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# Interactions Among Stickies, Fiber, and Water

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## ***Abstract***

The pulp-water distribution of polyvinyl acetate and styrene butadiene rubber was determined through a Britt jar separation technique. The affinity of polyvinyl acetate to fiber increased with increasing kappa number, suggesting a hydrophobic-hydrophobic interaction. Fiber-stickie association increased at  $\text{pH} \approx 4$ ; this was attributed to protonation of the lignin carboxylic acid groups which would increase lignin hydrophobicity. Microparticle retention aids directed the stickie from the water to the mat phase by associating either the stickie, or the stickie-bound fines to the mat. Temperature had a significant effect on the breakup of two hot melts that were applied to linerboard. The most important finding was that fibers inhibit stickie reagglomeration. Polyvinyl acetate agglomerated completely when added to water in a methanol carrier. However, when added to a pulp slurry, a large fraction of the polymer was found as an apparently free suspension and transferred to the filtrate. It is proposed that stickie particles are trapped in fiber flocs or are otherwise associated with fiber, and are unable to interact with other stickie particles. The tendency of the polymer to reagglomerate in the absence of fiber could be a mechanism for stickie reagglomeration in white water.

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## ***Introduction***

The presence of stickies in recycled fiber can cause runnability problems, lead to hole and spot formation, and to decreased felt lifetime. The industry has principally focused on practical aspects of stickie prevention and removal, e.g., through more frequent pulper cleaning, and optimizing screens and cleaner efficiency. Detackifiers (1), talc (2), synthetic fibers (3), retention aids (4), and a variety of chemicals (5,6) have had some success in minimizing the effects of stickies, but a universal set of solutions has not emerged. Our approach is mechanistic in nature; it seeks to understand the chemistry of the interactions among fiber, water, and stickie, and to then apply the principles developed towards stickies control. In this paper we describe laboratory procedures to study the distribution of model stickies between fiber and water, and identify some of the governing factors.

### ***Technique for measuring fiber:water distribution***

Consider the relationships in Table 1. A pulp water slurry containing a mass of  $w_1$  of fiber is agitated in a Britt jar, and stickie ( $w_2$ ) is slowly added with a syringe in a small volume of methanol. The mixture is agitated at 200 rpm for 15 minutes, after which the water is drained through a 200-mesh screen and collected. Agitation at 400 rpm leads to substantially similar results. The solids retained on the 200-mesh screen and a measured aliquot of the filtrate are dried and weighed to give bone dry weights of  $w_3$  (mat) and  $w_4$  (water). A companion experiment with an identical mass of fiber ( $w_1$ ) is performed 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  $M_r$ , the mass ratio, can be defined as in Table 1 as the fiber:water distribution coefficient of the stickie. However, 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, and 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. For this case,

$$M_r = [\text{stickie}]_{\text{mat}} / [\text{stickie}]_{\text{water}} \quad (1)$$

where  $[\text{stickie}]_{\text{mat}}$  and  $[\text{stickie}]_{\text{water}}$  are stickie concentrations in the mat and in water respectively. As will be discussed later, there are instances where this assumption breaks down and  $M_r$  no longer represents the distribution coefficient. For these cases,

$$M_r = \{[\text{stickie}]_{\text{mat}} + \Delta\text{fiber}_{\text{mat}}\} / \{[\text{stickie}]_{\text{water}} + \Delta\text{fiber}_{\text{water}}\} \quad (2)$$

where  $\Delta\text{fiber}$  is the stickie-induced difference in fiber mass. Equation (1) reflects the true mat:water stickie distribution, whereas equation (2) is an approximate measure of the changes in distribution under different conditions. Either equation allows us to at least qualitatively

relate 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. Thus, a low  $M_r$  indicates a weak stickie-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.

In order to compare results among different experiments it is necessary to use a constant quantity of fiber. We accomplished this for never-dried fiber by preparing wet handsheets in a Formette Dynamique, and cutting 0.625" cross-directional strips for each experiment. In order to determine uniformity, 10 strips were cut in alternating segments from a sheet containing 20 strips. The weight of these averaged to 0.585 g ( $\sigma=0.004$  g) which translates to a standard deviation of 0.7%.

$M_r$  values for polyvinyl acetate (PVAc, MW:90,000, Polysciences) in a water and a kappa 23 pulp system are presented in Table 2. 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 it is associated with the mat, then  $M_r=77$ . This uncertainty range is typical of  $M_r$  values determined by this approach. All  $M_r$  measurements reported in this paper were made at least in duplicate.

The advantage of the technique is that changes in the fiber:water distribution are easily measured. The principal disadvantage is that the mass of the stickie is inferred by difference rather than through direct determination. Since the stickie is added as small particles, our  $M_r$  values relate to the whitewater loop where the stickies are likely to be in 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  $M_r$ -kappa relationship is clearly linear for PVAc, suggesting 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 non-polymeric species where distribution coefficients are linear with kappa number (7-9). The situation for SBR is more difficult to interpret since the substrate was introduced as a latex, and surfactant was, therefore, already present in the system. Since surfactants stabilize aqueous phase suspensions, lower  $M_r$  values are to be expected. Evidently, in our case, the surfactant masks the effect of the lignin. The practical implication of these findings is that (in the absence of surfactants) stickies will associate more strongly to brown pulp than to bleached.

These results potentially explain the behavior of pitch in a virgin mill processing a mixture of sulfite pulp and TMP (10). Pitch problems are observed in the absence of TMP, but disappear when TMP is mixed in with the sulfite pulp. Since pitch is expected 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. The following retention system was used: anionic colloidal silica (0.06 g); cationic starch (0.06 g); alum (0.03 g.); fiber (3 g); resin (0.15 g); water (600 mL). The system is similar to microparticulate retention systems, e.g. as described by Doiron (4). Three types of PVAc were used, and for each, parallel experiments were done with and without the cationic starch. The results shown in Table 3 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 for the stickies to be removed from the aqueous phase. First, they can be directly attached to the pulp by the retention aid. Second, if the stickie is already substantially associated with the fines, then the retention aid will collect the fines together with the bound stickies.

### ***Dependence of $M_r$ on freeness***

The mass ratio ( $M_r$ ) varies inversely with freeness for bleached Kraft pulp as shown in Table 4. Three possible explanations were considered: (i) most of the stickie is tied up with the fines which are retained to a greater extent in the mat; (ii) the decreased mat porosity filters out both stickie and fines which are not necessarily associated; and (iii) the stickie associates strongly with the fibrils in the refined fibers.

The “fines in filtrate” column in Table 4 measures the fines in the filtrate *without* the stickie, i.e. it represents  $w_6$  in Table 1. The “apparent stickie weight in filtrate” represents  $w_4 - w_6$  in Table 1. The fourth column is the apparent stickie: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 was identical for the two experiments with and without the stickie. The relatively constancy of this column suggests that most of the PVAc could be associated with fines. However, phase contrast microscopy of fresh filtrate showed the presence of both free and fines-associated PVAc, negating this possibility. Stickie-fines association did increase with time, but this is not germane to the  $M_r$ -freeness relationship which depends on the stickie distribution at the time of filtration. While we are unable to distinguish between mechanisms (ii) and (iii) above, we have noted through phase contrast microscopy that stickies have a particular affinity to fibrils (11). On this basis, the refined pulp should have a greater affinity for the stickie which could account for the inverse  $M_r$ -freeness relationship. Results from related experiments with SBR latex emulsion (with alum added) are also included in Table 4. Weights of stickies and fines are omitted since the alum will partition differently into the filtrate in the presence of the SBR. These data also show the inverse  $M_r$ -freeness relationship seen for PVAc.

### ***Dependence of $M_r$ on pH***

$M_r$  increases for the unbleached pulp at low pH as shown in Table 5. The probable reason is that the ionization of lignin acid groups is suppressed (12,13), 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***

Two types of experiments were conducted. First, PVAc in methanol was added to the slurry, and Britt jar measurements were made as before. Second, each of two hot melts was softened in an oven and then poured on linerboard. This material was too rigid to be broken up in a Britt jar, and it was repulped in either a British disintegrator (50,000 revolutions) or a Waring blender (5 minutes). Companion control experiments were conducted without added stickie, and the stickie transferred to the filtrate was obtained by comparing the dried mass in the filtrate from the two measurements. The results are reported in Table 6.

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:fiber interactions, any additional temperature-induced transfer to the aqueous phase is probably undetectable with our technique. For the two hot melts at 80°F, the percent weight of added stickie in the filtrate is negative, indicating that more fiber is retained in the experiment with the hot melt than in the control without it, because the hot melt entraps the fiber. In this case, increasing temperature would weaken the stickie-fines association and release the fines into the filtrate. In addition, components of the hot melt would soften and disperse into the aqueous phase.

Our PVAc was unable to trap fiber because it was introduced as small particles. Had it been pre-applied to the fiber as was the hot melt, we would have expected to see much higher fiber retention. In other words, we attribute differences in the amount of 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 PVAc is added to water in the absence of fiber it quickly aggregates, and no PVAc transfers to the filtrate. As shown in Figure 2, addition of bleached fiber to the system increases the amount of PVAc entering the filtrate. The data are reported as water:mat distribution ratios instead of  $M_r$  in order to accommodate the zero solids point which would be infinity in an  $M_r$  plot. Thus, we have the curious situation where the fiber inhibits

agglomeration, and we have free stickie in the filtrate despite its propensity to instantly agglomerate in the absence of fiber. The phenomenon can be rationalized on the basis of kinetic vs. thermodynamic control, a well-known 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-stickie collisions are infrequent. Thus, the weaker PVAc-fiber attachment is formed in preference to the thermodynamically more stable PVAc-PVAc association because a PVAc particle collides with fiber much more often than it does with another PVAc particle. Thus, the fiber protects the captured PVAc from an encounter with another PVAc particle, thereby preventing agglomeration. Now consider the stickie-fiber floc network. If the network is disturbed through agitation, the free stickie particle enters the aqueous phase. However, since the probability of a stickie-stickie collision is very much lower than that of a stickie-fiber encounter, it is recaptured by fiber.

Ultimately, the stickies will agglomerate into a separate phase as it does in the absence of fiber since this is a thermodynamically more stable situation. However, the preferred kinetics of the PVAc-floc collisions prevent this from occurring in the time frame of our measurements. The Figure 2 relationship steadily increases beyond a consistency of about 0.5, probably because stickie-stickie collisions are eliminated and virtually all the stickie particles are captured by fiber. 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 whitewater system.

### ***Dependence of $M_r$ on the method of stickie application***

In the above experiments, the stickie was applied to the pulp slurry in a methanol carrier. In order to determine the strength of the stickie-fiber attraction, a number of experiments were run where pulp was saturated with 19% by weight of PVAc in methanol,

dried, mixed with untreated pulp, and run through our Britt jar procedure. The results are as follows:

Percent 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

Note that the amount of PVAc in water does not change appreciably as the blends change, suggesting that the PVAc in the pulp does not readily transfer to water under our experimental conditions. This is further confirmed by the solids ratio column. 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. This result is not surprising since the PVAc in this experiment is soaked into the matrix of the fiber, and is much more difficult to dislodge than the PVAc added through methanol which associates with the fiber surface.

### ***Conclusions***

We have demonstrated a simple Britt jar approach to the study of stickie-fiber interactions. Our principal findings are that polyvinyl acetate has a greater affinity to brown pulp than to white, and that this affinity increases at low pH and in the presence of retention aids. Temperature has a significant effect on the disintegration of hot melts during repulping. Most important, fiber interrupts the agglomeration of small stickie particles. This last observation could be the basis of stickie reagglomeration in low consistency regions such as the whitewater loop.

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Table 1: Fiber:water distribution of stickies				
	solids in		solids out	
	fiber	stickie	fiber	water
sample	$w_1$	$w_2$	$w_3$	$w_4$
blank	$w_1$	0	$w_5$	$w_6$
difference in fiber mass: $(w_3-w_5)$ ; difference in water mass: $(w_4-w_6)$				
$M_r = m_w(w_3-w_5)/m_f(w_4-w_6)$ ; $m_w$ : mass of water; $m_f$ : mass of fiber				

Table 2: $M_r$ values of polyvinyl acetate						
	solids in (g.)			solids out (g.)		
	fiber	PVAc	total	fiber	water	total
sample	1.7416	0.1	1.8416	1.7088	0.1062	1.815
blank	1.7416	0	1.7416	1.6898	0.0365	1.726
PVAc weight		0.1	0.1	0.019	0.0697	0.088
$M_r = 48$						

**Table 3: Effect of retention systems on  $M_r$**

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resin: 2873 flexible cross-linking PVAc latex for PSA ( $T_g = -36$ )  
 without starch:  $M_r = 62$ ;      with starch:  $M_r = 1,630$  (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)

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Table 4: Dependence of $M_r$ on freeness				
freeness	fines in filtrate (g)	apparent stickie weight in filtrate (g)	apparent stickie/fines ratio	$M_r$
<b>PVAc</b> (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
<b>SBR</b> (0.3 g. SBR, 3g. fiber (kappa 37 unbleached softwood Kraft), 600 mL water, 1.66% alum)				
732				1060
588				1730
134				4310

Table 5: Dependence of $M_r$ on pH		
pH	$M_r$	
	kappa=0	kappa=81
4	156	410
7	131	96
9	113	149

Table 6: Percent of added stickie transferred to filtrate <sup>1</sup>			
	80°F	120°F	140°F
PVAc (kappa=0)	93	81	86
PVAc	64	72	90
Hot melt A <sup>2</sup> (British)	-26	-8	19
Hot melt A (Waring)	-52	7	
Hot melt B <sup>3</sup> (British)	-17	7	14
Hot melt B (Waring)	-18	33	28
<sup>1</sup> A negative value indicates that fines are held by the stickie in the mat. A kappa 81 pulp was used unless indicated otherwise. <sup>2</sup> Fuller HM3108 (softening temperature: 168°F). <sup>3</sup> Fuller HM2042 (softening temperature: 197°F)			

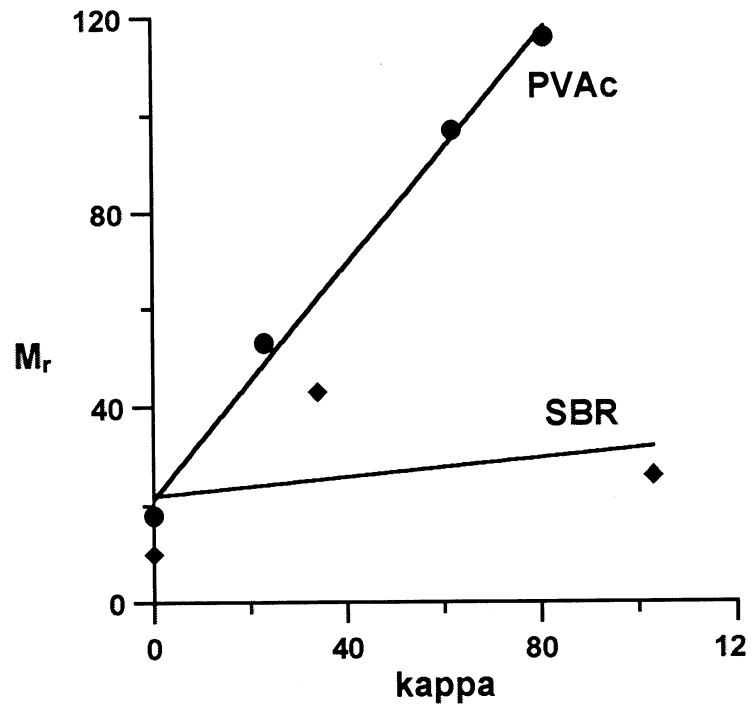


Figure 1: Variation of  $M_r$  with  $\kappa$  for PVAc and SBR.

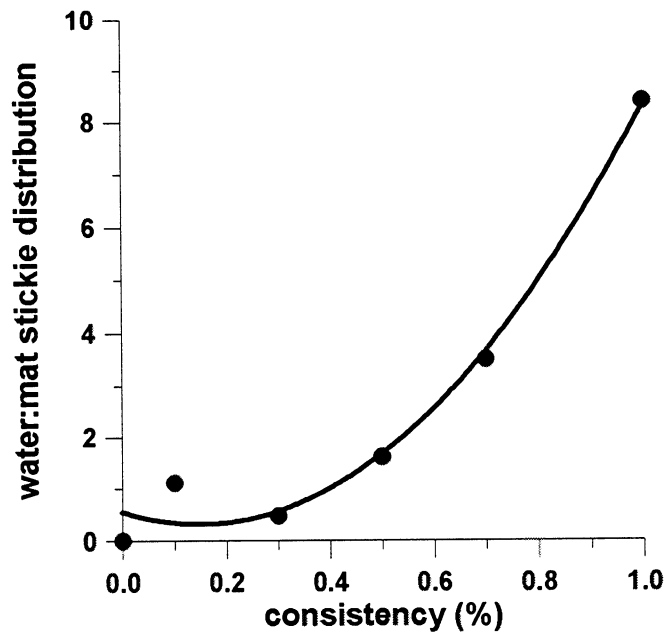


Figure 2: Dependence of the water:mat distribution of PVAc on consistency.

