RECYCLING

A sensor for microstickies

Jere T. Koskinen, Dong-Jin Sung, Feroz Kazi, Ji Yang, and Sujit Banerjee

SUMMARY
Because stickies can cause major operational problems, their detection and control has long been an industry priority. While several methods are available for determining macrostickies – adhesives caught in a 0.006-in. screen – a rapid, consistent procedure for microstickie analysis is unavailable. We propos that the high molecular weight (MW >3000 dalton colloidal) material in process streams of secondary fiber mills is mainly microstickies. This material can be determined by first filtering a sample and measuring its total organic carbon (TOC) content. The filtrate is then ultrafiltered through a membrane that only allows passage of compounds of MW< 3000 D. The TOC of this low-MW permeate is then obtained. The difference in TOC represents high-MW (>3000 D) material, which corresponds to microstickies. A sensor that makes the entire measurement in 8 min has been built for online use. We validated the technique by comparison with two independent techniques using lab-derived samples as well as those collected from several locations at six mills.

Application statement: A method for sensing microstickies can alert mills to high incoming microstickie loads, help test strategies to remove microstickies, and serve as a quality control tool.

The detection and control of stickies has long been an industry priority [1]. Stickies are classified as microstickies if they pass through a 0.006-in. screen; larger particles are termed macrostickies. Several methods for determining macrostickies are available [2]. Typically, the contaminants are isolated through screening, transferred to a sheet, and imaged [2-9]. Methods reported for quantifying microstickies include the Berol/polyethylene film method [10], the polyethylene bottle technique [11], the Doshi procedure [12], the Pira papermachine wire test [13], and the PAPRICAN/Hobart mixer method [14]. The turnaround time of all these methods is too long for process control applications.

The adhesives comprising stickies are polymeric and are, therefore, of high molecular weight (MW). In a secondary fiber facility their concentration should be highest at the pulper and should then fall progressively as they are removed through screening, cleaning, flotation, and other operations. The other high-MW chemicals likely to be present at the repulper are residual process polymers. This study is based on the hypothesis that microstickies constitute the majority of the colloidal high-MW material in the front end of the mill. In this paper we show that isolating and measuring this high-MW (operationally defined as >3000 D) fraction leads to a microstickie sensor that can be deployed online.

EXPERIMENTAL

The high-MW material was determined as follows. The sample was filtered through Whatman #4 paper and the total organic carbon (TOC) of the filtrate determined with an Ionics Model 1555B Carbon Analyzer (Ionics Inc., Watertown, Massachusetts, USA). The filtrate was then ultrafiltered through a membrane (Amicon membranes obtained from Millipore, Inc.) that allowed pas-

sage of compounds of MW< 3000 D. The TOC of this low-MW permeate was determined. The difference in TOC represents high-MW (>3000 D) material.

To measure the tack of the components in a process stream, we first gently boiling down 700 ml of the filtered sample to 5 mL. A 1-mL aliquot of this concentrate was painted on a metal coupon, which was dried overnight at 25 ^{o}C-40^{o}C. The coupon was warmed in water, the water was shaken off, and the tack measured with a ProbeTack PT-500 tack tester (ChemInstruments, Fairfield, Ohio, USA) at different temperatures as the coupon cooled. Water was used to warm the coupon, since cracks occasionally developed on the surface of film heated in the air. We interpolated the tack results to 40^{o}C to enable comparison across samples.

The model stickie used was BF Goodrich Carbotac 26171 (48.9% total solids).

RESULTS AND DISCUSSION

We validated the method in the laboratory against a technique proposed by Robert de Jong [15] where macrostickies are first screened out and the screenate maintained at 4^{o}C for two weeks. The microstickies agglomerate over this period and are screened and weighed. A minor modification was made in that the microstickies were agglomerated by acid-shocking rather than through screening, which eliminated the need for a holding period. Four Carbotac suspensions were acid-shocked with 96% H_2SO_4 (6 mL/100 mL) to agglomerate the latex, settled overnight, and then filtered. We weighed the recovered solids and measured TOC before and after agglomeration. The difference in TOC should correspond to the quantity of solids agglomerated. The results in **Table I** demonstrate an acceptable comparison between the two methods.

We then repeated the measurements in the presence of fiber. Five sheets of Avery return labels (No. 5267) were pulped with 750 g of water in a Waring blender at 50^{o}C for 5 min. The slurry was diluted to 2 gal and screened through a 100-mesh screen. Three aliquots of the screened sample were subsequently acid-shocked as described above, with TOC being determined before and after acid-shocking. The results, presented in **Table II**, translate to an average recovery of 66%. The variability on TOC is small; that for gravimetry is much higher because of the uncertainty involved when weighing small quantities of solids. Fiber debris was collected with the stickies in the gravimetric technique, which also would bias the results high. We conclude that the comparison between the two methods is adequate.

In order to demonstrate that the high-MW dissolved components caught on the membrane were, indeed, stickies, samples from various process streams in a newsprint mill were collected and filtered to remove particulates. The filtrate (20 mL) was then ultrafiltered, and water (10 mL) was flushed through the membrane to remove inorganic salts. We then washed the membrane surface with acetone (5 mL) to remove the trapped material. The acetone was dried at room temperature to 0.5 mL, transferred to a slide, taken to dryness, and analyzed by infrared reflectance (IR) using a microscope attachment. No meaningful spectra were obtained when a water sample was processed as a control. The results from the mill samples show that stickies constitute a significant fraction of the material caught by the membrane (**Table III**). Of the other components trapped, the inorganics would not appear in our TOC measurement, and the surfactants, defoamers and extractives are likely to be of low molecular weight. Hence, the high-MW material isolated is predominantly stickies. We obtained similar results from a recycle linerboard mill (**Table IV**).

We compared the high-MW TOC with the tack of the components in samples collected from various process streams in six mills for a final validation of our method. We use tack, because it is a *direct* measure of all adhesive material in the sample. The results, illustrated in the

left panel of **Fig. 1**, demonstrate a relationship between tack and high-MW TOC. The curve flattens out at the top, probably because the coupon has more than just thin-layer coverage at this point, and the internal bond strength of the residue film contributes to the tack measurement. The intercept is near zero, as would be expected. Only broad generalities can be drawn from a plot of total TOC *vs.* tack as shown in the right panel of Fig. 1. For example, we can say that the samples from Mill 1 lie in the right upper quadrant, while those from Mill 4 are located in the left lower quadrant of the plot, but further interpretation cannot be supported. The variability in low-MW TOC is evidently high enough to obscure the contribution of stickies to the total TOC. The relationship with high-MW TOC in Fig. 1 is compelling because it is drawn from several sampling points across different types of mills. Clearly, high-MW TOC tracks the tack in the sample. The scatter in Fig. 1 (left panel) probably derives from the tack measurements, whose uncertainty approaches 30%. The uncertainty in the high-MW TOC values is less than 10%.

We compared the performance of the microstickies sensor to the more traditional Pulmac shive analyzer using samples taken from various points (repulper to thick stock) at a newsprint mill. Note from the results in **Fig. 2** that the Pulmac values drop rapidly after the coarse screen accepts as the macrostickies are removed, whereas the microstickies drop more gradually. The two sets of data are complementary; the Pulmac measures macrostickies, whereas the high-MW method determines microstickies. There is a weak relationship between micro- and macrostickies beyond the feed to fine screens (**Fig. 3**). Pulmac data are typically associated with high uncertainty, and the scatter in Fig. 3 almost certainly arises from variability in the Pulmac values. Since the population of one size-fraction should relate to that of another, a relationship of the type seen in Fig. 3 is expected.

The high-MW method [16] is easily automated. We anticipate that the method will have at least four potential applications. One is in process control where a high microstickies count could serve as an early warning for developing problems. We have seen a major difference in repulper microstickies in one mill, which means that we have the ability to flag a bad batch of wastepaper, adjust chemical use, and make other process changes to mitigate its effect. A second application lies in testing strategies for evaluating wastepaper batches that enter the mills. A third application focuses on removing microstickies from various process streams. This has been difficult in the absence of an accurate measurement technique. Finally, the sensor can serve as a quality control device. The Pulmac analyzer presently fills this role, and the microstickies sensor would complement the Pulmac instrument. However, the Pulmac device characterizes material that would be screened out anyway in most cases, whereas the microstickies sensor represents the stickies that are able to traverse the screens and are more likely to enter the system. As such, high-MW TOC may be a more appropriate measure of quality than Pulmac counts.

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Koskinen, Sung, Kazi, Yang, and Banerjee are with the Institute of Paper Science and Technology, 500 10th Street, NW, Atlanta, GA 30318, USA. Email Banerjee at s.banerjee@ipst.edu.

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Table 1. Recovery of Carbotac by TOC.				
initial solids (g)[1]		**Agglomerated solids (g)**	**remaining solids (g)**	
added	**by TOC**		**by difference**	**by TOC[2]**
0.753	0.736	0.712	0.041	0.025
0.723	0.719	0.703	0.020	0.032
1.497	1.46	1.473	0.024	0.036
1.489	1.45	1.456	0.033	0.035
[1]in 100 ml for the first two entries and in 200 ml for the next two; [2]TOC was multiplied by 1.8 since carbon constitutes approximately 55% of the acrylate.				

Table 2. Mass balance for the pulped return labels.					
volume (ml)	**TOC (ppm) before acid shock**	**TOC (ppm) after acid shock**	**ΔTOC as grams solids[1]**	**Weighed solids recovered (g)**	**recovery (%)**
200.5	185	70	0.0415	0.065	63.8
201.7	185	70	0.0418	0.051	81.9
199.6	185	70	0.0413	0.078	52.9
[1]TOC was multiplied by 1.8 since carbon constitutes 55 % of the acrylate latex.					

Table 3. FTIR-identified contaminants at a newsprint mill.		
alkaline loop	feed to coarse screen	PVAC[1], extractives, surfactant
	feed to fine screen	PVAC, phthalate, extractive, defoamer
	feed to alkaline flotation cell	PVAC, clay, surfactant, SBR[2], acrylate
	feed to alkaline DNT washers	PVAC, clay, SBR, defoamer
	alkaline press accepts	clay, PVAC
acid loop	feed to flotation cell	PVAC, defoamer, surfactant
[1]polyvinyl acetate; [2]styrene butadiene rubber		

Table 4. FTIR-identified contaminants at a linerboard mill.	
thickener accepts	extractives, acrylate
fine screens feed	extractives, starch, groundwood
fine screens accepts	retention aid, clarifier polymer, acrylate
fine screens rejects	PVAC[1], primary clarifier polymer, acrylate, starch, polyvinyl alcohol
reverse cleaner feed	retention aid, clarifier polymer, acrylate
reverse cleaner accepts	groundwood, PVAC
reverse cleaner rejects	PVAC
[1]polyvinyl acetate	

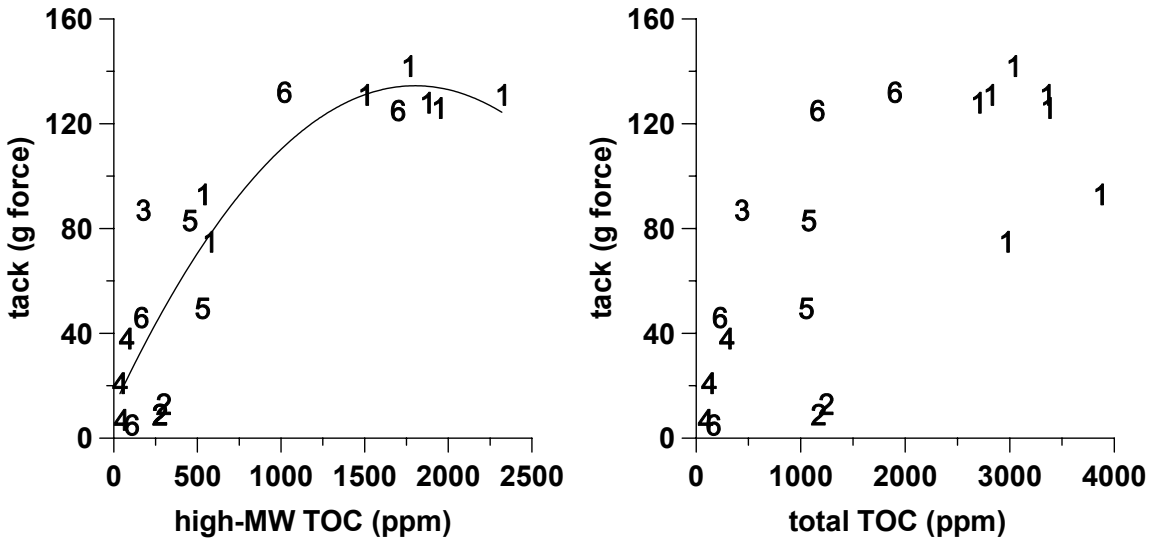

Figure 1: Relationship between tack and high-MW TOC (left) and total TOC (right). Samples were taken from the following types of mills: linerboard/medium (1), linerboard (2), newsprint (3, 5), tissue (4), specialty paper (6).

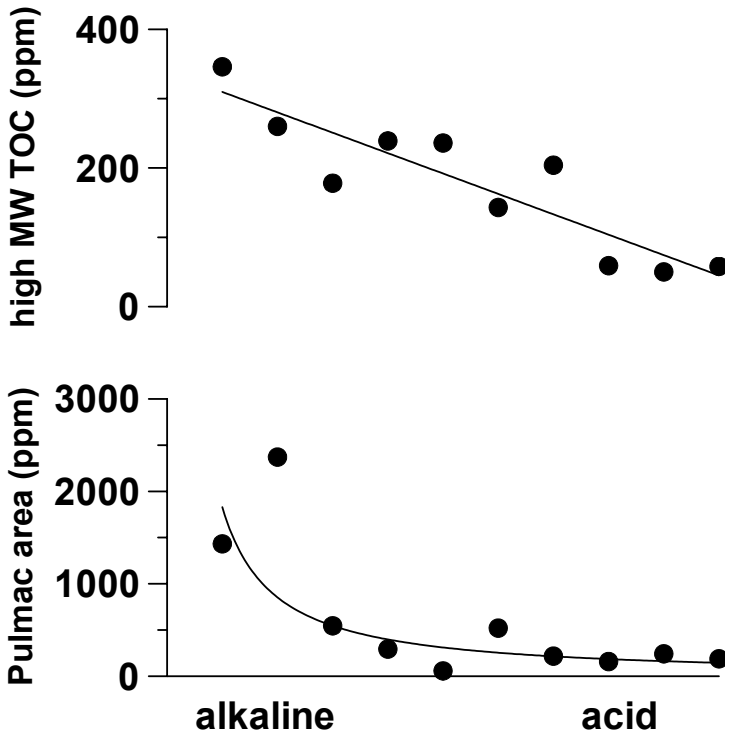

Figure 2: Relationship between micro- and macrostickies across a newsprint mill.

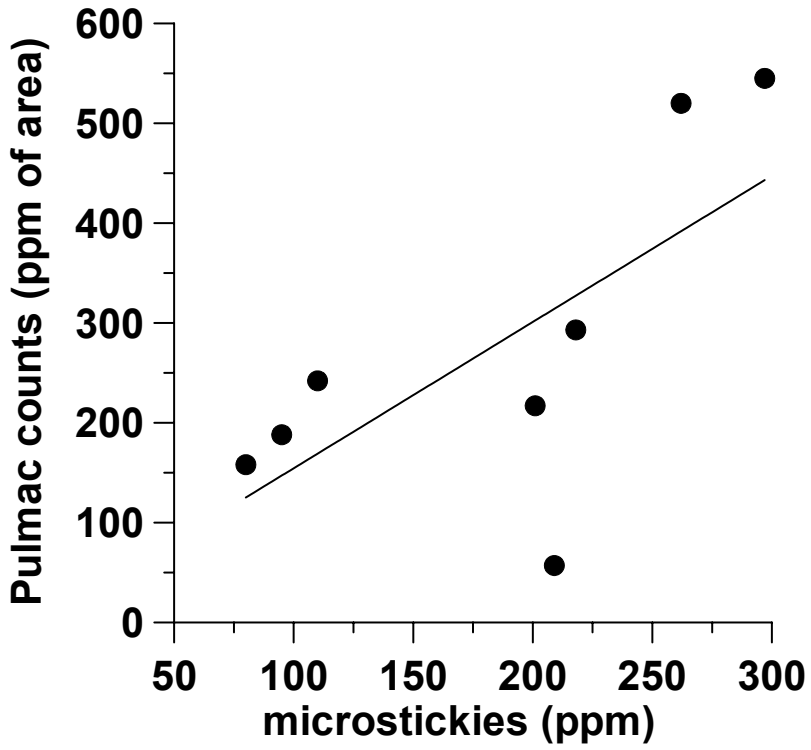

Figure 3: Relationship between micro- and macrostickies at locations beyond the coarse screens.