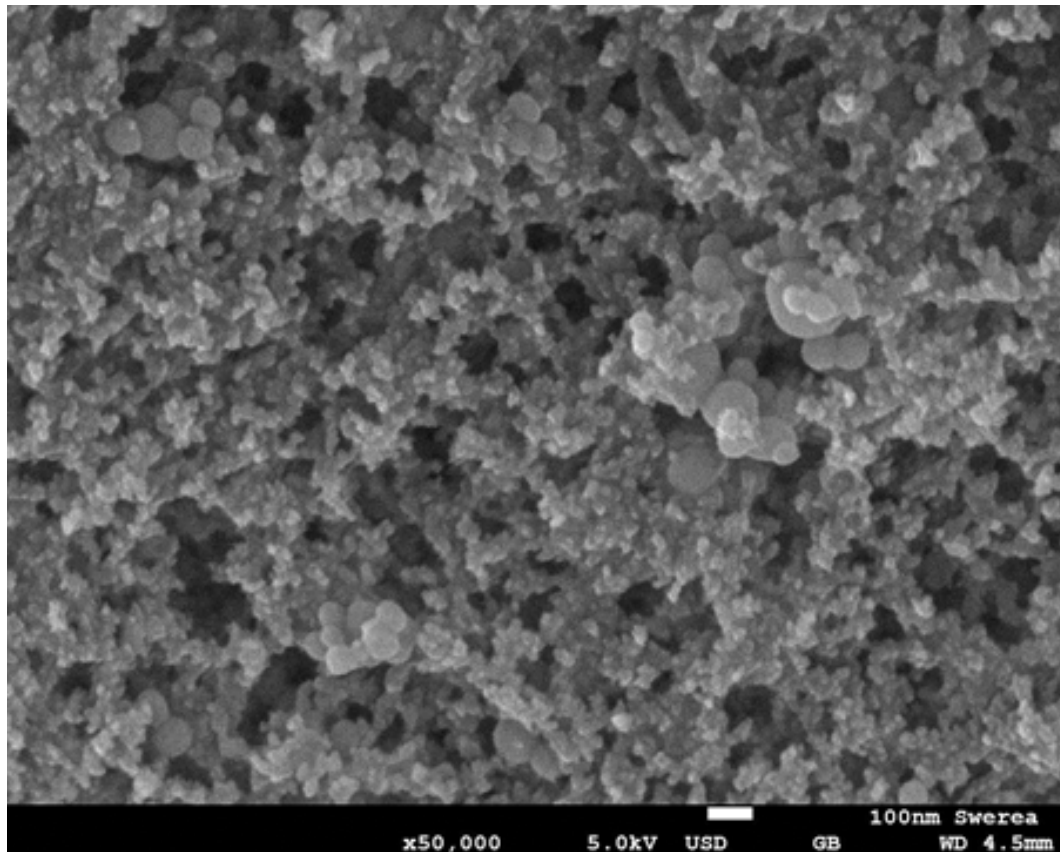


CHALMERS



Creating super hydrophobic surfaces for
moisture protection of biobased
composites

*Master of Science Thesis in the Master's Programme Materials
Chemistry and Nanotechnology*

EMELIE BENGTTSSON

Department of Chemical and Biological Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2013

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EMELIE BENGTTSSON

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Department of Chemical and Biological Engineering

Chalmers University of Technology

SE-412 96 Göteborg

Sweden

Telephone + 46 (0)31-772 1000

Cover: [A SEM image at x50,000 magnification of an unworn epoxy-containing coating which has been hydrophobized by Ruco-guard AFR 6. More information can be found in figure 4.9.]

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Master of Science Thesis

Super hydrophobic surfaces for moisture protection of biobased composites

EMELIE BENGTTSSON

Examiner: Prof. Anders Palmqvist
Supervisor: Karin Lindqvist

This work was performed at Swerea IVF AB, Mölndal, Sweden

swerea|IVF



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Department of Chemical and Biological Engineering
Division of Applied Surface Chemistry
Chalmers University of Technology
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Abstract

Polymer composites are useful construction materials due to their favorable properties. Due to an increasing price as well as the recognition of the environmental burden of petroleum-based composites the interest of biobased polymeric composites has increased. One major problem with these composites is, however, their susceptibility towards moisture penetration. The absorbed water causes weight gain and can lead to an acceleration of the degradation process.

A super hydrophobic coating could possibly be used to protect the composites from the water penetration. These coatings can be created by mimicking the surface roughness of lotus leaves. Super hydrophobic surfaces have been created in many different ways, however, none have been satisfactory industrially applicable. Plasma technology is an industrially applicable technique which possibly could improve the bond strength between the surface and the super hydrophobic coating by activating the substrate surface.

The aim of this master thesis was to create a super hydrophobic coating on a biobased composite by using silica nanoparticles, polymer binders and hydrophobizing agents. The influence of various parameters of the systems; such as particle size, surface modification, polymer binder type and hydrophobization agents were evaluated. Polydimethylsiloxane (PDMS) and epoxy resin were examined as possible polymer binders and different fluor-containing chemicals were examined as potential hydrophobization agents for the epoxy system. The wear resistance and the super hydrophobic properties of the coating were evaluated by a modification of the Martindale abrasion test method and dynamic contact angle measurements, respectively.

The results showed that a system using epoxy resin as polymer binder and the commercial Ruco-guard AFR 6 as hydrophobization agent created the most wear resistant super hydrophobic coating. Plasma treatment proved to be unessential to create a strong bonding between the coating and the substrate.

A system using the polymer binder PDMS showed to exhibit lower wear resistance than the epoxy system. Different plasma pre- and after-treatments were investigated in hope of increasing the bonding strength between the coating and the surface, without success.

Keywords: biobased composite, super hydrophobic, silica nanoparticles, PDMS, epoxy, plasma treatment, wear resistance

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1

Introduction

POLYMER COMPOSITES is a useful group of materials due to their light weight combined with their high strength & stiffness, corrosion resistance and their ability to be tailored into different shapes (GangaRao & Vijay 2010). These properties have led to an increasing use of polymer composites as construction materials for wind mills, bridges and for automotive applications. During recent years the increasing price as well as the recognition of the environmental burden of petroleum-based composites have led to an increasing interest of biobased composites (Zhan & Wool 2010). One major problem with biobased polymeric composites, as for all polymeric composites, is their susceptibility towards moisture penetration. The absorbed water causes weight gain and can lead to an acceleration of the degradation by lowering of the glass transition temperature, plasticization and reduction of the fiber-matrix interfacial bonding (Moalli 2001).

One possible way to solve the problem of moisture sensitivity is to create a highly water repellent surface. This has been achieved in many ways for different kinds of materials by mimicking the surface roughness of the self-cleaning lotus leaves. The surface structure of the leaves enables entrapment of air between water droplets and the surface. This contributes to less wetting and adherence between the water droplets and the surface, thus creating a highly water repellent surface (Ma & Hill 2006). A combination of this surface structure and a hydrophobic outermost molecular layer has proven to create super hydrophobicity. Various techniques have been used to manufacture super hydrophobic surfaces on different kinds of materials. In numerous studies surface roughness has been created on a low surface energy material, through e.g. oxygen plasma treatment, laser etching or nanocasting. Other studies have first created a favorable roughness, through e.g. etching or electrochemical deposition of particles, which later has been modified with a low surface energy material (Ma & Hill 2006). Silica nanoparticles are one type of particle which has been used in numerous studies to build up these surface structures together with different polymer binders and hydrophobic agents. None

of the different manufacturing processes used has, however, been satisfactory industrially applicable which means that an easy and effective method for producing this type of surface in a large scale is still missing.

One technique which is industrially applicable and which could be used for modifying this type of surfaces is plasma treatment. The plasma treatment can activate the surface which possibly could improve the bond strength between the surface and the super hydrophobic coating making the coating more robust.

It is important that the super hydrophobic coating is robust since it should be able to resist typical wearing conditions in its field of application. The micro- and nanostructures of super hydrophobic surfaces often results in a coating which easily can become distorted by abrasion. Surface abrasion can also lead to detachment of the hydrophobic layer which consequently reduces the surface water repelling properties (Xiu et al. 2012).

1.1 Aim

This project aims to prevent moisture penetration of biobased composites by creating a super hydrophobic surface. An important requirement is that the coating system is industrially applicable in large scale. The surface coating will be created by applying a dispersion of silica nanoparticles in a polymer binder solution. The influence of various parameters of the systems; such as particle size, surface modification, polymer binder type and hydrophobization agents will be evaluated. The coating should be both robust as well as super hydrophobic. These properties will be evaluated by a modification of the Martindale abrasion tester method respectively dynamic contact angle measurements. The influence of vacuum plasma treatment will also be studied as a possible method to increase the performance of the coating.

2

Theory

IN THIS SECTION a short introduction to important expressions, phenomena and techniques will be given to increase the understanding of this thesis. It will start with describing the basic concepts of hydrophobicity and continue with a description of plasma technology. Finally ways of creating super hydrophobic surfaces will be described.

2.1 Hydrophobicity

Solid surfaces are often defined in terms of hydrophilicity or hydrophobicity which describes the materials ability to be wet by water. A surface which is easily wet by water is referred to as hydrophilic while a surface which is unwettable is considered to be hydrophobic. These different behaviors can be correlated to the surface energies of both the water and the solid material.

Other factors that may influence the wetting behavior can be the parameters of the surface structure such as porosity, roughness, chemical heterogeneity or reactivity (Holmberg et al. 2002).

2.1.1 Surface energy

The surface free energy of a material, for liquids often called surface tension, depends on the intermolecular forces within the material. A strong interaction between the molecules gives a material with a high surface free energy and vice-versa. Water, as an example, has a high surface tension of approximately 73 mN/m due to its ability to form strong hydrogen bonds within itself (Holmberg et al. 2002). The biobased composite used in this thesis exhibits a surface energy corresponding to that of the unsaturated polyester resin which is approximately 45 mN/m (Dhakal et al. 2012). The fibers within the composite do not affect the surface energy as they are completely embedded in the polymer matrix.

The degree of wetting and thus the contact angle (θ), is controlled by the surface tension of the liquid (γ_{lv}) the surface free energy of the solid (γ_{sv}) and the interfacial tension between the two medium (γ_{sl}) according to Young's law, equation 2.1, which is displayed schematically in figure 2.1. To obtain a high contact angle towards water, hence exhibit a hydrophobic character, a material must have a low surface energy.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2.1)$$

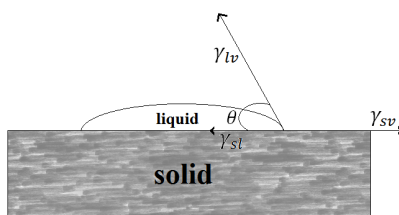


Figure 2.1: A schematic picture of the parameters included in Young's law

2.1.1.1 Molecular interactions

The strength of the intermolecular forces depends on the nature of the molecular interaction. Hydrogen bonding, i.e. the bonding which occurs between hydrogen atoms that are bonded to nitrogen, oxygen or fluorine atoms, is the strongest intermolecular interaction. The attraction between the partial charges in polar molecules, dipole-dipole interaction, and the attraction between instantaneous fleeting dipole moment of nonpolar molecules, van der Waals forces, are weaker examples of intermolecular forces. However, none of the intermolecular forces are close in magnitude to the strength of intramolecular forces, e.g. covalent bonding. Table 2.1 displays typical dissociation energies, i.e. the energy required to break the bond, for the different types of interactions (Atkins & Jones 2008).

Table 2.1: Typical dissociation energies for different types of molecular interactions (Atkins & Jones 2008).

Type of interaction	Dissociation energy (kJ/mol)
Covalent	400
Hydrogen bonds	20
Dipole-dipole	0.3-2
van der Waals forces	2

2.1.2 Contact angle

The contact angle is the angle between the liquid and the solid which appears when the solid is not completely wetted, as can be seen in figure 2.1. A low contact angle indicates a good wetting, hence a hydrophilic surface and vice versa. A stationary contact angle can easily be determined by using a contact angle goniometer, which is explained in more detail in chapter 3.2.

However, the static contact angle alone is not sufficient when describing the hydrophobicity of a surface (Chen et al. 1999). In fact, both the advancing (increasing the volume of the drop) and the receding (decreasing the volume of the drop) angles must be taken into account since a high stationary contact angle does not always guarantee a poor water-surface adhesion (Miwa et al. 2000). This surface adhesion can be evaluated by examining the sliding contact angle. The sliding angle is the angle needed for a droplet of a specific size to start sliding down a tilted surface. A low sliding angle correlates to poor adhesion and vice versa. The contact angle hysteresis, i.e. the difference between the advancing and receding contact angle, has shown to be important when assessing the hydrophobicity. Surfaces with high advancing angle but low receding angle may show poor hydrophobicity and leave water drops “pinned” to the surface (Youngblood & McCarthy 1999).

Equation 2.2 describes the force needed for a drop to start sliding over a solid surface. In this equation α is the sliding angle, γ_{lv} is the surface tension of the liquid, θ_R/θ_A is the receding respectively advancing angle, d and m is the diameter respectively the mass of the droplet and g is the gravitational acceleration (Chen et al. 1999). An illustration of some of these parameters can be seen in figure 2.2. The equation implies that a surface with very low hysteresis also will have a very low sliding angle, regardless of the magnitudes of the different contact angles (Youngblood & McCarthy 1999).

$$F = \frac{mgs\sin\alpha}{d} = \gamma_{lv}(\cos\theta_R - \cos\theta_A) \quad (2.2)$$

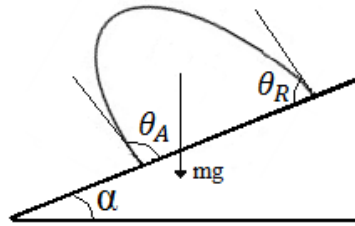


Figure 2.2: An illustration of some of the parameters influencing the force needed for a drop to start sliding down a tilted surface.

2.1.3 Super hydrophobicity

A surface is often considered as super hydrophobic when it exhibits a contact angle above 150° and a low sliding angle (and thereby a low contact angle hysteresis) (Nosonovsky & Bhushan 2009, Quéré et al. 2003). This behavior exists in the nature and is called the “lotus effect”, named after the leaves of the lotus plant which show excellent water-repelling capacity. The underlying cause of its super hydrophobicity has been correlated to the leaves surface roughness in both nanometer- and micrometer-scale as well as the low surface energy of the outermost molecular layer, which consists of wax crystals (Ma & Hill 2006).

There are two hypotheses to explain this enhanced hydrophobicity by surface roughness phenomena. One of these theories is the Wenzel model which describes the wetting when the liquid fills the cavities of the surface, figure 2.3 (a). In this model the static contact angle will increase due to the increasing surface area of the roughened surface, compared to the surface area of a smooth surface. The increase can be described by equation 2.3 where θ^* is the apparent static contact angle, θ is the static contact angle if the surface would be ideally smooth and r is the ratio between the actual surface area and the projected surface area (Quéré et al. 2003).

$$\cos\theta^* = r\cos\theta \quad (2.3)$$

The other theory is the Cassie-Baxter model which relates to the case where air is trapped in the pockets underneath the liquid drop, which is shown in figure 2.3(b) (Lafuma & Quéré 2003). Here the rough surface is considered to be a porous hydrophobic material unfavorable for the liquid to penetrate. This leads to the entrapment of air, which can be considered as a hydrophobic phase, and thereby a higher exhibited contact angle of the liquid (Quéré et al. 2003).



Figure 2.3: The different wetting models (a) Wenzel and (b) Cassie-Baxter (Yan et al. 2011).

A drop in the Wenzel state have been shown to adhere more to the substrate compared to a drop in the Cassie-Baxter state, even if it exhibits a higher static contact angle (Quéré et al. 2003). This is due to the filling of the surface cavities by water. The air-pockets in the Cassie-Baxter state gives fewer points of contact which leads to lower adhesion and thereby lower contact angle hysteresis. This consequently gives lower sliding angles and a better water repelling surface (Quéré et al. 2003).

2.2 Plasma treatment

Plasma is a state of matter which consists of a mixture of electrons, positive and negative ions, atoms, molecules, radicals and photons all together in one. The plasma shows a collective behavior due to long-range Coulomb interactions and is sometimes referred to as the fourth state of matter (Perucca 2010). The generation of plasma involves appliance of energy onto a gas with the purpose of rearranging the electronic structure of the atoms and molecules as well as producing excited species and ions (Tendero et al. 2006).

There are two types of plasma treatments available today. One is called thermal or hot plasma, and relates to plasma in thermal equilibrium. This means that all the different species have the same temperature, the thermodynamic equilibrium temperature, due to an efficient collision frequency within the plasma. Consequently, hot plasma has a high energy content which limits the use to thermally stable inorganic materials. The other classification of plasma is non-thermal or cold plasma. This, unlike hot plasma, relates to plasma which is not in thermal equilibrium and therefore contains species with different temperatures. The electrons possess a high temperature while the ions and neutral species exhibit almost ambient temperature. Since the electrons cannot efficiently heat the larger species, the plasma stays close to room temperature. This enables the plasma to be used for thermally unstable materials such as plastics (Perucca 2010). Hence, non-thermal plasma will be used for treating the plastic composite in this master thesis.

2.2.1 Vacuum plasma

Vacuum plasma can be generated by applying electromagnetic energy upon a process gas which is kept at a sufficiently low pressure. Depending on the frequency of the electromagnetic energy, different pressures of the process gas is needed. A frequency in the radio wave range typically requires that the process gas is kept below 0.1mbar whereas microwave frequencies can utilize pressures between 0.5-1mbar (Lippens 2007). To obtain and maintain these low pressures a vacuum pump is needed which results in a batch-wise process.

2.2.2 Plasma surface treatment

Plasma treatment can be used for modifying material properties in many different ways. The treatment is limited to the outermost layer of the surface thus protecting the bulk material from being affected (Perucca 2010). It can induce grafting and polymerization as well as perform etching and sterilization of the surface. An increase or decrease of the surface activity of the substrate can also be obtained by introducing different precursors before, in or after the plasma zone (D'Angelo 2010). This makes it possible to tune properties such as the surface adhesion and wettability.

The underlying cause for the wide range of modification possibilities lies in the high amount of chemically active species in the plasma which easily react with the processed

surface. Furthermore, the high temperature of the electrons in the plasma leads to a decrease of the activation energy thresholds which can promote chemical reactions which would otherwise need catalysts or a very high energy input (Perucca 2010).

Due to the high reactivity of plasma; the duration and power of the plasma treatment is of great importance. A prolonged treatment time and/or a high intensity may result in etching and degradation of a polymer substrate due to chain scissions in the bulk (Hegemann et al. 2003).

Plasma treatment using oxygen as processing gas will temporarily increase the surface energy of a substrate due to an incorporation of oxygen-containing groups to the surface. This effect is, however, only temporarily since nature always pursues having as low energy as possible. The material will eventually return to a lower level of surface energy by reorienting the newly created groups into the bulk, a phenomena usually known as ageing (Buyle et al. 2010).

Plasma treatment can also activate a substrate by creating radicals upon its surface. These radicals are very reactive and can be utilized to graft different species onto the surface (Kumar et al. 2010). This method could thereby be utilized to bind a coating onto a substrate.

2.3 Creating super hydrophobic surfaces

Super hydrophobic surfaces can be created in many different ways by combining surface roughness and low surface energy. The focus in this thesis has been to use a combination of silica particles, polymer binders and hydrophobizing agents. This section will describe the materials used as well as present how super hydrophobic surfaces have been created in previous studies.

2.3.1 Silica

Silica consists of tetrahedral $[\text{SiO}_4]^{4-}$ which are connected by Si-O-Si bridges. The surface of silica is very easily modified owing to its silanol groups, i.e. Si-OH. These groups exist mostly at the surface and only to a limited amount in the bulk. The silanol groups affect the charge as well as the reactivity of the surface which can be utilized to functionalize the surface in different ways (Cademartiri & Ozin 2009).

An increase of the number of silanol groups present, and thus an increase in the surface reactivity, can be achieved by exposing the silica to oxygen or air plasma treatment. The plasma treatment breaks the Si-O-Si bridges which gives an increase in concentration of silanol groups according to the equilibrium reaction which can be seen in figure 2.4. This increase, however, is temporary and exposure to air leads to a return to the equilibrium level within a few hours. If instead a decrease of the silanol groups is desired; the silica can be heat treated. The applied heat will condense the silanol groups and form Si-O-Si bridges (Cademartiri & Ozin 2009).

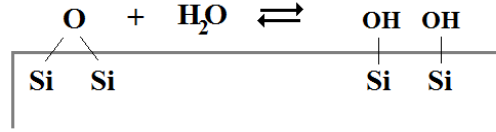


Figure 2.4: The equilibrium reaction present at the surface of silica.

2.3.1.1 Surface modification of silica

Silica is often utilized in the form of silica sols which is a colloid dispersion with solid silica particles suspended in an aqueous phase. The sol can be used in sol-gel reactions where a combination of hydrolysis and condensation is used to create oxide structures (Cademartiri & Ozin 2009). The basic concepts of the sol-gel reaction are displayed in figure 2.5 below.

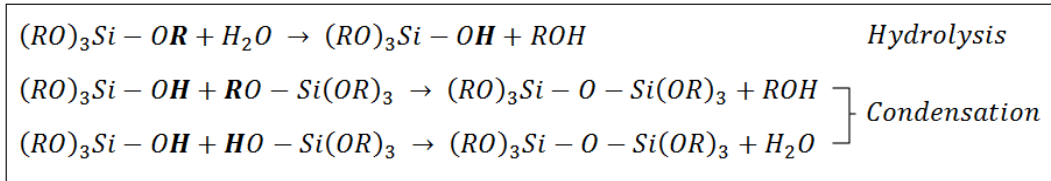


Figure 2.5: The basic concept behind silica sol-gel chemistry.

Silica particles can easily be hydrophobically functionalized with different kinds of silanes. This modification occurs through a dehydration reaction between the silanol groups of the silica surface and the silane as shown schematically in figure 2.6.



Figure 2.6: The dehydration reaction between the silanol groups of the silica and a silane.

2.3.2 Polymer binder

Polymer binders can be used to increase the robustness of a coating by bonding with the surface. The polymer binders can also contribute to a better dispersed silica particle dispersion as they will adsorb to the silica/solvent interface and stabilize the dispersion (Holmberg et al. 2002). The polymer binders used in this thesis is polydimethylsiloxane and epoxy resin.

2.3.2.1 Polydimethylsiloxane

Polydimethylsiloxane (PDMS) is a polymer which is built up of dimethylsiloxane, figure 2.7. It is inert and heat resistant and has mechanical properties which can be tuned by controlling the length of the polymer chains, branching and crosslinking. Contrary to silica, PDMS has a very low concentration of silanol groups at the surface. Instead methyl groups reside at the interface rendering low surface energy and a very hydrophobic character. Due to the low surface energy of the material, poor adhesion towards other surfaces often becomes a problem. This can, however, be solved by exposing the PDMS to oxygen or air plasma treatment. As for silica, the plasma treatment increases the density of silanol groups on the surface of PDMS giving it a higher surface energy and thus generally a better adhesion to other surfaces (Cademartiri & Ozin 2009). There is, however, also a risk of decreasing the hydrophobicity of the PDMS surface.

When a PDMS layer, spread over a plasma pre-treated glass substrate, is exposed to plasma treatment the chemical bonds within the PDMS break and recombine with the active species on the glass surface. This results in a formation of a coating consisting of methyl groups as well as different hydrophobic groups containing silicon. As for all plasma treatment there is always a risk of over treating the material. An excessive treatment will lead to plasma etching which will destroy the formed bonds between the surface and the PDMS (Zhi et al. 2007).

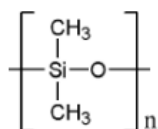


Figure 2.7: The monomer dimethylsiloxane builds up PDMS.

2.3.2.2 Epoxy resin

Epoxy is a thermosetting polymer which contains reactive epoxy-groups, shown in figure 2.8. It is generally produced through a condensation reaction between epichlorohydrin, bisphenol-A and a curing agent.

Epoxy resins are commonly used as strong, fast-setting adhesives, as heat resistant coatings/binders or in reinforced plastics (Gooch 2011).

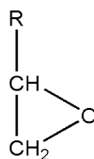


Figure 2.8: The reactive epoxy-group which is found in epoxy polymers.

2.3.3 Hydrophobizing agent

Fluor-containing compounds work as excellent hydrophobizing agents due to their low surface energy. Their high reactivity also enables a relatively high bonding strength towards the sample surface (Atkins & Jones 2008).

Perfluorinated compounds are, however, environmentally harmful since they are persistent materials and in some cases bioaccumulative. The bioaccumulation has proven to be correlated to the length of the carbon chain. If the chain consists of 8-12 carbons the perfluorinated compound is considered bioaccumulative (Kemikalieinspektionen 2006).

Different types of fluor containing chemicals such as fluor plasma, fluorosilanes and fluorocarbons can be used to hydrophobize a surface.

2.3.4 Literature review

Many techniques have been developed over time to successfully mimic the lotus effect. These can often be divided into two categories; roughening of a surface with low surface energy or modifying an already rough surface with a low surface energy material (Ma & Hill 2006).

Ming et al. created a super hydrophobic film by grafting silica-based raspberry-like particles onto an epoxy-based polymer via silica nanoparticle suspensions and an automatic film applicator. An additional hydrophobization by grafting of PDMS was needed to reach the super hydrophobic region. The stability of the coating was tested by immersing the substrate in water overnight followed by a measuring of the different contact angles. No alternation of the surface wetting properties was detected (Ming et al. 2005).

Xiu et al. used a mixture of silica nanoparticles and epoxy resin to coat glass slides via dip coating. After curing the polymer coating was subjected to oxygen plasma to expose the embedded silica particles and thereby create a surface roughness. The roughened surface was then hydrophobized by treatment with a fluorosilane to render a super hydrophobic coating. To examine the robustness of the coating an abrasion test was performed by sliding the sample 25 cm along a technicloth wiper with the applied pressure of 3.45 kPa. The effect was measured by means of contact angle and contact angle hysteresis and it was found that the sample was affected only to a very little extent (Xiu et al. 2012).

Ke et al. have fabricated a super hydrophobic surface by sequential drop coating of silane-modified-silica solutions onto glass substrates. This was followed by a hydropho-

bization with PDMS. The robustness of the coating was evaluated by a shear resistance test where a flat PDMS elastomer, with an applied pressure of 10-18 kPa, was slid along the surface of the test sample. The test resulted in only a small alteration of contact angle and sliding angle suggesting that the coating was robust. The authors claim that the robustness was created by the layer of PDMS which, besides introducing more hydrophobicity, also enhanced the robustness by enabling a linkage between itself and the silica particles (Ke et al. 2011).

Sun et al. fabricated super hydrophobic films by assembling silica micro- and nanoparticles on glass substrates. Two methods were used to create surface roughness that mimic the lotus leaves. One approach was to use 8 μm sized silica particles as a template that was coated with smaller particles by electrostatic deposition. The other approach was based on casting a PDMS mold on the template particles array. The mold was then used to cast a suspension of silica nanoparticles on the glass substrates. The silica structures were coated with a fluoroalkyl silane in order to obtain a hydrophobic behavior. High contact angles, $161\pm 0.5^\circ$ were obtained for the second approach. This could be compared to the result for the structure created by the first approach which obtained a contact angle of $148\pm 0.5^\circ$. The difference may be explained by the larger porosity included in the micrometer sized spherical structure consisting of silica nanoparticles particles (Sun et al. 2007).

Karapanagiotis et al. investigated the effect of particle size on the hydrophobicity of polymer-particle films. Alumina particles of different size ranges (20-30nm, 27-43nm, 150nm) were dispersed in a siloxane solution which was sprayed onto a glass substrate to create the super hydrophobic coating. It could be concluded that all of the particle size ranges could result in super hydrophobicity if a high enough particle concentration was used. The concentration required for super hydrophobicity was named critical particle concentration (CPC) and was correlated to the specific surface area of the particles. A particle with low specific surface area needs a higher particle concentration than a particle with a higher specific surface area to create the needed surface roughness for super hydrophobicity (Karapanagiotis et al. 2012).

The referred articles are examples of research involving the use of silica particles and a polymer binder to achieve super hydrophobic surfaces, which has been a successful approach in many cases. The silica particles were used to create the "porous" structure necessary for enabling air entrapment. The polymer has contributed to a robustness to the system and in some cases also hydrophobized the silica structure. This literature review makes up the background for the choice of silica nanoparticles for building a structure and PDMS or epoxy for creating a robust surface coating in this study.

To create a particle structure with high porosity the opposite thinking of maximizing the packing density was used. To maximize the packing density there should be a large difference between the size of small and large particles so that the small particles can fill the interstices between the large ones. The proportion of small particles should not be too large around 20 wt.% (Randall 1989). The opposite thinking meant that the amount of small particles was the double of the large ones (by weight) i.e. the ratio of

large/small particles was set to 0.5. Also, when considering the particle sizes chosen the large particles were 100 nm and the small particles 12-16 nm which gave a size difference of 1: 6-8. Particles in the nanometer range were chosen since agglomerates easily form which also could contribute to the porous structure that is desired in order to create a super hydrophobic coating.

A system with all components included and a coating procedure with as few steps as possible is desired in order to make it industrially applicable, economically feasible and robust. The property "robustness" is ambiguous. It should include aspects of withstanding wear and abrasion as well as retained properties over time. In this work it also includes the coating procedure which should be robust in the sense that a coating with repeatable properties is obtained.

3

Materials and Methods

IN THE FOLLOWING section the materials and methods used in this master thesis will be explained in short. The coating procedure and the dispersion manufacturing will be described to enable reproduction of the coatings. General recipes for the dispersions can be found in appendix A.

3.1 Materials

Four main types of materials were used; the biobased composite, silica particles, polymer binders and hydrophobization agents.

The biobased composite used in this master thesis was produced at Swerea SICOMP in Piteå and consisted of a matrix of the unsaturated polyester resin Envirez with fibers manufactured from linen.

Many different kinds of silica particles were used in the experiments. In table 3.1 the different particles used can be found together with information of size, modification and manufacturer.

Table 3.1: The different silica particles used in this master thesis.

Name	Producer	Specific surface area [m ² /g]	Size range [nm]	Modification
NanoSilica Powder Grade 999	Elkem	45-60	~100	Unmodified
Sidistar T120U	Elkem	20	~100-150	Octyltriethoxysilane
Aerosil 200	Evonik	200 ±25	~12	Unmodified
Aerosil R972	Evonik	110 ±20	~16	Dimethyldichlorosilane

Two different polymer binders were used in this thesis; polydimethylsiloxane and epoxy resin. The polydimethylsiloxane used was a two part silicone elastomer called Sylgard 184 which was provided by Dow Corning. The epoxy resin was also a two part system with the base NM Laminering 625A and the curing agent NM Härdare 650 M both provided by Nils Malmgren AB. The solvent used for the PDMS containing dispersions was cyclohexane provided by Fisher Scientific with a percentage of purity of 99.99. For the epoxy containing dispersions methyl ethyl ketone was used as the solvent. It was provided by Merck KGaA with a percentage of purity of 99.5.

Hydrophobization of the silica/epoxy containing system was performed by applying a fluorocarbon containing substance on top of the particle coating. Three types of fluorocarbon films were evaluated:

1. Fluor plasma - The fluor plasma was created in a vacuum plasma by using the process gas CF_4 .
2. Fluorosilane - The fluorosilane used was called (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trimethoxysilane and was provided by Gelest, Inc.
3. Ruco-guard AFR 6 - Ruco-guard AFR 6 is a fluorocarbon-containing impregnation product intended for the use on textiles. It was provided as a waterborne emulsion by Rudolf Group.

3.2 Equipment

To evaluate the different plasma treatments characterizations through contact angle measurement, scanning electron microscopy and Martindale abrasion tests were performed. In this section short introductions to the different techniques will be provided.

Contact angle measurement

Both the static and the dynamic contact angles can be determined by using different variations of the sessile drop method. The method uses a contact angle goniometer to measure the angle by taking a picture of the drop on the surface with a microscope camera. This image is then analyzed by the software to determine the contact angle (David et al. 2010).

The contact angle measurement instrument used in the experiments was a Krüss DSA30E from Krüss GmbH which together with the accompanying software enabled the determination of dynamic contact angles. The advancing contact angle was measured for a drop volume increase between 10-20 μl and the receding contact angle was measured for a drop volume decrease between 20-10 . The majority of the resulting contact angles were based on three measured drops on five different samples from each sample group. Exceptions existed where the results were based on only three different samples from each sample group.

Scanning electron microscopy

Scanning electron microscopy (SEM) is an excellent method to create magnified images of the surface of a material. The technique creates the image by detecting the emitted species which arise when a surface is bombarded with an electron beam. The electron beam causes various kinds of emitted species; primary backscattered electrons, primary electrons, secondary electrons, Auger electrons and electrons of the continuum (Lampman et al. 2010). Of these only the backscattered electrons and the secondary electrons are used to form the SEM image.

The SEM analyses were performed by Lars Eklund at Swerea IVF in a JSM-7800F from JEOL. Before measurement the samples were coated with a 1 nm thick Pt layer to prevent charging of the substrates. Measurements were carried out on samples from both the PDMS as well as the epoxy system. Both unworn and samples tested in the Martindale equipment were analyzed to establish possible differences in the coating structure.

Martindale abrasion test method

The Martindale test is usually used to determine the abrasion resistance of fabrics. The procedure is then performed according to the standard EN ISO 12947-2:1998 where the sample is mounted in a specimen holder and then rubbed against an abrasive medium under a specified load. This is continued until breakdown of the fabric occurs (EN-ISO-12947-2: 1998). The test method was modified to enable usage of solid composites as sample substrate.

The robustness tests were conducted in a Martindale abrasion tester from James H. Heal Co LTD where the composite substrates ($\sim 3 \times 3$ cm) were attached with double-coated adhesive tape onto a specimen holder. The samples were then rubbed against a Teflon baking sheet under a pressure of ~ 2.18 kPa corresponding to the weight of the specimen holder for a predetermined amount of cycles.

The test method was chosen to enable comparative measurements between the various coatings applied to the composite samples. The rubbing motion between the sample holder and the Teflon sheet gave an indirect measure of the "robustness" of the coating. The results indicated the adhesion of the coating to the substrate and/or the internal bonding strength of the coating itself.

Vacuum plasma

The vacuum plasma equipment used in the experiments was a Technics Plasma 440G from Technics Plasma GmbH with the physical parameters shown in table 3.2. The plasma source was a 2.45 GHz microwave generator.

The substrate was placed in the chamber which was evacuated to ~ 0.20 mbar before inlet of the chosen process gas. The plasma was ignited when the pressure had reached ~ 0.70 mbar and the treatment time was recorded manually from the plasma ignition.

Table 3.2: The parameters of the vacuum plasma equipment used.

Property	
Max Power	600W
Working Pressure	~0.5 mbar
Possible gases	Ar, CF ₄ , O ₂

Certain sample groups were pre-treated with vacuum plasma, for more information about the different sample groups see table 3.3. Both oxygen plasma and argon plasma was used for the pre-treatments. The effect of both plasma treatments was set to 300W and the exposure time was varied between 5-15s. To preserve the plasma treatment until coating; the samples were covered in aluminum foil which had been sterilized by 300W oxygen plasma for 15s. The plasma pre-treatment and the coating procedure were both carried out within 8 hours to prevent deactivation of the substrate.

When hydrophobizing the epoxy-containing coatings with fluor plasma, the substrates were treated in the vacuum plasma using CF₄ as the process gas. The samples were treated for 180s at 300W.

3.3 Coating procedure

Before coating the composite substrates were cleaned with ethanol to remove possible contaminations and thereafter exposed to chosen pre-treatments. The coating procedure was carried out by hand with an airbrush purchased at Biltema using different dispersions. The distance between the airbrush and the composite sample was approximately 30 cm and the nozzle was tuned to give a thin coating. The substrate was completely wetted by the dispersion and after solvent evaporation another thin layer was applied in the same manner. The solvent evaporation was detected by a whitening of the coating corresponding to the color of the silica particles. To give a rough estimate of the amount of dispersion applied to each substrate the sample container was weighed before and after coating. The procedure was repeated to ensure repeatability of the coatings.

Two different kinds of dispersions were used in this thesis; one using PDMS as the polymer binder and another using epoxy resin. However, the particle concentration for all dispersions was 2wt% and the weight ratio of large/small particles was 0.5. The particles/polymer binder weight ratio was varied between 0.5-5.0.

To generate a simple coating procedure with few process steps and easy handling; a dispersion containing both the silica particles and the PDMS components was manufactured. Cyclohexane was used as the solvent due to its ability to dissolve the two PDMS components as well as its high vapor pressure, which gave a fast evaporation upon airbrushing. The process of applying the epoxy-containing coating, on the other hand, was separated into two different steps. First a dispersion, containing the silica particles and the epoxy resin, was created by the use of methyl ethyl ketone as the solvent. This dispersion was applied to the substrate followed by a subsequent hydrophobization step.

To simplify the weighing of both the two highly viscous PDMS components as well the two highly viscous epoxy resin components; solutions of the components dissolved separately in respective solvent were manufactured. All the polymer binder component solutions contained 5wt.% of the specific component dissolved in either cyclohexane or methyl ethyl ketone. From these solutions the specific amounts of the components were weighed-in to the dispersions by considering the solution concentrations.

The general procedure of manufacturing the dispersions was:

1. Weigh-in the amount of polymer binder-base solution needed.
2. Dilute the polymer binder-base solution to desired dispersion volume.
3. Weigh-in the silica particles for the specific dispersion and add to the diluted polymer binder-base solution.
4. Expose the dispersion to ultra-sonic treatment for approximately 5 minutes under stirring to ensure well-dispersed silica particles.
5. Weigh-in the amount of polymer binder-curing agent solution needed.
6. Add the curing agent solution to the particle dispersion and stir for approximately 2 minutes.

Examples of more detailed recipes can be found in appendix A.

In the case of hydrophobization by fluorosilane, a dispersion of approximately 5 wt.% silane in methyl ethyl ketone was manufactured. This dispersion was applied to the composite sample in the same manner as the particle dispersion, however, only in one layer. In the case of hydrophobization by Ruco-guard AFR 6 the emulsion was diluted to 5 wt.% in distilled water before applying in the same manner as the fluorosilane. After hydrophobization by either the fluorosilane or the Ruco-guard AFR 6 the substrates were heat treated in a furnace at 160°C for 3 minutes.

A pre-treatment with oxygen plasma followed by a PDMS-curing agent dispersion was also conducted for a sample group of PDMS-containing coatings. The composites were then pre-treated with 300W oxygen plasma for 15s before a dispersion consisting of solely PDMS-curing agent and cyclohexane was applied. This was followed by an application of the original silica particle/PDMS dispersion. The two dispersions were of the same PDMS-curing agent concentration.

In table 3.3 the different sample groups examined in this project are described. A short explanation of the purpose of each specific experiment is also given in the table.

Table 3.3: An overview of the different sample groups investigated in this thesis. The first two sample groups concern experiments that could be applied to both the two systems while the other sample groups concern solely the PDMS- respectively the epoxy-system. Since PDMS is hydrophobic no hydrophobization was needed for these samples. The plasma column indicates whether or not plasma treatment was used for that specific sample group.

System	Particles	Binder	Hydrophobization	Plasma	Purpose
General	Unmodified 100+12 nm	PDMS			Evaluate optimal particle/binder weight ratio
	Unmodified 100 nm	PDMS			Evaluate influence of one size vs. mixture of particle sizes
PDMS	Modified 100+16 nm	PDMS			Compare the influence of hydrophobically modified particles with unmodified
	Unmodified 100+12 nm	PDMS		x	Evaluate the influence of different plasma pre- & after-treatments
	Unmodified 100+12 nm	PDMS+ curing agent		x	Evaluate the influence of plasma + PDMS-curing agent pre-treatment and compare to system with no pre-treatment
Epoxy	Unmodified 100+12 nm	Epoxy	CF ₄ plasma	x	
	Unmodified 100+12 nm	Epoxy	Fluorosilane	x	Compare hydrophobization agents in order to find the most efficient
	Unmodified 100+12 nm	Epoxy	Ruco-guard AFR 6	x	
	Unmodified 100+12 nm	Epoxy	Ruco-guard AFR 6		Evaluate the effect of plasma pre-treatment and compare to system with no pre-treatment

4

Results

THE RESULT can be divided into three parts. The first part deals with results concerning the particle/polymer binder structure that is built up. The following parts concern the results which are specific for the PDMS- respectively epoxy-system. To be able to estimate the increase in contact angle created by the coating it is relevant to know that the uncoated biobased composite exhibits a contact angle of approximately 88° .

4.1 Generally applicable results

The following results are generally applicable but were, however, all produced from PDMS-systems. The idea of particle sizes and the size relationship of large/small particles 0.5 turned out to be successful since the obtained particle structure turned out to give high contact angles when covered by a hydrophobic coating.

Different particle/polymer binder weight ratios

The optimal weight ratio between particles and polymer binder was investigated by measuring the dynamic contact angles of a series of different ratios. These results are displayed in figure 4.1.

A ratio of 2.5 yielded the most optimal coating. It obtained higher dynamic contact angles as well as a smaller contact angle hysteresis than the other weight ratios. The standard deviation was approximately 2 which indicated a small contact angle interval and thereby a good stability of the measurements.

Weight ratios above 2.5 resulted in less homogenous particle dispersions which formed two more defined phases. The silica particles resided in a more viscous phase than the solvent and polymer binder. This made it more difficult to apply an even coating since the low viscosity phase easily passed through the nozzle while the high viscosity phase tended to clog the nozzle.

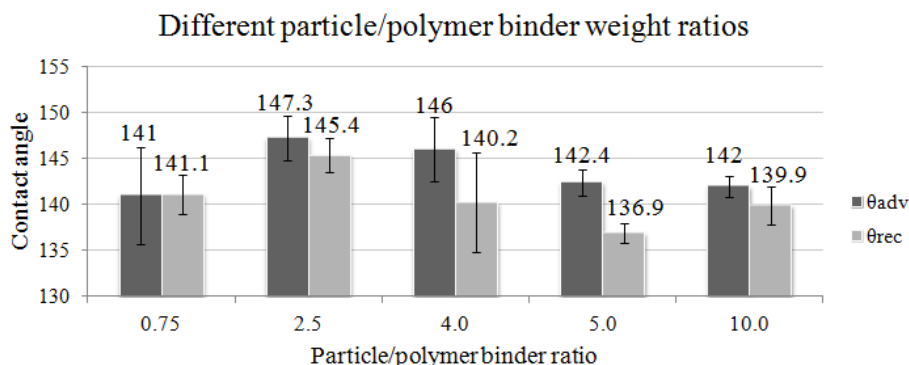


Figure 4.1: A comparison of the dynamic contact angles for coatings with different particle/polymer binder weight ratios. The weight ratio 2.5 gives the highest dynamic contact angles as well as the smallest contact angle hysteresis. The results for ratio 2.5 & 4.0 are based on 3 measurements on 5 different samples while the results for the other ratios are based on 3 measurements on 3 different samples from each sample group.

In figure 4.2 SEM images of the 2.5 weight ratio coating at $\times 10,000$ respectively $\times 100,000$ magnification are displayed. The images show a "porous" surface structure with different levels of roughness.

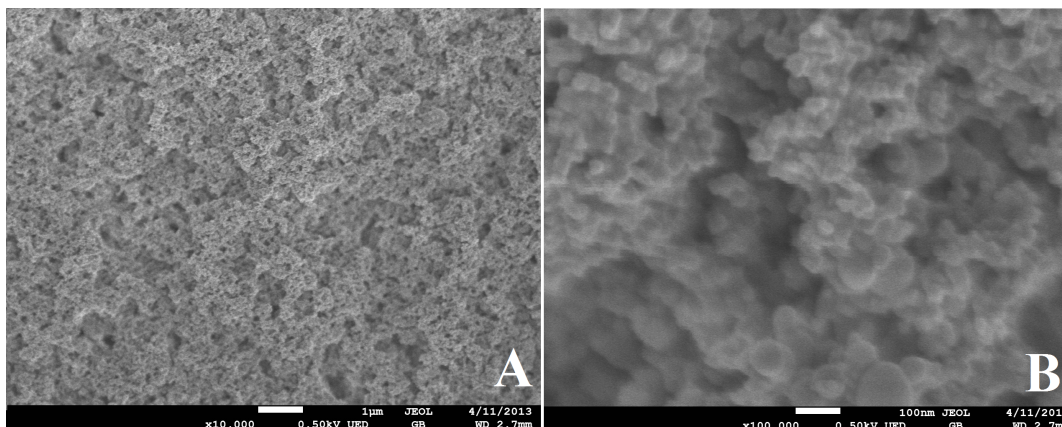


Figure 4.2: SEM images at $\times 10,000$ (A) respectively $\times 100,000$ (B) magnification of a coating with the particle/polymer binder weight ratio 2.5 showing multiple levels in the surface structure.

Large particles vs. mixture in particle sizes

An experiment using dispersions with two different particle compositions was conducted in order to examine the influence of particle size on the wear resistance of the coatings. One dispersion contained solely large particles with the size of about 100 nm while the other dispersion contained a mixture of the large particles and smaller particles of

approximately 12 nm. The weight ratio of large/small particles was set to 0.5. The wear resistance of the different samples was evaluated by the difference in dynamic contact angles before and after treatment in the Martindale equipment. The results from the measurements are displayed in figure 4.3.

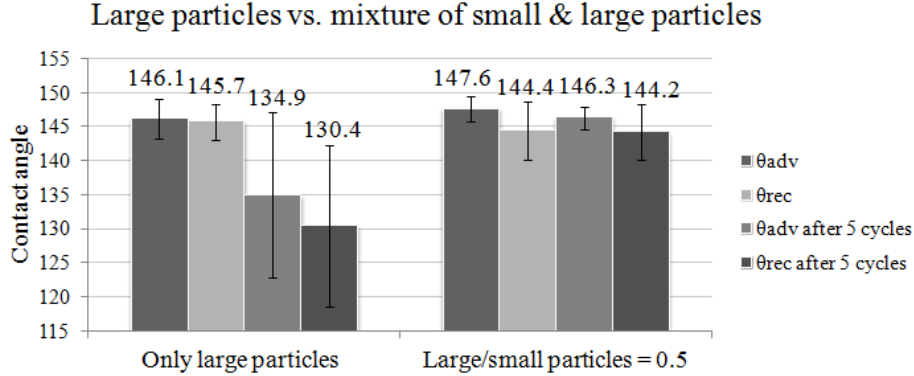


Figure 4.3: A comparison of the wear resistance of a coating containing solely large particles and a coating with a mixture of small and large particles. The coating consisting of a mixture of large and small particles exhibit better results after 5 cycles in the Martindale equipment than the coating containing solely large particles. These results are based on 3 measurements on 5 different samples from each sample group.

The coating which consisted of only large particles showed a lower wear resistance than the coating with a mixture of particle sizes. Already after 5 cycles in the Martindale equipment the large particle coating appeared to be very worn and exhibited low dynamic contact angles as well as high standard deviations.

4.2 PDMS system

In the following section results which solely concern the system using PDMS as the polymer binder as well as the hydrophobizing agent will be presented. Pure PDMS coating without silica particles exhibits a contact angle of 110° .

Different plasma pre- & after-treatments

To investigate if plasma treatment could have an effect on the wear resistance of the coating a series of different plasma pre- and after-treatments were carried out on coatings with particle/PDMS weight ratio 2.5. The different pre-treatments used were oxygen respectively argon plasma for 15s at 300W whereas the after-treatment solely consisted of argon plasma for 5s at 300W. The wear resistance was evaluated by the difference in dynamic contact angles before and after test in the Martindale equipment. Figure 4.4 shows the result from these measurements.

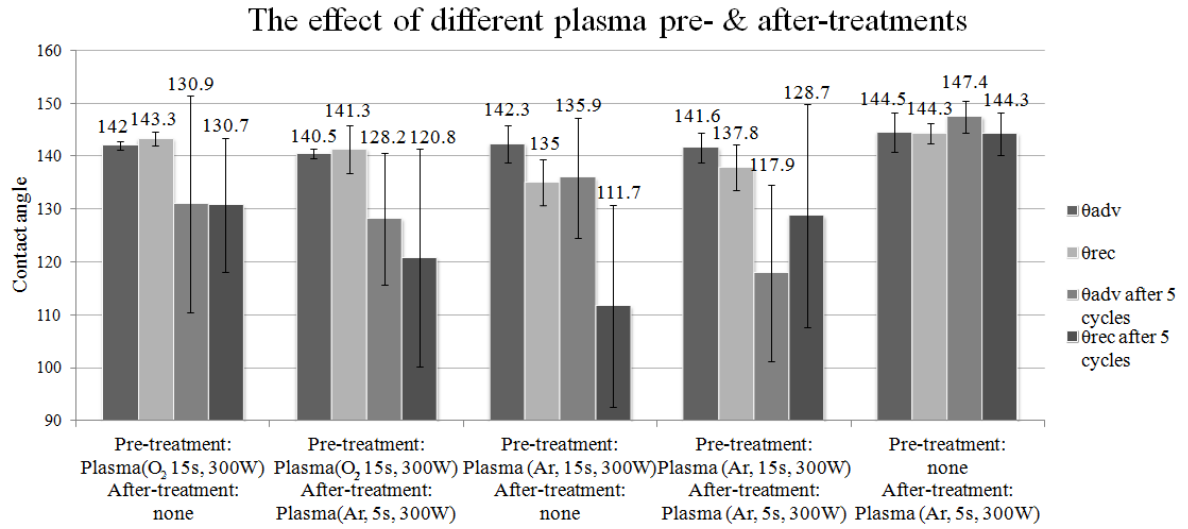


Figure 4.4: A comparison of the wear resistance, of coatings with particle/PDMS ratio 2.5, created by different plasma pre- and after-treatments. All plasma pre-treatments result in a poor wear resistance while the effect of solely plasma after-treatment is unclear. The results are based on 3 measurements on one sample from each sample group.

From figure 4.4 it is clear that a pre-treatment with oxygen as well as argon plasma yielded a lower adhesion between the surface and the coating.

Whether or not an after-treatment with argon plasma was beneficial could not be determined by this test and further investigation of this treatment was carried out. Sample groups with/without argon plasma after-treatment were compared over a more detailed Martindale cycle-spectrum. The result is shown in figure 4.5.

A distinct difference in wear resistance could not be detected between the two sample groups.

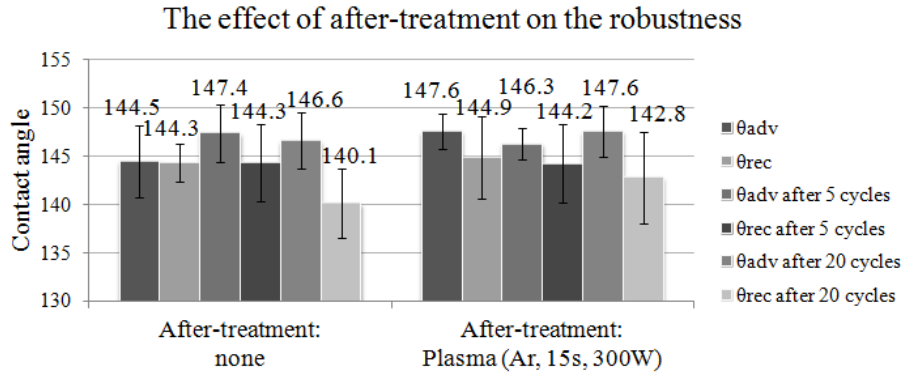


Figure 4.5: A comparison of the wear resistance between samples with an argon plasma after-treatment and samples without after-treatment. It is difficult to detect a distinct difference in wear resistance between the two sample groups. The results are based on 3 measurements on 5 different samples from each sample group.

Pre-treatment with plasma and PDMS curing agent

A hypothesis arose in the course of the project that a pre-treatment with PDMS curing agent possibly could increase the wear resistance of the coating by an initial reaction with the substrate surface before application of the particle/PDMS containing coating. The idea was to apply a coating of the reactive curing agent onto an oxygen plasma pre-treated composite surface. The curing agent would react with the surface but still leave some reactive groups on its surface. These groups would then be used to react and bind with the PDMS-base in the original particle/PDMS dispersion leaving a robust coating. Figure 4.6 shows the result from these measurements.

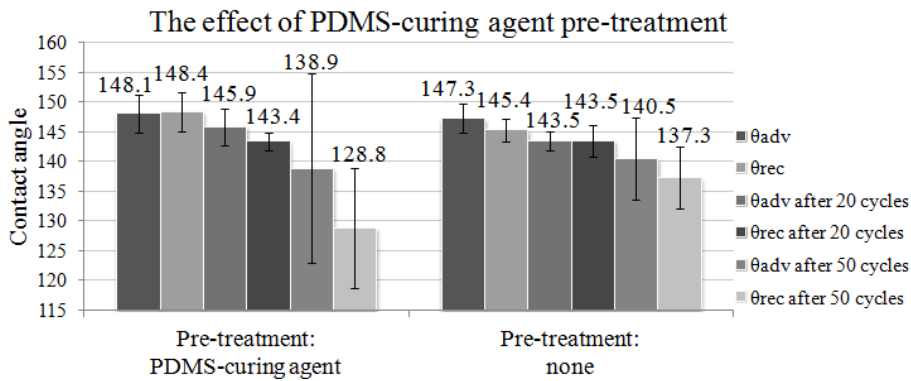


Figure 4.6: A comparison of wear resistance between sample groups with and without a pre-treatment of argon plasma in combination with PDMS-curing agent. Both sample groups show good results after 20 cycles in the Martindale equipment but give poor results after 50 cycles which makes it difficult to say which sample group has the best wear resistance. These results are based on 3 measurements on 5 different samples from each sample group.

Unfortunately, it was difficult to determine if the pre-treatment increased the wear resistance since both sample groups showed poor result after 50 cycles in the Martindale equipment. The evaluation method chosen may be too rough to detect the small difference in wear resistance. However, the dynamic contact angles and the standard deviations were higher respectively smaller for those without pre-treatment than for the samples with pre-treatment. This could imply that a pre-treatment with plasma and PDMS-curing agent had a negative effect on the wear resistance.

Unmodified vs. hydrophobically modified particles

The influence of using hydrophobically modified silica particles in the coating was examined by dynamic contact angle measurements in combination with treatment in the Martindale equipment. The result from the measurements is displayed in figure 4.7.

By using hydrophobically modified particles a more homogenous dispersion was created which made it easier to apply an even coating onto the composite substrate. Slightly higher contact angles were also obtained for the coatings containing hydrophobically modified particles.

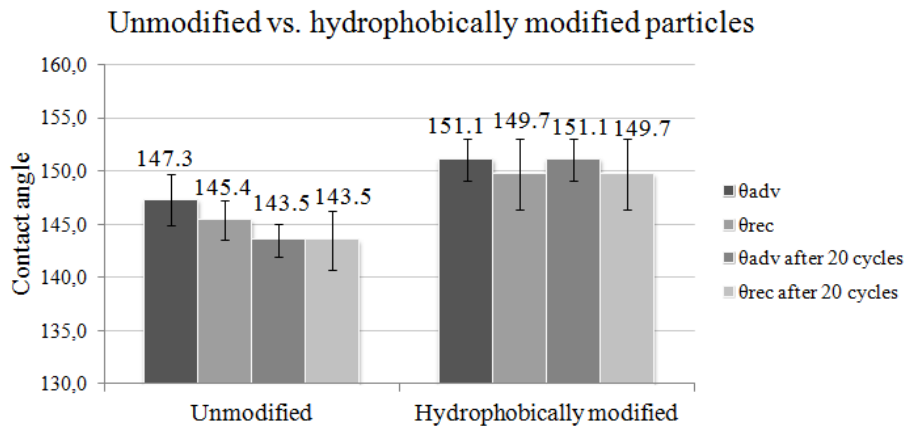


Figure 4.7: A comparison of wear resistance between a coating containing unmodified particles and a coating containing hydrophobically modified particles. It is hard to detect a distinct difference in wear resistance between the hydrophobically modified particles and the unmodified ones. These results are based on 3 measurements on 5 different samples from each sample group.

A distinguishable difference in wear resistance could not be detected between the two sample groups.

4.3 Epoxy system

In the following section results which solely concern the system using epoxy as polymer binder will be presented. As received polyester composites which have been hydropho-

bized by different hydrophobization agents exhibits the following contact angles; fluor plasma $\sim 100^\circ$, fluorosilane $\sim 115^\circ$ and Ruco-guard AFR 6 $\sim 120^\circ$.

Hydrophobization agents

Three different hydrophobization agents were examined for the epoxy system; fluor plasma, fluorosilane and Ruco-guard AFR 6. The hydrophobization methods were evaluated in means of dynamic contact angle measurements and treatment cycles in the Martindale equipment. In figure 4.8 the results for the different hydrophobization agents are displayed.

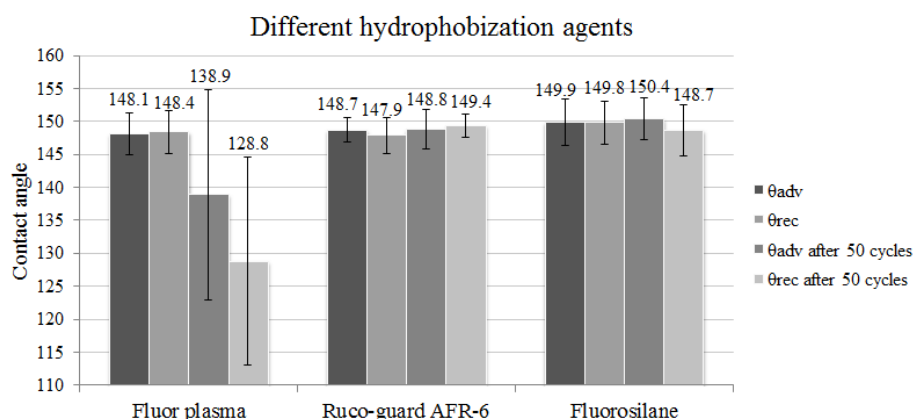


Figure 4.8: The dynamic contact angles, of coatings with different hydrophobizing agents, before and after 50 cycles in the Martindale equipment. The coating hydrophobized by fluor plasma exhibits low dynamic contact angles as well as high standard deviations after 50 cycles. Both the other two hydrophobization agents give good result after 50 treatment cycles. These results are all based on 3 measurements of 5 different samples from each sample group.

After 50 cycles in the Martindale equipment the particle coating hydrophobized by fluor plasma appeared intact as the white coating was visible over the sample surface. However, the dynamic contact angles showed a dramatic decrease in magnitude and large standard deviations which indicated that the fluor containing coating was damaged by the wear.

The other hydrophobization methods exhibited better wear resistance and withstood 50 cycles in the Martindale equipment. Since the Ruco-guard AFR 6 was waterborne while the fluorosilane was dispersed in methyl ethyl ketone; Ruco-guard AFR 6 was preferred as hydrophobizing agent.

In figure 4.9 SEM images at x50,000 magnification of an unworn coating hydrophobized by Ruco-guard AFR 6 is shown. A "porous" surface structure with multiple levels where both large and small particles as well as agglomerates were detected was obtained.

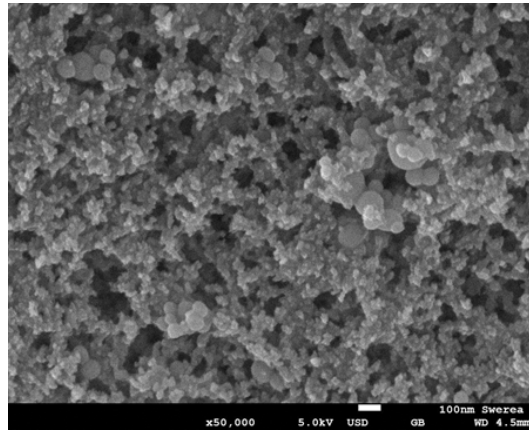


Figure 4.9: SEM image at x50,000 magnification of an unworn epoxy-containing coating hydrophobized by Ruco-guard AFR 6. Multiple levels in the surface structure can be seen which explains the coating's good super hydrophobic properties.

The samples which were tested in the Martindale equipment exhibited both darker and lighter areas of the coating. Figure 4.10 shows x10,000 magnified SEM images of these light (A) and dark (B) areas of a coating tested 200 cycles in the Martindale equipment.

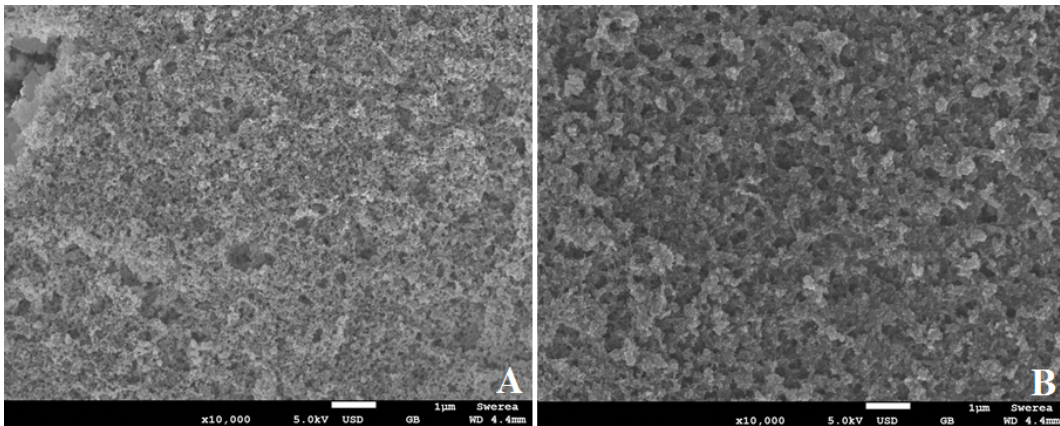


Figure 4.10: SEM image at x10,000 magnification of the coating hydrophobized by Ruco-guard AFR 6. Image A shows the light area while image B shows the dark areas of a coating tested 200 cycles in the Martindale equipment. The light areas appear to be more worn than the darker areas.

The light area of the coating appeared to be more worn and flattened than the dark area.

SEM images at x50,000 magnification of the same light and dark areas of the coatings are shown in figure 4.11. SEM images of the darker areas are shown in the upper images (A & C) while the lighter areas are shown in the lower corners (B & D). Images A

and B correspond to 50 treatment cycles and the images C and D corresponds to 200 treatment cycles. When comparing to the unworn SEM image in figure 4.9 the lighter areas appeared to be more worn and flattened than the darker areas while the dark area gave the impression that there was a phase holding the particles together.

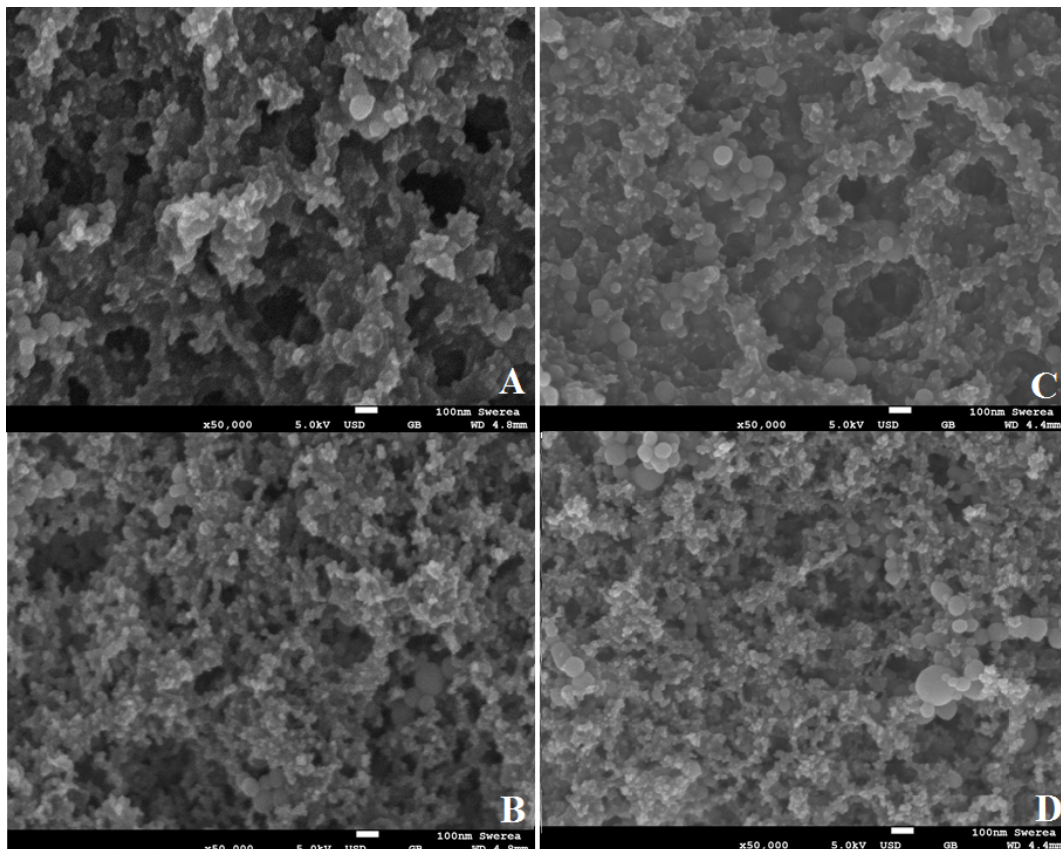


Figure 4.11: SEM image at x50,000 magnification of coating hydrophobized by Ruco-guard AFR 6 and tested in the Martindale equipment. Image A shows a dark area coating after 50 cycles and image B shows a light area after the same amount of treatment cycles. Image C shows a dark area coating after 200 cycles and image D shows a light area after 200 cycles. The light areas appear to be more worn than the dark areas.

Plasma pre-treatment

The epoxy-system hydrophobized by Ruco-guard AFR 6 was investigated further to determine if the plasma pre-treatment could possibly be excluded without affecting the wear resistance of the coating. The plasma pre-treatment was performed on the composite substrate before applying the coating. The influence was examined by measuring the dynamic contact angles over a more detailed Martindale spectrum for sample groups with/without the oxygen plasma pre-treatment. The result from the experiments can be found in figure 4.12.

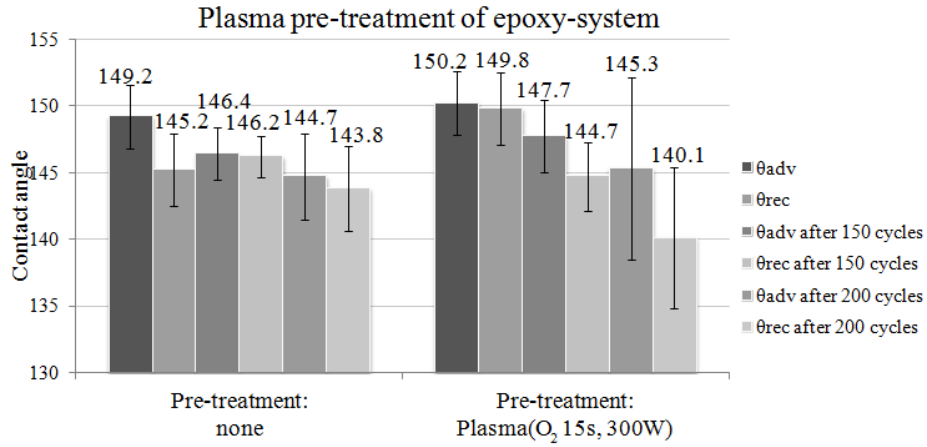


Figure 4.12: A comparison of the wear resistance between a sample group which was pre-treated with oxygen plasma and a sample group without any pre-treatment. The sample group without pre-treatment exhibits better results after 200 cycles than the samples with plasma pre-treatment. The results are based on 3 measurements on 5 different samples from each sample group.

The result indicated that a pre-treatment with oxygen plasma was not necessary to achieve a good wear resistance. In fact, the result implied that a pre-treatment might even create a lower adhesion between the surface and the coating.

5

Discussion

THE OPTIMAL particle/polymer binder weight ratio was found to be 2.5. A lower amount of polymer binder, and thus a higher ratio, led to a less homogeneous dispersion where the silica particles formed one phase while the polymer binder/solvent formed another phase. Increasing the amount of polymer binder contributed to a better dispersion, probably due to adsorption to the surface of the silica particles which led to a stabilization of the particles. The polymer binder can in other words be considered to be a dispersing agent.

However, a too large amount of polymer binder will fill up the surface structure created by the silica particles and result in a coating with wetting properties corresponding to the pure polymer binder.

The attempt to create super hydrophobic surfaces from dispersions containing solely large particles (~ 100 nm) and from dispersions containing a mixture of large and small particles (~ 100 respectively 12 nm) showed that both systems gave high contact angles. This is in agreement with the findings published by Karapanagiotis et al. They proved that a super hydrophobic surface could be created independent of the size range of the particles used if the particle concentration was equal or higher than the critical particle concentration (Karapanagiotis et al. 2012).

However, it was found that the coatings consisting of solely large particles exhibited lower wear resistance than the coatings with a mixture in particle size. This can be explained by the attractive van der Waals forces acting between the particles. The small particles will have many contact points to neighboring particles and it is evident from the SEM photos that the agglomerates in the porous surface structure survived the Martindale test. These agglomerates are held together by van der Waals forces working on the contact points. There will be a lower number of contact points between larger particles and thus the agglomerates in the coating will be weaker. This explains the observed difference in wear resistance after Martindale test.

5.1 PDMS system

This section will concern the parts of the result which only applies to the system using PDMS as the polymer binder.

From the results presented in figure 4.4 it is clear that a pre-treatment with oxygen as well as argon plasma yields a lower bonding adhesion between the surface and the coating. Most likely, the surface becomes too hydrophilic by the plasma which makes it incompatible with the hydrophobic particle/PDMS dispersion.

The results obtained by plasma treatment as an after-treatment of the particle/PDMS-system or as combined in the case of plasma+PDMS-curing agent pre-treatment, do not show any improvement of the wear resistance. It could therefore be concluded that the best method to prepare a super hydrophobic surface with silica particles and PDMS is without plasma treatment.

No difference in the wear resistance was found when PDMS-systems with unmodified or hydrophobically modified particles were compared even though the unmodified particles could have stronger agglomerates due to the possible polar interactions between the silica surfaces. It is believed that the particle surfaces are coated by at least a molecular layer of PDMS since the contact angle is very high. Thus, the unmodified particles will be separated by a hydrophobic layer and exhibit the same properties as the modified particles.

However, the particle dispersion with hydrophobically modified particles is much more homogenous than the unmodified particle dispersion. This makes it easier to handle and apply to the substrate which makes the coating containing the hydrophobically modified particles the most preferable. The modified silica particles were, according to the suppliers, hydrophobized by chemically reacting the silica surface with a silane. This results in covalent bonding of the silanes and any phase separation during particle dispersion preparation could therefore be avoided.

5.2 Epoxy system

This section will concern the parts of the result which only applies to the system using epoxy resin as the polymer binder.

When exposing the coating which had been hydrophobized by fluor plasma to Martindale treatment it was discovered that the hydrophobicity decreased rapidly. The coating lost its super hydrophobic properties already after 50 treatment cycles in the Martindale equipment. However, the whitish silica particle/epoxy coating seemed visually unworn which could indicate that the decrease in dynamic contact angles instead was a consequence of detachment of the fluor plasma from the surface.

The coatings hydrophobized by fluorosilane and Ruco-guard AFR 6 showed much better wear resistance and could withstand at least 50 treatment cycles without a reduction on its super hydrophobic properties.

Ruco-guard AFR 6 is purchased as a waterborne emulsion while the fluorosilane has

to be dispersed in a solvent before spraying it onto the substrate. The Ruco-guard AFR 6 has however been diluted to 5 vol.% to minimize the use of fluor as well as to make sure that a thin layer is applied to the coating. Since a waterborne emulsion is both more environmentally friendly and creates a better working environment, due to the absence of harmful solvents, it is to be considered the most optimal choice. Ruco-guard AFR 6 also has shorter fluorinated carbon chains than the (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane and is therefore an environmentally better choice since it should not be bioaccumulative.

After testing the coatings hydrophobized by Ruco-guard AFR 6 in the Martindale equipment it was noticed that there existed darker and lighter areas in the coating. SEM images, which are shown in figure 4.10 and 4.11, were taken of these different areas. The lighter areas appeared to be more worn and flattened than the darker areas. The whitish coating of the substrates, however, still seemed intact which implies that the particles still remained at light and dark areas. A hypothesis is that some of the fluorinating chemicals were removed and re-deposited to the substrate at the dark areas, thus creating a “coarsened” structure.

If a pre-treatment of oxygen plasma could be excluded from the coating process it would render an easier and cheaper manufacturing process which is desirable.

From the result presented in figure 4.12 it is clear that a pre-treatment of oxygen plasma is not necessary to achieve a good wear resistance. In fact the measurements indicates that not pre-treating the substrate may contribute to a better wear resistance.

The unsaturated polyester matrix contains anhydride groups which react well with epoxy groups. Oxygen plasma may possibly destroy the anhydride groups of the composite which would lead to a lower bonding strength towards the epoxy groups of the coating. This may be the reason why plasma pre-treatment lowers the wear resistance of the system.

5.3 Comparing the systems

From the results described in chapter 3 and the discussion it is clear that the most wear resistant coating is obtained by the silica particle/epoxy-system with a Ruco-guard AFR 6 hydrophobization layer on top. The wear resistance seems to be 10 times higher for the epoxy system than for the PDMS. A two-step coating process is, however, necessary for the epoxy-system. The higher wear resistance could be explained by the fact that the epoxy-based system is hydrophilic and thereby has a good wetting of the composite substrate. There are reactive hydrophilic groups on the polyester surface that can react with the epoxy system during crosslinking and thus create a covalent bonding between the epoxy and the polyester. The fluor-containing coating created by application of Ruco-guard AFR 6 requires a heat treatment of 160°C and some covalent bonds could be developed during this heat treatment.

The low wear resistance of the PDMS-system can be explained by the fact that

the polymer is completely hydrophobic and does not have any groups that can react with the polyester surface. The attempts to initiate a reaction with the PDMS-curing agent was not successful although the curing agent has hydrophilic groups which possibly could react with a plasma treated surface. When comparing the dissociation energies of different bonds and surface interactions, see table 2.1, it is clear that it requires about 10 times the energy of a van der Waals interaction to dissociate a hydrogen bond and about 200 times higher energy to dissociate a covalent bond. This comparison illustrates the weak interaction between hydrophobic substances and surfaces since only van der Waals forces are at hand in those cases.

6

Conclusion

A ROBUST INDUSTRIALLY applicable system for creating super hydrophobic surfaces on biobased composites has been developed. The silica nanoparticle/polymer binder dispersion for creating the hydrophobic system can be prepared by means of large scale available equipment and can be sprayed in the same manner as paint.

Of the two examined polymer binders; epoxy resin yielded the best adhesion towards the composite surface and thereby the best wear resistance. This coating was then hydrophobized by different fluor-containing chemicals where fluorosilane and Ruco-guard AFR 6 gave the best result. Since the use of Ruco-guard AFR 6 minimizes the use of harmful solvents, this is to be considered the preferable hydrophobization agent. Vacuum plasma treatment proved to be unessential for creating a wear resistant coating.

Polydimethylsiloxane has also been examined as a possible polymer binder/ hydrophobization agent but have, unfortunately, given unsatisfactory result. The wear resistance of the coating has been low compared to that of the epoxy-system. Attempts to improve the wear resistance by different vacuum plasma treatments were made without success. If the PDMS-system would have been able to create a good wear resistance it would have been preferred over the epoxy-system since the PDMS works as both the polymer binder and the hydrophobizing agent. This would have rendered an easier and cheaper production process. It would also have been more environmental friendly since there would not have been any use of harmful fluor chemicals as there is for the epoxy-system.

6.1 Future work

Since the coating should be able to withstand a varying environment, such as high humidity and varying temperature, without losing its super hydrophobic effect investigations of these properties should be carried out, e.g. immersion in water.

It is also desirable to create a more environmentally friendly coating by eliminating the usage of hazardous fluorocarbons. This could be done by investigating new possible hydrophobization agents such as non fluor-containing silanes.

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A

Dispersion recipes

PDMS system

The following recipes refer to the PDMS-system using a large/small particle weight ratio of 0.5 and a particle/PDMS weight ratio of 2.5. In table A.1 and A.2 general recipes for the PDMS-base respectively PDMS-curing agent solutions are displayed. Table A.3 displays the general recipe for the dispersion using the above mentioned PDMS component solutions.

Table A.1: Above the line are the weighed-in amounts of the different ingredients. Below the line is the corresponding concentrations of the PDMS-base solution.

PDMS-base solution		
m(base)	5	g
m(cyclohexane)	95	g
Concentration	5.00	wt.%

Table A.2: Above the line are the weighed-in amounts of the different ingredients. Below the line is the corresponding concentrations of the PDMS-curing agent solution.

PDMS-curing agent solution		
m(curing agent)	5	g
m(cyclohexane)	95	g
Concentration	5.00	wt.%

Table A.3: Above the line are the weighed-in amounts of the different ingredients. Below the line is the corresponding ratios, concentrations and amounts of PDMS components respectively particles.

Dispersion		
m(base solution)	5	g
m(cyclohexane)	29.3	g
m(NanoSilica)	0.23	g
m(Aerosil 200)	0.46	g
m(curing agent solution)	0.5	g
Large/small particle weight ratio	0.5	
m(PDMS-base)	0.25	g
m(PDMS-curing agent)	0.025	g
m(total PDMS)	0.275	g
m(total particle)	0.69	g
Particle/PDMS weight ratio	2.5	
Particle concentration	2	wt.%

Epoxy system

The following recipes refer to the epoxy-system using a large/small particle weight ratio of 0.5 and a particle/epoxy weight ratio of 2.5. In table A.4 and A.5 general recipes for the epoxy-base respectively epoxy-curing agent solutions are displayed. Table A.6 displays the general recipe for the dispersion using the above mentioned epoxy component solutions.

Table A.4: Above the line are the weighed-in amounts of the different ingredients. Below the line is the corresponding concentrations of the epoxy-base solution.

Epoxy-base solution		
m(base)	5	g
m(methyl ethyl ketone)	95	g
Concentration	5.00	wt.%

Table A.5: Above the line are the weighed-in amounts of the different ingredients. Below the line is the corresponding concentrations of the epoxy-curing agent solution.

Epoxy-curing agent solution		
m(curing agent)	5	g
m(methyl ethyl ketone)	95	g
Concentration	5.00	wt.%

Table A.6: Above the line are the weighed-in amounts of the different ingredients. Below the line is the corresponding ratios, concentrations and amounts of epoxy components respectively particles.

Dispersion		
m(base solution)	5	g
m(methyl ethyl ketone)	31.8	g
m(Sidistar)	0.25	g
m(Aerosil R972)	0.5	g
m(curing agent solution)	1	g
Large/small particle weight ratio	0.5	
m(epoxy-base)	0.25	g
m(epoxy-curing agent)	0.05	g
m(total epoxy)	0.3	g
m(total particle)	0.75	g
Particle/epoxy weight ratio	2.5	
Particle concentration	2	wt.%

Hydrophobization agents

The following recipes refer to the dissolution and dilution of the hydrophobization agents. Table A.7 refers to the dissolution of fluorosilane and A.8 refers to the dilution of Ruco-guard AFR 6.

Table A.7: Above the line are the weighed-in amounts of the different ingredients. Below the line is the corresponding concentrations of the silane solution.

Fluorosilane		
m(silane)	0.5	g
m(methyl ethyl ketone)	9.5	g
Concentration	5.00	wt.%

Table A.8: Above the line are the measured amounts of the different ingredients. Below the line is the corresponding concentrations of the Ruco-guard AFR 6 solution.

Ruco-guard AFR 6		
V(Ruco-guard AFR 6)	5	cm ³
V(distilled water)	95	cm ³
Concentration	5.00	vol.%