

RESEARCH

# Powdercoating on Plastics

Effects of gas plasma on adhesion



Professorship for Polymer Engineering



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## Colophon

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# Effects of plasma surface treatments on morphology and surface chemistry: Improving adhesion of powder coating systems to polypropylene substrates

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*"Test ideas by experiment and observation. Build on those ideas that pass the test. Reject the ones that fail. Follow the evidence wherever it leads, and question everything. Accept these terms, and the cosmos is yours."*

- Neil deGrasse Tyson  
*Cosmos: A Spacetime Odyssey*

## Abstract

Powder coating on plastics such as polypropylene is a new development which is made possible by low temperature powder coating curing systems. This coating technique is relevant to recycling and of major interest in industries such as automotive. Application on polypropylene is difficult because of poor wettability and adhesive properties. Surface treatment, mainly plasma, is extensively used in the industry to improve all kinds of adhesive bonds. How plasma treatment can improve powder coating adhesion, and how this adhesion mechanism works, is not studied before.

In this study polypropylene panels were treated using different plasmas and varying treatment times. Plasma treated panels were stored over time to study the shelf life. Treated panels were also stored under water to study preservation of treated surfaces. Thereafter panels were studied on wettability, morphological and chemical changes. Subsequently three different powder coating were applied and evaluated. The powder coating performance was studied by pull-off strength tests and cross-cut tests.

This study showed that plasma treatment has a great effect on the surface properties of treated polypropylene substrates. Chemical changes were characterized with X-ray photoelectron spectroscopy showing up to 23% of introduced oxygen and 4% of nitrogen. Atomic-force microscopy studies showed that surface roughness at the nanoscopic scale had no effect on coating adhesion. Type of plasma gas as well as treatment time both have a significant influence on polar surface energy and also show to be directly related with wettability. Hydrophobic recovery of the plasma treated surfaces occurs for a great deal within the first 2 days after plasma treatment. Under water storage proved to be helpful to preserve polar groups. However, the degree of (polar) surface energy is not related to the coating adhesion performance or the coating appearance (orange peel). It is found that only a relative small amount of polar surface energy is needed for powder coatings to adhere. Degradation of the surface involved with plasma treatment is affecting powder coating adhesion in a negative way. Therefore plasma treatment time is involved in adhesion performance in different ways.

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# 1. Introduction

Polypropylene is after polyethylene the most used plastic in many applications. Worldwide plastic production in 2014 was about 311 million tonnes worldwide of which 19.2% was polypropylene. And these numbers are growing exponentially [1] because of population growth and increasing prosperity. This means that this year and in the years to come, more plastic will be produced than ever before. At the same time raw materials are getting scarcer. Together with a growing concern for a more sustainable world, this urges to make more work of recycling.

To increase the use of recycled plastics, different challenges need to be overcome. These challenges are for instance improving the mechanical, thermal and chemical properties of recycled materials. All of these subjects are already widely studied [2, 3]. Another challenge that is not so widely studied yet is the colouring of recycled polypropylene. Most of the available recycled polypropylene is greyish or black but users often demand different colours. According to Plastics Europe, the organisation that represents the interest of the plastics manufacturing industry in Western Europe, about 29.7 % of the discarded plastics in Europe find their way into new recycled products [1]. Compared to many other materials this is a very low figure. A reason for this low recycle figure lies among others in the difficulties to colour polypropylene. To increase the use of recycled polypropylene in an attractive way, better ways to colour this material should be found. Besides the colouring and pigmentation issue of recycled polypropylene there is also a growing interest in coating consumer goods using new plastics. One major industry that asks for recycled and coloured polypropylene is for example the automotive.

Generally pigments are used as colourant in almost all plastics, however a solution to remove them is not there. Therefore the act of coating recycled plastic products seem to be a promising solution. Wet coating of polymers is possible but powder coating has many advantages. Main advantages of powder coatings are the efficiency and solvent free way of painting [4]. This is a reason to further develop this technique for plastics.

The first step to make this possible was the development of curing temperatures that are getting lower [5] and ways to make polymer substrates electrically conductive. This is needed for the powder to adhere during application. There are several challenges facing the application of a powder coating on a polymeric substrate. An electrostatic mechanism is used to apply a powder coating to a substrate. Since plastic is an electric insulating material this is a difficult process. Afterwards, a coating needs to be cured, which is done in an oven. Generally plastic substrate tends to warp when heated. Preventing this substrate from warping is difficult because relative high temperatures are needed to cure the (conventional) coating system.

Subsequently there is a challenge in the adhesion between the powder coating system and polymer substrate. At present first steps are made making a powder coating possible on polypropylene. Recent performed research [6] shows that using additives, a low-cure powder coating systems and applying a plasma surface treatment make a powder coating applicable.

The plasma treatment shows a significant improved adhesion of the powder coating. However, a clear understanding of the working principles between polypropylene substrate and powder coating systems is lacking.

This study is about the adhesion of powder coatings to surface treated polymeric substrates with focus on polypropylene. Plasma treatment will be used as pre-treatments technique. Plasma is widely used on polymers to increase adhesion with glues and paints. Good adhesion of a powder coating system to a polymeric substrate involves a lot of different parameters. Within this study there will be a closer look on adhesion which is defined by pull-off strength and cross-cut performance. The effect of different plasmas on a polypropylene surface will be studied. This will particularly involve their effect on morphological changes and surface chemistry. Also the wettability will be studied. Ultimately different powder coating systems will be applied, tested and evaluated. The goal of this research is to gain insight into the adhesion between polypropylene substrates and powder coating systems.

## 2. Literature

This chapter is a short introduction to the literature about powder coating systems, plasma treatment and adhesion mechanisms improved by plasmas. More information can be found in the document: *“Literature review on plasma treatment for improved adhesion of powder coating systems to polypropylene”*.

### 2.1 Powder coatings

Powder coating is a solvent free and clean way of painting. Powder particles are electrostatically applied on a surface and baked in an oven. The fact that it is solvent free makes it more environmental friendly than wet coatings. Advantages are also in the efficiency, energy consumption and processing time [4]. Development of low cure powder coating systems makes application on non-metal substrates possible. Plastics [6], composites [7], and wood (Medium-Density Fibreboard) [8, 9] can be powder coated and are subject of many studies because of a variety of challenges. A major challenge is the powder coating adhesion. Important to note here is that powder coatings are polar.

Almost all powder coating systems are thermosets of which a great deal are polyesters. Besides a polymer resin a powder coating systems consists of a cross-linker, pigments and additives [10]. The functionality of the polyester resin can either be hydroxyl (OH-functional) or carboxyl (COOH-functional). This is achieved through synthesis with either an excess diol or diacid. Often triols or polyols are used for branching the polymer resin. Also higher functional acids can be used. For curing different cross-linkers are being used. All have different characteristics including among others flexibility of coating, exterior durability, color stability and processing [11, 12]. Cross-linkers that are often used are TGIC and Primid [13].

A commonly used polyester powder coating systems uses Poly Bisphenol A diglycidylether (BADGE) as cross-linker. This powder coating is known as ‘Hybrid’. BADGE can make up 30 to 50% of the total binder system. Other types of polymer resins that are being used are polyamides [14, 15], epoxies [11] and acrylics.

The development of low temperature and ultra violet (UV) cure systems makes possible the application of powder coating systems on temperature sensitive substrates. Conventional curing temperatures of around 200 °C are lowered towards 120 °C [5]. The application of a UV-curable powder coating also needs less heat. This brings new opportunities such as application on wood (MDF) and plastics [16]

A powder coating is applied by the use of a spraygun. This spraygun charges the particles which will then adhere to the substrate electrostatically. Curing involves the flow and wettability of the substrate, moreover heating up the substrates. Powder adherence, wettability and elevated temperatures are all three critical for polypropylene as substrate. More about powder coatings regarding polypropylene is described in the next chapter.

## 2.2 Polypropylene

Polypropylene is a versatile plastic that is widely used in many applications. It is used in films, packaging and household appliances. It also finds a way in many applications in industries such as automotive, aerospace, marine and medical devices. Within these industries there is also a growing demand for coating of the products [17-20], including powder coating [7, 21]. Also the recycling of polypropylene [1] shows that there is room for increased use. This may be possible by making recycled products more attractive through coating. As mentioned before, in order to use more some challenges about polypropylene regarding powder coatings need to be overcome.

Polypropylene is generally electrical insulating. However, for the application of a powder coating, electrical conductivity is needed. A simple and cheap, conductive additive is carbon black. A weight percentage between 12 and 20 is needed for a surface resistivity which is low enough for powder adherence [6, 22].

Another concern when powder coating plastics is the temperature that is needed for curing. The melting temperature (peak) of polypropylene is about 170 °C [23]. The semi-crystalline morphology of polypropylene makes it relatively form stable close up to its melting temperature. However, the curing temperature should be well under 170°C. With the use of low-curing systems it is possible to apply powder coatings to polypropylene.

Finally, the wettability is an important factor regarding the application of powder coatings on polypropylene. The wettability is the ability of a fluid to wet a surface, or in other words: to get in contact with a surface. A proper wettability is needed for a good adhesion of glues, prints or coatings [24]. The wettability is related to the surface energy of a material. The surface energy consists of both a dispersive and a polar part. When the surface energy is low, the wettability is poor. Polymeric materials generally have low surface energies. Polypropylene is a nonpolar plastic with a low dispersive surface energy, hence exhibiting a very poor wettability. The wettability can be improved by using different treatment techniques. One of them is plasma treatment, which is described in more detail after the next paragraph. First there is a closer look on adhesion.

## 2.3 Adhesion

Adhesion can best be defined as: the adhering effect of two (unlike) material surfaces in close contact through inter- as well as intramolecular forces. It cannot be explained by one single theory or model [25]. Adhesion involves different phenomena of which often more than one is involved in bonding two materials. It is widely accepted that there are six major mechanisms:

## **Adsorption**

Also known as dispersive adhesion theory or physisorption, this theory is based on the belief that adhesion is obtained through intermolecular forces at the interface between adhesive and substrate [25]. These intermolecular forces are known as van der Waals forces and may also involve hydrogen bonding. For a good adsorption, wetting is essential [26]. Adsorption is widely viewed as the most important adhesion mechanism [25, 26], and should in fact always be present in an adhesion bond [27].

## **Chemical bonding**

This theory involves the formation of ionic and/or covalent bonds between glue or coating and substrate. Covalent bonds are proved in adhesive bonds in literature [25] and can greatly participate to the level of adhesion between two materials.

## **Other mechanism**

Furthermore there is *mechanical interlocking* which is about a glue or coating anchoring itself to a porous or open substrate such as wood or textile [27]. *Diffusion theory* describes that polymers can interdiffuse. This kind of bond can be obtained when polymer chains are mobile through heat or using solvents [27]. In fact, diffusion makes the initial interface being removed. *A weak boundary layer* is a theory that proposes that clean surfaces are needed for good adhesive bonds. *Electrostatic theory* [27] is proposed between metals thus not of interest here.

## **2.4 Plasma treatment**

There are many different surface treatment techniques which can be used on polymers [28]. These techniques can involve the use of ion beam, ultraviolet, laser or ozone [29, 30]. Commonly used techniques for improving the wettability by increasing the surface energy are: flame treatment [31, 32], corona treatment [33-35] and plasma treatment [29, 36]. Corona is commonly used by industry to improve wettability of polymers in continuous operations such as film or sheet production [33]. Flame treatment is used for over 40 years [37] in the automotive industry to improve the wettability of robust car parts prior to painting [32]. Plasma surface treatment is a versatile technique for the pre-treatment of all kinds of material surfaces including paper, glass, metals and polymers. It is extensively used in the aircraft and automotive industry [29].

The versatility comes from the different gases that can be used with plasma, discharge type and parameters, pressure and treatment time all having a different effect on the chemical, physical and mechanical properties of a surface. Corona, flame and plasma treatment all have their own characteristics, advantages and disadvantages. These are in the shelf-life, applicability at 3D shaped models, temperature, process control and costs.

Taking into account all of these factors, then plasma treatment is the best technique for further investigation on polypropylene. Plasma treatment has the best process control, relative low temperatures and can be used on complex shaped products.

Plasma treatment is a clean and solvent free process that only modifies the surface without affecting the bulk property of the material [7, 24, 38]. By using an atmospheric pressure plasma (APP) Jet, pre-treatment is relatively easy and fast. However, by using plasma in vacuum conditions (low pressure plasma (LPP)), process time goes up. This makes LPP less attractive for industrial application. An advantage of LPP is that it offers some more controlled conditions. Therefore LPP is probably a more appropriate technique for researching plasma altered surface properties.

### **Surface energy versus wettability**

As described earlier, the wettability of a polymeric surface depends on its surface energy. The surface energy, composed of a dispersive and a polar part, both increase as a result of plasma treatment. Dispersive surface energy increases through cross-linking [17, 24, 39, 40] of the polymeric molecules at the surface. This is only several molecular layers [41], so it does not affect the bulk properties of the material. Reactive species in the plasma break covalent bonds at the surface at which point free radicals are formed [41]. Interaction of two or more formed radicals at the surface will then establish a covalent bond [24]. This cross-linking makes the material surface consist of more strong bonds instead of weak intermolecular bonds and therefore increases its surface energy. Free radicals at surface can also react with oxygen and moisture in the air to produce polar functional groups on the surface [41]. In case of LPP this happens shortly after releasing the vacuum. Also the introduction of polar groups is referred to as a part of increased surface energy [24]. This is called polar surface energy.

### **Surface functionalisation**

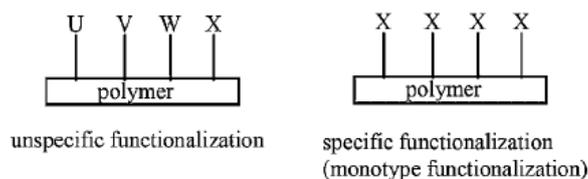
Oxygen containing functional groups introduced through plasma can be: C-O, C-OH, C=O, O-C-O, O-C=O, COOH and O-CO-O [39, 41]. It is reported that some groups only appear through high plasma energy (power) levels [39]. Functional groups generally also increase with longer treatment time and higher power [39, 41-43]. However, a long treatment time can also lead to degradation which is suggested to be possible after only seconds of treatment [44]. G. Borcia et al. [44] showed that wettability of various polymeric surfaces increase with higher discharge power and longer treatment time.

Introduced functional groups may contribute in adhesion through chemical bonding with a powder coating. Based on earlier describes coating systems, -COOH and -OH functional groups which may be present after plasma treatment are interesting. These may form covalent bonds with the polyester coating resin or cross-linkers as described earlier.

Adhesion can also come from hydrogen bonding. Hydrogen bonds are sometimes referred to as chemical bonds but are also mentioned in adsorption theory.

In a way it is a physical bond. However, there is also something changing on molecular scale from chemical point of view. In this study hydrogen bonds will not be discussed as chemical bonds but as part of adsorption theory.

The introduced groups with plasma treatment remain predominantly unspecific [45, 46]. Unspecific refers to the fact that the plasma treatment involves the introduction of a variety of oxygen and/or nitrogen containing functional groups. Not just one sort of group as can be seen in Figure 1 (taken from [46]).



*Figure 1. Unspecific versus specific functionalization*

There are also ways to create a more specific (monosort) functionalized surface with plasma. This is interesting for further chemical surface engineering for different purpose such as corrosion-inhibition, chemical, scratch and abrasion resistance, lubrication, permeability, biocompatibility, antistatic or optical properties [47]. Regarding adhesion [48] of e.g. coating systems, some monosort functional groups may be interesting. This process is called plasma polymerisation. Plasma polymerisation refers to the use of monomers instead of gases [45-47, 49]. By using pulsed plasma polymerisation with monomers such as acrylic acid [46, 48], allyl alcohol [46] or allylamine [46] subsequently carboxyl, hydroxyl and amine groups can be introduced. A disadvantage of this technique is that like LPP this process can only be done in vacuum. This even more complex technique is also not commonly used in industrial application.

### **Morphology effects**

Besides surface energy and functional groups there is one more aspect of plasma treatment which may help improve coating adhesion. This is the etching effect of plasma. Etching is a consequence of plasma treatment and will always take place. It will introduce new, roughened surface. The exact morphology depends on the gas being used [41]. A rougher surface does probably improve adhesion through dispersive adhesion because of a larger surface. Likewise, increased surface roughness may also contribute to an improved adhesion through an anchoring effect (mechanical adhesion). It is stated that an increased surface roughness is a very important phenomenon that can be exploited for adhesive properties through an increased number of chemical links between a coating and substrate [24].

Another improved adhesive effect with relevance to plasma etching is explained through cleaning the surface. Plasma is often used, with a specific gas, to clean a surface by removing dirt [50]. With etching, old surface can entirely be removed to improve any form of adhesion.

This is explained through removing a so called weak boundary layer. A weak boundary layer can be seen as a layer containing different kinds of contaminants near the surface however not the surface itself. The theory states that often an adhesive bond fails because of this weak boundary layer and not necessarily the adhesive bond itself [51]. Weak boundary failures often involve a cohesive failure within either coating or substrate. This can be the effect of a previous environment, proceeding, air contaminant, or even surface treatment itself. A weak boundary layer from a surface treatment may be the result of a long treatment time causing surface degradation.

### **Shelf life of plasma treatment**

The shelf life of a plasma treatment depends on many aspects and varies from hours to years [36]. It is clear that it depends on the sort of plastic on which the treatment has taken place. The storage stability of polypropylene after plasma and corona treatment has also been examined by M. Wouters [22]. This research pointed out that storage of samples in water improves the shelf life of treated polypropylene. An explanation for this increased shelf life is given through the mechanism that water molecules are adsorbed by the hydrophilic polar groups on the surface, preventing them to rotate/reorient towards the bulk, or to diffuse into the bulk of the material [43]. Both rotation and diffusion is suggested as the most important mechanism for polar groups to disappear. Rotation of polar groups (within mainly the amorphous regions of the material) occurs more easily when the chain segments have more mobility. Therefore heating a sample has a negative effect on wettability [22, 43]. On the other hand, as the semi-crystalline regions of polypropylene doesn't have much mobility because of the orderly packed structure, increased crystallinity is favorable for the shelf life. Yo Il Yun et al. concluded in their research [43] that less crystalline PP had a higher susceptibility to be attack by plasma and had a higher oxygen concentration on the surface because of the more amorphous fraction on its surface. But during aging, the more crystalline PP had lower water contact angle and a higher oxygen concentration than the less crystalline PP. Since it's known that crystallinity effects of polypropylene can be altered through process settings [52] as well as post-processing proceedings [53, 54] (e.g. annealing) this may be interesting to explore further in future research.

## **2.5 Analysing techniques**

The study of the influence of plasma treatment on polymeric substrates involves many different analysing techniques. Frequently used techniques that are mentioned in literature are described in this paragraph.

Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Atomic-force microscopy (AFM) and Sessile drop technique (SDT) are analysing techniques that are extensively

used for the characterisation of polymeric substrates after plasma treatment. FTIR is used frequently for the surface characterization of surface treated polymers [19, 42, 55]. IR light is absorbed depending on the chemical properties of the sample. Every type of bond absorbs IR light at a different wave length.

The intensity of each absorption quantifies the amount of each chemical component on the surface. XPS is extensively used for the characterization of the elemental composition of polymer surfaces [39, 44, 56]. It's a non-destructive technique and able to detect all elements with a concentration > 0.5 atomic % except H and He. Atomic-force microscopy can be used to perform force measurements but also for imaging the dimensional shape (topography) of a surface. The basic working principle of AFM is that a spring-like cantilever with a small radius tip on the end of it is dragged along the surface. An optical detector measures the deflection of the cantilever on each coordinate. Sessile drop technique (SDT) is a method used for the characterization of surface energies. The surface energy can be calculated with the contact angles of liquids of which surface tension is known. Besides calculating the surface energy also the contact angle itself is used as a direct measurement of the wettability of a surface.

Each technique has its own lateral resolution and information depth. Both are key factors when collecting data from surfaces and interpreting them. Table 1 gives both surface analysis area and depth of information from some common analytical techniques [57].

<i>Technique</i>	<i>Information</i>	<i>Smallest analysis surface [nm] (XY size or diameter)</i>	<i>Depth of information [nm]</i>
XPS	Elemental	30,000	1 – 12
EDX (SEM)	Elemental	800	500 – 3,000
SEM	Topographical	10	1 – 6
AFM	Topographical	1,000	0.1 – 0.2
ToF-SIMS	Elemental	200	0.2 – 0.4
FTIR	Elemental	5,000	500 – 15,000

*Table 1. Surface analysis areas & depths of information of common analytical techniques*

### **Main conclusion from literature**

Surface treatment techniques have been proven to be very effective when dealing with adhesion issues within all kinds of industries. Surface treatment techniques which have been proven to work very well for different situations are flame, corona and plasma treatment. Plasma treatment can either be in vacuum as well as in atmosphere. This latter is favourable for use on industrial scale regarding

costs. The surface modification of polymeric materials involves a lot of different phenomena: Dispersive and polar surface energy and their effect on wettability, functional groups and the etching effect of plasma involving increased surface and roughness, different adhesion theories. This makes it all together a complex matter. Main conclusion is that plasma surface treatment is very well applicable in improving adhesion issues. However, an optimisation of many parameters is required and needs to be tested for each particular case.

### **A new study**

There is few literature that deals specific with functional groups that can be introduced through gas plasma treatment and which are favourable for a specific adhesive or coating system, or how adhesion is obtained. Therefore a new study about the effects of plasma surface treatment on morphology and surface chemistry to improve adhesion of powder coating systems to polypropylene is needed. This new study will try to find out which effects of the plasma surface treatment are accountable for improved adhesion, whether or not chemically. Comparing surface chemistry and morphology of treated substrates with coating systems and their performance will gain new insights. This will help the development of future powder coatings for application on polymers. Research questions, hypotheses and an experimental approach are presented in the beginning of the next chapter.

### 3. Methodology

The goal of this study is to gain more insight into the adhesion of powder coatings on polypropylene substrates when treated by plasmas. The following main research question is formulated:

'How do plasma surface treatments enhance the adhesion between a polypropylene substrate and binders of different powder coating systems?'

Hence, the following sub-questions are formulated:

1. How does plasma treatment (plasma type, used gas and treatment time) of polypropylene relate to surface energy and wettability?
2. What is the effect of the amount of surface energy on coating adhesion and quality?
3. Which functional groups are formed with different plasma treatments?
4. Do morphological changes e.g. increased roughness improve coating adhesion?
5. What kinds of bonds are formed between coating and substrate?
6. What is the shelf life of different plasma treatments and can these be extended with under water storage of substrates without affecting the coating adhesion?

The following hypotheses are formulated to be tested:

1. A higher surface energy and better wettability yields a better powder coating adhesion and quality
2. Surface energy increases with treatment time
3. Long plasma treatment times deteriorates the surface, affecting the powder coating adhesion in a negative way
4. Surface energy and wettability of substrate decrease with storage time, hence the adhesion of freshly applied powder coating as function of storage time of the substrate too
5. Surface energy and wettability remain through under water storage and does not affect powder coating adhesion
6. Increased surface roughness improves powder coating adhesion

Within this study three different plasmas and three different coating systems were used to study the effect of plasma with respect to adhesion. Samples were studied direct after plasma treatment and powder coating. Samples that were plasma treated and powder coated were also studied over time to investigate the time effect on wettability. This was done for samples that were stored under normal conditions as well as samples that were stored under water. Also the effect of different plasma treatment times was investigated. The flowchart in Figure 2 shows the overall course of the entire study.

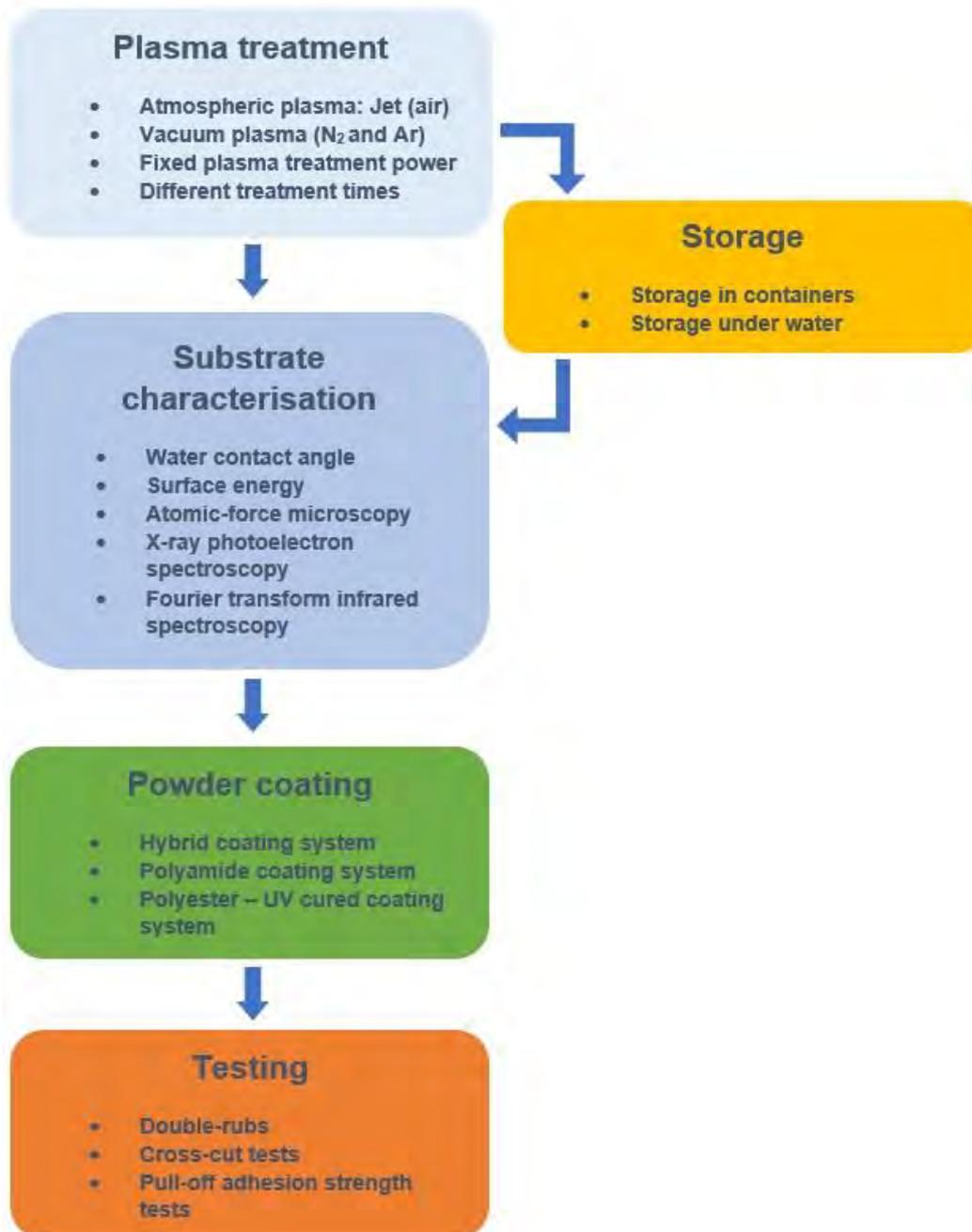


Figure 2. Overall setup of experimental research

### **3.1 Sample preparation**

This paragraph describes the preparation of the samples. This includes the polypropylene panel production, storage and plasma treatments.

#### **3.2.1 Material and specimen**

Polypropylene grade PP-HI-EC from the company Witcom Engineering Plastics B.V. was used. The material is filled with 20 wt% carbon black to obtain a low surface resistivity. The particle size of the carbon black is below 45 nm according to the supplier.

Panels for powder coating of 180x115x4 mm were produced by injection moulding. Process settings can be found in Appendix A table 1. Smaller panels of 115x80 mm and 90x80 mm were cut out of these bigger panels for a more compact storage system under water. These smaller samples were also required for some analyzing machines on which the original sized panels did not fit. Even smaller samples of 10x10 mm were made for both Atomic-force microscopy and X-ray photoelectron spectroscopy. Surface resistivity was tested according to ASTM-D257-07. A picture of a panel is shown in Appendix A Figure 35. The produced panels had no moulding defects like remarkable flow lines, weld lines, voids, flash or jetting.

#### **3.2.2 Preservation system**

Within this study samples were preserved in two ways. Samples were stored in air and under water. For both types of preservation a storage system was created. Within both systems samples are only in contact with either air or water. This was achieved by placing the panels in a round chamber. This way surfaces are prevented from contact with other materials to exclude possible contamination of the samples after plasma treatment. A picture of this storage system can be found in Appendix A Figure 36. In the same way containers for storage under water were fabricated. A picture of this system is included in Appendix A Figure 37. Normal tap water was used.

### **3.2 Plasma treatments**

Two types of plasma were used. Low pressure – and atmospheric pressure plasma (LPP and APP). The used parameters and setup is described in this paragraph. All samples were only treated at the front side. The rear side of the panels can easily be recognized by the ejector pin marks. Before plasma treatment the sample surfaces were cleaned using a cloth and isopropanol.

### Low pressure plasma

Low pressure plasma treatment (LPP) was done in a PORTA 400 plasma unit equipped with an Advanced Energy Cesar 1325 400 V at 500 watt. This radio frequency generator was operated at 13.56 MHz. A maximum of eight full-sized rectangular panels were placed in the chamber at once. The samples were attached to a polymer plate using double-sided tape so the front side faced the electrode at the bottom of the chamber. The distance between electrode and panel was 36 cm. A schematic representation of this setup is given below in Figure 3. The treatment times that were chosen in this study varied from 5 to 120 seconds. The applied gases in the low pressure plasma apparatus were N<sub>2</sub> and Ar. N<sub>2</sub> gas flow into the chamber was set to 200 cc/min. Argon gas flow was 144 cc/min to compensate for gas density.

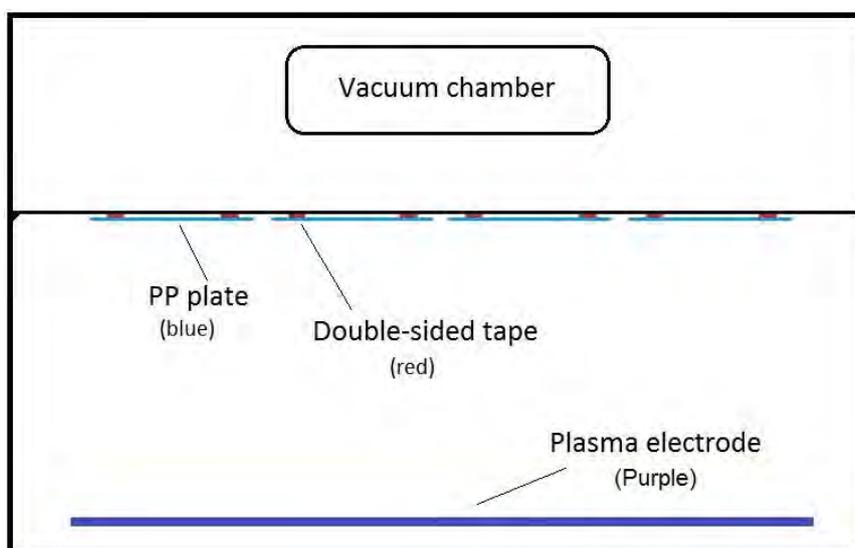


Figure 3. Schematic setup of the low pressure plasma with PP samples

### Atmospheric pressure plasma

Atmospheric pressure plasma (APP) treatment was done using a PlasmaJet®DC from the company Raantec using a pendulum nozzle. This system uses an AFS G12 P plasma generator. The power was set at 500 Watt. The Pendulum swept a distance of about 20 mm. Compressed air was used as plasma gas. The PlasmaJet unit was bolted on a rigid aluminium frame with the nozzle directed downwards. The nozzle distance to the substrate was kept at 12 mm. Panels were pushed past the sweeping nozzle manually counting 4 seconds to cover the length. Six tracks were needed to cover the whole panel. A picture of this setup is shown in Figure 4.

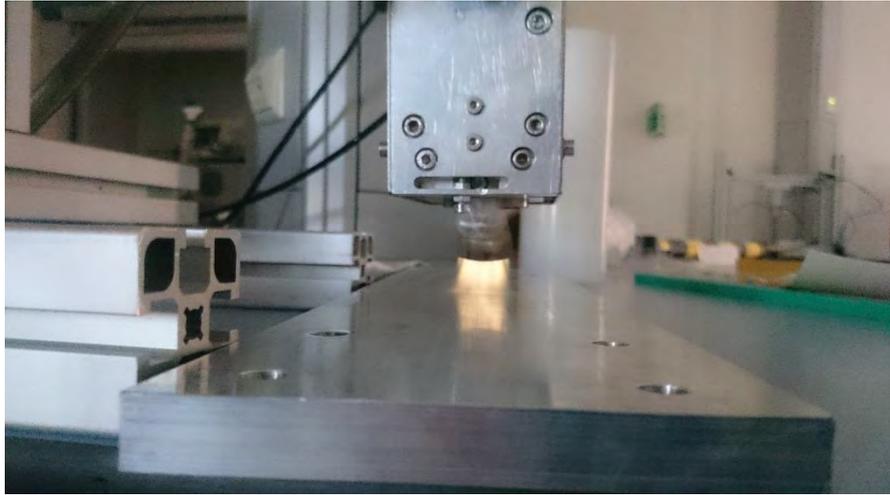


Figure 4. Atmospheric pressure plasma setup. The PlasmaJet unit

Four different sets of panels were treated with plasma within this study:

Series	Purpose
1	Different plasma treatments to investigate contact angles and surface energies over a period of time. This is also done for panels stored under water.
2	Different plasma treatment to test three powder coating systems and their adhesion direct after plasma treatment.
3	A series to test adhesion as a function of storage time after plasma treatment
4	Varying treatment times to study contact angles and surface energies as function of treatment time. Powder coating adhesion was also studied as function of treatment time, storage time and storage time under water.

Table 2. Plasma treatment series

### 3.3 Applied powder coating systems

Three different model powder coating systems were made for this study by DSM. The average molecular weight of each system is around 2000 – 4000 g/mol. The white pigment used in each system is Kronos® 2360, which is about 33 % of the total formulation. All three systems also contain 0.5 – 1.5 % Resiflow® PV 5 as flowing agent and 1 – 3 % Benzoïn as air-release agent. The formulation of each binder system is given hereafter.

#### Hybrid

A hybrid binder system is made out of a polyester and an epoxy resin. The used hybrid resin is Uralac® P 3150 from DSM. The polyester is based on terephthalic acid and neopentyl glycol

monomers and is terminally functionalized using trimellitic anhydrides to create four carboxyl end groups.

Poly Biphenol A diglycidylether was used as epoxy resin. About 0.1 – 0.5% catalyst based on a tertiary amine was used to catalyse the curing process.

### **Polyamide**

The polyamide binder system was prepared out of a selection of aliphatic dicarboxylic acids and diamines. The exact composition is not available. Monomers which are generally used in DSM polyamide resins are: phthalic acid, isophthalic acid, terephthalic acid, adipic acid, sebacic acid, isophorondiamine, 1,2-ethylenediamine, 1,3-propylenediamine, 1,6-hexamethylenediamine etc. [14]. The polyamide resin was made carboxyl functional and cross-linked using Huntsman Araldite® PT910. Accelerator DT 3126-2 (Huntsman) was added as accelerant.

### **Polyester – ultraviolet cured**

The used polyester resin was Uracross® UV cure P 3125 from DSM. This resin is based on terephthalic acid and neopentyl glycol with hydroxyl functional end groups. Double bonds are introduced by using maleic anhydride and fumaric acid. The weight per unsaturation is 1000 g/mol. Around 80 % of the total binder system consists of this unsaturated polyester. The other 20 % is a hydroxybutyl vinyl ether based cross-linker. Around 1 % of Irgacure® 2559 and around 2 % of Irgacure® 819 photo initiator on total formulation is used to initiate the UV cure.

### **Powder coating application**

The powder coating systems were all applied using a Wagner sprint X spray gun. Powder adherence was achieved using corona at 60 kV. An average of 4 grams of powder was applied on the earlier described rectangular panels as measured by weighing before and after. The powder coating was only applied at the plasma treated front side. To apply, the polypropylene panels were laid down flat on a workbench as can be seen in Figure 5.



Figure 5. Manual application of a powder coating

Curing of the hybrid and polyamide coating system was done in a Thermo Scientific Heraeus laboratory oven at 130 °C for 30 minutes.

Curing of the polyester UV powder coating was done in two stages in a laboratory machine of Triab. Specific type of machine is unknown. In the first stage the powder has time to melt and flow before getting cured. Heating in this machine was done by infrared heaters for 2 minutes at 120 °C. Thereafter the samples were transported on a conveyor where they received a total UV dosing of 6000 mJ/cm<sup>2</sup>. At this second stage no heating was applied. A schematic representation of the UV curing is given in Figure 6. Double rub tests were performed on all coating systems to verify that they cured completely.

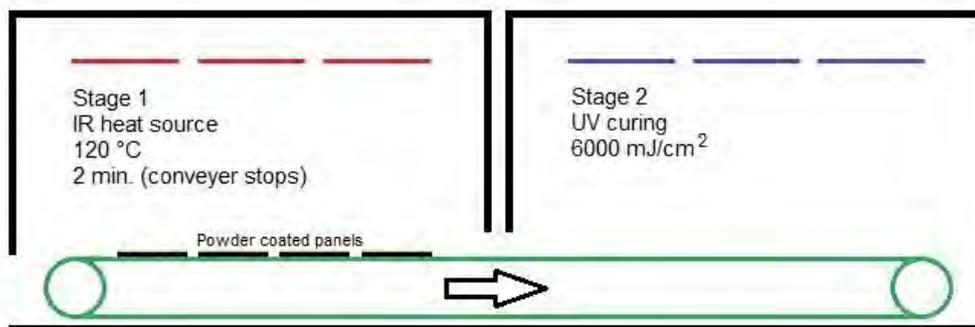


Figure 6. Schematic representation of the Triab UV curing machine

### 3.4 Characterisation

This paragraph describes all characterisation techniques that were used to study physical, chemical and morphological changes to the surface as a result of plasma treatment. Also methods for the characterisation of the coating adhesion are described.

### **Sessile drop technique**

The sessile drop technique (SDT) is a method to determine water contact angles and surface energy. Measurements were performed over a period of time to study the development of contact angles and surface energies with time. Measurements were performed on a Krüss DSA100 drop shape analyser. Demineralized water drops of 4  $\mu\text{L}$  were used to determine water contact angles. Additional 2  $\mu\text{L}$  drops of diiodomethane were placed to calculate surface energy. A picture of a water droplet and diiodomethane can be found in Appendix A Figure 38. Each measurement was taken with 10 drops of water and between 3 and 5 drops of diiodomethane. Contact angles were calculated using the Young-Laplace fitting. This method offers the most exact contact angle. The total surface energy composed of a dispersive and a polar part was calculated by computer using the Owens, Wendt, Rabel and Kaelble (OWRK) method [58].

### **Atomic-force microscopy**

Atomic-force microscopy (AFM) images were obtained under ambient conditions in tapping mode with a Nanoscope V multimode atomic force microscope (Bruker Nano Surfaces, Santa Barbara, USA) using silicon cantilevers with resonance frequencies of 300-400 kHz (model: TESP, Bruker Nano surfaces). Imaging was carried out on either 1x1, 5x5 and 10x10  $\mu\text{m}$  area's to reveal surface morphology at different scales. The scan rate was set between 0.5 to 1.5 Hz with the number of pixels set at 512. The scan angle was set to 0°.

### **X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy (XPS) was used to characterise the chemical surface composition. Measurements were taken by a Quantera SXM (scanning XPS microprobe) from Physical Electronics. The X-ray anode used for radiation was an Al  $K\alpha$ , monochromatic at 1486.6 eV. The power of the x-ray beam was manually set at 50 Watt. The base pressure of the analyser chamber was  $< 4.5 \times 10^{-8}$  Pa and the working pressure around  $4.25 \times 10^{-6}$  Pa. The greatest part of the remaining pressure was argon for neutralisation. 4 square 10x10 mm samples (Reference, Jet plasma, Ar plasma and  $\text{N}_2$  plasma) were attached to a plate using double sided tape.

Survey scans were made to see the gross overall atomic content of the surface layer. Element spectra scans were made with a better energy resolution and lower noise than the survey spectra. Therefore five areas of 600 x 300  $\mu\text{m}$  per sample were chosen for acquisitions. The investigated element spectra besides the C1s spectra were the N1s and O1s. Fitting of spectra is mostly done after shifting of the measured spectra with respect to known reference binding energies. The software used was Compass for XPS control, Multipak v.9.6.1.7.

### **Fourier transform infrared spectroscopy**

A Bruker LUMOS FTIR microscope with a motorized micro ATR crystal was used. IR spectra were obtained using low ATR pressure in order not to damage the surface. Spectra were obtained from untreated as well as plasma treated panels.

### **Double rub test**

Double rub tests were performed with acetone according to ASTM D5402 – 15 to be sure that applied coating systems were fully cured. Within this test, an acetone soaked cloth is repeatedly moved back and forth over the sample. The score is quantitatively measured by the total rubs before the cloth rubs through the coating. After 100 repetitions, and no breakthrough, the coating is assessed on a scale of 1 to 5. 5 for good and 1 for bad (but not through). Ethanol was used for a double rub test on the polyamide coating system since this is a more suitable solvent for polyamides.

### **Pull-off tests**

Pull-off tests were performed according to ISO 4624 using a DeFelsko Positest AT-M Pull-Off Adhesion tester. The tester has a resolution of  $\pm 0.01$  MPa. 20 mm diameter aluminium dollies were glued to the coating surface using 3M Scotch-Weld DP 460 Epoxy Structural Adhesive. The adhesive was left to dry for 24 hours. Before testing the surrounding coating area was drilled away by a hole saw. Thereafter the dollies were pulled off. The coating adhesion performance is measured in MPa. Stress was applied with  $< 0.25$  MPa/s. In Appendix A Figure 39 a picture is included of the adhesion tester in action.

### **Cross-cut test**

Cross-cut tests were performed to obtain quick and indicative information about a coating performance. This method is used for determining the parallel groove adhesion of one or many coating layers on a substrate. A Byk Cross-Cut Tester Kit 2mm (Cat. No. PE-5126) was used. The tests were performed and rated according to ISO 2409:2013. A table with the classification of Cross-Cut adhesion test results is included in Appendix A Figure 40.

## 4. Results

In this chapter the results of different plasmas, treatment times and powder coatings are shown. Also effects in the course of time and of storage methods were studied. Characterization of the plasma treated panels which includes the effect on wettability, morphological and chemical changes are presented in succession in paragraphs 4.1, 4.2 and 4.3. Paragraph 4.4 and 4.5 is about test results of applied powder coating systems.

### 4.1 Effect of plasma treatment on wettability

The effects of low pressure plasma treatment (Ar and N<sub>2</sub>) as well as atmospheric pressure plasma treatment (Jet) on water contact angle and surface energy was studied. The result of decreased water contact angle for each plasma and thereafter increasing water contact angle with time, called hydrophobic recovery, is given in Figure 7.

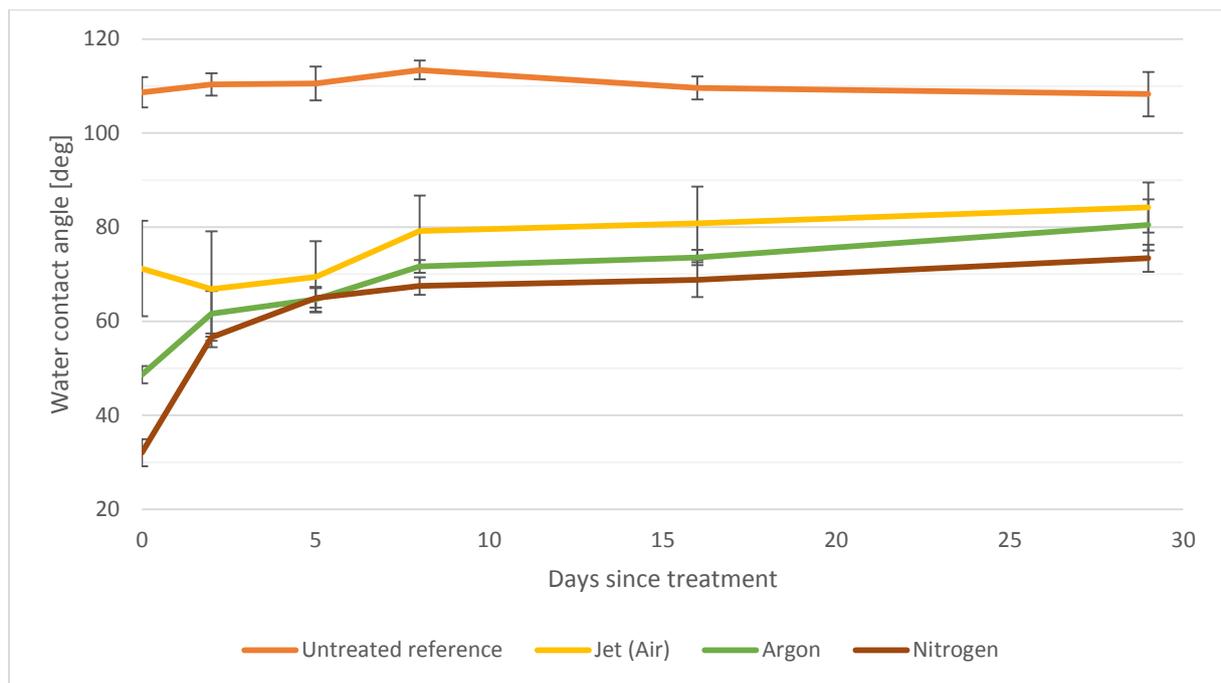


Figure 7. Effect of plasma treatment by different gases and influence of storage time as measured by water contact angle

The untreated reference shows an average contact angle of 110°. The effect of different plasma treatments on wettability is clearly visible at t=0 (measured directly after plasma treatment). All contact angles are at least 30° lower compared to the reference. N<sub>2</sub> plasma gives the smallest contact angle (30°) followed by Ar plasma (50°). Jet plasma treatment results in a contact angle of around 70°, however with some larger deviation. Jet plasma treatment shows a decrease of water contact angle 2 days after treatment which is probably due to the deviations across the surface.

The use of each plasma treatment shows that the wettability increases significantly. Another observation is that the most hydrophobic recovery for N<sub>2</sub> and Ar LPP occurs within the first 2 days after treatment. After 8 days the contact angles remain more stable for each plasma treatment, however all remain significantly lower with respect to the reference. The effect of hydrophobic recovery is also studied by looking at the surface energies after plasma treatment.

Surface energy is generally expressed by only two terms: a dispersive component and a polar component [25]. Both can be calculated from the average water contact angle and contact angle of diiodomethane droplets. The result for each plasma treatment and time effect is given in Figure 8. There is a consistent inverse similarity between the amount of the total surface energy and the development of the water contact angle.

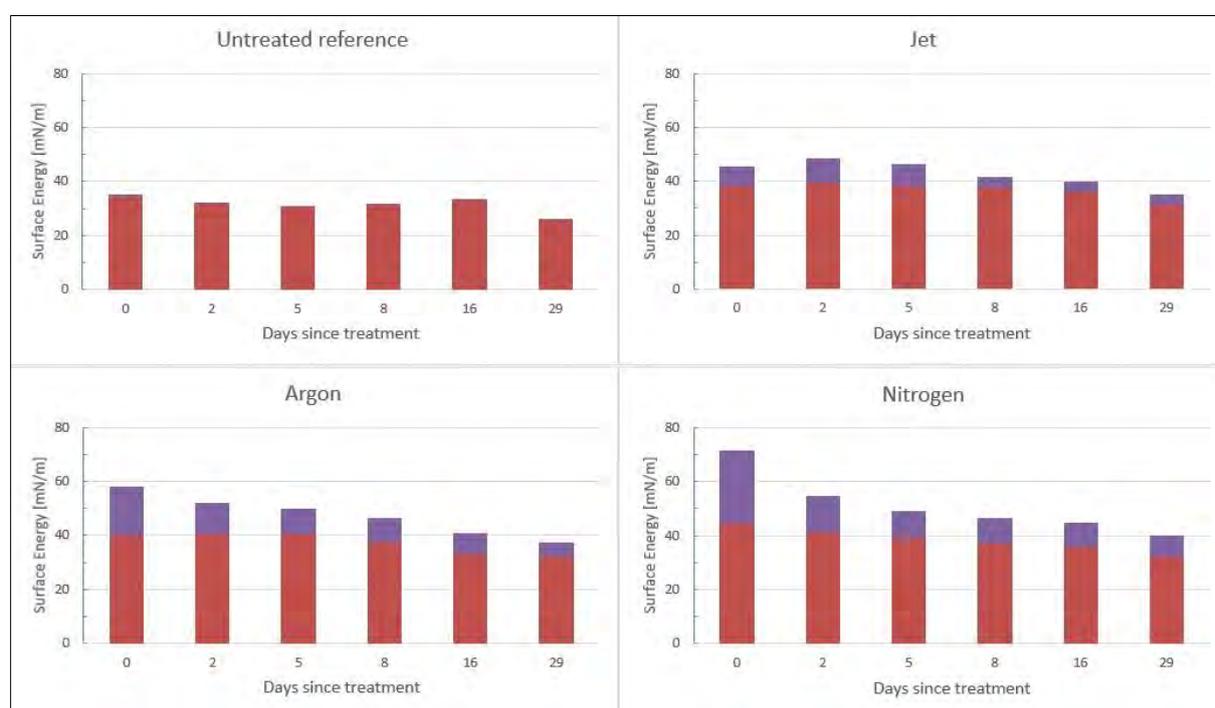


Figure 8. Effect of plasma treatment by different gases and influence of storage time on surface energy. Surface energy is composed of dispersive (red) and a polar (purple) part. The deviations of all surface energy measurements are within 2 mN/m based on the untreated reference.

The untreated reference in Figure 8 shows an average surface energy of around 30 mN/m which is only dispersive surface energy. After plasma treatment the total surface energy increases. For each plasma treatment the dispersive surface energy increases. But most of all a significant amount of polar surface energy emerges. The increased dispersive surface energy is attributed to cross-linking of the surface [17, 24, 39]. As can be seen in Figure 8, the dispersive surface energy decreases with storage time as also the polar surface energy. This suggests that there is a de-crosslinking with time. The decrease of polar surface energy shows that introduced polar groups disappear with time. The best performing plasma (nitrogen), in terms of wettability, was subsequently used to study the effect of varying treatment times.

## Effect of varying plasma treatment time on wettability

Varying treatment times were used to study the effect on wettability. Panels were treated using low pressure plasma (nitrogen) for 5, 15, 30, 60, 90 and 120 seconds. Figure 9 shows the development of both contact angle and polar surface energy.

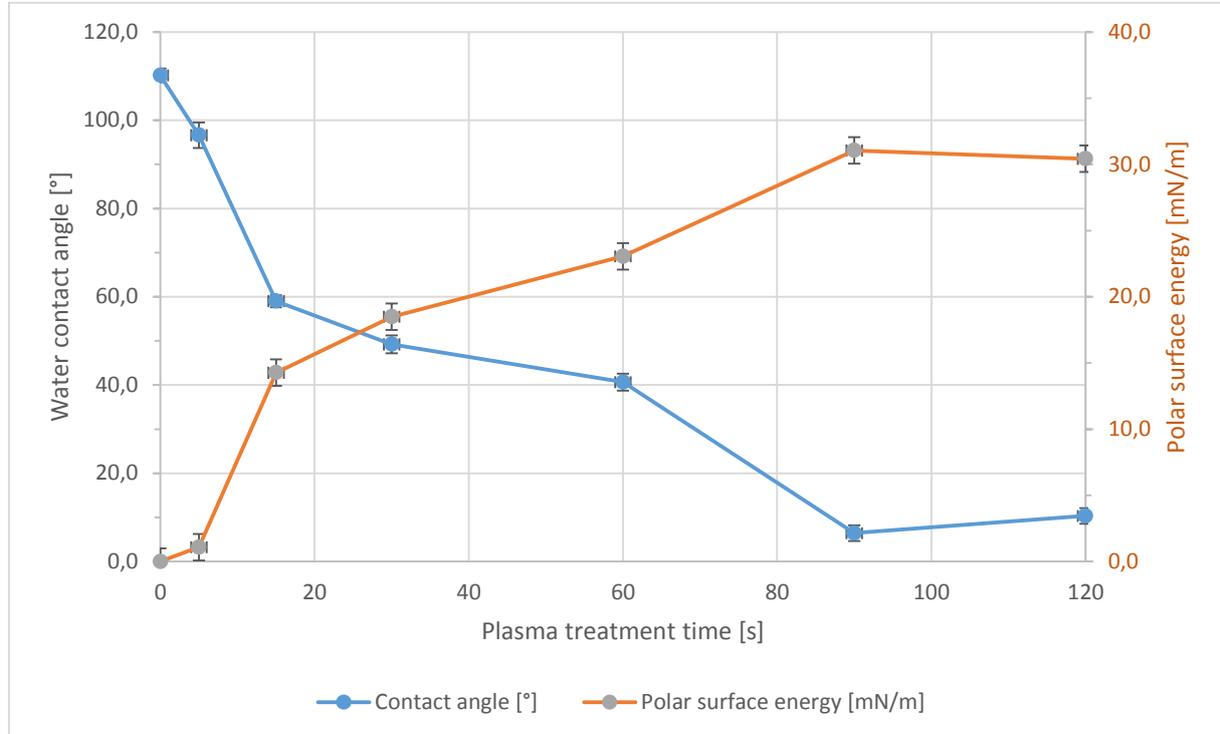


Figure 9. Water contact angle and surface energy (polar part) as function of nitrogen plasma treatment time - measured directly after plasma treatment ( $t=0$ )

The contact angle at  $t=0$  in Figure 9, which in this figure is basically the untreated reference, is  $110^\circ$  and shows no polarity. While plasma treatment time increases, the contact angle decreases and the polar surface energy increases. An optimum wettability is reached after 90 seconds. As can be seen, a major effect is reached within the first 30 seconds of treatment time. This shows that there is a nonlinear relationship between treatment time and surface energy.

Measurements of contact angle and surface energy were repeated 36 days after plasma treatment. As can be seen in Figure 10, after 36 days, remarkably, there are no clear differences between the treatment times above 15 seconds anymore. Both contact angle and polar surface energy show the same values upwards of 15 seconds. The polar surface energy shows a small part of around 7 mN/m and the water contact angle around  $76^\circ$ . Thus, independently from treatment time both wettability and (polar) surface energy reach a stable state that no longer seems to change with time.

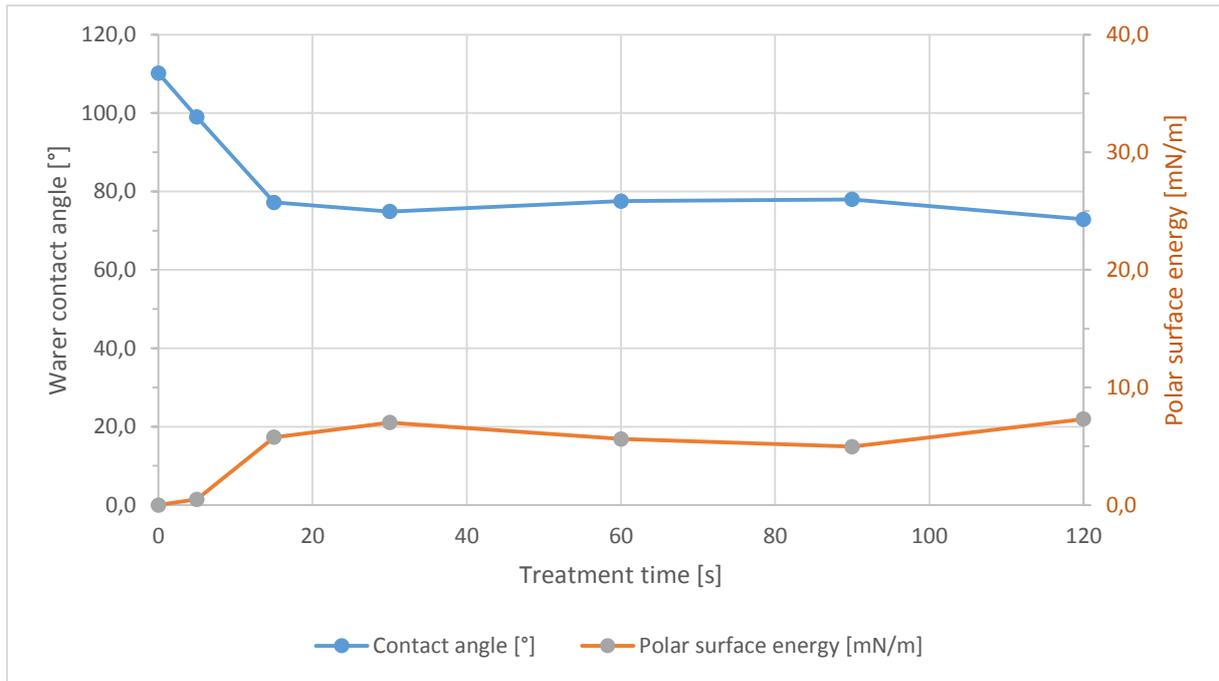


Figure 10. Water contact angle and polar part of surface energy as function of nitrogen plasma treatment time - measured after 36 days of normal, dry storage

### Under water storage of plasma treated panels

The effect of water contact angle and surface energy was also studied for samples that were preserved under water. The results of different plasmas are presented in Figure 11 and Figure 12. The outlier of the contact angle for Jet is believed to be a measurement error or an error in the sample preparation. Figure 11 shows that the water contact angle of the untreated reference decreases with time. This is probably due to the uptake of some water. After five days this uptake of water can also be noticed from the upcoming polar part of surface energy (Figure 12).

When looking at the contact angle of Jet, Ar and N<sub>2</sub> in Figure 11 it looks if they remain the same after 5 days. As can be seen the water contact angle of the untreated reference dropped about 30° after 29 days. Taking into account that this effect from the uptake of water is also present in the measured plasma treated panels, it is not certain that storage in water helps to improve the shelf life of plasma treated surfaces. However, when looking at the polar surface energies a different conclusion can be drawn.

The untreated reference in Figure 12 shows that it obtained a polar surface energy of only 8 mN/m after 29 days under water. The nitrogen plasma treatment remained 28 mN/m after being stored 29 days under water. This compared to 8 mN/m after normal storage (Figure 8). From this it is clearly evidenced that storing under water helps to remain polar groups on the nitrogen plasma treated panels and that this effect is not just from the uptake of water. The same can be concluded for the argon treated panels. Under water storage does not seem to hinder the decrease of dispersive surface energy. This can be observed from all the different tests.

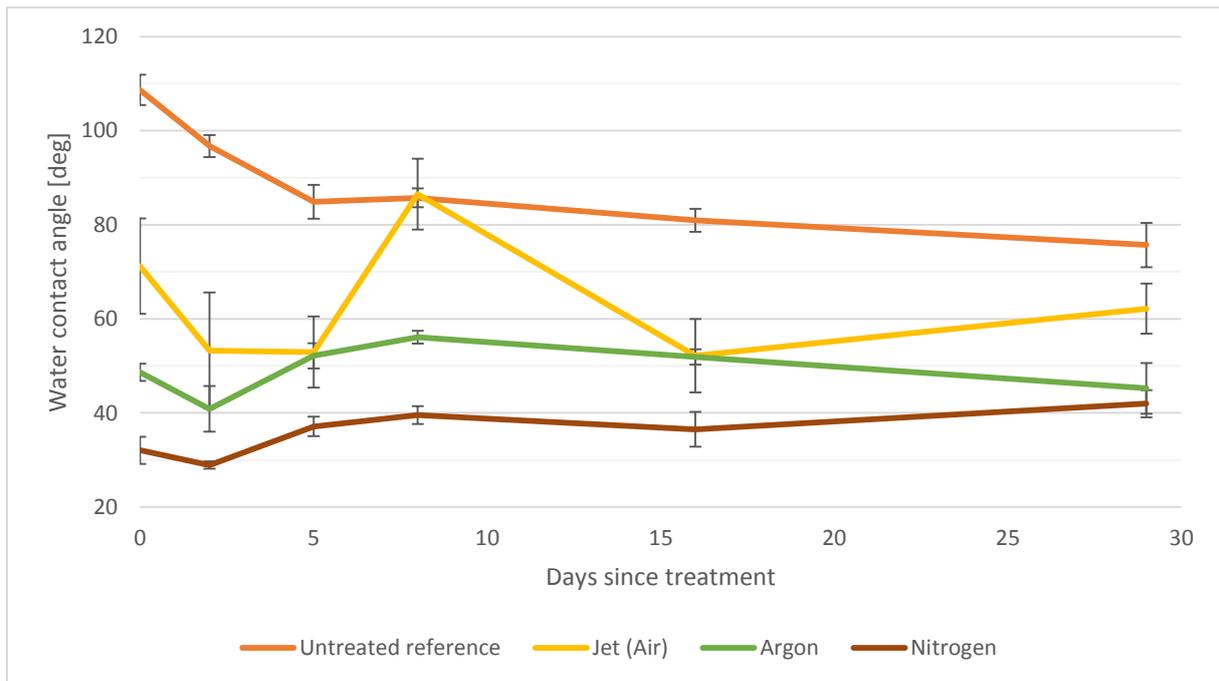


Figure 11. Effect of plasma treatment by different gases and influence of storage time as measured by water contact angle – stored under water

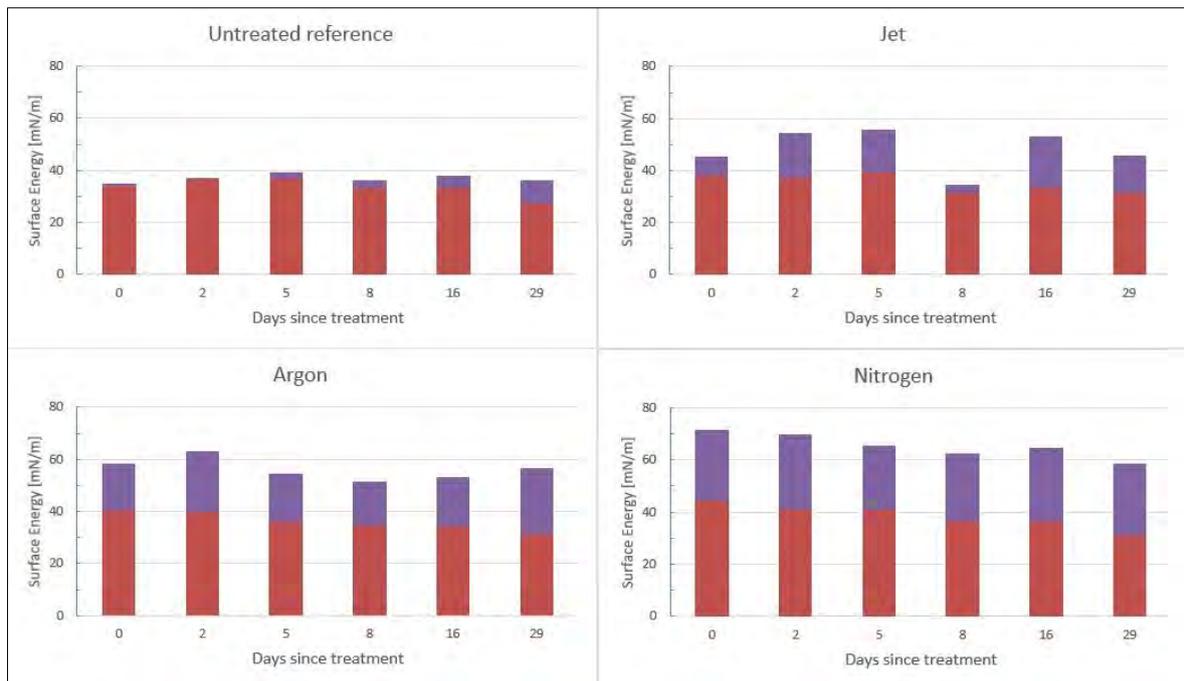


Figure 12. Effect of plasma treatment by different gases and influence of storage time on surface energy. Surface energy is composed of dispersive (red) and polar (purple) part – stored under water. The deviations of all surface energy measurements are within 2 mN/m based on the untreated reference.

## Storage of plasma treated panels in a freezer

In an additional experiment Ar and N<sub>2</sub> plasma treated panels were stored in a freezer at -20 °C. The result of the N<sub>2</sub> treated panel can be found in Figure 13. Storing panels in a freezer proved also the hindering of hydrophobic recovery. A significant amount of polar surface remained after 27 days, however not as much as compared to under water storage. Another noticeable difference is the fact that the amount of dispersive surface energy did not decrease much compared to both storage methods for 29 days. The same results are found for the Ar plasma treated sample. The figure showing this is included in Appendix B Figure 41.

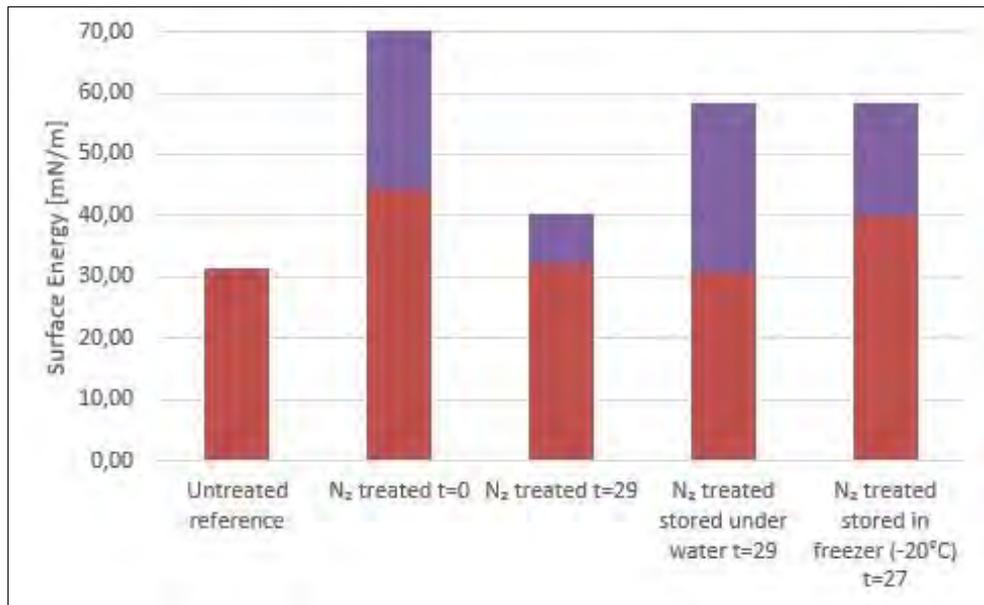


Figure 13. Surface energy of reference, N<sub>2</sub> plasma treated at t=0 and N<sub>2</sub> plasma treated panels after different kinds of storage. Including in a freezer.

## Short conclusion

Atmospheric Jet plasma treatment is not as in control as the low-pressure plasmas. Further results involving Jet plasma should be carefully evaluated. Nitrogen plasma treatment yields the highest surface energy as well as polar surface energy and lowest contact angle. From all measurements it is clear that both are consistent inversely related to each other. An optimum plasma treatment time with nitrogen was found using 90 seconds.

For an optimum use of the wettability and introduced functional groups on the surface, application of powder coatings should be done soon as possible after plasma treatment. Hydrophobic recovery takes place for the most part within 2 days but some polar surface energy will remain with time. Storing plasma treated panels in a freezer or under water seems a good solution when plasma treatment and powder coating application cannot quickly follow each other. Both storage methods proved to be able to preserve polar surface energy.

## **4.2 Morphological effects of plasma treatment**

After studying the physical effects of different plasmas treatment, the morphological and chemical changes were studied. Atomic force microscopy is used to study the effect of the different plasma types on the morphological structure of the surface. Three height images were made of each sample which are presented in Figure 14.

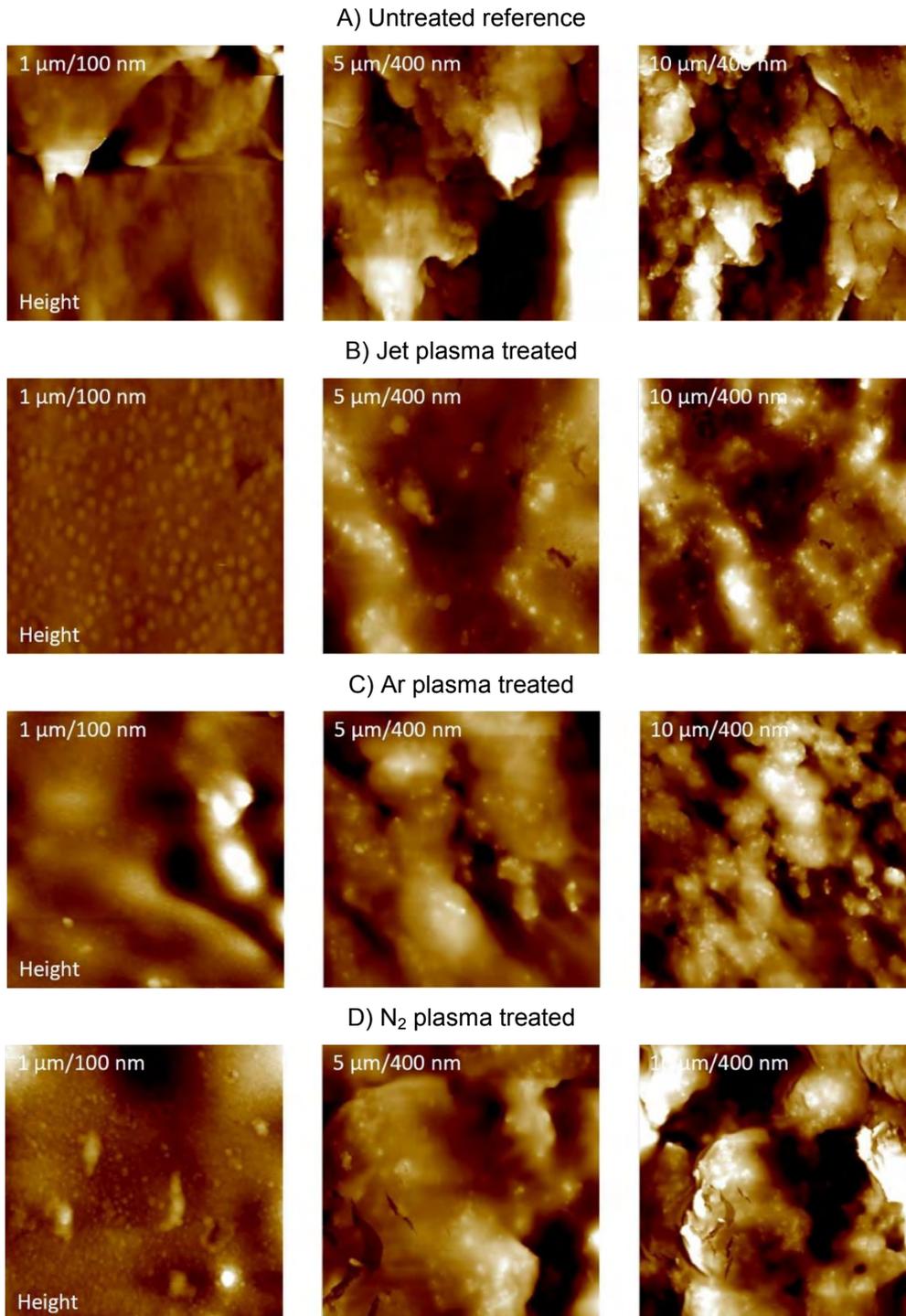


Figure 14. AFM height image of a) untreated reference, b) Jet plasma treated, c) Ar plasma treated and d) N<sub>2</sub> plasma treated surface after 60s of treatment time. Surface area left to right: 1x1, 5x5 and 10x10 μm. Total height difference (white represents high, black represents low) left to right: -50 + 50 nm, -200 nm +200 nm and -200 nm +200 nm.

The height images show that all three plasmas had an effect on the morphology of the surface. Root mean square roughness values ( Figure 15) were calculated by the software of the apparatus to quantify roughness differences. It shows that the surface after Jet plasma is the smoothest. This can also be seen in the height images. N<sub>2</sub> plasma proved to roughen the surface a bit compared to the untreated reference.

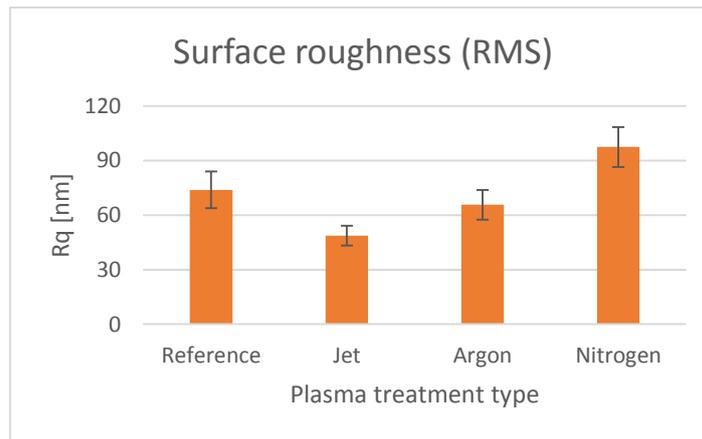


Figure 15. Calculated RMS surface roughness

Looking at the first height image of the Jet treated surface (Figure 14 B) particle-like round features can be seen. The diameters are all in the region of 40 nm. Even smaller round features in the region of 10 nm can be seen on both the Ar and N<sub>2</sub> plasma treated surfaces (Figure 14 first image C, D). Phase images obtained with AFM show these features more clearly and are given in Figure 16.

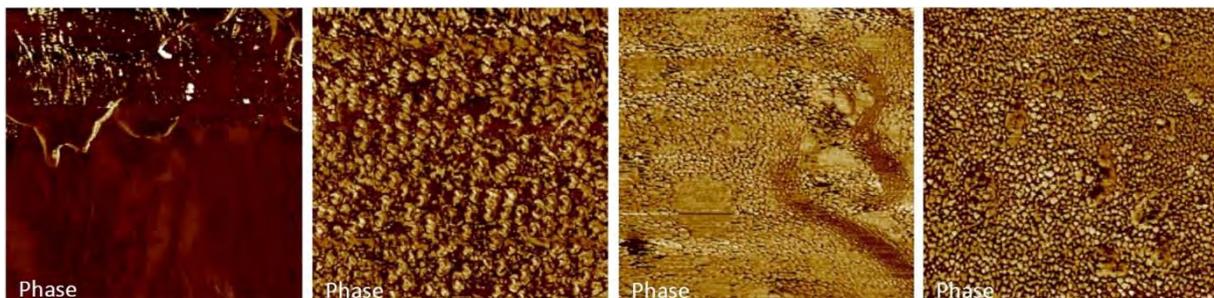


Figure 16. AFM phase image (surface area 1x1  $\mu\text{m}$ ) with round features on plasma treated surfaces. Left to right: a) untreated reference, b) Jet plasma treated, c) Ar plasma treated and d) N<sub>2</sub> plasma treated surface

These particles are believed to be the low molecular weight oxidized materials (LMWOM) as is reported in literature [59, 60] as an effect of plasma treatment. This literature also shows different size LMWOM particles as a result of different plasmas. To what extent these round nodular features helps in coating adhesion is unsure. It can help the performance by giving some mechanical anchoring points. The effect of the different plasmas on surface chemistry is discussed in next paragraph.

### Short conclusion

AFM height images show a small effect of used plasmas on morphology. While Jet smooths the surface, N<sub>2</sub> roughens it. Phase images show the presence of round features which are also noted and explained in literature.

### 4.3 Chemical effects of plasma treatment

X-ray photoelectron spectroscopy (XPS) was used to characterise the chemical surface composition of different plasma treated surfaces. Jet atmospheric pressure plasma (APP) and Low pressure plasmas (LPP) were studied. Survey scans were made to see the gross overall atomic content of the surface layer. The atomic content was also measured by element spectra scans. The overall average measured atomic content of C, O and N is presented in Table 3.

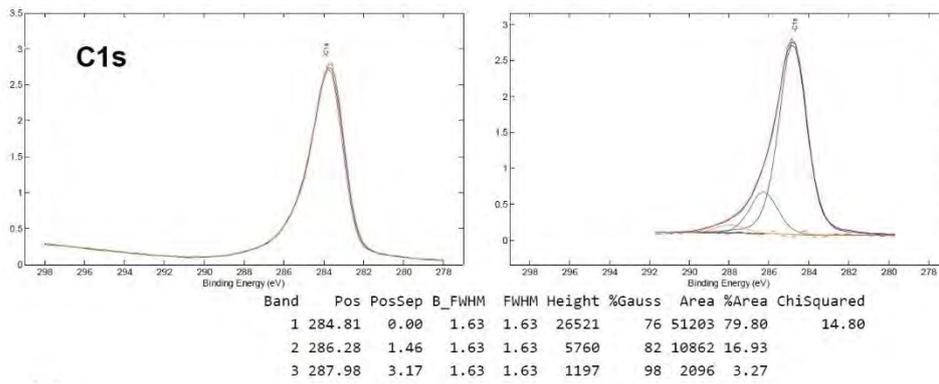
Element Plasma treatment	C [%] ( $\pm 1.25$ )	N [%] ( $\pm 0.4$ )	O [%] ( $\pm 0.8$ )	Other [%]
Untreated	95.2	0.2	4.6	
Jet (APP)	81.8	1.9	16.3	
Ar (LPP)	79.8	0.2	19.1	0.8
N <sub>2</sub> (LPP)	70.6	3.6	23.2	2.6

*Table 3. Atomic concentrations obtained from XPS survey and element spectra of polypropylene substrates exposed to Jet, Ar and N<sub>2</sub> plasma – after 60s of treatment time*

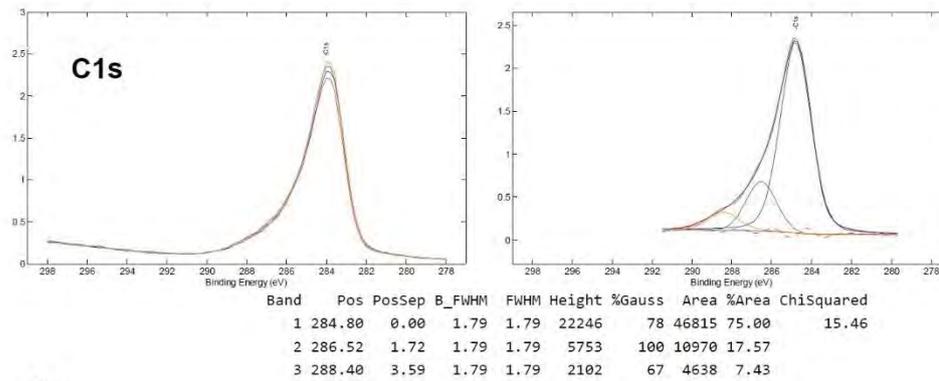
The untreated reference contains a small amount of oxygen which is probably from some water. After plasma treatment there is between 16 - 23% more oxygen and up to 4% nitrogen. The results show clear differences between the plasmas. The introduction of nitrogen to surface with gases that contain nitrogen is also seen in literature [7]. When comparing the polar surface energy of Figure 8 (0 days since treatment) with Table 3, it is evident that the amount of introduced polarity corresponds to the combined amount of oxygen and nitrogen.

Element spectra scans were made to investigate the O1s, N1s and C1s element spectra. The decomposition fit of the C1s spectra was done with 3 bands to study which kind of functional groups were introduced with plasma treatment. These C1s decompositions of all plasmas are shown in Figure 17. Between the reference and the plasma treated samples it can be seen that a broad shoulder appears left of the main band with its peak at 284.8 eV. Furthermore, this figure also shows that the decomposition of the C1s spectra does not show big differences between the different plasmas.

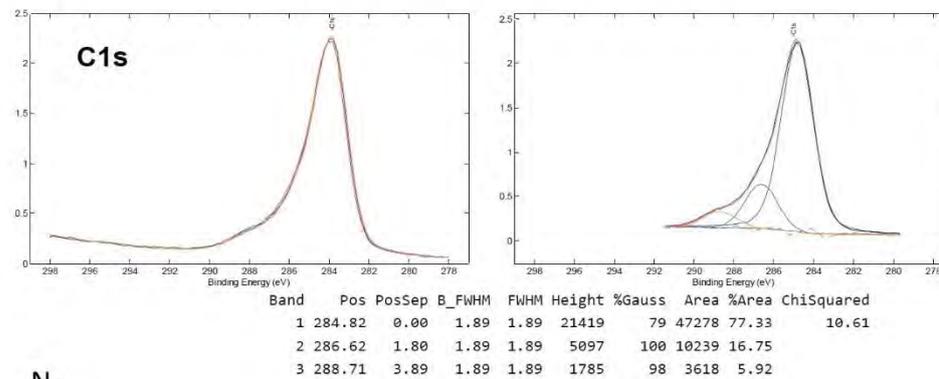
## Reference



## Jet



## Ar



## N<sub>2</sub>

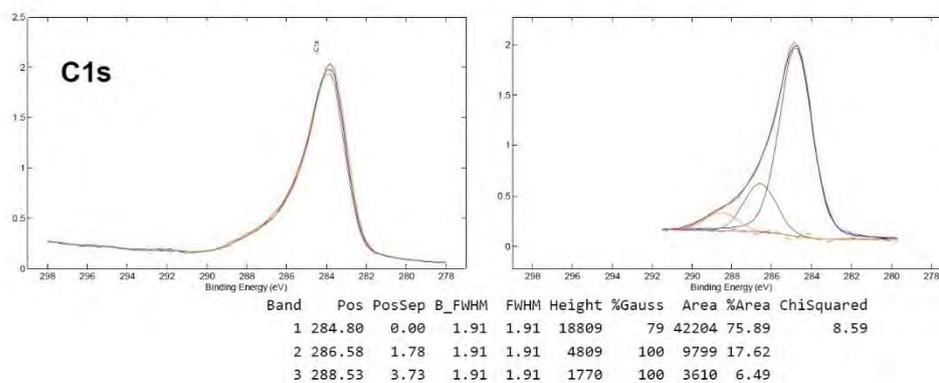


Figure 17. XPS C1s spectra of in succession: 1. Untreated reference, 2. Jet plasma treated, 3. Ar plasma treated and 4. N<sub>2</sub> plasma treated. Left: C1s spectra as measured and right: C1s decomposition fits after shift of the main C1s band.

Figure 18 shows the difference between the reference and the N<sub>2</sub> plasma treated substrate (both spectra extracted from Figure 17). Band 1 is the main band at 284.8 eV which is from the C-C-C bonds. Band 2 has its peak at around 286.6 eV. This shift is most likely from hydroxyl, ether or other C-O containing functional groups [39, 44, 56, 61]. The third band has its peak at around 288.5 eV, which is a shift of 3.7 eV. This band is attributed to carbonyl and carboxylic acid groups.

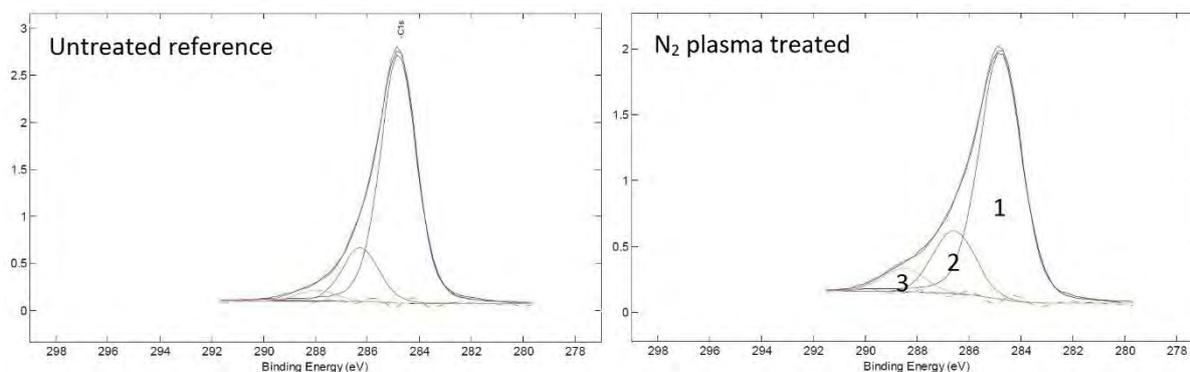


Figure 18. C1s element spectra of the untreated reference (left) and N<sub>2</sub> plasma treated (right) with upcoming shoulder and deconvolution fit of two shifted bands.

Jet and N<sub>2</sub> plasma treated samples also showed an increase of introduced nitrogen to the surface. Their N1s spectra are presented in Figure 19. Both element spectral regions show the existence of a peak at around 400 eV. This band is formed due to nitrogen, which is triple bonded to carbon only, forming a nitrile group. The peak at around 407 eV is from nitrogen bound to carbon and oxygen at the same time.

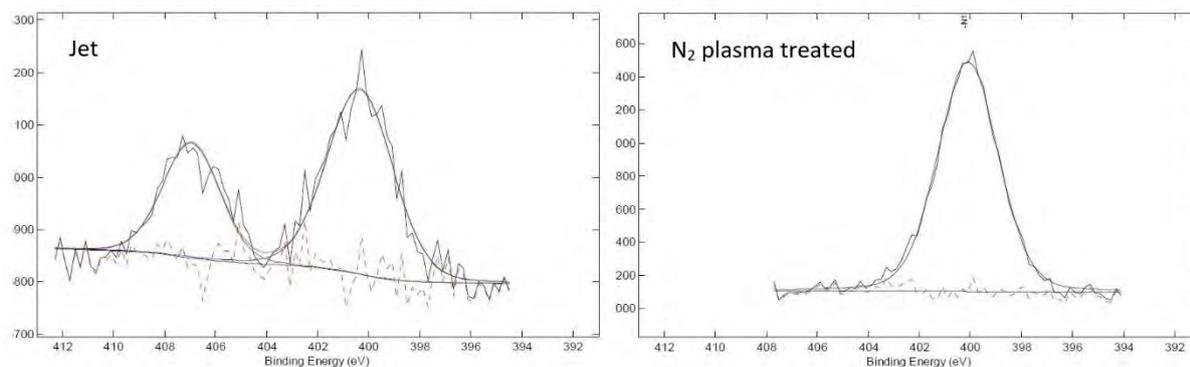
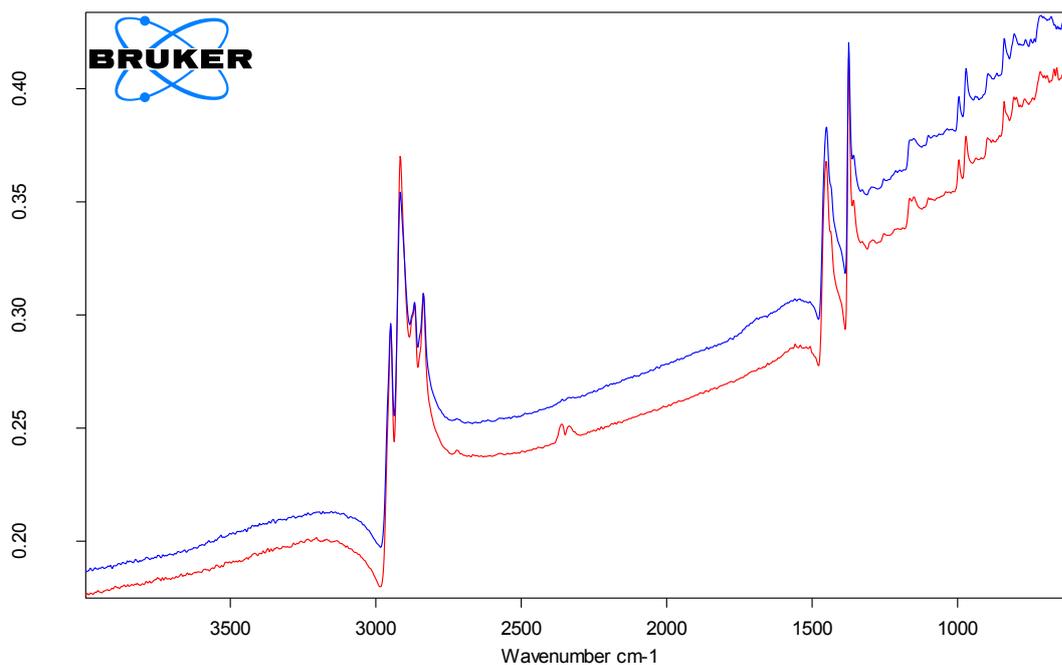


Figure 19. N1s element spectra of Jet (left) and N<sub>2</sub> plasma treated (right)

FTIR measurements were performed using a low pressure micro ATR. Surfaces which were exposed for 120 seconds to N<sub>2</sub> plasma were chosen for acquisition expecting some chemical changes. Literature [19, 42, 55] describes specific bands and wavenumbers which are associated with oxygen containing groups as a result of plasma treatment. Bands around 1640 cm<sup>-1</sup> and 1730 cm<sup>-1</sup> from C=O bonds and a broad band between 3100 and 3600 cm<sup>-1</sup> were expected. Spectra obtained of a reference and a 120s N<sub>2</sub> treated panel are included in Figure 20.



C:\DATA\AN2016\Req-000PSP-Gydo\G4 120 s high press ATR.0	G4 120 s high pres	sample form ATR	16/06/2016
C:\DATA\AN2016\Req-000PSP-Gydo\pp-ec-hi ref .0	pp-ec-hi ref	sample form ATR	16/06/2016

Page 1/1

Figure 20. FTIR spectra overlay of reference (red) and 120s N<sub>2</sub> plasma treated panel (blue)

There are distinct differences between both spectra. However, the absorption towards the fingerprint region (small wavenumbers) is remarkable. This high absorption may disturb or predominate the overall acquisition. Another reason for not finding chemical changes may be due to the significant higher acquisition depth of FTIR compared to XPS (paragraph 2.4).

### Short conclusion

All plasmas introduced oxygen to the surface. N<sub>2</sub> plasma yields the most oxygen. It also introduced the most nitrogen. Earlier measured polar surface energy can be related to both. Thus more introduced oxygen and nitrogen means more polar surface energy and thus better wettability.

XPS measurements show for all plasmas an upcoming shoulder in the C1s spectral region. The C1s spectra show that there are no big differences between the different used plasmas. Decomposition of this region shows the existence of hydroxyl, ether or other C-O containing groups, carbonyl and carboxylic acid groups. Both introduced hydroxyl and carboxyl groups are favourable because both may interact with either amines, epoxies or the hydroxyl and carboxyl which are present in the different powder coating systems. Based on the upcoming bands in the C1s, which are related to the amount of introduced hydroxyl and carboxyl, there is no plasma treatment that seems to be more favorable than the others. FTIR is not a suitable analysing technique to study effects of plasma treatment on polypropylene.

## 4.4 Powder coating results

Paragraphs 4.1, 4.2 and 4.3 demonstrated that plasma treatment alters the polypropylene surface in different physical and chemical ways. Three different powder coating systems were applied on different plasma treated surfaces. This paragraph is about the overall results of these applied powder coatings. Paragraph 4.5 is about the performance of these coatings in more depth.

### 4.4.1 Powder coatings on an untreated reference

The three powder coatings used in this study (paragraph 3.2) were applied on untreated polypropylene panels. As is clear from Figure 21, without any form of treatment there is absolutely no form of adhesion. After curing, coatings can be removed by a gentle rub or leave hold of themselves because of crimp effects.

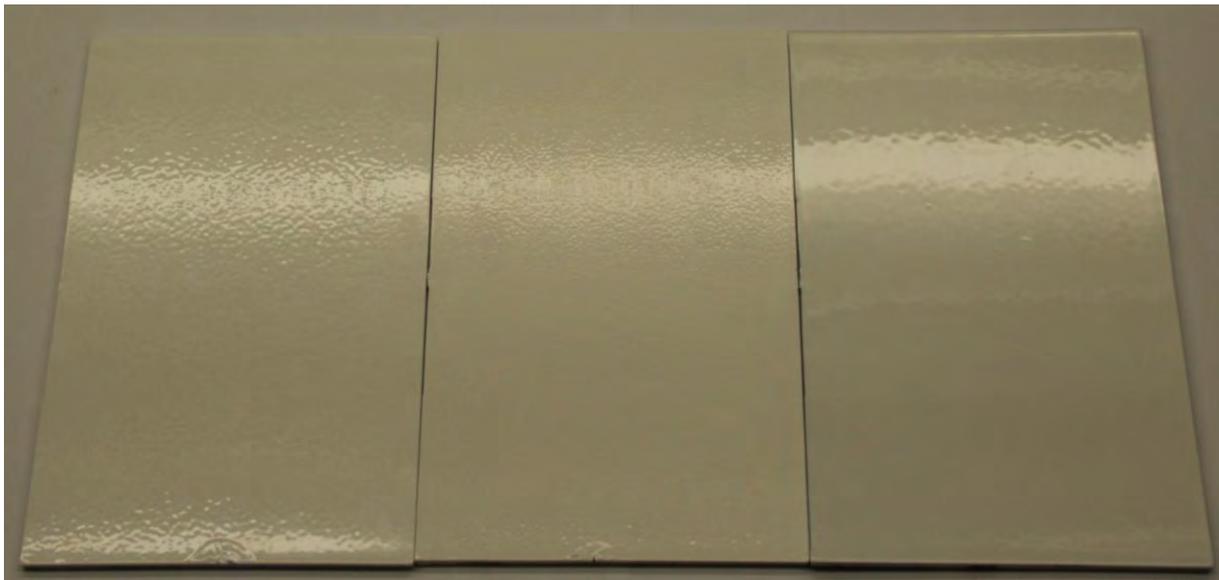


*Figure 21. Total absence of adhesion on untreated panel. Left to right: polyamide coating, hybrid coating and polyester UV coating system*

#### 4.4.2 Powder coating appearance

The effect of plasma treatment on the three applied coating systems is clearly observed. After plasma treatment the coatings instantly obtain adherence to the substrates. The powder coatings were subjected to double rub tests to know that they were fully cured. All three powder coatings were not affected by the used solvent end therefore passed the test with the best possible score of 5.

The different applied powder coating systems showed significant differences in appearance between each other. The whiteness of all three systems was about the same. The main difference between the powder coatings systems is their orange peel effect. The effect was independent of the plasma being used. As an example here, the effect on N<sub>2</sub> plasma treated panels is given in Figure 22. The hybrid coating shows the most distinct orange peel effect with a relative wavy surface. The polyamide coating also has a clear orange peel but a more fine structure. The polyester UV cured system flowed best and shows a minor orange peel effect. Close up images of the three coating systems are included in Appendix B Figure 42, Figure 43 and Figure 44. Besides the orange peel effect, the coatings shown a little difference in gloss. The polyester UV powder coatings has the most glossy finish while the polyamide has the least glossy finish.

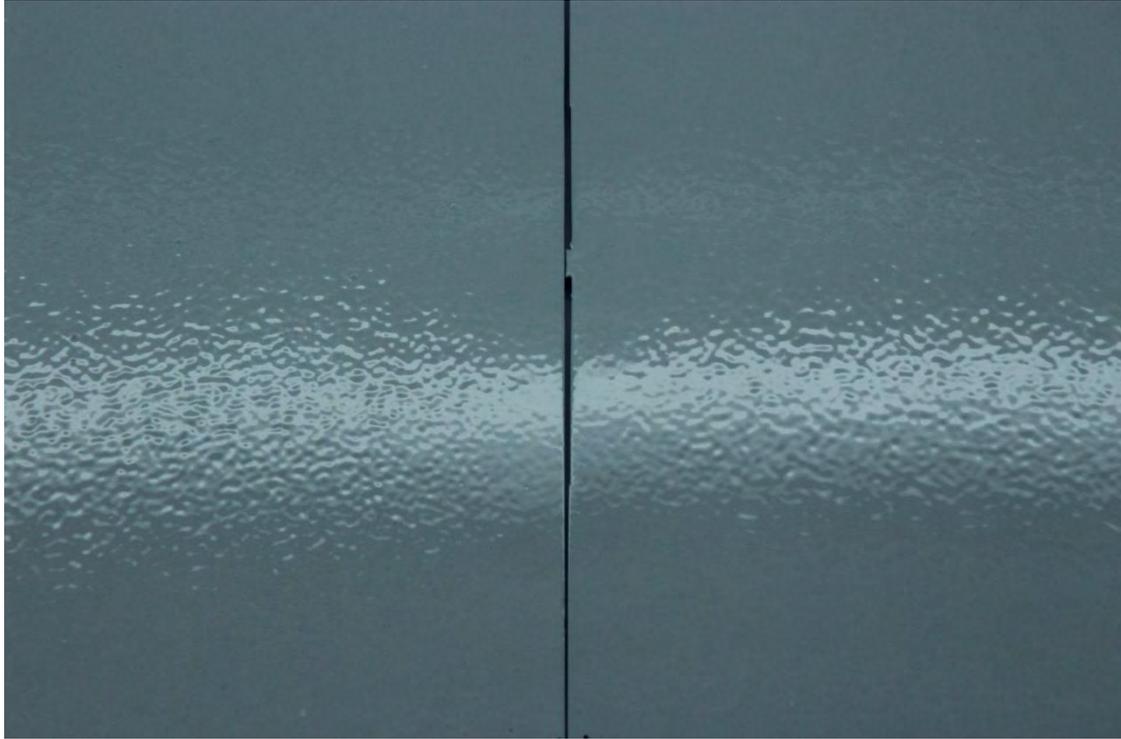


*Figure 22. Orange peel effect on N<sub>2</sub> plasma treated panels (60 seconds) under TL-84 light in ColorBox cabinet. Left to right: hybrid coating, polyamide coating and polyester UV coating system. Powder coatings applied direct after plasma treatment.*

The optical appearance of the coating systems on the substrates looks very promising. The used formulations were very basic, which means that flow and therewith orange peel but also gloss can be improved in many different ways. Experts were asked to review the coatings. All agreed that these panels were looking good. In fact, the same result could be expected from these coatings on traditional aluminium and steel substrates.

### Effect of wettability on orange peel

The effect of wettability on orange peel was studied comparing panels with very different surface energies. Nitrogen plasma treatment was chosen because earlier in this study was shown that the best wettability was obtained with this plasma. Varying treatment times of 5 and 120 seconds (the limits within this study) showed that surfaces energies were far apart from each other. Figure 23 shows both samples.



*Figure 23. Very small orange peel effect difference of the hybrid coating system applied on N2 plasma treated surface. Left: plasma treatment time 5 s, right: plasma treatment time 120 s. Surface energies differ 50 mN/m. The orange peel on the left side looks to have a bit finer structure.*

An effect on orange peel is hardly observed. The orange peel difference is not significant compared to the very significant surface energy difference of around 50 mN/m. It was expected that with higher surface energy and thus better wettability the appearance would improve with a less distinct orange peel effect.

### Short conclusion

Powder coatings applied on untreated surfaces have absolutely no adherence. After plasma treatment there is a clear adhering effect. The used powder coating systems have varying degrees of orange peel, however the actual amount of surface energy has little influence to the appearance. From the applied powder coatings could not be noticed that they were applied to a plastic substrate. This indicates how good the powder coatings, from aesthetic point of view, are performing.

## 4.5 Powder coating performance

This paragraph is about the powder coating performance of the different used powder coating systems. The performance was measured by pull-off strength tests and cross-cut tests. Next subparagraph 4.5.1 is about the performance of the different powder coatings systems applied on the different plasmas. Subparagraph 4.5.2 is about the performance related to plasma treatment time.

### 4.5.1 Performance of hybrid, polyamide and polyester UV

All three different powder coatings were applied on three different plasma treated surfaces. Figure 24 shows the pull-off adhesion strength of the powder coatings applied on different plasma treated surfaces. As can be seen, the hybrid and the polyester UV coating on Jet seems to be performing not as well as the Ar and N<sub>2</sub> plasmas. Also the deviations of the Jet are somewhat larger. On Ar and N<sub>2</sub> the polyester UV powder coating proved to be significant better than the hybrid and polyamide powder coating. An average pull-off strength of 2 MPa is found for the polyester UV on both plasmas. The average pull-off strength of the polyamide seems to be continuously stable on all three plasmas. To put the results into perspective, pull-off values around 3.5 MPa (500 PSI) are considered to be 'good' when powder coatings are applied on conventional metal substrates.

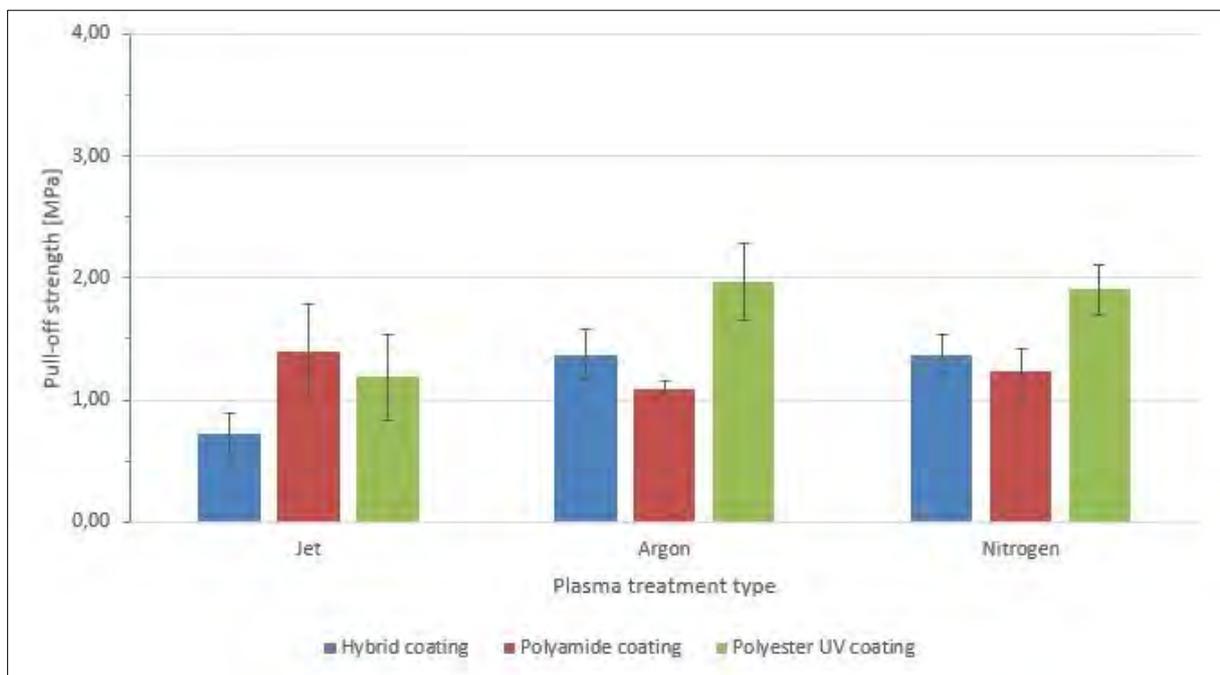


Figure 24. Pull-off adhesion strength of powder coating systems on plasma treated surfaces. Treatment time 60s. Application direct after plasma treatment.

Cross-cut tests, which involves another type of failure mechanism, were also performed to test the powder coating performance (Figure 25). Only the polyester UV cured powder coating scored fairly well on Ar and N<sub>2</sub> with a classification 1. All the powder coatings applied on the Jet plasma treated panels in this series performed badly. From the results it can be seen that the polyamide powder coating on all plasmas shows about the same pull-off strengths. When looking at the cross-cut test results the polyamide scored significantly better on the Ar and N<sub>2</sub> treated panels. This results shows that pull-off adhesion strength and cross-cut results are not proportional to each other.

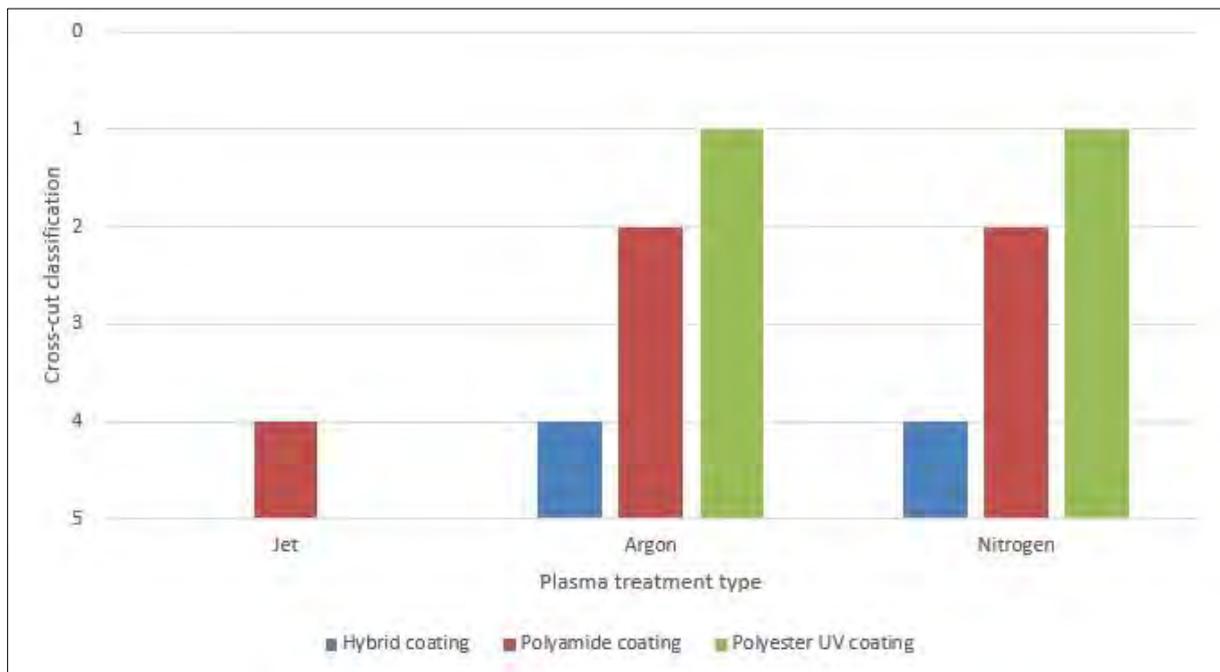


Figure 25. Cross-cut classification of powder coating systems on plasma treated surfaces. Treatment time 60s. Lower classification is better, no bar is classification 5. Application direct after plasma treatment.

### Performance 29 days after plasma treatment

Pull-off adhesion strength tests were also performed on powder coatings that were applied 29 days after plasma treatment. Between plasma treatment and application panels were stored in boxes. The results of these pull-off tests are shown in Figure 26. The plasma treatment was done in another series independently of the panels used for the pull-off tests directly after plasma treatment. The pull-off strength of the powder coatings on Ar and N<sub>2</sub> did not drop or significantly changed after 29 days compared to those directly after plasma treatment. This result shows that storage time has no influence on pull-off strength. It was expected that performance would decrease.

Remarkable are also the pull-off strengths of all three powder coatings on Jet treated panels after 29 days. The average pull-off strength values are well above 3.0 MPa, which is more than a 100% increase compared to the earlier results direct after plasma treatment. There is no clear explanation for this result. Between both batches settings and methods were kept the same. The only parameter not fully controlled was the treatment time.

As described in the methodology, panels were guided underneath the Jet flame by hand. A small variation in treatment time may cause these differences in pull-off strength. This indicates that there is a very small process window in which optimum results can be yielded.

Cross-cut tests were also performed on the 29 days stored plasma treated panels (Appendix B Figure 45). The Jet plasma treatment shows a classification 2 for the polyester UV and a classification 1 for the polyamide powder coating on the 29 day old Jet treated panels. This is also far better than earlier results. The hybrid scored a classification 5. This shows again that a relative high pull-off strength not necessarily leads to a good cross-cut classification.

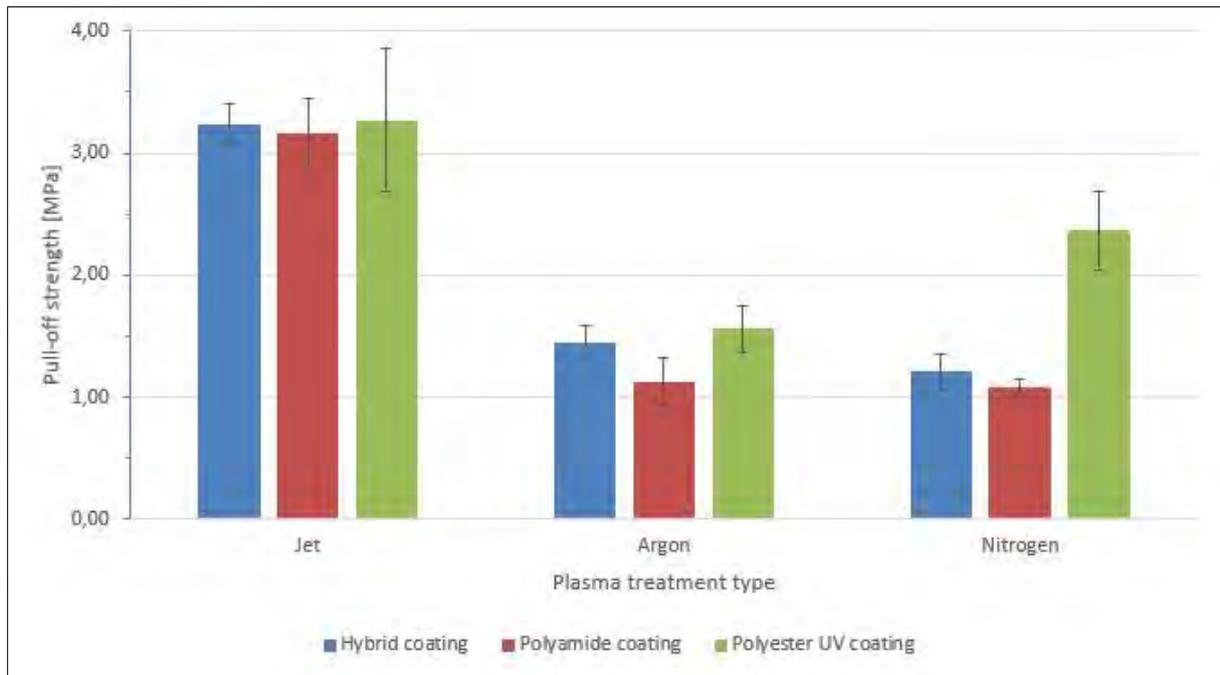


Figure 26. Pull-off adhesion strength of powder coating systems on plasma treated surfaces. Treatment time 60s. Application 29 days after plasma treatment. Stored in air

The results of the pull-off strength tests and the cross-cut tests are summarized in Figure 27. Based on these results some conclusion can be drawn.

### Short conclusion

The polyester UV powder coating proved to be the best performing in this study. Pull-off as well as cross-cut tests showed that this polyester UV, directly applied after treatment, performed best on the (LPP) Ar and N<sub>2</sub> plasmas. Further testing, comparing other powder coatings on different plasmas, showed that pull-off strength performance and cross-cut tests are not proportional to each other. Overall the hybrid powder coating was performing the least well based on primarily the cross-cut results. This powder coating seems to be too brittle to offer resistance to the failure mechanism of cross-cut tests.

High pull-off adhesion strengths were found with Jet (APP) treatment on which powder coatings were applied after 29 days. This shows the astonishing potential of adhesion strengths that can be yielded with Jet plasma treatment. In fact these pull-off strength are close to powder coating on metal performance. Better control of the Jet plasma process parameters are needed to obtain reproducible results.

From the performance results in this paragraph can also be concluded that there is no similarity with the amount of wettability. Earlier in this study it was shown that nitrogen plasma yielded the best wettability. However, this plasma does not show that powder coatings perform better. Besides, with 29 days of storage time, involving a significant amount of hydrophobic recovery, performance also remained more or less the same. There were also no similarities found between the performance of the different coatings and the chemical and morphological changes. This all together shows that powder coating performance, which clearly improved by plasma treatment, cannot be simply explained by one single parameter such as wettability. Different phenomena are at work effectuating adhesion between coating and substrate.

<b>Application direct after plasma treatment</b>				
		Average pull-off strength		Cross-cut classification
		[Mpa]	S.D.	
Hybrid coating	Jet	0,72	0,17	5
	Argon	1,38	0,21	4
	Nitrogen	1,37	0,16	4
Polyamide coating	Jet	1,39	0,39	4
	Argon	1,09	0,06	2
	Nitrogen	1,23	0,19	2
Polyester UV coating	Jet	1,19	0,35	5
	Argon	1,97	0,32	1
	Nitrogen	1,91	0,21	1
<b>Application 29 days after plasma treatment</b>				
<b>Panels stored in boxes</b>				
		Average pull-off strength		Cross-cut classification
		[Mpa]	S.D.	
Hybrid coating	Jet	3,24	0,16	5
	Argon	1,45	0,14	3
	Nitrogen	1,21	0,14	3
Polyamide coating	Jet	3,16	0,28	1
	Argon	1,13	0,19	1
	Nitrogen	1,08	0,06	1
Polyester UV coating	Jet	3,27	0,58	2
	Argon	1,56	0,19	2
	Nitrogen	2,37	0,32	2

Figure 27. Comparison of pull-off and cross-cut test results of all three powder coatings applied on all three plasmas. Treatment time was 60 seconds. 29 days storage was done in boxes (not under water)

#### 4.5.2 Performance related to varying treatment times

The powder coating performance was also studied on panels which were treated using varying treatment times. As described earlier, nitrogen plasma was used because of its best wettability results. Only the hybrid powder coating was applied. This is done to study the effect of powder coating adhesion strength related to measured differences in polar surface energy. The result is shown in Figure 28.

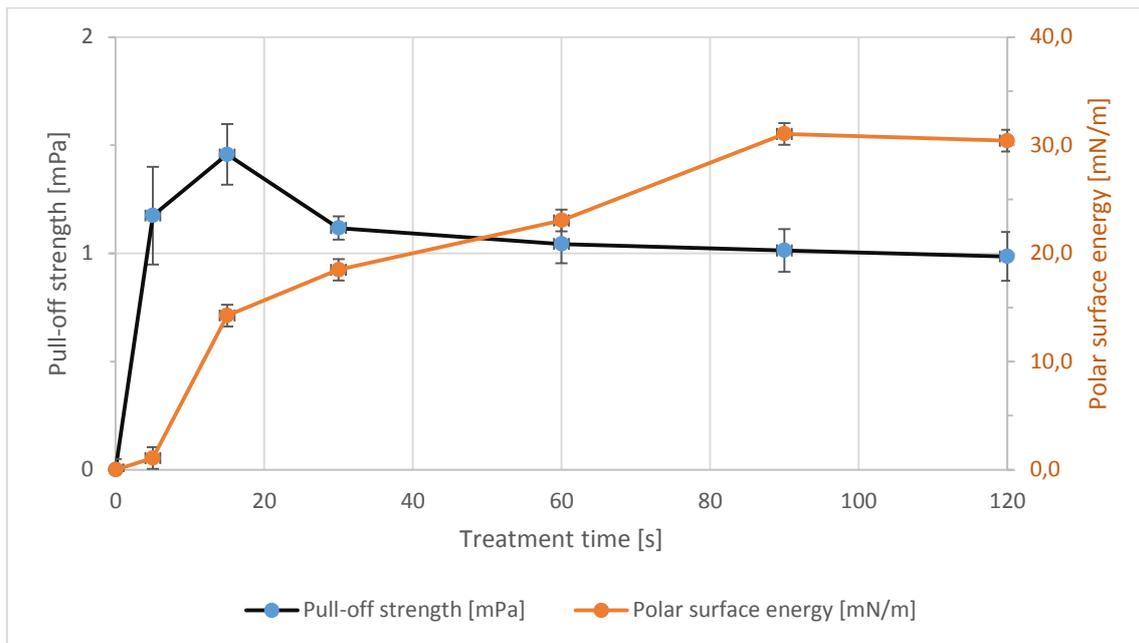


Figure 28. Hybrid powder coating pull-off strength and polar part of surface energy as function of treatment time – application of powder coating direct after plasma treatment as well as for the measured polar surface energy.

From Figure 28 it can be seen that already a small part of polar surface energy is obtained with 5 seconds of treatment time. At the same time a significant coating adhesion is obtained. The optimum pull-off strength is obtained with 15 seconds of treatment time. Upwards of 15 seconds the pull-off strength first drops a bit and then stabilizes at around 1 MPa while the polar surface energy increases with longer treatment time. From this it is clear, as also shown in previous paragraph, that the amount of (polar) surface energy is not related to powder coating performance. However, it can be concluded that only a small part of polar surface energy is needed to obtain adhesion. This result, together with earlier results, suggests that there is a link between the obtained (polar) surface energy of the substrate and the applied powder coating.

This result is similar to earlier results. From tests on panels that were stored, as well as stored under water, it is found that storage has little influence on the powder coating pull-off strength. Pull-off strengths did not change much with storage time. At the same time it is evidenced from experiments (paragraph 4.1) that polar surface energies do change with storage time. It decreases with storage

time while it remains when stored under water. Overall it can be concluded that an ever increasing amount of polar surface energy does not contribute to a better powder coating pull-off performance.

Based on the result that the surface energies of both powder coating and substrate maybe related, the surface energies of the cured powder coatings were studied. This was done by measuring the contact angles on the cured surfaces. This gives the best indication of the amount of surface energy since these are not known. It should be noted that these probably differ from uncured powder coatings. Figure 29 shows that the total surface energy of the hybrid and polyamide are both about the same. The polyester UV has the lowest surface energy.

The polar parts of the surface energies are also not significantly different from each other. The polyamide has 6.7, the hybrid 4.3 and the polyester UV has 5.1 mN/m.

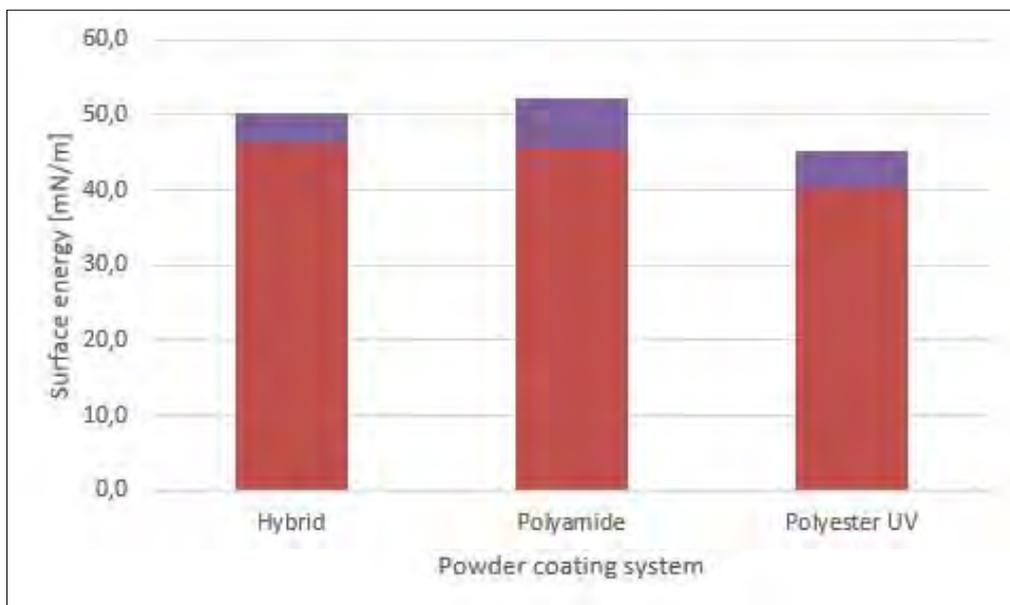


Figure 29. Surface energy of powder coating systems. Surface energy is composed of dispersive (red) and polar (purple) part

The link between the obtained (polar) surface energy of the substrate and the applied powder coating can be explained by the adsorption theory. The adsorption theory involves van der Waals forces including hydrogen bonding and is the most widely used approach in adhesion science at present [25, 26].

Optimum adsorption of the powder coatings, during curing, is reached when surface energies are matched. This is generally explained as the work of adhesion [62]. The work of adhesion is maximized when the surface energies of the adhesive and the adherend are as large as possible but at the same time the interfacial tension is as small as possible [63]. This can best be clarified by some figures (Figure 30 and Figure 31) - taken from Krüss [62]:

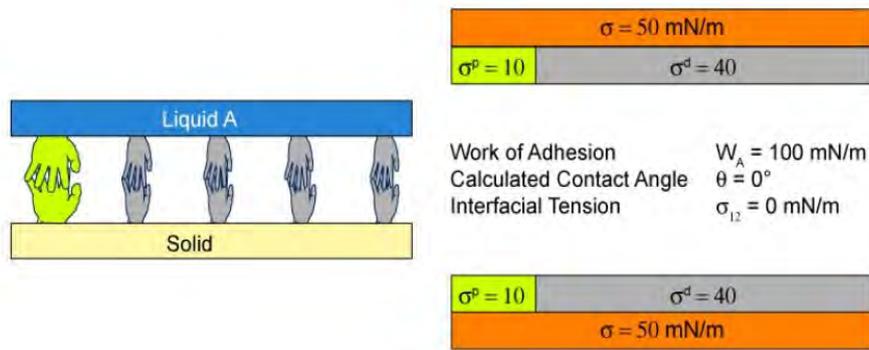


Figure 30. Good adhesion through good match of surface energies

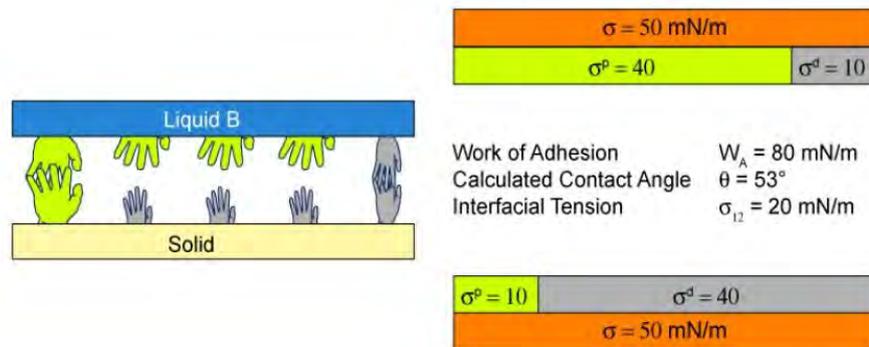


Figure 31. Bad adhesion through bad match of surface energies

As can be seen from Figure 30 and Figure 31 it can be seen that it comes down to matching polar ( $\sigma^p$ ) and dispersive ( $\sigma^d$ ) surface energy to obtain best work of adhesion. The work of adhesion is used to explain wetting behaviour but different workers also proved the relation between the work of adhesion and actual adhesive bond strength between adhesives and polymers [63]. When comparing the approximate surface energies of the powder coatings and obtained surface energies after plasma treatment (Figure 29 and Figure 8), adsorption is an important adhesion mechanism that could explain the adhering force at work between powder coating and substrate in this study.

## Interfaces

Dollies from the pull-off tests were studied after they were pulled off. The interfaces show differences in colour with different experiments. A hybrid coating interface is shown in Figure 32. It was applied on panels treated with varying  $N_2$  plasma treatment times.

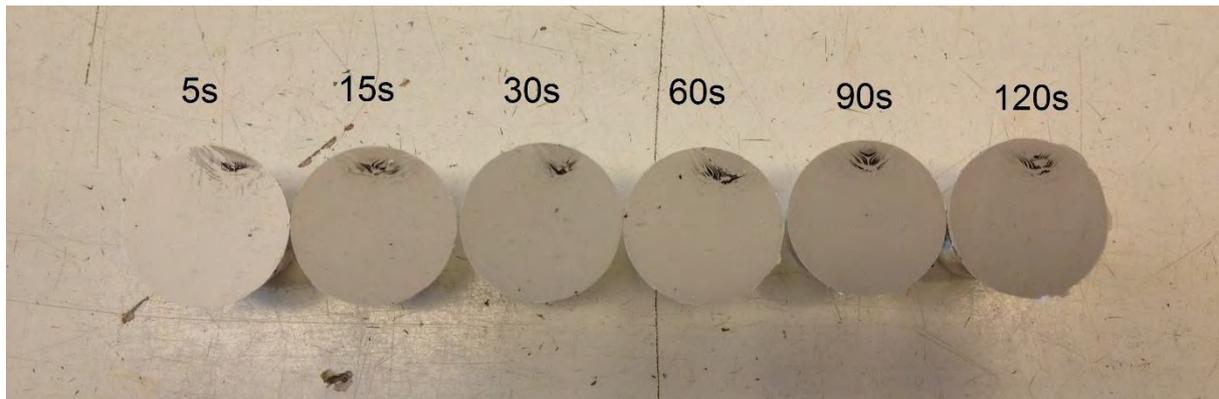


Figure 32. Coating interface on dollies after pull-off test of hybrid coating on  $N_2$  plasma treated panels with varying treatment times

Interfaces in most pull-off experiments have a dark/black coloured spot. In Figure 32 these spots are all lined up at the upside. As can be seen, the colour of the rest of the interfaces are not white as the powder coating itself, but comes in different shades. The dolly from the 5s plasma treatment is significantly lighter of colour while the 90s and 120s are significantly darker/greyish of colour. This greyish colour is probably due to degradation of the polypropylene surface as an effect of a long treatment time and is probably earlier described low molecular weight oxidized material. The interfaces were investigated using FTIR. The grey areas did not show existence of polypropylene, but this is probably due to the limitations of FTIR regarding the depth of acquisition as also earlier concluded from FTIR scans on plasma treated surfaces. However, the dark black spot, which clearly was a thicker layer pulled out of the substrate, proved to be polypropylene.

#### **Cross-cut test results with varying treatment times**

Cross-cut tests also show the optimum reached with shorter treatment times. Figure 33 shows the distinct differences. Between 5 and 15 seconds of treatment time the cross-cut classification is in the range of 0-1. At 30 seconds the classification is 2. Upwards of 30 seconds the classification is 4-5. Comparing the pull-off test and cross-cut results in this experiment it seems that there is a similarity between both. This is in contradiction with earlier result were pull-off and cross-cut test did not seem to show similarities.

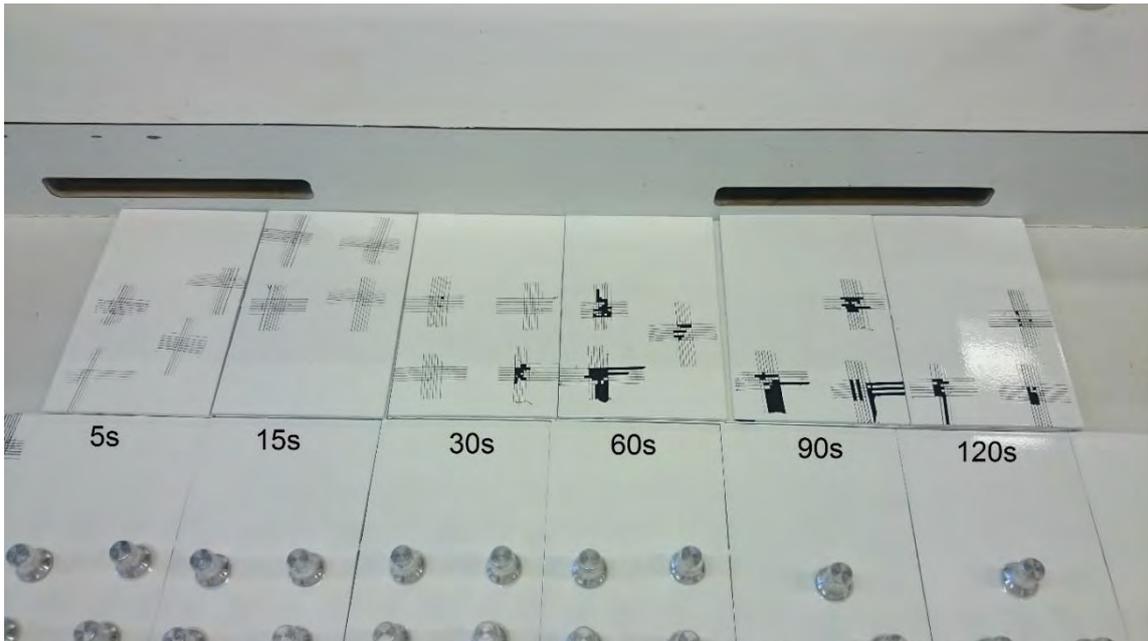


Figure 33. Panels after cross-cut classification. hybrid powder coating applied on panels treated with varying  $N_2$  treatment times. Application was direct after plasma treatment. Classification left to right: 1-1-2-4-5-5

#### **Stored and under water stored panels after varying treatment times**

Pull-off tests were also performed on normally stored and under water stored panels. The storage time was 36 days before powder coating. In Figure 34 these two series of pull-off strengths are added to the known result of Figure 28. As can be seen, after 36 days there is no distinct optimum at 15 seconds of treatment time anymore. In general, the differences of all three series are small. Difference in polar surface energy between the series was big, as described in paragraph 4.1.

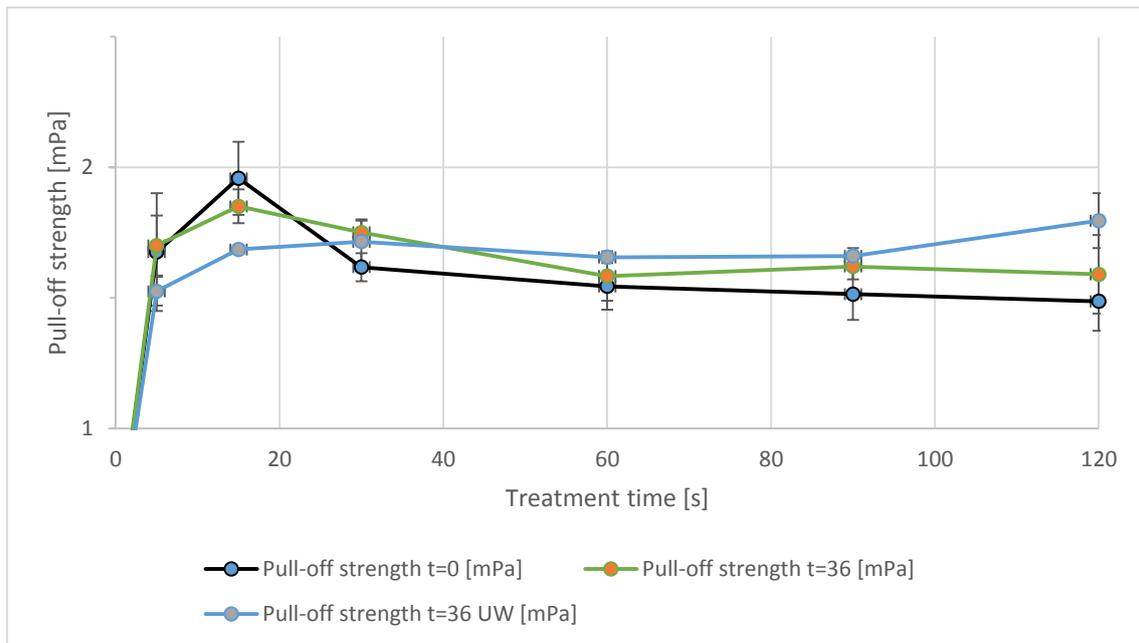


Figure 34. hybrid powder coating pull-off strength as function of treatment time – application on stored panels and on under water stored panels (UW). Stored for 36 days.

Panels powder coated after 36 days had the same cross-cut classification compared to those directly after plasma treatment. This can be seen in Figure 46 of Appendix B. This shows, together with the pull-off tests, that storage time is of minor influence on performance. Cross-cut test were also performed on the panels stored under water. A picture of these panels are included in Appendix B, Figure 47. These panels performed worse compared to the normal 36 days stored. Classifications were between 3 and 5. While the pull-off strength did not suffer from under water storage, the cross-cut test showed the opposite. There is no clear explanation why storing under water only deteriorated the cross-cut results.

### Short conclusion

Optimum powder coating performance is obtained with relative short treatment times involving small amounts of polar surface energy. A long treatment time yields a good wettability, however coating performance decreases. This decrease of performance can be explained by increasing surface tension between powder coating and substrate. The optimum is reached by matching the surface energies of both powder coating and plasma treated substrate as explained by adsorption theory. However, long treatment times seem to involve degradation. Interfaces from dollies that were pulled from panels which were treated with varying treatment times showed different shades of grey. All dollies also show a dark spot which is polypropylene pulled from the substrate. Degradation of the surface can form a weak boundary layer affecting the powder coating performance.

The study using varying treatment times combined with under water storage showed that powder coating performance suffers from under water storage. The cross-cut classifications were poor after 36

days. Moreover, storing under water is probably unnecessary since preservation of high amounts of polar surface energy is not needed. This together makes under water storage of little use.

## **5. Conclusions, discussion and future work**

The work in this study brings many new insights into adhesion of powder coatings to polypropylene through plasma treatment. This was also the main goal of the study. Many different conclusions can be drawn based on the results. This chapter is about the conclusions, discussion and future work.

### **5.1 Conclusions**

Plasma treatment has a great effect on the surface properties of polypropylene substrates. Chemical changes were evidenced with XPS and morphological changes were observed using AFM. Without plasma treatment, powder coatings don't adhere to polypropylene.

#### **Morphology**

Morphological changes on the scale of nanometres in this study were not able to be linked to the adhesion performance of the powder coatings. Some plasma treatments even smoothed the surface so adhesion through mechanical interlocking is not dominant. This rejects hypothesis 6 which postulates that increased surface roughness improves powder coating adhesion.

#### **Surface chemistry and wettability of substrate**

Plasmas introduce significant amounts of oxygen to the surface. Also some nitrogen is introduced with low pressure N<sub>2</sub> plasma and Jet APP. XPS peak shifts revealed that oxygen is present in the form of hydroxyl, ether or other C-O containing functional groups, carbonyl and carboxylic acid groups. The distribution of these groups are similar for the used plasmas. Introduction of these oxygen containing groups leads to a higher polar surface energy. Cross-linking of the surface witnessed from the increase of dispersive energy also adds to the total amount of surface energy. Increased surface energy clearly leads to an improved wettability as measured by water contact angle. Water contact angle and surface energy showed to be consistent related to each other by inverted value. The amount of polar surface energy and amount of oxygen / nitrogen evidenced with XPS are also consistent. N<sub>2</sub> yields the highest polar surface energy while this also increases by longer treatment times. This latter approves hypotheses 2: surface energy increases with treatment time.

### **Shelf life of plasma treated surfaces**

Polar surface energy decreases with storage time. This effect is called hydrophobic recovery. A significant amount of hydrophobic recovery takes place within the first two days after treatment. Thereafter, there is a more gradual decrease in polar surface energy. Also the dispersive surface energy decreases with time. Both surface energy effects are similar for all plasmas.

The shelf life of plasma treated panels can be extended through storing them under water. Experiments showed that after 29 days polar surface energy did not decrease as much as panels that were stored in boxes in laboratory conditions. Under water storage cannot prevent the decrease of dispersive surface energy. Storing plasma treated panels in a freezer at  $-20^{\circ}\text{C}$  also improves the shelf life. It slows hydrophobic recovery but also the decrease of dispersive surface energy.

### **Surface energy and powder coating performance**

A high surface energy does not yield better powder coating performances. Performance was measured by pull-off and cross-cut tests. A higher surface energy also has no distinct positive effect on orange peel effect. Therefore hypothesis 1 is rejected: a higher surface energy and better wettability yields a better powder coating adhesion and quality. Only a small amount of polar surface energy is needed for adhesion of a powder coating. An optimum is reached somewhere between 1 – 18 mN/m based on experiments with varying treatment times. A polar surface energy upwards of 18 mN/m does not yield a higher coating performance. This optimum can best be explained by adsorption theory which is about matching surface energies. The discussion, next paragraph, will be in some more detail about this.

Experiments involving storage of plasma treated panels also proved the insignificance of a high polar surface energy. The performance of powder coatings remained with storage time. Enough polar surface energy thus remains. This means that under water storage, to prevent hydrophobic recovery, is not of much use. It even has a negative influence on powder coating performance as seen with cross-cut tests. Also long treatment times proved to have a negative effect on performance. From this hypothesis 3 is approved: long plasma treatment times deteriorates the surface, affecting the powder coating adhesion in a negative way. Hypotheses 4 and 5 are rejected. Hypothesis 4 stated: surface energy and wettability of substrate decrease with storage time, hence the adhesion of freshly applied powder coating as function of storage time of the substrate too. And hypothesis 5 stated: surface energy and wettability remain through under water storage and does not affect powder coating adhesion.

### **Plasma performance**

Different plasma gases were used on the polypropylene substrates. Surface energies prove to differ with use of plasma gas and therewith the wettability of the treated panels. Ar and  $\text{N}_2$  plasma gas were

initially performing better (regarding powder coating performance) than Jet which uses compressed air. Between Ar and N<sub>2</sub> LPP no big differences in performance of powder coatings were found.

A second time that Jet plasma was used, to study the performance after storage, it showed far better powder coating performance while conditions were kept the same to earlier Jet plasma treatment. These unexplained findings however does prove some important things. It shows the potential of powder coatings applied on polypropylene and the effect by use of plasma treatment. But it also shows that the key to optimal performance lies within the ability to control plasma parameters to obtain reproducible results. From this it is also concluded that the yielded (polar) surface energy has not on its own influence on performance. The used treatment/discharge type and perhaps treatment gas eventually does too.

### **Overall performance of used powder coatings**

From many tests it is found that pull-off tests and cross-cut tests are not always consistent. A high pull-strength not necessarily lead to a good cross-cut classification or visa versa. Jet results showed (after 29 days), that pull-off strengths of all three coatings were exceptional high, however the hybrid clearly underperformed with cross-cut tests. From this is concluded that, for a good assessment of the overall powder coating performance, both tests should be used.

By looking at the overall performance of the three different powder coatings it is concluded that the polyester UV cured system performed best on all plasma treated surfaces. The hybrid powder coating performed clearly least well on all plasma treated surfaces. It can thus be concluded that, besides the plasma treatment itself, performance of the powder coatings also depends on the binder system itself.

### **Research question**

Answer to 'How do plasma surface treatments enhance the adhesion between a polypropylene substrate and binders of different powder coating systems?'

Plasma treatment enhances the adhesion of a powder coating systems to polypropylene through either or both chemical and physical interactions with the surface. Morphological changes as an effect of plasma treatment are not dominant.

Improved wettability by increased (polar) surface energy is certainly one condition that is obtained with plasma treatment and needed for powder coatings to adhere. However, a high (polar) surface energy is no guarantee for a good powder coating performance. The best explanation for optimum surface energy and adhesion is given by the adsorption theory (work of adhesion) as explained in paragraph 4.5.2. However, also degradation effects of plasma treatment are very likely to play a role. Different adhesion mechanisms and other effects are involved at the same time. The discussion in next paragraph is about this is some more depth.

## 5.2 Discussion

This study started with the goal to gain more insight into the adhesion between powder coating and substrate. While different new insights were found, as shown in the conclusion, there is no final conclusion how powder coating performance is exactly obtained and which bonds are involved. This discussion is about the adhesion mechanism that certainly play a role in this study in some more depth.

First it is important to note that the adhesion of the powder coatings, as obtained and proved after plasma treatment, cannot be explained by one model or theory. Based on different adhesion theories it is very likely that multiple effects are involved at the same time. Main mechanisms of adhesion that probably exist between plasma treated substrate and powder coating are:

- Adsorption (including hydrogen bonds)
- Chemical bonds

Earlier in the conclusion it was already stated that mechanical interlocking, which is proved to be an significant adhesion mechanism in other cases [27], is not dominant on the roughness scale involved with plasma treatment. Furthermore, there is a weak boundary layer to take into account.

### Adsorption

Almost certain adsorption (through van der Waals interactions) plays a role. Induced by good wettability, this type of adhesive interaction is always present between matter. From literature [64, 65] it is found that this type of adhesion mechanism, at ideal circumstances, can yield up to about 0.24 MPa of adhesive strength from only these van der Waals forces. Adhesive strengths well above this value should thus be from other kinds of bonds. Most likely chemical and/or hydrogen bonds.

The presence of adsorption can be derived from the fact that an optimum of polar surface energy and coating adhesion is found. The maximum work of adhesion is obtained when surface energies of adhesive and adherend, or in this case, powder coating and substrate are as large as possible but at the same time the interfacial tension is as small as possible [63]. It comes down to matching the dispersive and polar surface energies.

The obtained adhesion between powder coating and substrate can not only be explained by van der Waals forces. As mentioned earlier, most likely chemical and/or hydrogen bonds are also present. Based on the measured polar surfaces energies of both powder coating and substrate and also witnessed functional groups by XPS after plasma treatment, both are likely to be present.

## **Chemical bonds**

Covalent bonds between powder coating and substrate are well possible. By looking at the introduced groups as witnessed by XPS, it is shown that there is carboxyl and hydroxyl present. Both are functionalities which are also part of the powder coating curing chemistry.

Functional end-groups of the powder coating system can react during curing with introduced functional groups on the substrate to form covalent bonds. However, based on the pull-off strength tests, covalent bonds are probably not the primary form of binding. Much higher pull-off values can be expected from proper chemical adhesive bonds. For this study there are two possible explanations why chemical bonds are not dominant: The amount or sort of functional groups introduced by the different plasma treatment are not suitable to the functionalities of the powder coatings. Or: the powder coating systems don't offer enough reactive functionalities. Besides functional end groups in the powder coating systems there are double bonds in one powder coating system that may also contributes.

The polyester UV cured powder coating system in this study performed clearly better on the LPP Ar and N<sub>2</sub> treated surfaces than the polyamide powder coating system. From hydrogen bonding perspective it was expected that the polyamide would perform better because of its somewhat higher polarity. This was not the case. However, the polyester UV has double bonds formed in its binder system. These double bonds are known to be reactive and probably interacts with double bonds formed at the cross-linked plasma treated surface or with some kind of functional group. The differences between the powder coatings and experiments in this study show that, by all means, powder coating performance is thus also related to the composition and sort of binder system of the powder coating itself.

## **Hydrogen bonds**

Hydrogen bonds are physical intermolecular bonds which therefore are often part of adsorption theory. Based on the polarities of powder coatings and plasma treated substrate, these kinds of bonds are well possible. Also with hydrogen bonding an optimum is reached by matching the amount of polar groups between powder coating and substrate.

## **Weak boundary layer**

A weak boundary layer, as also mention in the literature chapter, is not a adhesion mechanism by itself but can play a major role in the total adhesion mechanism. A weak boundary layer can be formed by pollutants on the surface or involve the cohesive failure of the substrate itself. In fact, a weak boundary layer is also likely to be present in this study given the degradation effect found on the coating interfaces with increasing plasma treatment times. Also the AFM study showed features explained as low molecular weight oxidized materials that can act as a weak boundary. Interfaces after pull-off tests show to become increasingly darker of color with longer treatment time.

Thus combined there are two adhesion mechanisms that explain powder coating adhesion on plasma treated substrates and one mechanism that involves failure:

1. Adsorption: matching high as possible surfaces energies with minimal surface tension, including adhesion through polar interaction by hydrogen bonding.
2. Chemical bonds between plasma introduced functional groups on the substrate and powder coating, including chemical bonds between reactive double bonds present in the powder coating system and substrate.
3. A weak boundary layer formed with increasing (too long) treatment times. This probably deteriorate the surface so much that powder coating adhesion at the (near) interface fails. The netto overall effect is a decrease of adhesive performance.

By combining all results from the conclusion and statements from the discussion, the following statements can be made to obtain optimized powder coating performance:

- All used plasmas are suitable based on introduction of similar functional groups and presence polar surface energy.
- An optimized (short as possible) plasma treatment time to obtain matched polar surface energies between the substrate and powder coating and minimal degradation of the substrate.

This means that there is a contradictive effect involved with plasma treatment. This also implies that there is a clear optimum between both effects. The high pull-off strengths found with Jet could be explained by the optimum of both: A very short treatment time not effecting the surface layer while just enough oxygen and or nitrogen is introduced to the surface for optimal hydrogen bonding and/or chemical bonds.

### **Pull-off adhesion strength versus cross-cut classification**

This study showed that pull-off strength and cross-cut classification are not proportional to each other. This is clearly witnessed from the Jet results involving very high pull-off strengths while the hybrid powder coating performed very poor with cross-cut tests. That there is such a difference is not strange since there is a big difference in both failure mechanisms. The hybrid powder coating clearly performed worse compared to the other powder coatings in all tests. Based on this result, the cross-cut performance seems to be related to the type of powder coating system.

### **Shelf-life**

The storage of plasma treated samples in a freezer proved to preserve polar surface energy. However, storing under water did as well and even better. Storing in a freezer at -20°C preserved the dispersive surface energy better. How this exactly works is not known. Literature suggests rotation and/or diffusion of the polymer chain as the most important mechanism for polar groups to disappear.

While storing the polypropylene panels under the glass-transition temperature this could indeed be used as explanation.

However, an explanation can also be theorized considering other preserving mechanism in both storage methods. Placing sample under water may help to prevent air contaminants to reach the surface. And by storing in a freezer, functional groups may not react that easily with contaminants anymore.

### **Analysing techniques**

Fourier transform infrared spectroscopy (FTIR) did not yield results as presented in literature. This may have to do with the following two things, or a combined effect:

- The carbon black which is added for electrical conductivity absorbs the IR light. This is witnessed from the spectra which are deformed (high absorption) towards the fingerprint region with low wavenumbers.
- The depth of information. FTIR starts from 500 nm into the surface. The surface treatment may not be that deep.

It may be interesting to use ToF-SIMS in further research. However, based on many literature articles, this technique is not regularly used to study surface chemistry after plasma treatment. When looking at the depth of information at which this technique acquires information, it is far better compared to FTIR (Table 1). It does even obtain information much closer to the surface than XPS. Some more measurements should be taken to compensate for the relative small analysis surface area.

### **5.3 Future work**

Based on literature study and this study itself, recommendation for further study are:

- Extensive testing with Jet atmospheric plasma. Can reproducible high pull-off strengths be obtained? If so, use XPS and AFM again to study chemical and morphological changes.
- Optimize plasma parameters, specifically plasma treatment time. Test a variety of short treatment times. Make sure that degradation is as little as possible.
- Try powder coating formulations (polyester UV cured) with more introduced double bonds to see if performance increases.
- Test with varying polarities of one sort of powder coating system. See if more polarity can be built in the powder coating systems and test if performance depends on it.
- Stop with under water storage. Preserved higher surface energy is not of much use. It's however useful when studying chemical surface changes after plasma treatment.
- Try use ToF-SIMS to see if this technique can obtain more detailed information about surface chemistry after plasma treatment.

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# Appendices

## Appendix A. Attachments to chapter 3

<i>Parameter</i>	<i>Setting</i>
Material drying	4 hours at 80 °C
Temperature profile (back to front) [°C]	190, 200, 210, 210
Injection speed [mm/s]	20
Injection pressure [bar] (results from injection speed)	54
Holding pressure [bar]	35
Holding Pressure time [s]	10
Cooling time [s]	35

*Table 4. Injection moulding process settings*



*Figure 35. PP-EC-HI panel*



*Figure 36. Preservation of full-sized panels made out of 180 mm PVC DN 125 piping. Stories were separated sing a thin foamed polystyrene sheet. A lid was used to close the container.*



Figure 37. Preservation system for small panels under water. A rubber seal watertight container staked with two 90 mm PVC pipes.

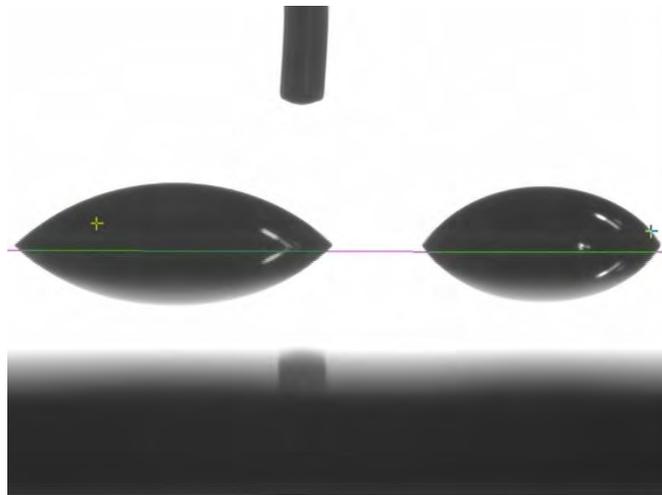
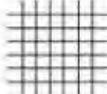
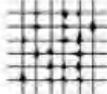
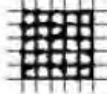
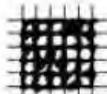
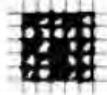


Figure 38. SDT – drop of water (left) and Diiodomethane (right) on plasma treated surface



Figure 39. DeFelsko Positest AT-M Pull-Off Adhesion tester in action

Table 1 - Classification of test results

Classification	Description	Appearance of surface of cross-cut area from which flaking has occurred <sup>a</sup>  (Example for six parallel cuts)
0	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5 % is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5 %, but not greater than 15 %, is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15 %, but not greater than 35 %, is affected.	
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35 %, but not greater than 65 %, is affected.	
5	Any degree of flaking that cannot even be classified by classification 4.	—

<sup>a</sup> The figures are examples for a cross-cut within each step of the classification. The percentages stated are based on the visual impression given by the pictures and the same percentages will not necessarily be reproduced with digital imaging.

Figure 40. Classification of Cross-Cut adhesion test results

# Appendix B. Attachments to chapter 4

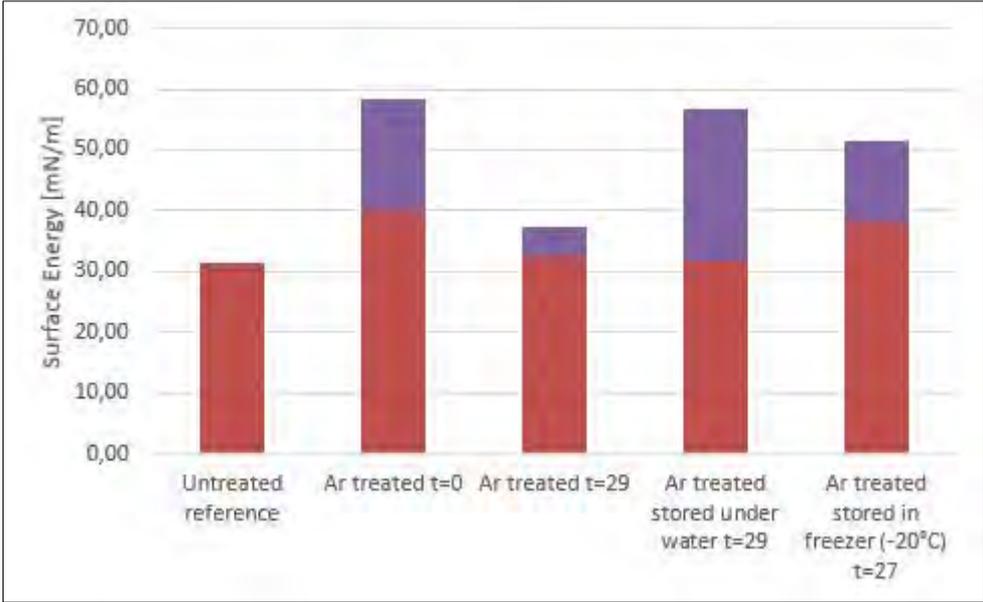
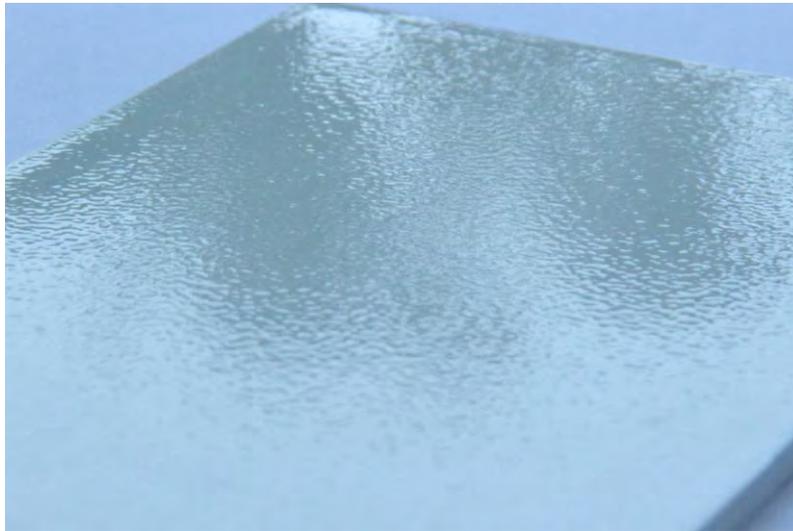


Figure 41. Surface energy of reference, Ar plasma treated at t=0 and Ar plasma treated panels after different kinds of storage. Including in a freezer.



*Figure 42. Close up visual appearance of the hybrid coating system applied on  $N_2$  plasma treated surface - treatment time 60 s*



*Figure 43. Close up visual appearance of the polyamide coating system applied on  $N_2$  plasma treated surface - treatment time 60 s*



*Figure 44. Close up visual appearance of the polyester UV cured coating system applied on  $N_2$  plasma treated surface - treatment time 60 s*

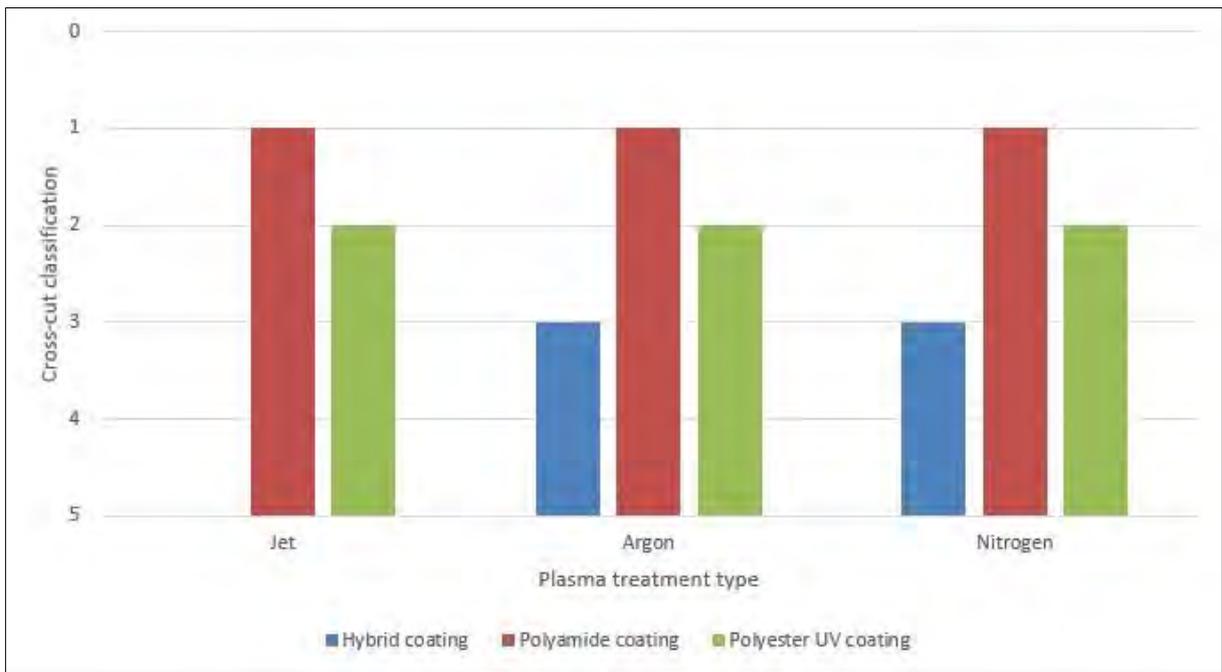


Figure 45. Cross-cut classification of powder coating systems on plasma treated surfaces (60s). Lower classification is better, no beam is classification 5. Application 29 days after plasma treatment.

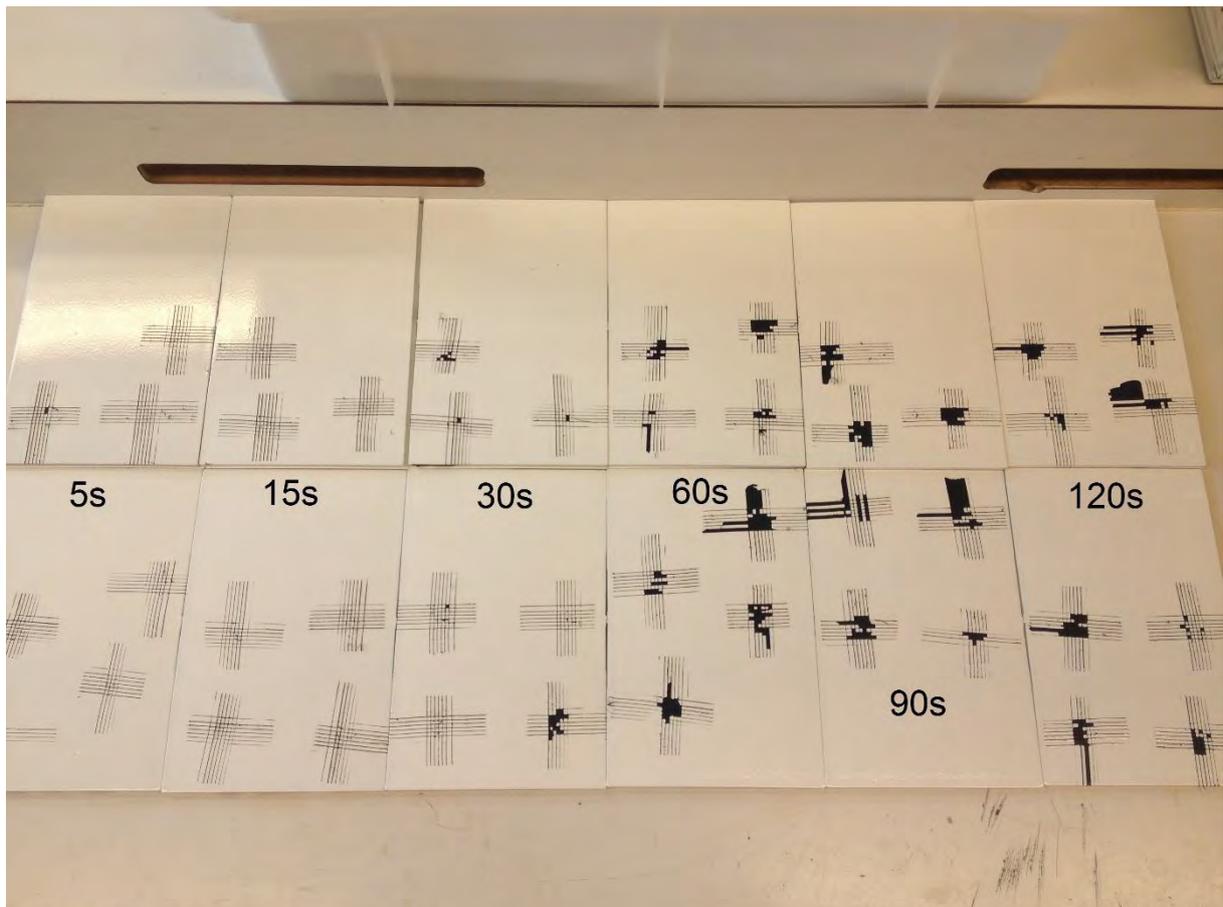


Figure 46. Panels after cross-cut classification. Hybrid powder coating applied on panels treated with varying N<sub>2</sub> treatment times. Row above is application after 36 days. Row below is application direct after plasma treatment. Classification left to right for both series: 1-1-2-4-5-5

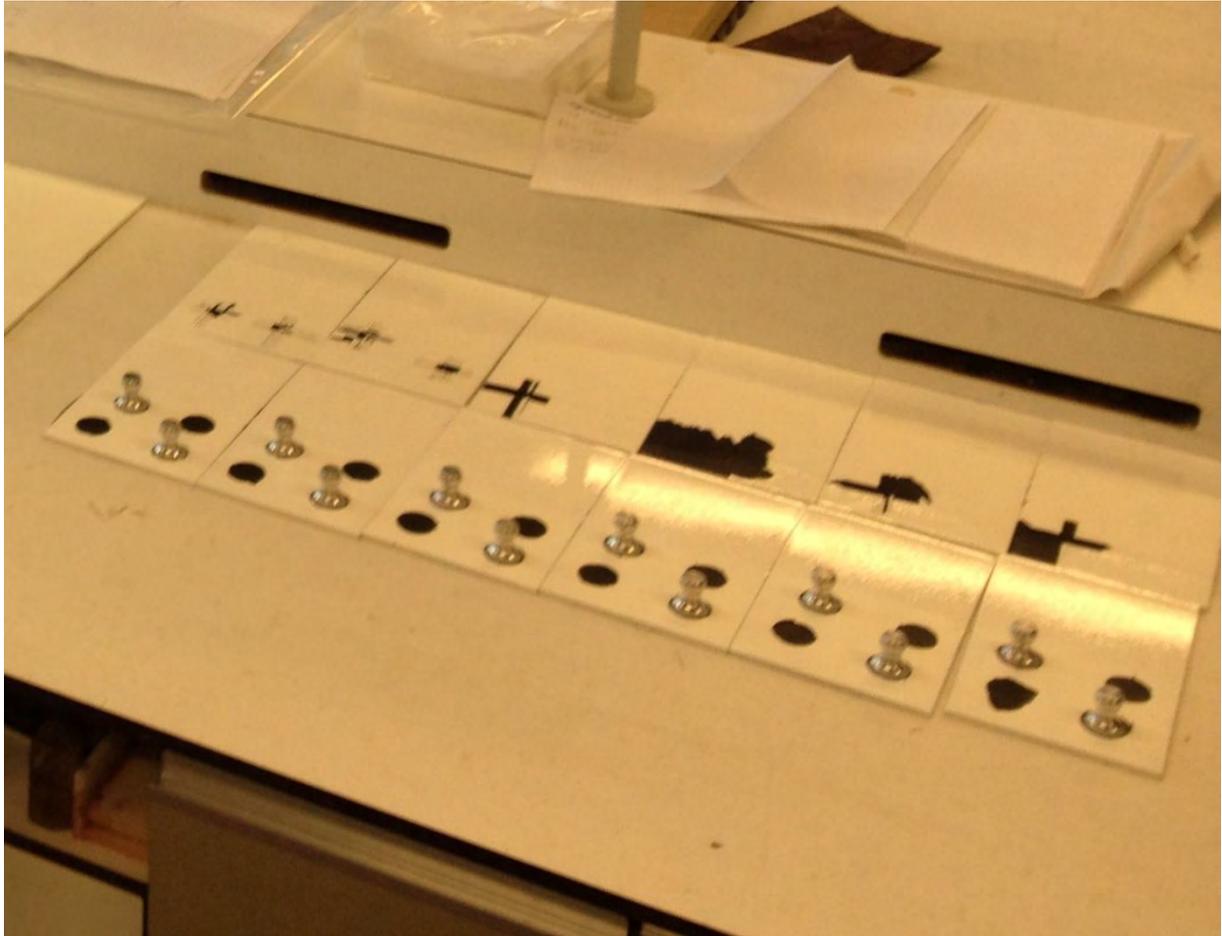


Figure 47. Panels after cross-cut classification. Hybrid powder coating applied on panels treated with varying  $N_2$  treatment times. Application after 36 days, storage under water. Classification left to right: 3-3-5-5-5-5

# Professorship for Polymer Engineering

The Professorship for Polymer Engineering of University of Applied Sciences Windesheim was founded in 2009; the group's objective is to improve the knowledge base on sustainable processing of plastics and composites within and through the higher education system. Its primary function is as a research group in Polymer Engineering, delivering output in the field of applied science. The team operates within market based projects and comprises lecturers from Civil Engineering, Industrial Product Design and Mechanical Engineering. The output of the projects is integrated into the curriculum of these study programmes.

The team has worked on Powder Coating on Plastics since 2014. This report describes the effects of gas plasma treatments to improve adhesion of the coating on the plastic substrate.

