Fiber to water distribution of stickies

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ABSTRACT

A Britt jar separation technique can determine the pulp and water distribution of polyvinyl acetate and styrene butadiene rubber. The affinity of polyvinyl acetate to fiber increases with increasing kappa number. Stickie association to fiber increases at pH approximately 4. Microparticle retention aids direct the stickie from the water to the mat phase by associating either the stickie or the stickie-bound fines to the mat. Temperature greatly affects the breakup of two hot melts applied to linerboard. An important finding was that fibers inhibit stickie reagglomeration.

Application:

Fiber flocs can trap stickie particles, preventing interaction with other stickie particles. Polymer reagglomeration without fiber could be a mechanism for stickie reagglomeration in white water.

THE PRESENCE OF STICKIES IN recycled fiber can cause runnability problems, lead to hole and spot formation, and decrease felt lifetime. The industry has principally focused on practical aspects of stickie prevention and removal. Examples are more frequent pulper cleaning and optimization of screens and cleaner efficiency *(1)*. Detackifiers *(2)*, talc *(3)*, synthetic fibers *(4)*, retention aids *(5)*, and various chemicals *(6, 7)* have had some success in reducing the effects of stickies. There is no universal set of solutions, however.

Our approach to the problem of stickies is mechanistic. It seeks to understand the chemistry of the interactions among fiber, water, and stickie. Then we apply the principles developed toward stickies' control. In this paper, we describe laboratory procedures to study the distribution of model stickies between fiber and water and identify some governing factors.

TECHNIQUE FOR MEASURING FIBER TO WATER DISTRIBUTION

Consider the relationships in **Table I**. In the table, the difference in fiber mass is $W_3 - W_5$, and the difference in water mass is $W_4 - W_6$. The following hold true:

$$M_r = m_w(W_3 - W_5)/m_f(W_3 - W_6) \quad (1)$$

where

M_r = mass ratio
m_w = mass of water
m_f = mass of fiber.

We agitated a slurry of pulp in water containing a mass of fiber, W_1, in a Britt jar and slowly added stickie, W_2, with a syringe in a small volume of methanol. We agitated the mixture at 200 rpm for 15 min, drained the water through a 200-mesh screen, and collected it. Agitation at 400 rpm gave similar results. Drying and weighing of the solids retained on the 200-mesh screen with a measured aliquot of the filtrate gave bone dry weights of W_3 for the mat and W_4 for the water. We performed a companion experiment with an identical mass of fiber, W_1, without the added stickie. The dried materials in the mat and water for this control experiment weigh W_5 and W_6, respectively. If the stickie does not change the quantity of fines transferred to the filtrate, then the definition of mass ratio, M_r, is the fiber to water distribution coefficient of the stickie. This distribution coefficient may represent a steady-state condition rather than true thermodynamic equilibrium.

The solids in the water phase for the blank, W_6, are fiber fines. For M_r to represent the distribution coefficient, the same mass of fiber fines must transfer to the water layer from both the sample and the blank. Here the following equation is true:

$$M_r = (\text{stickie})_{mat}/(\text{stickie})_{water} \quad (2)$$

where $(\text{stickie})_{mat}$ and $(\text{stickie})_{water}$ are stickie concentrations in the mat and water, respectively.

As we will discuss later, there are instances where this assumption fails. Then M_r does not represent the distribution coefficient. For these cases, the following equation holds:

$$M_r = [(\text{stickie})_{mat} + \Delta\text{fiber}_{mat}]/[(\text{stickie})_{mat} + \Delta\ \text{fiber}_{water}] \quad (3)$$

where

Δfiber= the stickie–induced difference in fiber mass.

Equation 2 reflects the true mat to water stickie distribution. Equation 3 provides an approximate measure of the changes in distribution under different conditions. Either equation allows us to relate qualitatively the trends in M_r to changes in stickie behavior. If the stickie helps retain fines that would otherwise transfer to the filtrate, then $W_4 < W_6$, and M_r is negative. A low M_r therefore indicates a weak stickie to fiber interaction; a high M_r suggests a strong attraction; and a negative M_r represents a situation where the stickie helps retain fines in the mat.

To compare results among different experiments, it is necessary to use a constant quantity of fiber. We accomplished this for never-dried

	SOLIDS IN		SOLIDS OUT	
	Fiber	Stickie	Fiber	Water
Sample	W_1	W_2	W_3	W_4
Blank	W_1	0	W_5	W_6

I. Fiber to water distribution of stickies

fiber by preparing wet handsheets in a Formette Dynamique and cutting 0.625-in. cross direction strips for each experiment. To determine uniformity, we cut 10 strips in alternating segments from a sheet containing 20 strips. The weight of these averaged to 0.585 g (σ = 0.004 g). This translates to a standard deviation of 0.7%.

Table II presents M_r values for polyvinyl acetate (PVAc) of 90,000 molecular weight in a water and a kappa no. 23 pulp system. The difference in weight in the "solids out" columns, i.e., 0.019 g for the fiber and 0.0697 g for the water, leads to a M_r value of 48, after normalizing for the mass of fiber (1.6898 g) and the volume of water present (300 mL). The difference in weight between the stickie added and recovered (0.012 g) is probably due to a small difference in weight between the fiber used in the sample and blank. If this uncertainty is assigned to the stickie in water, then M_r = 42. If associated with the mat, M_r = 77. This uncertainty range is typical of M_r values determined by this approach. We made all M_r measurements reported in this paper at least in duplicate.

The advantage of the technique is the easy measurement of changes in the fiber to water distribution. The principal disadvantage is inference of the mass of the stickie by difference rather than through direct determination. Since stickie addition involves small particles, our M_r values relate to the white water loop, where the stickies are likely present as small particles—having successfully navigated the screening and cleaning system.

DEPENDENCE OF M_r ON KAPPA NUMBER

Figure 1 illustrates the dependence of M_r on kappa number for PVAc added as a methanol solution and styrene butadiene rubber (SBR) added as a latex emulsion. The PVAc in methanol falls out of solution as particles of approximately 1–5 μm. The M_r to kappa number relationship is clearly linear for PVAc. This suggests that the pulp is progressively more attractive to the hydrophobic polymer as its own hydrophobicity increases. This follows the pattern established for lower molecular weight nonpolymeric species where distribution coefficients are linear with kappa number *(8–10)*. The situation for SBR is more difficult to interpret. This is because the substrate is a latex. Surfactant was therefore already present in the system. Since surfactants stabilize aqueous phase suspensions, one would expect lower M_r values. Surfactant may also form associative thickener barriers over hydrophobic regions of the fiber and mask the effect of the lignin. The practical implication of these findings is that in the absence of surfactant, stickies will associate more strongly to brown pulp than to bleached pulp.

These results potentially explain the behavior of pitch in a virgin mill processing a mixture of sulfite pulp and TMP *(11)*. Pitch problems occur without TMP but disappear when sulfite pulp contains TMP. Since one would expect pitch to parallel the behavior of PVAc in its attraction to lignin, TMP should decrease pitch problems as observed.

EFFECT OF RETENTION SYSTEMS ON M_r

Since retention systems reduce the fines fraction, their effect on M_r should reflect the amount of stickies associated with the fines. We used the following retention system: anionic colloidal silica (0.06 g), cationic starch (0.06 g), alum (0.03 g), fiber (3 g), resin (0.15 g), and water (600 mL). The system is similar to microparticulate retention systems described by Doiron *(4)*. We used three types of PVAc. For each, we did parallel experiments with and without the cationic starch. The results in **Table III** illustrate the dramatic effect of the retention aid on M_r. The variability of the retention aid measurements is high because very little material remained in the filtrate, leading to a high uncertainty in weight.

There are two possible ways to remove the stickies from the aqueous phase. In one case, the retention aid can directly attach them to the pulp. If the stickie already associates with the fines, then the retention aid will collect the fines with the bound stickies.

DEPENDENCE OF M_r ON FREENESS

Table IV shows that the mass ratio, M_r, varies inversely with freeness for bleached kraft pulp. Three possible explanations were considered:

- Most of the stickie associates with the fines retained to a greater extent in the mat.
- The decreased mat porosity filters out both stickie and fines that do not necessarily associate.
- The stickie associates strongly with the fibrils in the refined fibers.

The "fines in filtrate" column in Table IV measures the fines in the filtrate without the stickie—it represents W_6 in Table I. The "apparent stickie weight in filtrate" represents $W_4 - W_6$

	SOLIDS IN, g			SOLIDS OUT, g		
	Fiber	PVAc	Total	Fiber	Water	Total
Sample	1.7416	0.1	1.8416	1.7088	0.1062	1.8150
Blank	1.7416	0	1.7416	1.6898	0.0365	1.7263
PVAc weight	...	0.1	0.1	0.019	0.0697	0.0887

II.* M_r *values of PVAc

in Table I. The fourth column is the apparent stickie to fines mass ratio in the filtrate. The "apparent stickie weight" would correspond to the true stickie weight, if the mass of fines transferred to the filtrate were identical for the two experiments with and without the stickie. The relative constancy of this column suggests that most of the PVAc could associate with fines. Phase contrast microscopy of fresh filtrate showing the presence of both free and fines-associated PVAc negated this possibility. Stickie to fines association did increase with time. This is not germane to the M_r to freeness relationship that depends on the stickie distribution during filtration. While we are unable to distinguish between the final two mechanisms above, we have noted through phase contrast microscopy *(12)* that stickies preferentially attach to fibrils over fiber *(13)*. On this basis, the refined pulp should have a greater affinity for the stickie. This could account for the inverse M_r to freeness relationship.

Table IV also includes results from related experiments with SBR latex emulsion with alum added. The table omits weights of stickies and fines, since the alum will partition differently into the filtrate in the presence of the SBR. These data also show the inverse M_r to freeness relationship seen for PVAc.

Resin: 2873 flexible cross-linking PVAc latex for PSA (T_g = -36)
Without starch: M_r = 62; with starch: M_r = 1630 (355 - 3400)

Resin: 1105 rigid PVAc latex for paper coating (T_g = 29)
Without starch: M_r = 66; with starch: M_r = 690 (235 - 1060)

Resin: 9003-20-7 PVAc homopolymer (T_g = 29)
Without starch: M_r = 33; with starch: M_r = 380 (210 - 480)

III. Effect of retention systems on M_r

Freeness, m L CSF	Fines in filtrate,g	Apparent stickie weight in filtrate, g	Apparent stickie/fines ratio	M_r
PVAc (3 g PVAc, fiber, 600 mL water)				
641	0.0854	0.2093	2.45	27
575	0.0403	0.1447	3.59	151
441	0.0409	0.1142	2.79	131
335	0.0264	0.0901	3.45	486
200	0.0202	0.0612	3.03	779
SBR (0.3 g SBR, 3 g fiber (kappa no. 37 unbleached softwood kraft), 600 mL water, 1.66% alum)				
732				1060
588				1730
134				4310

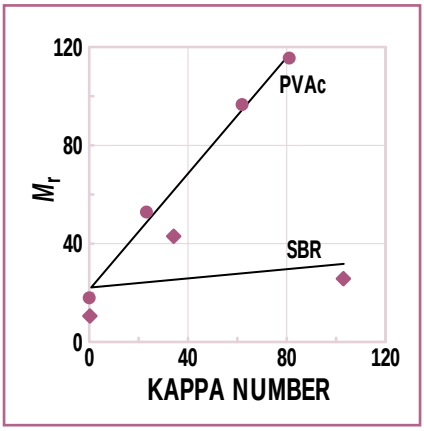
IV. Dependence of M_r ***on freeness***

DEPENDENCE OF M_r ON pH

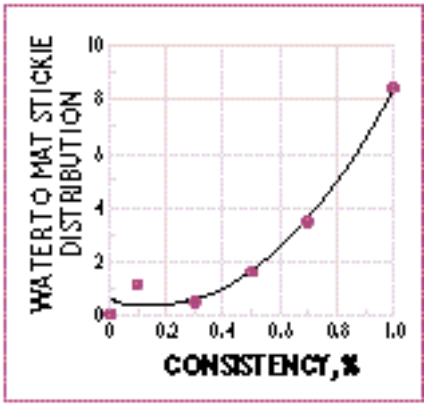
Table V shows that M_r increases for the unbleached pulp at low pH. The probable reason is suppression of the ionization of lignin acid groups *(14, 15),* making the mat more hydrophobic and therefore more receptive to PVAc. This argument is consistent with a much smaller effect observed for the bleached pulp.

DEPENDENCE OF M_r ON TEMPERATURE

We conducted two types of experiments. First, we added PVAc in methanol to the slurry and made Britt jar measurements as before. Second, we softened two hot melts—softening temperatures of 168°F and 197°F—in an oven and then poured them on linerboard. This material was too rigid to be broken in a Britt jar. We therefore repulped it in a British disintegrator (50,000 revolutions) or a Waring blender (5 min). We conducted companion control experiments without added stickie and compared the dried mass in the filtrate from the two experiments to obtain the stickie transferred to the filtrate. **Table VI** reports the results



1. Variation of M_r with kappa number for PVAc and SBR



2. Dependence of the water to mat distribution of PVAc on consistency

of the duplicate measurements. In this table, a negative value indicates that the stickie in the mat holds the fines. Except as noted otherwise, the kappa number of the pulp was 81.

PVAc distributions show no significant temperature dependence, especially for the bleached pulp. The stickie predominantly proportions into the aqueous phase. Since a temperature increase should weaken stickie to fiber interactions, any additional temperature–induced transfer to the aqueous phase is probably undetectable with our technique. There is a definite temperature effect on the two hot melts. For the hot melts at 80°F, the weight percentage of added stickie in the filtrate is negative, indicating more fiber retention in the experiment with the hot melt than in the control without it. This is because repulping does not dissociate the hot melt from the fiber. Heating the slurry softens the hot melt and allows the fiber to debond and release fines into the filtrate. In addition, components of the hot melt soften and disperse into the aqueous phase.

Our PVAc could not trap fiber because of its small particle size. If we had preapplied it to the fiber like the hot melt, we would have expected to see much higher fiber retention. In other words, we attribute differences for stickie transferred to the filtrate to differences in the mode of application between the two stickies and not to any physicochemical differences between them.

DEPENDENCE OF M_r ON CONSISTENCY

When adding PVAc to water without fiber, it quickly aggregates and no PVAc transfers to the filtrate. As **Fig. 2** shows, addition of bleached fiber to the system increases the amount of PVAc entering the filtrate. The table shows the data as water to mat distribution ratios instead of M_r to accommodate the zero solids point that would be infinity in an M_r plot. We therefore have the curious situation where the fiber inhibits agglomeration. There is free stickie in the filtrate despite its propensity to quickly agglomerate without fiber. One can rationalize the phenomenon using kinetic vs. thermodynamic control—a common mechanism in organic chemistry.

Consider a drop of PVAc in methanol contacting water. The methanol dissolves, and the PVAc falls out of solution in particulate form. If a PVAc particle contacts a fiber, it is entrained in the fiber floc or is otherwise trapped by the fiber. Since the surface area of fiber in the system is much larger than that of stickie, stickie to stickie collisions are infrequent. The weaker PVAc to fiber attachment therefore forms instead of the thermodynamically more stable PVAc to PVAc association. This is because a PVAc particle collides with fiber much more often than it does with another PVAc particle. The fiber therefore protects the captured PVAc from an encounter with another PVAc particle and prevents agglomeration. Consider also the stickie to fiber floc network. If agitation disturbs the network, the free stickie particle enters the aqueous phase. Since the probability of a stickie to stickie collision is very much lower than that of a stickie to fiber encounter, fiber recaptures it.

The stickies will ultimately agglomerate into a separate phase as they do without fiber, since this is a thermodynamically more stable situation. The preferred kinetics of the PVAc with floc collisions prevents this from occurring during our measurements. The Fig. 2 relationship steadily increases beyond a consistency of approximately 0.5. This is probably because of elimination of stickie to stickie collisions. Fiber captures most stickie particles. While the addition of stickies via a methanol carrier has no practical relevance, the finding that fibers can interrupt stickie agglomeration will apply to situations where stickies are present as small particles. For example, stickie reagglomeration should be highest in low consistency regions such as a white water system.

DEPENDENCE OF M_r ON THE METHOD OF STICKIE APPLICATION

In the above experiments, we

KEYWORDS
Contraries, deinked stock, fibers, polymers, reclaimed fibers, recycling, stickies, surface properties, water repellence, water.

pH	M_r kappa no. = 0	kappa no. = 81
4	156	410
7	131	96
9	113	149

V. Dependence of M_r on pH

	80 °F	120 °F	140 °F
PVAc (kappa no. = 0)	93	81	86
PVAc	85	70	93
Hot melt A (British)	-26	-8	19
Hot melt A (Waring)	-52	7	...
Hot melt B (British)	-17	7	14
Hot melt B (Waring)	-18	33	28

VI. Percentage of added stickie transferred to filtrate

Treated pulp, %	PVAc in solids, g	PVAc in water, g	Solids in water/solids on Britt jar screen
0	0	0.00	0.02
50	0.20	0.038	0.03
80	0.40	0.010	0.02
100	0.64	0.035	0.02

VII. Strength of stickie to fiber attraction

applied the stickie to the pulp slurry in a methanol carrier. To determine the strength of the stickie to fiber attraction, we conducted experiments saturating pulp with 19% by weight of PVAc in methanol, drying, mixing with untreated pulp, and running through our Britt jar procedure. **Table VII** shows the results. Note that the amount of PVAc in water does not change appreciably as the blends change. This suggests that the PVAc in the pulp does not readily transfer to water under our experimental conditions. The solids ratio column further confirms this. Although the amount of fiber and PVAc increases in both water and fiber phases as the amount of PVAc increases, the ratio does not. This indicates that the distribution of PVAc between water and fiber is constant because the PVAc remains attached to the fiber. The result is not surprising, since the PVAc in this experiment bonds into the matrix of the fiber and is more difficult to dislodge than the PVAc added through methanol that associates with the fiber surface.

CONCLUSIONS

We have demonstrated a simple Britt jar approach to the study of stickie to fiber interactions. PVAc has a greater affinity to brown pulp than to white. This affinity increases at low pH and in the presence of retention aids. Temperature greatly affects the disintegration of hot melts during repulping. Fiber interrupts the agglomeration of small stickie particles. This last observation could be the basis of stickie agglomeration in low consistency regions such as the white water loop. **TJ**

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LITERATURE CITED

1. Spangenberg, R. J., in *Secondary Fiber Recycling* (R. J. Spangenberg, Ed.), TAPPI PRESS, Atlanta, GA, 1993, p. 261.
2. Moreland, R. D., *TAPPI 1990 Recycling Paper Symposium Notes*, TAPPI PRESS, Atlanta, p. 508.
3. Fogarty, T. J., *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 429.
4. Wade, D. E., *TAPPI 1990 Recycling Paper Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 536.
5. Doiron, B . E ., *TAPPI 1994 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 603.
6. Goldberg, J. Q., *TAPPI 1990 Recycling Paper Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 496.
7. Dykstra, G. M. and May. O. W., *TAPPI 1990 Recycling Paper Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 527.
8. Severtson, S. J. and Banerjee, S., *Environ. Sci. Tech.* 30: 1961(1996).
9. Garbarini, D. R. and Lion, L. W., *Environ. Sci. Tech.* 20: 1263(1986).
10. Daube, A. K., Karim, M. R., Dimmel, D. R., *et al., Environ. Sci. Tech.* 26: 1324(1992).
11. Mulcahy, J., personal communication.
12. Barer, R. and Cosslett, V. E., *Advances in Optical and Electron Microscopy*, Academic Press, London, 1966, Vol. 1.
13. Diaz, R., "Measurement of interactions between fibers and styrene butadiene rubber pressure sensitive adhesives," M.S. thesis, Institute of Paper Science and Technology, Atlanta, GA, 1995.
14. Scallan, A. M., *TAPPI J.* 66(11): 73(1983).
15. Katz. S., Beatson, R. P., and Scallan, A. M., *Svensk Papperstid.* 87(6): 248(1984).