Study of binding strength development inmultiple coating systems



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Abstract :

Binding strength development in multiple coating systems was studied and the proposed "Weakest link in the chain" model was tested. The strength of a multiple coating system was found to be determined by its weakest coating layer. Binder movement between the coating layers and its impact on the strength of the multilayer structure was studied using a range of starch binders with different molecular weight (MW) and thereby, different hypothesized mobility of dissolved starch. Using starch binder of different MW, multilayer strength was greatly affected by the binder enrichment or depletion in the weakest link. The starch mobility between the coating layers could be clearly linked to its MW.

The weakest link model can help to design new approaches for optimizing binder use and strength in multilayer structure.

Introduction :

The main function of a binder in a coating layer is to bind the pigment particles together and onto the base paper. The dry and wet strength of latex-based coatings has been studied extensively (1, 2). In addition to the cohesive and adhesive strength of the latex, it is understood that, in an offset printing process, the ability of a coating to resist picking is dependent on the rate of ink tack build-up (3, 4). It has also been demonstrated (5-7) that the coating strength of a single coating layer is dependent on the movement of latex particles during coating consolidation and drying.

The fundamental binding mechanisms and critical variables, related to the strength of starch-based paper coatings are less well documented. Starch film (8) and paper strength studies (9, 10) however suggest that dry strength increases with molecular weight. Starch is generally known to be more prone to migration than latex. Dobler et al showed in pioneering work (11) that the strength of a pre-coat can be reduced due to the re-solubilization and subsequent migration of starch into the topcoat.

The majority of literature references discus binding strength mechanisms within a single coating layer and do not take into account the possibility of one layer affecting the strength one of an adjacent. The effect of binder movement from one layer to an adjacent layer on the strength of the first layer has received little attention. The objective of this work is to investigate the strength development in a multilayer coated paper using latex and starch as binders. The hypothesis is that different binder mobility can increase or decrease the strength throughout the z direction of the layered structure resulting in different locations of failure.

Experimental

Paper coating and characterization

Coating colors were formulated using commercial grades of ground calcium carbonate (90 % of particles < **2 µm), carboxylated styrene butadiene latex, CMC and enzymatically degraded starch. Wood free paper (61 g/m^2) was blade coated with a laboratory coating device (30 m/min, drying web temperature 61-66** C). Coating parameters were set to target 14 ± 1 g/m^2 coat weight and typical final moisture ranging between 4.5 – 5.5 %. Uncalandered coated papers were conditioned under controlled atmosphere (23 C, 50% r. H.); paper samples were allowed to equilibrate 24 hrs prior to their characterization.

Dry strength was measured using medium ink viscosity and an IGT device (Pendulum). IGT strength scale ranges from 20 to 110 cm/sec.

Color coating dewatering was determined using (ABO) AA-GWR Water Retention Meter Model 250 (1 bar pressure for 90 sec). Gravimetric analysis of the wet and dry AA-GWR blotted paper was applied to determine the solid content of the filtrate.

Starch degradation

Alpha-amylasewas added in different quantity (0.5, 0.1, 0.05, 0.01 mL) in 1000 mL calcium chloride solution (1.0 g/L) to produce four enzymatic solutions. Waxy-rich starch (500 g) was dispersed under stirring and the pH was adjusted to 6.5 with 10% caustic soda solution. The slurry was cooked under vigorous agitation at 90 C and pH 6.5 for 20 minutes, and then at 95-100 C at pH 4.3 (citric acid addition) for further 10 minutes. The slurry was cooled to 25 C and a small quantity of biocide was added resulting in a viscous and translucent solution (solid 32±1%, pH 4.3).

Analytical methods

Molecular weight of starch was characterized in aqueous phase adapting the method described by Fishman and Hoagland (12). Filtered starch samples were characterized by aqueous SEC (Agilent 1260 Infinity LC fitted with Tosoh Bioscience GMPWXL column and RI detector), PEG standards were used for the calibration.

Electron microscopy images of paper cross sections (cutting in epoxy resin embedding and iridium coating) were generated with backscatter electron (BSE) imaging mode using a FEI Nova NanoSEM.

Results and discussion

This study is based on the proposed "weakest link in the chain" model and investigates the hypothesized model by using starch and latex as coating binders. It has previously been demonstrated that starch and latex have different mobilities during coating consolidation (5-7, 11). The experimental coating systems aim at investigating the fundamental mechanism of coating strength development and are not necessarily typical for the paper industry.

Strength development in double coated latex formulation: weakest link model

In order to study the strength development of a multilayered coating structure, wood free paper was double coated to produce combinations of low latex level pre-coats and high latex level top-coats as reported in table 1. IGT characterization (figure 1) demonstrates that irrespective of the top-coat latex amount (latex rich layer) coating strength is controlled by the latex amount in the pre-coat layer (low latex level layer). Failure occurred in the low latex level layer (pre-coat) when external stress was greater than the cohesive strength for a given latex amount. Therefore, the weakest link model (figure 2) seams to apply when describing the failure mode of this type of coating structure. The chain (or multilayer) strength is determined by the strength of its weakest element (related to the latex amount in the formulation). Reinforcing the strongest link does not increase the overall strength.

The results collected did not suggest latex binder movement across the layers.

Although not specifically investigated, no evidence could be found that failure happened between the pre- and top-coat interface. In case of weak layer adhesion, strength is expected to be independent from the latex amount, which was clearly not the case.

	P1		P2		P3	
coat layer	pre	top	pre	top	pre	top
GCC pts	100	100	100	100	100	100
SB latex	*6*	10	*6*	14	*8*	10
CMC	0.45	0.45	0.45	0.45	0.45	0.45
Solid	65.5%	65.5%	65.5%	65.5%	65.5%	65.5%
PH	8.5	8.5	8.5	8.5	8.5	8.5
Brookfield (mPas)	670	790	670	850	740	790
CW (g/m^2)	14.0	12.2	14.0	13.0	14.0	12.7

Table 1: samples P1-P3 color formulations and coating structures for samples P1-P3 (low latex level layer in italic font).

Strength development in single coated starch formulations

In order to study the effect starch mobility has on strength development, starch samples differing in MW were prepared using alpha-amylase. The experimental samples were produced to minimize other variation in starch chemistry and to cover a typical range seen in commercial coating starch grades, figure 2. Literature references (12,13) reports MW of 18-22x10^6 g/mol for untreated waxy corn starches characterized in aqueous phase. Molecular weight characterization of sample MW4 revealed a similar MW range (figure 2) suggesting that the sample possibly had a very limited enzymatic degradation. However, it is noteworthy to mention that great differences in MW estimation of native starch are reported (12, 15) and attributed also to sample preparation, solvent and detector used (13). Therefore the MW characterization of sample MW1 to MW4 should merely be interpreted as apparent MW.

The extent of MW reduction was controlled by the enzyme concentration in the cooking vessel. The enzymatically degraded starch showed the expected molecular weight and viscosity reductions with increasing enzyme concentration.

Starch samples were directly formulated with GCC and coated on wood free paper as described in table 2. The viscosity of starch sample MW4 was too high for coat weight control and the sample was not further considered.

It was initially hypothesized that starch retention and mobility correlates with its MW. This hypothesis was investigated by studying the ABO dewatering behavior and solid content of the filtrate penetrating

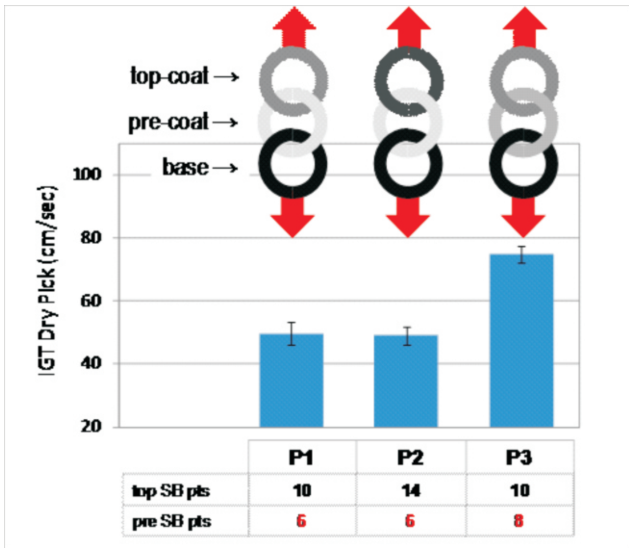


Figure 1: IGT strength for sample P1-P3 for combinations of latex amount in pre- and top-coating. The analogy to the weakest link chain model (grey intensity corresponds to layer inner strength) is made: the overall chain is defined by the weakest element.

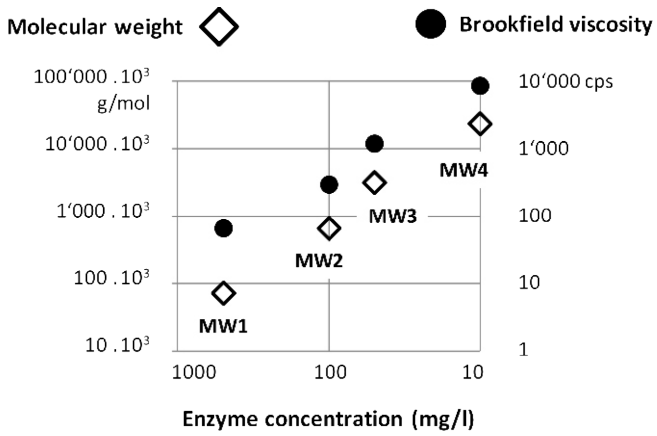


Figure 2: starch viscosity (circle) for 32±1% solid and weight averaged molecular weight (diamond) as function of enzyme concentration in the cooking vessel.

into the blotting paper. Results for simple formulations made of 100 pts GCC and 10 pts starch at 65% solid are plotted in figure 3, and suggest that there is indeed a correlation between starch mobility and its MW: higher retention was observed for higher MW starch.

Coating strength of sample P4-P6 (figure 4) correlates with starch MW. These results can be explained by the MW-controlled retention behavior of starch in the coating layer.

Despite evidences pointing towards a retention mechanism, it is not possible to entirely rule out the contribution of the mechanical strength of the starch film. Typical for many polymers, mechanical strength correlates to MW. However, results presented later in this paper suggest mechanical strength not to be the dominant mechanism determining the MW correlation here observed. Differences are also hardly related to pigment packing variation as coating structure in electron microscopy pictures (figure 5) appeared similar.

		P4	P5	P6
coat layer		single	single	single
GCC pts		100	100	100
SB latex		-	-	-
Starch	type	MW1	MW2	MW3
	pts	10	10	10
CMC		0.6	0.3	-
Solid		65.5%	65.5%	65.5%
PH		8.5	8.5	8.5
Brookfield (mPas)		750	850	810
CW (g/m^2)		15.9	15.6	15.3

Table 2: samples P4-P6 colors formulation with MW1-MW3.

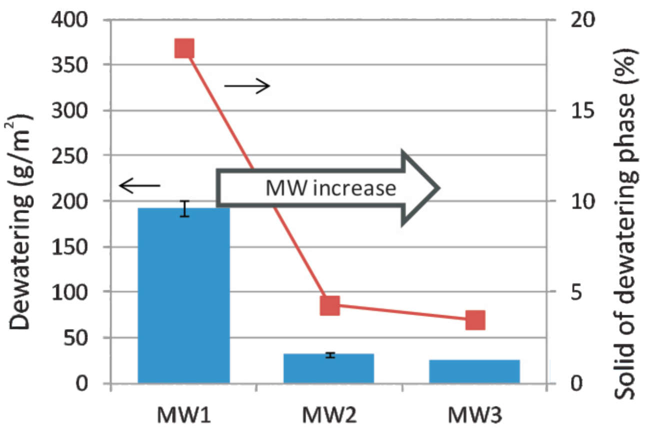


Figure 3: dewatering (bars) and solid content of dewatered phase (squares) for simple formulations made of 100 pts GCC and 10 pts MW1-MW3 (TS 65%).

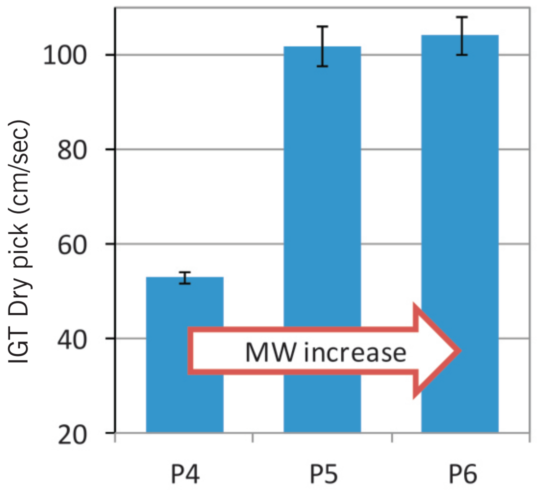


Figure 4: coating strength for starch formulation F6 (MW1) to F8 (MW3).

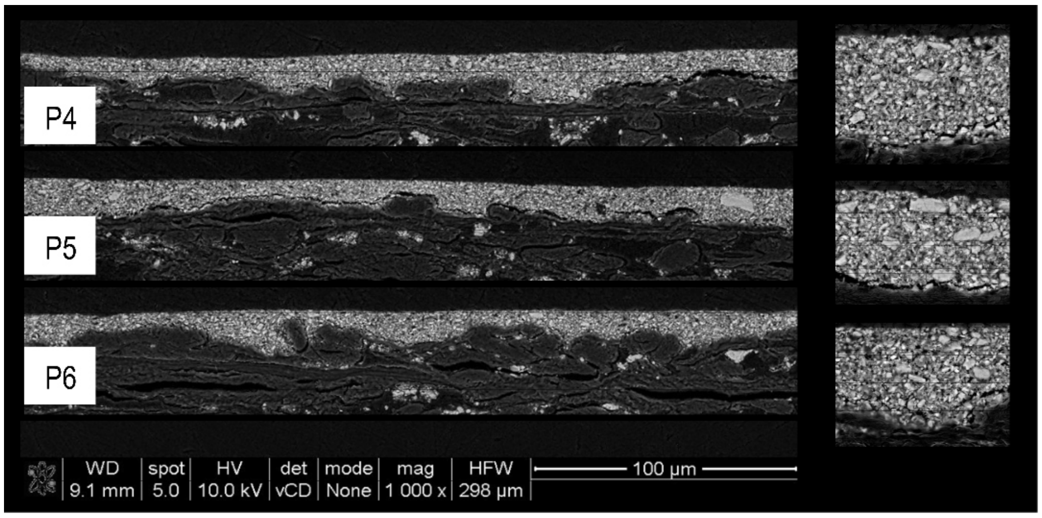


Figure 5: cross section electron microscopy imaging for P4-P6.

Strength development in double coated latex and starch formulations

Starch mobility was previously suggested to relate to its MW and, in case of a single layer, to reduced binder content in the coating layer and therefore to reduced strength. A set of starch solutions of varying MW was then used to investigate the effect of binder mobility on the strength development of multilayer paper coatings. In two experiments, starch was separately applied in top- and pre-coat formulations and the development of strength was studied.

Binder rich formulations comprising latex and starch were top-coated on a relatively weaker pre-coat layer to produce samples P7-P10 (table 3). Samples P11-P14 were similarly produced as in table 3 but reducing latex to 4 pts instead.

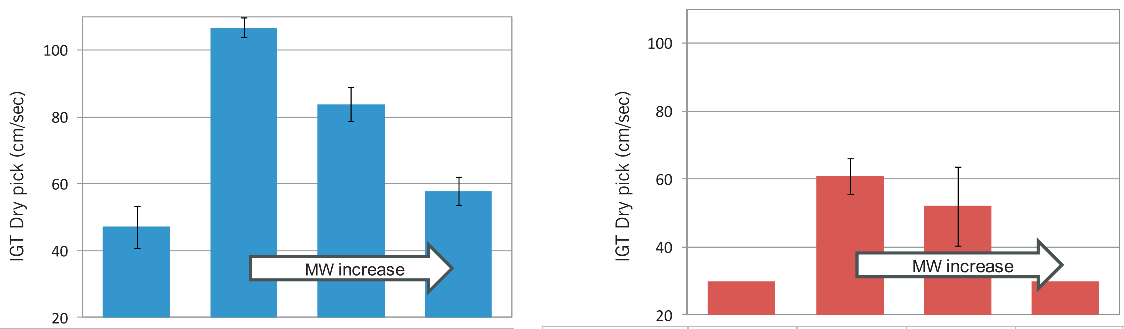
Coating strength measurements shown in figure 6a (P7-P10) and 6b (P11-P14) reported higher strength for papers containing starch in the top-coating (P8-P10). This is not obvious because the pre-coat contains a constant and lower binder amount which should make it the weakest link in the chain. This implies that starch applied into the top coat influences the strength of the pre-coat layer. The extent of the effect could be clearly linked to starch MW.

It was previously observed that the weakest link model applies for double coating (figure 1) and latex mobility across layers is rather low. However, in these results an explanation is that starch migration from the stronger top-coat into the pre-coat has occurred, reinforcing the weakest link. The lower strength of the high-MW starch system is due to the lower mobility of higher MW starch between the layers.

The results also suggest that possible MW-related differences in mechanical strength of the starch film must not play a significant role since the opposite MW-trend seen in figure 6 is otherwise expected.

		P7		P8		P9		P10	
	coat layer	pre	top	pre	top	pre	top	pre	top
GCC pts		100	100	100	100	100	100	100	100
SB latex		6	6	6	6	6	6	6	6
Starch	type				MW1		MW2		MW3
	pts				10		10		10
		0.4	0.4	0.4	0.6	0.4	0.4	0.4	-
		65.5%	65.5%	65.5%	65.5%	65.5%	65.5%	65.5%	65.5%
		8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
		610	610	610	740	610	1040	610	730
		14.0	14.1	14.0	12.6	14.0	12.4	14.0	13.6

Table3: coating color formulation P7-P10.



		P7	P8	P9	P10
top	starc pts	-	10	10	10
	SB pts	6	6	6	6
pre	SB pts	6	6	6	6

		P11	P12	P13	P14
top	starc pts	-	10	10	10
	SB pts	4	4	4	4
pre	SB pts	4	4	4	4

Figure 6a, 6b: Dry strength (IGT) for combinations of pre- and top coating formulations.

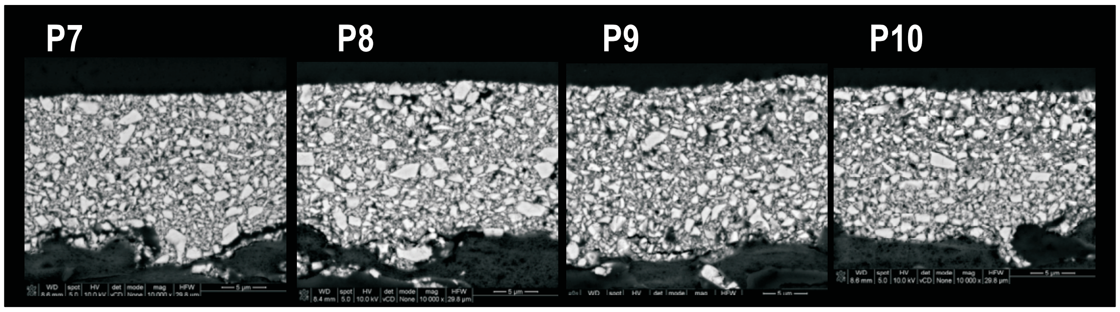


Figure 7: cross section electron microscopy imaging of double coated P7-P10 samples.

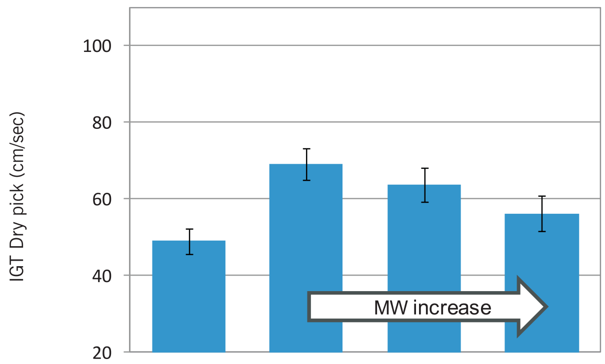
Dobler et al. previously showed (11) that the strength of pre-coat can be reduced due to the re-solubilization and subsequent migration of starch during the application of topcoat. A similar experiment was here tried using the starch MW-family to determine whether MW plays a role also for this case.

High binder level pre-coats comprising latex and different MW starch was applied. A relatively weaker (low binder level) top-coat was subsequently applied to each pre-coat to produce the coating structures summarized in table 4.

Higher strength was observed (figure 8) for samples containing starch in pre-coating (P16-P18). This is interesting because the top-layer is coated with a constant and lower binder level which should make it the weakest link in the chain. This result is believed to be due to starch migrating from the pre-coat into the weaker top-coat reinforcing it. Importantly, the effect was linked to starch MW: greater reinforcement was observed when using lower MW starch, which indicated greater accumulation in the top-coat due to higher mobility.

		P15		P16		P17		P18	
		pre	top	pre	top	pre	top	pre	top
GCC pts		100	100	100	100	100	100	100	100
SB latex pts		10	10	10	10	10	10	10	10
Starch	type			**MW1**		**MW2**		**MW3**	
	pts			**10**		**10**		**10**	
CMC pts		0.4	0.4	0.6	0.4	0.4	0.4	-	0.4
Solid		65.5%	65.5%	65.5%	65.5%	65.5%	65.5%	65.5%	65.5%
PH		8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Brookfield (mPas)		770	770	790	770	1070	770	610	770
CW (g/m2)		14.1	7.5	14.2	8.2	14.1	7.8	14.1	10.8

Table 4 : coating color formulation P15-P18.



		P15	P16	P17	P18
top	SB pts	**10**	**10**	**10**	**10**
pre	starc pts	-	10	10	10
	SB pts	**10**	10	10	10

Figure 8: Dry strength (IGT) for combinations of pre- and top coating formulations P15-P18(higher viscosity ink applied).

Conclusion

This work suggests that strength development in multilayered paper coating structures can be described with the weakest link model. Failure happens when the stress experienced is greater than the cohesive strength of the weakest link in the chain. The overall strength of the multilayer is therefore as good as its weakest link. The weakest link model approach should be applied when optimizing strength of multilayered structures.

A starch family with a controlled range of MW values was used to study the MW dependence of starch mobility. Results suggest that indeed mobility between coating layers strongly depends on starch MW. For single coating, starch mobility can lead to weakening, resulting from binder depletion in the coating layer. In multilayered structures starch mobility leads to binder redistribution across layers, strengthening or weakening the overall structure. Within the framework of the study, latex migration could not be detected.

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