Relative humidity and moisture impact on décor polyethylene adhesion

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Master thesis

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Abstract

Adhesion is the force keeping different materials together. In packaging materials this is important due to the many layers needed to protect its content. Retaining the packaging integrity is necessary to keep the long term storage capabilities of the packaging.

This thesis will focus on the outermost interface for adhesion in Tetra Pak packaging material. The interface in this case is polyethylene film laminated on a coated paperboard where moisture has been found to have an impact on adhesion levels, potentially causing problems to arise in filling machines and with end product.

By using standardized methods for measuring adhesion and moisture content, a strong relationship between the two was found and investigated. By mixing different compositions of clay coating it was possible to relate adhesion results to moisture content in the coating rather than in the board. It was also possible to relate commercial supplier board contents to adhesion results. A small series of atomic force microscope experiments were tried and seems like a promising tool for future investigation. No correlations were found between production settings and material properties for the samples investigated in this study.

Sammanfattning

Adhesion är kraften som håller samman olika material. I förpackningsmaterial är det viktigt eftersom det finns flera lager som måste hålla samman för att hålla förpackningen tät och skydda innehållet. Den här rapporten fokuserar på yttersta gränssnittet för adhesion i Tetra Pak förpackningsmaterial. Det här gränssnittet består av en polyeten film laminerad på lerbestrykt kartong. Det har upptäckts att adhesionen i gränssnittet påverkas av fukt vilket kan skapa problem i fyllmaskiner eller med slutprodukten.

Genom att använda standardiserade metoder för att mäta adhesion och fukthalt så upptäcktes och undersöktes förhållandet mellan dem. Genom att blanda olika sammansättningar av lerbestrykningen så gick det att koppla resultaten från adhesionsmätningarna till fukthalten i bestrykningen. Det var även möjligt att koppla uppbyggnaden av kommersiella förpackningsmaterial till resultaten i adhesionsmätningarna. Atomkraftsmikroskåp användes i mindre skala och ser lovande ut för fortsatt undersökning av gränssnittet. Inget samband upptäcktes mellan produktionsinställningar och materialegenskaper för materialen som användes i den här studien.

Acknowledgements

1. Background

Tetra Pak has noted that moisture reduces the adhesion between the décor polyethylene (PE) layer and the board interface. This can cause delamination in the filling machines where the packaging material encounters moisture. Delamination in the décor PE means that the package must be discarded and could cause issues in the machines.

Better understanding the cause could lead to reduced waste, increased quality for Tetra Pak and their customers.

1.1 Scope

The purpose of this study was to increase the understanding of the moisture-adhesion phenomenon by evaluating different board suppliers and print surfaces and relating their compositions to the results of adhesion measurements.

Materials used were limited to commercially used products and reference materials to ensure that results can be related to real world cases. Board substrate was limited to unprinted surfaces to allow comparison between samples as well as to reduce the size of the study. Thickness of the utmost polymer layer was limited to 12 gram per square meter packaging material to avoid differing stretching properties of the peel arm.

1.2 Tetra Pak

Tetra Pak was founded in 1951 as they launched their first packaging system. They have been improving their systems continuously since then and are currently one of the world leaders of the packaging industry. Tetra Pak is currently active in over 160 countries and in 2018 they sold over 189 billion packages. [1][6]

1.3 Packaging material

The Tetra Pak packaging material is used to pack a wide variety of drinks and foodstuffs, to prevent the product from spoiling the material needs good barrier properties.

The packaging material typically consists of six layers. The outermost layer is a thin PE layer, next is the paperboard, then another PE layer, then an aluminium foil, and lastly the inside consists of an adhesive and yet another PE layer. Figure 1 below displays the typical packaging material structure in a schematic way. [5]
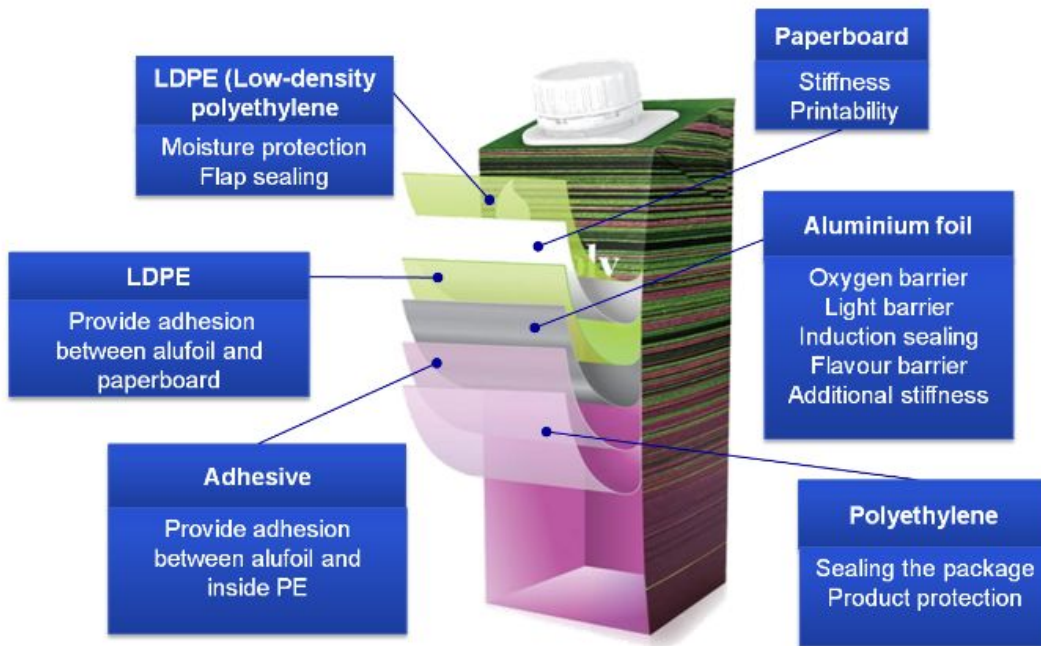
Figure 1: A schematic view of typical packaging material explaining the purpose of each layer. The structure may vary over different packaging solutions. [5]

Paperboard is the main component of the packaging material. It provides the largest share of structural integrity, and mechanical strength of the package.
The paperboard is coated with a mixture of clay, chalk, and a binding agent. This layer is called "clay coat" and provides the packaging material with a smooth, white, printable surface. The purpose of polyethylene (PE) in Tetra Pak packaging material is to provide a barrier for liquids, moisture, and microorganisms, as well as working as an adhesive between the aluminium and the paperboard. The PE on the inside works as a seal to protect the product inside the packaging. The PE in packaging material is low density polyethylene (LDPE) to reduce the total weight of the packaging. [5] [7] [8]

The aluminium layer provides a barrier for light, oxygen, and odours to prevent the contents from spoiling. It also increases the strength of the package. Due to its small thickness the foil is highly flexible but also quite fragile, as such it is laminated onto a PE layer. The conductive properties of aluminium also allow the package to be sealed by induction heating, packaging without the foil requires other methods for sealing. [5] To ensure that the PE on the inside sticks to the aluminium foil, a layer of adhesive polymer is used. [5][9][10]

1.4 Method
The method for the adhesion and moisture content measurement used in this thesis were chosen as they represent the industry standard. This allows for a comparison between studies as well as ensuring a large collective knowledge of the methods and their pitfalls. The mixing of unique coatings was deemed necessary to secure a more exact knowledge of the contents than what was readily available from paperboard manufacturers.

1.5 Adhesive test methods

1.5.1 Peel test

It is possible to measure adhesion levels using a peel test, most commonly the international standard ASTM D 903 – 98 is used, with or without modifications. The test is performed by loosening a part of the adhesive layer creating a free "peel arm" and then fastening the peel arm in a movable clamp and the non-modified part of the sample in another clamp. The machine then peels at a constant speed until a stable force is measured. The angle relative to the surface of the sample at which the peel test is performed has a major impact on the results. In fact, the actual work needed to create the surface when peeling at 180° is twice as high as when peeling in 90°. Measuring at the same speed at both angles means that the area of surface created increases twice as fast when peeling at 90°. A common problem is the elasticity of the peel arm which results in the PE deforming during the test, causing the measured adhesion value to be lower than the theoretical values. [11] [12][13]

1.5.2 Tape peel test

If for some reason it is impossible to perform the peel test using a machine, it is possible to instead use the "tape peel test" which is a quick and simple test. An operator applies a tape to the test surface and then peel the tape off in a specified approach. There are a couple of problems with this method, mainly because the results are impacted by trivial parameters such as operator mood (a tired operator might peel with less force/speed than an energetic one) as well as having an inherent operator dependency. The results from this test should mainly be used when fast results are necessary or when a comparative result is sufficient e.g. is one material better than another. [13]

1.5.3 Pull test

A pull test involves applying the test sample to an instrument capable of pulling at specified forces. The machine pulls in a 90° angle relative to the surface, in contrast to the peel test this does not require a peel arm due to applying the traction at the surface fastened to the machine. While this method diminishes the elasticity problem of the peel test it instead has other disadvantages. The test is highly sensitive to imperfections in the application of the specimen, an uneven surface or contaminants create loci of failure which are not inherent to the material, possibly causing faulty data. However, the main issue with applying the pull test to packaging material lies with the paperboard. Pulling at the surface this way causes the paperboard fibres to rupture before the adhesive delaminates from the sample resulting in the method instead measuring the cohesion strength of the paperboard. [13]

1.5.4 Mode of failure

When measuring adhesion on the outside layer of packaging material, it is possible for the sample to fail in multiple ways. To be certain of what is measured, the mode of failure must be determined. Note that failure does not necessarily mean that the data is not meaningful, it simply refers to how and where the sample was separated. [15]

When performing adhesion tests on packaging material it is quite common for the sample to break in the thin PE arm. This means that the sample gave no numerical result. However, it could be argued that the adhesion is at least decent, since a very weak adhesion would more likely peel as intended. Figure 2 below illustrates an example of this. [14][15]
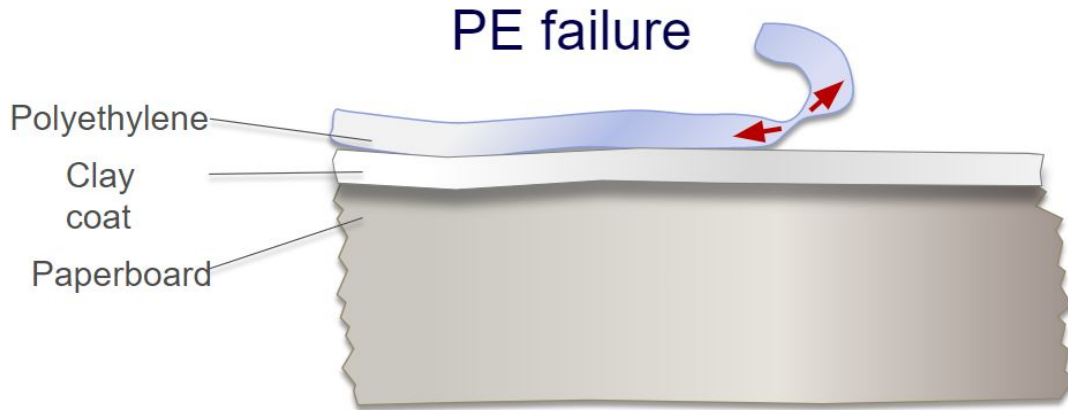
Figure 2: Illustration of PE failure. Note that the figure is not to scale.

An adhesive failure happens when the sample fails in the interface between two layers. Here it would mean that the PE delaminates from the clay coat without either material being damaged. Adhesive failure is illustrated below in Figure 3. [14] [15]

Figure 3: Adhesive failure. Note that the figure is not to scale.

When the sample breaks in the substrate layer it is labelled cohesive failure. In this case the substrate is the clay coat. An example of substrate failure is found in Figure 4. [14] [15]
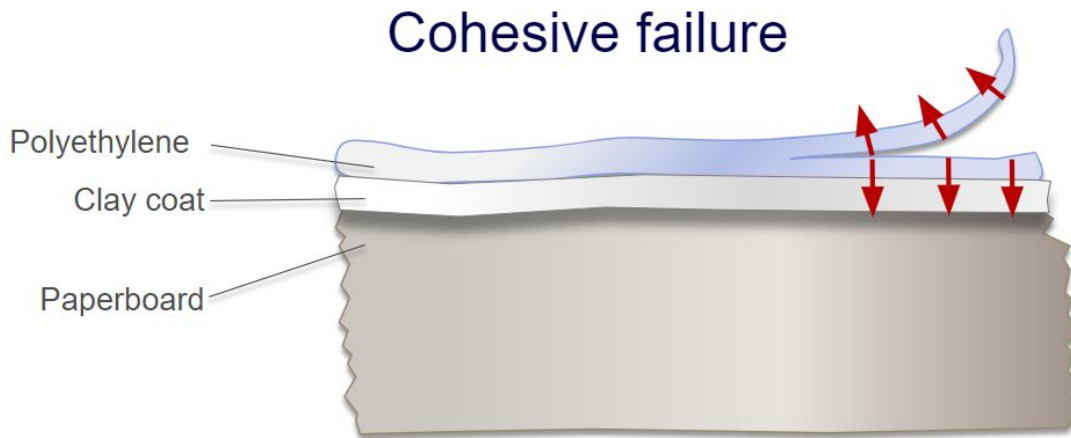
Figure 4: Cohesive failure. Note that the figure is not to scale.

In the case of packaging material there is also the possibility of samples tearing in the paperboard fibres. Numerical results obtained from this type of failure are not comparable to adhesive failure even though they might look similar. At best, it tells you that the adhesion is greater than the forces required to change fracture interface. An illustration of this type of failure is found in Figure 5. [14]
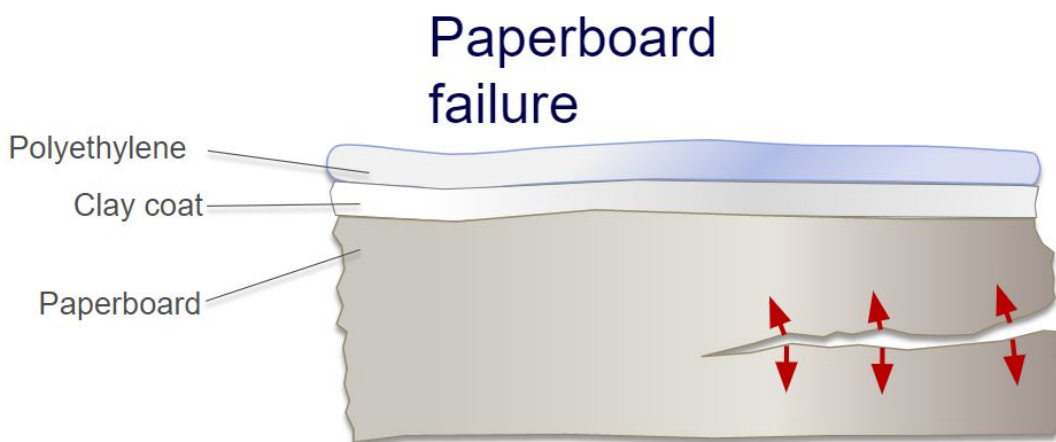
Figure 5: Paperboard failure. Note that the figure is not to scale.

If the failure starts in one layer and then progresses to another, or continuously switch between layers the failure is considered an alternating failure. For example, if the sample starts separating in the interface of PE and clay coat and then the PE breaks apart. [14] [15]

2. Theory

2.1 Adhesion

While cohesion is the effect of surface bonding or attraction between identical molecules, adhesion is the same effect between two surfaces of different constitution. There are several theories on how adhesion works: mechanical theory, electronic theory, adsorption theory, diffusion theory, and chemical bonding theory. Since adhesion is rarely explained by one

single theory, and different theories are more important in some scenarios than other, it is difficult to model or otherwise predict adhesion levels. [2]

2.1.1 Mechanical theory

Mechanical theory provides perhaps the simplest explanation for the phenomenon by stating that adhesion arises from the adhesive and adherend physically interlocking. This has been proven to be an unlikely case except when referring to materials which are extraordinarily rough or porous, where it often is a significant factor. [2]

2.1.2 The electrostatic theory

The electrostatic theory is based on Coulomb's law which states that an electromagnetic force causes the adhesive and adherend to attract each other and thus adhere. While the electromagnetic forces have been proven to be always present, they often only represent a tiny amount of the total adhesive force. [2]

2.1.3 Adsorption theory

Adsorption theory is considered the most applicable theory and is founded on the idea that interatomic and intermolecular forces (dipole effects and London dispersion) between the surfaces are the source of the adhesion. These forces are only relevant when the distances are at molecular level. This implies that to achieve good adhesion the adhesive is a good wetting agent on the adherend. Theoretically modelling adhesion with adsorption theory is possible with equation 1:

$$w_{adh} = \gamma_1 + \gamma_2 - \gamma_{1,2} \quad (1)$$

Where w_{adh} is the work of adhesion, γ_i is the surface free energy of substance i and $\gamma_{i,j}$ is the surface free energy of the interface of substance i and j. This equation becomes increasingly more complicated when more components are added, for example if a liquid penetrates the adhesive or the adherend equation 1 would have to be modified to equation 2:

$$w_{adh,l} = \gamma_{1,l} + \gamma_{2,l} - \gamma_{1,2} \quad (2)$$

Where $\gamma_{i,l}$ is the surface free energy of the interface between substance i and the liquid. Adhesion of a partially moist interface would then be represented by equation 3:

$$w_{adh,tot} = x * \left(\gamma_1 + \gamma_2 - \gamma_{1,2} \right) + (1-x) * (\gamma_{1,l} + \gamma_{2,l} - \gamma_{1,2}) \quad (3)$$

Where x represents the fraction of the interface which is dry.
To calculate the surface free energy of an interface equation 4 is used:

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - 2\left(\gamma_{1,D}\gamma_{2,D}\right)^{\frac{1}{2}} - 2\left(\gamma_{1,P}\gamma_{2,P}\right)^{\frac{1}{2}} \quad (4)$$

where $\gamma_{i,D}$ is the dispersion component of the surface free energy, and $\gamma_{i,P}$ is the polar force component of the surface free energy. Inserting equation 4 into equation 3 yields the following equation 5:

$$W_{Adh,\,max} = 2 * \left(\left(\gamma_{1,D}\gamma_{2,D}\right)^{\frac{1}{2}} + \left(\gamma_{1,P}\gamma_{2,P}\right)^{\frac{1}{2}} \right) +$$

$$2 * (1-x) * \left(\gamma_l - \left(\gamma_{1,D}\gamma_{l,D}\right)^{\frac{1}{2}} - \left(\gamma_{1,P}\gamma_{l,P}\right)^{\frac{1}{2}} - \left(\gamma_{2,D}\gamma_{l,D}\right)^{\frac{1}{2}} + \left(\gamma_{2,P}\gamma_{l,P}\right)^{\frac{1}{2}} \right) \quad (5)$$

Which would be used to calculate the theoretical maximum work of adhesion at specified conditions. [2] [3]

2.1.4 Diffusion theory

Diffusion theory explains adhesion through the concept of solubility and random movement diffusion. This means that molecules, often polymers, migrate between the adhesive and adherend creating a zone where it is difficult to determine where the adhesive ends and the adherend starts. Applying this theory would mean that the highest adhesion would be found in interfaces where the components are easily soluble in each other, i.e. the components are chemically similar and have high mobility. [2] [4]

2.1.5 Chemical bonding theory

Chemical bonding theory states that the adhesive and adherend create chemical bonds, mainly covalent, hydrogen, and ionic bonds, between each other, meaning that to separate the two would require breaking the bonds. For bonds to form in a meaningful amount the two substances must have a high reactivity, generally polymers do not react without any reactive agents. [2]

2.2 Moisture hysteresis

The moisture retention capabilities of paperboard depend on which environments the material has previously been exposed to. This phenomenon is called hysteresis. It means that a material which has been stored in a high humidity environment will never reach the same moisture content as a material which has been stored in a low humidity environment. As seen in Figure 6, the moisture content of materials stored in high humidity has an equilibrium moisture content of about 8%, while the materials stored in a low humidity has an equilibrium around 7% moisture content. The climates initially used in this thesis were 23°C, and relative humidity (RH) 25, 50, and 75% respectively. These climates were chosen because 23°C/50% is the industry standard for paperboard testing. [16] [17]
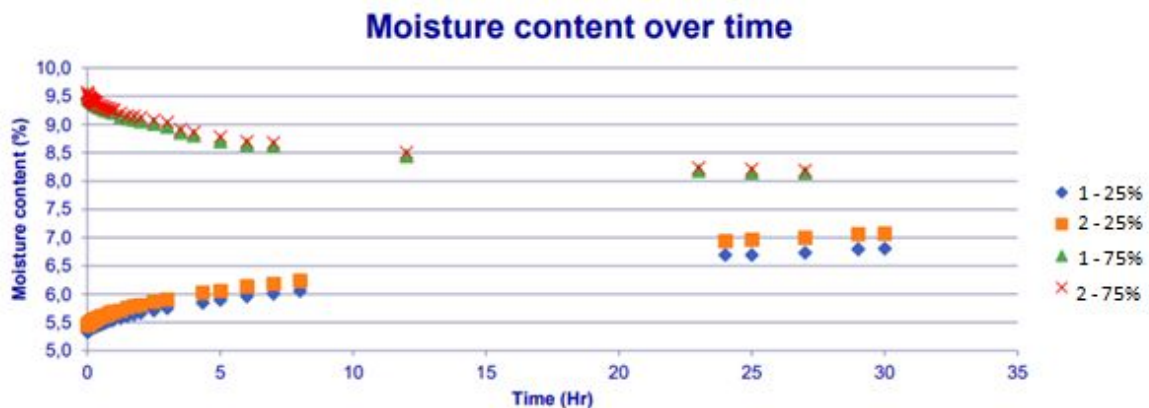
Figure 6: Moisture content over time for packaging materials previously stored in different environments. [16]

Interestingly, adhesion measurements do not exhibit the same hysteresis effect as the board moisture content. [16]

2.3 Microscopy

2.3.1 SEM
Scanning electron microscopy (SEM) utilizes an electron probe to scan a surface. The electrons from the probe are scattered in a variety of angles and trajectories. The software analyses the quality and quantity of scattering and forms an image. [19]

2.3.2 AFM
Atomic force microscopy (AFM) is a powerful tool for determining topography, by analysing the topography of the area where adhesion measurements were performed it is possible to gain information about the fracture. AFM moves a tip along a sample surface and measures the atomic forces between the tip and the sample. By analysing the attractive and repulsive forces they can be translated into images of the surface. [20]

2.4 Commercial Board supplier contents
Board suppliers share varying amounts of information about what their boards contain. Due to company interest, Tetra Pak has investigated the contents of commercial clay coatings. However the knowledge is not exact, and all information is not known. Estimations relevant for this thesis are displayed in Table 1.

Table 1: Estimated information about Tetra Pak board supplier coating contents. Each letter represents a supplier used in this thesis.

CaCO3 – Clay ratio	Binder SA[2]	Binder PVAc + SB[2]	Binder SB[2]	Binder PVAc[2]
80-20		A[1]		
70-30	B[1], F[1]			
60-40				
50-50	D[1]			E[1]
40-60			C[1]	

[1]A through F are letters representing different commercial board supplier material used in this thesis.
[2]SA represents a styrene acrylic based latex binder. SB represents a styrene butadiene based latex binder. PVAc represents a polyvinyl acetate based latex binder.

3. Sample preparation
Commercial materials used in this study will be referred to by letters ranging from A – H with the letter representing the board supplier, this is due to suppliers not wanting to share their specific compositions to the public. Naming the suppliers is not relevant to the results and conclusions.

3.1 Décor adhesion
The samples were prepared according to ASTM standard D903 with changes to sample dimensions according to Tetra Pak internal method. The samples were then placed in the specified climate for at least 48 hours to ensure that the moisture in the samples had stabilized before measuring. All samples were taken from unprinted surfaces to keep the samples comparable.

3.2 Moisture content

Investigating the moisture content in the packaging material is paramount to understanding its effect on adhesion. Samples were prepared according to Tetra Pak internal method and then placed in the specified climate for at least 48 hours before measuring. It is assumed that the PE and aluminium layers do not retain any moisture. As such the moisture content of packaging material was calculated by finding the mass of dry paperboard and clay coat. This mass is found by separating and weighing each layer until the mass of each component is known.

3.3 Clay coat samples

A deeper understanding of how moisture affects the clay coating and how the different components change the behaviour had to be achieved. To do this an experimental set up was created. The components, kaolin, calcium carbonate of two different grades, and binders were mixed in varying amounts to construct a matrix intended to cover as much as possible. The samples are then dried at 90℃ for three hours at which point they are completely dry. After drying, the samples are immediately weighed and put in the specified climate.

4. Execution

4.1 Décor adhesion

After storing the samples in their climates, they are transported in sealed bags which were also stored in the climate, to the Instron 3345 dynamometer. The total time from when the samples leave the climate, to being tested is assumed to be short enough to not impact the moisture content in the samples. During testing most samples coming from 23°C/25%RH climate failed by breaking in the PE. The samples were therefore repeated, with equally poor results. Due to the lack of results on the dry climate it was decided to add another dry climate, 23°C/35%RH to be able to evaluate the results in a more satisfying way.

4.2 Moisture content

After the samples have reached the equilibrium moisture content for their respective climate, they are weighed. The samples are then placed in an oven until the samples contain zero moisture and are once again weighed. The difference in weight is the weight of the water in the sample and is used to calculate the moisture percentage of the sample before drying.

4.3 Clay coat samples

After weighing the completely dry samples they were transported to the driest climate (23°C/25% RH) where they were stored until equilibrium was reached. When equilibrium was confirmed the samples were weighed again and then transported to the next driest climate. This process was repeated until the samples had been weighed at equilibrium moisture at all three original climates. To investigate the hysteresis effect on pure clay coating the samples were then put in the middle ground climate (23°C/50% RH) and weighed repeatedly until equilibrium was once again established. This yields results where there should be no difference between the moisture in samples stored in the drier climate, and the ones stored in the wetter climate. Otherwise there is hysteresis in the clay coat samples.

23°C/35% RH climate was not used in clay coat testing as this climate was added at a later stage. The intended mixture matrix is found in Appendix A1.

4.4 AFM – Nanosurf Naio

An AFM was used to investigate the topography after performing adhesion measurements on sample H. Sample H was chosen because it gave multiple results on each climate, allowing a good comparison between them. The used AFM was "Nanosurf Naio" and can be seen in Figure 7.
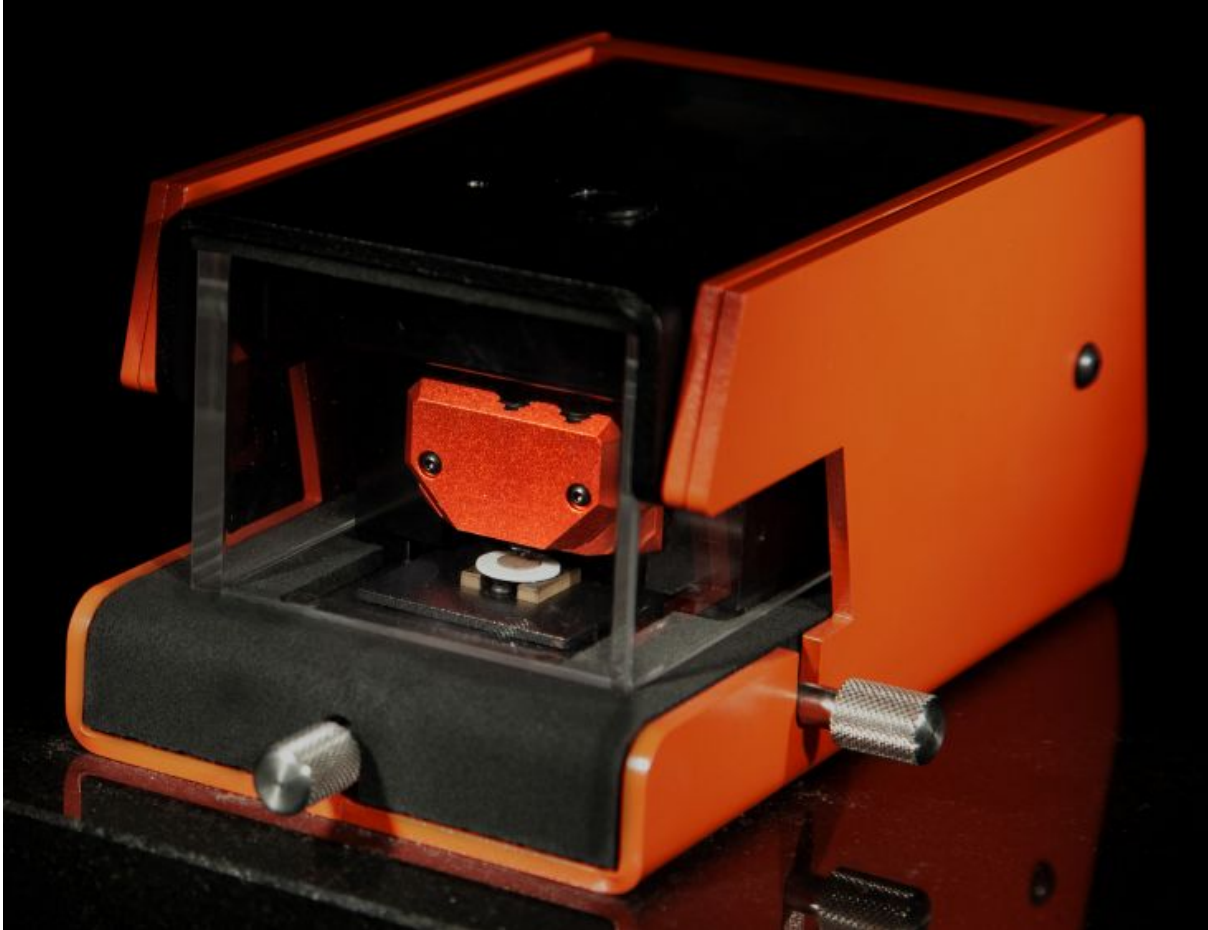
Figure 7: The AFM used in this thesis, Nanosurf Naio, picture from
https://www.nanosurf.com/en/products/naioafm-the-leading-compact-afm#overview, accessed 3 September 2019.

The samples were placed in the microscope in such a way that the area on which the adhesion measurements were performed was centred under the tip. An area of 25 times 25 micrometres was examined after which the tip of the AFM was moved to another location (still in the relevant region) and measured again. A total of three repetitions were done on each sample.

5. Results & Discussion

5.1 Moisture content

Raw data for moisture content measurements is found in Appendix A. The average moisture content of each material is displayed below in Table 2. The data from Table 2 was drawn in Figure 8.

Table 2: Average moisture content and standard deviation (SD) data from the moisture content measurements.

Board supplier	Average moisture in sample after storing in 25% relative humidity (%)	SD 25% (%)	Average moisture in sample after storing in 35% relative humidity (%)	SD 35% (%)	Average moisture in sample after storing in 50% relative humidity (%)	SD 50% (%)	Average moisture in sample after storing in 75% relative humidity (%)	SD 75% (%)
C 1	5.3	0.15	6.3	0.06	7.7	0.04	10.7	0.06
No coat	5.8	0.03	6.4	0.05	8.2	0.07	11.6	0.05
C 2	5.3	0.11	6.4	0.05	7.8	0.07	10.7	0.05
B	5.3	0.19	6.4	0.07	7.9	0.09	10.8	0.07
E	4.8	0.04	5.8	0.05	7.2	0.10	10.2	0.05
F	5.2	0.04	6.5	0.18	7.9	0.08	10.6	0.17
G	4.8	0.02	5.8	0.08	6.8	0.04	9.7	0.08
H	4.9	0.12	5.9	0.06	6.6	0.05	9.6	0.06
D	5.2	0.09	6.6	0.06	7.4	0.07	10.6	0.06
A	5.4	0.06	6.4	0.04	7.3	0.13	10.5	0.04
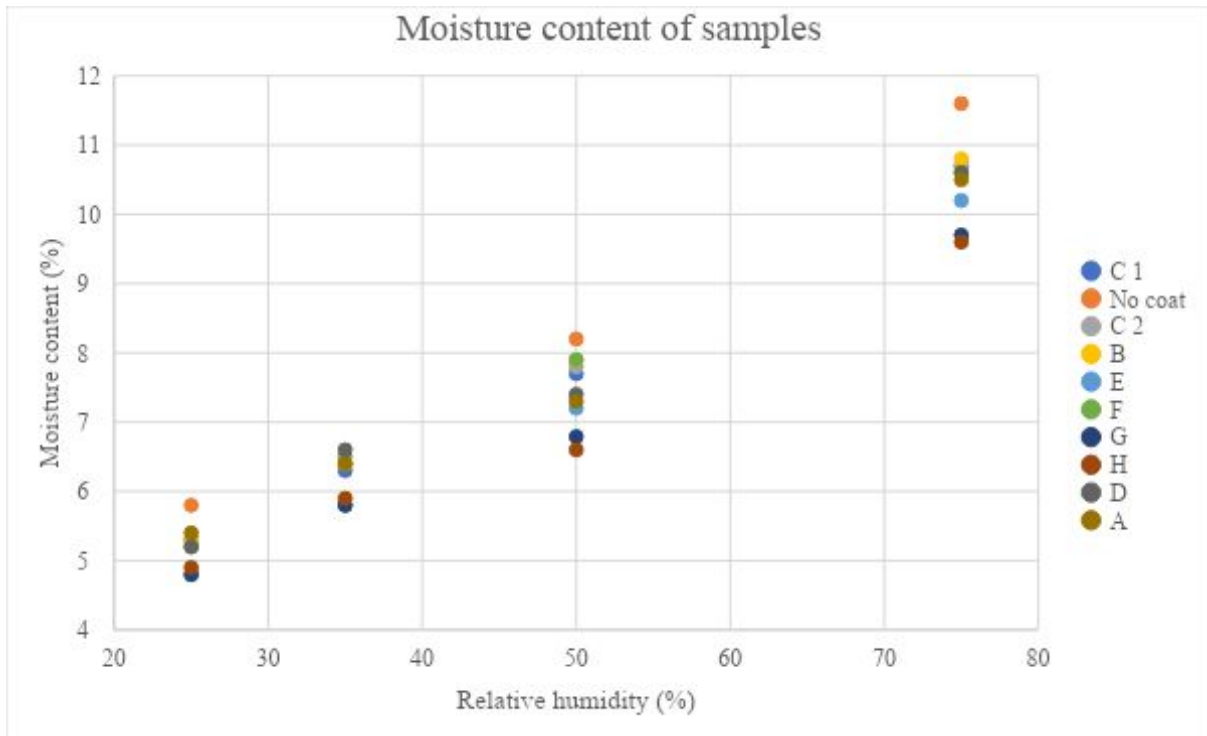
Figure 8: Data from Table 2, average moisture content vs relative humidity in storage.

While most of the samples group together with little spread, the sample without coating absorbs a higher amount of moisture. This is due to the clay coating absorbing less moisture than board fibres and since this sample has no coating its board consists of relatively more fibres than the other samples. Sample G and H absorb less than the other samples. This is due to their board being constructed in a different manner. Sample E also has this different construction and it also absorbs a bit less, although harder to see it is more obvious at the wettest climate.

5.2 Décor adhesion

Raw data for décor adhesion measurements is found in Appendix A.
Mean adhesion results along with number of successful specimens are displayed in Table 3.
Table 3: Average adhesion for samples & standard deviation (SD) along with number of successful specimen (N) at different climates.

Board supplier / sample	25%			35%			50%			75%		
	Mean adh. (N/m)	SD (N/m)	N	Mean adh (N/m)	SD (N/m)	N	Mean adh. (N/m)	SD (N/m)	N	Mean adh (N/m)	SD (N/m)	N
C 1	-	-	0	84.7	1.5	3	61.5	1.3	5	43.4	1.6	5
No coat	67.1	6.4	4	65.8	5.0	3	61.0	9.1	4	42.7	1.4	3
C 2	-	-	0	94.5	2.1	2	74.3	4.8	4	50.6	4.3	5
B	-	-	0	-	-	0	103.7	9.6	3	55.1	3.3	5
E	-	-	0	-	-	0	116.7	6.4	2	22.4	4.9	5
F	120.5	14.5	2	-	-	0	93.0	6.5	3	45.3	3.2	5
G	-	-	0	-	-	0	63.4	-	1	19.1	1.0	5

	140.3	6.8	3	125.7	4.0	3	103.6	13.0	5	51.0	2.1	5
H	140.3	6.8	3	125.7	4.0	3	103.6	13.0	5	51.0	2.1	5
D	-	-	0	-	-	0	89.5	6.4	2	40.2	3.7	4
A	-	-	0	-		0	111.5	3.5	2	63.3	7.2	3

The average adhesion data from Table 3 is drawn in Figure 9 versus moisture data from Table 2 for visual purposes.
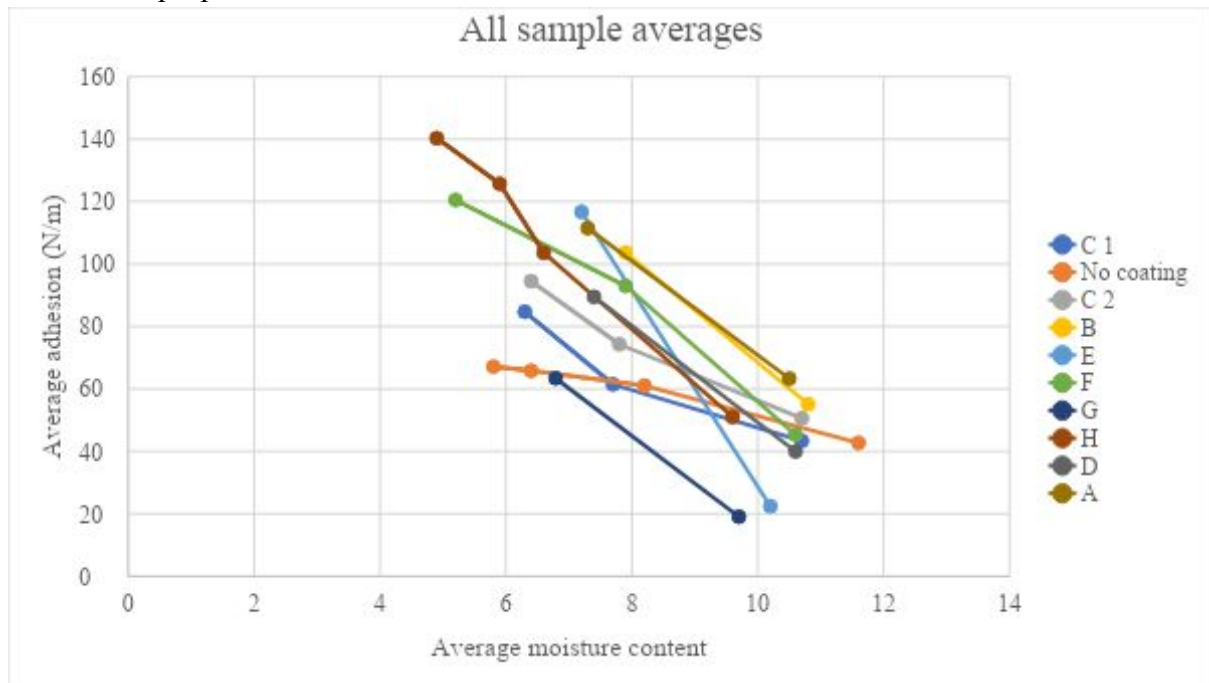
Figure 9: Data from Table 2 and 3 combined, average adhesion vs average moisture in packaging material. Lines connect to the next data point, no regression is displayed in this figure.

The change in adhesion over moisture is displayed in Table 4:

Table 4: The slope of adhesion data (N/m/%).

Board supplier	Slope (N/m/%)
C 1	8.9
No coating	4.3
C 2	9.9
B	16.8
E	31.4
F	13.9
G	15.2
H	19.3
D	15.5
A	15.1

Most samples have a slope around 15 N/m/% but sample E deviates from this with twice as steep slope. Sample C 1 and C 2 deviates from this with a flatter slope ~10 N/m/%.

In cases where less than 5 results were obtained for a sample it is likely that the mean adhesion is skewed towards a lower average than the true value. This effect is due to samples with less adhesion are more likely to be successfully measured than samples with high adhesion.

5.3 Clay coat

A matrix containing the target mixtures can be found in Appendix B1. Actual dry content percentages and results are found in Table 5, type of binder used is found in Appendix B1.

Table 5: Dry content percentages and sample moisture.

Sample	Dry % CaCO3 coarse	Dry % CaCO3 fine	Dry % Kaolin	Dry % binder:	Average 25% RH (%)	Average 50% RH (%)	Average 75% RH (%)	Average 75->50 RH (%)
1	100	0	0	0.	0.25	0.35	0.48	0.33
2	0	100	0	0.	0.26	0.45	0.70	0.43
3	93.75	0	0	6.25	0.30	0.46	0.63	0.37
4	88.95	0	0	11.05	0.24	0.36	0.46	0.37
5	0	93.73	0	6.27	0.32	0.53	0.76	0.52
6	0	90.36	0	9.64	0.27	0.44	0.60	0.45
7	87.27	0	0	12.73	0.31	0.56	0.82	0.56
8	86.50	0	0	13.50	0.24	0.38	0.48	0.38
9	0	86.52	0	13.48	0.33	0.61	0.95	0.61
10	0	87.09	0	12.91	0.24	0.40	0.54	0.41
11	83.10	0	0	16.90	0.28	0.60	0.94	0.57
12	0	79.96	0	20.04	0.54	0.87	1.26	0.88
13	84.46	0	0	15.54	0.20	0.34	0.46	0.35
14	0	83.40	0	16.60	0.49	0.59	0.77	0.64
15	43.59	43.66	0	12.75	0.25	0.52	0.81	0.51
16	42.62	44.29	0	13.10	0.26	0.40	0.52	0.39
17	0	0	100	0	0.57	1.34	2.10	1.29
18	0	0	83.39	16.61	0.64	1.01	1.97	1.09
19	0	0	86.56	13.44	0.39	0.91	1.34	0.80
20	48.60	0	51.40	0	0.38	0.85	1.29	0.82
21	40.62	0	45.23	14.15	0.38	0.67	1.34	0.69
22	43.94	0	43.09	12.96	0.22	0.55	0.78	0.52
23	84.46	0	0	15.54	0.30	0.62	0.90	0.57
24	86.80	0	0	13.20	0.25	0.61	0.92	0.61
25	44.66	0	43.72	11.62	0.45	0.89	1.29	0.91
26	25.35	20.79	44.13	9.73	0.36	0.65	1.34	0.69
27	19.82	25.25	42.52	12.41	0.27	0.47	0.86	0.51

[1]Averages represent the mean moisture content of 3 replicates.
[2]This column displays moisture in samples which had been stored in a climate of 75% RH then put into a 50% RH climate, this result is used to investigate hysteresis

Comparing the averages of samples stored first in a dry climate then put in to the standard climate to the ones stored in a wet climate and then put in the standard climate using a T-test at 95% significance revealed that there is no statistical difference between the two and as such moisture exhibits no hysteresis.

The standard deviations in water content for clay coat samples at different climates are displayed in Table 6.

Table 6: Standard deviations (SD) for values in Table 5.

Sample	SD 25% (%)	SD 50% (%)	SD 75% (%)	SD 75->50% (%)
1	0.016	0.017	0.014	0.017
2	0.022	0.018	0.018	0.022
3	0.029	0.025	0.020	0.011
4	0.019	0.022	0.022	0.021
5	0.013	0.011	0.008	0.012
6	0.018	0.017	0.015	0.024
7	0.013	0.017	0.019	0.028
8	0.015	0.015	0.013	0.014
9	0.017	0.019	0.023	0.041
10	0.017	0.019	0.023	0.041
11	0.015	0.014	0.015	0.013
12	0.019	0.025	0.030	0.038
13	0.013	0.013	0.013	0.014
14	0.090	0.051	0.054	0.058
15	0.009	0.008	0.005	0.040
16	0.031	0.027	0.028	0.018
17	0.048	0.015	0.014	0.061
18	0.021	0.039	0.050	0.078
19	0.098	0.097	0.086	0.092
20	0.027	0.030	0.032	0.092
21	0.016	0.016	0.015	0.023
22	0.018	0.019	0.020	0.012
23	0.018	0.009	0.018	0.053
24	0.010	0.011	0.013	0.012
25	0.013	0.021	0.029	0.030
26	0.010	0.022	0.027	0.011
27	0.025	0.029	0.030	0.029

The results from pure pigment samples in Table 5 were drawn in Figure 10. Results from Table 5 grouped by binder and climate was drawn in Figure 11.
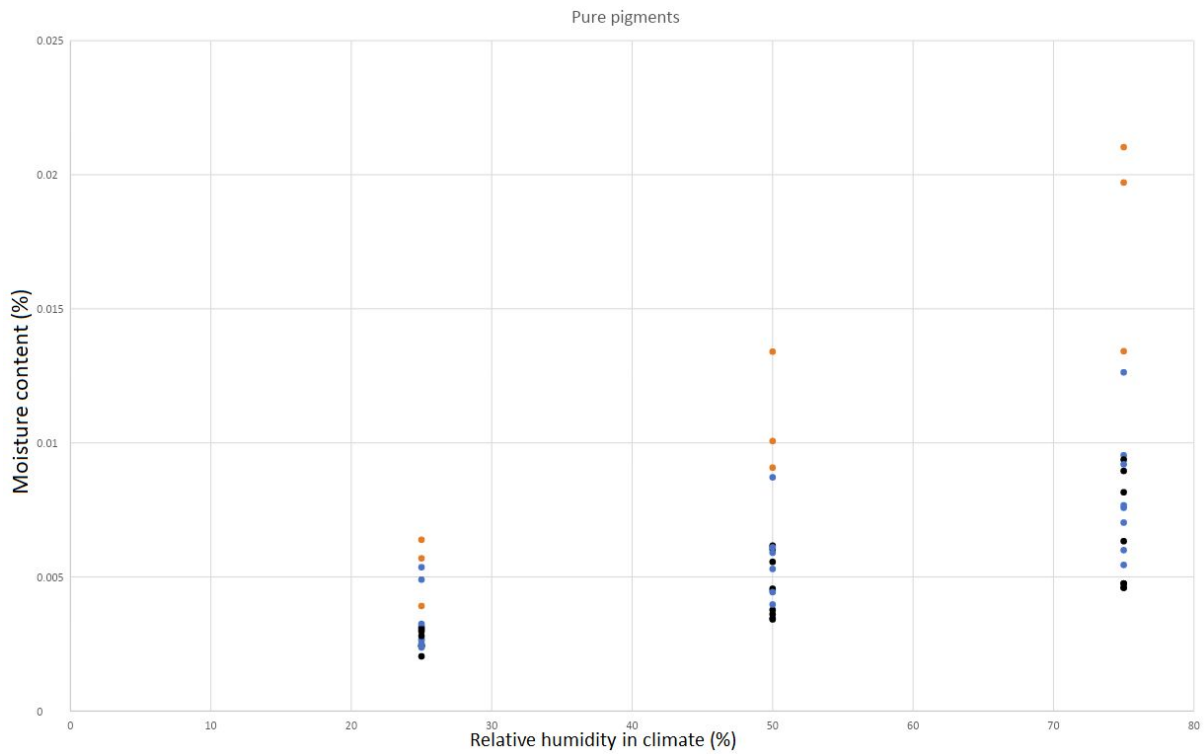
Figure 10: Pure pigment samples, teal, black, and orange dots represent fine carbonate, coarse carbonate, & Kaolin respectively. Y-axis represents moisture content by weight and the x-axis represents moisture in storage climate.
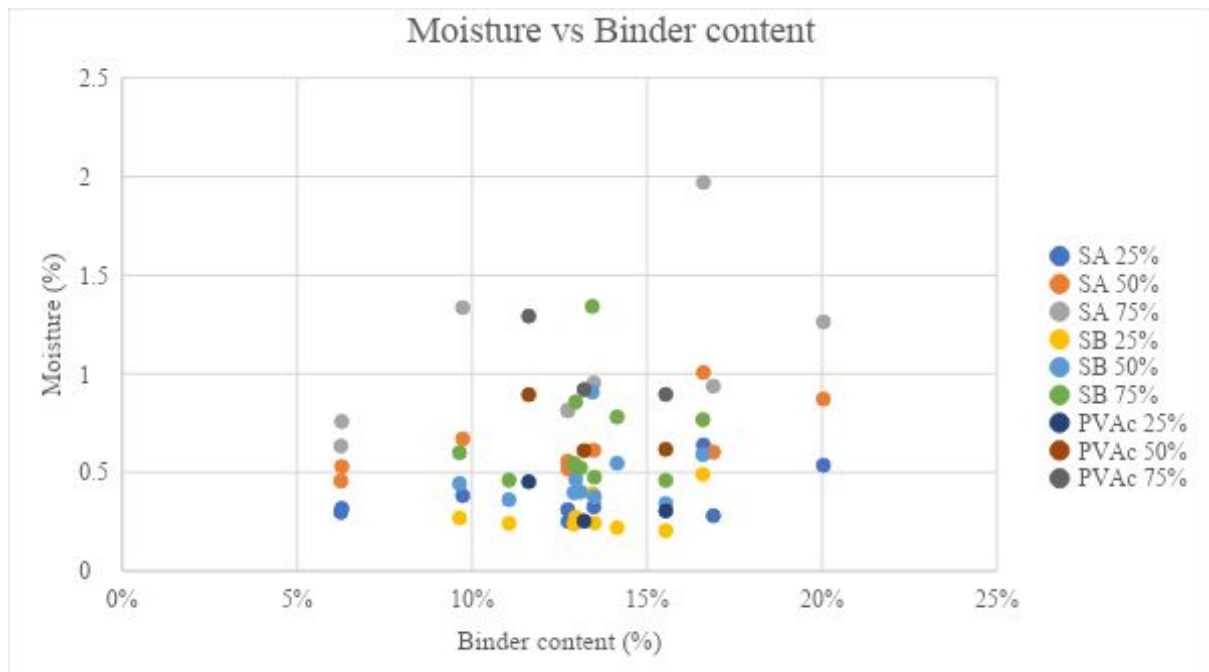
Figure 11: Average moisture vs binder content, displaying different climates and binder type as different colors.

Coating mixtures absorb between ~0,5 – 2% moisture compared to packaging material which absorbs ~5-11% moisture.

Kaolin mixtures absorb more moisture than carbonates, the fine carbonate absorbs more moisture than the coarse carbonate as seen in Figure 10. Binder SB absorbs less moisture than SA & PVAc which are difficult to distinguish. Using T-test at 95% significance it is possible to eliminate the possibility of hysteresis in clay coating. As such hysteresis is found in fibre moisture but not in adhesion level or coating moisture. This means that adhesion is affected by coating moisture rather than by fibre moisture.

5.4 Commercial board coatings vs adhesion

As explained in section 5.2, sample E had the steepest slope and in Table 1 E can be found to contain PVAc as binder and 50-50 mixture of clay and carbonate. PVAc was (together with SA) the most absorbent binder, and 50% clay being a higher than most amount could mean that coatings from supplier E absorbs more moisture and as such is affected more by a change in storage climate. Sample C had the flattest slope and is found to contain a high amount of clay, and using binder SB, the least absorbent binder, making it seem as though the effect of having a less absorbent binder outweighs the influence of a high clay ratio.

5.5 Impact of laminator speed

Laminator speed is thought to have an impact on the adhesion of the end product, to investigate this its relation to the results was explored. The laminator speeds for each material is found in table 7.

Table 7: Laminator speed (meters per minute) for the materials.

Board supplier	Laminator speed (m/min)
C 1	500
No coating	500
C 2	600
B	650
E	600
F	650
G	650
H	500
D	400
A	500

The data from Table 7 was drawn versus the average moisture content to investigate if there was any relation between laminator speed and moisture absorption in end product in Figure 12. Laminator speed was also drawn versus the adhesion measurements to examine the

relation between laminator speed and adhesion in Figure 13 and 14.
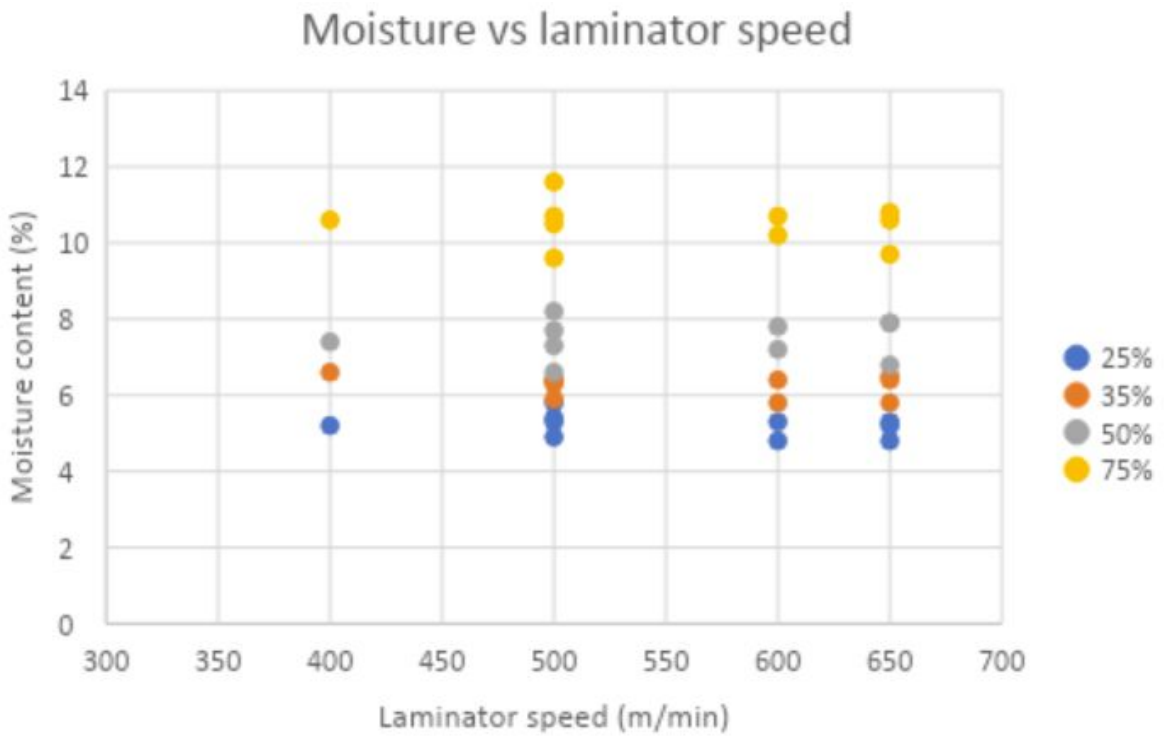
Figure 12: Moisture content in end product versus laminator speed. Colors indicate storage climate.
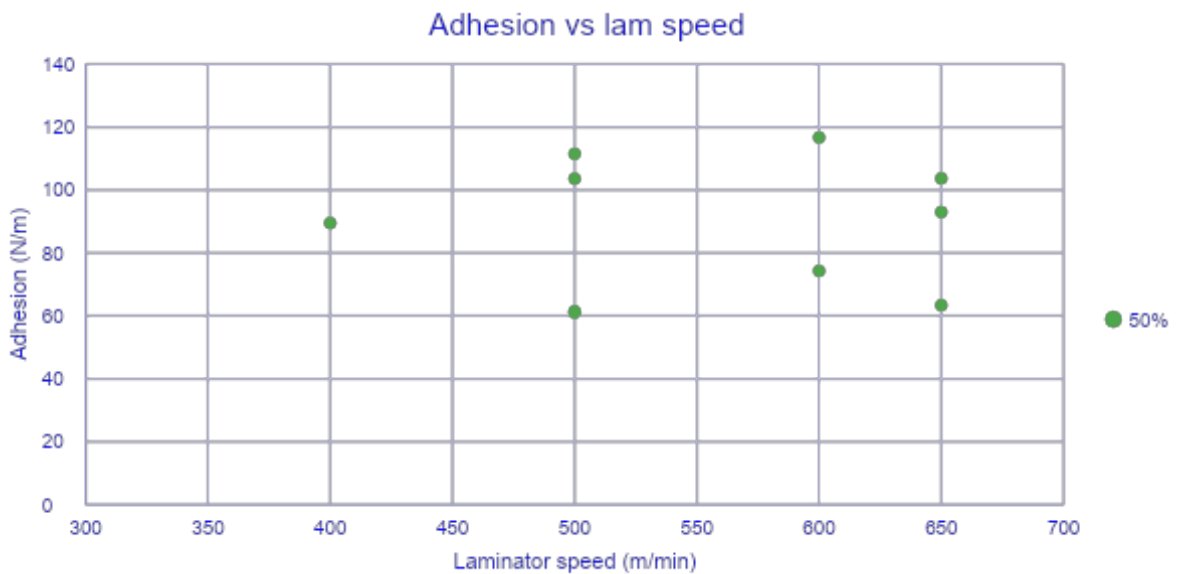
Figure 13: Adhesion versus laminator speed after storage in 50% relative humidity.
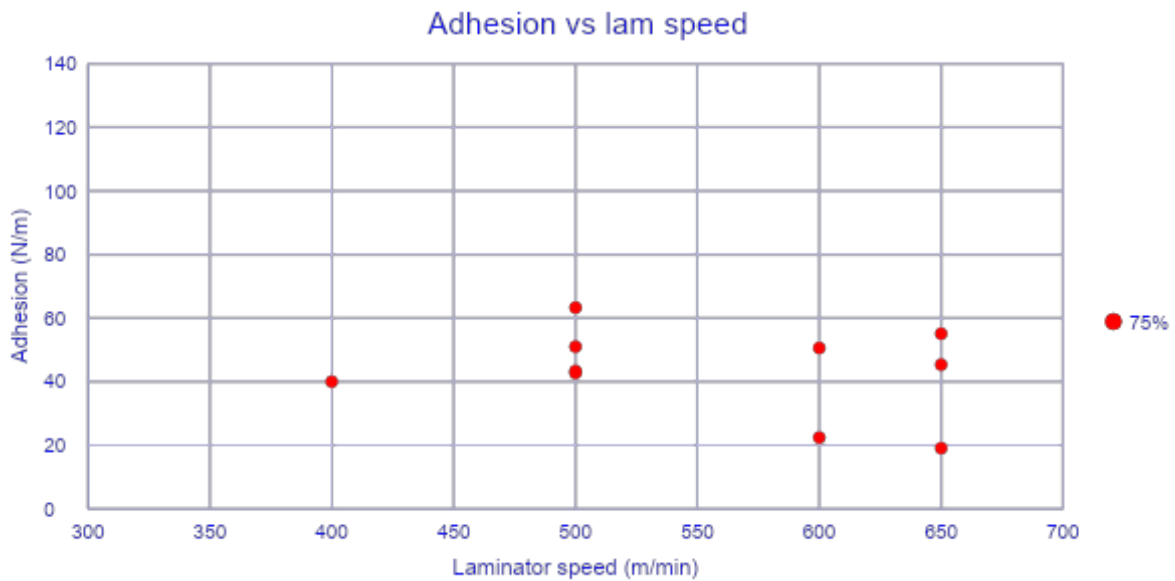
Figure 14: Adhesion versus laminator speed after storage in 75% relative humidity.

Adhesion versus laminator speed was only presented in two climates since the dryer two climates would not have enough data points. No strong correlation was found between laminator speed and the results obtained in this study. It is not possible to rule out the impact of laminator speed on adhesion for the general case since the materials in this study vary on several other factors as well.

5.6 AFM

Roughness data from Gwyddion software calculations are displayed in table 8.

Table 8: Roughness data from Gwyddion software calculations.

Sample:	Roughness (nm)
50% RH 1	571
50% RH 2	335
50% RH 3	158
75% RH 1	1271
75% RH 2	864
75% RH 3	759

AFM microscopy was put on hold after analysing the data from the first sample due to inexperience. As such the data should be considered with caution. However, using existing software "Gwyddion" to calculate root mean square surface roughness seemed to yield that a higher moisture resulted in a rougher surface. This is explained by the clay coating becoming weaker with more moisture.

6. Conclusions

It was concluded that there is a strong relationship between adhesion and moisture content. Extra care should be considered to make sure that samples for adhesion testing have been stored in proper climate.

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No correlation was found between obtained results and laminator speed for the materials used in this study. From the clay coat experiments it was concluded that kaolin is the most absorbent pigment and can be explained by its lower density allowing more water to be retained. SB is the least absorbent binder of the components used in this study. SB being a less polar polymer than SA and PVAc provides a reasonable hypothesis to why it absorbs less moisture than the others. No hysteresis was found in moisture content of clay coating, combined with the fact that there is hysteresis in fibre moisture and no hysteresis in adhesion it was concluded that adhesion is related to moisture in clay coating rather than moisture in fibres. By comparing contents of commercial materials to absorption of mixtures with similar compositions, it was possible to relate adhesion behaviour to the composition of the material.

7. Future work

A deeper understanding of how moisture affects adhesion may be achieved if the moisture content of each adhesion sample was known, rather than the average of the material. This is currently hard to do because both the adhesion measurement and the moisture content measurement are destructive tests. By creating a continuous graph of number of successful specimens over relative humidity a better cut off for future studies could be found. Using 25% relative humidity mostly serves as a waste of time due to the low amount of results obtained. This, however, would take a significant amount of time to perform. Fully mapping the effects of laminator conditions would improve knowledge about which parameters affect adhesion and would ease elimination of such factors. Continuing microscopy, whether it is with AFM, SEM or some other method would improve understanding of fracture mechanics and could lead to valuable conclusions. Correlating clay coat experiments with real board coatings could lead to improved understanding of how the components affect properties as it seems quite possible to link commercial material contents to moisture absorption.

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Appendix A – Raw data

Table A1: Raw data from adhesion measurements. Values are displayed in N/m (newtons per meter width of sample).

Sample C1	25%		50%		75%		35%
1	-	1	60.5	1	42.28	1	83
2	-	2	60.85	2	44.46	2	-
3	-	3	-	3	43.83	3	86
4	-	4	-	4	41.23	4	85
5	-	5	62.94	5	45.03	5	-
Mean	-	Mean	61.46	Mean	43.36	mean	84.7
Std	-	Std	1.3	Std	1.58	std	1.5
No coating	25%		50%		75%		
1	68.35	1	59.47	1	-		
2	60.76	2	74.11	2	42		
3	63.9	3	57.85	3	44.3		
4	75.53	4	52.7	4	41.83		
5	-	5	-	5	-		
Mean	67.13	Mean	61.03	Mean	42.71		
Std	6.4	Std	9.19	Std	1.38		
Sample C 2	25%		50%		75%		35%
1	-	1	76	1	55.05	1	93
2	-	2	67.5	2	50.14	2	96
3	-	3	-	3	54.39	3	-
4	-	4	75.2	4	48.85	4	-
5	-	5	78.7	5	44.46	5	-
Mean	-	Mean	74.3	Mean	50.58	mean	94.5
Std	-	Std	4.8	Std	4.34	std	2.1
Sample B	25%		50%		75%		
1	-	1	-	1	51.93		
2	-	2	-	2	59.51		
3	-	3	114.7	3	51.82		
4	-	4	97	4	56.57		
5	-	5	99.4	5	55.26		
Mean	-	Mean	103.7	Mean	55.08		
Std	-	Std	9.6	Std	3.29		
Sample E	25%		50%		75%		
1	-	1	-	1	30.01		
2	-	2	121.2	2	22.32		
3	-	3	-	3	17.78		
4	-	4	112.1	4	23.58		
5	-	5	-	5	18.36		

Mean	-	Mean	116.7	Mean	22.41		
Std	-	Std	6.4	Std	4.92		
Sample F	25%		50%		75%		
1	110.28	1	87.2	1	49.93		
2	130.76	2	-	2	41.98		
3	-	3	91.9	3	44.23		
4	-	4	100.1	4	43.4		
5	-	5	-	5	47.15		
Mean	120.52	Mean	93	Mean	45.34		
Std	14.49	Std	6.5	Std	3.19		
Sample G	25%		50%		75%		
1	-	1	-	1	18.29		
2	-	2	63.4	2	19.22		
3	-	3	-	3	20.51		
4	-	4	-	4	19.37		
5	-	5	-	5	17.94		
Mean	-	Mean	63.4	Mean	19.07		
Std	-	Std	-	Std	1.01		
Sample H	25%		50%		75%		35%
1	-	1	87	1	51	1	130
2	135	2	93	2	54	2	122
3	148	3	109	3	48	3	-
4	-	4	111	4	51	4	-
5	138	5	118	5	51	5	125
Mean	140.3	Mean	103.6	Mean	51	mean	125.7
Std	6.8	Std	13	Std	2.1	std	4
Sample D	25%		50%		75%		
1	-	1	85	1	44		
2	-	2	-	2	40		
3	-	3	94	3	-		
4	-	4	-	4	35		
5	-	5	-	5	41		
Mean		Mean	89.5	Mean	40		
Std		Std	6.4	Std	3.7		
Sample A	25%		50%		75%		
1	-	1	-	1	67		
2	-	2	-	2	68		
3	-	3	-	3	-		
4	-	4	109	4	55		
5	-	5	114	5	-		
Mean		Mean	111.5	Mean	63.3		

Std		Std	3.5	Std	7.2		

Table A2: Raw data from moisture content measurements. Values are written in weight %..

Sample C 1	25 %	Sample C 1	50 %	Sample C 1	75%	Sample C1	35%
1	5.70	1	7.75	1	10.72	1	6.21
2	5.68	2	7.67	2	10.60	2	6.30
3	5.75	3	7.69	3	10.64	3	6.26
4	6.09	4	7.72	4	10.86	4	6.21
5	5.82	5	7.77	5	10.74	5	6.33
6	5.72	6	7.73	6	10.74	6	6.36
No coating	25 %	No coating	50 %	No coating	75%	No coating	35%
1	5.33	1	8.23	1	11.59	1	6.46
2	5.36	2	8.20	2	11.47	2	6.45
3	5.29	3	8.13	3	11.69	3	6.50
4	5.36	4	8.26	4	11.60	4	6.42
5	5.38	5	8.14	5	11.68	5	6.36
6	5.36	6	8.08	6	11.46	6	6.44
Sample C 2	25 %	Sample C 2	50 %	Sample C 2	75%	Sample C2	35%
1	5.27	1	7.80	1	10.79	1	6.43
2	5.49	2	7.71	2	10.70	2	6.43
3	5.28	3	7.77	3	10.70	3	6.49
4	5.33	4	7.89	4	10.60	4	6.44

5	5.27	**5**	7.79	**5**	10.85	**5**	6.38
6	5.17	**6**	7.72	**6**	10.77	**6**	6.52
Sample B	**25 %**	**Sample B**	**50 %**	**Sample B**	**75%**	**Sample B**	**35%**
1	4.77	**1**	7.90	**1**	10.82	**1**	6.35
2	4.78	**2**	7.89	**2**	10.65	**2**	6.38
3	4.82	**3**	7.94	**3**	10.86	**3**	6.51
4	4.79	**4**	7.92	**4**	10.82	**4**	6.45
5	4.77	**5**	8.14	**5**	10.80	**5**	6.53
6	4.79	**6**	7.91	**6**	10.81	**6**	6.46
Sample E	**25 %**	**Sample E**	**50 %**	**Sample E**	**75%**	**Sample E**	**35%**
1	5.26	**1**	7.27	**1**	9.73	**1**	5.76
2	5.27	**2**	7.05	**2**	9.70	**2**	5.74
3	5.18	**3**	7.11	**3**	9.54	**3**	5.85
4	5.18	**4**	7.12	**4**	9.61	**4**	5.87
5	5.24	**5**	7.24	**5**	13.11	**5**	5.82
6	5.26	**6**	7.28	**6**	9.60	**6**	5.83
Sample F	**25 %**	**Sample F**	**50 %**	**Sample F**	**75%**	**Sample F**	**35%**
1	4.76	**1**	7.78	**1**	10.45	**1**	6.58
2	4.80	**2**	7.92	**2**	10.58	**2**	6.17
3	4.77	**3**	7.87	**3**	10.51	**3**	6.43
4	4.76	**4**	7.88	**4**	10.80	**4**	6.64
5	4.81	**5**	7.78	**5**	10.61	**5**	6.46
6	4.85	**6**	7.97	**6**	10.44	**6**	6.64
Sample G	**25 %**	**Sample G**	**50 %**	**Sample G**	**75%**	**Sample G**	**35%**
1	5.18	**1**	7.13	**1**	9.65	**1**	5.73
2	5.14	**2**	7.14	**2**	9.90	**2**	5.71
3	5.20	**3**	7.08	**3**	9.68	**3**	5.78
4	5.20	**4**	7.05	**4**	9.70	**4**	5.92

5	5.18	**5**	6.20	**5**	9.77	**5**	5.73
6	5.17	**6**	6.79	**6**	9.68	**6**	5.77
Sample H	**25 %**	**Sample H**	**50 %**	**Sample H**	**75%**	**Sample H**	**35%**
1	4.86	**1**	6.66	**1**	9.59	**1**	5.91
2	4.91	**2**	6.55	**2**	9.56	**2**	5.82
3	4.86	**3**	6.64	**3**	9.59	**3**	5.89
4	4.85	**4**	6.67	**4**	9.74	**4**	5.88
5	4.91	**5**	6.69	**5**	9.60	**5**	5.86
6	5.16	**6**	6.64	**6**	9.62	**6**	5.74
Sample D	**25 %**	**Sample D**	**50 %**	**Sample D**	**75%**	**Sample D**	**35%**
1	5.28	**1**	7.44	**1**	10.53	**1**	6.70
2	5.06	**2**	7.56	**2**	10.60	**2**	6.53
3	5.20	**3**	7.43	**3**	10.47	**3**	6.60
4	5.26	**4**	7.43	**4**	10.54	**4**	6.64
5	5.30	**5**	7.38	**5**	10.52	**5**	6.58
6	5.25	**6**	7.34	**6**	10.67	**6**	6.56
Sample A	**25 %**	**Sample A**	**50 %**	**Sample A**	**75%**	**Sample A**	**35%**
1	5.52	**1**	7.26	**1**	10.41	**1**	6.49
2	5.35	**2**	7.17	**2**	10.51	**2**	6.47
3	5.41	**3**	7.32	**3**	10.46	**3**	6.44
4	5.40	**4**	7.22	**4**	10.49	**4**	6.46
5	5.39	**5**	7.50	**5**	10.44	**5**	6.43
6	5.44	**6**	7.47	**6**	10.45	**6**	6.37

Appendix B – Mixture matrix

Table B1: Intended mixture matrix for clay coat experiments. Values are written in parts rather than percentage. Actual mixture proportions are found in the results section.

Sample no	1	2	3	4	5	6	7	8	9
CaCO3 coarse	100		100	100			100	100	
CaCO3 fine		100			100	100			100
Kaolin									
SA			10		10		15		15
SB				10		10		15	
PVAc									

Sample no	10	11	12	13	14	15	16	17	18
CaCO3 coarse		100		100		50	50		
CaCO3 fine	100		100		100	50	50		
Kaolin								100	100
SA		20	20			15			15
SB	15			20	20		15		
PVAc									

Sample no	19	20	21	22	23	24	25	26	27
CaCO3 coarse		50	50	50	100		50	25	25
CaCO3 fine						100		25	25
Kaolin	100	50	50	50			50	50	50
SA			15					15	
SB	15			15					15
PVAc					15	15	15		