at the third overtone (15 MHz) of the samples from Mill-B, DIP-I. The Loop I FT-A and FT-B were the flotation cell for process water treatment, and the Sec. FT was the flotation cell for the froth treatment of primary flotation cell in stock preparation. It was clear that the deposition of filtrate from Loop I FT-A was twice as large as that of filtrate from Loop I FT-B, even the consistency of filtrates were the same. The turbidity of filtrate from the FT-B inlet was 765 ppm, and that of FT-A inlet was 860 ppm. Therefore, the data obtained from QCM-D did not depend on the consistency and turbidity of the filtrate.

![Figure 7](image)

Figure 7 Relationship between the concentration of filtrate and the frequency shifts (\( \Delta f \)) at the third overtone (15 MHz) of QCM-D. The Loop I FT-A and B were the flotation cell for process water treatment, and the Sec. FT was the flotation cell for the rejects treatment of primary flotation cell in stock preparation, in the DIP line-I from Mill-B. The QCM-D measurements were conducted about filtrate and the twice-dilute filtrate.

As shown in figure 8, the \( \Delta f \) values were different from each flotation cell. The \( \Delta f \) value of DIP line-I was higher than that of DIP line-II. In process water, the FT-A gave the largest \( \Delta f \) and this implied that microstickies had accumulated in the system. It was also clear that the \( \Delta f \) values before and after flotation did not change significantly. Thus, it was thought that the removal efficiency of microstickies was low, especially in the FT-A and B in DIP line-I, and secondary FT in DIP line-II. The \( \Delta f \) value from Loop II FT outlet was higher than that of inlet and the result was reproducible. It might be affected by other factors. The estimated reject percentage of FT-A and B was around 5 % and it was relatively low, and this seemed to be one of the reasons for these results.
Figure 8  Comparison of frequency shifts ($\Delta f$) at the third overtone (15 MHz) of QCM-D for different flotation cells in DIP line I and II from Mill-B. The Loop FTs were the flotation cells for process water treatment, and the Sec. FTs were the flotation cells for the froth treatment of primary flotation cells in stock preparation. The before FT was the sample for the inlet of flotation cell, and the after FT was the outlet.

The relationships between QCM-D data and wet-end parameters, turbidity and static surface tension were shown in Figure 9. The two parameters have the possibility to mislead the QCM-D data. Turbidity, which was almost similar to ash content in case of DIP, gave a significant influence for gravimetric measurement, and surface tension, which was strongly correlated to deinking agents in DIP. According to the results shown in Figure 5, it was considered that the correlation among these parameters was low. The influence of deinking agents was verified by other adsorption experiments and the shift in frequency was much smaller than the results obtained from filtrates in the range of deinking agent used in DIP process. Therefore, QCM-D measurements were thought to give new information about the deposition of hydrophobic colloidal materials, especially microstickies.

Figure 9  The relationships between QCM-D measurement and turbidity (left), and surface tension (right) of the samples before and after flotation cell in Mill-B.
QCM-D Measurements of Varied Mill Samples

According to these results described in before, a trial that increased the rejects rate of flotation cells was done in Mill-B. Figure 10 shows the results of the resonance frequency shift ($\Delta f$) at the third overtone (15 MHz) of the samples from inlet and outlet of flotation cell during the trial in the Loop I FT-A, DIP line-I, Mill-B. It was clear that the $\Delta f$ values of filtrate after flotation were smaller than the values before flotation, except for the samples from March 15th. The removal efficiency rose to 25-45%. The reason for the significant decrease of $\Delta f$ in the flotation cell inlet from March 15th was not clarified.

![Figure 10](image)

**Figure 10** The frequency shifts ($\Delta f$) at the third overtone (15 MHz) of filtrate from the inlet and outlet of the flotation cell (Loop I FT-A) in the DIP line-I of Mill-B. The samples were collected from March 14th to 22nd.

![Figure 11](image)

**Figure 11** The effect of flotation and dewatering on the frequency shifts ($\Delta f$) at the third overtone (15 MHz) of QCM-D. The samples from the inlet, outlet and filtrate of the final thickener, and the inlet and outlet of Loop II flotation cell that clarified the filtrate of the thickener and other process waters in Mill-C were measured.

Next, the effect of flotation and dewatering on the deposition microstickies was investigated by using the samples from Mill-C. Figure 11 shows the results of frequency change of filtrate from the inlet and outlet of the final thickener and the Loop II flotation cell that clarified the filtrate of the thickener and other process water in Mill-C. It was found that the $\Delta f$ of flotation cell outlet decreased about 20% of the inlet, and $\Delta f$ of thickener outlet decreased
60% of the inlet. It seemed reasonable to take into account the rejects rate of flotation cell and thickener. Therefore, these results suggested that the replacement of process water acted as an important factor for microstickies control.

It is well known that the mixing of DIP and mechanical pulp (MP) increases the deposition of DCS including pitch and microstickies at certain conditions. Therefore, the influence of MP addition to DIP on the deposition of DCS was measured. The final DIP and RGP from Mill-C were mixed at the ratio 7/3, respectively, and the results of frequency change of filtrate, consistency of the filtrate and turbidity were summarized in Table 2. The mixing experiment was conducted twice.

Table 2  The influence of RGP addition to DIP on the deposition of dissolved and colloidal materials. The final DIP and RGP from Mill-C were mixed at the ratio 7/3. The frequency shift, consistency and turbidity of filtrates of DIP and the mixture were measured, respectively. The mixing experiment conducted twice.

<table>
<thead>
<tr>
<th></th>
<th>Run #1</th>
<th>Run #2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>DIP only</td>
<td>DIP/RGP=7/3</td>
</tr>
<tr>
<td>( \Delta f )</td>
<td>Hz</td>
<td>Hz</td>
</tr>
<tr>
<td>Consistency*</td>
<td>0.102</td>
<td>0.092</td>
</tr>
<tr>
<td>Turbidity FTU</td>
<td>439</td>
<td>201</td>
</tr>
</tbody>
</table>

*consistency of filtrate through a 500-mesh sieve (opening 25 \( \mu \)m)

After mixing the RGP, the turbidity decreased by 50-60% of the value of DIP only and the consistency of the filtrate decreased approximately 10%, as well. The \( \Delta f \) value of the mixture was 30% lower than that of DIP only, and the result was quite reasonable. From these results, again, it was thought that the QCM-D measurements gave new information about deposition of DCS.

**Effect of Enzyme on the Deposition of Microstickies**

One of the countermeasures for the microstickies problem, the use of enzymes, was nominated. Therefore, the effects of enzyme treatment for DIP were evaluated by QCM-D measurements. The results of enzyme addition to the final DIP from Mill-C were also summarized in Figure 12. The filtrates were obtained from the samples 1 or 2 hours after enzyme addition. The dose of enzyme was fixed at 300 ppm by weight.

![Figure 12](image)

**Figure 12**  The effect of enzyme addition to the DIP from Mill-C on the frequency shift (\( \Delta f \)) and dissipation shift (\( \Delta D \)) at the third overtone (15 MHz) of QCM-D. The QCM-D measurements were conducted on the filtrates from the DIP after 1 or 2 hours enzyme addition.

It was clear that the \( \Delta f \) value was decreased by enzyme treatment. The consistency of filtrate with and without...
enzyme treatment was almost the same (ca. 0.10 %). However, the turbidity after 2 hours of enzyme treatment was 253 FTU and that of without enzyme was 439 FTU. Therefore, the turbidity was decreased by 40 % without enzyme and that of $\Delta f$ value was decreased 50 %.

Figure 13 shows the photomicrograph before and after the enzyme treatment. After the enzyme treatment, the size of deposits on the sensor surface decreased significantly. Thus, it was thought that stickies surrounded the filler particles to be resolved by the enzyme treatment, and this prevented the growth of secondary stickies. According to this result, the enzyme treatment was conducted in the DIP process of Mill-C, and the improvement of paper machine runability was verified.

![Figure 13 The photomicrograph of deposit from DIP without enzyme treatment (left) and with enzyme treatment (right) on the surface of polystyrene-coated QCM-D sensor.](image)

CONCLUSIONS

The QCM-D technique was employed to measure microstickies deposition and it was found that this method was able to measure microstickies deposition both qualitatively and quantitatively in a short period of time. The information from QCM-D measurements was not always subordinate to wet-end parameters like turbidity, cationic demand, static surface tension and consistency of filtrate. By using this method, the behavior of microstickies deposition in mill samples could be evaluated and found as follows.

1) Flotation decreased the deposition of filtrate from DIP by 0-40 %, and the efficiency of removal could depend on the operating conditions.
2) The replacement of process water by dewatering was highly effective, and that might act as an important factor for microstickies control.
3) The enzyme treatment decomposed stickies/filler complex and prevented the growth of secondary stickies.

Overall, it was considered that this technique gave significant information concerning the deposition of microstickies.

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References