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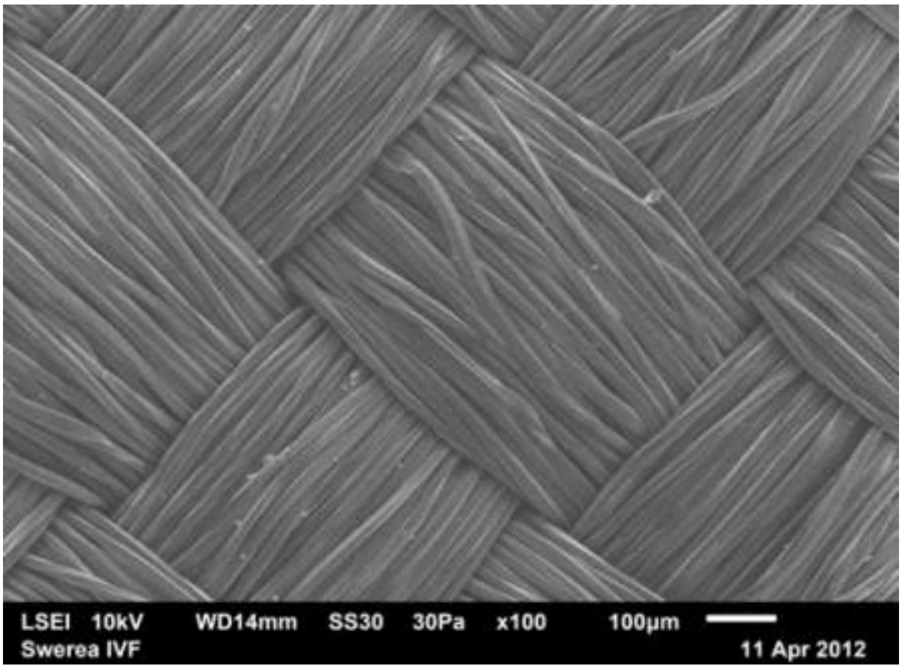

Improved Adhesion of Polyolefin Laminates to Textiles Using New Plasma Technology

Master of Science Thesis

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Abstract

Coatings and laminates introduce new properties to fabrics, such as improved durability and barrier properties to gasses and liquids. For the coatings and laminates to work properly the adhesion to the fabric needs to be good. Today adhesion is obtained by treating the surfaces with different chemicals, which may be harmful to the environment. In this project it is investigated if plasma treatment of the surfaces can be employed to increase the adhesion instead.

Atmospheric pressure plasma treatment was used to treat both the textiles and the polymer films that were used for the lamination. The adhesion was evaluated by peel testing and it was seen that the plasma treatment enhanced the adhesion several times the original value. However, both the textile fabric and the polymer film used as laminate need to be plasma-treated to achieve high adhesion.

Also XPS and SEM have been employed for characterization. From the XPS measurement it was seen that there was a significant increase in the amount of oxygen groups on the surface after plasma treatment. This supports the assumption that such functional groups are responsible for the enhanced adhesion between the fabric and the polymer film. Plasma treatment of a material brings a lot of energy to the surface. From the SEM pictures taken in this project however, it is concluded that the plasma treatment can be made without damaging the textile fibers.

The number of functional groups that are introduced on the surface by the plasma treatment will decrease with time and the surface will eventually go back to its initial state. To investigate how long this will take, fabrics were plasma-treated and then stored in a room of constant climate for a certain time, before laminated to the polymer film. From this experiment it was seen that the fabric surfaces will lose some of their reactivity, needed to obtain high adhesion, but not at a high rate and the material will still obtain high adhesion if laminated one week after the plasma treatment.

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1 Introduction

The Swedish textile industry face some big challenges, companies in Asia and other parts of the world can often produce the same products but at a lower cost. In order for the Swedish textile industry to compete they need to focus on advanced materials of high quality. It is then important to find improved ways of production. Plasma treatment is one such technique that has the potential of improving textile materials without a big increase in production cost.

Plasma technology has been used for about 60 years but then as a vacuum technique where the first area of application was surface treatment within the microelectronics industry. The reasons for this is that only batch-wise production is possible and because the energy and equipment needed to reach and maintain the low pressure, makes this technique complicated to use in a continuous process. However, in recent years atmospheric pressure plasma has been developed into a new and promising technique for surface treatment. In atmospheric pressure plasma there is no need for vacuum making it possible to use in a continuous process for surface treatment of materials such as textiles and paper. The technique is also possible to directly introduce into today’s production. However, more research is needed to investigate how the technique best is utilized to improve the performance of the textile. One promising field of application is adhesion enhancement of coating and laminates.

For many textiles a coating or laminate is applied in order to improve the material properties, chemical resistance, appearance and waterproofing. A good coating or laminate needs to have good adhesion to the textile, or the coating will fall off. To achieve a good adhesion between the applied coating or laminate and the fabric the fabric surface is generally treated by chemicals, which are applied as a solution, making it necessary to dry the fabric after the chemical treatment. This process is expensive, since a lot of chemicals and energy are used. If instead a plasma technique could be used the need for chemicals would be reduced, and since plasma is a dry technique there would be no need for drying.

Another problem with the coatings and laminates used today is that a lot of chemicals need to be added to the polymer to make a useful coating. One such example is poly vinyl chloride (PVC) which is a common polymer in coatings. The PVC used for coatings and laminates contains a lot of plasticizers which are harmful to the environment. Therefore, it would be a significant advantage if plasma could make it possible to use plastics which are less harmful to the environment but still cheap and easy to use.

There are however some challenges related to plasma treatment, one is the ageing of the surface after the treatment. After surface activation by plasma the material will relax and go back to its normal, low-energy state. How long this relaxation takes is affected by the plasma parameters and the material treated, and must be investigated in each case. Other challenges are about optimization of the plasma parameters, such as gas type, power and exposure time etc. Another concern is that plasma treatments have the potential of harming the surface of the fabric if too much energy is added to the surface. Hence, the plasma parameters need to be optimized in order to achieve the desired effect of the treatment without harming the fabric surface.

1.2 Aim

This project aims to use atmospheric plasma treatment to improve the adhesion between a synthetic textile fabric and a polymer film based on ethylene. A first step of the project will be to investigate if the plasma treatment can improve the adhesion. The treatment will then be optimized to improve the adhesion without harming the surfaces of the materials. Finally, the aging of the plasma-treated surfaces will be investigated.

2 Theory

2.1 Fabrics

Different materials can be used for the production of fabrics. The first fiber used for textile production and the most important even today is cotton.

Nowadays there exist not only natural fibers such as cotton but also synthetic fibers. Examples of synthetic fibers are nylon, polyester and acrylic fibers. All of these synthetic fibers are polymers produced from petroleum products. Depending on the desired properties of the final product different fibers should be used. Synthetic fibers of infinitive length are called filament fibers. The fabric used in this project was produced from polyester fibers of filament yarn. [1]

2.1.1Polyester fabrics

Polyester fabrics are made of polyethyleneterephthalate (PET), which is produced by a transesterification reaction between ethylene glycol and the ester dimethyl terephthalate. In the production of PET dimethyl terephthalate are initially reacted with an excess of ethylene glycol, this reaction is made with the aid of the catalyst sodium methoxide. From this reaction bis(2-hydroxyethyl) terephthalate and methanol are produced, the methanol is removed by distillation. When the methanol have been removed the temperature is raised in order to achieve a transesterification between the bis(2-hydroxyethyl) terephthalate which forms the polymer and ethylene glycol. The structure of the final polymer can be seen in Figure 1.[1]

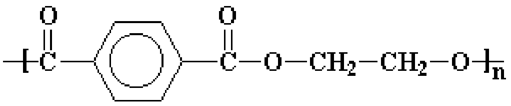

Figure 1. Chemical structure of the repeating unit in polyethyleneterephthalate.

In order to create the filament yarns the molten polymer is extruded into thick bands which are then cooled only to be re-melted and spun into filaments. [1] The normal finished PET fiber is smooth and has a diameter that varies between 12-25 micrometers. Generally the cross section of PET fibers is nearly circular but the structure in this project has been one with edges. The polymer itself are linear and have a crystallinity of approximately 35 %.[2]

A standard PET fiber is hydrophobic which make it hard to color with an aqueous solution of ionic dye, which is the normal procedure when coloring for example cotton. This will make the coloring of PET fabric more complicated since they need to be colored by non-ionic dispersive dyes which have low water solubility. Because of the low solubility of the dyes a lot of surfactant is used in order to improve the solubility. But even by the aid of surfactant the solubility is low. This will give a slow uptake of the dyes into the fibers making the coloring process time demanding if run at normal temperature. If the temperature is raised above the T_g of the PET the polymer chains will have a higher mobility and an increased ability for uptake of the dye. Therefore the dyeing is made at temperatures of approximately 130 ˚C, this high temperature have the potential of changing the surface properties of the PET. The reason the surface properties are change are that raising the temperature above the T_g will give a more amorphous polymer, this is also the reason for the faster uptake of the dye. [1][3]

2.1.2 Nylon fabrics

Nylon was the first synthetic fiber to be produced and it exists in several forms, where nylon 6.6 and nylon 6 are the most abundant. The name nylon is a trade name, the chemical name is polyamide. Nylon 6 and nylon 6.6 are both polyamides but produced in slightly different ways giving different structure of the polymer chains and therefore also different properties of the finished polymer. [1][2]

Nylon 6.6 is produced by heating a mixture between the salt of adipic acid and hexamethylene diamine in a concentrated aqueous solution in the presence of a some acetic acid. When most of the hexamethylene diamine has reacted most of the water is removed by distillation. The mixture is then heated in a nitrogen atmosphere to about 280 ˚C, the reason a nitrogen atmosphere is used is to prevent oxidation. The obtained polymer is finally extruded and cut into chips from which the filaments can be created.

Nylon 6 is produced in a similar way to nylon 6.6 but from caprolactam instead of hexamethylene diamine and adipic acid. For the rest of the polymerization the process is basically the same. There is however a differens when it comes to the production of the filament from the polymer. Since nylon 6 has a lower melting point than nylon 6.6 the filament can be created directly from the polymerization reactor.

For a comparison, the repeating units of nylon 6.6 and nylon 6 are shown I Figure 2.

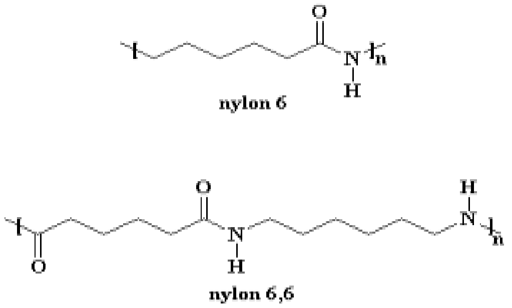

Figure 2. Chemical structure of the repeating units of nylon 6 and nylon 6,6.

2.1.3 Acrylic fabrics

Acrylic fabrics are made from the polymer polyacrylonitrile (PAN), which is also a common polymer in coatings. PAN is described further in section 2.3.3.

2.3.4 Cotton

Also cotton can be considered to be a polymer, the difference is that cotton comes from cellulose which is the basic building stone for all vegetation. Therefore the cellulose used for cotton fabric production is not produce by man but is a naturally occurring material that is harvested and spun into fibers.

Cotton comes from the seed pod of the plant family *Gossypium*, where the cotton fibers grows out from the seeds in the closed pod. When the pod burst and the seeds are released the fibers will stay and after a while dry out where-after they can be harvested and used for the production of cotton fabrics. [1]

2.2 Coated and laminated textiles

For as long as man have been wearing clothes made from fabrics there has always been the need for improving properties such as water and wind proofing. For examples the Maya Indians began to improve their fabrics by applying the sap from the rubber tree onto the fabric and then dry it. However, to find the beginning of the modern form of coating and laminating industry one has to go all the way up to 1823 when Charles Macintosh patented the first raincoat. This first raincoat was made by applying rubber dissolved in naphtha between two pieces of cloth which was then dried for evaporation of the naphtha creating a rubber film in between the two cloth pieces. [4][5]

The fabrics created this way had several disadvantages. One was the smell of the fabric, but the fabrics were also uncomfortable to wear and the rubber film had a tendency to soften and melt in hot weather. New ways of production and the use of new materials soon made the fabrics better and today the techniques and materials used are quite different from the one used by Macintosh in 1823.[4][5]

2.2.1 Coating and laminating methods

Textile materials can be coated or laminated with a polymer for a number of reasons such as increased resistance to soling and penetration of liquids and gases, improvement of abrasion resistance, but it can also be made for esthetic reasons. Hence, a coating is made in order to introduce new properties to the fabric. [4][5]

The coating can be made by several different methods and the method used depends on several factors such as the polymer used, what kind of fabric the coating is applied on, how the end product are to be used and for economic reasons. The methods used to coat a textile fabric can be divided into two main groups which are fluid coating and dry coating. [4]

Fluid coating

In fluid coating the polymer is applied as a solution to the textile where-after the solvent are evaporated and the polymer is solidified into a film. There are several different techniques to apply the polymer solution and also many different machines can be used. A general structure for a fluid operation involves four steps. The first is the fabric let-of arrangement where the fabric is drawn under uniform tension. The second step is application and spreading of the polymer solution on the fabric surface from the coating head, to achieve an even polymer film with the desired thickness. There exist many different methods to achieve the correct thickness of the coating they are however outside of the scope of this report and are therefore not explained here but the interested reader can find them in [4][5] and [6]

The third step is the drying oven where the coating is solidified and all the solvent are evaporated in order achieve a polymer film. The fourth and final step is the winding section where the fabric is cooled and winded up on rolls. [4]

Dry coating

In the dry coating process, no solvents are used in the application of the polymer. One simple application method is melt coating where the polymer is melted and applied onto the fabric where-after it is cooled to solidify. Another method for dry coating of plastic films is lamination where the plastics are first made into a film with a certain thickness which is then laminated onto the fabric by means of heat or certain chemicals, called adhesives. [4]

Lamination can be seen as a special case since an already prepared film is applied to the substrate. Therefore a distinction is sometimes made between coating and laminating. The final product is however often called a coated product.

2.3 Polymer coatings

The main polymers used for polymer coatings and laminations of textiles today are polyvinyl chloride (PVC), polyurethanes, acrylics and rubbers [5]. These polymers will here be briefly explained and also polyethylene (PE), which is the polymer of choice in this project. PE however, is not frequently used in coating and laminations.

2.3.1 Polyvinyl chloride

Polyvinyl chloride (PVC) is polymerized from the monomer vinyl chloride $CH_2{=}CH\text{-}Cl$ by a free radical polymerization mechanism. The monomer vinyl chloride has been found to be toxic in large dosages and standards have been set for the exposure levels of the monomer. These exposure levels include exposure during the polymerization but also on the amount of monomer residue left in the final product. Thanks to these standards the amount of monomer residue in PVC is today close to zero. [4][7]

PVC is usually produced by suspension polymerization but solution, emulsion and bulk polymerization techniques can also be used. The product is normally atactic, independent of the polymerization technique, but also isotactic and syndiotactic PVC can be made. The combination of an atactic polymer chain with the relative bulkiness of the chlorine atom will give a highly amorphous polymer with about 10% crystallinity. The bulkiness of the chlorine atom also makes the polymer more sensitive to solvents compared to similar polymers such as polyethylene. This sensitivity is used in the production of PVC products since the addition of certain solvents, called plasticizers, will significantly change the properties of PVC. The most common plasticizers used for PVC are phthalates. Phthalates is toxic and can cause some serious health problems such as cancers and damages to kidneys or the reproductive system of mammals. Addition of plasticizers will give a softer and more flexible polymer, this form of PCV is normally called soft PVC. Without the addition of the plasticizers the polymer will be harder and more rigid and is therefore called rigid PVC. For coating and lamination of textiles the soft PVC is used. [4][7][8]

A general property of PVC is that it is sensitive to degradation by both heat and light. If degraded, the polymer will release hydrochloric gas, which is corrosive and toxic. Stabilizers must therefore be added to PVC in order to increase the lifespan of the polymer. The release of HCL gas when degraded also makes PVC self extinguishing when exposed to a fire, a property that makes PVC suitable for many applications where there is a risk of fire. [4][7]

2.3.2 Polyurethanes

Polyurethanes are a family of polymers that is formed by the interaction between diisocyanates and diols. The general reaction for forming polyurethane is: [9]

$$OCN\text{-}R\text{-}NCO + HO\text{-}R^1\text{–}OH \longrightarrow (\text{-}O\text{-}R^1\text{-}O\text{-}CO\text{-}NH\text{-}R\text{-}NH\text{-}CO\text{-})_n$$

The reaction mechanism can be seen as a step growth reaction since two monomers react in a head to tail manner except that no condensate is formed, differentiating it from a normal step growth polymerization. The reaction is often made in two steps where the first are the production of a prepolymer by a reaction between diisocyanate and dihydroxy-terminated short-chain polyether or polyester. In this first step the diisocyanate is used in excess to ensure isocyanates end–capped blocks. These prepolymers are then chain extended by reaction with a diol. [9]

Since the groups R and R^1 as seen in the above reaction can be varied, the properties of the polymer changes accordingly . This gives a polymer that can be designed for many different applications and the use of polyurethanes is therefore wide. [7]

Advantages of using polyurethanes as material for coatings and laminates compared to other polymers include: high toughness, abrasion resistance, flexibility, fast curing and good chemical resistance. Many polyurethanes is however sensitive to UV, humidity and certain temperatures and are therefore unsuitable for some coating and lamination applications. [7]

2.3.3 Acrylics

The monomers used in creating the acrylic polymers are esters of acrylic and methacrylic acid. The chemical structure of an acrylic ester can be seen in Figure 3.[4]

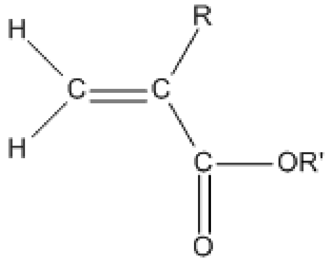

Figure 3. structure of an acrylic ester.(figure redrawn from [4])

Acrylic polymers are created in a free radical polymerization mechanism. For the acrylic group two main polymers are created, namely Polymethyl methacrylate (PMMA) and polyacrylonitrile (PAN). The properties of these polymers differ significantly, PMMA is a hard and rigid polymer with excellent optical clarity and PAN is mainly used as a fiber or for creating copolymers with other polymers. Mixing of those two monomers creates copolymers that obtain flexibility and softness according to the ratio between the monomers. [4][7]

Acrylic polymers can be produced by bulk, suspension, solution and emulsion polymerization techniques. When the polymer is to be used as a coating or laminate the normal production techniques are emulsion and solution polymerization. Acrylic coatings have excellent resistance to UV, heat, ozone and chemicals. [4]

2.3.4 Elastomers

Rubbers or elastomers, which is a more suitable name of this material group, are materials that are highly elastic. Elastomers can be elongated several times their original length and directly retracted when the tensile stress is released. [9] The property of elastomers to be stretched and their direct retraction is mainly due to entropic effects. In their outstretched state the polymer chains will be highly ordered which is unfavorable in terms of entropy and the material will therefore retract, giving a less ordered state with higher entropy. [9]

The first elastomers discovered and used was natural rubber which have the chemical name cis-poly isoprene. The first use of natural rubber was by the Maya Indians who used it as a coating to waterproof clothing and footwear. The Maya Indians obtained this rubber by drying the sap from the rubber tree (Hevea braziliensis). The poly isoprene obtained by this method only contains the cis-form while the synthetically produced poly isoprene will also contain some amount of trans poly isoprene making the synthetically produced poly isoprene somewhat harder to process. [7]

Today there are many different elastomers used for coating and laminations. Apart from poly isoprene, a few of those are styrene‑butadiene rubber (SBR), poly chloroprene rubber (CR), nitrile–butadiene rubber (NBR) and silicone rubber. Those elastomers have different properties and hence, are useful in different applications [4]

All elastomers are used above their T_g and are amorphous. If the temperature is lowered below the T_g of the polymer it will become more rigid and will no longer function as an elastomer. Many elastomers are also slightly cross-linked something that may seem counterintuitive since crosslink's normally provides a higher stiffness and strength in a polymer, making it more rigid. This is to some extent also true for elastomers, but if the crosslink's are few enough they may give the elastomers a higher strength without affecting the materials ability to elongate. This since there will be many atoms in-between every crosslink and therefore the material will still be able to elongate, making it suitable for a wider range of applications. Elastomers are crosslinked in a process called vulcanization. . [7][9]

2.3.5 Polyethylene

Polyethylene (PE) is produced from the monomer ethylene $CH_2{=}CH_2$ and is the simplest polymer available, consisting only of only carbon and hydrogen. Polyethylene is also the most common polymer used and can be found in applications such as plastic bags, packaging film, children's toy and many other. The main reasons for the widespread use of polyethylene are that it is cheap to produce and easy to process. Another advantage of polyethylene is that the temperature needed to process polyethylene into its final shapes is low, keeping the energy consumption at a low level. [7] [10]

Polyethylene can be found in many different forms and the three main types are high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). All of these various forms of polyethylene will differ in their general properties and it is important to use the right type of polyethylene for the right application. The main difference between these various forms of polyethylene is the amount of side chains present in the molecule. [7] [10]

In HDPE the amount of side chains is low making it possible for the polymer chains to pack close together which gives a material with a high density. HDPE is therefore more rigid and harder compared to LDPE and LLDPE. To produce HDPE a catalyst is required since the temperature and pressure must be kept low to avoid chain branching during the polymerization process. [7] [10]

LDPE contains a lot of side chains giving a material with a lower density compared to HDPE, this since the side chains will prevent close packing of the polymer chains. LDPE is the easiest type of PE to produce and was also the first type of PE discovered. For the production of LDPE the temperature and pressure can be higher compared to the production of HDPE reducing the need for a catalyst. Properties of LDPE include good flexibility, low water absorption and good resistance to chemicals and weather. [7] [10]

LLDPE is similar to LDPE in that it contains a lot of side chains, these side chains is however shorter in LLDPE compared to the side chains found in LDPE. The side chains in LLDPE will prevent close packing of the polymer chains giving a lower density compared to HDPE, however since the side chains are short the polymer will have a linear structure similar to HDPE. LLDPE can be seen as a mixture between HDPE and LDPE and its properties are also somewhere in between those of HDPE and LDPE. To make the short side chains of LLDPE a co-monomer is added during the polymerization. These co-monomers consist of a short carbon chain (normally 2-6 carbons) with a double bound between the first and second carbon. The co-monomers will bind to the polymer chain, creating the short side chains necessary to produce LLDEP. For production of LLDPE a catalyst is used, as in the case of HDPE. [7] [10]

2.4 Adhesion

Adhesion is the ability of two different materials to stick together, by mutual interactions and formation of chemical bonds. Adhesion is important for most applications where two surfaces are joined together. For applications such as painting and coating it is important to have as high adhesion as possible but for some applications such as lubrication it is instead important to have as low adhesion as possible. [4][11]

There are four main mechanisms that contribute to the total adhesion between two polymer materials and those are *mechanical interlocking, interdiffusion of chains, electrical interactions and chemical interactions.* [4][11]

Mechanical interlocking states that an adhesive will adhere more strongly to a rough surface than one that is completely smooth. This is because if a surface is rough the adhesive can penetrate into the pores and then lock mechanically to the surface. Mechanical interlocking are however a bit controversial and some mean that it is not a valid theory since there are experiments showing that an increased roughness of a surface in some cases can decrease the adhesion. This is however dependent on the materials used and for some materials the mechanical interlocking can be important for achieving a good adhesion. [4][11][12]

Interdiffusion of chains are the interaction between different polymer chains. If the polymers are above their T_g, segments of long polymer chains can diffuse into the other polymer moiety. This theory however only applies to the case when both moieties are polymers and their compatibility is high enough. [4][11]

Electrostatic attraction is the effect that similar charges will repel each other while charges with different signs will attract each other. This is a well known fact and if dealing with surfaces of different charges the electrostatic interaction will contribute to the adhesion. But also the opposite effect can be found if two surfaces with the same charge are put together, in this case the electrostatic effect will lower the adhesion. [4][11]

The fourth and final form of adhesion is the *chemical interactions*. In the case of chemical interactions there are many different forces that contribute to the adhesion such as London interactions, dipole-dipole interactions, dipole induced dipole interactions, hydrogen bonding and chemical bonding (covalent bonds). [4][11][12] Another chemical interaction that affects the adhesion is the acid/base character of the surfaces which is a polar interaction. [13]

All of these interactions have to be considered to achieve good adhesion but generally it is the chemical interactions that play the biggest roll in how strong an adhesive will adhere to a substrate. It is also only the chemical interactions that are applicable to all surfaces, the other mechanisms are more or less special cases that can have some effect for some materials but not for all. The chemical interactions are also the strongest and in order to create a coating or laminate with strong adhesion to the substrate chemical interactions are preferable.

2.5 Surface tension and surface energy

Achieving a strong interlaying bonding between two materials is central to achieve a good adhesion as was explained in the previous section. Achieving this strong interlaying bonding between two surfaces is strongly dependent on the interlaying strength of the two surfaces. The interlaying strength is called surface tension for a liquid and surface energy for a solid and is here shortly explained. To achieve high adhesion, the joined materials need to have high surface energies. [6]

The surface tension is what gives liquids the ability to form drops, and is central when it comes to the wetting of a surface. The surface tension occurs because the attractive forces between the molecules of the liquids is stronger compared to the forces between the liquid molecules and the surrounding medium. Depending on the strength of these forces, different surface tensions will occur. A good example where strong forces are present is in water, since water has the capability of forming hydrogen bonds. The great number of hydrogen bonds and the high polarity of a water molecule will give a liquid with a high surface tension. If this is compared to ordinary oil where no hydrogen bonds can be formed and the molecular structure is non-polar the difference in surface tension is significant. [14]

The explanation above has focused on the surface tension of liquid, for a solid the case is somewhat different. A solid surface is defined as portions of matter able to withstand stress without deformation. Therefore the methods used to measure the surface tensions of liquids cannot be used for solids. The surface energy of a solid not only depends on the interaction between the molecules at the surface and the bulk of the material, but also on functional groups present on the surface. The easiest way to measure the surface energy of a solid is by measuring the contact angle between liquids with known surface tensions and the solid surface. [11][14]

Measuring surface energy of a solid surface is, easiest done by contact angle measurement and the procedure used is explained below.

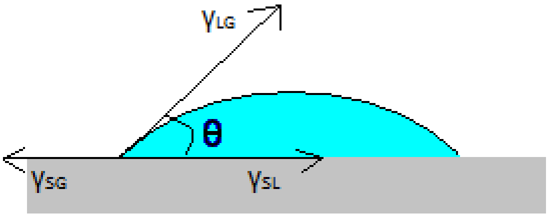

Figure 4. Contact angle between a liquid and a solid surface.

The contact angle θ between a liquid and a solid surface is illustrated in Figure 4. The surface energy of the solid can be calculated by the use of Youngs equation:

γ_{SG}-γ_{SL}=γ_{LG}*cosθ

In Youngs equation γ_{SG} is the interfacial tension between the solid and the gas, γ_{SL} is the interfacial tension between the solid and the liquid and γ_{LG} is the interfacial tension between the liquid and the gas (surface tension). By plotting cos θ against the surface tension (Zisman plot) one will get a straight line and the point where the line cuts the cos θ=1 is the critical surface energy of the solid.[11] [14]

The spreading of a liquid on a surface requires that the surface energy of the solid is higher than the surface tension of the liquid. It is thus important to achieve as high surface energy as possible to ensure a good spreading of a coating on a substrate. [14]

2.6 Plasma

Plasma was explained by Faraday as the fourth state for matter even though Faraday called this state radiant matter instead of plasma. [15] Plasma is simply ionized gas existing of electrons, ions and neutrals in excited states. Plasmas are electrically conductive and free charges exist but seen from a macroscopic view all plasmas are electrically neutral and is therefore said to be quasineutral. Plasma is the most common state in the universe and approximately 99% of the matter is in the plasma state. [16] For technical applications the plasma is created by an electrical discharge where a gas is led in between two electrodes. A high voltage over the electrodes generates a gas discharge and thereby a plasma is created.

Plasmas can be divided into two different forms, one is the *local thermodynamic equilibrium plasma* denoted LTE. The LTE plasma is in thermal equilibrium and both the electrons and the more heavy particles have the same temperature, this will give a high overall temperature of the plasma. Because of the high temperatures of the LTE plasma it is often called hot or high temperature plasma. For surface treatment of textiles LTE plasma is useless since the plasma would burn the fabric as soon as they come into contact. But for applications such as welding or plasma cutting the LTE plasma is excellent. The form of plasma used in this project is the *non-local thermodynamic equilibrium plasmas,* denoted non-LTE plasma. In non-LTE plasmas the electrons and the heavier particles are not in thermal equilibrium giving the electrons one temperature and the heavier particles another where $T_e>>T_h$. This gives the effect that even though the electrons have a high temperature the total temperature of the plasma can be kept low since the heavy particles have a much lower temperature and due to their heavier weight gives the main contribution to the overall temperature. [16]

In order to produce non-LTE plasmas the feeding power supply must have a low density or be pulsed. The plasma will then be prevented from reaching equilibrium. [16]

A plasma treatment can essentially change a material surface in two different ways. The first is removal of particles from the surface. This will lead to cleaning, sterilization and etching of the surface. [17]

Plasma treatments can also introduce particles on surfaces. One typically speaks of three different effects: activation, functionalization, and finishing/coating. [17]

Activation of a surface is made by temporarily increasing its surface energy. This is made by the incorporation of oxygen-containing groups such as –OH, =O and –COOH onto the surface. This is the desired effect of the plasma treatment in this project. The oxygen bound to the surface in this way is however un-stable and will orient into the bulk of the material with time. This process is called ageing and is explained in section 2.6.1 [17]

In *functionalization* specific chemical groups is permanently grafted to the surface of the material. One example of functionalization of a surface is the introduction of nitrogen-based groups onto the surface creating a permanent primer layer. This is essentially done by the use of nitrogen as process gas in the plasma treatment. [17]

Plasma finishing/coating is the deposition of a thin layer or coating of a specific material onto the surface. This is done by using a plasma device in combination with a liquid evaporator, to vaporize a liquid precursor directly into the plasma field; the precursor is applied to the surface in situ. Depending on the precursor chosen several different surfaces can be created. [17]

2.6.1 Ageing after plasma treatment

The improved adhesion achieved by plasma treatment comes from the creation of new functional groups on the material surface. These functional groups will increase the surface energy of the material and interact with other surfaces creating an enhanced adhesion. However since everything in nature wants to have as low energy as possible these new functional groups bounded to the surface will eventually reorient into the bulk of the material and the effect of the plasma treatment will therefore decrease with time. Depending on which functional groups that are present on the surface the aging time will vary and in order to use plasma for the activation of a surface it is essential to know how long after the treatment the surface can be coated or laminated. [17]

2.6.2 Plasma treatments

Two different forms of non-LTE plasma treatments exists, vacuum plasma and atmospheric pressure plasma treatment. The plasmas created by these techniques are basically the same, the difference lies in how the plasma is created.

Vacuum or low pressure plasmas have been used in the microelectronics industry since the 1960s. In the 1980s their usages started to broaden and more areas where plasmas could be used were investigated. Soon research within plasma for textile applications started and this is an ongoing field ever since. [18]

In vacuum plasma the gas pressure needs to be low in order to produce the plasma. Hence, a vacuum chamber and pump is needed. This will make the technique energy-demanding since the pump needs to be powerful in order to be able to reach the low pressures needed for the plasma to be generated and maintained. This also makes it demanding to use a vacuum plasma treatment as part of a continuous process and only batch-wise processes are realistic.

Atmospheric pressure plasma is a technique in which there is no need for low pressures hence, the treatment can be made at a normal pressure. This makes it possible to use atmospheric plasma treatments in a continuous production line. The energy use for an atmospheric plasma treatment will also be significantly lower compared to vacuum plasma since no pump is needed.

Some different forms of cold atmospheric plasmas exist examples of this are corona discharge, dielectric barrier discharge and glow discharge.

The corona discharge is the oldest and most widely used of the atmospheric pressure plasma techniques. It is however a weak form of plasma and cannot penetrate deep into textiles. [18] The corona treatment is also inhomogeneous making it unsuitable for use when treating textiles since homogeneity is an important factor in textile applications. [15]

The dielectric barrier discharge uses an insulating (dielectric) layer made of for example quarts or a ceramic material, covering at least one of the electrodes. The technique is often used in the packaging industry in order to increase the wettability of polymer films. The homogeneity of the plasma is however not that good and can cause an uneven treatment of the textile [15][18][19].

Glow discharge is a homogenous, uniform and stable technique for producing plasma. The plasma is created by applying radio frequency voltages across two parallel plate electrodes, the gas used for glow discharge is often helium or argon [18].

In this project the atmospheric plasma equipment used has been based on dielectric barrier discharge plasma.

2.7 Characterization methods

Different characterization methods were employed, to evaluate the effect the plasma treatment had on the material surfaces and to increase the understanding of the chemical and physical mechanisms that are taking place.

2.7.1 Measurement of adhesion

Depending on the nature of the polymer and the substrate some different methods can be used to measure the adhesive force between two materials. If the coating is flexible the preferred method used is the peel test, in a peel test the coating is simply peeled of the substrate at a specific angle. If both the coating and the substrate are flexible normally a T-peel test is used, see Figure 5A. This is the method used in this project, since both the textile and the polymer films are flexible. If a flexible coating is applied on a more rigid surface the peel tests used is normally the 90^o and the 180^o peel-test, see Figure 5B-C. [20]

If both the coating and the substrate is rigid the butt joint test or the lap shear test can be used instead, see Figure 5D-E.

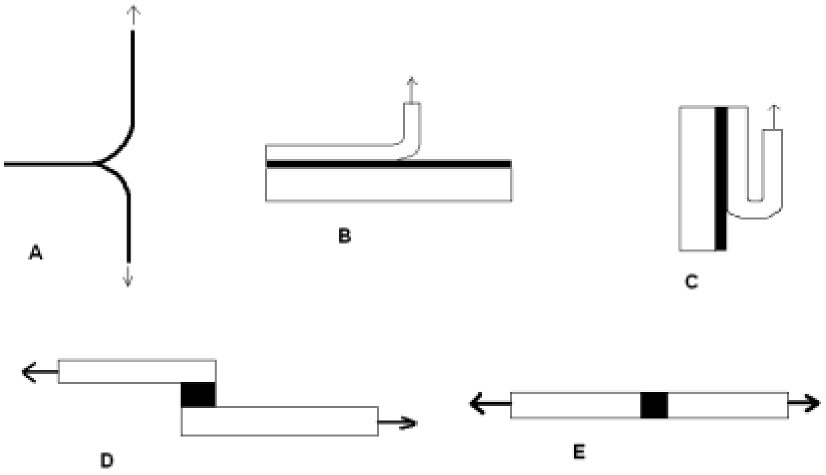

Figure 5. A=T-peel test, B=90° peel test, C=180° peel test, D=lap shear test, E=but joint test

The techniques seen in Figure 5 all have one big disadvantage in that the sample is destroyed during the measurement. There exist also nondestructive tests for adhesion measurements. Those methods however, are generally more complicated and therefore also more expensive to run. In this project no such technique was used and for most purposes the techniques seen in figure 4 are sufficiently reliable.

2.7.3 Scanning electron microscopy

In scanning electron microscopy (SEM) a surface is bombarded by an electron beam, this will result in emission of electrons from the surface. These emissions can be categorized into groups, depending on how they have interacted with the surface these groups are:

- Primary backscattered electrons without energy loss
- Primary backscattered electrons with energy loss
- Secondary and Auger electrons
- Electrons of the continuum

In SEM the image is created by the backscattered and secondary electrons. To achieve the primary electrons necessary for a SEM experiment, a tungsten filament with a low beam current is normally used. Other sources can be used to produce primary electrons as well, but the most common is the tungsten filament. Different detectors are used for detection of different kinds of electrons. For secondary electrons a Thornley-Everhart scintillator/photomultiplicator can be used, while backscattered electrons normally are detected by silicon diodes. [17]

2.7.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is used for elemental surface characterization of materials. The theory behind the technique comes from Einstein's explanation of the photoelectric effect for which he received the Nobel prize in 1905. [21] However, the technique was developed in Uppsala in the 1950s, by Siegbahn et al. They first called the technique electron spectroscopy for chemical analysis (ESCA) and later it has also been known as XPS. [22]

In an XPS experiment the sample is irradiated with soft X-rays photons with a specific energy $h\upsilon$. The X-ray photons will eject photoelectrons from the sample and the energy of those photoelectrons can be calculated according to;

$E_K = h\upsilon - E_B$

Where E_K is the kinetic energy of the emitted photoelectrons, $h\upsilon$ is the incident photon energy and E_B is the binding energy of the photoelectrons. From the kinetic energy of the photoelectrons E_B can be calculated. E_B is elemental-specific and hence, allow for the elemental composition of the surface to be determined. [17][22]

One advantage of using XPS for surface characterization of plasma-treated samples is that it is a surface sensitive technique with a sampling depth of approximately 10 nm. Another advantage is that the irradiation damage is low, since soft X-rays are used and XPS can therefore be regarded as a nondestructive technique. [17]

3 Materials and Method

3.1 Materials used

3.1.1 Fabrics

The fabric used in this project is made of 100% polyester filament yarn, supplied by FOV fabrics AB, located in Borås Sweden. For a more detailed description of the fabric see table 1. Two types of the fabric have been used, one colored orange with a coumarin based dispersion and one uncolored. The fact that one is colored will give slightly different properties, due to the coloring process but also from the fact that the added dye can have an effect on the chemical properties of the fabric.

Table 1. Properties of the fabric used in the project.

Properties of the PET fabric	
Quality number	8209
Weight	126,5 g/m^2
Binding	2/1
Warp	167 dtex, 40 treads/cm
Weft	167 dtex, 23 treads/cm

3.1.2 Polymers

In this project two different polymers have been used to laminate the fabrics. The first is called Engage 8100 and is supplied by DOW Chemical Company. Engage 8100 is a copolymer of ethylene and octane and is therefore non-polar. Information of the octene content in this copolymer is not provided by the supplier. The ethylene/octene copolymer will be called ETO in the rest of this report.

The second plastic used is supplied by Arkema and is called Lotryl 17BA07. Also this polymer is a copolymer, this time of ethylene and butyl acrylate, giving a more polar polymer. The butyl acrylate content in this copolymer is between 16-19 wt %. The ethylene/butyl acrylate polymer will be called EBA in the rest of this report.

Both of the copolymers were delivered as pellets, some of the basic properties of the copolymers can be seen in table 2.

Table 2. Comparison of some central properties of the copolymers used in the project.

Properties of the copolymers		
	ETO	**EBA**
Melt index (190 ˚C / 2,16 kg)	10 g/min	6,5-8 g/min
Density	0,87g/cm^3	0,93 g/cm^3
Vicat softening point	45 ˚C	60 ˚C

The values in table 2 are supplied by the manufacturers and may differ depending on subsequent process parameters.

3.2 Methods

All lab work was conducted at Swerea IVF in Mölndal, Sweden, unless otherwise stated.

3.2.1 Pressing of the polymer films

For the lamination of the polymer films (explained in section 3.2.3) the copolymer first needed to be pressed into polymer films. To make the polymer films, a compression mold from J. Wickert & Söhne Maschinenbau, Germany, was used. An appropriate amount of pellets where placed between two sheets of Teflon film and metal pieces with a thickness of 1 mm. The metal pieces were placed so that the melted copolymer only came in contact with the Teflon sheets the reason for using the metal pieces was to ensure that the films always gained the same thickness.

The films were pressed at 95 ˚C for the ETO copolymer, and 110 ˚C for the EBA copolymer. The pressure was slowly raised from 0 to 50 kg/cm^2, where it was kept for about 15 s where-after the pressure was released and the film collected. The pressure applied were the same for both copolymers.

3.2.2 Plasma treatment

Atmospheric plasma treatment

The atmospheric plasma treatment was performed on a Platex 600 lab plasma from Grinp S.r.l, Italy. The plasma is based on the DBD technique and have two parallel electrodes placed horizontally. One electrode is placed upwards and the other downwards. The plasma zone is generated in the gap between the two electrodes. Following parameters of the plasma was varied:

- The process gas used
- The gas flow
- Time in the plasma zone
- The power
- The distance between the electrodes
- Temperature of the electrodes

Pure He was used as process gas, if not otherwise noted, but also N_2 and O_2 have been used, either pure or mixed with He. The total gas flow was kept constant at 7,5 l/min for all samples, independent of the gas used. The time in the plasma zone was controlled by regulating the speed of a tender frame on which the fabric was mounted. The treatment was generally repeated three to six times and the total time in the plasma zone calculated.

The power of the plasma can be set to values in between 500 and 8000 W, depending on the electrode distance. The electrode distance can be varied between 1-500 mm and in this project distances between 1-60 mm has been used. The temperatures of the electrodes can also be varied and was set to 50 ˚C when treating the fabric and 30 ˚C when treating the polymer films.

The polymer films was too small to be mounted on the tender frame normally used for the fabrics and was therefore placed on top of a large piece of fabric, which was then mounted on the tender frame.

The different parameters were used to calculate the total plasma energy per square meter of treated surface (treatment energy). The calculations are described by equations 1-6 seen below.

In equation 1 the total time the material has spent in the plasma zone was calculated. The total energy is given by equation 2, where t_{tot} and the power of the plasma is multiplied. The power of the plasma is set by the operator, which means that it is known.

$$(1)\ Total\ time\ (t_{tot}) = \frac{Plasma\ lenght\ * Cycles\ through\ plasma}{Fabric\ speed}$$

$$(2)\ Total\ energy\ (E) = Power * t_{tot}$$

Equation 3 and 4 are combined into equation 5, which expresses the area of the treated material. Combination of equation 3 and 4 removes the *Fabric speed*.

$$(3)\ Time\ for\ one\ cycle\ (t_1) = \frac{Length\ of\ plasma}{Fabric\ speed}$$

$$(4)\ Area\ of\ fabric\ (A) = Width\ of\ the\ plasma * \ t_1 * Fabric\ speed$$

$$(5) Area\ of\ fabric\ (A) = Width\ of\ the\ plasma * length\ of\ the\ plasma$$

Combining equation 2 and 5 will give equation 6 which is the plasma energy applied per square meter of material. This is called the Treatment Energy (TE).

$$(6)\ Treatment\ energy (TE) = \frac{Total\ energy (E)}{Area\ of\ fabric (A)} = \frac{E}{A}$$

The calculations don’t account for all of the parameters that can be varied during the plasma treatment. The type of gas used, the gas flow, the distance between the electrodes and the temperature of the electrodes are not accounted for in the calculations. Furthermore, the calculation of the Treatment power is only valid for atmospheric pressure plasma and not for vacuum plasma.

Vacuum plasma treatment

The vacuum plasma treatment has been performed with 440 Plasma-System from Technics Plasma GmbH, Germany. The vacuum plasma equipment has been used for treatment of the polymer films. Following parameters were varied to obtain the optimal conditions:

- The gas used
- The power
- Time in the plasma
- The pressure in the vacuum chamber

The process gasses used for vacuum treatment were O_2 and N_2. Those gasses were also used to clean the plasma chamber from other gasses prior to any treatment. This is done by first lowering the pressure in the chamber to about 0,22 mbar. The pressure in the chamber is then raised to about 1,4 mbar by the connected process gas. This procedure was repeated 3 times. When the chamber had been cleaned from other gases the pressure was adjusted to the desired value by controlling the flow of the process gas. The gas pressure was 0.7 mbar in all treatments.

The plasma parameters were kept constant once optimized. The power of the plasma can be varied between 0 and 600 W and was set to 500 W. The total exposure time to the plasma was 60 s, divided into two periods of 30 s each, with 10 s delay time between them.

3.2.3 Lamination

Lamination of the plastic films to the fabric has been achieved by using a laboratory hydraulic press from Graseby Specac. The following parameters can be varied:

- Lamination temperature
- Lamination time
- Lamination pressure

All the samples have been laminated the same way independent of the copolymer used. The temperature used was 180 ˚C, and the lamination time 1 min. The lamination pressure is applied manually

The fabrics and the polymer films were placed between two Teflon sheets during the lamination. The fabrics were also laminated on the backside with a supportive polymer film of the same type.

3.2.4 The adhesion measurements

20 mm wide stripes of the laminate were punched pressed out to be tested for adhesion. The adhesion testing is performed by an Instron 1122, connected to a computer with the program Test Works 4. The samples are pulled by the Instron at a constant rate of 100 mm/min, while the applied force is measured. The measurement has been performed as a T-peel test se figure 5A. The measurement is stopped when all the plastic has been peeled off the fabric. The program plots a graph, with the extension in mm on the x-axis and the force in N on the y-axis, see figure 6. The average force is calculated by choosing a representative interval of the graph.

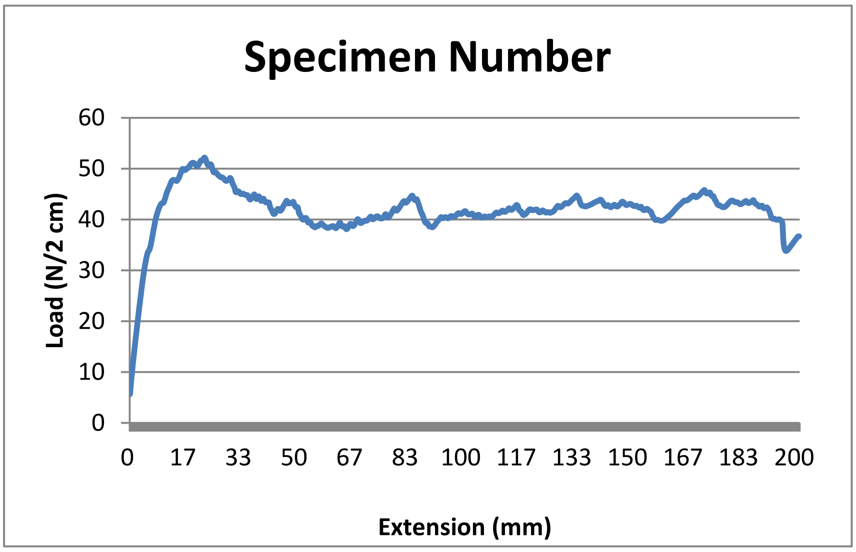

Figure6. A typical load-extension graph, the way is it generated by Test Works 4.

From each sample laminated, three stripes were measured for adhesion. The average forces from these three measurements are then combined to give an average. Those averages are the values presented in this report.

3.2.5 Ageing test

The ageing test has been made by first treating the uncolored and the colored fabric in the atmospheric plasma device. For different samples with different plasma treatments were made for both of the fabrics, the treated fabrics were large enough to ensure that at least 8 different pieces could be used for lamination.

The fabric was laminated with ETO copolymer films treated in the vacuum plasma. The parameters used for the vacuum treatment of the film can be seen in table 3.

Table 3. Parameters used for the vacuum plasma treatment of the polymer films used for the ageing test

Parameters for the vacuum plasma treatment	
Process gas	O_2
Pressure in the vacuum chamber	0.7 mbar
Time in the plasma	30+30 s
Power	500 W

All the films used in the aging test have been treated this way and the plasma treatment has been made no longer than 2 h before the lamination of the film.

When the fabrics had been plasma-treated they were place in a room with a controlled atmosphere (65 % rh and 20 ˚C). The plasma-treated fabrics were kept up to 50 days before laminated and tested for adhesion.

3.2.6 Treatment of plastic powder and fabric at the same time

Fabrics have been treated by the atmospheric plasma after a powder of the ETO copolymer pellets had been spread on the fabric. The powder was obtained by grinding the polymer pellets in a variable speed rotor from Fritsch, called Pulverisette 14. The pellets were cooled by liquid nitrogen before fed into the Pulverisette.

The powder was spread on the fabric with an ordinary kitchen strainer. After the powder had been applied to the fabric it was treated in the atmospheric plasma device. After the fabric and the polymer powder had been plasma treated it was laminated with the same polymer used to produce the powder.

3.2.7 SEM analysis

The SEM analysis where performed on the fiber structure of the untreated fabric and on fabric treated with a relatively low treatment power, and one that has been treated with a high treatment power. The SEM analysis was performed with a 6610 LV from JEOL, Japan, employing a secondary electron detector.

Pictures have also been taken on the fabric after plasma treatment. For this, two different plasma treatment have been performed, one with a treatment power of 150 kJ/m^2 and one with a treatment power of 1060 kJ/m^2. For both of these plasma treatments helium has been used at an electrode distance of 1 mm. The plasma treatments was made one day before the pictures was taken and the fabric was place in aluminum foil during that time.

3.2.8 X-ray photoelectron spectroscopy

XPS was performed on a Quantum 2000 scanning ESCA microprobe from Physical Electronics located at Chalmers University of Technology in Gothenburg, Sweden. The setup used during the XPS measurement can be found in Table 4.

Table 4. The setup used for the XPS measurements

X-ray source	**Al Kα (1486.6 eV)**
Beam size	100 μm
Analyzed area	Approx 500 x 500 μm
Take off angle (with respect to sample surface)	45 °
Information depth	Approx 4-5 nm

The XPS was made for both plasma-treated and untreated samples of EBA films and the colored fabric. The plasma-treated samples were treated one day before the experiment and kept in aluminum foil during that time.

4 Results/discussion

4.1 Results of the peel test for plasma treated fabrics

The primary method used to evaluate the adhesion and the improvement achieved by the plasma treatment has been the peel tests. Since the focus mainly has been on plasma treatment of the fabric this is presented first. The first results presented here are the colored fabric (orange), laminated with either the ETO or the EBA copolymer. All of the points in the graphs below are average values, derived from three measurements. Turn to the appendix for a complete list of all measured adhesion values and their standard deviations, last in the appendix the atmospheric plasma parameters used for the different treatments can also be found.

4.1.1 Colored fabric

The result from the atmospheric plasma treatment of the colored fabrics can be seen in figure 7. The electrode distance was 1 mm and the process gas helium, for all the samples in figure 7. All samples were laminated within an hour after the plasma treatment.

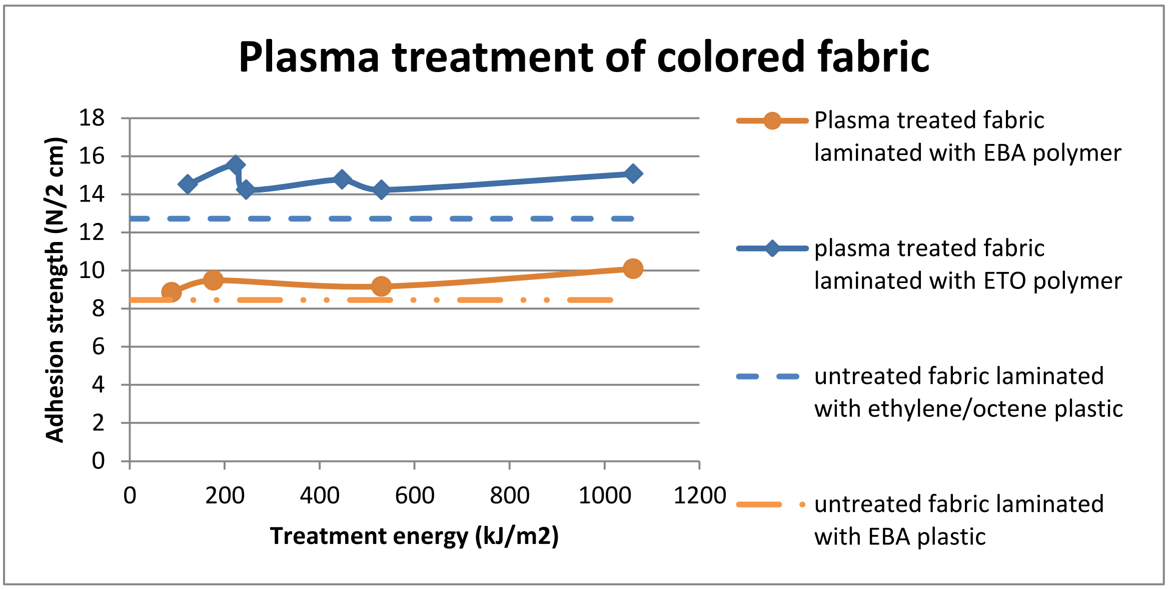

Figure 7. This graph show how the treatment effect of the orange fabric affects the adhesion when laminated with either the EBA or the ETO copolymer film.

Something that is interesting in figure 7 is that the EBA copolymer clearly has a lower adhesion than the ETO film to the PET fabric. This is the opposite effect from what was expected since the EBA has a more polar structure and therefore should interact strongly with the polar structure of the PET fabric. What instead is seen is that the completely non-polar copolymer ETO has higher adhesion than the EBA copolymer to the PET fabric. The reasons for this could be that the EBA copolymer has stronger intermolecular bonds between the polymer chains, which could lead to a higher crystallinity and hence, a weaker polymer-fabric interaction. A higher crystallinity will also give less penetration of the polymer chains of the film into the polymer chains of the fabric, giving an overall lower adhesion. Other factors that could contribute to the lower adhesion of the EBA film could be the molecular weight of the polymers and the amount of crosslink’s on the surface of the plastic film. The amount of crosslink's would in this case be higher for the EBA than for the ETO copolymer, giving a less reactive surface for the EBA copolymer.

Interesting however, is the fact that the plasma treatment of the fabric increases the adhesion for both EBA and ETO. Even though the adhesion is slightly higher for the samples where the fabric has been treated with a high treatment energy the differences between high and low plasma treatment energies are small. This indicates that the need to treat the fabric with a high treatment power is small, at least for fabrics that are laminated directly after the plasma treatment.

The adhesion improvement is approximately the same independent of if the fabrics are laminated with the ETO or the EBA copolymer. At least as long as only the fabric and not the polymer film has been plasma-treated.

As mentioned above, all of the plasma treatments presented in figure 7 have been made at an electrode distance of 1 mm. A higher electrode distance gave a more uneven plasma zone, which lead to damaging of the fabric since there were a high number of discharges which burnt small holes in the fabric.

4.1.2 Uncolored fabric

Most of the fabric used in the project has been the colored but also an uncolored variant of the same fabric has been used in order to see if the coloring of the fabric has an effect on the adhesion properties.

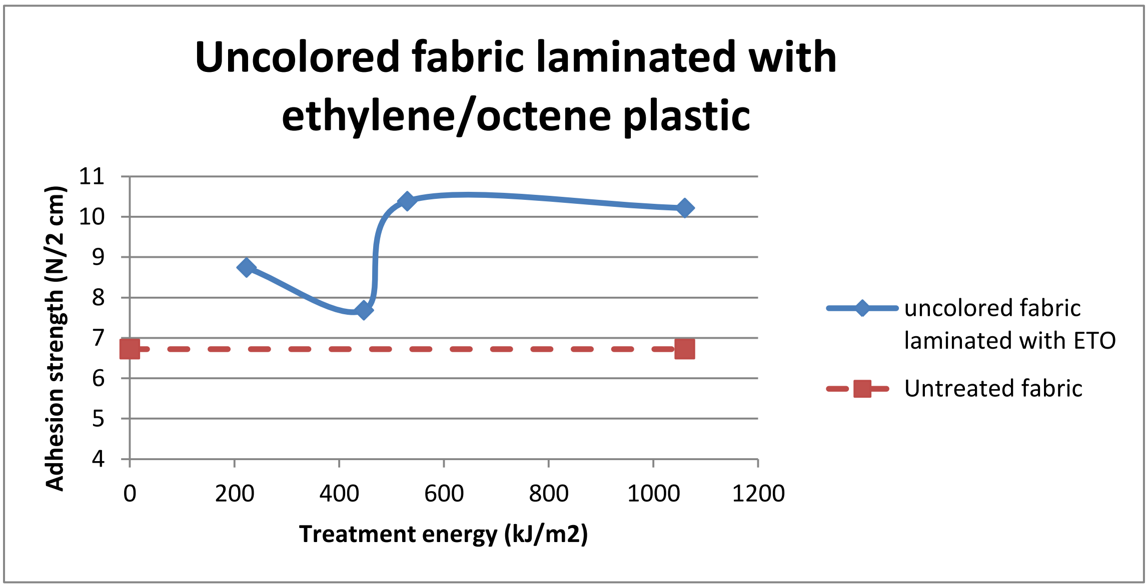

Figure 8. Peel test results of the uncolored fabric laminated with the ETO copolymer.

The result of the He plasma treatment of the uncolored fabric can be seen in Figure 8, from the graph it is clear that the uncolored fabric have a lower adhesion compared to the colored one. The higher adhesion of the colored fabric could be explained by the surface properties of the fabric, induced by the adsorbed dye molecules and also by the process used to color the fabric[1], which was explained in the theory section.

If the higher adhesion seen for the colored fabric are because of the dye this could be because the dye contain a lot of groups capable of forming hydrogen bonds. One effect the dye could have on the surface is that more groups capable of forming hydrogen bond are bond to the surface, making it more reactive. Another reason for the higher adhesion could be that the dye dispersion probably contains a lot of surfactants, these could be left on the surface giving a better wetting and therefore improving the adhesion.

The higher adhesion for a colored fabric could also be because of the treatment used to color the fabric. As mentioned in section 2.1.1 the coloring process involve water at temperatures up to 130 ˚C and treating a PET fabric at this temperature can significantly change the surface properties of the fabric, since the T_g of PET is around 70 °C. [9] The changes may involve chemical crosslinking and increase of the total surface area of the fabric, which both will have an effect on the adhesion properties of the fabric.

The increased adhesion for the colored fabric can be because of either one of the factors mentioned above or it can be a combination of all of them. But clear is that there is some difference in the surface properties of the fabric before and after the coloring of the fabric.

Another interesting aspect of the results in Figure 7 and 8 are that even though the adhesion is lower from the start for the uncolored fabric the adhesion enhancement seems to be approximately the same after plasma treatment. This indicates that the properties of the surface before plasma treatment are of less importance to reach high adhesion and that the plasma treatment induces the same kind of surface functionality, irrespective of the surface properties of the untreated materials.

4.2 Result of the peel test for the plasma treated polymer films laminated to untreated fabric

Not only the fabrics have been treated in the atmospheric plasma, also the polymeric films have been treated in a few cases, see Table 5. The reason for the low number of plasma-treated polymer films, is that the atmospheric plasma treatment performed in the beginning of the project was made with an electrode temperature of 50˚C. That temperature had a tendency to soften the polymer films making them curl up and a high electrode distance had to be used in order to prevent the films from getting stuck inside the plasma zone. The solution to this problem was to lower the electrode temperature to 30 °C. This was however not made until late in the project and the main focus was then to plasma-treat both the fabric and the polymer film, see section 4.3.

For the values presented in table 5 the electrode temperature has been 30 °C, the electrode distance 2,5 mm and helium was used as process gas.

Table 5. Peel test results for when only the polymer films has been plasma treated, prior to lamination.

ETO	
Treatment power kJ/m²	**Adhesion strength N/2 cm**
1060	**19,1**
1471	**19,8**
EBA	
1471	**18,0**

From the values found in Table 5 it is clear that treating only the polymeric films will give a higher adhesion compared to when only the fabric is treated. The reasons for this could be that more oxygen-containing functional groups will be incorporated on the surface of the polymer film during the plasma treatment, as compared to when the fabric is plasma-treated. Several different explanations exist however, such as changed amount of crosslink's or making the surfaces more rough, but the most probable cause of the adhesion enhancement is the incorporation of new functional groups onto the surface.[23]

4.3 Result of the peel test when both films and fabric have been treated

The results presented in section 4.1 and 4.2 are for treatment of either the fabric or the polymer film. The results presented in Figure 9 are instead when both of the material surfaces have been plasma treated by the atmospheric plasma, prior to lamination.

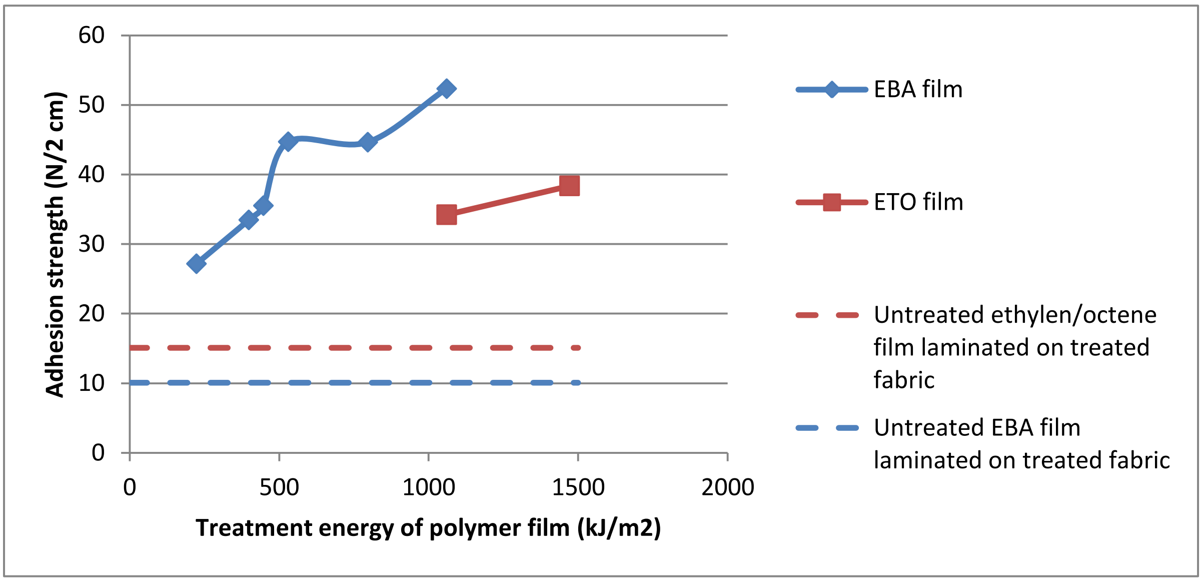

Figure 9. Peel test results for when both the fabric and the polymer films has been plasma treated, prior to lamination.

In figure 9 the x-axis is for different plasma treatment of the polymer films. The plasma treatment of the fabric has been the same for all results fund in Figure 9 For the results presented in Figure 9 the colored fabric was plasma-treated with a treatment power of 1060 kJ/m^2 in helium gas, an electrode distance of 1 mm and an electrode temperature of 50 °C. The treatment of the polymer films have been performed at an electrode distance of 2,5 mm in helium gas with an electrode temperature of 30 °C.

The Adhesion was several times higher after treating both the polymer film and the fabric, compared to when either of them was treated. Noticeable is also that when both the polymer film and the fabric were plasma-treated, the fabric laminated with the EBA copolymer shows stronger adhesion than the fabric laminated with the ETO copolymer. This is the opposite from when only the polymer film was plasma-treated and indicates that the difference in the chemical properties between the ETO and EBA copolymer make the EBA copolymer more suitable for plasma treatment.

Not all the values of the adhesion measurement are presented in the graph seen in Figure 9. The EBA copolymer has also been plasma-treated with of 1471 kJ/m^2. In this case the adhesion became so high that the polymer film broke in the tensile testing machine, before it was peeled off the fabric. Hence, no adhesion values could be obtained, but the film broke at a load of 70 N/2 cm.

There can be several different reasons for the high adhesion when both the polymer and the fabric have been plasma-treated. One explanation could be that the introduced functional groups are reactive and create covalent bonds, resulting in strong adhesion.[23] The reason could also be because a formation of hydrogen bonds between the two materials surfaces. This is a possible explanation since the plasma treatment will incorporate many oxygen-containing groups on the surface, capable of forming hydrogen bonds. These examples would all be regarded as chemical interactions, further explained in section 2.4. After all, it is unlikely to reach the high adhesion here reported, without the involvement of chemical interactions.

Also other factors may contribute to the adhesion enhancement; one such factor is that the plasma treatment will break the molecular structures of some of the polymer chains. This would affect the interlocking of chains since the plasma then would give a more amorphous structure at the surfaces, enhancing the interlocking of the chains. The same goes for the mechanical interlocking. Since plasma energy has the potential of harming surfaces by etching, those surfaces will become less smooth and this should contribute to the enhanced adhesion.

For the present case it is clear that the plasma treatment has changed the surfaces of both the fabric and the polymer, giving two more reactive surfaces, capable of forming strong interactions between them. From the result seen in Figure 9 it is also clear that plasma treatment is a good method for enhancing the adhesion between a PET fabric and an ethylene-based polymer.

4.4 Result from the peel test when other gases than He has been used

Not only helium has been used for the atmospheric plasma treatment, also nitrogen and oxygen have been evaluated. These gases has been used both pure and in mixtures with Helium. In the case of gas mixtures the ratio between helium and the other gas has been 4/1. The peel test results for the colored fabric, plasma-treated in pure nitrogen and laminated with untreated ETO film, can be found in Figure 10.

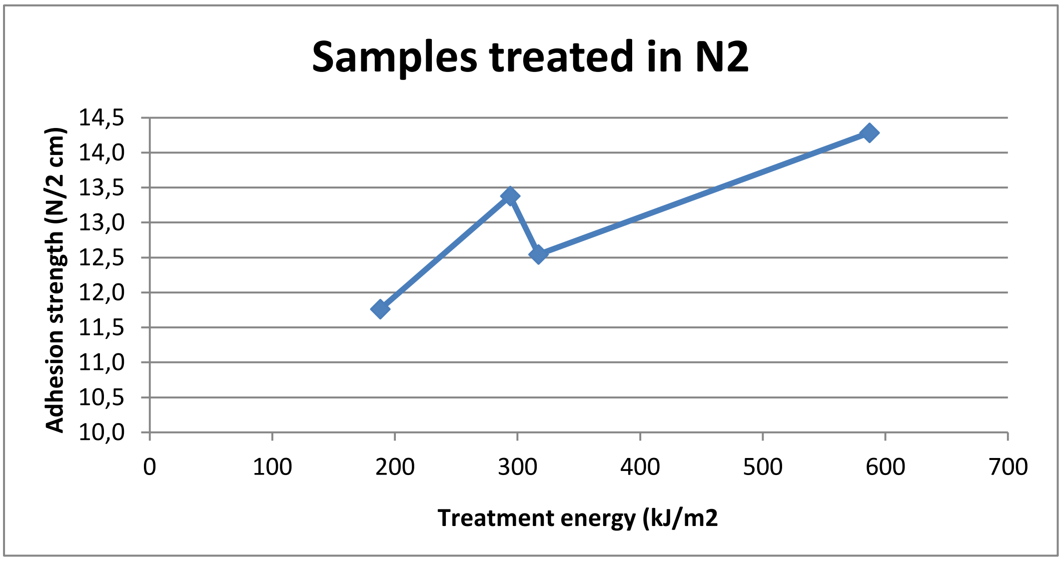

Figure 10. Peel test results of the treatment of the fabric in nitrogen gas

From the results found in Figure 10 it can be seen that the adhesion is approximately the same as when helium was used. What is not seen in Figure 10 is that the treatment made with nitrogen damaged the fabric to a higher degree, compared to the fabric treated with helium. Still, the treatment energy was kept at a low level when using nitrogen, in order not to damage the fibers too much. For the oxygen-treated samples the damage to the fabric was so extensive that there was no point in performing the lamination.

The fabrics treated with a mixture of gases have been laminated with a film treated by vacuum plasma. The process gases used for the vacuum plasma treatment were O_2 and N_2. The reason for evaluating both O_2 and N_2 were to investigate if different functional groups can be incorporated on the plasma-treated surface, by using different gases. And if this is the case, to see if surfaces plasma-treated a certain gas will interact more strongly with a another surface treated with the same gas. The vacuum plasma parameters used in the treatment of these films have been the same as those used in the ageing tests, described in section 3.2.5. The results can be found in Table 6, where the electrode distance has been 1 mm.

Table 6. Results of the peel test when a gas mixture has been used, the gas used beside helium can be seen in brackets for the values given in the table. The polymer was treated by vacuum plasma and the fabric by atmospheric pressure plasma. For a comparison where only He has been used se Figure 7 and 8.

Laminate with polymer film treated in N_2	
Treatment power of the fabric (kJ/m^2)	**Adhesion strength (N/2 cm)**
176 ($He:N_2$, 4:1)	29,34
1060 ($He:N_2$, 4:1)	29,14
176 ($He:O_2$, 4:1)	29,09
587 (($He:O_2$, 4:1)	28,30

Laminate with polymer film treated in O_2	
Treatment power of the fabric (kJ/m^2)	**Adhesion strength (N/2 cm)**
176 ($He:N_2$, 4:1)	28,27
1060 ($He:N_2$, 4:1)	31,88
176 ($He:O_2$, 4:1)	26,43
587 ($He:O_2$, 4:1)	33,18

From the values in Table 6 it is seen that O_2 and N_2 are equally good to use for the vacuum plasma treatment of the polymer film, when the gas mixture of helium and nitrogen has been used for the atmospheric plasma treatment of the fabric.

When a gas mixture of helium and oxygen has been used for the atmospheric plasma treatment the best results seems to be achieved when laminating with a film where oxygen was used in vacuum plasma treatment. The variations are small however and more measurements need to be made in order to make a correct assumption of the influence of the process gases.

From Table 6 the assumption can be made that the effect of the gas composition is small to the adhesion results. Worth mentioning here is also that the damaging of the fabric when it was treated by the gas mixture of helium and oxygen was more pronounce compared to when a mixture of helium and nitrogen was used. The treatment power was lower for He/O_2 than for He/N_2, in order to minimize the fabric damage.

4.5 Result of the peel test when treating fabric together with a polymeric powder

For the treatment of the fabric together with a polymer powder on top it was a bit complicated to find a working setup for the plasma treatment. Previous results had shown that in order to get the most effective plasma treatment the electrode distance should be around 1 mm. For this electrode distance the powder was scraped off the fabric when it entered the plasma zone. Because of this a longer electrode distance had to be used to get the plasma treatment to work. The electrode distance has therefore been varied between 2-6 mm and the results from the adhesion measurements can be found in Figure 11.

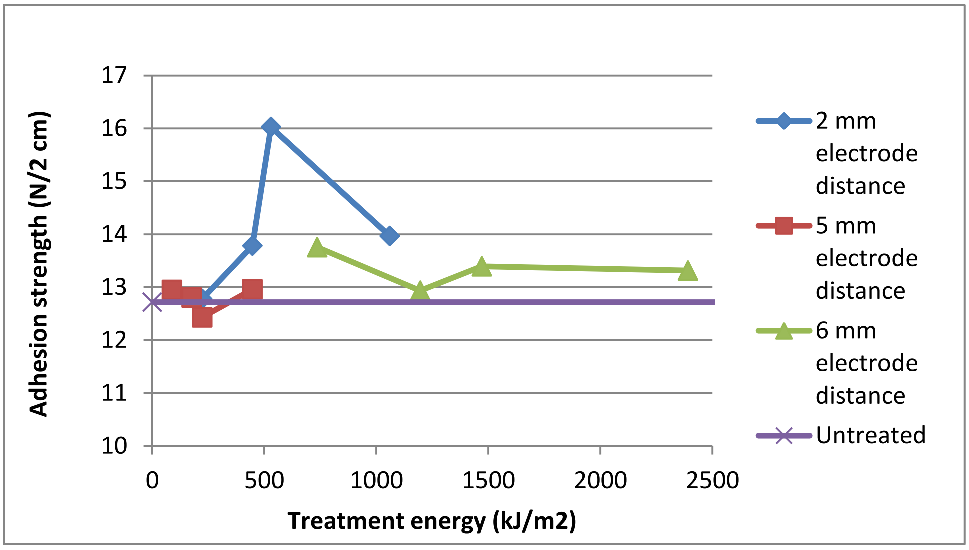

Figure 11. Peel test results from when the fabric has been plasma treated together with a polymer powder, prior to lamination.

In Figure 11 there is no clear trend of how the adhesion values depend on the plasma treatment. The values of the adhesion are also low compared to the ones from where both the fabric and the polymer films have been plasma treated. It seems as the plasma treatment made at an electrode distance of 2 mm is the most effective but this is also the sequence of measurements that varies the most with the treatment energy. The reason for the high variation might be that the electrodes scraped off some of the powder from the fabric so that the distribution of the powder became uneven after the plasma treatment.

For electrode distances of 5 and 6 mm, the plasma treatment provide none or low extra adhesion, independent of treatment energy.

Altogether, treating the fabric together with a polymer powder seems to be ineffective and complicated. This is regretful since treating the fabric this way would be one way of eliminating the need for two plasma treatments; one of the film and one of the fabric. However, it is possible that the technique would be useful if more work is made into finding a better way of distributing the powder on top of the fabric and to make sure that the powder stays on the surface also for shorter electrode distances.

4.6 Ageing results

Aging tests have been made for both the uncolored and the colored fabric. The plasma parameters were the same for the colored and the uncolored fabrics, and the results of these experiments can be found in Figure 12 and Figure 13.

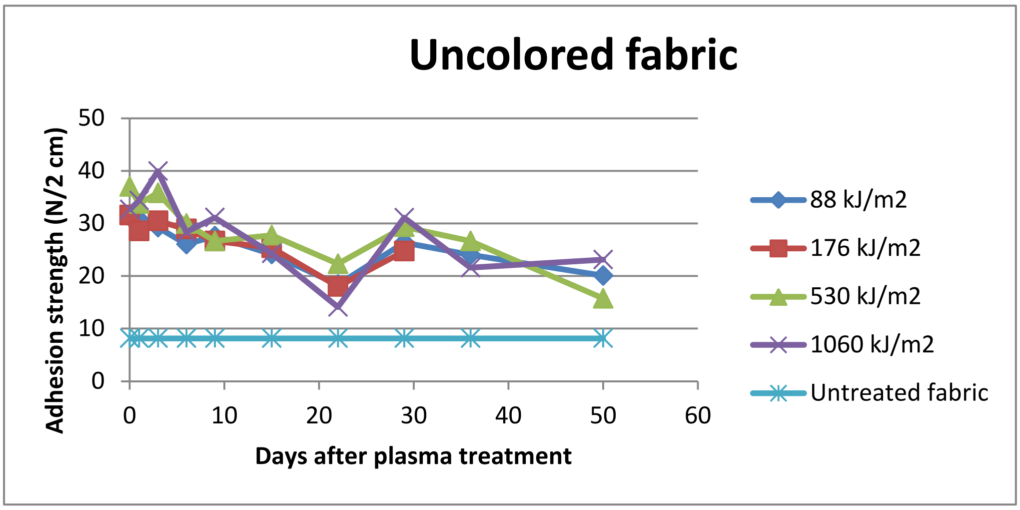

Figure 12. Ageing results for the uncolored fabric

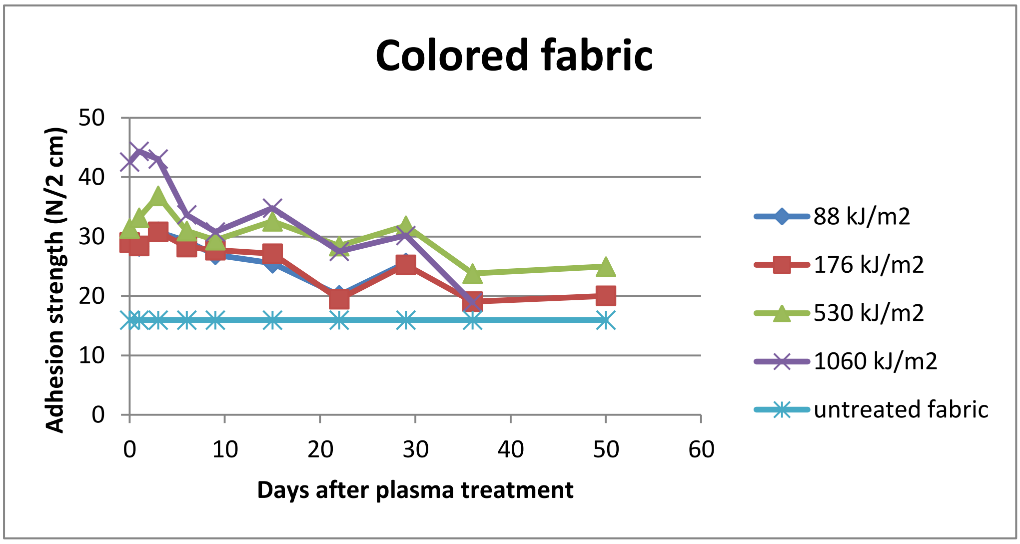

Figure 13. Ageing results for the colored fabric

The colored and the uncolored fabric show the same trend: the adhesion is highest for the samples laminated soon after the plasma treatment and decreases with time. This was expected and the results confirm that the aging after plasma treatment is worth taking into account when working with plasma treatment for adhesion enhancement.

Interesting from the results of the ageing is that the effect of the plasma treatment can last 50 days after the fabrics has been treated. It is also interesting to see that even though a decrease can be seen already after a week the adhesion-decrease is not so significant and a good adhesion can still be achieved if the lamination is made within one week after the plasma treatment.

From the graphs in Figure 12 and 13 it is also seen that higher plasma treatment power generally gives higher adhesion, even a long time after plasma treatment of the fabric. This is not true for all of the values in Figure 12 and 13 but a general trend.

4.7 SEM pictures

SEM pictures were captured in order to investigate if the plasma treatment damaged the surface of the fabrics. Pictures were captured on both the uncolored and the colored fabric, to investigate if any differences could be seen, since the adhesion values have been different depending on whether the fabric had been colored or not. SEM micrographs of the colored and the uncolored fabrics, without plasma treatment, are presented in Figure 14.

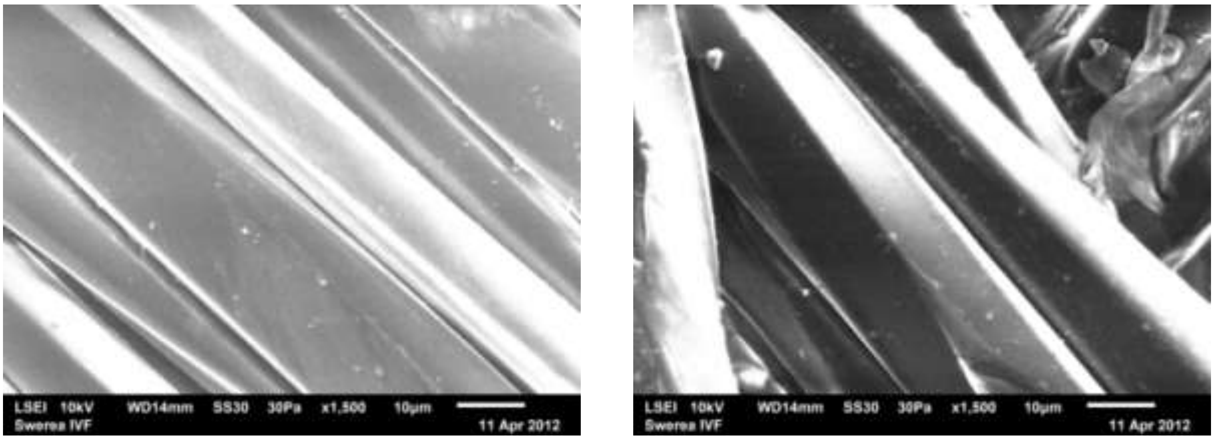

Figure 14. SEM pictures taken at a magnification of 1 500. The left picture is the uncolored fabric and the right picture is of the colored fabric

From the SEM pictures seen in Figure 14 it seems as the coloring process has left the fibers unharmed. Slightly more contaminants can be seen on the surface of the colored fabric, but the fibers seem to be smooth and unharmed in both cases.

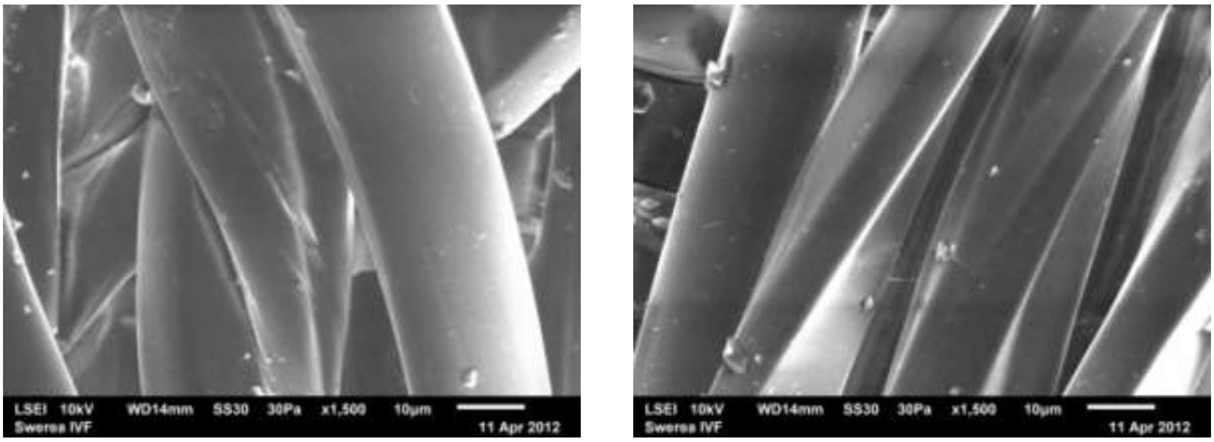

Figure 1. SEM pictures taken at a magnification of 1 500. The left picture is the colored fabric treated with a treatment energy of 150 kJ/m^2 and the right picture is of the colored fabric treated with a treatment energy of 1060 kJ/m^2

SEM pictures were also captured on plasma-treated colored fabrics, shown in Figure 15. Two different plasma treatment were performed, both was made in He and with an electrode distance of 1 mm. The first fabric was treated with a treatment energy of 150 kJ/m^2 and the second with a treatment energy of 1060 kJ/m^2.

In figure 15 a small damage can be seen for the fabric treated by a plasma energy of 150 kJ/m^2 this kind of damages could however also be seen for the untreated fabrics and is therefore not considered to be because of the plasma treatment. For a plasma energy of 1060 kJ/m^2 no signs of damages can be seen on the fabric fibers with SEM. This indicates that the plasma treatment of the fabrics has been performed without harming the fiber surface.

4.8 XPS results

The elemental surface compositions of some selected materials were determined by XPS and the results are shown in Table 7.

Table 7. Result of the XPS measurements

	C1s	N1s	O1s	F1s	Si2p	S2p	Na1s	Ca2p
Un treated fabric	72.8	-	27.2	-	-	-	-	-
Fabric treated by 150 kJ/m²	65.9	0.8	32.0	-	0.8	0.2	-	0.3
Fabric treated by 1060 kJ/m²	64.3	2.1	32.8	-	-	-	0.3	0.4
Untreated EBA	89.7	0.4	8.0	1.8	-	0.2	-	-
EBA treated by 1471 kJ/m²	71.0	2.8	24.8	0.7	0.7	-	-	-

From the result of the XPS measurement it is clear that the oxygen content on the surface of the fabric has increased for the plasma treated samples. To be able to decide which functional groups of oxygen that has been bound to the surface of the fabric the carbon peaks has been studied more closely. The different carbon bands of the untreated fabric is presented in Table 8.

Table 8.The carbon bands found for the untreated colored fabric

Band	Pos (EV)	%Area
1	284.2	67.0
2	285.8	21.6
3	288.2	11.5

As can be seen in Table 8, there are three different carbon peaks present for the untreated fabric. From these values and the repeating unit of PET the different carbons to which the bands belong can be decided. This is illustrated in Figure 16.

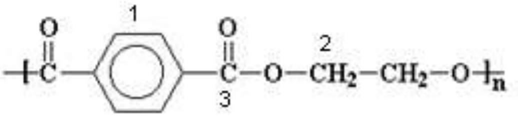

Figure 16 The functional groups connected to the bands seen in table 8

Looking at the carbon bands of the plasma-treated fabrics, it is possible to make an estimation of which type of oxygen groups has been bond to the fabric surface.[22] For the two plasma-treated fabrics, those bands can be found in Table 9.

Table 9 The carbon bands found for the plasma-treated colored fabric

Fabric treated by 150 kJ/m^2			Fabric treated by 1060 kJ/m^2		
Band	Pos (EV)	%Area	**Band**	Pos (EV)	%Area
1	284.2	56.3	**1**	284.2	52.6
2	285.8	25.4	**2**	285.7	26.5
3	288.1	18.4	**3**	288.1	21.0

Comparing table 8 and table 9 one can see that the bands present are approximately the same for all the fabrics. The main difference is the area of the bands. For the plasma-treated samples the area of band 2 and 3 are larger than the corresponding bands of the untreated fabric. This indicates that after the plasma treatment oxygen has been bound to the surface in the form seen as group 2 and 3 in Figure 16. Band 3 has increased the most, meaning that the carboxyl is the type of functional group that has increased the most on the surface.

From Table 9 it is also interesting to see that the area differences between the bands of the plasma-treated samples are small, for the two treatment powers evaluated. This is supported by the peel tests of the plasma-treated fabrics, in which approximately the same adhesion was reached, independent of plasma power.

From the values found in Table 7 it can be seen that not only oxygen have been bound to the fabric surface, some amount of nitrogen has also been introduced. The amount of nitrogen seems to be higher for the fabric treated with a high treatment power indicating that a lot of energy is needed in order to bind nitrogen to the fabric surface. According to the XPS results there are also some other elements on the plasma-treated fabrics, such as Si and Na. It is hard however, to see a general trend for the occurrence of these components, and therefore hard to say if their presence is a result of the plasma treatment or if they are part of a contamination on the surface.

XPS measurements were also performed on the EBA copolymer. The oxygen content on the surface of the EBA copolymer has increased significantly after plasma treatment. This would explain the higher increase of the adhesion when only the polymer film has been treated, compared to when only the fabric has been treated. For the EBA results the band can also be studied, as in the case of the fabric, and these bands can be seen in Table 10 for the untreated copolymer.

Table 10 The carbon bands found for the untreated EBA film

Band	Pos (EV)	%Area
1	283.9	90.7
2	285.4	7.1
3	287.8	2.2

In Table 10 band 1 should be a normal carbon-carbon bond. This assumption is based on the position of the band and the fact that it constitutes 90,7 % of the total area. The second band should be a -CH-O bound, this assumption is made from the bonds known to exist in the structure and the fact that a C=O band theoretically would have a higher energy, compared to a -CH-O bound. This would then mean that band 3 corresponds to a group with a C=O bond and from the molecular structure of the repeating unit of EBA, it is assumed that this band corresponds to the carbon in the following group: –O-CH=O.

This can now be compared to the XPS results for the plasma treated EBA seen in table 11 .

Table 11 The bands found for the treated EBA film

Band	Pos (EV)	%Area
1	283.96	69.55
2	285.53	14.47
3	286.91	7.51
4	288.06	8.47

Here four bands can be found, indicating that one new functional oxygen group has been introduced into the surface that was not present in the untreated EBA. Looking more closely at the band position it is seen that band 1, 2 and 4 are very similar to the ones found in the untreated EBA. Those bands are therefore assumed to represent the same functional oxygen groups that were found for the untreated copolymer. Band number 3 in Table 11 can be of different origins: one is a carbon atom in a ketone group, but a more likely explanation is that the band comes from hydroxyl groups. Such hydroxyl groups are generated in a known plasma process, in which water molecules in the air are dissociated and the products are covalently anchored to the surface. [18]

Table 7 also shows that there are low amount of some other substances present on the surface of the EBA copolymer. One of these is fluorine. The fluorine content present on the surface is probably due to the teflon films used in the pressing of the polymer films, possibly the plasma has etched away some of the fluorine present on the surface, explaining the lower fluorine content for the plasma treated EBA than for the untreated EBA. The silicon and sulfur are probably contaminant on the surface and not a result of the plasma treatment.

5 Conclusion

In this project it has been shown that an atmospheric plasma treatment can significantly enhance the adhesion between a PET textile and a copolymer of ethylene. The results indicate that in order to achieve the best adhesion both the polymer film and the textile need to be plasma-treated. Treatment of only one of them will enhance the adhesion, but the effect will be significantly lower compared to when both of the surfaces have been plasma-treated, if however only one surface is to be plasma treated it is most effective to treat the polymer film.

From the experiments made in the project it is clearly seen that higher adhesion can be achieved when a slightly polar polymer is used for the coating of the fabric, compared to when a completely nonpolar polymer is used.

The aging of the plasma-treated PET fabric has been investigated and it has been shown that the effect of the plasma treatment can be seen as long as 50 days after the treatment. However, even though the effect could be seen 50 days after the treatment it had decreased during this time.

The best adhesion has been achieved when using helium as a process gas for the plasma treatment. The use of nitrogen and oxygen seem to damage the fabric surface too much to make them useful for the present application. From the SEM pictures taken in this project it is also found that the helium plasma treatment has no damaging effect on the surface of the fabric.

From performed XPS measurements, it is clear that the plasma treatment will bind functional groups to the surface of the treated materials. It is also clear that these functional groups are mainly oxygen-based, giving a surface with a higher surface energy after the plasma treatment. Also nitrogen has been found to be bound to the surface by the plasma treatment.

6 Future work

In this project only ethylene based copolymers have been used for the lamination and plasma treatment, in future studies it would be interesting to investigate how other polymers could be plasma-treated in order to improve the adhesion. Only PET fabric has been used in this project, natural and other synthetic fibers would be very interesting in order to see if how they will respond to the plasma treatment.

Only fabrics were age-tested in this project and another thing that would be interesting to investigate is the ageing of the polymer films. Also a combined investigation, where both the polymer and the fabric are age-tested at the same time would be interesting to perform.

Since only lamination has been used as the coating method in this project it would be interesting to see if another way of applying the polymer to the fabric surface could be used and still achieve high adhesion. Here it would also be interesting to see if different application methods would give different results, depending on the polymer and fabric used.

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9 Appendix

In this appendix the adhesion values used to create the figures seen in the report are presented together with the standard deviation. The average values found in these tables are the values that are presented in the figures found in the chapter Results/Discussion. The two last tables in this appendix presents all the parameters used for the atmospheric plasma treatment used in the project.

Table 12 The values used to create figure 7.

Atm plasma treated colored fabric lam with untreated EBA					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
0 (untreated)	8,598	8,475	8,283	0,159	**8,452**
88	9,084	8,9	8,571	0,260	**8,852**
176	9,46	9,487	9,494	0,018	**9,480**
530	9,226	9,248	8,999	0,138	**9,158**
1060	9,83	10,334	10,099	0,252	**10,088**
Atm plasma treated colored fabric lam with untreated ETO					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
0 (untreated)	12,685	12,466	12,998	0,267	**12,716**
122	15,735	13,844	13,97	1,057	**14,516**
223	16,14	15,394	15,073	0,547	**15,536**
245	14,813	14,35	13,548	0,640	**14,237**
447	15,834	14,03	14,458	0,943	**14,774**
530	14,678	13,345	14,656	0,763	**14,226**
1060	15,257	14,478	15,488	0,529	**15,074**

Table 13 The values used to create figure 8

Atm plasma treated colored fabric lam with untreated ETO					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
223	8,93	8,291	9,011	0,394	**8,744**
447	7,867	7,487	7,702	0,191	**7,685**
530	11,78	9,97	9,41	1,239	**10,387**
1060	10,86	10,291	9,501	0,682	**10,217**

Table 14 The values used to create figure 9, the energy is in this case the one used for the treatment of the copolymer films the fabric has been treated with a treatment power of 1060 kJ/m^2

Atm plasma treated ETO film laminated onto treated fabric					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
1060	37,038	35,688	29,921	3,780	**34,216**
1471	37,875	38,992	38,21	0,573	**38,359**
Atm plasma treated EBA film laminated onto treated fabric					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
223	27,297	27,322	26,88	0,2483	**27,166**
398	31,232	35,028	34,132	1,9842	**33,464**
447	37,053	37,55	31,934	3,1089	**35,512**
530	43,206	44,872	46,015	1,413	**44,698**
796	42,314	44,323	47,265	2,4901	**44,634**
1060	53,205	51,118	52,647	1,080	**52,323**

Table 15 The values used to create figure 10

Atm plasma treatment of fabric with N_2 laminated with ETO film					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
188	11,66	11,554	12,069	0,272	**11,761**
317	12,395	12,472	12,76	0,192	**12,542**
294	14,076	13,447	12,611	0,735	**13,378**
587	14,278	14,443	14,126	0,159	**14,282**

Table 16 The values used to create figure 11

Atm plasma treatment of fabric with polymer powder at an electrode distance of 2 mm					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
223	12,79	12,633	12,907	0,137	**12,777**
447	14,02	13,924	13,403	0,332	**13,782**
530	15,993	17,197	14,89	1,154	**16,027**
1060	14,388	13,411	14,1	0,502	**13,966**
Atm plasma treatment of fabric with polymer powder at an electrode distance of 5 mm					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
88	12,945	12,657	13,237	0,290	**12,946**
176	13,311	12,749	12,349	0,483	**12,803**
223	12,158	12,729	12,399	0,287	**12,429**
447	12,828	13,164	12,883	0,180	**12,958**
Atm plasma treatment of fabric with polymer powder at an electrode distance of 6 mm					
Energy (kJ/m2)	Point 1	Point 2	Point 3	Standard deviation	**Average**
736	12,851	12,752	15,66	1,651	**13,754**
1196	12,743	13,368	12,688	0,378	**12,933**
1471	13,375	13,283	13,522	0,121	**13,393**
2391	13,235	13,56	13,144	0,219	**13,313**

Table 17 All of the vales used to create figure 12

Uncolored fabric treated by 88 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**
After 0 days	33,025	30,459	30,218	1,556	**31,234**
After 1 days	31,243	31,051	29,993	0,673	**30,762**
After 3 days	23,235	31,734	32,811	5,246	**29,260**
After 6 days	27,636	26,986	23,488	2,231	**26,037**
After 9 days	26,656	28,022	27,97	0,774	**27,549**
After 15 days	23,595	20,463	28,428	4,013	**24,162**
After 22 days	22,874	16,338	15,852	3,921	**18,355**
After 29 days	26,041	28,132	24,925	1,628	**26,366**
After 36 days	28,277	22,501	21,258	3,746	**24,012**
After 50 days	19,997	20,139	20,062	0,071	**20,066**
Uncolored fabric treated by 176 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**
After 0 days	32,662	31,078	30,954	0,952	**31,565**
After 1 days	31,1	27,874	26,679	2,287	**28,551**
After 3 days	26,433	30,452	34,542	4,055	**30,476**
After 6 days	28,101	29,082	29,612	0,767	**28,932**
After 9 days	28,648	27,332	23,913	2,444	**26,631**
After 15 days	24,912	24,308	26,838	1,321	**25,353**
After 22 days	18,895	15,333	19,749	2,342	**17,992**
After 29 days	25,6	23,988	24,586	0,815	**24,725**
Uncolored fabric treated by 530 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**
After 0 days	39,417	35,754	35,841	2,090	**37,004**
After 1 days	32,803	37,289	31,198	3,157	**33,763**
After 3 days	38,471	35,039	33,869	2,392	**35,793**
After 6 days	30,894	30,355	28,595	1,202	**29,948**
After 9 days	26,469		26,792	0,228	**26,631**
After 15 days	27,628	28,374	27,216	0,587	**27,739**
After 22 days	21,993	24,701	20,23	2,252	**22,308**
After 29 days	31,43	30,793	25,806	3,080	**29,343**
After 36 days	26,81	24,076	29,027	2,480	**26,638**
After 50 days	16,32	16,451	14,437	1,127	**15,736**
Uncolored fabric treated by 1060 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**

After 0 days	32,107	30,768	35,079	2,206	**32,651**
After 1 days	36,173	31,344	35,535	2,623	**34,351**
After 3 days	34,186	40,722	44,893	5,397	**39,934**
After 6 days	32,348	25,394	27,248	3,601	**28,330**
After 9 days	29,207	30,294	33,858	2,433	**31,120**
After 15 days	27,393	23,026	22,422	2,713	**24,280**
After 22 days	13,866	13,194	15,227	1,036	**14,096**
After 29 days	28,878	32,974	31,365	2,064	**31,072**
After 36 days	18,37	23,651	22,698	2,815	**21,573**
After 50 days	24,457	22,073	22,796	1,222	**23,109**

Table 18 All of the vales used to create figure 13

Colored fabric treated by 88 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**
After 0 days	30,792	29,141	28,883	1,036	**29,605**
After 1 days	26,826	26,082	32,12	3,292	**28,343**
After 3 days	32,141	29,268	30,983	1,445	**30,797**
After 6 days	29,123	29,05	29,528	0,258	**29,234**
After 9 days	25,499	25,167	30,126	2,772	**26,931**
After 15 days	28,006	26,35	22,165	3,010	**25,507**
After 22 days	20,054	19,609	20,635	0,515	**20,099**
After 29 days	26,696	25,722	24,269	1,221	**25,562**
Colored fabric treated by 176 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**
After 0 days	28,888	29,497	28,612	0,453	**28,999**
After 1 days	26,254	28,428	30,595	2,171	**28,426**
After 3 days	30,08	30,69	31,62	0,776	**30,797**
After 6 days	28,367	27,811	28,534	0,379	**28,237**
After 9 days	27,396	28,906	26,83	1,073	**27,711**
After 15 days	28,628	26,358	26,336	1,317	**27,107**
After 22 days	18,707	20,839	18,859	1,189	**19,468**
After 29 days	24,242	25,217	26,242	1,000	**25,234**
After 36 days	18,295	18,701	20,156	0,979	**19,051**
After 50 days	20,217	19,08	20,778	0,865	**20,025**
Colored fabric treated by 530 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**
After 0 days	32,492	30,265	31,328	1,114	**31,362**
After 1 days	33,093	35,934	30,448	2,744	**33,158**
After 3 days	36,783	35,664	38,108	1,223	**36,852**
After 6 days	31,345	31,952	29,479	1,289	**30,925**
After 9 days	33,27	30,65	24,269	4,630	**29,396**
After 15 days	31,851	32,159	33,714	0,999	**32,575**
After 22 days	27,12	30,78	27,294	2,065	**28,398**
After 29 days	34,643	29,136	31,674	2,756	**31,818**
After 36 days	23,293	23,162	24,843	0,935	**23,766**
After 50 days	27,324	24,083	23,412	2,092	**24,940**
Colored fabric treated by 1060 kJ/m^2					
	Point 1	Point 2	Point 3	Standard deviation	**Average**
After 0 days	41,725	41,67	44,234	1,465	**42,543**

After 1 days	41,154	45,174	46,7	2,865	**44,343**
After 3 days	44,369	43,656	41,11	1,713	**43,045**
After 6 days	39,157	28,17	33,66	5,494	**33,662**
After 9 days	33,518	26,084	32,712	4,079	**30,771**
After 15 days	35,808	34,968	33,565	1,133	**34,780**
After 22 days	27,825	23,785	30,91	3,573	**27,507**
After 29 days	31,091	29,085	30,328	1,013	**30,168**
After 36 days	18,32	17,805	20,561	1,465	**18,895**

Table 19 The parameters used for the different atmospheric plasma treatment of the fabrics used in the project.

Treatment energy kJ/m²	Process gas	Electrode distance	Electrode temp	Number of cycles	Treatment power	Value of tender frame speed control
88	He	1	50	3	1000	2,5
88	He	2	50	3	1000	2,5
88	He	5	50	3	1000	2,5
122	He	1	50	3	1000	2
176	He	1	50	6	1000	2,5
176	He	5	50	6	1000	2,5
176	He/N_2	1	50	6	1000	2,5
176	He/O_2	1	50	6	1000	2,5
188	N_2	1	50	3	1500	2,5
223	He	1	50	3	2000	2,5
223	He	2	50	3	2000	2,5
223	He	5	50	3	2000	2,5
245	He	1	50	6	1000	2
294	N_2	1	50	3	2500	2,5
317	N_2	1	50	6	1500	2,5
447	He	1	50	6	2000	2,5
447	He	2	50	6	2000	2,5
447	He	5	50	6	2000	2,5
530	He	1	50	3	4000	2,5
530	He	2	50	3	4000	2,5
587	N_2	1	50	6	2500	2,5
587	He/O_2	1	50	6	2500	2,5
736	He	6	50	3	5000	2,5
1060	He	1	50	6	4000	2,5
1060	He	2	50	6	4000	2,5
1060	He/N_2	2	50	6	4000	2,5
1196	He	6	50	3	7000	2,5
1471	He	6	50	6	5000	2,5
2391	He	6	50	6	7000	2,5

Table 20 The parameters used for the different atmospheric plasma treatment of the polymer films used in the project.

Treatment energy kJ/m²	Process gas	Electrode distance	Electrode temp	Number of cycles	Treatment power	Value of tender frame speed control
223	He	2,5	30	3	2000	2,5
398	He	2,5	30	3	3000	2,5
447	He	2,5	30	6	2000	2,5
530	He	2,5	30	3	4000	2,5
796	He	2,5	30	6	3000	2,5
1060	He	2,5	30	6	4000	2,5
1471	He	2,5	30	6	5000	2,5