Comparison of Microstickies Measurement Methods
Part I: Sample Preparation and Measurement Methods

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BACKGROUND

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Recently, we completed a project on the comparison of macrostickies measurement methods (1). Based on the success of the project, we decided to embark on this new project on comparison of microstickies measurement methods. When we started this project, there were some concerns and doubts principally due to the lack of an accepted definition of microstickies. However, we agreed to undertake the project due to its importance to the industry.

As one can see from the list of authors and organizations above, we were fortunate that eight organizations/institutions agreed to participate in the project. Furthermore, Carl Houtman and his group at Forest Products Laboratory volunteered to prepare pulp samples in their pilot plant and ship them to all participants.

FPL was requested to prepare two pulps: sticky-containing pulp (Pulp A) and sticky-free pulp (Pulp B). Participants were then asked to prepare 5 pulp samples by mixing pulp A and pulp B in 25% increments:
Sample (i): 100% A; 0% B
Sample (ii): 75% A; 25% B
Sample (iii): 50% A; 50% B
Sample (iv): 25% A; 75% B
Sample (v): 0% A; 100% B

Additionally, a sample of deinked pulp (Pulp C) was also sent to all participants.

The current definition of microstickies is stickies particles that are smaller than 100 μm or smaller than 150 μm in size. These particles would pass through a 4-cut (0.1 mm, 0.004 in) or 6-cut (0.15 mm, 0.006 in) slotted screen. We let the participants decide whether to use whole stock or fractionated stock for testing. We did not set any lower limit though particles smaller than 5 μm are usually classified as colloidal and dissolved material - CDM or DISCO. We also did not specify the use of any chemical additive to promote the formation of secondary stickies.

In Part I of the paper we present details of sample preparation and description of various methods used for the measurement of microstickies. Results of sample analysis from these methods will be presented in Part II.

1.0 SAMPLE PREPARATION

Karen Scallon and Carl Houtman, USDA Forest Products Laboratory Madison, WI.

1.1 INTRODUCTION

As mentioned above, we were requested to prepare pulp samples in our pilot plant for collaborative microstickies investigation in cooperation with recycling experts world-
wide. Before presenting details of sample preparation a brief description of our pilot plant is appropriate.

The USDA Forest Products Laboratory (FPL) Pulp and Paper Pilot Plant provides the opportunity for companies and research organizations to collaborate with federal and university experts on all aspects of paper recycling. The pilot plant offers a state-of-the-art recycling system that utilizes similar processes and equipment found in mills today. The 45,000 sq. ft. pilot plant has the capacity to recycle five dry metric tons of paper per day. The plant is configured for continuous, dosed-loop operation for conservation and reuse of process water.

1.2 FPL PILOT PLANT CLOSED-LOOP PROCESS

The paper recycling pilot plant has seven stages: (1) high consistency pulping; (2) pressure screening; (3) forward cleaning; (4) through-flow cleaning; (5) flotation; (6) washing/dewatering; and (7) water clarification. The process is started with fresh city water, but once generated, clarified process water is recycled for use in pulping of subsequent batches and as dilution water for pressure screening and cleaning stages. Plant operations are typically performed at 46 ± 2°C. Process temperature is maintained by temperature controllers and heat exchangers. A data acquisition system records flow rate at 33 locations in the process, temperature at four locations, pulper power, and clarifier inlet and outlet turbidities.

High Consistency Pulping
Each pulper batch is typically pulped for 20 minutes at 14% consistency and 46 ± 2°C in a Voith HC 1.5 pulper. Pulper batches are timed to allow continuous operation of subsequent unit operations. Fresh water is used in the first batch and clarified process water is used for all subsequent batches.

Pressure Screening
The pressure screening stage consists of four slotted pressure screens in a feed-back, feed-forward configuration. Feed to the first primary pressure screen (0.3 mm milled slots) is diluted in-line to approximately 1% consistency (esc.). Rejects are fed to a secondary screen (0.2 mm c-bar slots). Accepts from the first primary and two secondary screens are collected, diluted to 1% csc., and fed to the second primary screen (0.15 mm c-bar slots), with the final accepts being fed to the cleaning stage. The rejects from the second primary screen are fed to another secondary screen (0.15 mm c-bar slots). Screen banding is used to increase passing speeds to 1 m/s.

Forward Cleaning
The forward cleaning stage consists of two primary forward cleaners (Celleco 270) and one secondary forward cleaner (Voith) for fiber recovery.

Through-flow Cleaning
The through-flow cleaning stage consists of two stages of through-flow cleaners (first stage: Black-Clawson Xclone; second stage: Beloit Uniflow).

Flotation
The flotation stage consists of a 2,000 L two-stage La Mort vertical flotation cell. The flotation aid is DI-700 (Manufacturer: Highpoint), a nonionic surfactant that is added at 0.1% loading level. Flotation rejects are sent to the drain and accepts are sent to the washing/dewatering stage.

Washing/Dewatering
A pilot drum washer having a 75-mesh screen is used to dewater the pulp to approximately 24% csc.

Water Clarification
Drum washer effluent and through-flow cleaner rejects are sent to the dissolved air flotation unit (Poseidon PPM-25) for process water clarification and recovery. A coagulant (Cytec C-577) and a flocculant (Cytec Superfloc 48 18) are added to the feed, typically in concentrations of 6 ppm and 10 ppm, respectively. The clarified process water typically has a turbidity of 35 NTU or lower and a flow rate averaging 380 Lpm. Clarified process water is collected in a holding tank equipped with a heat exchanger to maintain temperature near 46°C.

1.3 MATERIALS AND METHODS

A closed-loop pilot plant recycling trial with a mixture of eight pressure sensitive adhesives (PSAs) was performed at FPL on April 29, 2003 to investigate the generation and impacts of microstickies in the closed water loop and also to compare various test methods for the quantification of microstickies. The eight PSAs are identified in Table 1. Acrylic, vinyl alcohol, microsphere, and rubber PSAs were used. One of the PSAs was known to be difficult to remove due to its small pulper particle size.

<table>
<thead>
<tr>
<th>Adhesive No.</th>
<th>Adhesive Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Ethylhexyl acrylate</td>
</tr>
<tr>
<td>2</td>
<td>2-Ethylhexyl acrylate</td>
</tr>
<tr>
<td>3</td>
<td>Butylacrylate</td>
</tr>
<tr>
<td>4</td>
<td>Butylacrylate w/ Vinyl acetate copolymer</td>
</tr>
<tr>
<td>5</td>
<td>2-Ethylhexyl acrylate with Vinyl acetate copolymer</td>
</tr>
<tr>
<td>6</td>
<td>Styrene butadiene rubber emulsion</td>
</tr>
<tr>
<td>7</td>
<td>Styrene butadiene rubber emulsion</td>
</tr>
<tr>
<td>8</td>
<td>Styrene butadiene rubber hot melt</td>
</tr>
</tbody>
</table>
In the trial, equal weights of eight different PSAs were combined to achieve a PSA mass loading of approximately 0.5% per pulper batch. Stock materials identified in Table 2 having a total weight of 159.58 kg (148 kg OD) per pulper batch were pulped for 20 minutes at 46 ± 2°C. No chemicals were added for upling. A total of four pulper batches were processed through the recycling system resulting in approximately 240 minutes of operating time. Table 3 shows some important pilot plant operation parameters for the trial.

Table 2. Stock materials used for the trial, per pulper batch

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight in Pulper</th>
<th>Weight (kg) in Pulper</th>
<th>Oven-Dried Weight (kg) in Pulper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copy paper (Zero recycled content)</td>
<td>47.5</td>
<td>77.02</td>
<td>71.25</td>
</tr>
<tr>
<td>Envelope Paper (Zero recycled content)</td>
<td>47.5</td>
<td>77.02</td>
<td>71.25</td>
</tr>
<tr>
<td>PSA Facepaper</td>
<td>5</td>
<td>5.54 (0.692 per PSA)</td>
<td>5.21</td>
</tr>
<tr>
<td>TOTAL:</td>
<td>100</td>
<td>159.58</td>
<td>147.71</td>
</tr>
</tbody>
</table>

Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Batch #1</th>
<th>Batch #2</th>
<th>Batch #3</th>
<th>Batch #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulper Csc. (%)</td>
<td>14.58</td>
<td>14.50</td>
<td>13.31</td>
<td>13.42</td>
</tr>
<tr>
<td>Pulper Power Used (kWh/dry metric ton)</td>
<td>53.1</td>
<td>62.5</td>
<td>64.9</td>
<td>64.7</td>
</tr>
<tr>
<td>Pulping Time (min.)</td>
<td>20.5</td>
<td>20.8</td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>Temperature Before Pulping Before Paper is Added (deg. C)</td>
<td>42.3</td>
<td>Not recorded</td>
<td>44.0</td>
<td>44.0</td>
</tr>
<tr>
<td>Temperature After Pulping (deg. C)</td>
<td>49.2</td>
<td>48.2</td>
<td>50.1</td>
<td>49.3</td>
</tr>
</tbody>
</table>

To start up the pilot plant, clean city water was used in the following locations and quantities:
- First batch pulping and dilution: 5,810 liters
- Filling dissolved air flotation (DAF) clarifier: 6,700 liters
- Initial clean pulp feed to DAF at 0.5% csc until drumwasher effluent is generated: up to 2,000 liters

Immediately after start-up, clarified water from the DAF clarifier was reused in subsequent pulping operations (i.e., batches), and for screening and cleaning dilution water.

Pulp samples were taken at nine locations that encompassed the pulper, screening feed, screening accepts (2 screens), cleaner feed, cleaner accepts, flotation feed, flotation accepts, and final pulp. Pulp samples were taken during the fourth and final batch of the trial, except that a pulper sample was taken for each batch. Pulp samples were taken for consistency measurement, handsheet preparation and for microstickies analysis. DAF clarifier effluent samples were taken (for our own testing) every half hour during the trial for COD analysis.

Three types of pulp samples were shipped to all participants for microstickies content analysis. The three types of pulp samples were: (1) Pulper sample from the trial, fourth batch, 13.45% consistency, PULPA; (2) Clean pulp consisting of only clean copy and envelope paper (no PSA) that was pulped in a small 50 L Hydropulper the day before the trial, 13.20% consistency, PULP B; and (3) Final deinked pulp from the trial, fourth batch, 23.31% consistency, PULP C.

2.0 METHODS FOR MICROSTICKIES ANALYSIS

2.1 UCM Deposition Test

Angeles Blanco and Carlos Negro, Complutense University of Madrid, Madrid 28040, Spain.

UCM deposition tester (2, 3) consists of a rotor joined to a shaft with an axial flow propeller in the bottom. The shaft is connected to an electric drill in such a way that the rotational speed can be controlled. The rotor presents holes in the top, in the bottom and in the side in such a way that the pulp suspension enters through the top and bottom holes and goes out through the side holes due to the centrifugal force. Therefore, if a surface is placed in front of the side holes, the sample hits this surface and the sticky material is deposited by the collision mechanism. In this system, there is a perpendicular flow to the rotor and also a parallel flow on the outside surface of the rotor.

This method can be used to study sticky deposits formed by impact of pulp suspension with surfaces in papermaking (internal depositions), as well as stickies deposits due to the flow of a pulp suspension (external depositions). The sticky material can be determined by extraction, surface weighing or by image analysis. We have used scanner and image analysis in this trial.

Internal depositions are produced by collision of the DCM on the internal surface of the collector due to the centrifugal forces generated by the deposition rotor. It simulates what happens in a turbulent flow with collisions (it is similar to the deposition in the impinging jet equipment).

External depositions are due to the transference of DCM to the surface due to the fluid dynamic of the system. It simulates what happens in a pipe without disturbances.

In this way two different deposition mechanisms are simu-
lated and the results do not necessarily go in parallel, it again depends on the type of DCM. With pitch, for example, the deposition by collision (in the internal surface) is much higher than by transference (in the external). In white pitch the opposite effect is observed.

When analyzing pulp samples, whitewater containing microstickies is collected by filtering through Britt jar as shown in Figure 1. Macrostickies and long fibers are retained in the jar.

2.2 Paprican’s Thermogravimetric Method

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Introduction

A new thermogravimetric (TG) technique for the determination of synthetic polymers in recycled pulp, paper, process water, and deposits has recently been reported (4). The technique is based on the observation that the pyrolysis in nitrogen of the major synthetic polymers such as EVA (ethyl vinyl acetate), PVA (polyvinyl acetate), PP (polypropylene), PS (polystyrene) and SBR (styrene-butadiene rubber) takes place at higher temperatures than those of natural polymers (i.e., cellulose, lignin and hemicelluloses) in wood fibers. With this technique, synthetic polymers are reported as a single class but each type of synthetic polymer included in the determination may have a wide range of natural tackiness. When the analysis is carried out on pulp samples, the synthetic polymer content pertains to particles greater than 0.22 µm but smaller than ~75 µm.

Experimental

The original plan was to prepare 5 pulp samples by mixing sticky pulp (A) and sticky-free pulp (B) in 25% increments. Though the 5 samples were prepared, we realized after analyzing the sticky pulp A, called sample (i) in the study, that its microstickies content was at the limit of detection of our TG method. Hence mixtures of A and B were not analyzed (i.e. samples ii, iii, iv).
Figure 2. Analytical scheme to determine microstickies content by thermogravimetry; optional analyses also done for this comparative study (i.e. Chloroform extract of whole pulp and fractionated pulp; macrostickies content of whole pulp).

The overall analytical scheme is shown in Figure 2. Though Paprican’s thermogravimetric method aims to quantify the content of micro particles of synthetic polymers of which stickies belong, optional analyses were done for this comparative study. We also made a very rough estimate of macrostickies content (weight, count, area, diameter) in the whole pulp B (sample v) using only 5 g samples instead of the usual 25 g samples. Macrostickies were isolated with a Pulmac 150 µm (0.006”) slotted screen and then deposited on a black filter paper. The weight of these macrostickies was also determined. The sample was not hot pressed prior to scanning and image analysis. Chloroform extract in whole pulps A and B (samples i and v) were also determined using a Soxtec extractor (Soxtec System HT).

For TG and solvent extraction of microelements in the two pulp samples (see Figure 2), pulps were first diluted to 0.5% with deionized water and then fractionated using a 1 L DDJ equipped with a 200-mesh screen. This step removed long fibers and stickies greater than about 75 µm from the samples. An aliquot of the pulp accepts (50 mL) was filtered through a 0.22 µm Millipore membrane filter and the film of filtered solids was then gently peeled from the membrane for TG analysis.

Another aliquot was filtered on a Whatman filter #42. The filtrate was recirculated until a clear liquid was obtained. Retained solids (suspended and colloidal) were dried and then extracted with chloroform extraction using a Soxtec system.

A detailed description of the procedure has been presented elsewhere (4). Briefly, the method relies on the comparison of pyrograms ran in nitrogen of pulp sample containing synthetic polymers, with that of a reference sample free of polymers. In this study, the reference sample was sample B after it had been processed in a similar way to Sample A (i.e. after pulp fractionation in the DDJ followed by micro filtration of accept sample for TG analysis in a nitrogen atmosphere).

2.3 Rotating-Wire-Mesh-Analyzer

Axel Hamann, Institute of Chemical Engineering and Macromolecular Science, Darmstadt University of Technology, Darmstadt, Germany.

A 5 cm X 45 cm piece of polyester-wire is cleaned with deionized water, dried overnight at 105°C and weighed. 800 milliliters of the sample (fractionated or whole stock) is filled into the sample trough, stirred (300 min⁻¹) and heated (45°C if not indicated otherwise). Even when the whole stock is used without fractionation only stickies smaller than 150 µm appear to deposit on the wire.

The wire mesh is attached to the rotating metal-frame. The wheel, which dips by 1/3 into the sample, is put to
rotation (15 min⁻¹), as shown in Figure 3. The drying hood is operated by a hair-dryer, which is set to a drying-temperature of 90°C. After 2 hours exposure the wire is detatched and rinsed with deionized water, dried overnight (105°C) and weighed again.

2.4 IPST Method


The IPST detection method is based on the assumption that dispersed, colloidal and dissolved solids greater than a molecular weight of 5000 Dalton and smaller than 25 microns (Whatman #4) in process streams of secondary fiber mills are mainly microstickies. The concentration of microstickies can be determined by first filtering a sample through a Whatman #4 filter paper and measuring its total organic carbon (TOC) content of the filtrate. The filtrate is then ultra-filtered through a membrane that only allows passage of compounds of a molecular weight (MW) less than 5,000 Dalton. The TOC of this low-MW permeate is then measured. The difference in TOC is reported as microstickies in parts per million (5).

2.5 Chemical Oxygen Demand (COD) Method

Karen Scallon and Carl Houtman, USDA Forest Products Laboratory, Madison, WI.

Three pulp samples (Pulp A, Pulp B and Pulp C) were analyzed for microstickies content using chemical oxygen demand (COD) analysis.

In a first approach, six individual samples at 1% csc. were prepared. A 500 mL volume of each sample was filtered through a Britt jar equipped with a 150 micron (0.006 in) filter. The Britt jar filtrate was then separated and either filtered with a Whatman 42 filter or centrifuged, and the filtrate/supernate was analyzed in triplicate (duplicate for some) for COD according to Standard Methods, 5220 D Closed Reflux, Colorimetric Method.

In a second approach, pulp samples at their full consistency were used. Each individual pulp sample was squeezed manually, and the squeezeate was collected, filtered in a Britt jar, diluted with pilot plant water (1:1 and/or 1:4), centrifuged at 4,000 rpm for 30 minutes, and was analyzed in triplicate for COD as before.

2.6 PMV Micro Stickies Method

Hans-Joachim Putz, Paper Technology and Mechanical Process Engineering, Darmstadt University of Technology, Darmstadt, Germany.

The microstickies method of PMV is based on the INGEDE macrostickies method. Whereas in the macrostickies method the reject of a laboratory screening procedure of
50 g b.d. pulp on a 100 µm slotted plate is evaluated, the PMV microstickies method analyzes the accept of the laboratory screening. Instead of 10 min in macrosticky determination, for microstickies only 5 min screening time is used. The total accept volume of this 5 min screening will be collected (about 50 litre, because of 101/min water flow during screening). This water volume contains also almost all fibres. Therefore, samples to be prepared from this highly diluted accept volume, have to avoid the overlapping of stickies with fibres. The microstickies visualization method produces 5-10 samples of the homogenized accept sample, which will be dewatered in an identical way as in the macrosticky method. The solid content on the filter is limited to 200 mg for each filter sample to avoid overlapping of stickies with fibres. Visualization and image analysis is performed in the same way as in the macrosticky method and also the lower size limit of the sticky analysis is identical (100 µm). The average is calculated from the result of 5-10 samples and related to the total collected water volume which can afterward be related to the sample mass used for the screening (50 g b.d.). Therefore, the microstickies content can be expressed in mm²/kg pulp also.

By definition (of the German ZELLCHEMING) microstickies are those tacky particles from recycled fibre stock which are passing a 100 µm slotted screening plate. With the PMV microsticky method only a part of all microstickies are detected, those which have at least 100 µm equivalent circle diameter. The microsticky particle smaller than 100 µm equivalent circle diameter are still not detected with this method. Nevertheless, a shift from more macrosticky particles to more microsticky particles can be observed by the evaluation of complete recovered paper processing lines.

2.7 SCA Solvent Extraction Method


Our method measures total stickies and macrostickies by solvent extraction and microstickies are calculated by difference. First to determine total stickies, one part of the pulp sample is dewatered in a Buchner funnel into a cake and dried. The dried cake is extracted using dichloromethane (DCM). The extractives content represents the total stickies amount. The extract was stored for further analysis using FTIR.

Another part of the pulp sample is processed through Pulmac 0.10 mm slotted screen. The screening residue is dried, weighed and extracted using DCM. The extractive content represents macrostickies content of the pulp. The extract was stored for further analysis using FTIR.

All extracts were analyzed by FTIR to establish the composition of the extracts, as described in our earlier article (6). The results are given as: synthetic polymers; wood extractives; and unexplained (6).

2.8 Polyethylene Film Method

R.A. Venditti, K. Copeland and H-M Chang, North Carolina State University, Raleigh NC 27695-2005

The test device consisted of a four-place gang stirrer with 3-inch marine-style propellers operating at 600 RPM (see Figure 4). Pulp slurries (500 ml at 1% consistency and 65 °C) were agitated in four one-liter glass beakers positioned on hot plates. The pH of the slurries and tempera-
ture were recorded. Five pieces of LDPE film (Associated Bag Company) were cut into 2 X 5 cm pieces and the total weight of the five pieces was determined for each beaker. Five film pieces were added to each beaker with the slurry and the contents agitated for one hour. The pieces were then taken out of the slurry, gently dipped into a 4000 mL beaker of cold tap water to remove fibers and solidify the stickies. All of the pieces of film were air dried overnight and then weighed. The mass of the microstickies adsorbed was determined by subtracting the initial mass of the film pieces from the final mass after the test. The test is based on a procedure outlined by Elsby (7).

2.9 Other Methods

There are many other methods used by researchers to quantify microstickies. These include for example, deposition of stickies on HDPE (8, 9), or on microfoam (10) or on paper machine wire (11, 12, 13). Two other methods simulates deposition of microstickies on paper machine dryers (13, 14). Proposed TAPPI method for measuring microstickies in process water requires 14 days sample storage in refrigerator (15).

3.0 SUMMARY

Pulp samples containing macrostickies and microstickies plus a stickie-free pulp were analyzed for microstickies by various methods. Sample preparation details and a brief description of the methods used are provided here. Results and discussion will form Part II of the article that will appear in the next issue of Progress in Paper Recycling.

4.0 LITERATURE CITED


