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Film formation of latex in dry coating films

Master Thesis of 20 credit points
Surface Treatment Technology

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Abstract
The objective of this master thesis was to investigate the possibility to measure the gain in stiffness of the dry coating due to film formation of latex with a Dynamic Mechanic Thermal Analyzer (DMTA). This could tell when and to which extent the latex forms a film after the drying process.

Two latices with different \( T_g \) was used for the experiments, one with a \( T_g \) of 36°C, denoted hard, and the one with a \( T_g \) of 8°C, denoted soft. The hard latex was used to make coating samples that would not form a film when dried at room temperature and the soft latex was used as a reference to the coating with hard latex since it would form a film at room temperature.

It was shown that a gain in stiffness due to film formation of latex in coating can be measured with a DMTA. It was also shown that that the film forming of latex in coatings depend on time, temperature and the history of the sample. Further investigations were carried out to try to determine the time for film formation to be completed at a certain temperature. These investigations showed that this type of trials cannot be carried out in a DMTA directly since the stiffness seemed to increase monotonically during a very long time. This might be due to the rearrangements in the pigment structure that might affect the gain in stiffness. Therefore, a method involving oven curing was developed. Only one series of test were performed with this method due to lack of time but the method showed promising results.
**Sammanfattning**

**Filmbildning av latex i torra bestrykningsfilmer**

Syftet med detta examensarbete var att undersöka möjligheten att använda en Dynamic Mechanic Thermal Analyzer (DMTA) för att mäta ökningen av styvhet som följd av filmbildning av latex i en torr bestrykning.

Två olika latexer användes för experimenten, en med $T_g = 36^\circ$C (hård) och en med $T_g = 8^\circ$C (mjuk). Den hårdare latexen användes för att kunna göra tester på prover som ännu inte filmbildat när de torkat vid rumstemperatur och den mjuka latexen användes för att göra referens prover mot bestrykningen med hård latex.

1. Introduction

1.1 Coating

Paper and paperboard are coated to improve the surface properties such as gloss, brightness, opacity and printability. The coating layer consists of pigment particles that are bond together by latex bridges, giving a porous structure of the coating layer. Most coated products are used for printed magazines and consumer packages, where demands in print quality are high.

During the printing process with off-set, the board is subjected to a high mechanical stress at the exit of the nip and after the coated paper product has been printed, it usually goes through subsequent operations like cutting, creasing or folding. During these operations, the coating is exposed to mechanical stress. Resistance of mechanical stress is therefore a coating characteristic of great importance.

1.1.1 The coating process

The coating is applied on the paper or paperboard in a thin layer either in connection to the paper machine, on-line, or in a separate unit, off-line. The most common types of coating system is the blade coater where a large amount of coating colour is applied to the paper and the surplus is scraped off by a blade. The solids content on the coating applied is in the range 62-67 percents. The blades that are used to scrape off the excessive amount of coating are made of steel and some of them are equipped with a ceramic tip that makes them last longer. After the coating is applied it passes through a dryer, the dryers that are used are IR-dryers, hot air driers and cylinder driers.

The coating colour is added to the paper by an applicator. Common applicators are jet applicator, roll applicator and short dwell time applicator (SDTA). Roll applicator is the most widely used applicator in the paper industry. The advantage of roll applicators is that a bad formation of the base paper is less critical for the roll applicator and it is therefore best suited when a thick coating is desired. Disadvantages with the roll applicator is for example film splitting phenomena at high speeds that can hurt the coating layer so much that these effects will remain after the metering blade. The roll application also exert a higher pressure on the substrate compared to jet and SDTA applicators where the pressure is close to atmosphere. Rewetting of the base paper caused by the long dwell time can result in web breaks. Coat weights below 6 to 7 g/m² are generally difficult to achieve with roll applicators. The SDTA applicator are better suited for low coat weights and weak sheets, because it does not rewet the paper as much as other applicators and it requires lower blade loads to achieve a certain coat weight. The time between the applicator and the blade is short for SDTA compared to roll and jet applicators, leading to a short time for the paper to absorb the coating colour before the blade. One disadvantage with the SDTA applicator is streakiness i.e. the coat weight profile is uneven. Jet applicator is the newest applicator introduced to the market. Due to increasing machine speed the quality are more difficult to maintain with the other
mentioned applicator techniques. The jet applicator was design to eliminate the disturbing film split as well as the short dwell streakiness.

The last stage to perform a fine coating is to calender it. The reason to calender the coating is to make the surface of the coating smooth and glossy. If the surface is smooth the printing colour will distribute more uniformly which will create a sharp print. The main difference between calenders is weather a hard nip or soft nip is used. In a hard nip, two steel cylinders is used while a soft nip uses at least one polymer covered roll.

1.1.2 Coating colours
The coating colour consists manly of pigment, binder and water. A high dryness of the coating is usually the aim because it will give a short drying time and low rewetting of the paper it is added to. The viscosity becomes high with a high dryness which demands a higher blade load. Some benefits with a high dryness on the coating are that the energy consumption for drying is lower and it is easier to make thick coating layers. Disadvantage with high dryness is that it can give runnability problems such as scratches and web break.

1.1.3 Pigment
The pigment is the main component in the coating colour. Pigments in coating colours are white and together with the binder they make the coating porous which is important for the brightness and opacity. Important pigment properties are refractive index, particle size and particle size distribution. A high refractive index and a small particle size give many light scattering surfaces leading to a high opacity. The particle size must, however, exceed the wavelength of visible light (around 400 nm) in order for scattering to occur. The particle size distribution governs the pigment packaging and therefore the porosity of the coating layer. A broad distribution gives a dense coating because the fine particles are located in the space between the coarser particles whereas a narrow distribution with low percentage of fines gives a porous coating due to the fact that there are no small particles to fill up the voids between the larger pigment particles.

The pigment used in the coating colour is usually a Kaolin clay or ground calcium carbonate. Some other pigments, such as talk or titanium dioxide, exist but are not so frequently used in paper coatings. Kaolin clay is a weathering product of feldspar from gneiss and granite. In clay the main mineral is kaolinit and it is a platy mineral, therefore it gives good cover ability. Ground calcium carbonate (GCC) originates from three different rocks: chalk, limestone and marble. It has a significant higher brightness than clay but it does not give the same good coverage as clay because of its spherical shape.

1.1.4 Binder
The main functions of binder are to bind the pigment particles together and to bind to the substrate. There are two different types of binders, water soluble binders and latex binders. The most commonly used latex binder is Styrene-Butadiene followed by styrene-n-butyl acrylate (SA-latex) and Polyvinylacetate (PVAc). In addition to its binding properties the water soluble binder is also a thickener and water retention agent. The later properties are
usually the most important for the water soluble binder and it is therefore often called thickener or water retention agent. If a latex binder is used, a co-binder is usually added in order to control the water retention. The most commonly used water soluble binders are starch and the sodium salt of carboxymethylcellulose (NaCMC). Polyvinyl alcohol (PVA), alkali swellable polyacrylates and associative thickeners are other less used water-soluble binders.

2.1.5 Additive chemicals

Additive chemicals are a group of chemicals that are added to receive certain properties. Dispersants are added in order to reduce flocculation, biocides are added to prevent biological growth and wet strength agents are added to make the coating withstand rewetting during printing. Lubricants are added to save calendar rolls from wearing and optical brighteners might be added to increase brightness of the coating.

1.2 Film formation of latex

The latex binder is a colloidal dispersion of spherical polymer particles and looks like a white milky substance because of the polymer particles ability to scatter light when dispersed in water. The latex is very sticky and the adhesive properties or stickiness provide the binding strength that is desired in paper coatings. The average particle size in the latex is between 1000Å to 3000Å. To understand how small the latex particles are one could ponder the example that if the particles are 2000Å a cubic centimetre would contain $10^{12}$ particles (Klun 1988). A typical dryness for the latex is 50 weight percent polymer solids concentration. The particles are made through free radical emulsion polymerization. This makes it possible to control the particle size, composition, molecular weight and degree of cross linking. The development of emulsion polymerization occurred over the period from 1930 to 1950 (Klun 1988).

The colloidal dispersion has to be stabilized because the van der Waals forces between the particles will make the system coagulate if no stabilizer is added. The function of the stabilizer that is uses either electrostatic repulsion between the latex particles or steric stabilization by using non-ionic macromolecules (Klun 1988). The spherical latex particles contain hundreds of polymer chains of different length and it is often constructed of two different types of polymers for example styrene-butadien (SB-latex), styrene-n-butyl acrylate (SA-latex) or polyvinylacetate (PVAc latex). Most of the PVAc latex is homopolymer latices and the SA and SB lattices are copolymers.

The latex polymer core is hydrophobic and it is therefore surrounded by a hydrophilic shell making it soluble in water. To receive different properties of the latex, functional groups are often added to the latices. This is done with monomers containing carboxylic acids (-COOH); anides (-CONH$_2$), hydroxyl groups (-OH), etc., and are modified with monomers such as acrylonitrile (VCN) and methyl methacrylate (MMA) (E. Lehtinen 2000). One of the most important properties is the latex glass transition temperature ($T_g$). $T_g$ is the temperature when softening of the polymer occurs, this is manifested by a large drop in E-molulus. The physical state below $T_g$ is called the glassy state, which is characterized as the temperature when the
polymer chains no longer have any freedom of motion, and when it is heated over \( T_g \) it goes from the glassy state to the rubbery state (Klun 1988). This is illustrated in Figure 1.

The system Styrene-Butadiene is one of the few compatible copolymer systems resulting in one single and well defined \( T_g \). Butadiene makes the latex soft and styrene makes it stiff, therefore the latex \( T_g \) is controlled by the ratio of styrene to butadiene. Due to the fact that the SB latex polymer chain is a co-polymer of styrene and butadiene the SB-latex \( T_g \) are very stable, i.e. styrene and butadiene monomers are polymerised in the same macromolecule which will give a even distribution between the styrene and butadiene within the system. In contrast to Styrene-Butadiene, some PVAc lattices consists of a mix of different macromolecules where each of the macromolecules are built up of only one type of monomer which might result in an uneven distribution of the different macromolecules that will make it difficult to control the \( T_g \).

\[ \text{log} G' \ [\text{Pa}] \]
\[ T \ [\text{°C}] \]

Glassy state

Rubbery state

\( T_g \)

Figure 1. The modulus as a function of temperature.

Gel content or cross linking is defined as the amount of chemical bonds between polymer chains. This occurs when the content of the solids is high enough and the latex is heated above \( T_g \) (Klun 1988). Minimum Film Formation Temperature (MFFT) is the minimum temperature at which latex will form a continuous film. Most of the lattices have a MFFT that is higher than the lattice \( T_g \). Klun (1988).
Figure 2. Schematic illustration of the film formation process.

The general opinion of how film formation occurs is that when the latex has a volume fraction of 0.5 the particles move freely, but as the drying process starts and water evaporates the movements of the particles becomes more limited and collision among the particles occurs more often. When the volume fraction reaches 0.70-0.75 the movement of the particles decreases because they are in contact with each other and the remaining water is filling up the void between the particles, demonstrated as stage 1 in Figure 2. At this point or shortly thereafter the particles may deform to a honeycomb pattern due to surface and capillary forces, illustrated as stage 2 (Vanderhoff and Bradford 1963). In stage 3 the latex undergoes ageing or coalescence which means that the polymer chains are starting to cross the interface of the particles which leads to a gain in strength. Stage 4 shows a fully coalesced film where the functional groups that created the hydrophilic shell now are scattered in the structure. How extensive the film formation is depends on the history of the coating i.e. how intense the drying is and at which conditions it is kept after it has dried considering temperature and time (Carlsson et al. 2005). In some cases the latex particles create a continuous film and in some cases they retain their spherical form during the drying process which will result in a friable discontinuous film (Vanderhoff and Bradford 1963).

If the film is cast at a temperature well above the MFFT, deformation and cohesion of the latex particles can take place and formulate a transparent film. If the film is cast below the MFFT the particles will not deform and a discontinuous opaque film is formulated. The film becomes opaque because of the presence of voids in the film which are capable of scattering light. A compromise between these two conditions is desired due to the fact that if the particles deform too much it will result in a permanently tacky film. P.A. Steward, et al (2000). If the latex is too hard, it will be porous and fragile and will not meet the demands of mechanical strength that are necessary to keep the pigment particles together and to bind them to the paper or paperboard. The latex that creates a continuous strong film is characterised as soft lattices and the ones that results in a discontinuous film is called hard lattices (Vanderhoff and Bradford 1963).
1.2.1 Theoretical aspects of film formation

The history of evolving the theory of film formation started in 1951. Dillon et al. (1951) assumed that the driving force for film formation is provided by the decrease in surface tension force as the surface area reduces when the particles coalesce. To describe the theory they applied a model developed by Frenkel (1945), cf. Figure 3.

![Figure 3. model of two coalescing spheres as proposed by Frenkel (1945).](image)

The coalescence is of the latex film was described by Frenkel (1945) as:

\[ \theta^2 = \frac{3 \gamma t}{2 \pi r \eta} \]  

[1]

Where \( \theta \) is the half angle of coalescence shown in Figure 3, \( r \) is the radius of the sphere, \( \gamma \) is the surface tension of the latex, \( \eta \) is the viscosity of the latex and \( t \) is the time. The properties \( \gamma \), \( \eta \) and \( t \) do not vary between particles and such variations are therefore negligible. Dillon et al. (1951) used an electron microscopy to determined \( \theta^2 \) as a function of \( r \) and found that \( \theta^2 \) is proportional to \((1/r)\). They concluded that the coalescence of latex particles occurs due to viscous flow driven by the surface tension forces. Brown (1956) presented a capillary force theory five years later:

\[ F_s + F_c + F_{vdW} + F_g > F_e + F_r \]  

[2]

Where the left hand of the equation describes the driving forces for particle deformation and the right hand describes the forces resisting particle deformation. The different terms on the left hand describes the following functions: \( F_s \) is the force produced of the negative curvature of the polymer surface, \( F_c \) is the capillary forces from the water in the interstitial between the particles during the period of water loss, \( F_{vdW} \) is the force resulting from the van der Waals forces between the particles and \( F_g \) is the gravitational force. The different terms in the right hand hand describes the following functions: \( F_e \) is the electrostatic and steric repulsive forces and \( F_r \) is the elastic resistance of the particles. Brown’s (1956) idea was that the driving forces had to be greater than the resisting forces if coalescence of the particles would take place. In a
stable emulsion, i.e. $F_c > F_{vdW}$, and if $F_s$ and $F_g$ are negligible eq. 2 can be reduced to eq. 3 indicating that capillary forces are the driving force for coalescence.

$$F_c > F_r \quad [3]$$

Brown (1956) used Laplace’s Principle of capillary pressure to a system of three contiguous spheres together with Hertz contact theory and created an equation that described how film formation occurs:

$$G \left( \frac{35\sigma}{R} \right) \quad [4]$$

where $G$ is the elastic shear modulus of the polymer and $\sigma$ is the surface tension of the water in the capillary. Some imperfections were found in this theory and an attempt to correct them where performed by Mason (1973):

$$G \left( \frac{166\sigma}{R} \right) \quad [5]$$

An other theory is that film coalescence depends on the pressure generated by interfacial tensions between latex and water (Vanderhoff 1966). This theory implies that as the water evaporates, the particles stabilizing interfaces will get in contact with each other. As the water continues to evaporate the pressure on the particles will increase and result in rupture of the interfaces and a polymer to polymer contact will be established. This process is called the wet sintering theory. Sperry et al. (1990) performed measurements on minimum film temperature, both on wet and pre dried latex film to distinguish water evaporation and coalescence during dry conditions. They came to the conclusion that the driving force for coalescence is van der Waals attractive forces and polymer-air surface tension. Ecersley and Rudin (1990) concluded that both capillary and surface forces act together to promote coalescence where the capillary forces are important to rupture the particle to particle boundary which results in a polymer to polymer diffusion. The capillary forces are, in this case, complemented by interfacial forces to create a permanent deformation of the particles.

1.2.2 Mechanical behaviour of the latex film

Latex is a viscoelastic material and since the latex builds bridges between the pigment particles in the paper coating, the paper coating possess viscoelastic properties (Kan et al. 1996). Viscoelasticity means a material that is an intermediate between a completely elastic material and a completely viscous.

Dynamic Mechanic Thermal Analyzer (DMTA), also mentioned under the names Dynamic Mechanic Analyzer (DMA) or Dynamical mechanical spectroscopy (DMS), has been used to determine the viscoelastic properties of paper coatings (Kan et al. 1996, Prall et al. 2000, Mikkilä et al. 2001, Carlsson et al. 2006). The DMTA expose the materials to an oscillation strain ($e$) at different temperatures and measures the response of the material that is called
stress (s). Some of the data that can be received from measurements with the DMTA is storage Modulus ($E'$) and the loss Modulus ($E''$) that can be presented as the loss factor (Tan $\delta$), these are both a product of the stress and strain, shown in (eq. 6) and (eq. 7).

\[
E = \frac{\sigma}{\varepsilon} \quad [6]
\]

\[
\tan\delta = \frac{E''}{E} \quad [7]
\]

Prall et al. (2000) introduced a method to determine the viscoelastic behaviour of thin free coating films in a tensile mode with the DMTA. With this method they evaluated how different types of pigments (Clay, GCC and Polystyrene) affect the modulus of the coating, depending of the pigment volume concentrations. They used two types of latices and the difference between them was the rate of carboxylation. The $T_g$ of the latices was about 1°C and the samples was oven cured for 1 minute at 80°C to make sure that the latex in the samples had coalesced. After making temperature sweeps between -50°C to +150°C they concluded that the polystyrene pigment only gave a reinforcing effect above the latex $T_g$ and below the pigment $T_g$ (if a polystyrene pigment was used). GCC pigments gave a reinforcing effect over the whole pigment concentration range and clay coatings showed a decrease in modulus in the temperature range 5°C to 25°C. This behaviour was reversible for high pigment volume concentrations. The highest modulus for the clay coating was obtained when the pigment volume concentration was at 50 percent. They also concluded that the modulus of the less carboxylated latex decreased more rapidly with increasing temperature than the latex that was carboxylated to a higher extent.

Kan et al. (1996) tested latices with different $T_g$ (+12°C, 3°C and 25°C) and different volume fractions of latex in paper coatings. To assure that the latex in the coating had coalesced, the coating samples were formed and dried in Teflon molds at 40°C. DMS of the samples were determined using torsional rectangular geometry. They concluded that a lower $T_g$ gave a higher modulus both over and below the latex $T_g$. They attribute this to porosity in the coating layer, i.e. the coating consisting of the latex with lower $T_g$ gives a coating with a less porous structure. They also concluded that an increase of the volume fraction of latex resulted in an increase of modulus at temperatures below latex $T_g$ and a decrease of the modulus at temperatures over the latex $T_g$. They also found that the viscoelastic properties of the coating correlated with the compressive behaviour of the coated paper during calendaring and the bending behaviour in Gurley stiffness testing.

Mikkilä et al. (2001) tested latices with different $T_g$ (-7°C, 20°C and 45°C). They performed temperature sweeps between -40°C and 140°C with a DMTA using a tree point bending system. The aim of their work was to explain the deformation during calendaring and its relationship with gloss. They concluded that DMTA analysis could not do this alone. One interesting result in their DMTA experiments was that the coating with the latex that had a $T_g$
of -7°C increased in stiffness at temperatures above the latex $T_g$. They stated that the increase could depend on a denser packing of pigments or that the crosslinking of the latex would increase due to higher temperatures.

Carlsson et al. (2005) studied how the mechanical properties of the coating are affected of calendaring and storing at different time and temperatures. They tested latices with different $T_g$ and different gel contents and measured the binding and wet binding strength of the coating. They also used AFM images to illustrate the film formation of the latex in the coating. They discovered that the high temperature calendaring clearly improved the strength of the coating when the coating strength was not fully developed during drying. In their study they showed that the strength build up depended to a great extent on the temperature that the latex was stored in. Storing the samples for two months at room temperature gave no clear increase of the strength, however storing samples at elevated temperatures (60°C and 80°C) for one or four hours increased the strength of the coating significantly. They concluded that the film formation occurred in the calender nip due to the temperature from the heated roll.

Prall et al. (2000), Kan et al. (1996), Mikkilä et al. (2001) and Carlsson et al. (2005) all used the Williams, Landel and Ferry’s (WLF) equation for time temperature superposition to estimate the viscoelastic properties that corresponds to the process conditions. This is done because the process conditions are not easy to reproduce in laboratory conditions due to the short residence time in the calender nip.

The cross linking process has been studied using two new methods to measure the degree of cross linking in coatings (Hellgren, et al 2001). Gradient At Right angles to the Field Magnet Resonance Imaging (GARField MRI) provides quantitative measurements of concentration and molecular mobility as a function of time and position (i.e. Depth) in the coating. Quartz Crystal Microbalance (QCM-D) can monitor mass gain, due to oxygen uptake, and mass loss, due to chemical reactions and evaporation. It measures the viscoelasticity of thin coatings during dynamic processes, such as crosslinking. They concluded that oxygen inhabitation strongly slows down the cross linking rate, and that the turbidity of the latex effects leads to a decreased rate of crosslinking near the substrate/film interface. These methods are applicable to measure how the film forming occurs through the structure and how it is affected by different process conditions. Testing with a DMTA has earlier been used to characterise the curing of rubber-to-metal bonding agent and the technique was found reliable (Persson et al. 2002). Due to the fact that gain of strength due to cross linking of rubber can be measured using DMTA it seems likely that DMTA can be used to measure the time/temperature influence of film formation of latex in paper coatings.
2. Purpose

The objective with this master thesis is to investigate the possibility of measuring the gain in stiffness of the dry coating with a Dynamic Mechanic Thermal Analyzer (DMTA). This could tell when and to which extent the latex forms a film in the coating, i.e. when the latex polymer bind together with the pigment particles to create a network that is resistant to mechanical stress. This could give extensive knowledge about how the different properties of the latices affect the coatings mechanical properties, which in turn could give the benefit to choose the latex characteristics to be more specific for a specific type of coating. It could also make it easier to optimise process parameters to perform a refined coating and reduce the energy consuming in the production. The work is supported by two hypotheses.

The first hypothesis is:

- The stiffness of the coating layer increases when the latex is film forming and that this increase in stiffness can be measured with DMTA.

The second hypothesis is:

- Latex film forming is influenced both of time temperature and the history of the sample.
3 Materials and methods

3.1 Material
Two different pigments were used; one clay and one Ground Calcium carbonate (GCC). The clay pigment was Caovit with a dryness of 70.16 % supplied by the company, Thiele Nordic AB and the GCC pigment that were used was Hydrocarb 90 with a dryness of 78.53 % supplied by the company, Omya AB.

Two latices from EKA polymer latex with different $T_g$ was used. The first latex had a $T_g$ of 36°C and a dryness of 51.20 %, and the second latex had a $T_g$ of 8°C and a dryness of 50.00 %. A co-binder, finfix 10 from noviant OY, Finland, was also added.

The composition of the coatings that were prepared is presented in Table 1. The coatings were prepared in the following order, first the clay or GCC were weight up then the latex were weight up an added to the Clay/GCC under stirring. The mixture was stirred for 5 minutes thereafter the amount of CMC were weighted up and added to the mixture. After that the mixture was stirred for 20 minutes and then the pH was adjusted to 8.5. The coating were stored for 24 hours in a refrigerator at 5°C, then the coating was filtered to remove lumps and air bubbles before any draw downs were made.

<table>
<thead>
<tr>
<th>Coating Nr.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td>GCC</td>
<td></td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Clay</td>
<td>100</td>
<td>100</td>
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<td></td>
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<tr>
<td>CMC</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Latex, $T_g$ = 36 (hard)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Latex, $T_g$ = 8 (soft)</td>
<td>10</td>
<td>10</td>
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</tbody>
</table>

3.1.1 DMTA
The DMTA that was used was a DMA/SDTA861e with the software Mettler Toledo STAR® System from Mettler Toledo. A picture of the DMTa is shown in Figure 4.
The DMTA tests were performed in shear mode. The samples are mounted in pairs between the three pucks. When the samples are in place the three pucks are fixated with two screws, cf. Figure 5, force or displacement is then applied to the middle puck leading to a shear force on the samples. For the trials, a maximum displacement or force is given and the DMTA will choose whichever of these values that is reached first. The force and displacement are registered during the measurement and the results are presented in terms of Storage modulus ($G'$) and phase angle ($\tan\delta$).
3.2 Methods

3.2.1 Draw downs
To make samples that would fit in the DMTA fixture, draw downs of coatings were made on aluminium foil. Aluminium foil was chosen since it has a smooth surface and due to the fact that it is easy to remove from the dry coating. To receive a thick, coating the draw downs were made for hand with an adjustable doctor, cf. Figure 6. To make the draw downs as even as possible the aluminium foil was taped to a glass plate before the coating was applied with the doctor.

After the draw downs were produced, they were left to dry in room temperature (23°C) for 24 hours. The aluminium foil was removed from the coating and pieces were cut out with a scalpel. The thicknesses of the dried samples were between 0.7 – 1.0 mm. At first, pieces of approximately 2.5 mm² were cut out but since the draw downs bended a bit during drying, the size of the samples were reduced to approximately 1.3 mm² after the pre-trials. To prevent the samples to coalesce before they were tested in the DMTA the samples were stored at a temperature of 5°C.

![Figure 6. Picture of the adjustable doctor that was used to make draw downs.](image)

3.2.2 DMTA Method 1
The trials performed using method 1 were the first trials and should be considered more or less as pre-trials, some modifications were made after these trials in order to improve the accuracy of test data. The samples were exposed to a force of 1 N at a frequency sweep from
0.1 Hz to 1 Hz. During the trials, the maximal displacement was set to 10µm. After the first measurement, the samples were cured in an oven at 105°C for 15 min, and thereafter the same DMTA test was performed once again. This test was performed on coating 2 and 3.

3.2.3 DMTA Method 2
The substrate temperature was heated with a rate of 4°C per minute and at the same time it was exposed to a shear force of 5 N at a frequency of 1 Hz. The maximum displacement in the substrate was set to 10 µm. Coating 2, 3 and 5 that contained latex with $T_g$ on 36°C was tested in the temperature interval of 0°C to 120°C and Coating 1 and 4 that contained latex with $T_g$ on 8°C was tested in the temperature interval of -28°C to 92°C.

3.2.4 DMTA Method 3
The substrates were exposed to a shear force of 5 N at a frequency of 1 Hz. The maximum displacement in the substrate was set to 10 µm. The substrate was heated to a target temperature with a heating rate at 2°C/min and then at the temperature was kept constant for a time period between 1 hour and 16 hours, depending on expected time for film formation at the target temperature. The different constant temperatures varied between 32°C and 110°C. This test was performed on coating 2, 3 and 5.

3.2.5 DMTA Method 4
In this method coating 2 were cured in an oven at 70°C and the samples were taken out at different times during a time period of 159 hours. The samples were then tested with two temperature sweeps as described in DMTA method 2. One sample was also cured for 24 hours at 105° and than tested with two temperature sweeps as described in DMTA method 2.

3.2.6 DMTA Method 5
In DMTA Method 5, two temperature sweeps were performed on coating 2 in a temperature interval of 0°C to 120°C. The heating rate was varied between 0.25°C/min to 12°/min.
4. Results

4.1 Pre-trials in the DMTA

Pre-trials were performed in the DMTA to evaluate the first hypothesis. During these trials Method 1 was used to measure if the gain in stiffness could be detected in coating 2 and coating 3. Coating 2 was based on Clay pigment and coating 3 was based on a GCC pigment and both coatings contained the harder latex. The results from the trials are presented in Figure 7 and Figure 8, for coating 2 and coating 3 respectively.

![Figure 7. Shows the gain in modulus on 4 samples of coating 2 (clay with hard latex after oven curing with method 1.)](image)

![Figure 8. Shows the gain in modulus on 6 samples of coating 3 (GCC with hard latex) after oven curing with method 1.](image)
Three out of four samples with coating 2 showed a gain in stiffness after oven curing, cf. Figure 7, and four out of six samples with coating 3 showed a gain in stiffness, cf. Figure 8. One of the samples also showed a large gain in stiffness, around 90%.

**4.2 trials with temperature in the DMTA**

When DMTA method 2 was used, two temperature sweeps was performed for each sample, i.e. the furnace was cooled down to the start temperature when the first temperature sweep was finished and a subsequent temperature sweep was performed without removing the sample.

![Figure 9. Shows the changes in modulus and tan δ with increasing temperature on coating Nr. 2 (clay with hard latex).](image)

Figure 9 shows two subsequent temperature sweeps for a sample with the compositions according to coating 2 (Clay with hard latex). The first temperature sweep is labelled “Before” and the second temperature sweep is labelled “After”. For the first temperature sweep the modulus decreased in the beginning of the temperature interval, between 45°C and 55°C the modulus flattened out and in the temperature interval between 55°C to 100°C, the modulus increased. Above 100°C the modulus decreased slightly. The second sweep showed a decrease in modulus at low temperatures with approximately the same rate as seen the in the first sweep. The only difference was that the modulus was considerably higher indicating a gain in stiffness between the first and second sweep. The shape of the curve started to differ from the first sweep at a temperature of 40°C where the decreasing rate of the modulus lessened, and the curve started to flatten out without the minimum observed in the first temperature sweep. The curves converged at approximately 100°C. Tan δ was slightly lower the second sweep and the structure of the curve were similar to the first temperature sweep. The latex T_g could be estimated as when tan δ reached its peak, i.e. approximately 46°C.
A test with DMTA method 2 of coating 5 (GCC with hard latex) is shown in Figure 10. The first temperature sweep labelled “Before” shows a decrease in modulus between 0°C to 50°C and after that it is plane between 50°C and 70°C. The modulus started to decrease again between 70°C and 120°C. In the second temperature sweep labelled “After” the modulus was similar to the first curve between 0°C and 40°C, with the difference that the modulus of the second temperature sweep was slightly higher. The modulus did not plane out in the same manner as the first temperature sweep, but decreased with a different rate during the whole temperature sweep. The two curves converged at approximately 80°C. The tan δ was slightly lower the second sweep and the structure of the curve were similar to the first temperature sweep. The latex $T_g$ could be estimated to approximately 46°C.

Figure 10. Shows the changes in modulus and tan δ with increasing temperature on coating Nr. 5 (GCC with hard latex).

Figure 11. Shows the changes in Modulus and tan δ with increasing temperature on coating Nr. 1 (Clay with soft latex).
A test with DMTA method 2 on coating 1 (Clay with soft latex) is shown in Figure 11. The first sweep labelled “Before” shows a decrease in modulus between -28°C to 40°C, above 40°C the curve levelled out after and remained flat for the rest of the measurement. In the second sweep labelled “After”, the modulus decreased between -28°C to 0°C. After that, the modulus made a little leap between 0°C to 20°C and above 20°C the curve levelled out. The modulus was lower in the second sweep than in the first temperature sweep. The latex T_g was estimated to approximately 18°C.

Figure 12. Shows the changes in Modulus and tan δ with increasing temperature on coating Nr. 4 (GCC with soft latex).

A test with DMTA method 2 on coating 4 (GCC with soft latex) is shown in Figure 12. The first sweep labelled “Before” shows a decrease in modulus between -30°C to 40°C, the modulus levelled out after 40°C and then the modulus increases a little for the rest of the measurement. In the second sweep the modulus decreases in the whole temperature range. The modulus in the second sweep labelled “After” is a little bit lower at first but at 0°C, the curves shift place. After that the modulus for the second sweep is a little bit higher than in the first sweep and at about 80°C the curves converge again. The latex T_g could be estimated to approximately 18°C.
Figure 13. The graph shows the modulus and tan $\delta$ for one hour at 60°C, the test is performed on coating 2 (clay with hard Latex).

Figure 13. shows a test on coating 2 (clay with hard latex) were tested according to DMTA method 3. The sample was exposed to a temperature of 60°C for one hour and the test were performed twice in the same way as in method 2. During the heating up to 60°C the modulus for the first curve labelled “Before” decreased between 0°C and 45°C then it started to flatten out and when the temperature was reached it started to increase at a slow rate. The modulus for the second curve labelled “After” is higher from start and the form of it is similar to the first curve with the difference that the minimum is slightly less pronounced. The difference between the two curves reduces during the sweep but it still remains to the end of the sweep even if it is small. The tan $\delta$ is slightly lower the second sweep and the structure of the curve are similar to the first one. The latex $T_g$ can be estimated to approximately 44°C.

Figure 14. The graph shows the modulus for nine hours at 85°C, the test is performed on coating 2 (clay with hard Latex).
Figure 14. Shows a graph with the results when coating 2 (clay and hard latex) were tested according to DMTA method 3. The sample were exposed to a temperature of 85°C for nine hours. The heating rate up to 85°C was 2°C/min and the modulus decreased during this part of the experiment. The elapsed time before reaching the target temperature was 32 min. The modulus started to increase when the sample had reached the target temperature. After approximately 90 minutes the temperature took a leap from 85°C to 88°C, at the same time the modulus decreased for a couple of minutes before it started to increase again. The modulus then increased during the remaining test. Note that the scale of the modulus is very narrow.

Figure 15. The graph shows the modulus divided by the start modulus. The data are from temperature sweeps made on samples of coating 2 (clay with hard latex) that have been oven cured for different time at 70°C according to DMTA method 4.

Figure 15 shows the results from a test with DMTA method 4 on samples of coating 2 (clay and hard latex). The samples had been oven cured at 70°C for 14 hours, 18.5 hours 136 hours and 159 hours. To eliminate eventual differences in physical properties of the samples (e.g. surface roughness and porosity), the modulus for each sweep was normalised by dividing the modulus with the modulus obtained at 0°C in order to make the four sweeps comparable. The sweep of the sample that had been cured for 14 hours shows a decrease in modulus between 0°C and 50°C, with an increase in the temperature interval 50°C to 80°C. Between 80° and 120°C the modulus decreases again but at a slower rate than before. The sweep with the sample that had been cured for 18.5 hours shows a decrease in modulus between 0°C and 55°C, and then the modulus increases a little between 55°C to 70°C. Between 70° and 120°C the modulus decreases but at a slower rate than before. The third sweep with the sample that had been cured for 136 hours shows a decrease in modulus over the whole sweep, the decrease in modulus is greater between 0°C and 60°C than it is between 60°C and 120°C. The last sweep was performed on the sample that had been cured for 159 hours is similar to the
third sweep with the exception that the modulus is a little higher during the whole sweep. The results of the samples cured during 136 and 159 hours must be considered as similar since eventual differences (~5%) between the results are probably due to experimental scatter.

Figure 16 shows the influence of heating rate on the modulus (DMTA method 5) on samples of coating 2 (clay with hard latex). The different heating rates that were used were: 0.25°C/min, 1°C/min, 4°C/min and 12°C/min. The time consumption of these tests was: 456 minutes, 114 minutes, 28.5 minutes and 9.5 minutes respectively. To make the results from the four sweeps comparable the modulus was normalised by dividing the modulus with the modulus measured at 36°C (which is the $T_g$ of the hard latex, supplied by the manufacturer). The test with the heating rate of 0.25°C/min shows a decrease in modulus that diminishes with increasing temperature over the whole sweep. A heating rate of 1°C/min gave results that were similar to the results when a heating rate of 0.25°C/min was used. One difference can be observed between them, the modulus is slightly lower for faster heating rate, 1°C/min. The test performed with a heating rate of 4°C/min showed a rapid decrease between 36°C and 50°C and an increase with approximately the same rate between 50°C and 80°C. Between 80°C and 150°C the modulus decreased at approximately the same rate as the tests with a heating rate of 0.25°C/min and 4°C/min. The test performed with a heating rate of 12°C/min showed a rapid decrease between 36°C and 50°C then the modulus increased with a little slower rate between 50°C and 70°C. Between 70°C and 90°C, the modulus decreased rapidly again and then the modulus levelled out and showed a similar shape as the three previous curves. The difference between the initial modulus (at 36°C) and the final modulus (at 150°C) was considerably greater.
5. Discussion

Latex A that had a T_g on 36 was chosen because the aim of the project was to do tests on latex that did not form a film during drying at room temperature. The first tests that were performed cf. Figure 7 and Figure 8, gave an indication that the DMTA was suitable to measure the gain in stiffness due to film formation of paper coating. The force that the samples were exposed to in these tests was 1 N. For the subsequent tests the force was adjusted to 5 N to improve the accuracy of the results. The purpose with the second tests (DMTA method 2) was to see if the development of stiffness could be measured during the actual film forming process. In Figure 9 that shows a test on coating 2 (clay and hard latex) a gain in stiffness with increasing temperature occurs between approximately 55°C and 100°C on the curve marked “Before”. This proves that the gain in stiffness can be used as a measure to prove that film forming has occurred. The curve marked “after” shows an increase in stiffness of about 30 percents from start, this proves that the gain in stiffness that is measured in the first sweep remains. That the curves converge at about 100°C could be interpreted as the point where film formation was complete, this will be further discussed below. The same test were performed on coating 5 (GCC and hard latex) and the results are illustrated in Figure 10. The gain in stiffness is not as obvious as in the test with clay, although the modulus showed an increase of about 15 percents between the two sweeps at the start temperature. Between 50°C and 120°C, the modulus from the first sweep had levelled out more than in the second sweep. This indicates an increase in stiffness in that temperature interval. The peak of tan d indicates the T_g of the latex and how viscous the coating are. The peak was more pronounced when the clay was tested, this could be due to that the platy structure of clay is easier to rupture when it is exposed to shear force. The T_g was estimated to 46°C, which is 10°C higher than the suppliers specification. This difference can depend on different measuring methods or that the composition of the coating affects the T_g.

Reference tests were performed on latex B with a T_g 8°C. The drying temperature was 23°C so these samples hade probably already coalesced when the tests were performed. The results for coating 1 (clay and soft latex) and coating 4 (GCC with soft latex) showed that no gain in stiffness could be observed during the temperature sweep. The result in Figure 11 showed that the modulus for clay and soft latex (coating 1) was much lower during the second temperature sweep. The curve from the second sweep is also very flat and the difference in modulus between the first and second sweep is large, which was quite unexpected and no good explanation for this can be offered. When GCC and soft latex (coating 4) were tested, the modulus from the two temperature sweeps seems to follow each other better, cf. Figure 12. In the second sweep, the modulus is a little lower from the start compared to the first sweep. The results from these two tests shows that no gain in stiffness occur when the coatings with the soft latex are heated up to 120°C. This indicates that the gain in stiffness obtained from the test on coatings with hard latex (coating 2 and coating 5) is due to film formation since the hard latex had probably not coalesced before the tests were performed. The fact that the starting modulus of the second sweep were lower than the first sweep for coating 1 (clay and soft latex) and coating 4 (GCC with soft latex) could be due to that the latex might start to
break down at elevated temperatures. The tan $\delta$ peak indicates a $T_g$ of 18°C which is 10°C higher than the supplier’s specification, i.e. the same difference as the $T_g$ on the hard latex.

Earlier in this chapter some results indicated that the film forming of the hard latex had been completed at about 100°C when a heating rate 4°C/min was used. Carlsson et al. (2005) have performed tests where they stored coating samples for one hour at 80°C using lattices of similar $T_g$ as the hard latex used in this work. They concluded that an increase of the coating strength was developed during the time the coatings were stored at an elevated temperature and that this increase in stiffness was due to film formation. They suggested that film formation depend both on time and temperature. In order to prove this hypothesis, DMTA method 3 was created. The idea with this method was to determine how long residence time the coating needed to coalesce completely at different temperatures. With such data it would be possible to predict the time needed for the latex to reach complete film formation at lower temperatures using the time-temperature superposition.

Figure 13 shows a test at a constant temperature of 60°C for one hour. Double tests were performed and the second measuring of the modulus is a little higher than the first one. This indicates that the film forming was not completed after one hour at 60°C. The temperature and time were extended several times and a lot of tests were performed. One is shown in Figure 14 and after magnifying the scale of the modulus it is clear that the modulus still is increasing after 9 hours at 85°C. Film formation might be the reason why the modulus is still gaining after so long time at that temperature. However, it is possible that the gain stiffness depend on rearrangement of particles within the coating which might increase the stiffness. The rearrangement in the coating could then be a result of the oscillating movement that the coating is exposed to during the DMTA measurements.

Since the tests at constant temperature in the DMTA were very time consuming and might affect the structure of the coating, DMTA method 4 was developed. When the coating samples are cured in an oven the particle arrangement of the coating should not change. Sample that had been oven cured for 159 hours were tested with double sweeps according to DMTA method 2 and after that it was still a significant increase in modulus after the first sweep, this support the theory of rearrangement of particles. A new angle was therefore tested and it was to make the first temperature sweeps for the different measurements comparable. To achieve this, the modulus was divided with the start modulus which gives a normalisation of the modulus during the sweep, this makes the results comparable. The result of this can be seen in Figure 15. A gain in stiffness at temperatures above $T_g$ could be observed for the temperature sweeps with the samples cured during 14 and 18.5 hours whereas the samples cured for 136 and 159 hours showed similar results without no gain in stiffness above $T_g$. This indicates that film formation has occurred after 136 hours. However before this test method can be used to estimate time for film formation at different temperatures it needs further investigation because there was only time to perform one series of tests.

The second hypothesis was that latex film forming is influenced both of time, temperature and the history of the sample. To test this hypothesis, DMTA method 5 was used and the results
are presented in Figure 16. The different sweeps was made comparable in the same way as in Figure 15, with the difference that the modulus was divided with the modulus measured at 36°C. This is the T_g of the latex given by the suppliers and this gives the value 1 at the point where the film formation should start. The sweeps with the heating rate of 0.25°C/min and 1°C/min showed curves without a minimum or stiffness build up at any temperatures indicating that film formation occurs gradually during the temperature sweep. Any differences between these two curves are also probably within experimental scattering. A heating rate of 4°C/min showed a large drop in modulus at first, with an increase in modulus at a temperature of about 50°C. The modulus curve from the sweep with the heating rate of 12°C/min also showed a large drop in modulus with an increase in modulus at about 50°C. The modulus then decreased considerably again at a temperature of about 70°C and did not recover. It shall, however, be remembered that the modulus for the fastest temperature sweep was not measured for more than 9.5 minutes. It can be compared to the sweep with the heating rate of 4°C/min that was at a temperature of 74°C after 9.5 minutes and the modulus was still increasing in this case. This indicates that the modulus from the fastest sweep might recover to the same level as the other sweeps, if it where left at the end temperature for as long time as it takes to perform a test with the heating rate 4°C/min. The difference in modulus between the modulus at T_g compared to the modulus at the end of the test was smaller for the sweep with the heating rate of 4°C/min than the tests with the heating rate of 0.25°C/min and 1°C/min. This indicates that film formation were closer to be complete for the slower heating rates at T_g.
6. Conclusions

The first hypothesis of the work was proven to be correct i.e. it is possible to measure the gain in stiffness during film formation in paper coatings. The second hypothesis was that latex film forming is influenced both of time, temperature and the history of the sample. The results in Figure 15 and Figure 16 indicate that this hypothesis was correct too. The oscillation movement in the DMTA seems to cause rearrangement within the coating structure that affects the gain in stiffness limiting the usefulness of the method to determine the time of film formation. Therefore a method without mechanical influence of the sample should be used. From this point of view, further investigations with DMTA method 4 should be performed. This might make it possible to predict the time needed for film forming to be complete at a specific temperature. This could give the answer to which optimal heat that should be added to the paper coating to get the best possible film forming online.
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8. References


Dillon, R.E., Matheson, L.A. and Bradford, E.B (1951); J. Colloid Sci. 6, p 108-117

Eckersley S. T., Rudin A. (1990); *Mechanism of Film Formation From Polymer Latexes*, J. Coat. Technol. 62 (780), p. 89-100

Frenkel, J. (1945); J. Phys. (U.S.S.R) 9, pp 385-391

Hellgren, A.-C., Wallin, M., Weissenborn. P.K., McDonald. P.J., Glover, P.M. and Keddie, J.L. (2001); *New techniques for determining the extent of cross linking in coatings*


Speary, P. R., Snyder, B. S., O’Dowd, M. L. and Lesko, P. M. (1994); *Role of Water in Particle Deformation and Compaction in Latex Film Formation*, Langmuir 10 (8), p 2619-2628


Vanderhoff, J.W. and Bradford, E.B. (1963); *Mechanism of Film Formation of Lattices*, Tappi Journal, Volume 46, No. 4,

Vanderhoff, J.W. (1966); *Film formation of lattices*, Emulsion Polymers Institute Lehigh University Betlehem, Pennsylvania 18015

Ward, I. M. (1979); *Mechanical Properties of Solid Polymers*, ISBN 0 471 91995 0