Master's Thesis
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Effect of Ozone Treatment on Molten LDPE on to Aluminum Foil

Astrid Nordin

Packaging Logistics
Lund University

ABSTRACT

BACKGROUND
In the lamination process the use of surface treatment is necessary to improve the adhesion between the different layers of the packaging material. Surface treatment can be described as *Techniques which change the surface characters without affecting properties of the bulk materials*.

One of the surface treatments is the ozone treatment where the ozone is applied to the hot melt just before the melt enters the nip and is put together with the board and aluminum foil. The treatment enables carbon-oxygen bonds to be formed which make the treated surface of the polymer melt oxidized which results in better adhesion.

METHOD
In this project the ozone treatment in the laminate station was examined. Different settings for the ozone parameters were altered in the desire to see which ones play an important role for the adhesion and the measured concentration in the nip region. The parameters that were changed were the ozone concentration [g/m^3], ozone flow rate [m^3/hour] and the ozone applicator angle [°].Furthermore the goal for the project was to get a better understanding of the ozone process.

RESULTS & PROPOSAL
From the results of this study a number of conclusions could be made. First of all the ozone treatment has a positive effect on the adhesion.

The measured concentration in the nip region is far from the same as the ozone concentration set in the generator. In addition the ozone concentration set from the generator fluctuates.

The results from the adhesion measurements showed that the model was poor and no analysis could be made regarding the settings and the adhesion values. The reason for the poor model is most likely caused by noise. The noise could be the test method for the adhesion measurements.

Suggested work regarding the ozone treatment is to improve the test method and equipment for measuring ozone concentration in the nip region. In addition the test method for analysing the adhesion results needs to be investigated to see if it produces reliable results. Finally, many more tests needs to be performed to get the whole understanding for the ozone treatment.

SAMMANFATTNING

BAKGRUND
Inom lamineringsprocessen är användandet av ytbehandling nödvändigt för att förbättra vidhäftningen mellan de olika lagren i förpackningsmaterialet. Ytbehandling kan beskrivas som *Tekniker som ändrar ytegenskaperna utan att påverka merparten av materialets egenskaper*.

Ozonbehandlingen är en ytbehandling där ozon appliceras på den varma smältan precis innan smältan når nypet och sätts samman med kartongen och aluminiumfoliet. Behandlingen möjliggör formering av koloxidbindningar som gör att den behandlade laminatytan oxideras och på så sätt uppnås bättre vidhäftning.

METOD
I projektet undersöktes ozonbehandlingen i laminatstationen. Inställningarna på ozonparametrarna ändrades med en önskan om att se vilka som spelar en stor roll för vidhäftningen och den uppmätta ozonkoncentrationen i nypområdet. Parametrarna som ändrades var ozonkoncentrationen [g/m^3], ozonflödeshastigheten [m^3/h] och ozonapplikatorns vinkel [°]. Vidare var målet för projektet att få en bättre förståelse för ozonprocessen.

RESULTAT & FÖRSLAG
Ett antal slutsatser kunde dras utifrån resultaten från undersökningen. Först och främst har ozonbehandlingen en positiv effekt på vidhäftningen.

Den uppmätta koncentrationen från nypområdet är långt ifrån densamma som den från generatorn. Dessutom fluktuerar ozonkoncentrationen från generatorn.

Resultaten från vidhäftningsmätningarna visade att modellen var dålig och inga analyser kunde utföras angående inställningarna och vidhäftningsvärdena. Orsaken för den dåliga modellen är troligen orsakad av brus. Bruset kan vara testmetoden för vidhäftningsmätningarna.

Förslag på ytterligare arbete inom ozonbehandlingen är att förbättra testmetoden och utrustningen för mätningar av ozonkoncentrationshalten i nypområdet. Ytterliggare så behövs vidhäftningstestmetoden undersökas för att se till att den producerar pålitliga resultat. Slutligen så behöver det göras många fler tester för att förstå hela bilden av ozonbehandligen.

PREFACE

This master's thesis work has been done at the department of Lamination Technology at Tetra Pak in Lund together with the department of Packaging Logistics at LTH during the fall and summer of 2009.

I would like to thank my supervisors at Tetra Pak; Francesco Pisciotti and Mattias Månsson as well as Annika Olsson at the division of Packaging Logistics for great guidance and help. A special thanks also to Guangju Zuo who has been a technical mentor and Sara Ghatnekar-Nilsson, my mentor.

Furthermore, I would like to thank Johan Nilsson for the help with planning the test run and analyzing the results, Rikard Palmqvist for his great assistance ahead and during the test run and the staff at the Pilot plant and Material Analysis for their great support.

Finally I would like to thank Günther Lanzinger together with the department of Lamination Technology for giving me this opportunity. It has been an interesting and enjoyable time with many lessons learnt.

Lund 2009

Astrid Nordin

TABLE OF CONTENT

1. INTRODUCTION

The introduction chapter introduces the reader to Tetra Pak and this project.

1.1 Background

Tetra Pak is a family owned Swedish company that develops, produces and markets complete processing, packaging and distribution systems for food stuffs. The company was founded in 1951 by Ruben Rausing and Erik Wallenberg. The aim was to create a package for milk that requires a minimum of material whilst providing maximum hygiene. Development involved introduction of new techniques for coating paper with plastics and for sealing below the level of the liquid. Over the next decades the company grew and today it employs more than 20 000 people in over 150 countries.[1]

Tetra Pak is one of three companies in the Tetra Laval Group created in 1993, the other two are DeLaval and Sidel. Tetra Pak's headquarter is in Switzerland.[2]

This master thesis is performed at the department of Lamination Technology at Tetra Pak in Lund, Sweden. Their main focus is to build up long term and edge knowledge about the lamination process in Tetra Pak's converting process of packaging material.[3]

The packaging material consists of layers with different materials which are put together in the lamination machine. The surface of the materials is treated in different ways to increase the adhesion between the layers. One of these treatments is the ozone treatment in which the ozone is applied to the polyethylene melt by an applicator formed as a tube with holes in it, see figure 1.

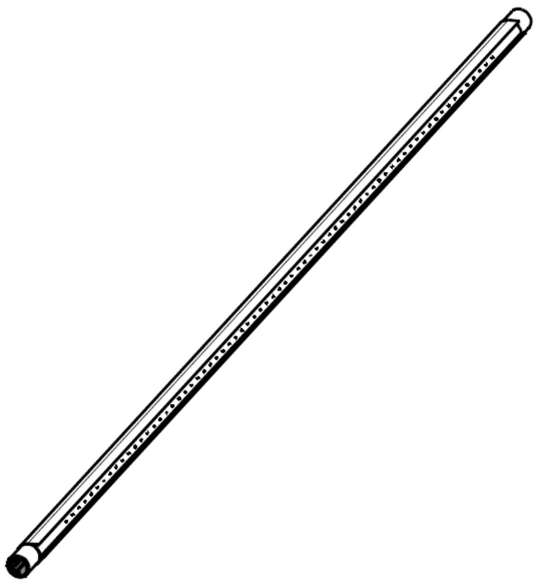

Figure 1: Ozone applicator

[1] Tetra Pak – Development in brief
[2] www.tetrapak.com 2009-02-17
[3] Tetra Pak's Intranät 2009-02-17

1.2 Problem statement

Tetra Pak has used the ozone treatment for many years but there is still a need to have more and deeper knowledge about the treatment. Since it's a small part of the machine it hasn't been examined as much as the other parts and processes in the lamination process. The positive effect of the treatment is known however the design, placement and settings of the applicator are not yet fully investigated.

The ozone applicator is placed just above the nip which is the point of contact between the chill roll and the pressure roll (nip roll) where the molten polymer first contacts the moving substrate[4]. (See figure 2)

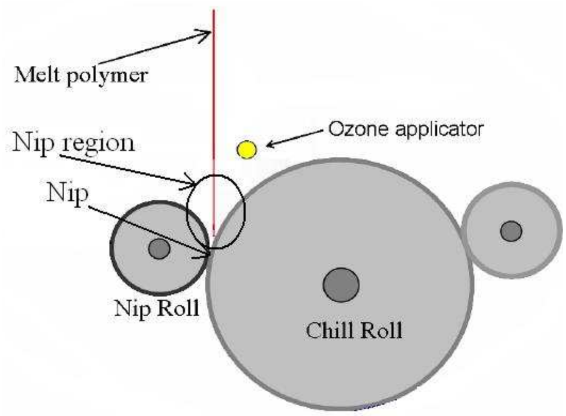

Figure 2: Ozone applicator position

The applicator treats the polymer melt which is positioned between the aluminum foil and the paperboard in the packaging material, see figure 3.

1. Outside layer: Polyethylene (PE)
2. Paperboard (printed or unprinted)
3. Lamination layer: Polyethylene (PE)
4. Aluminum foil
5. Adhesive layer: Polyethylene (PE)
6. Inside layer: Polyethylene (PE)

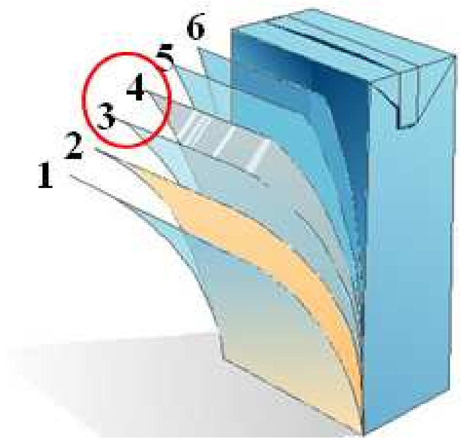

Figure 3: Layers of packaging material

These three materials (paperboard, aluminum foil and polymer melt) bring different air flows and temperatures into the nip. As a result of this the ozone concentration is diluted and the amount of ozone that reaches the polymer melt is not the same as the output from the applicator.

It is unclear how much the position of the ozone applicator in the nip area can affect and reduce the air flows, see figure 3 for the arrangement.

[4] Extrusion coating manual

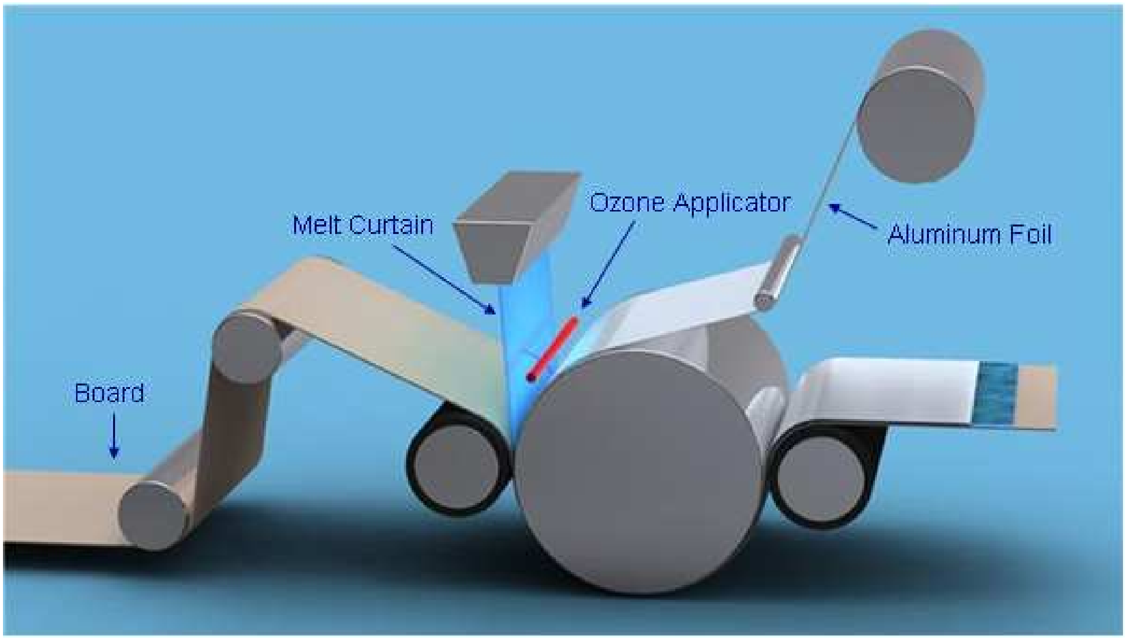

Figure 4: Ozone applicator position

In addition it's also uncertain how the ozone concentration and flow rate combined with the different placements of the applicator affect the rate of ozone that reaches the polyethylene melt.

1.3 Purpose

The purpose of this thesis is two-parted. Firstly it is to get a better understanding of the ozone treatment in the lamination process. Different angles of the applicator in the nip area as well as different variations of the ozone concentration and flow rate will be investigated. The evaluation will be based on in house testing's at the lab at Tetra Pak in Lund.

Secondly the aim is to find a setting that increases the ozone concentration in the nip and therefore improving ozone treating efficiency of the polyethylene melt and the adhesion of aluminum foil to the laminate layer.

1.4 Focus

The laminator has three stations where the different layers of the packaging material are created. As it is today the ozone treatment is used in two of the stations. For this project the chosen station is the laminate station where the ozone applicator treats the polyethylene melt to adhere better to the aluminum foil, see figure 5.

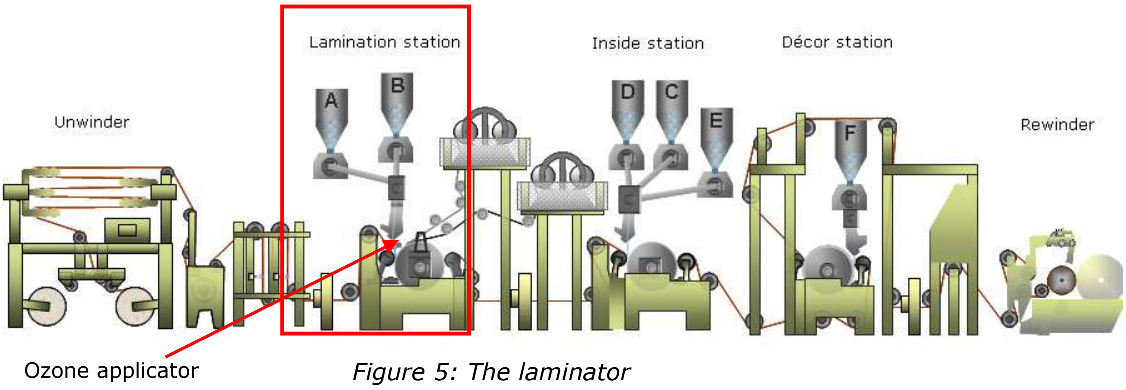

Figure 5: The laminator

The test run for the thesis was performed in the test factory in Lund, Pilot plant. Since there's many on-going projects at Tetra Pak the time in Pilot plant was restricted to one day. If more time was given more tests could have been performed.

The test run was planned with the help of the Design of Experiment program MODDE.

The test material for the test run was the following:

- Standard cartoon, 80 mN produced by Frövi, with no holes or creasing
- Low density polyethylene (LDPE)
- Aluminum foil was 6,35 µm from Hydro aluminum

The evaluation is based on adhesion ability and measured ozone concentration in the nip area.

No changes in applicator distances to melt and nip were able to be performed due to safety issues in the Pilot plant.

The area of ozone treatment is a relatively unexplored area. Its effects have never been quantified statistically in published data. Therefore it was rather difficult finding literature covering the area.

1.5 Target group

The main target group for this thesis is the employees at Tetra Pak that has an interest in the results and can use it for further development within the area of surface treatment. The thesis is also intended for engineering students with an interest in surface treatment.

2. METHODOLOGY

The chapter describes different approaches in choosing a methodology. It explains the chosen method for this project and motivation. The work procedure is also described.

2.1 Methodology approach

The chosen methodology depends on the goals and character of the project. The work can be divided into four different main objectives:

- *Descriptive studies* with its main objective to find out and describe how something works or performs.
- *Exploratory studies* aim to get at deeper knowledge of how something works or performs.
- *Explanatory studies* look at reasons and explanations for how something works or performs.
- *Problem solving studies* with its main objective is to find a solution for an identified problem. [5]

The different types of studies are mostly performed as separate studies but within bigger projects there's often more than one main objective that is performed.[6] [7]

It is important to find a suitable method or combination of methods to be able to perform the work. For different methods different tools can be used for the data collection. These could be interviews, observations, questionnaires and analyses of documents. The data can be quantitative or qualitative. Quantitative data is things that can be counted or identified. The data can be analyzed with the help of statistical analysis. The qualitative data consists of words and descriptions and sorting and categorization is how the data is analyzed. In many cases both quantitative and qualitative data is necessary.[8]

2.2 Choice of method and data collection

Since the purpose in this project is to get a better and deeper understanding of the ozone treatment in the lamination process the chosen methodology is the exploratory.

In this project both quantitative and qualitative data will be used. The quantitative data is the results from the test run. The qualitative data is information collected from literature study, interviews, earlier reports etc.

2.3 Work procedure

In the beginning of the project a project plan was established, see figure 6. The initial activity was a literature study in order to get a better understanding of the

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[5] Att genomföra examensarbete
[6] http://www.nationmaster.com/encyclopedia/Pure-research#Research_methods (2009-03-15)
[7] Forskningsmetodikens grunder: Att planera, genomfora och rapportera en undersokning
[8] Att genomföra examensarbete

subject. To facilitate the navigation in Tetra Pak's databases a meeting was held with a technology information researcher at Tetra Pak.

This literature study included:

- Books and articles concerning ozone and surface treatment
- Technical studies performed at Tetra Pak
- Reports published in different forums at the internet
- Interviews with employers at Tetra Pak and other companies (Epsilon)

These different sources were used as a reference base to get a theoretical input within the area.

Furthermore different computer programs and test methods have been studied in order to complete the project, these were:

- DoE, Design of experiment
- Minitab
- Test methods for
  - adhesion
  - wettability
  - ozone concentration

Simultaneously as the literature study was performed the test run for the tests in Pilot plant were planned. Throughout the project regular meetings with the mentors involved in the project were held.

The figure (Figure 6) below shows the work flow for the master thesis. See appendix 1 for a better view.

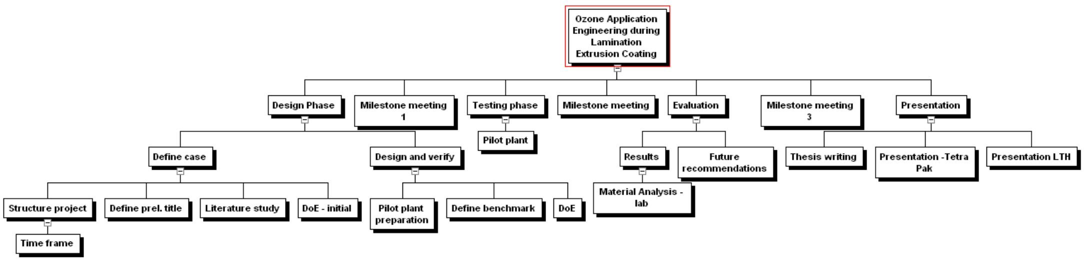

Figure 6: Work flow

2.4 Design of experiment (DoE)

Design of experiment is a statistical experimental design in which a set of carefully selected experiments is conducted in which all relevant factors are varied simultaneously.

There are three main types of problems, called experimental objectives, to which Design of experiment is applicable to:

1. Screening – identify the most influential factors and determine their appropriate ranges
2. Optimization – determine which combination of the essential factors that will result in optimal operating conditions.
3. Robustness testing – determine the sensitivity of a procedure to small changes in the factor settings.

Before conducting experiments there are some input conditions that needs to be specified. These are the number of factors and their ranges, the number of responses and the experimental objective. The factors are the tools that are used to manipulate the system. The responses informs about properties and general conditions of the studied system. See figure 7 for a figurative description.

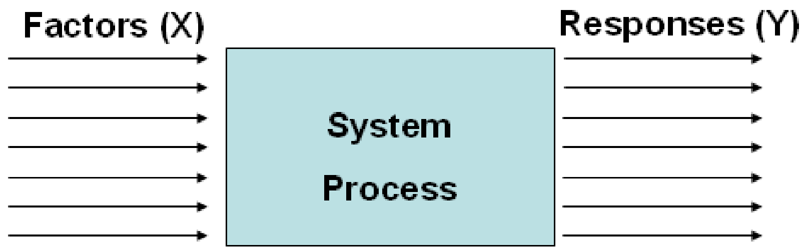

Figure 7: Design of experiment system

When the variables have been decided the design of the tests can be created and the tests can be performed. The results are then investigated using a regression analysis. The result is a model that will indicate which factors are most important and how they can be combined to influence the responses.[9]

2.4.1 Full factorial design, 2^3

The name of the design means that there are three factors that each has two levels (high and low). This result in 8 variants and then three centre points are added (with middle values). In total the experiment exists of 11 variants where the centre points have the same values. With the centre points it is possible to investigate the repeatability in the test run. See figure 8.

[9] Design of Experiments – Principles and Applications

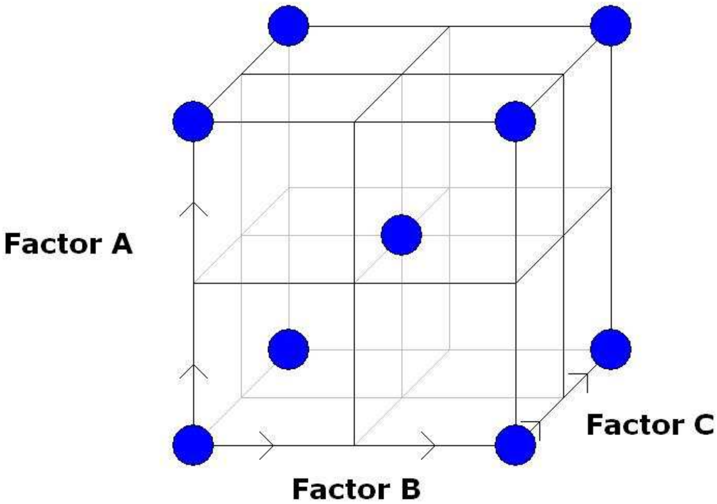

Figure 8: 3-dimentional overview of a 2^3 factorial test

The model looks like the following:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_{12} + \beta_{13} x_{13} + \beta_{23} x_{23} + \varepsilon$$

In the model y is the response, the x's are the three factors, β_0 is the constant term, β's the model parameters and ε is the residual response variation that is not explained by the model. The aim of the data analysis is to estimate numerical values of the model parameters (β), called regression coefficient, and these values will indicate how the factors influence the response. The regression coefficients are easy to overview when they are plotted in a bar chart, see figure 9.[10]

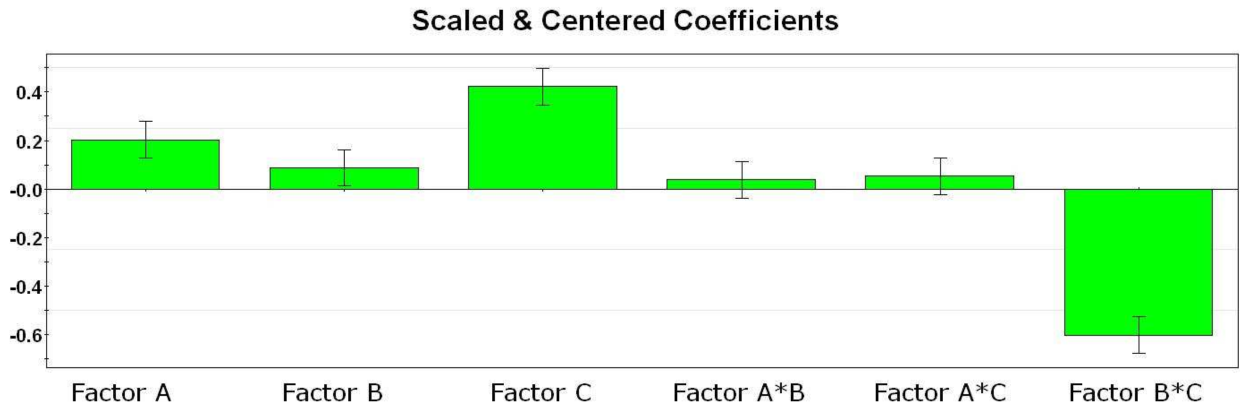

Figure 9: Coefficient plot

[10] Design of Experiments – Principles and Applications

2.4.2 Data analysis

The first part in the analysis is called Evaluation of raw data. When the factors and responses have been decided and the factors have been given a low and high value it is important to evaluate the performance of the experimental design prior to its execution. One tool that can be used for this is the condition number.

When the model is approved by the MODDE program (the design of experiment program) the test is ready to be performed. After the results are received they are put in the program which then uses the figures to analyze the material. The analysis consists of different steps and is called the regression analysis.

Finally when it is believed that the optimal regression model is obtained it is important to carry out the third stage of the data analysis, use of model. The aim of this part is to get a better understanding of the modeled system, to decide if it is necessary to continue experimenting. If that is the case the aim is to locate good factor settings for doing this. One way of finding these is to use the response contour plot.[11]

2.4.3 Example

To easier understand the way the data analysis works an example is given where parts of the three main steps (evaluation of raw data, regression analysis and use of model) are presented. The example is called Cake Mix and the outcome is to find out which ingredients play the most important role in deciding the best tasting cake.

The chosen factors are (see figure 10):

- Flour
- Shortening
- Egg powder

The response is:

- Taste

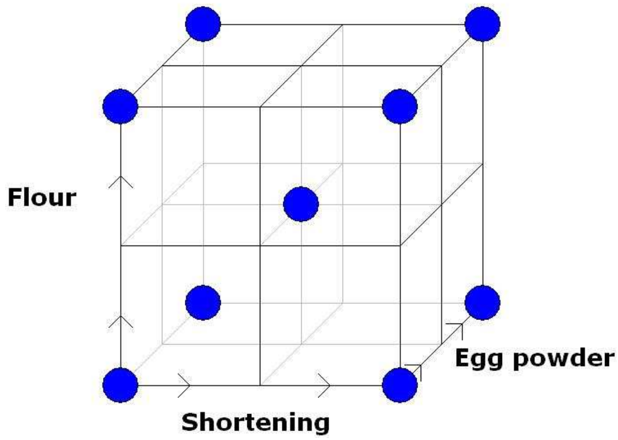

Figure 10: Cake Mix example

[11] Design of Experiments – Principles and Applications

Below the different steps in a regression analysis is listed with the example Cake Mix.

EVALUATION OF RAW DATA

Condition number

The condition number shows how balanced the design is. If the number is below 3, it's a good design. Up to the value 6 is ok, but above that the design should be remade for obtaining a reliable model.[12]
The condition number for the Cake mix design is 1,1726 and therefore the design is well balanced.

Replicate plot

In the replicate plot the measured values of a response are plotted against the unique number of each experiment. In the plot each variant is resembled by an own stick. Experiments with identical factor settings (the centre points) will show up in the same stick. Preferable the variation of the repeated experiments (the centre points) should be smaller than the overall variability.

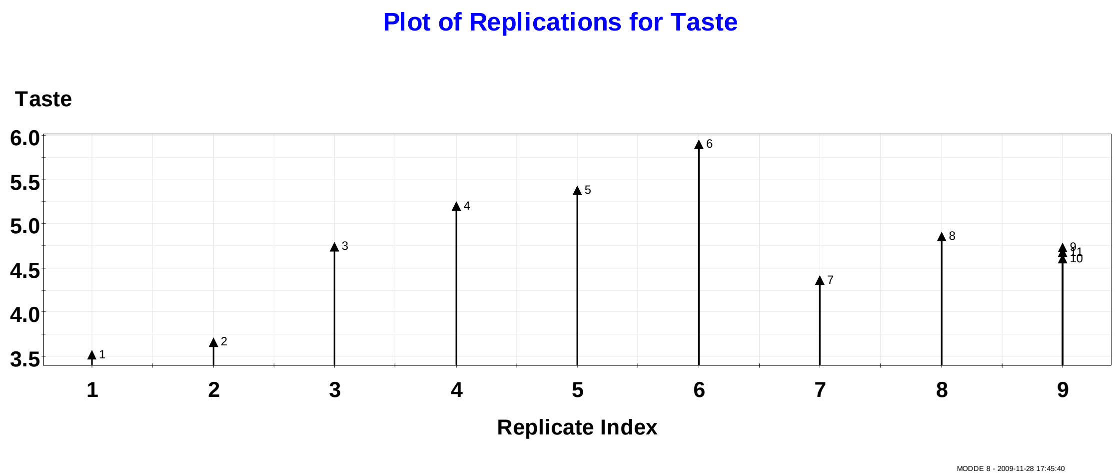

Figure 11: Replicate plot

The figure above shows the replicate plot for the Cake mix example. Number 9, 10 and 11 are the centre points as they're shown in the same stick. The variation of the repeated experiments (the centre points) is smaller than the overall variability which proves a good model.

REGRESSION ANALYSIS

The summary of fit plot

When fitting a regression model the most important tool consists of two parameters R^2 and Q^2.

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[12] Martin Berntsson, Senior Application Specialist, Umetrics

R^2 is called the goodness of fit and measures how good the regression model can be made to fit the raw data. R^2 varies between 0 and 1, where 1 indicates a perfect model and 0 no model at all. (R^2 is the green bar in figure 12)

As can be seen in the figure below (Figure 12) the Cake Mix example shows a R^2 of 0,995 which is very good.

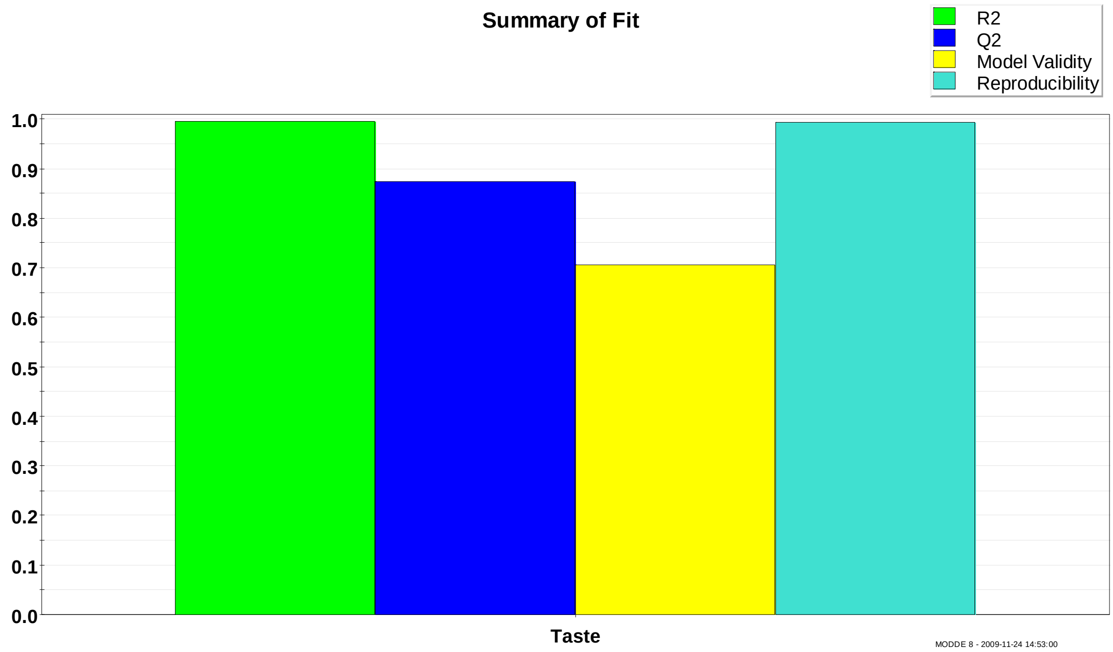

Figure 12: Summary of fit for Cake Mix

Q^2 is called the goodness of prediction and estimates the predictive power of the model. Therefore it is a more realistic and useful performance indicator than the R^2. The upper limit for Q^2 is 1 and its lower limit is minus infinity. If Q^2 is higher than 0.5 the model is considered good. If Q^2 is higher than 0.9 the model is considered as excellent.
For a model to pass the test both R^2 and Q^2 should be high and the difference between them should not exceed 0.2-0.3. A large difference is a warning of an inappropriate model. (Q^2 is the blue bar in figure 12.)

In the Cake Mix example the Q^2 is 0,874 which is also very good. The difference between R^2 and Q^2 is 0,121 which show that the model passes the test.

Other parameters to look at are the model validity and the reproducibility.
The model validity reflects whether the model is appropriate in a general sense. For example if the right type of model (linear, interaction, quadratic) was chosen from the beginning in the problem formulation. The higher the number is the more valid the model is. A value above 0.25 suggests a valid model. (The model validity is the yellow bar in figure 12.)

In the Cake mix example the value of the model validity is 0,705 which imply that the model is valid.

The reproducibility parameter is a numerical summary of the variabilities plotted in the replicate plot. The higher the value is the smaller the replicate error is in relation to the variability seen across the entire design. When the Reproducibility bar is 1.0, the pure error is 0. This means that under the same conditions the values of the response are identical. The value should be over 0.5. (The reproducibility is the turquoise bar in figure 12.)

In the Cake Mix example the reproducibility 0,992 which is extremely good.

Coefficient plot

The coefficient plot displays the regression coefficients with confidence intervals. This plot is used to interpret the coefficients.

By default the coefficient plot is for data centred and scaled. The scaling of the data makes the coefficients comparable. The size of the coefficient represents the change in the response when a factor varies from 0 to 1, in coded units, while the other factors are kept at their averages.

The coefficient is significant (different from the noise), when the confidence interval does not cross zero.[13]

In the plot in figure 13 the bars resembles the factors and also interactions between the factors.
The size of the bar indicates the impact on the response, the bigger the bar is the bigger influence on the response. The black small line represents the confidence interval. The coefficient is significant when the confidence interval does not cross zero.

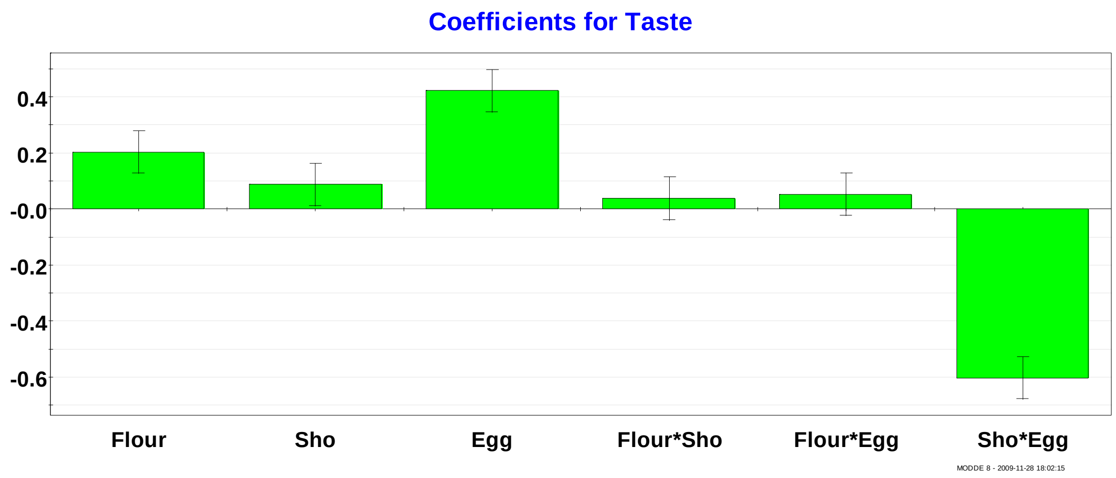

Figure 13: Coefficient plot for Cake Mix

[13] MODDE program version 8

The interpretation of the model indicates that in order to improve the taste one should concentrate on increasing the amounts off egg powder and flour.

The two-factor interaction between flour & shortening and flour & egg powder are statistically insignificant as their confidence intervals include the zero line. Therefore they can be removed from the plot in order to improve the model. The large two-factor interaction between shortening & egg powder has a big influence as well on the taste if they are varied at the same time. However the plot doesn't explain how they should be increased or decreased for a better taste of the cake.

Normal probability plot of residuals

Another important diagnostic tool is the normal probability plot of response residuals. The Normal Probability Plot of residuals displays the residuals on a double Log scale. With this plot it is possible to:

1. Detect outliers
2. Assess Normality of the residuals

In the plot the vertical axis shows the normal probability of the distribution of the residuals. The horizontal axis corresponds to the numerical values of the residuals. If the residuals are random and normally distributed, the Normal probability plot of the residuals has all the points lying on a straight line between -4 and + 4. All experiments outside $\pm$ 4 are considered as statistically significant outliers and may be deleted.

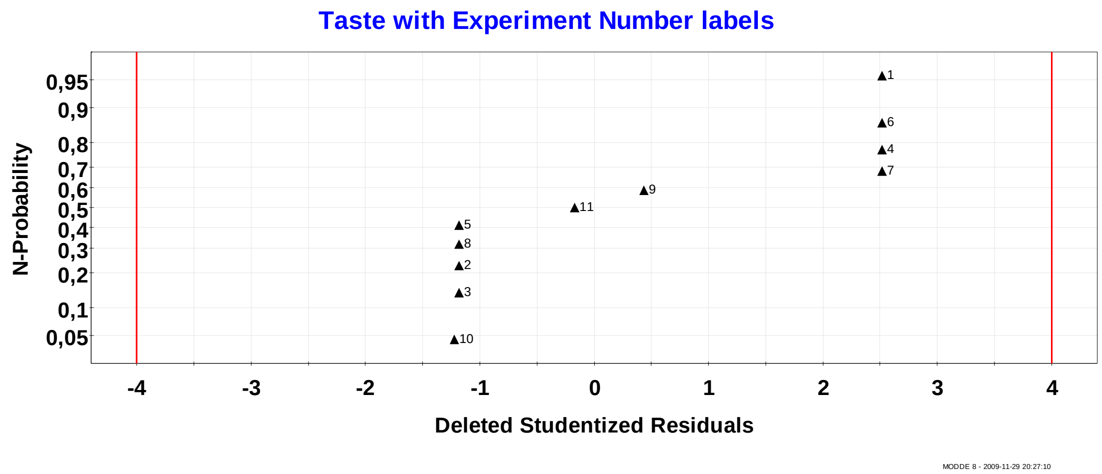

Figure 14: Normal probability plot of residuals for Cake Mix

In the plot displayed above it can be seen that there are no outliers (all residuals are within the $\pm$ 4 lines). The residuals in the figure above are not perfectly aligned on a straight line but they are within the $\pm$ 4 lines.

Observed vs. predicted plot

The plot displays the observed versus predicted values of the response. With a good model all the points will fall on the 45degree line. The plot below is an example of a good model.

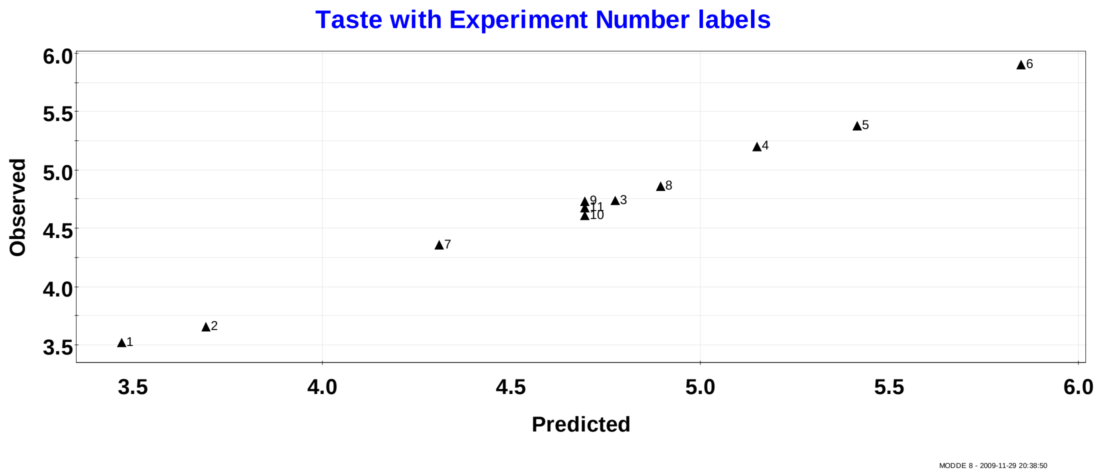

Figure 15: Observed vs. predicted plot for Cake Mix

USE OF MODEL

Response contour plot

The last stage in the analysis of the data is to use the regression model for making predictions. The aim is to gain a better understanding of the modelled system, to decide if it's necessary to continue experimenting and, if so, to locate good factor settings for doing this. In the response contour plot the modelling results are converted into maps which are used to clarify where the best operating conditions are to be expected.[14]

In the cake mix example it's interesting to look at the strong two-factor interaction between shortening and egg powder. The flour is fixed at its high level since that would give the best taste according to the coefficient plot.

[14] Design of Experiments – Principles and Applications

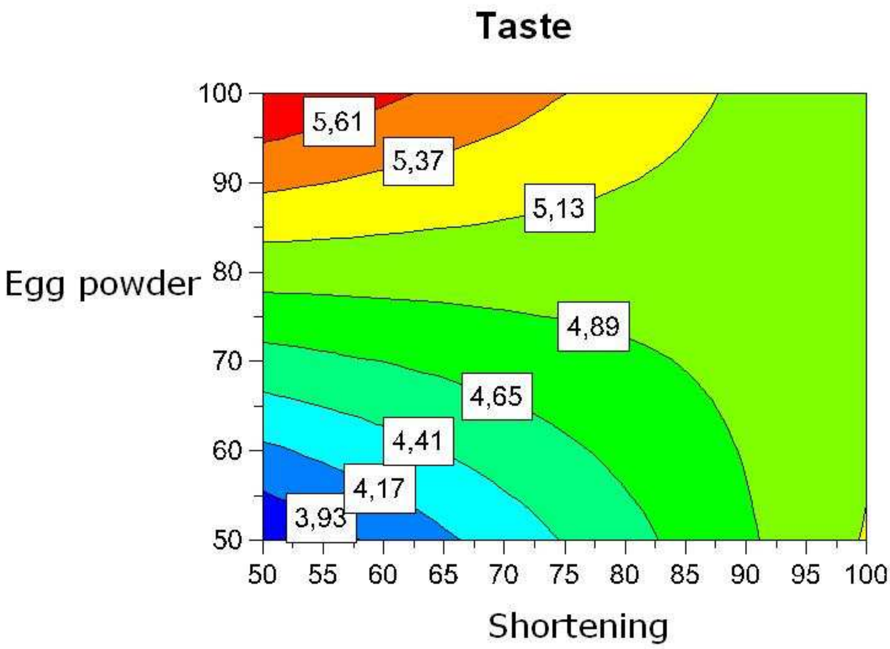

Figure 16: Contour plot for Cake Mix

The plot shows that the best tasting cake is achieved in the upper left corner (the red area) where the level of egg powder level is high and the shortening level is low.

2.5 Changes

Originally the purpose of the test run was to alter not only concentration, flow rate and application angle but also the distance from the applicator to the laminate and the distance to the nip. See figure 17.

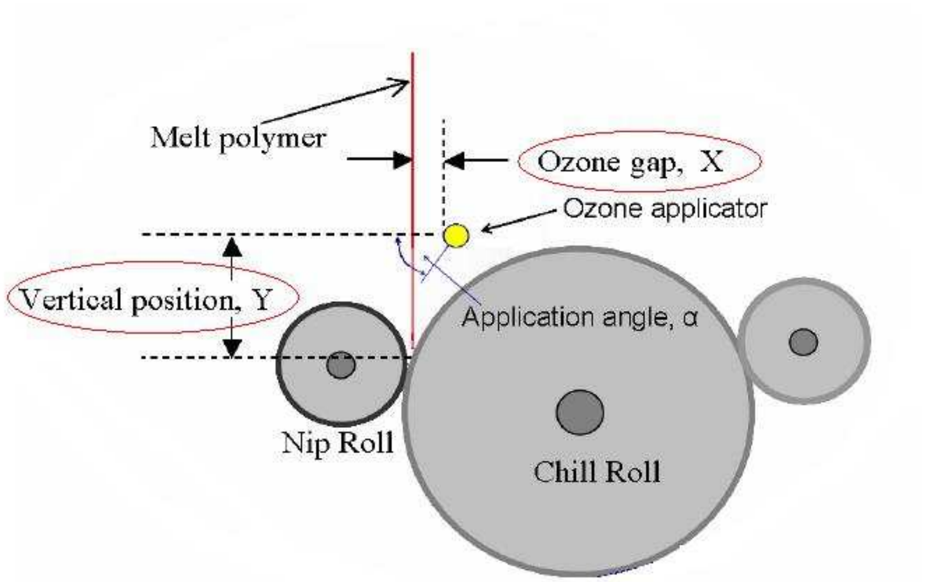

Figure 17: Ozone treatment settings

Due to safety issues and lack of time in Pilot plant the distance to the applicator and to the nip were cancelled. As a result of the changes the test plan became a full factor test where all variants were able to be tested. In the original plan the test plan was a reduced factor test which means that not all variants are tested.

3. THEORY

The chapter describes the lamination technology focusing on the surface treatment and foremost the ozone treatment.

3.1 Converting process/Lamination

Lamination is a process of binding different materials together to form a single whole. At Tetra Pak this means binding together laminate of paper, polymer and for aseptic packages aluminum foil into different combinations in order to create the carton-based packaging material. The combination of the different materials is varied to fit each of Tetra Pak's product categories[15]. See figure 18 for the different categories.

Figure 18: A part of Tetra Pak's product portfolio

Below is a description of the most common Tetra Pak packaging material structure.

1. **Décor layer –** Protects the package against external humidity. Also allows sealing of the package.
2. **Paperboard and printing** – Strengthens the package and offers a good printing surface.
3. **Lamination –** A plastic layer which allows the paperboard to stick to the aluminum foil.
4. **Aluminum foil –** Protects the product against oxygen and light.
5. **Internal coating –** A coating that offers good bond between the aluminum foil and the inside plastic layer.
6. **Inside plastic layer –** Prevents the liquid contents from soaking into the material. Also allows sealing of the package.[16]

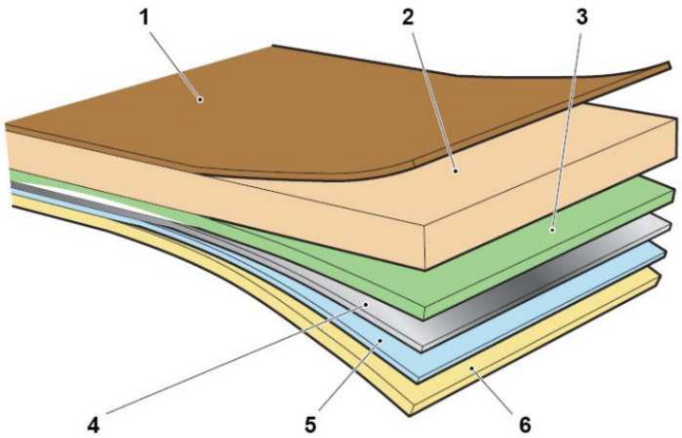

Figure 19: Different layers of packaging material

[15] Tetra Pak - development in brief
[16] Tetra Pak Internal

3.2 The laminator

In extrusion laminating two substrates are combined with the help of a polymer. In the laminate station the substrates are paper board and aluminum foil. The polymer exist the die as a hot thin film with a thickness of approximately 0,6mm. The polymer is drawn down into the nip and formed by the chill roll and the rubber sleeved pressure roll. The substrates are constantly fed to the same nip where they are combined with the molten polymer under pressure. [17]

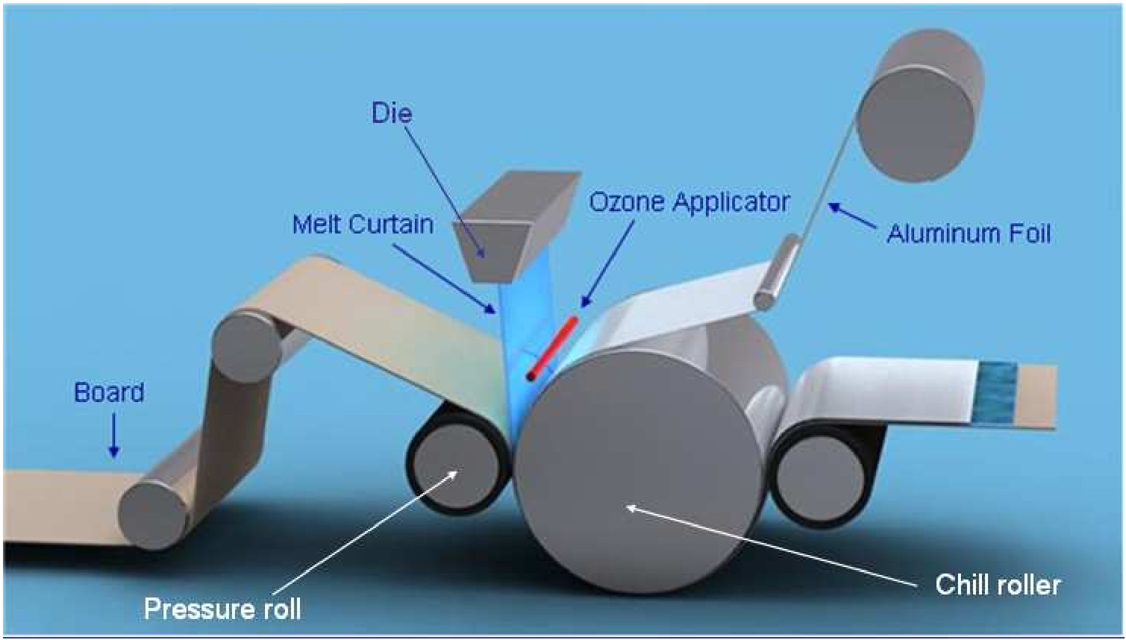

Figure 20: The laminate station

The whole laminator is approximately 60 m x 15 m x 6 m[18]. The machine consists of three different stations where the different layers of the packaging material are put together, these are:

- **Lamination station** – where the aluminum foil is glued to the paper board with a polymer layer
- **Inside station** – where the inside polymer layers is added to the packaging material
- **Décor station** – where the polymer is applied to protect the printed surface

[17] Extrusion coating
[18] Fredrik Persson, 2009-03-17

Tetra Pak has three different models/build-ups of the machine in the factories depending on the sequence of the stations. They are the following:

- **L-I-D**: laminate – inside - décor
- **D-L-I**: décor – laminate - inside
- **L-D-I**: laminate – décor - inside

The figure below (figure 21) shows an L-I-D laminator which is the most common one.[19]

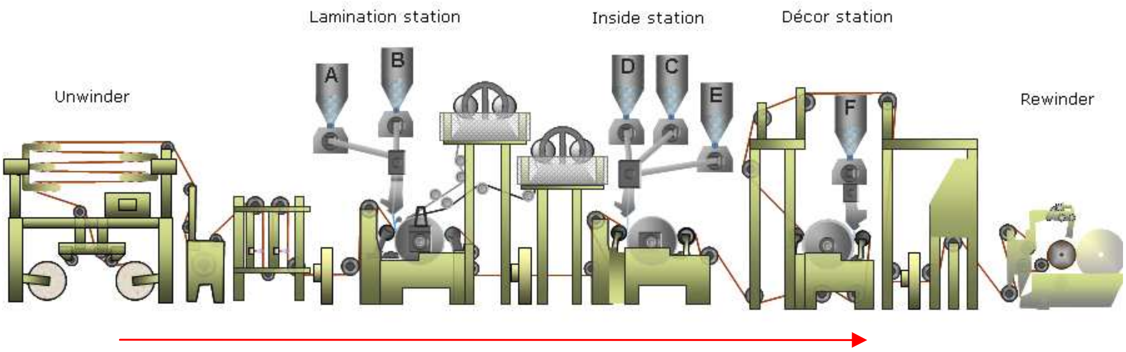

Figure 21: The laminator (the arrow shows the web direction)

[19] Tetra Pak - World Class Lamination material, Ulla Nimmermark

3.3 Adhesion

In extrusion coating and laminating one of the most important properties is adhesion of the polymer to the substrate. The adhesion is a value of the force that holds two different layers of material together. If the adhesion is bad the coating can easily be removed from the substrate.[20]

Adhesion is obtained by mechanical or chemical bonding. Mechanical bonding occurs where molten polymer physically penetrates the fibers of a porous substrate such as paper or board. Chemical bonding to nonporous substrates (such as aluminum foil) is achieved by the oxidation of the extrudate as well as by the treatment (or priming) of the substrate.[21]

Adhesion for a nonpolar polymer such as Low Density Polyethylene (LDPE) is accomplished by a combination of oxidation of the extrudate and treatment of the substrate (described in chapter 3.5). The level of a natural oxidation of the melt is a function of:

- Melt Temperature of laminate
- Line Speed
- Air Gap (see figure 21)
- Coating Weight [22]

Some combinations of these variables will give acceptable adhesion, but can also produce undesirable effects such as increased taste and odour or poor heat seal strength.[23]

Higher melt temperatures increase the oxidation of the extrudate which leads to higher adhesion. Slower line speed allows more time for oxidation in the air gap and enhancing the adhesion. Heavier coating weights carry more heat to the substrate with a result of enhanced adhesion.

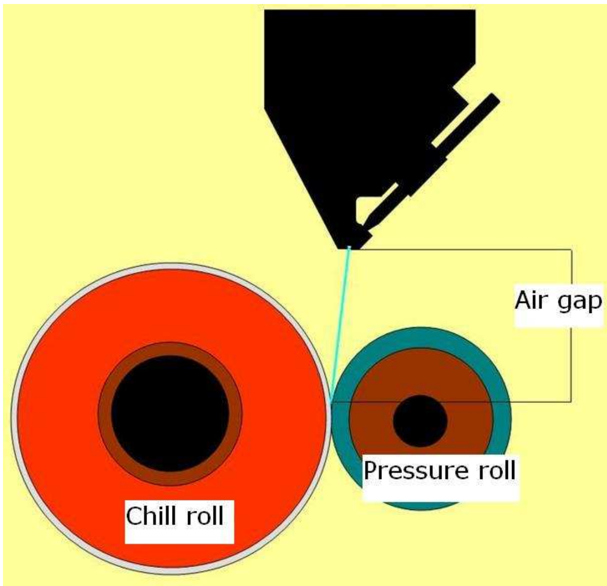

Figure 21: The air gap

[20] Atmospheric plasma -the new functional treatment for extrusion coating and lamination processes
[21] Extrusion coating manual
[22] Effect of time, temperature, and draw down on interlayer peel strength during co-extrusion coating, film casting, and film blowing
[23] Atmospheric plasma -the new functional treatment for extrusion coating and lamination processes

However changing either process parameters has its limitations as listed in the table below:[24]

Polymer melt oxidation	Process parameter	Quality limitations
High	Low line speed	Low production rate, high neck-in*, cooling of extrudate, odor/off-taste, poor sealing
High	High air gap	High neck-in, cooling of melt, odor/off-taste, melt instability
High	High melt temperature	Odor/off-taste, high neck-in, chill roll sticking, polymer degradation through chain scission and cross-linking

Table 1: Process parameters and limitations

> * Neck-in is when the laminate shapes like a curve on the sides instead of going straight down into the nip. The outcome is that the length of the laminate when it hits the nip is shorter than it is when it exits the holder.

To further improve the oxidation level different surface treatments are used, these will be described in chapter 3.5.

3.3.1 Theories of adhesion

There are four main theories of adhesion, they are:
- Adsorption
- Electrostatic
- Diffusion
- Mechanical keying

In the adsorption theory the macromolecules of the mobile phase (laminate) are absorbed onto the substrate (paperboard or aluminum foil) and held there by forces. These forces range from weak dispersion forces to chemical bonds where an interface exists.

In the electrostatic theory a transfer of charge happens between the mobile phase and the substrate so that they are held together by electrostatic forces.

The diffusion theory eliminates the interface by requiring the diffusion of the mobile phase into the substrate.

In the mechanical keying theory the mobile phase flows into the irregularities (pits and troughs) of the substrate surface. Then after hardening a keying action occurs.

The theory that is most generally applicable is the absorption theory.

But before an adhesion can occur it is necessary to have good contact between the two materials. Therefore wettability is of high importance. [25]

[24] Extrusion coating – there really is a good side to ozone
[25] Adhesion and bonding to Polyolefins

3.4 Wettability

To estimate the adhesion performance one can look at the spreading of a fluid drop on the surface, called wettability. This can be indicated by the water contact angle which is the angle between the sample surface inside the drop and the tangent of the drop at the sample surface (see figure 22). Good adhesion and wettability is indicated by a small angle. [26] When the attraction is poor a large contact angle is obtained, could be greater than 90°. See figure 23.

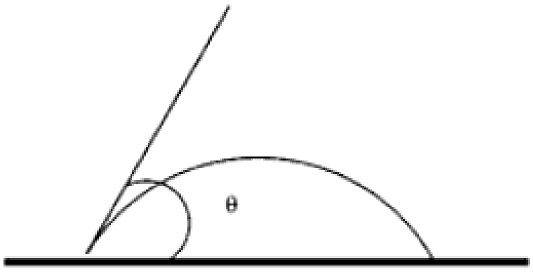

Figure 22: Water contact angle

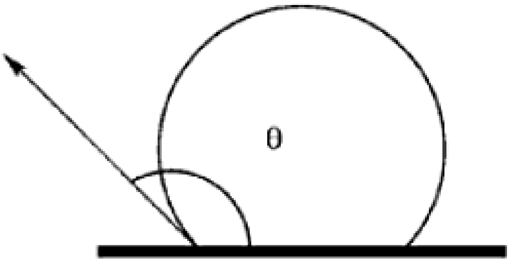

Figure 23: Large contact angle

To be able to estimate the surface free energy (SFE) of a substrate the contact angle values from various pure liquids can be used. One method is the Owens, Wendt and Kaelble which enables the polar and dispersion components of the surface free energy to be evaluated from the knowledge of the contact angle of various liquids of known polar and dispersion values.

The equation to use is:

$$\frac{(1+\cos\theta)\gamma_l}{2(\gamma_l{}^d)^{1/2}} = (\gamma_s{}^p)^{1/2}(\frac{\gamma_l{}^p}{\gamma_l{}^d})^{1/2} + (\gamma_s{}^d)^{1/2}$$

Where: γ_l is the SFE of the liquid

$\gamma_1{}^d$ is the dispersion component of the liquid SFE

$\gamma_1{}^p$ is the polar component of the liquid SFE

γ_s is the SFE of the solid

$\gamma_s{}^p$ is the polar component of the solid SFE

[26] Adhesion performance of UHMWPE after different surface modification techniques

$\gamma_s^{\ d}$ is the dispersion component of the solid SFE

This is the equation of a straight line where $\frac{(1+\cos\theta)}{2\gamma_l(\gamma_l^{\ d})^{1/2}}$ is plotted against $(\frac{\gamma_l^{\ p}}{\gamma_l^{\ d}})^{1/2}$. Hence the square of the gradient is $\gamma_s^{\ p}$, i.e., the polar component of the surface free energy of the solid and the square of the γ intercept is $\gamma_s^{\ d}$, i.e., the dispersion component of the surface free energy of the solid.

To contribute to the surface free energy of a polymer the easiest way is to alter the polarity of the surface (although the greatest contribution comes from the dispersion component). By doing this the adhesion can be increased ten times. The great improvement comes from better wetting and stronger interfacial attraction caused of the new functionality.[27]

[27] Adhesion and bonding to polyolefins

3.5 Surface treatment

When the parameters of extrusion and coating are optimized the final step is to enhance the adhesion between the polymer and substrate by the use of surface treatment.[28] When the surfaces are treated successfully the adhesion between them increases since the bonding ability improves.[29]

Surface treatment is *Techniques which change the surface characters without affecting properties of the bulk materials*.[30]

Surface treatment can be applied to plastic materials, paper and foil. Especially plastic is non receptive to bond with substrates, printing inks, coatings and adhesives. The reason for this is that plastics generally have chemically inert and nonporous surfaces with low surface tension.[31] Surface tension is what causes the surface portion of liquid to be attracted to another surface.[32]

Polyethylene and polypropylene have the lowest surface energy (see table 2) and are often surface treated to improve their bonding characteristics. [33]

Substrate		**Surface energy dyn/cm = mN/m**
Polycarbonate	PC	46,0
Polydimenthyldisiloxane		14,1
Polyethylene (low density)	LDPE	31,0
Polyethylene (high density)	HDPE	33,0
Polyethylenterephtalate	PET	43,0
Polyoxymethylene	POM	38,0
Polypropylene	PP	32,0
Polystyrol	PS	33,0
Polytetrafluorethylene	PTFE	18,0
Polyvinylchloride	PVC	39,0

[34]

Table 2: Substrates and their surface energy

The adhesion between the polyethylene and aluminum foil is generally very low. This is due to low wettability and the lack of polar or reactive groups on the surface which is what otherwise gives strong chemical bonds and interactions. One way to improve the adhesion is to introduce polar groups on the polyethylene surface through oxidation. The aluminum can also be treated in different ways to improve the adhesion but that will not be investigated further in this project.[35]

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[28] Extrusion coating
[29] Corona Treatment: an overview
[30] Guangju Zuo, Lamination technology
[31] Corona Treatment: an overview
[32] NE 2009-02-18 sökord Surface tension
[33] Polymers: Chemistry and Physics of modern materials
[34] PP surface treatments for lamination extrusion coating
[35] Tetra Pak internal development report 1992-09-24_DR0006500C[1]

The four surface treatments techniques used in Tetra Pak are:

- Ozone treatment
- Flame treatment
- Corona treatment
- Plasma treatment

3.5.1 Ozone treatment

(Standard treatment in Tetra Pak laminators.)

The ozone is applied to the molten polymer in the lamination station and the décor station. The treatment enables carbon-oxygen bonds to be formed which make the treated surface of the polymer melt oxidized which results in better adhesion.[36]
More information about ozone treatment is found in chapter 3.6.

3.5.2 Flame treatment

(Standard treatment in Tetra Pak laminators.)

Flame treatment is the normal technique to treat and modify paper board surface before extrusion coating in the lamination and décor stations.[37] See figure 24.

In the treatment air and fuel gas are premixed before entering the burner nozzle. During gas combustion in the flame, energised species such as free radicals, electrons, ions, and neutrals bombard the substrate surface. The energetic radicals react with the uppermost molecules at the surface which, in turn, lead to that polar functional groups are introduced at the material surface.

Figure 24: Flame treatment

The positive effects of the treatment are:

- Burning off dangling fibres that could create integrity problems
- Increasing the surface energy, wettability and adhesion by
    - Incorporation of polar groups
    - Cleaning
    - Cross-linking for adhesion
- Heating up the substrate which may be beneficial for adhesion[38]

[36] Tetra Pak – World Class Lamination material
[37] Lamination converting process
[38] Tetra Pak – World Class Lamination material

3.5.3 Corona treatment

(Used in some Tetra Pak factories for foil and paperboard treatment.)

Corona treatment is commonly used to surface modify paperboard, polymer films and foils and enhance adhesion against extruded polymers. See figure 25. The treatment involves the application of a high-energy electromagnetic field between an electrode and a ground roll. The air molecules in the air gap are ionised by the electric field. These species change and affect the surface characteristics without changing the bulk properties, and the result is improved wettability and increased surface energy.[39] It has been shown that the corona discharge leads to surface oxidation. [40]

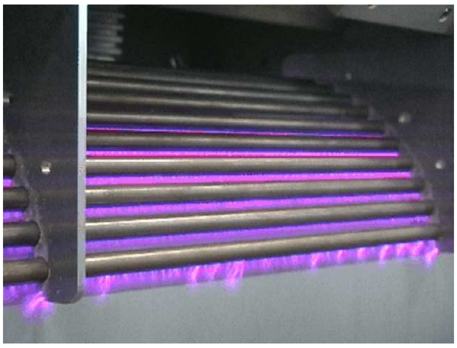

Figure 25: Corona treatment

3.5.4 Plasma treatment

(Under industrialization for aluminum foil treatment.)

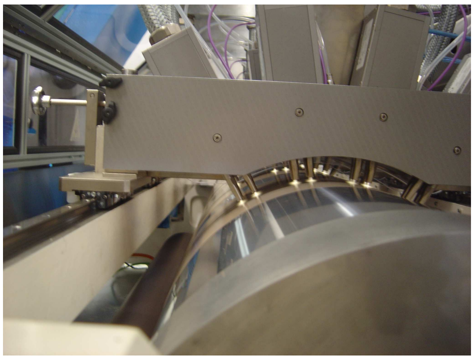

Figure 26: Plasma treatment

Plasma treatment is an ionized treatment like corona and flame.[41] See figure 26. The treatment helps both with generating radicals and oxidising the surface of the material.[42] The plasma treatment improve wettability of plastic materials with low surface energy, i.e. polyolefin materials, PE, PP and many others by raising its surface energy and improve adhesive characteristics by creating multiple bonding sites.[43]

[39] Tetra Pak – World Class Lamination material
[40] Extrusion coating
[41] http://www.sigmalabs.com/sigma/atmosplas.htm
[42] http://www.blurtit.com/q604329.html
[43] http://www.tantec.com

3.6 Ozone treatment

The ozone is used for treating the molten polymer in the lamination station and the décor station. The treatment enables carbon-oxygen bonds to be formed which make the treated surface of the polymer melt oxidized which results in better adhesion.[44] See figure 27.

The interest for ozone treatment began in the mid- to late 1970s when there was a dramatic increase in oil prices which lead to an urgent need to reduce polymer coating weights. Due to this, additional aids for increasing adhesion were needed and the ozone treatment was introduced.[45]

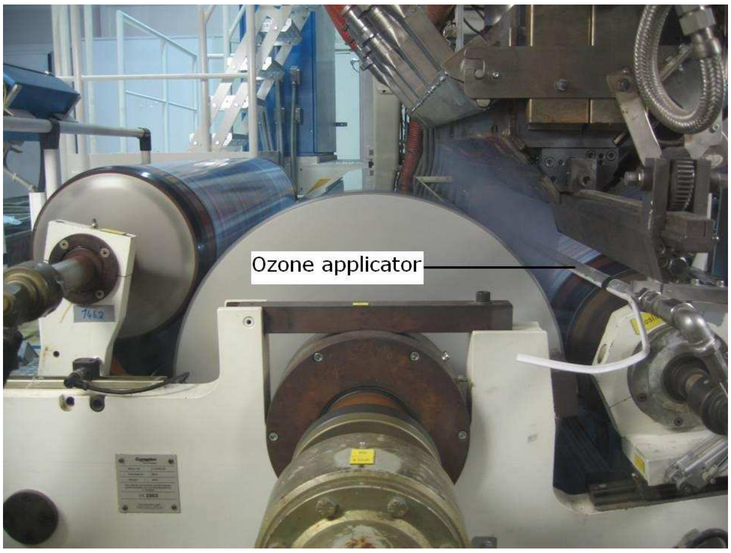

Figure 27: Ozone treatment

3.6.1 Ozone

Ozone is a natural, gaseous molecule and is frequently found in nature. The ozone layer protects the planet against ultraviolet solar radiation, and can be formed in low concentrations by lightening bolts or on hot summer days.[46]

Ozone (O_3) is a three atom allotrope of oxygen (O_2).[47] An allotrope is a substance consisting of only one type of atom. See figure 28. Ozone is formed from oxygen either from electrical discharge or by UV irradiation at specific wavelengths. The equation for the basic formation is:

$$3\ O_2 = 2\ O_3\ (\Delta H = 68\ \text{K cal})$$

The process is an endothermic process and therefore the equilibrium between O_2 and O_3 is shifted towards O_2 when the temperature is increased.

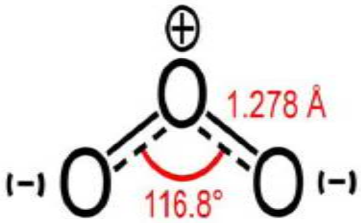

Figure 28: Ozone atom

[44] Tetra Pak Worl Class Lamination material
[45] Extrusion Coating Manual
[46] http://www.wedeco.com/index.php?id=91120&Lang=0&langID=117
[47] http://www.patentstorm.us/patents/5503968/description.html

Ozone oxidizes and decomposes substances at a higher rate than other reagents, only fluorine is a more powerful oxidant. This powerful oxidation nature is being used to treat the polymer melt for improved adhesion.

Ozone is a very unstable compound. Ozone's half life in room temperature (20°C) is 3 days but in 250°C it's only 1,5 seconds.[48] Half life is the time required to convert one half of a reactant to product.[49]

3.6.2 Treatment

It is very important that the temperature of the ozone that is applied to the polymer melt is closely controlled. If the temperature is too high the decomposition of ozone will be accelerated. If it's too low it will decrease the temperature of the polymer melt. In both cases the efficiency of the treatment deteriorates significantly.

Another important parameter is the distance between the applicator and the extruded polymer melt curtain. If the applicator is too close to the curtain it will affect its stability. If the distance is too great the efficiency of the treatment drops significantly.

The amount of ozone that is applied to the polymer melt is a crucial parameter for the outcome. If the amount is too low the degree of oxidation deteriorates. If it's too high the excess ozone in the ambient air can become a health hazard to the operating personnel.[50] Although the factories have exhausts for the excess ozone there's still some concern among some operators.

The amount of ozone treatment consumed on unit area of the melt curtain is specified as ozone dosage with the unit of mg/m^2. The ozone dosage is calculated by the formula:

$$Ds = \frac{C * F}{WW * LS}$$

Ds = ozone dosage
C = ozone concentration (g/m^3) from the ozone generator
F = the ozone/air flow rate (m^3/hour)
WW = web width (m) which represents the width of the melt polymer curtain being treated
LS = line speed m/min

The use of ozone treatment when extrusion coating has many advantages, namely:

- *Reduce coating weight* – instead of having to rely on high coating weights (thickness of laminate) the ozone polarizes the hot melt and thereby enhancing the adhesion

[48] Guangju Zuo, Lamination Technology
[49] http://chemistry.about.com/od/chemistryglossary/a/halflifedef.htm
[50] http://www.patentstorm.us/patents/5503968/description.html

- *Reduce melt temperature* – the temperature has a direct effect on the level of melt curtain surface oxidation. The oxidation yield to highly polar surface groupings which form strong bonds with substrates. By introducing ozone to the melt curtain the oxidation effect is encouraged whilst the melt temperature is reduced. No longer is the temperature required to help with the oxidation of the melt.
- *Enhance adhesion* – when the ozone oxidizes the melt surface and thereby produces a polarized surface the result is improved adhesion.
- *Achieve higher line speeds* – the residence time of the melt in the air gap is directly proportional to line speed. When line speed is increased the oxidation decreases as a result of the melt residence time being shortened. Since the melt requires oxidation in order to obtain adhesion the speed is reduced to achieve adhesion. Alternatively, ozone treatment of the melt curtain leads to controlled oxidation, and therefore removes line speed as the limiting factor in obtaining proper adhesion.
- *Optimize melt stability and neck-in (see figure 29)* – Die air gap and melt temperature has historically been manipulated to promote oxidation and therefore adhesion. This manipulation can cause high neck-in and instability of the melt. When ozone is used in the extrusion process the air gaps and the temperature can be reduced and therefore reducing the exposure to such problems.
- *Improve heat seal characteristics* – Traditional methods to enhance oxidation of the melt is heat and increased air gaps which means that oxidation occurs on both sides of the melt curtain. This leads to an oxidation on the surface on the opposite side which may not be wanted.
- *Reduce odour and off-taste* - a high melt temperature contributes to the package contents taking on an "off-taste" as a result. By applying ozone only to the contact side a preferential oxidation is achieved and thereby lessening exposure to heat seal or off-taste problems. [51]

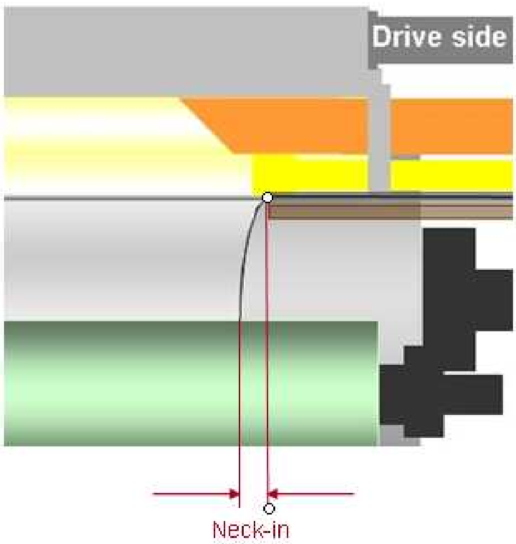

Figure 29: Neck-in

3.6.3 Settings

To be able to get good adhesion results there are special settings in the laminator. The settings concern both the placement of the applicator and parameters concerning the ozone. These parameters are:

- the concentration [g/m^3]
- the dosage [mg/m^2]
- the flow rate [m^3/h]

[51] Extrusion coating – there really is a good side to ozone

The position and application angle of the ozone applicator are important for treating efficiency. See figure 30 for the definition of the position and application angle of the ozone applicator. The ozone applicator will be described further in chapter 3.6.4.

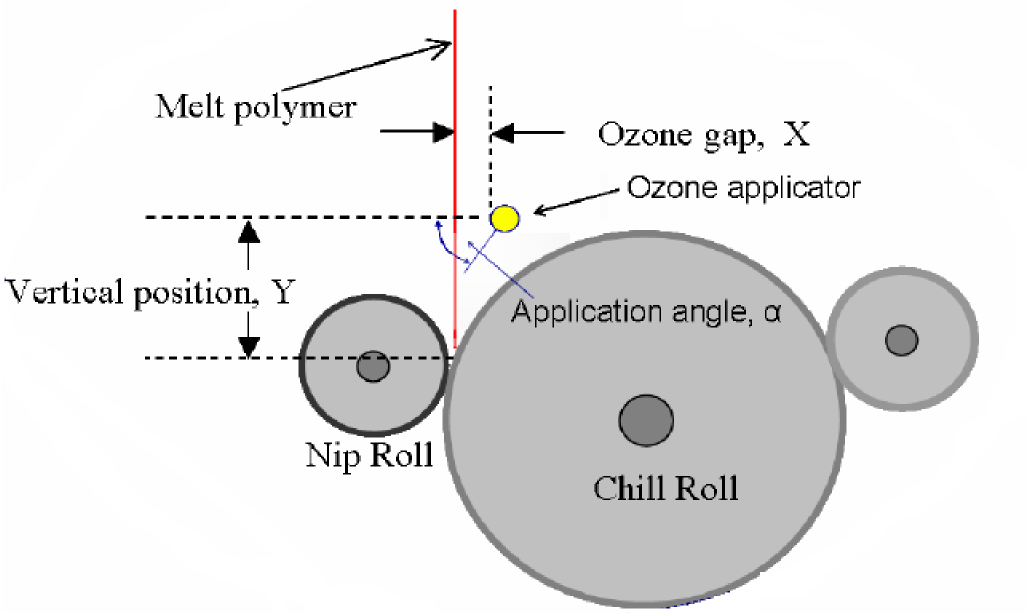

Figure 30: Ozone treatment parameters

The horizontal position is named ozone gap, symbolized X, is defined as the horizontal distance between the lip of the applicator and the melt curtain. The vertical position, symbolized Y, is the vertical distance between the horizontal centre line of the nip to the horizontal centre plane of the applicator. The ozone application angle is defined as the angle between the horizontal planes and the plane across the central line of the ozone applicator and the holes.[52]

In Tetra Pak's there's a specification regarding the Process parameter and machine settings for ozone treatment on melt laminate polyethylene, aluminum foil side.

3.6.4 Applicator

The ozone is applied to the polymer melt by an applicator that sprays out the ozone in the nip area towards the melt curtain. The applicator should meet the following process criteria:

- Provide full width ozone application to the extrudate

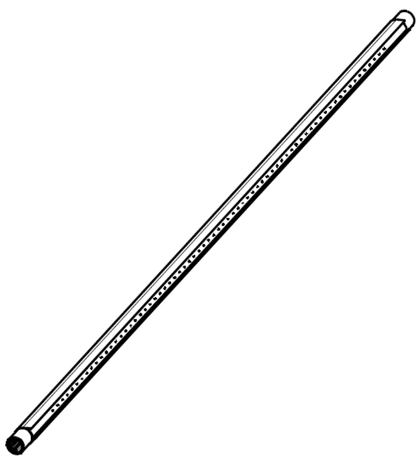

Figure 31: The ozone applicator

[52] DR0022199 - Tetra Pak Internal

- Permit deckling (cover to outer holes when a narrow web is used) to the minimum extrudate width
- Ensure a balanced constant ozone application velocity so not to disturb the extrudate

The ozone applicator used in the Tetra Pak factories is made of aluminum. As can be seen in figure 30 the applicator is shaped as a pipe with holes along the lengthwise direction. The wholes are spread out with equally distances. The size of the wholes differ, the ones furthest out on both sides are bigger than the ones in the middle. There are totally 34 (2x17) bigger holes with a diameter of 0,9 mm and 88 holes with a diameter of 0,75 mm. It isn't clear why the design is made like this; however the profile's look is mainly to stabilize the construction.[53] See figure 32.

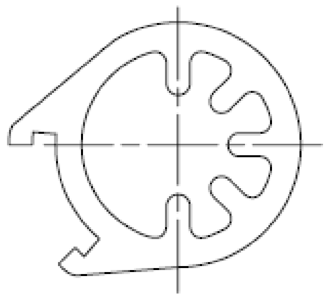

Figure 32: The profile of the ozone applicator

The ozone is created in a generator which is linked to the applicator by pipes. In the ozone generator pre-dried air is submitted to electrical discharge producing ozone gas and ionized species.[54]

3.6.5 Concerns

Despite the look of the profile there are still problems with the pipe as it misshapes after a whiles use.

Another difficulty with the design is that the holes sometimes get covered up by plastic so that the ozone is blocked on its way out of the applicator.[55] This happens since the ozone applicator is placed so close to the laminate which sometimes is unstable and therefore can end up on the applicator. The problem is solved by cleaning the pipe which should occur on a regularly basis. The cleaning process consists of both cleaning the pipe on the outside as well as penetrating each hole with a needle to ensure that the hole isn't covered.[56]

Another concern with the ozone treatment is the amount of air flow in the nip region. It is not known how much the air flow influence the ozone treatment but probably it

[53] Jan Bjädefors, Tetra Pak
[54] Surface Treatments for Lamination Extrusion Coating, Pisciotti F.
[55] Rikard Palmqvist, Tetra Pak
[56] Rikard Palmqvist, Tetra Pak

has some.[57] The air flow is created from the board, the aluminum foil and the melt curtain.

3.6.6 Safety issues

Ozone treatment raises some questions about the safety for the operating personnel. A concern is the issue of residual ozone that may linger around the coating area. However there is no cause for alarm providing that the applicator is correctly installed and can be properly deckled down to the minimum treat or application width.

The ozone that is applied in the nip area is under normal running conditions consumed by the heat of the extrudate. If there’s any remaining ozone it will be exhausted from the area.

If there’s an emergency stop it’s better to divert the ozone to a destruct unit instead of stopping the ozone generator. The main reason is that stopping and starting the ozone generator will lead to expansion and contraction stress being needlessly introduced to the dielectric tubes inside the ozone generator. Therefore is diverting the ozone a preferable way.[58]

[57] CFD analysis of ozone injection in a lamination station
[58] Extrusion coating – there really is a good side to ozone

4 EXPERIMENTAL FRAMEWORK

The chapter describes the test plan with factors and responses and how they were chosen. Further on the chapter also describes the methods for analyzing the material and results.

4.1 The experiment

The experimental objective was screening, to determine the impact of three factors on the adhesion and measured concentration in the nip.

Many factors in the lamination process might influence the adhesion between the laminate and the aluminum foil, for instance laminate temperature, line speed, air gap etc. For this experiment the chosen factors were ozone concentration, ozone flow rate and applicator angle. The factors were chosen since they were believed, due to long experience within Tetra Pak, to have an influence on the adhesion. The low and high values for each factor (see table 3) were chosen according to what was possible for the settings in Pilot plant (test machine) and previous knowledge within the area.

Factors	Levels (Low/High)	Centre point
Concentration [g/m^3]	L_c/H_c	M_c
Flow rate [m^3/hour]	L_{fr}/H_{fr}	M_{fr}
Angle [°]	-/+	0

Table 3: The factors

Due to Tetra Pak secrecy the values can not be revealed. However the settings for the concentration are in the relation 1:2:3 (L_c, M_c and H_c). For flow rate the relation is 1:2:4 (L_{fr}, M_{fr} and H_{fr}). The settings for the angle is -, 0 and +, where – means that the angle is pointing upwards, 0 means horizontal position and + means that the angle is pointing down in the nip.

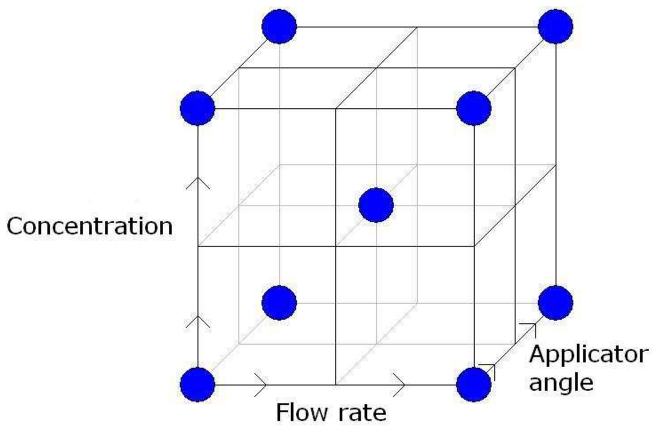

Figure 33: The design of the model

A standard experimental plan with eleven experiments was created. The design is shown in figure 32. Experiment number 9, 10 and 11 are the three centre points (in figure 33 these three points are represented by one circle).

A last, twelfth, experiment was added which excluded the ozone treatment. This variant was added to confirm that the treatment is beneficial for the adhesion.

Exp No	Run Order	Concentration	Flow rate	Angle
1	2	L_c	L_{fr}	-
2	7	H_c	L_{fr}	-
3	3	L_c	H_{fr}	-
4	8	H_c	H_{fr}	-
5	4	L_c	L_{fr}	+
6	9	H_c	L_{fr}	+
7	5	L_c	H_{fr}	+
8	10	H_c	H_{fr}	+
9	1	M_c	M_{fr}	0
10	6	M_c	M_{fr}	0
11	11	M_c	M_{fr}	0

Table 4: The experiments (without experiment no 12)

The run order that was random selected by the program was changed to fit the best order for the machine settings. Due to the limited time in the Pilot plant it was very important to reduce the time for the whole test. The factor that is the most time consuming to alter is the concentration and for that reason the run order was designed in a way where the concentration had the fewest changes. Since the centre points (Exp No 9, 10 and 11) have the exact same settings they can’t be run after each other and were spread out in the run order. See the new run order in table 5.

Exp No	Run Order	Concentration	Flow rate	Angle
9	1	M_c	M_{fr}	0
1	2	L_c	L_{fr}	-
3	3	L_c	H_{fr}	-
5	4	L_c	L_{fr}	+
7	5	L_c	H_{fr}	+
10	6	M_c	M_{fr}	0
2	7	H_c	L_{fr}	-
4	8	H_c	H_{fr}	-
6	9	H_c	L_{fr}	+
8	10	H_c	H_{fr}	+
11	11	M_c	M_{fr}	0

Table 5: The experiments with the improved run order

When the test is performed in Pilot plant there's a set-up time between each variant in order for the new settings (ozone concentration and ozone flow rate) to stabilize.

The responses for the test run were:

- adhesion
- measured ozone concentration in the nip region

Other parameters that were of interest were the logged ozone concentration from the generator as well as the ozone flow rate.

The other settings in the machine were set according to the standard when laminating packaging material.

The three different angles of the applicator are shown in the figures 34-36. Note that the positive angle is pointing downwards in the nip.

Figure 34: Application angle +

Figure 35: Application angle 0

Figure 36: Application angle -

4.2 Ozone concentration measurements

The measured ozone concentration in the nip region is an interesting parameter to investigate in understanding the whole ozone treatment process. The reason for the interest is all the air turbulence brought into the nip by the different materials. Besides the air turbulence brought into the nip region the lamination station is also equipped with an exhaust. All these flows in different directions make it more difficult for the ozone to reach the melt curtain.

To be able to measure the ozone concentration in the nip region a photometer (described in chapter 4.2.1) and a sniffer is needed. The sniffer collects the ozone in the nip region and transports the ozone to the photometer which analyses it and calculates the ozone concentration.

4.2.1 Ozone photometer

To be able to measure the ozone concentration a photometer is used.

Figure 37: The ozone analyzer

Measurement principle

The radiation source is a low pressure mercury lamp (in a UV photometer). Only the mercury line at 254 nm wavelengths (absorption wavelength for ozone) is used for measurement. To exclude the other spectral lines either narrow band UV detectors or narrow band filters are used.

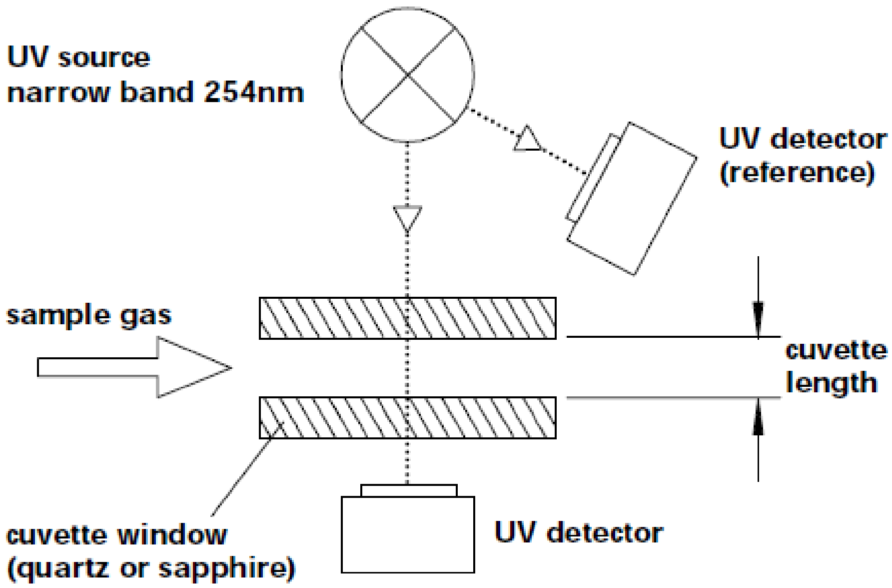

Figure 38: The system

The sample gas is ozone plus a carrier gas (normally oxygen or air), flows between two parallel cuvette windows. The windows are made of quartz or sapphire and are transparent for 254 nm radiation.

The distance between the windows (the cuvette length) defines the measurement range and the sensitivity of the instrument. For instance the range of 200 g/Nm^3 the cuvette length is only 0,8 mm, for the 400 g/Nm^3 the length is 0,4 mm.

The radiation is measured electrically by two different UV detectors. The reference detector measures the radiation before its passage through the cuvette. The other detector measures the radiation after the passage through the cuvette and the sample gas contained in the cuvette. From the signals from the detectors the instrument calculates the degree of extinction produced by the ozone contained in the cuvette. The carrier gas does not affect the result as long as it's clean oxygen or air.

What an ozone photometer measures

The ozone photometer only "see" the ozone, it's blind to the carrier gas. Because of this the photometer can measure ozone content in the sample only as "mass of ozone per volume of the sample". The dimension is g/m^3. To compensate that the photometer can't measure the temperature and the pressure of the sample gas it is equipped with sensors which gives this additional information of the carrier gas. An ozone analyzer consists of an ozone photometer, sensors which measures temperature and pressure and a computational unit which calculates the "mass of ozone per normal (or standard) volume of sample gas" at the arbitrary temperature and pressure of the sample gas, in g/Nm^3.

4.2.2 The sniffer and placement

The sniffer is used for collecting the ozone in the nip region and transporting it to the analyzer in order to measure the ozone concentration. The sniffer is made of stainless steel and is placed in a fix position in the middle of the web (see pictures below). The end of the sniffer which is placed in the middle of the web has an end with a hole pointing upwards. A special holder for the sniffer was designed to be able to measure the concentration in the nip area.

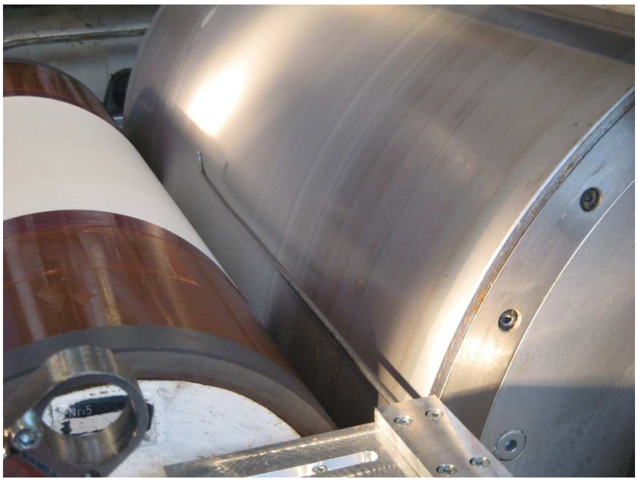

Figure 39: The sniffer placed between the chill roll and pressure roll

Figure 40: The sniffer with the bent end placed in the middle of the web

4.2.3 Data from the laminator

The ozone concentration and the flow rate are set by the operators. The values are logged in order to control that the generator is producing the right amount of ozone concentration and to see that the ozone flow rate is correct. It is also of interest to log these values since it takes a while for the system to stabilize after the settings has been changed.

4.3 Adhesion measurement

The adhesion test method described below is valid for checking adhesion between the lamination and aluminum foil layer.

Adhesion between the layers is an important property of the packaging material in order to form and seal packages. Since performance is not monitored during the lamination process, the level of adhesion must be checked regularly after production. Finished packaging material must guarantee adhesion values within the required specification.

The adhesion measurement is performed to measure the adhesion between the lamination layer and the aluminum foil. See figure 41.

1. Outside layer: Polyethylene (PE);
2. Paperboard (printed or unprinted);
3. Lamination layer: Polyethylene (PE);
4. Aluminum foil;
5. Adhesive layer: Polyethylene (PE);
6. Inside layer: Polyethylene (PE).

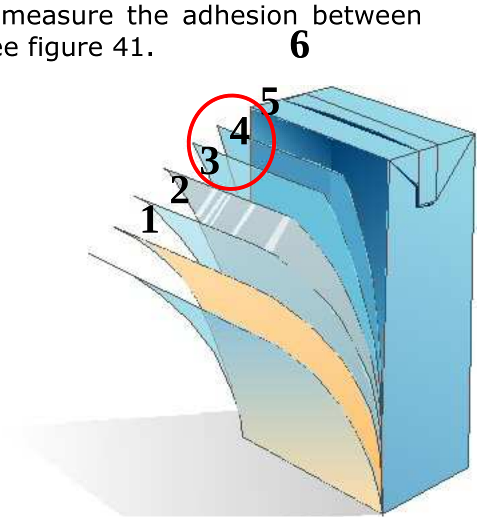

Figure 41: The layers of the packaging material

4.3.1 Procedure

Four strips are cut out from the packaging material. Each strip is split starting from the paperboard to eliminate the paper board fibers from the lamination layer (1). A wet rag is used to clean the remaining strip, removing as many fibers as possible (2). During this phase it's important to be careful not to damage the lamination layer.

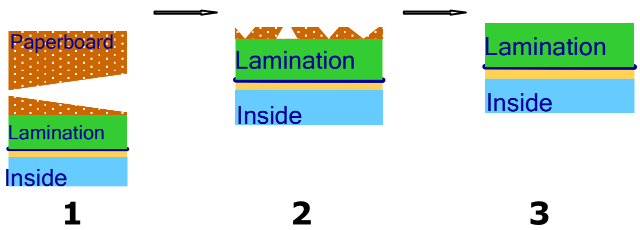

Figure 42: Removal of the paperboard

One end of the strip is dipped into hot alcohol for 5-10 seconds to start the delamination between the two layers (4). The lamination layer is separated from the aluminum foil layer while the strip is still wet (5). The strips are placed in an oven to dry. Tape is applied on both sides of the strip as support for the layers. Specimens are cut out from each of the prepared strips. The specimens are placed in the dynamometer with the two loose ends attached to the clamps (6). The tensile test is carried out and a graph is recorded. The graph shows the value of the adhesion between the lamination layer and the aluminum foil layer. The result is divided by the specimen width to obtain the adhesion in Newton per metre (N/m).[59]

4 **5** **6**

Figure 43: Removal of inside layer and adhesion test

[59] Adhesion of packaging material layers

5 RESULTS

In this chapter all the results from the tests will be presented.

The first step in analyzing the data is to evaluate the model. The test plan showed a good condition number, 1,1726, which means that the design is well balanced.

5.1 Measured concentration

The analysis of the measured ozone concentration in the nip is performed as described in chapter 2.4.3 with all the steps in the regression analysis and ending up with how the model can be used.

Replicate plot

As can be seen in figure 44 the variation of the repeated experiments (the centre points, no 9, 10 and 11) is smaller than the overall variability which proves a good model.

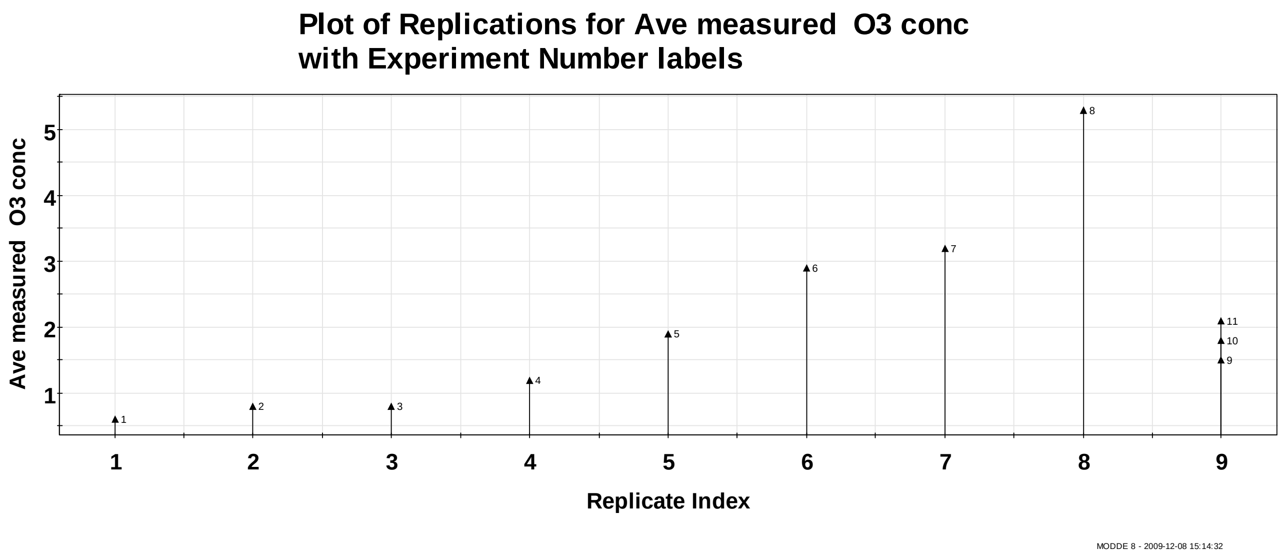

Figure 44: Replicate plot

Summary of fit

The bars in the summary of fit show all good results (according to the theoretical limits);
R^2 (the goodness of fit) is 0,96
Q^2 (the goodness of prediction) is 0,74
The model validity (whether the model is appropriate in a general sense) is 0,75
The reproducibility (numerical summary of the variabilities plotted in the replicate plot) is 0,95

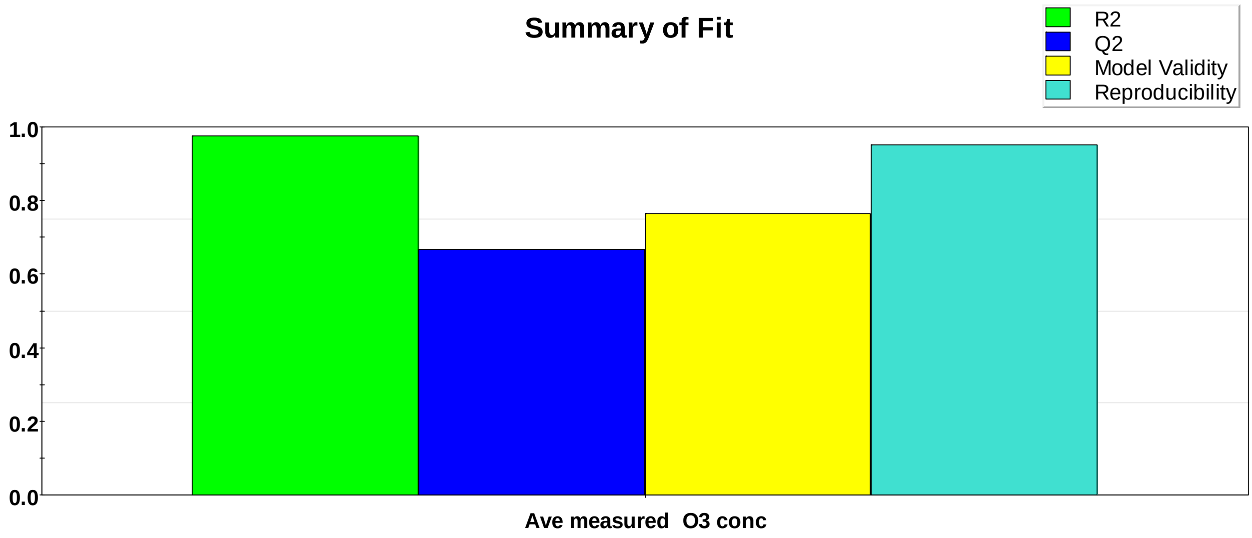

Figure 45: Summary of fit plot

Coefficient plot

The plot displays that the factor with the greatest influence on the measured concentration is the applicator angle. From the plot it can also be understood that the angle should be positive for a better result (pointing downwards). The flow rate and the applied concentration have roughly the same impact on the result.

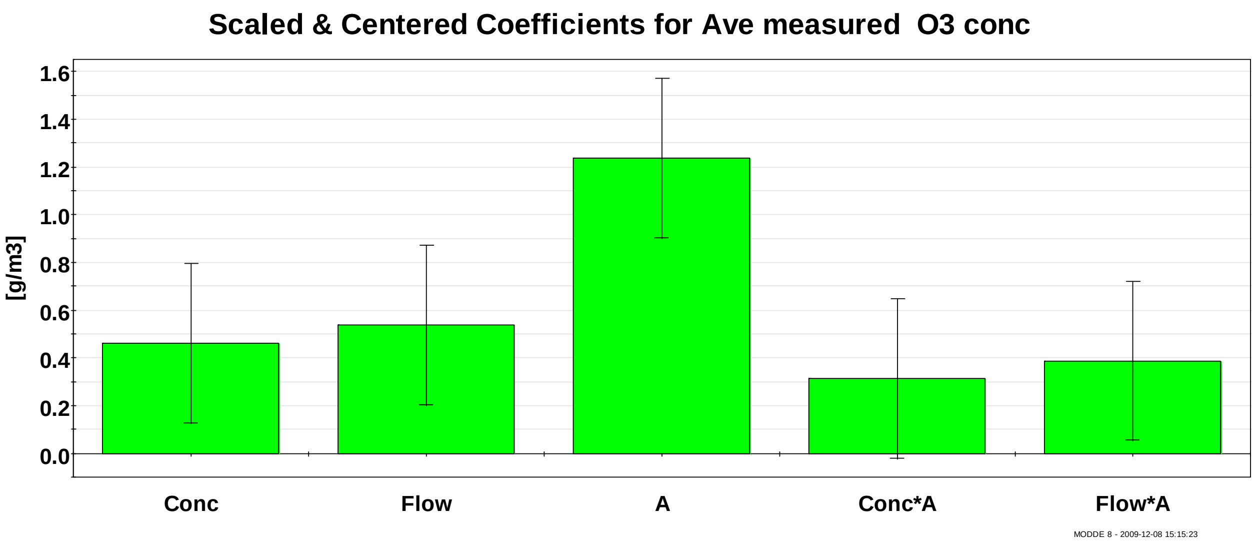

Figure 46: Coefficient plot (A= angle)

In the analysis of the plot the correlation bar for Conc*Flow has been removed in order to improve the model. The Conc*Flow coefficient was not significant since it crossed zero.

Normal probability plot of residuals

The plot shows that all values are within the + 4 lines which means that there's no outliers among the residuals. The residuals are also random and normally distributed since they are placed along a straight line.

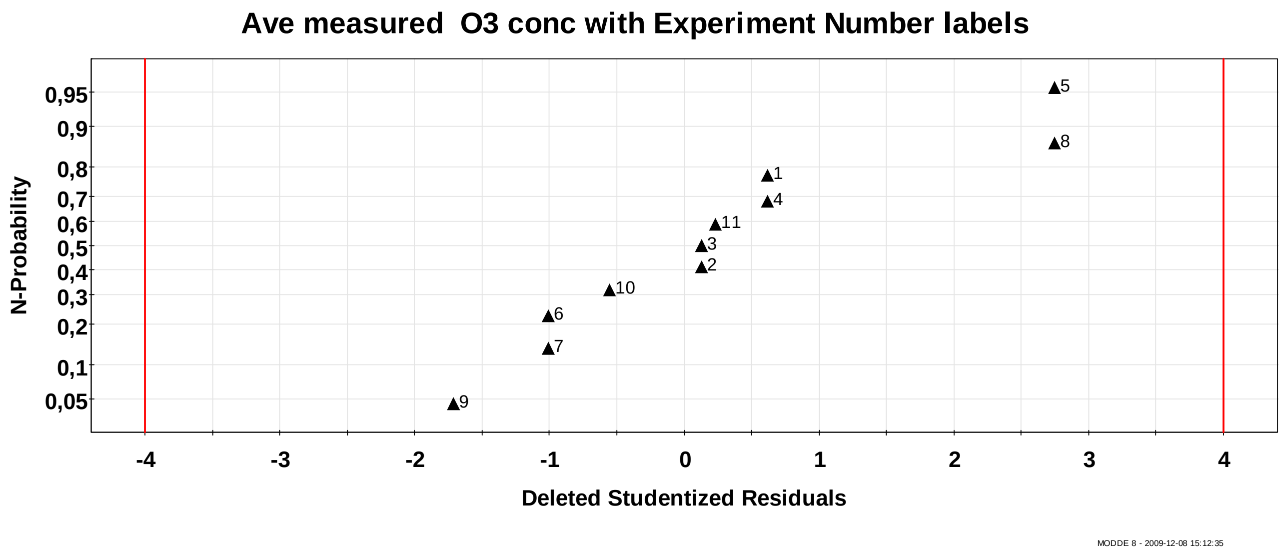

Figure 47: Normal probability plot of residuals

Observed vs. Predicted

In the plot the majority of the points fall on a 45 degree line which indicates a good model.

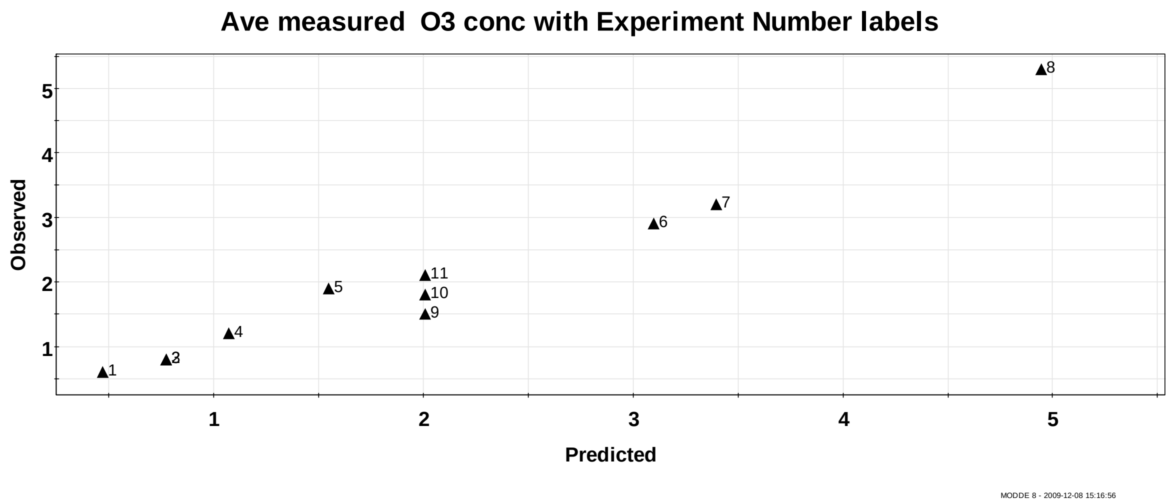

Figure 48: Observed vs. predicted

Contour plot

The coefficients with the biggest influence on the response were the angle and the flow rate. Therefore these two parameters were chosen as the x- and y-axis in the contour plot.

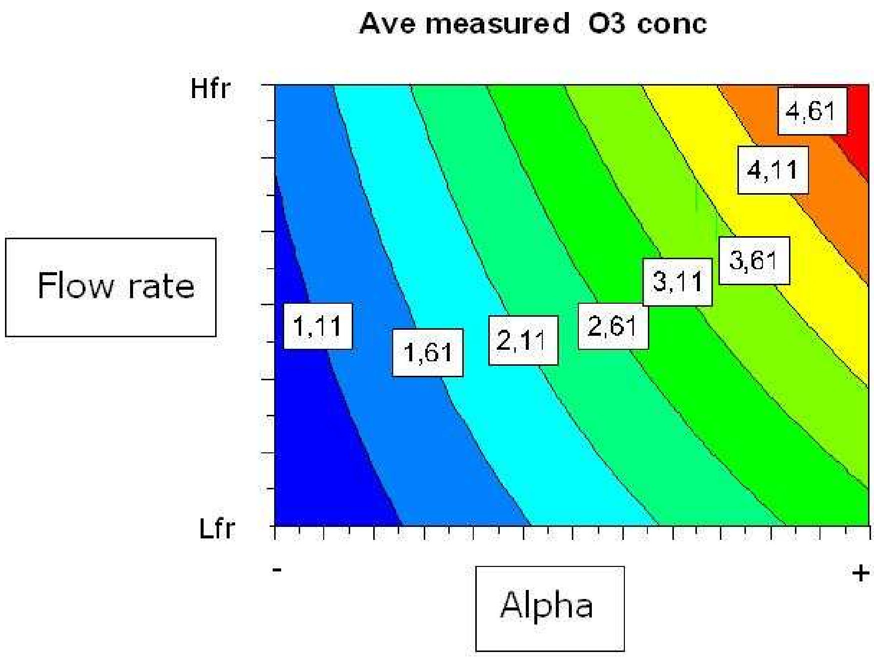

Figure 49: Contour plot when the concentration from the generator is set to highest (H_c)

The plot shows that the highest level of measured concentration in the nip region is reached when the angle is positive (pointing downwards) and the flow rate is at a high level.

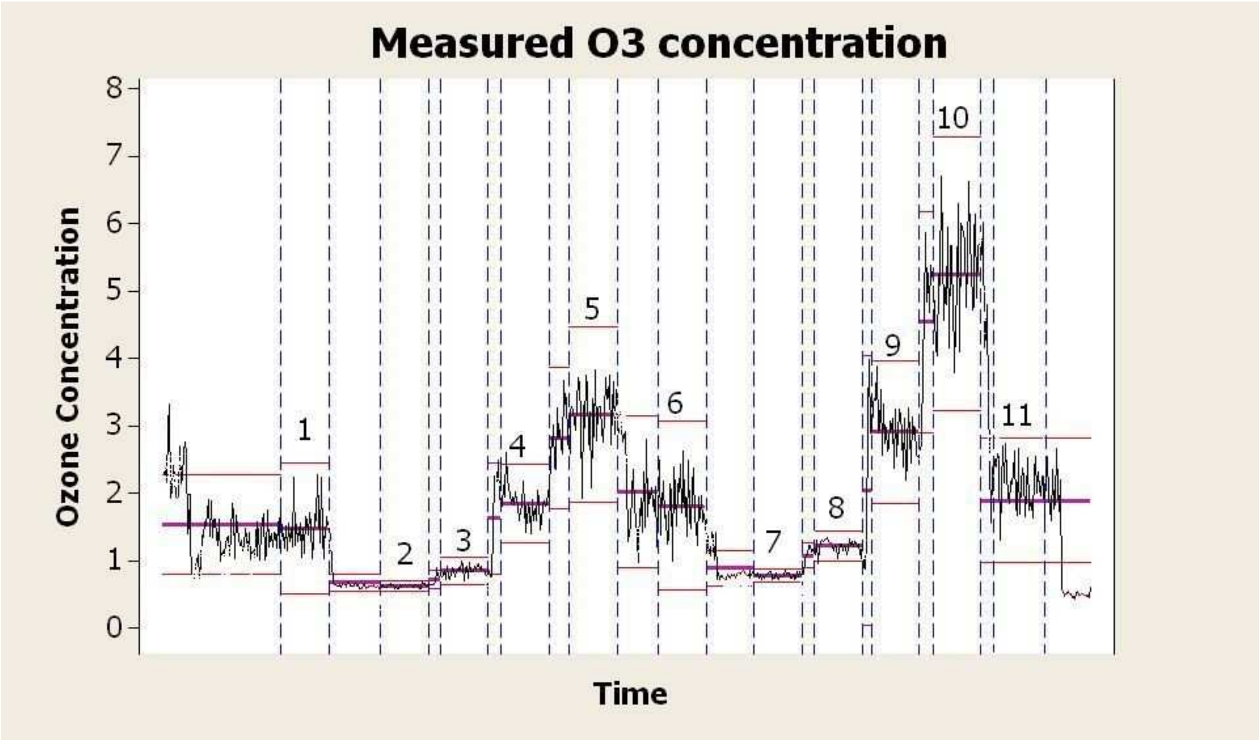

Figure 50: The measured ozone concentration for the experiments. N.B the Y-axis does not show the actual values for secrecy reasons

The figure above shows the different experiments and the measured ozone concentration for each experiment. The experiment without ozone treatment (no 12) is not in the picture as there's no ozone to measure. Besides showing which experiments giving the highest measured ozone concentration the figure is also interesting since it shows how the measured concentration fluctuates depending on the settings.

The columns without numbers represents the set-up time between the variants. As can be seen in the figure the set-up time differs according to which settings are changed.

The highest value of measured ozone concentration is obtained with experiment number 10. As can be seen in table 6 (next side), number 10 is the experiment with the highest concentration, highest flow rate and the angle pointing downwards.

The two second best measured concentrations are experiment number 5 and 9. Number 5 is the experiment with low concentration, high flow rate and a positive angle (pointing downwards). Experiment number 9 is the experiment with high concentration, low flow rate and positive angle (pointing downwards).

The lowest measured adhesion is experiment number 2, 3 and 7. All of these three experiments have a negative applicator angle (pointing upwards) and one or both of the parameters concentration and flow rate set to a low level.

The settings where the fluctuation is the least is when the angle is negative (pointing upwards).

Exp No	Run Order	Concentration	Flow rate	Angle
9	1	M_c	M_{fr}	0
1	2	L_c	L_{fr}	-
3	3	L_c	H_{fr}	-
5	4	L_c	L_{fr}	+
7	5	L_c	H_{fr}	+
10	6	M_c	M_{fr}	0
2	7	H_c	L_{fr}	-
4	8	H_c	H_{fr}	-
6	9	H_c	L_{fr}	+
8	10	H_c	H_{fr}	+
11	11	M_c	M_{fr}	0

Table 6: The experiments

5.2 Data from the laminator

The logged ozone concentration and flow rate can be seen in the figure below (figure 51). Unfortunately the two first variants were not logged. And therefore the actual values can not be displayed. The columns without numbers represents the set-up time between the variants. As can be seen in the figure the set-up time differs according to which settings are changed.

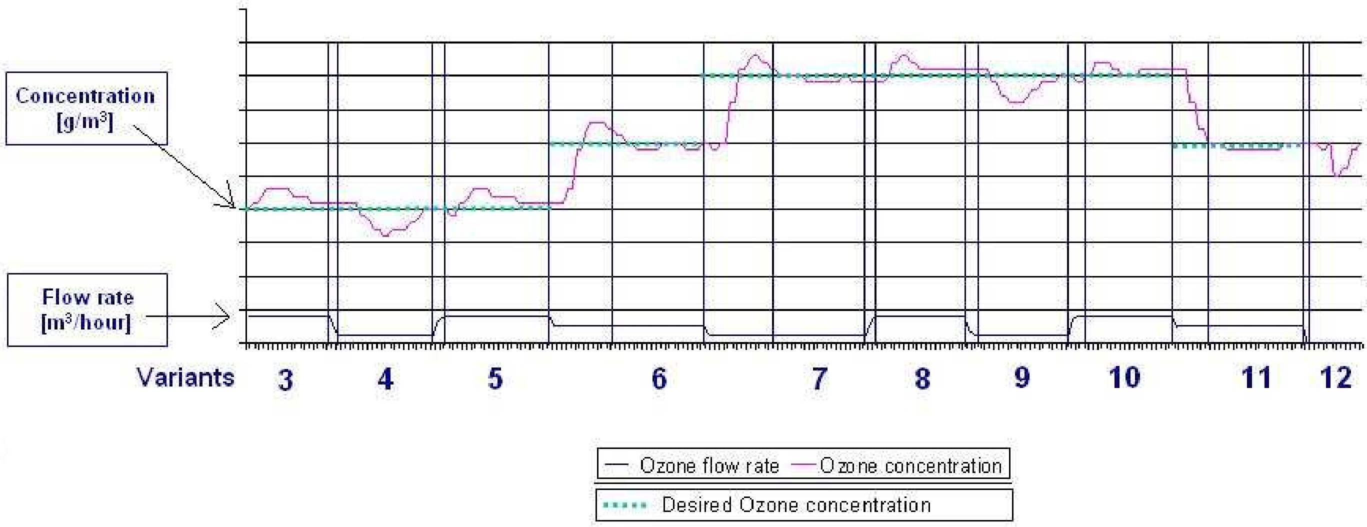

Figure 51: Data from the laminator

5.2.1 Concentration

As can be seen in the figure above the concentration from the generator fluctuates a great deal.
Worst is the case for variant 4 and 9 where the ozone concentration is up to almost 25 % lower then the set value.

5.2.2. Flow rate

The flow rate shows really good values. The actual flow rate doesn't deviate from the desired one (the same line in figure 51). When the flow rate is changed the output is quickly adapted and does not fluctuate.

5.3 Adhesion

The analysis of the adhesion between laminate and foil is performed as described in chapter 2.4.3 with all the steps in the regression analysis and ending up with how the model can be used.

Replicate plot
The replicate plot shows that the model is not good. There's a big variation among the centre points (1, 6 and 11). The replicates vary as much as the other experiments (can indicate a lot of noise).

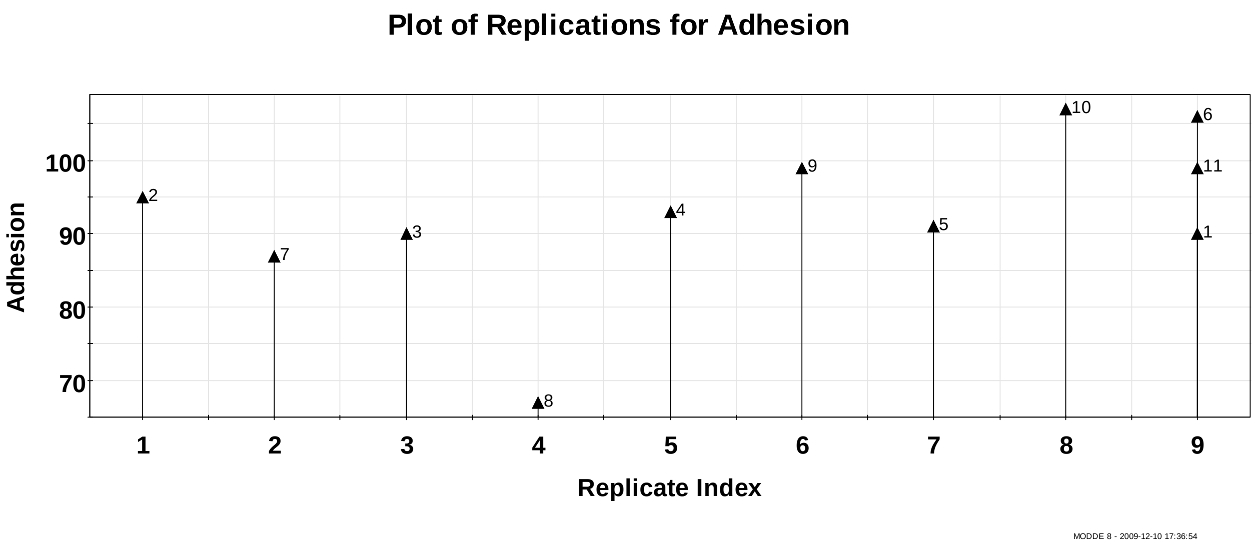

Figure 52: Replicate plot

Regression analysis
The bars in the summary of fit do not show good results (according to the theoretical limits);
$\mathbf{R^2}$ (the goodness of fit) is 0,73
$\mathbf{Q^2}$ (the goodness of prediction) is 0,13
The model validity (whether the model is appropriate in a general sense) is 0,77
The reproducibility (numerical summary of the variabilities plotted in the replicate plot) is 0,45

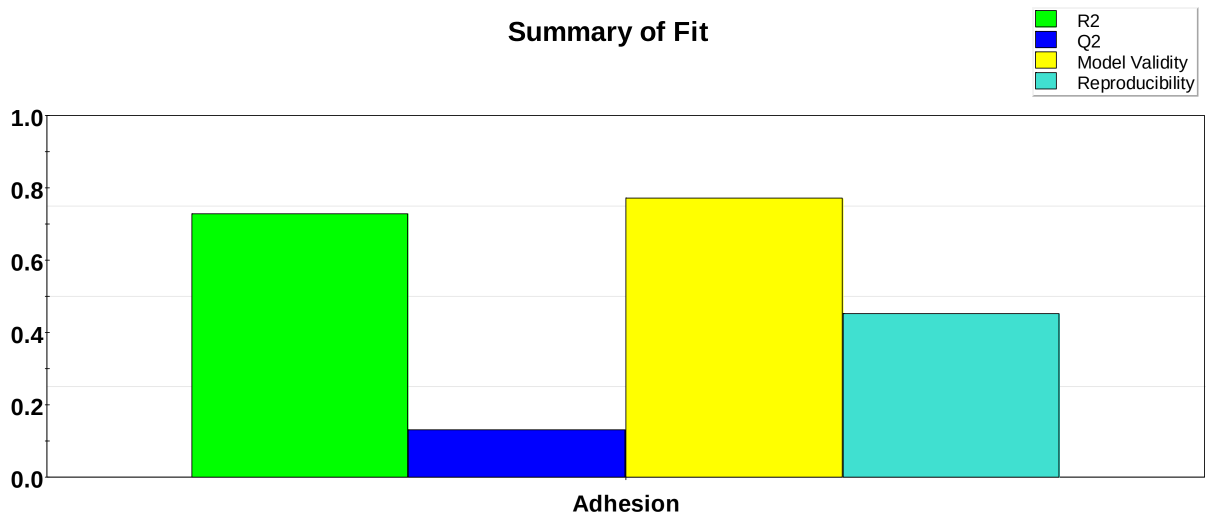

Figure 53: Summary of fit plot

R^2 is ok, but Q^2 is way to low, the difference between R^2 and Q^2 should only be 0,2-0,3 which is not the case in these results. Here the difference is as much as 0,6. This means that the model is poor.

Coefficient plot

Also the coefficient plot shows the same result, that the model is poor.

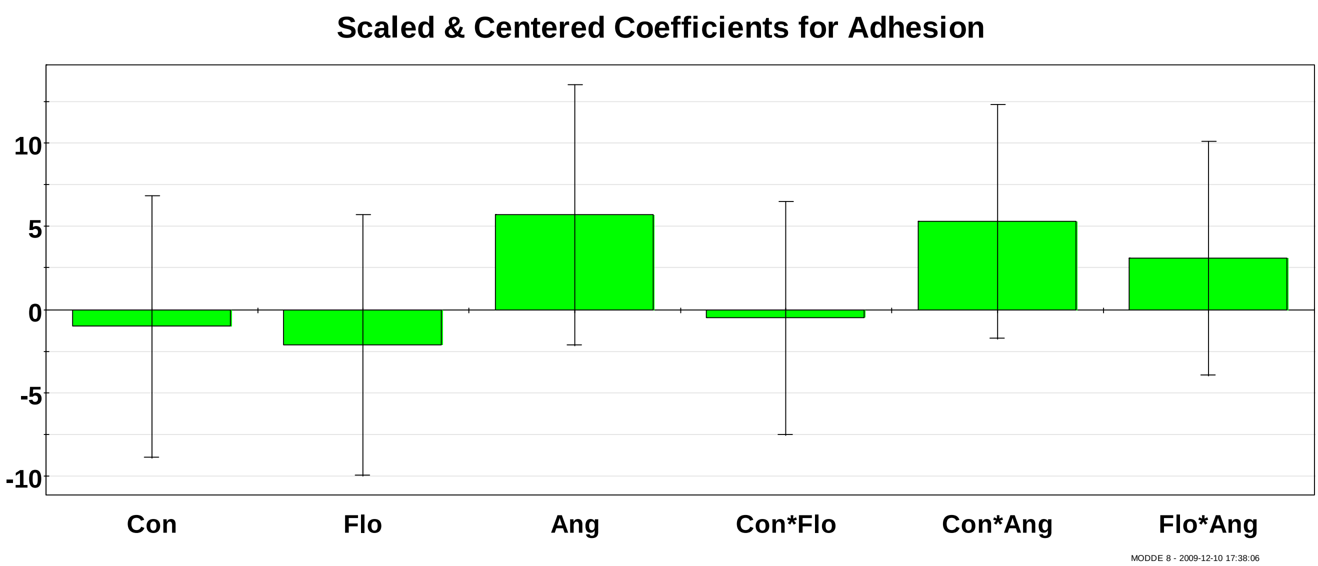

Figure 54: Coefficient plot

Conclusion – the error is so large that a good model can not be obtained and further model interpretation is excluded.

5.3.1 Ozone treatment's impact on the adhesion

Although the model for the adhesion measurement is poor there was one interesting result from. When there's no ozone treatment the adhesion values drops significant. With the ozone treatment the adhesion values reaches more than twice as high compared to no treatment.

6 ANALYSIS / DISCUSSION

The content of this chapter is the analysis from the test run.

First of all it’s important to remember that the ozone treatment is an area in which very little research has been made so far. All of the results analyzed in this project are the outcome from the certain setting of both the ozone applicator as well as all the other settings in the lamination process. Settings that most probably also are of importance in the surface treatment process but couldn’t been included in this study are the X-and Y-distances. Another parameter that probably is of importance is the exhaust.

6.1 Measured concentration

The factor with the biggest influence on the measured ozone concentration is the application angle. This seems reasonable since the opening hole of the sniffer is pointing upwards and will receive more ozone from the applicator when the applicator is spraying the ozone almost directly into the sniffer.

The ozone concentration and the ozone flow rate seem to play an equal role for the measured ozone concentration.

The highest value of measured ozone concentration is obtained with the highest concentration, highest flow rate and the angle pointing downwards.

The highest level of ozone concentration is still rather small compared to the one set by the generator. This outcome could be caused by the air turbulence caused by the speeds that the board, the aluminum foil and the hot laminate bring into the nip region. Another factor that contributes to the low measured concentration could be the exhaust. The exhaust is necessary but the question is if it could be reduced or used in a different way.

The settings where the fluctuation is the least is when the angle is negative (pointing upwards).

The method for measuring the ozone concentration in the nip region is not optimized since it’s impossible to measure at different points in the same test run without stopping the machine.

6.2 Adhesion

The model for the adhesion between the laminate layer and aluminum layer was poor. Therefore no conclusions could be made regarding which factors impact the result the most and how the settings should be made for optimized adhesion. The reason for the poor model can be many. Some reasons could be:

- *The settings doesn't affect the result*

This means that the high and low values for the factors weren't chosen in a good way. This is not so likely since the chosen values are the one's that are possible for the machine.

- *There can be an influence of a factor which is not included among the factors*

As mentioned in chapter 4.1 there are many factors affecting the ozone treatment of which not all could be included in the test run due to limited time. However the chosen factors are still believed to be among the most important and should show some impact on the adhesion.

- *There can be noise disturbing the model*

This reason is probably the most likely since there are many factors around the treatment process affecting the adhesion. It could be the surface of the aluminum that is not even resulting in different adhesion values for the same experiment settings. Most likely it's the test method for the adhesion measurements that causes most noise. The method is dependant on people performing different steps that could be made differently depending on how's doing it. Also there's no time limit for when the measurements should be made. Best would probably be if the adhesion tests were performed directly after the packaging material is produced. The situation today is that the tests are made whenever there's time in the lab and there can be days between when the different experiments are tested.

7 CONCLUSION

In this chapter the conclusions from the test and what new knowledge that is achieved by this work will be presented.

OZONE TREATMENT
Ozone treatment has a positive impact on the adhesion.

MEASURED CONCENTRATION
Regarding the measured concentration in the nip the setting which gave the highest concentration was not surprisingly the one where the applicator is pointing down and with highest ozone concentration and ozone flow rate.

The ozone concentration from the generator fluctuates.

The measured concentration in the nip is far from the same concentration as the one the generator produces.

ADHESION
Due to poor model in MODDE there can't be any conclusions made about the settings in regards to the adhesion. The adhesion results vary a lot and have also a big variation which indicates that they can't be trustworthy.

8 RECOMMENDATION

Further work is where the author has the possibility to recommend Tetra Pak how to continue the work with the ozone treatment.

First of all, more tests need to be made concerning the ozone treatment to get a better understanding of the treatment. Different things to look at are changing the X- and Y-distances together with the ozone concentration, ozone flow rate and the applicator angle.

To facilitate the measuring of the ozone concentration in the nip region a new sniffer should be made for enabling easy and accurate measurement. The new set up should be made so that measurements in different points can be made in the same test run without stopping the machine (very cost consuming). This is of interest for mapping up how the ozone concentration varies in the whole nip region.

It would be interesting to evaluate the test method for the adhesion measurements. The method seems a bit old and is not as precise as is wished. The parts where the human hand can play a role need to be eliminated. Also, it would be good if there is a timeframe for when the measurements should be made.

The fluctuation of the ozone concentration from the generator needs to be investigated. Does the fluctuation play a role in the efficiency of the treatment or are other parts more crucial?

NEW APPLICATOR

Once the ozone treatment process is "under control" it would be interesting to look into modifications of the ozone applicator.

It could be interesting to change the way the ozone exits the pipe. Maybe it could be a long slit along the pipe instead of many small holes. In that case the ozone wouldn't be sprayed out with the same pressure so it wouldn't affect the melt in the same way (cooling down and stability). However the applicator would have to be placed closer to the melt due to the lessening of pressure.

It could also be interesting to investigate if it would be possible to remove some of the air turbulence in the nip region and by doing so get a more stable ozone treatment.

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Appendix – Work flow