

Mecanismos de Resistência a Seco e a Úmido em Tintas para Revestimento de Papel: Parte 1 – Estudos Experimentais

On the Mechanisms of Wet and Dry Strength of Paper Coatings: Part 1 - Experimental Studies

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RESUMO

Um detalhado estudo experimental foi conduzido, visando o melhor entendimento dos fundamentos de resistência a seco e a úmido em camadas de tinta. Foram utilizadas medidas de tração e cinética de absorção de água em filmes de tinta não suportados. Experimentos cobrindo uma ampla faixa de concentrações volumétricas de pigmento – PVC (nível de latex) foram desenhados para investigar o impacto do tipo de pigmento, estrutura de tinta, adesão pigmento-latex, e resistência coesiva do filme polimérico. Os resultados obtidos com os filmes pigmentados não suportados demonstraram boa correlação com medições de propriedades em laboratório de impressão para resistência a seco e a úmido de papéis revestidos. Experimentos comparando a razão da resistência do filme pigmentado com a resistência do filme polimérico no estado seco e úmido demonstraram que a adesão entre o latex e o pigmento é enfraquecida na presença de água. Os resultados sugerem que o modo de falha da tinta no estado seco é mais coesivo, porém que a falha adesiva é predominante na presença de água. Elevados níveis de ácido carboxílico no latex foram benéficos para a resistência a seco, porém reduziram a resistência a úmido em filmes com elevado PVC. Experimentos adicionais demonstraram que o dispersante introduz uma camada sensível à água entre o pigmento e o ligante resultando em uma redução da resistência a úmido.

ABSTRACT

A large experimental study aimed at a better fundamental understanding of the dry and wet strength of coating layers has been carried out, using in-plane tensile properties and water absorption kinetics of unsupported coating films. Experiments over a broad range of pigment volume concentrations (latex levels) were designed to investigate the impact of the pigment type, the coating structure, the pigment-latex adhesion and the polymer film cohesive strength. Results obtained with the unsupported pigmented films showed good correlation with the lab print tested dry and wet strength measurements of coated paper. Experiments comparing the ratio of the pigmented film strength to the strength of the polymer film in the dry and wet state showed that the adhesion between the latex and the pigment is weakened in presence of water. The results suggest that the coating failure mode in the dry state is more cohesive but that adhesive failure dominates in the presence of water. Higher levels of carboxylic acid in the latex were beneficial for dry strength, but reduced wet strength in high PVC films. Further experiments showed that the dispersant can introduce a water sensitive layer between the pigment and the binder resulting in a reduction of wet strength.

INTRODUCTION

During calendering and printing, the paper coating layer is subjected to external stresses. The surface strength and cohesion of the coating are critical to maintain its integrity during calendaring and printing. Binders are used to provide the adhesion between the base paper and the coating layer as well as between the pigment particles. In the offset printing process, the integrity of the coating layer needs to be maintained both in dry and wet state. During modern multi-press offset printing, the ink solvent penetrates into the porous coating layer resulting in an increase of the ink layer tack and viscosity. This viscosity increase results in an increase of the force being applied onto the coating by the ink when the paper exits the printing nip. When the stress applied onto the coating layer exceeds its cohesion or critical strength, picking will occur (Figure1).

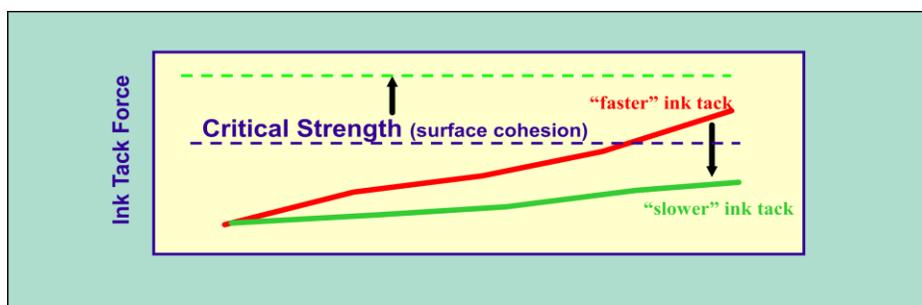


Figure 1: Picking during offset printing

Several studies have identified technologies to control the speed of ink solvent penetration and to slow down the rate of ink tack build-up (1,2,3,4). They were not the subject of this experimental work which concentrated on understanding how we can maximize the critical strength or resistance of the coating layer. Especially one objective of our study was to understand the mechanisms controlling the coating layer strength when latexes are used as paper coating binders.

In offset printing, aqueous fountain solution is applied to the non-image areas. The water can weaken the coating and lead to wet pick. Therefore a second objective was to understand which parameters are impacting the coating resistance in wet state.

Three main parameters control the critical strength of a coating layer: the coating structure, the adhesion between the polymer and the pigment particles and the cohesive strength of the polymer film bridges between the pigments. The pigment type, size and shape, the pigment volume concentration are important parameters controlling the coating structure. To achieve good adhesion between polymer and the pigment, the latex particles need to be soft enough to be deformable and spread on the surface of the pigments (5). Interactions between both surfaces, like acid-base interactions will further promote the adhesive contribution to strength. The presence of dispersant on the pigment surface adds an additional interface between pigment and polymer and its impact was analyzed in this study. Finally the polymer links between pigment particles need to have a high cohesive strength: good particle coalescence, molecular weight and crosslinking will enhance the cohesive strength. Therefore an additional objective was to understand the relative contributions of the adhesive and cohesive failures during dry and wet picking.

Our approach to gain a better understanding of the mechanisms controlling the dry and wet strength of paper coatings consisted in studying the dry and wet mechanical properties in tensile mode and the water absorption kinetics of unsupported pigmented films covering a broad range of pigment volume concentration. The results obtained with the unsupported pigmented films showed good correlation with the lab print tested dry and wet strength measurements of coated paper

MATERIALS AND METHODS:

MATERIALS:

Three pigment types were used in this study: a ground calcium carbonate (GCC), Hydrocarb 90 supplied by Omya, a clay type pigment with a shape factor of 15, Hydragloss 90 from KaMin LLC and a precipitated calcium carbonate pigment, Opacarb 40 from SMI. In the study, Hydrocarb 90, Hydragloss 90 and Opacarb 40 will be referenced as respectively GCC, Clay and PCC. Different carboxylated styrene butadiene latexes were evaluated in combination with the different pigments. The latexes were synthesized using a semi-continuous emulsion polymerization process and their main properties are described in the respective sections of the text.

Coating formulations were prepared covering a large range of pigment volume concentration preparation. The formulation solids content was 65 % and 0.3 parts carboxymethyl cellulose (Finnfix 10) based on 100 parts pigments were used as thickener.

METHODS:

Pigmented and unpigmented film preparation: The latex pH was adjusted to 8.5 prior to addition to the pigment dispersion. After addition of Finnfix 10, the solids content was adjusted to 65 %. A 200 micron wet film was applied onto a Mylar film and dried at 130 degrees Celsius for 3 minutes. Unpigmented latex films were prepared by applying a 600 micron wet film onto a Mylar foil and dried for 2 hours on a hot plate heated at 30 degrees Celsius.

Unpigmented and pigmented films were aged at 22-25 °C and 50 % humidity for at least 3 days before measuring mechanical properties.

Samples were punched out of the prepared films according to DIN 53455 (PK 3-1/2) having a total length of 75 mm, a testing length between specimen shoulders of 35 mm and a width of 5 mm in the middle section. Mechanical properties in tensile mode were measured using a deformation speed of 6 mm/min for the pigmented films and 100 mm/min for the unpigmented polymer films. The tensile strength when the film breaks (or maximum tensile strength) was recorded.

For wet testing, film specimens were immersed into water for different times. Water absorption was measured by the film weight difference before and after water immersion.

RESULTS AND DISCUSSION

DRY STRENGTH: ADHESIVE OR COHESIVE FAILURE?

Pigment volume concentration (PVC) and critical pigment volume concentration (CPVC). The latex amount in a pigmented formulation greatly impacts the mechanical properties of the pigmented films and the binding strength of coated paper. Due to the density differences between different pigments and latex, it is more relevant to describe a pigmented formulation by its pigment volume concentration. The pigment volume concentration (PVC) corresponds to the ratio of the volume occupied by the pigments over the volume of pigments and binders.

$$\text{PVC} = (\text{Volume pigment}) / (\text{Volume pigment} + \text{Volume binder})$$

The pigment and binder volumes are obtained by dividing their weight fraction in the coating formulation by their respective density.

The critical pigment concentration (CPVC) corresponds to the minimum binder quantity required to fill all the pores between the packed pigment particles. Below CPVC, the polymer forms the continuous phase and the pigment particles are dispersed in the polymer matrix. Above CPVC, the binder quantity is too low to fill all the spaces between the pigment particles and the coating consist of three phases: pigment particles, polymer bridges and air voids. Most properties of pigmented films will drastically change when the PVC exceeds CPVC: paper gloss and brightness, coating porosity and water absorption will increase. On the contrary mechanical resistance of pigmented films and coated paper binding strength will decrease as the volume of air voids is increasing.

Relation between polymer film strength and pigmented film strength. To assess the adhesion between polymer and pigment particles, we have used an approach developed by Perera (6). Perera used the ratio between the maximum tensile strength of the pigmented film (σ) over the maximum tensile strength of the unpigmented film or pure polymer film (σ_0). Especially he showed that the evolution of this ratio (σ/σ_0) with pigment volume concentration (PVC) was an indicator of the adhesion between the polymer and the pigment. In case of weak adhesion between the polymer and the pigment particles, there is no reinforcement of the film due to the presence of pigments and the ratio (σ/σ_0) will continuously decrease as pigment volume concentration increases. On the contrary, in case of good adhesion between polymer and pigment, the film will be reinforced by the presence of pigments and the maximum tensile strength will increase with increasing PVC. The ratio (σ/σ_0) will be higher than 1 and increase continuously with PVC until we reach the critical pigment volume concentration (CPVC). Above CPVC, the amount of binder is not sufficient to fill all spaces in the pigment packing resulting in the presence of air voids which will weaken the film: the tensile strength of the pigmented film (σ) will decrease rapidly. Therefore the ratio (σ/σ_0) against PVC will initially increase, go through a maximum at CPVC and then decrease due to the presence of voids.

Figure 2 shows an example of our experimental data obtained for three different latexes in combination with the GCC pigment. The three latexes have a glass transition temperature of 12 °C, a particle size of 100 nm and differ by their crosslinking density, measured by the % gel or polymer fraction being insoluble in toluene. The high gel latex has a high fraction of crosslinked polymer chains, while this fraction is lower for the medium gel latex and even more for the low gel latex. The ratio (σ/σ_0) is higher than 1 and increases until a maximum value when the pigment concentration reaches the critical pigment volume concentration (which is around 0.59 or 59%), then decreases rapidly to low values due to the presence of the voids. Similar curves were obtained for all latexes in combination with the three studied pigment types. In accordance with the approach of Perera, this indicates that in the systems we studied, we have a good adhesion between the polymer and the pigment particles.

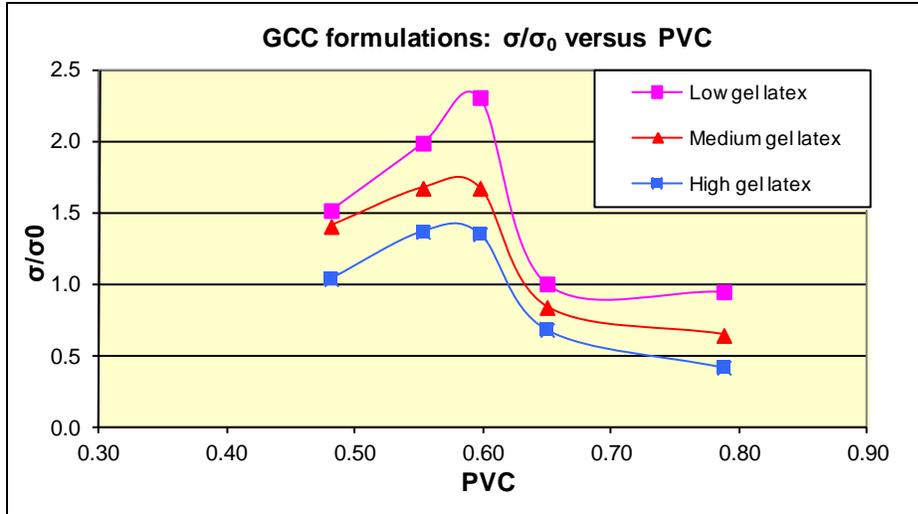


Figure 2: σ/σ_0 against pigment volume concentration for three different latexes

Having a good adhesion between polymer and pigment, it was interesting to study if there is a correlation between the polymer film strength and the strength of the corresponding pigmented film. In other words, does a higher tensile strength of the polymer film lead to a higher tensile strength of the pigmented film? We prepared pigmented films using respectively 10 and 20 dry weight parts of latex for 100 dry weight parts GCC pigment, both latex levels correspond to pigment concentration well above CPVC. The study was done with carboxylated styrene/butadiene latexes which all were film forming below 20 °C. All latexes had similar composition, except that the styrene and butadiene content was varied to obtain a range of glass transition temperatures from 5 to 19 °C. Results are presented in figure 3.

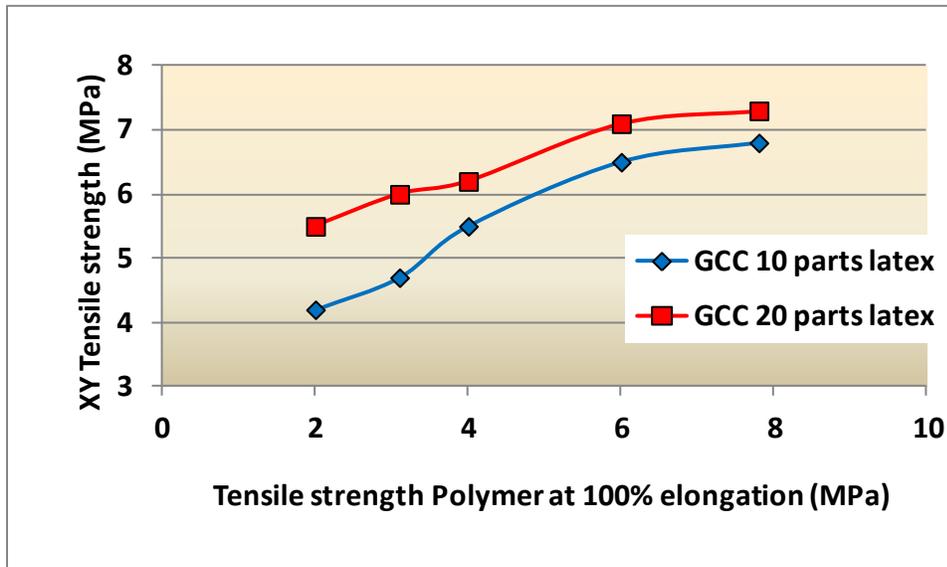


Figure 3: Relation between polymer film strength and pigmented film strength

For both levels of binder, the maximum tensile strength of the pigmented films increases when the tensile strength of the unpigmented film increases. The increase of the binder level from 10 to 20 parts reduces the void volume of the pigmented film and increases the maximum tensile strength. In addition, one can observe that there is a positive correlation between the polymer film strength and the strength of the corresponding pigmented film: a stronger polymer film leads to a higher pigmented film strength. The combination of good polymer-pigment adhesion and the correlation between polymer film strength and its corresponding pigmented film indicates that in dry state the failure is cohesive, the failure occurs in the polymer film between the pigment particles.

Correlation between pigmented film strength and coated paper binding strength. Two formulations A and B were prepared using two different latexes in combination with the same pigment slurry consisting of 80 parts Covercarb 75 (supplied by Omya) and 20 parts of Amazon Premium (supplied by Cadam). The styrene butadiene latexes used to prepare formulations A and B have a glass transition temperature of 5 °C and a particle size of 130 nm but differ by their crosslinked polymer fraction which is higher for latex A. These formulations were used to prepare on one side films for tensile strength measurements and were also used to coat paper. Binding strength of the coated paper was measured using IGT and Deltack equipments. Figure 4 shows that the maximum tensile strength of the pigmented film correlates well with the binding strength of the coated paper measured by IGT. Films based on formulation A have higher tensile strengths than those corresponding to formulation B for both binder levels. Same trend is seen for IGT binding strength measured on the coated paper samples: paper sheets coated with formulation A show higher IGT binding strength than those coated with formulation B.

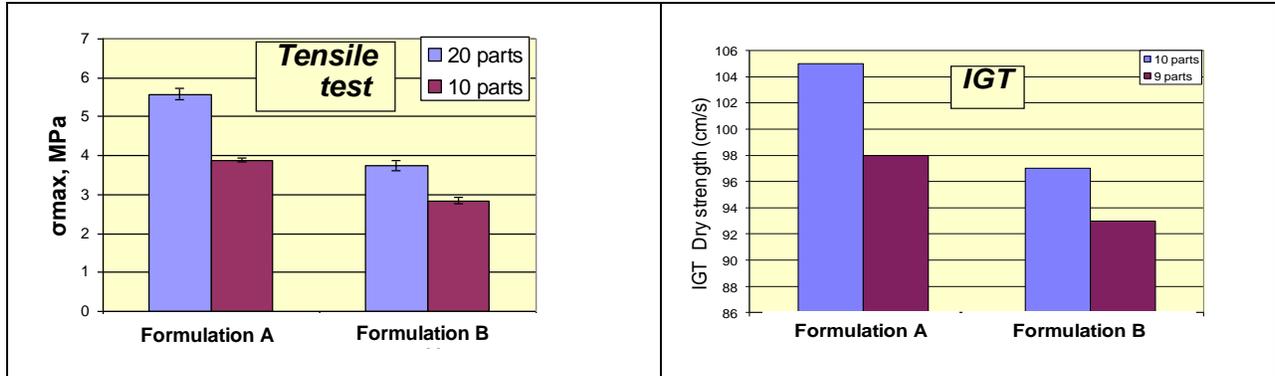


Figure 4: Correlation between film tensile strength and IGT binding strength

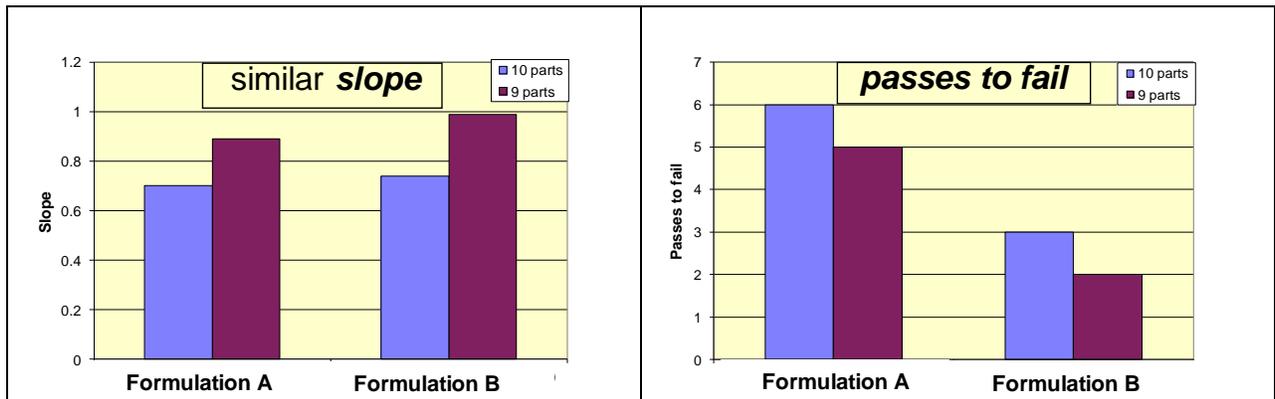


Figure 5: Correlation between film tensile strength and Deltack passes to fail

Figure 5 shows that both formulations at same binder content have similar ink coating interaction and therefore ink tack slope. The higher internal cohesion of the formulation A coating results in a greater number of passes before coating failure is observed. Both figures indicate that there is a good correlation between the maximum tensile strength measured in dry state and the binding strength measured on coated paper.

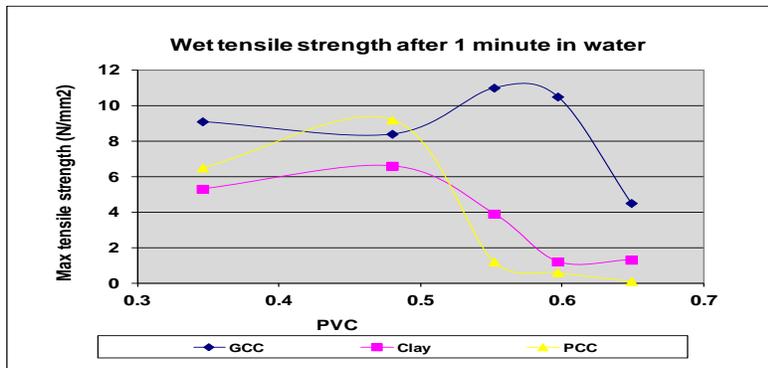
WET STRENGTH: INFLUENCE OF COATING STRUCTURE

Two latexes C and D were used to prepare paper coating formulations using GCC and 20 parts latex. Latex C has a particle size of 140 nm and a glass transition temperature of 1 °C. Latex D has the same particle size, a glass transition temperature of 5 °C and is less hydrophilic than Latex C. Dry and wet tensile strengths were measured for the pure polymer film and the pigmented films. Both latexes have similar dry polymer film strength and same dry strength of the pigmented formulations, showing again good correlation between polymer film strength and pigmented film strength in dry state. In wet state, polymer film strength of latex D is much higher than for latex C. However wet strength of pigmented films for both latexes are similar, indicating that there is no correlation between wet tensile strength of pure polymer films and the wet strength of corresponding coatings (Table 1).

Table 1: Dry and wet strength of polymer and coatings

	Tensile strength dry (MPa)		Tensile strength wet (MPa)	
	Polymer film	GCC, 20 parts latex	Polymer film	GCC, 20 parts latex
Latex C	10.8	4.3	3.1	0.9
Latex D	11.4	4.5	11.3	1.2

To get a better understanding of the factors influencing wet tensile strength of pigmented coatings, formulations based on the three different pigments GCC, clay and PCC were studied over a broad range of PVC. The formulations contained a carboxylated styrene butadiene latex (Latex E) having a glass transition temperature of 12 °C and a particle size of 140 nm. Wet tensile strength was measured after 1 minute immersion in water (figure 6). For all pigments, when increasing PVC, wet strength goes through a maximum but trends towards low values at high PVC. The reduction of wet tensile strength at high PVC is linked to the structure change of the pigmented film at CPVC from a polymer continuous film to the three phase structure containing air voids. Highest wet strengths over the full PVC range are obtained with GCC pigment. Clay containing coatings always show lower wet strength than GCC based formulations. PCC containing coatings, while close to values observed for GCC at low PVC, reach similar low wet strength values as clay based formulations at high PVC.

**Figure 6: Wet tensile strength for three pigment types**

The table 2 compares dry and wet strength measured on paper coated with formulations based on GCC and clay pigments. For same binder level, dry strength of GCC based coatings is higher than for clay coatings. With the used wet pick test, low values indicate better wet strength. So while for GCC coatings excellent wet strength was already obtained with 7 parts of binder, more than 10 parts binder were needed in combination with clay to reach excellent wet strength. These coated paper wet strength results correlate well with the observations made on the pigmented films in wet state.

Table 2: Dry and wet strength of GCC and Clay coatings

Pigment	Parts Latex	IGT	Wet pick
GCC	7	44	0
	10	49	0
	25	99	0
	50	>105	0
Clay	7	0	97
	10	23	85
	25	61	0
	50	79	0

It was interesting to evaluate the water absorption of coatings using the same latex (latex E) as above and the three pigments previously studied for pigmented film wet strength. Water absorption was measured after 15 seconds immersion of the pigmented films in water. At low PVC, water absorption is mainly controlled by the polymer continuous film: water absorption is low and shows little variation with PVC. When reaching CPVC, water absorption increases sharply in line with the increasing void volume in the pigmented film. Below CPVC, GCC and PCC coatings have a lower water absorption compared to clay based formulations. At high PVC, coatings containing PCC or clay have much higher water absorption than GCC coatings.

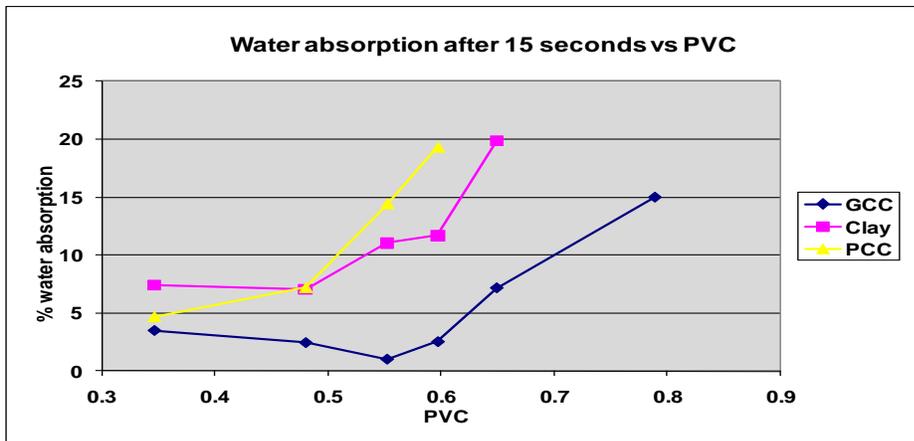


Figure 7: Water absorption after 15 seconds

A further study was measuring the water absorption kinetic as well as the rate of wet strength decrease. For films containing 20 parts of the same latex (Latex E) and the three pigment types, the water absorption and wet strength were measured after 15 seconds, 1 and 3 minutes.

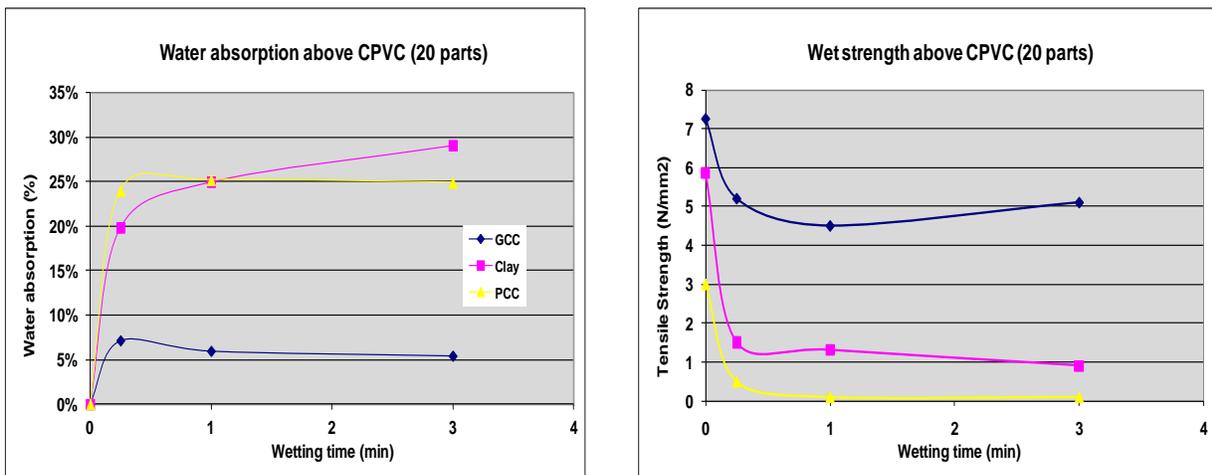


Figure 8: Kinetic of water absorption and wet strength decrease

Even with 100 micron thick pigmented films, most of the water absorption and the wet tensile strength occur during the first 15 seconds. Wet strength was highest for the GCC based coating. Wet strength of the clay formulation was much lower. Lowest wet strength was obtained for the PCC based coating.

It was interesting to compare the total coating porosity to the measured water absorption values. In this study we compared GCC and clay coatings over a broad range of PVC. Water absorption was measured after 1 minute immersion in water. The water absorption values measured as weight changes were converted to percent volume change. The total coating porosity was calculated comparing the measured dried coating density to the calculated density based on the relative weight of pigments and binder. In the calculations we assumed a GCC pigment density of 2.7, clay pigment density of 2.6 and a polymer density of 1. Figure 9 compares the water absorption and the porosity for GCC and clay coatings.

For GCC coatings, porosity at low PVC is in the range of a few percents. Water absorption is low and is controlled by the polymer. When increasing PVC, porosity increases very rapidly. Water absorption also increases but the volume occupied by the water remains lower than the total porosity, indicating that not all pores are filled with water. For clay coatings, a low porosity is observed at low PVC, but the water absorption is higher than the porosity and higher than the water absorption of the pure polymer film. This might be due to the more hydrophilic character of clay pigments. The high water absorption at low PVC was also confirmed by measuring the sample dimension

changes. When PVC increases, porosity increases and water absorption remains higher than the porosity values, but follows the same increasing trend: it seems that all voids are accessible to water.

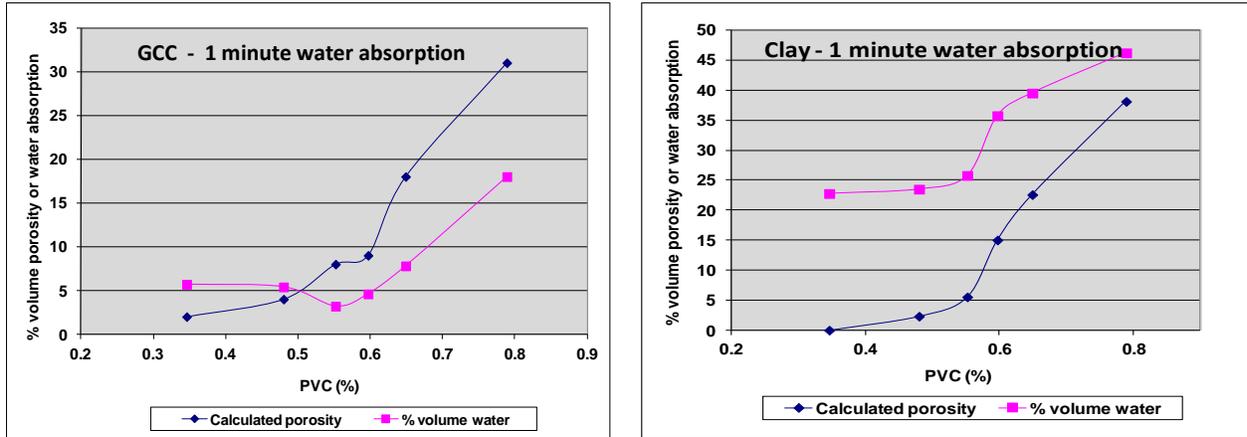


Figure 9: Water absorption and coating porosity

WET STRENGTH: INFLUENCE OF PIGMENT-POLYMER ADHESION

Tensile strength ratios as indicative of polymer pigment adhesion. Pigmented films were prepared using respectively GCC and clay pigments and covering a broad range of PVC. Latex F with a particle size of 130 nm and a glass transition temperature of 9 °C was used as binder. Dry and wet strength after 1 minute immersion in water were measured. To assess the pigment-polymer adhesion we used the approach described by Perera. For dry strength, we measured the maximum tensile strength of the polymer (σ_0) and the pigmented films (σ) corresponding to the different pigment volume concentrations. The ratio σ/σ_0 versus pigment volume concentration is indicative of the adhesion between pigment and polymer in dry state. In a similar approach, we measured the maximum tensile strength of the polymer film ($\sigma_{\text{latex wet}}$) and the maximum tensile strength of the pigmented films (σ_{wet}) after immersion in water. The evolution of the ratio $\sigma_{\text{wet}}/\sigma_{\text{latex wet}}$ was taken as an indicator of the adhesion between polymer and pigment in presence of water.

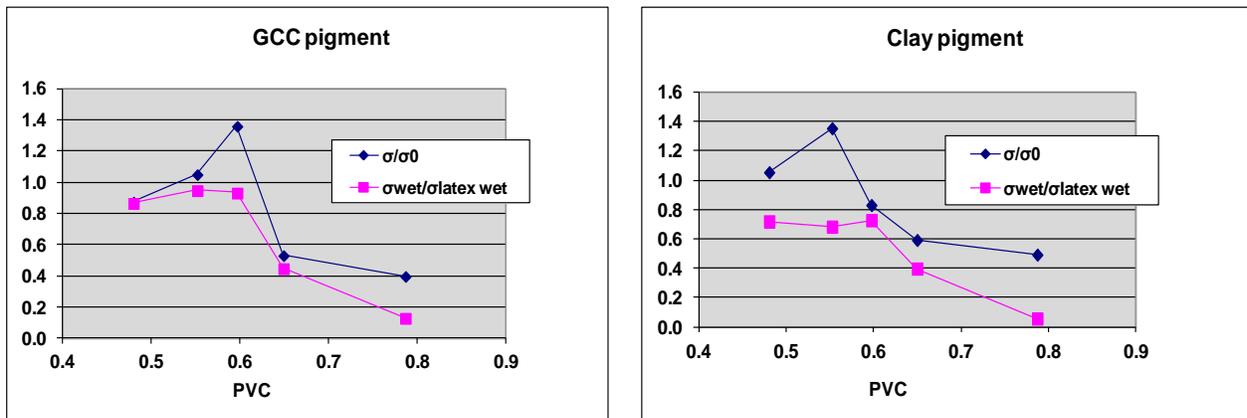


Figure 10: Tensile strength ratios as indicative of polymer pigment adhesion

As described previously, for dry strength we observe an initial reinforcement ($\sigma/\sigma_0 > 1$) until a maximum value of σ/σ_0 for the CPVC. This reinforcement is indicative of a good adhesion between pigment and polymer. For film strength after immersion in water, the ratio $\sigma_{\text{wet}}/\sigma_{\text{latex wet}}$ is smaller than 1 and there is no pronounced maximum at CPVC. The reinforcement disappears indicating weaker adhesion between polymer and pigment in presence of water. The impact of water is even more pronounced for films containing the clay pigment: the ratio $\sigma_{\text{wet}}/\sigma_{\text{latex wet}}$ is only 0.7 for low PVC. The importance of adhesive failure in presence of water has previously been reported by Husband (7).

Impact of latex carboxylation. Two styrene-butadiene latexes having same particle size (140 nm) and glass transition temperature (12°C) were synthesized using two levels of acrylic acid. Pigmented films covering a broad range of PVC were prepared using GCC as pigment. The maximum tensile strengths were measured in dry state and after 1 minute immersion in water.

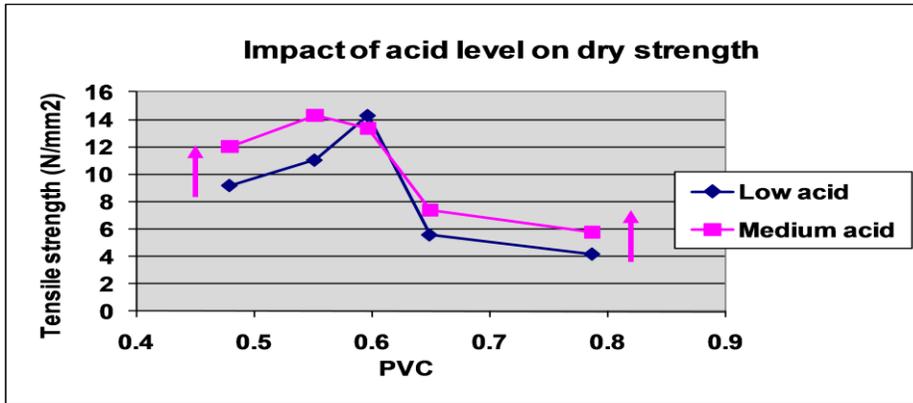


Figure 11: Impact of latex carboxylation on dry strength

In dry state (figure 11), increasing the amount of acrylic acid in the latex increased the maximum tensile strength both below and above CPVC. This increase results from the combination of two factors: a higher tensile strength of the polymer film when increasing the latex carboxylation and a stronger interaction between the carboxylic groups on the surface of the latex particles and the pigment surface.

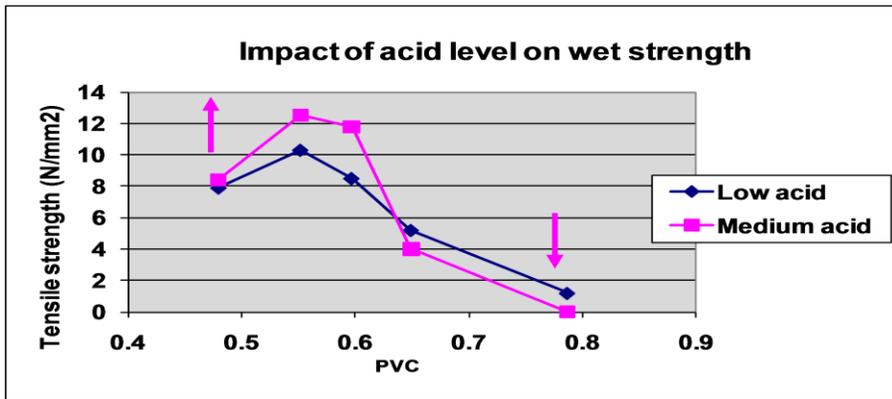


Figure 12: Impact of latex carboxylation on wet strength

After immersion in water for 1 minute, the maximum tensile strength increases with increasing carboxylation for pigmented formulations below CPVC where the polymer constitutes the continuous phase. On the other hand, above CPVC where the polymer no longer forms the continuous phase the maximum tensile strength after immersion in water decreases when increasing the latex carboxylation level. Higher carboxylation increases the water sensitivity of the pigment polymer interface, thus reducing the wet adhesion between pigment and polymer.

Impact of pigment dispersant. Dispersants used to prepare pigment slurries are often low molecular weight acrylic acid based polymers. They adsorb onto the pigment particle surface creating a more complex interface, pigment-dispersant-polymer. The presence of the water soluble dispersant might impact the water sensitivity of the pigmented films and their wet tensile strength. An experiment was set up to study the impact of dispersant level on dry and wet strength of pigmented films.

To the PPC slurry we added additional PCC pigment until reaching half the initial dispersant level based on total pigment content. Pigmented films were prepared with this modified PCC slurry and the original PCC dispersion using latex E as binder. Their maximum tensile strengths were measured in dry state and after immersion in water for 15 seconds.

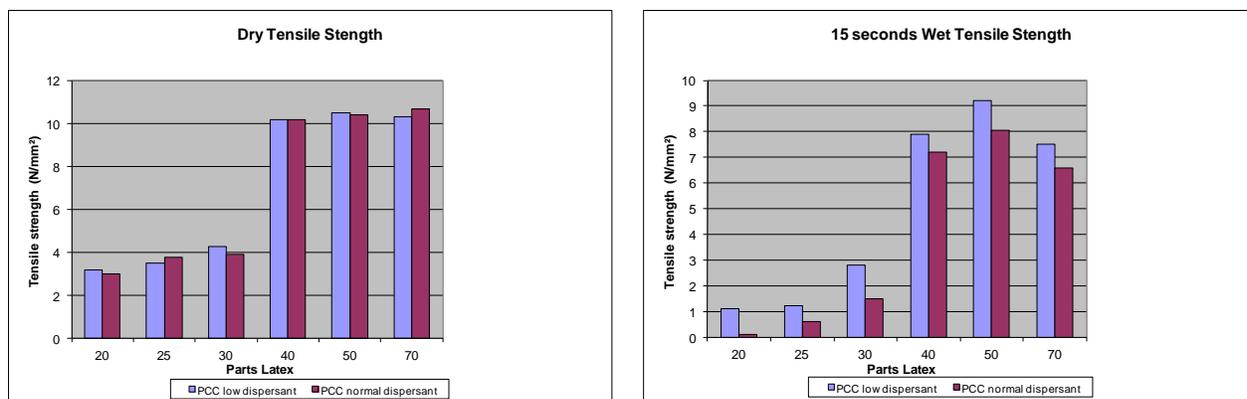


Figure 13: Impact of dispersant on dry and wet strength

Reducing the dispersant level to half of the initial value had no impact on dry tensile strength (Figure 13). However the dispersant level reduction significantly increased the pigmented film maximum tensile strength after immersion in water for 15 seconds and reduced the water absorption of the pigmented films. Lowering the dispersant amount present at the pigment particle surface increased the interactions between the polymer and the pigment, resulting in better adhesion between polymer and pigment in wet state.

CONCLUSION

Studying the dry and wet mechanical properties in tensile mode and the water absorption kinetics of unsupported pigmented films covering a broad range of pigment volume concentration provided insights into the mechanisms controlling dry and wet strength of pigmented coatings. The results obtained with the unsupported pigmented films showed good correlation with the lab print tested dry and wet strength measurements of coated paper. The impact of coating structure, pigment-polymer adhesion and polymer film cohesive strength on dry and wet strength could be identified. Experiments have shown that in dry state good adhesion between pigment and polymer is achieved and that the strength of pigmented films correlates with the strength of the polymer film: cohesive failure dominates in dry state. Water reduces the pigment-polymer adhesion, leading to a major contribution of adhesive failure in wet state. The presence of dispersant on the pigment surface increases the water sensitivity of the pigment-polymer interface and reduces wet strength.

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