

## SOLUBILIZING AND DETACKIFYING STICKIES WITH $\beta$ -CYCLODEXTRIN

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$\beta$ -Cyclodextrin ( $\beta$ -CD) solubilizes stickies from deinked pulp, commercial adhesive formulations, or magazine inserts, which demonstrates its potential as a washing aid. A new test to simulate coater scratches is described; it involves scraping the test paper sample across the surface of a thin layer chromatography plate and measuring the degree of scratching on the plate. Scratching was significantly reduced when the paper was pre-treated with  $\beta$ -CD. A trial at a recycle paper mill confirmed that  $\beta$ -CD reduces the tack of filtrate components.

*Keywords:* Stickies; Cyclodextrin; Tack; Recycle; Coater

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### INTRODUCTION

Cyclodextrins (CDs) are cyclic oligomers with glucose molecules arranged in a ring. The structure of  $\beta$ -cyclodextrin ( $\beta$ -CD) is illustrated in Fig. 1. CDs uniquely combine a hydrophobic cavity with a hydrophilic surface and are used in odor control (Trinh and Phan 1995; Trinh et al. 1997), sludge dewatering (Hartong et al. 2007; Banerjee 2010), and many other applications (Hedges 1998; Szejtli 1998; Buschmann and Schollmeyer 2002; Lo Nostro et al. 2003). They are relatively inexpensive and are prepared by the action of bacteria on starch (Tonkova 1998).  $\beta$ -CD increases the wettability of microstickies and reduces their tack, which inhibits their tendency to agglomerate and deposit on surfaces (Banerjee and Haynes 2008; Haynes 2009). This study demonstrated the effectiveness of  $\beta$ -CD in pulp washing and illustrated its ability to reduce tack in a mill application. Moreover, the study developed a new test that showed that  $\beta$ -CD reduces stickies-related scratches on sensitive surfaces.

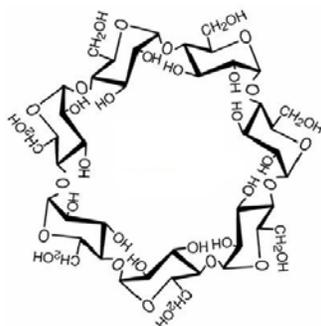


Fig. 1. Structure of  $\beta$ -cyclodextrin

## EXPERIMENTAL

The pulp used was “HQ” grade (made from heavily coated recycle paper) from the NewPage mill in Duluth, MN. Paper machine whitewater was taken from the NewPage mill at Stevens Point, WI. The pressure sensitive adhesive (PSA) formulation used was Carbotac XPD 1811 from Noveon. Total Organic Carbon (TOC) measurements were made with a Shimadzu TOC-V<sub>CSH</sub> instrument.

The tack of components in the filtrate was measured as described earlier (Koskinen et al. 2003) by filtering the samples through Whatman 4 filter paper. The samples (ca. 500 mL) were evaporated down to about 2 mL, transferred to metal coupons, and dried overnight at 45°C. The coupon was then immersed in hot water, shaken dry, and the tack measured with a Polyken tack tester at various temperatures as the coupon cooled. The tack values were interpolated to 40°C. Although not used in this study, a very recent adaption provides equivalent results much more rapidly (Haynes 2011).

In order to simulate the potential of a dried stickie to cause scratching, a section of the adhesive flap of a US Post Express mail envelope was soaked in 10,000 ppm CD for 30 minutes and air dried. The high CD level was necessary to treat the extremely tacky labels. A control sample was similarly treated with water. A 14 x 1 cm section of the label was weighted by a 130 g stainless steel coupon and manually dragged over a thin layer chromatography (TLC) plate coated with silica (Aldrich Z12, 269-6) over 5 seconds, whereupon the adhesive pulled off some of the silica from the surface of the plate. The difference in weight of the TLC plate was recorded.

## RESULTS AND DISCUSSION

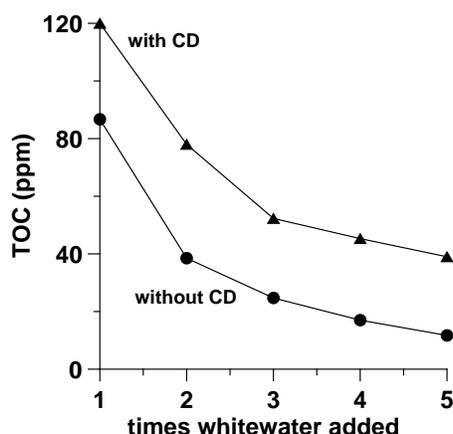
### Solubilization Experiments

The solubilization of stickies and other organic material from pulp through a CD-wash was investigated. First, dried stickies were prepared by drying 5 mL of a PSA acrylate emulsion overnight to a film. Water (100 mL) containing various amounts of  $\beta$ -CD was added and the mixture shaken at 50°C for an hour. TOC measurements showed that the amount of stickies solubilized was negligible, which emphasizes the need to control stickies *before* they dry. To demonstrate that CDs are able to remove stickies from wet pulp, HQ lap pulp from NewPage was mixed with water containing various amounts of  $\beta$ -CD at 4% consistency for 5 minutes at 40°C. The results (Table 1) show that the TOC increases in the presence of  $\beta$ -CD. The values were corrected for the carbon content of the CD itself, which does not associate with pulp. Indeed, without the correction the apparent amount solubilized would have been larger.

The mechanism through which the CD increased solubilization was probed by sequentially washing the same pulp with different batches of whitewater. The pulp was mixed for 5 minutes with whitewater at 4% consistency at 40°C, separated, the filtrate discarded, and the pulp washed again with a fresh batch of whitewater and so on. One set of whitewater was spiked with 50 ppmv  $\beta$ -CD. TOC measurements were taken of each filtrate (with and without CD) after its separation from pulp. The results in Fig. 2 show

**Table 1.** Stickies Removal with  $\beta$ -CD

|  | TOC (ppm)               |
|--|-------------------------|
| water + 4% pulp  | 67 $\pm$ 6              |
| 10 ppm CD + 4% pulp  | 74 $\pm$ 3 <sup>1</sup> |
| 20 ppm CD + 4% pulp  | 75 $\pm$ 3 <sup>1</sup> |
| 50 ppm CD + 4% pulp  | 91 $\pm$ 4 <sup>1</sup> |
| <sup>1</sup> corrected for the TOC contributed by the CD; the CD dose is based on od fiber |                         |

**Fig. 2.** Effect of  $\beta$ -CD on progressive pulp washing

that higher TOC values are obtained in the presence of the CD. The CD increases the amount of organics removed from the pulp, confirming its effectiveness as a washing aid. The constant difference between the two curves suggests a partitioning mechanism, i.e. the CD systematically increases the solubility of the TOC components in water.

While stickies are certainly a significant component of the dissolved/suspended material in deinked pulp, there are several other components present. TOC is an indirect measure of stickies, and a more direct demonstration of the ability of CD to solubilize stickies was necessary. Accordingly, an acrylate PSA formulation was added to Duluth pulp at 4% consistency. CD was included in the mixture in some cases. Results from TOC measurements taken of the filtrates are shown in Table 2 and clearly demonstrate that the CD promotes dissolution of the PSA. The CD dose of 10 ppm had the greatest proportional effect.

A second trial was conducted with magazine inserts, where 4.5 g of the inserts were mixed with 500 mL of deionized (DI) water for 1 hr at 60°C. CD was added in some cases. Associated TOC measurements listed in Table 3 show that the CD washes out the adhesive into solution. Again, the 10 ppm CD dose has the greatest proportional effect. The solubilizing ability of the CD is, in some ways, similar to the function of a surfactant, but the applied dosage is much lower. Indeed CDs have been used in place of surfactants in polymer synthesis. For example, Rimmer and Tattersall (1999) used  $\beta$ -CD in place of a

surfactant in emulsion, and Storsberg et al. (2003) replaced surfactants with methylated CD for the polymerization of styrene or methyl methacrylate.

**Table 2.  $\beta$ -CD Treatment of PSA-spiked Pulp**

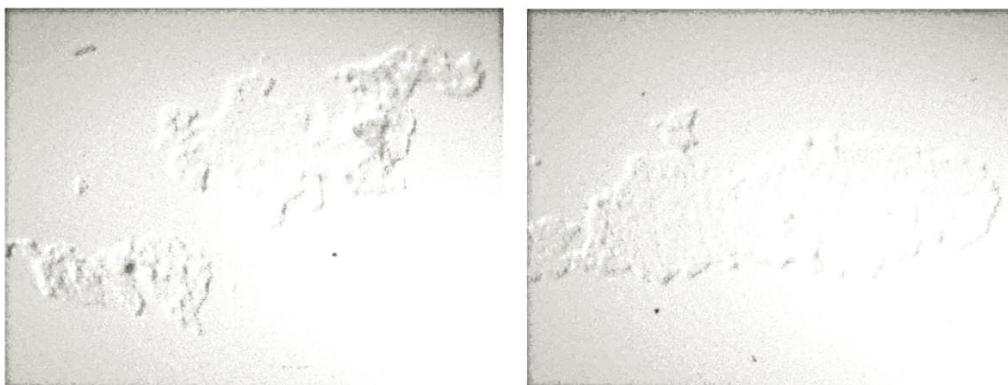
|  | TOC (ppm)    |
|--|--------------|
| 100 ppm PSA (no pulp)                                    | 48 $\pm$ 3   |
| pulp + 100 ppm PSA                                       | 124 $\pm$ 7  |
| pulp + 100 ppm PSA +10 ppm CD                            | 140 $\pm$ 8  |
| pulp + 100 ppm PSA + 50 ppm CD                           | 158 $\pm$ 13 |
|  |              |
| 200 ppm PSA (no pulp)                                    | 74 $\pm$ 6   |
| pulp + 200 ppm PSA                                       | 141 $\pm$ 3  |
| pulp + 200 ppm PSA +10 ppm CD                            | 166 $\pm$ 11 |
| pulp + 200 ppm PSA + 50 ppm CD                           | 179 $\pm$ 9  |
|  |              |
| <sup>1</sup> corrected for the TOC contributed by the CD |              |

**Table 3.  $\beta$ -CD Solubilization of Stickies from Magazine Inserts**

|  | TOC (ppm)                 |
|--|---------------------------|
| inserts only   | 138 $\pm$ 6               |
| inserts + 10 ppm CD                                      | 156 <sup>1</sup> $\pm$ 17 |
| inserts + 50 ppm CD                                      | 183 <sup>1</sup> $\pm$ 9  |
|  |                           |
| <sup>1</sup> corrected for the TOC contributed by the CD |                           |

### Simulating Coater Scratches

Scratches on coated recycled paper are a common problem that can be caused by stickies (Varsa et al. 1997). A new test was developed to quantify the benefit of CDs on coater scratches, where a thin layer chromatography (TLC) plate was used to simulate the coated paper surface. An adhesive coated paper containing stickies was weighted and scraped over the TLC plate, where it removed some of the silica and gouged the surface. Micrographs taken of the plate surface (Fig. 3) showed that the CD reduced the degree of indentation. A similar difference was found with filter paper impregnated with a PSA formulation with and without CD treatment. Because the images in Fig. 3 are difficult to evaluate quantitatively, the weight loss of the TLC plate caused by the partial removal of silica by the stickies was measured. The plate exposed to CD-treated paper lost 4  $\pm$  1 mg, whereas the corresponding value for the control was 11  $\pm$  2 mg with n=6 for both cases. CDs are known to soften the structure of stickie agglomerates (Banerjee and Haynes 2008), which reduces the strength of the deposit and, in turn, the degree of scratching. It follows that treating the papermaking furnish with CD should reduce the degree of scratching. The results from the TLC plates will not apply directly to coated paper. Nevertheless, both surfaces are sensitive to indentations caused by adhesives, and the overall trends should be similar.

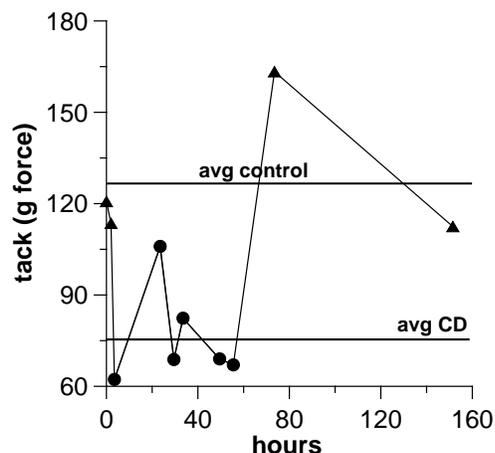


**Fig. 3.** Surfaces of thin layer chromatography plates contacted by an adhesive label (left) and with the label treated with  $\beta$ -CD

An important advantage of using TLC plates is that the coating is very uniform and any differences in the properties of the silica surface should be small. Certainly, the standard deviations cited above are low enough to differentiate the results obtained with and without the use of CD.

### Mill Trial

Previous laboratory work has shown that  $\beta$ -CD can detackify stickies (Banerjee and Haynes 2008). The dosage applied is important because overdosing can reverse the benefit for reasons described earlier (Wang and Banerjee 2009). A trial was run at a mill in Southern Sweden producing 900 tpd of deinked pulp.  $\beta$ -CD was added to the pulper as an aqueous concentrate at 45 kg/day. The pulper was followed by coarse screens, a swelling/homogenization tower, and 0.15 mm fine screens. Samples were taken at the fine screen accepts. Values for filtrate tack are provided in Fig. 4. The triangles represent control values taken before and after the trial; the circles are for tack measured in the presence of the CD. Although brief, the trial shows that the average tack of filtrate components in the presence of the CD is about 40% lower than that for the control.



**Fig. 4.** Effect of  $\beta$ -CD on filtrate tack. The triangles and circles represent control and CD samples, respectively. The abscissa represents time elapsed from the start of the trial.

## CONCLUSIONS

1. Stickies from lap pulp or magazine inserts are solubilized by  $\beta$ -cyclodextrin ( $\beta$ -CD).
2. A new test to evaluate coater scratches showed that the severity of scratching was reduced when the surface of the sheet was treated with  $\beta$ -CD.
3. A trial at a recycle mill shows that  $\beta$ -CD detackifies stickies in screened pulper filtrates.

## ACKNOWLEDGMENTS

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