Surface Polymerisation Methods for Optimised Adhesion

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Surface polymerisation methods for optimised adhesion

Joanna Maria Drews

Ph.D. Thesis

2008
SURFACE POLYMERISATION METHODS FOR OPTIMISED ADHESION

Ph.D. thesis

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April 2008

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Preface

This thesis is submitted in partial fulfilment of the requirements for obtaining the Ph.D. degree at the Technical University of Denmark (DTU). The manuscript presents the results of work carried out at the Polymer Department, Risø-DTU, and the Danish Polymer Centre, Technical University of Denmark. The Ph.D. project was supervised by Dr. Keld West (presently at NanoGeoScience, University of Copenhagen), Dr. Kristoffer Almdal (former Head of the Polymer Department, Risø-DTU; currently at MIC, DTU), Dr. Peter Kingshott (presently at iNano, Aarhus University) and Dr. Søren Hvilstved (main supervisor, Danish Polymer Centre, DTU).

The Ph.D. study is part of a framework programme on “Interface design for composite materials”, financed by the Danish Technical Research Council (STVF fund no. 26-03-0160) and coordinated by senior scientist Bent F. Sørensen. The programme is a collaboration between the Materials Research and Polymer Departments of Risø-DTU; Department of Building Technology and Structural Engineering and Institute of Mechanical Engineering of Aalborg University; Force Technology; and two industrial partners: LM Glasfiber A/S and NKT Flexibles I/S. The overall ideas are

- To establish characterisation and modelling tools for studying the mechanical behaviour of the fibre/ matrix interface in glass- and carbon fibre composites.

- To improve the understanding of how the chemistry of the fibre/ matrix interface influences the macroscopic properties of composites.

- Based on the above, to design and test optimised composite materials, e.g. composites which higher load carrying capabilities.
The research programme comprises both experimental work and modelling, covering the range from nanoscale interface properties (surface chemistry, topography, etc.) to macroscale material properties (mechanical performance).

Roskilde, April 2008

Joanna Maria Drews
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In general I want to thank the staff at the Polymer Department and the Materials Research Department, Risø-DTU, as well as the Danish Polymer Centre, DTU, in particular Bent F. Sørensen, Tom Løgstrup Andersen, Frank Adrian, Christian H. Madsen, Yukihiro Kusano (OPL-Risø) for help in understanding the cold plasma processes, and last but not least Noemi Rozlosnik and Lene Hubert for their help with AFM and XPS measurements, respectively. Finally, I would like to thank Nanon A/S for using their equipment stationed at Risø-DTU.
A special thank to all my friends, who helped me through this Ph.D. study, by patiently sharing my laughs and cries, and to my family for endless support during times, when things did not work out.

Finally, I would like to thank my husband for his support, love, and for just being there, when I needed him.
Summary

This thesis examines the use of plasma polymerisation as a surface modification technique, in general, and as means to improve the adhesion between carbon fibres and a polymer matrix, in particular. The thesis contains 8 chapters, which are based on a combination of unpublished and published material, the latter appearing in four articles that are reprinted in Appendix A through D.

The first chapter gives an introduction to the research project as a whole and includes a general discussion of plasma polymerisation.

The second chapter provides a comprehensive overview of experimental methods used to perform chemical as well as mechanical characterisation of plasma modified specimens. These methods include X-Ray Photoelectron Spectroscopy (XPS), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), Atomic Force Microscopy (AFM), contact angle measurements, the toluidine blue staining technique and Double Cantilever Beam (DCB) mechanical tests. A Quartz Microbalance Crystal (QCM) was used to monitor the rate of plasma deposition. Lastly, a proposed peel-off test is described.

In Chapter 3-4 and 7 the plasma polymerised layers derived from maleic anhydride (MAH), 1,2-methylenedioxybenzene (MDOB), and a co-polymer formed from these two monomers are investigated as a function of the plasma conditions, i.e. the plasma polymerisation time and power. It is well known that surface functional groups of carboxylic acid may increase the adhesion to an epoxy resin. In case of plasma polymerised MAH carboxylic acid groups are created by subsequent hydrolysis,
whereas in case of MDOB the carboxylic acids are created during the plasma
treatment. Here the increased strength of these interfaces is reported and related to
observed changes in the surface chemistry. Moreover, the stability performance of the
plasma polymerised layers in terms of their resistance to an alkaline hydrolysing
media and to certain thermal conditions is evaluated.

The last part of the thesis documents the results of several minor “pilot studies” that
spawned from work already mentioned. By means of AFM it is not only possible to
obtain information about the thickness of the polymerised layers but also to carry out
detailed topographical analyses of fracture surfaces, which may help to understand the
mechanical properties and the failure mechanism (Chapter 5). Furthermore, it is
demonstrated, how amine functional groups may be derived from plasma polymerised
MAH (Chapter 6). Finally, a simple peel-off test has been explored (section 7.3). The
potential in this technique, as a possible qualitative measure of interfacial strength, is
explained and exemplified using plasma polymerised coatings of MDOB.
Resumé


Første kapitel er en general introduktion til dette forskningsprojekt og beskriver bl.a. plasma polymerisations teknikken.

I andet kapitel gennemgås de eksperimentelle metoder, der er blevet brugt til kemiske såvel som mekaniske analyser af substrater, som er blevet overfladebehandlet ved hjælp af plasma polymerisation; herunder X-Ray Photoelectron Spectroscopy (XPS), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), Atomic Force Microscopy (AFM), kontaktvinkel-målinger, ”toluidine blue staining” og mekaniske Double Cantilever Beam (DCB) tests til bestemmelse af bindelagets styrke. Brugen af en Quartz Microbalance Crystal (QCM) krystal giver endvidere mulighed for at følge og delvist kontrollere polymerisationen af monomerer på overfladen. Endelig beskriver kapitlet, hvorledes en simpel ”peel-off” test kan udføres.
Kapitel 3-4 og 7 omhandler plasma polymeriserede film, der er dannet ved at polymerisere MAH (maleic anhydride), henholdsvis, MDOB (1,2-methylene-dioxybenzene). Desuden er en co-polymer film, der er dannet ved at blande disse to monomerer, blevet undersøgt. I alle tilfælde varieres forholdene under selve plasma polymerisationen for at kunne bestemme, for eksempel hvordan tykkelsen af den deponerede film afhænger af plasma-energien. Det er velkendt, at overflader indeholdende reaktive grupper af carboxylsyre binder stærkt til epoxy. Ved at hydrolysere en film bestående af plasma polymeriseret MAH er det muligt at opnå en film med høj koncentration af carboxylsyre grupper på overfladen. Tilsvarende kan der også dannes carboxylsyre på overfladen under plasma polymerisation af MDOB - om end koncentrationen af de derved dannede grupper er lav. I denne del af afhandlingen diskuteres, hvorledes målte forstærkninger i bindelaget hænger sammen med observerede ændringer i filmenes kemiske sammensætning. Desuden beskrives filmenes egenskaber i forbindelse med hydrolyse i basiske opløsninger samt under særlige termiske forhold.

Afhandlingens sidste del tager udgangspunkt i tre små “pilot-studier”, der er motiveret af ovenstående. I det første (kapitel 5) benyttes AFM som ”lup” for at kunne studere topografien (nanostrukturen) af de brækkede overflader og dermed de mekaniske processer, der finder sted under belastningen. I det andet (kapitel 6) demonstreres, hvordan amino grupper kan sættes fast på en overflade af plasma polymeriseret MAH og derved give filmen nogle nye kemiske egenskaber. Endelig (sektion 7.3) foreslås en ny simpel kvalitativ mekanisk test til evaluering af styrken i bindelaget, og der gives eksempler, hvor der er brugt plasma polymeriserede film af MDOB.
List of papers

The following manuscripts are included in the thesis (Appendix A through D):


The following paper from the Ph.D. period has not been included in the thesis:

List of abbreviations

AFM: Atomic Force Microscopy
ATR-FTIR: Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy
DCB: Double Cantilever Beam
EDA: 1,2-ethylenediamine
GC: glassy carbon
HDA: 1,6-hexanediamine
HDPE: High Density Polyethylene
MAH: maleic anhydride
MDOB: 1,2-methylenedioxybenzene
XPS: X-ray Photoelectron Spectroscopy
PDLLA: Poly (D,L-lactide)
PE: Polyethylene
ppMAH: plasma polymerised maleic anhydride
ppMDOB: plasma polymerised 1,2-methylenedioxybenzene
QCM: Quartz Crystal Microbalance
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1 Introduction

1.1 Background
In present years the demands for renewable energy sources are growing rapidly, e.g. as prompted by the concerns of climate change. Modern societies are consuming ever more energy, rapidly depleting our reservoirs of natural resources such as coal, oil and gas. Meanwhile anthropogenic CO₂ emissions produced by the burning of fossil fuels influence our climate, i.e. by increasing temperatures and causing sea level rises, affecting both humans and the environment [1]. Methods and chemicals used by industry and in agriculture also cause growing strains on the natural world. Taking all these issues into account it is not surprising that the protection of our green planet has become an important political question, and that the developments in present-day energy technologies are directed towards “cleaner” and sustainable energies.

Wind power is a clean and renewable energy resource, which has already been adopted by power companies worldwide, and thus the exploitation of wind power is subject to intensive research and development. The technological development is particularly directed towards more efficient and larger wind turbines, which are capable of producing more energy.

Currently, Denmark is the leading country in the world with regards to wind power production. Danish industry started their exploration of wind power as far back as the 1970’s, and today holds one of the world leading positions in manufacturing wind turbines. In fact Denmark is the first nation to cover almost 20% of its electricity demands from wind power (2004) [2]. The aim of the Danish government is to increase this number to a least 30% of energy derived from sustainable energy sources by 2025 [3]. One way to achieve these goals is to expand the number of existing wind
mills or to replace them with bigger and better ones. Currently, the size of state-of-the-art wind turbines is limited by the properties, in particular the strength, of existing materials, and therefore the need for new materials that are both stronger and more flexible is urgent. Using specially designed composite materials that combine the physical properties of its constituents will make it feasible to facilitate the building of larger wind mills, e.g. it is possible to realize rotor blades that are strong, durable and light at the same time. Not surprisingly, such composites are therefore well sought-after by industry.

1.2 Composite materials
Throughout history mankind have always been looking for new materials in order to overcome challenges, e.g. put forth in terms of infrastructure and industry. Many ancient civilisations developed techniques for producing various forms of composite materials [4, 5], since the size and design of complex structures, like the wind turbine blades mentioned above, often proves to be severely limited by the mechanical properties of the building materials. In this way advances, e.g. in architecture and technology, frequently become entirely dependant on the utilization of new materials.

A composite material is a mixture of at least two components with different physical and/or chemical properties. By mixing the two different components one can obtain a material that has completely different properties or, as it is usually the case, a material which has a favourable combination of properties from the two compounds. Perhaps the simplest example of a composite material is clay and straw [6]. Clay is very strong and resistant to compression but not very flexible. Straw on the other hand is very flexible in terms of elongation but not very resistant to compression. Mixing the two materials, however, we get a simple composite material which is very resistant because of the clay and at the same time has increased tensile strength due to the embedded straw. Such a composite is very useful, e.g. for building constructions, and present-day builders thus use a similar mixture of iron and concrete for contemporary works.

In terms of macro mechanical properties composite materials are generally characterized by their strength and toughness. The strength governs the initiation/formation of cracks within the material under external stress while the toughness determines the speed of crack propagation. Nowadays, composite materials that
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Combine carbon fibres with a polymer matrix are of special interest for many applications, including the production of wind power turbines. Here the fibres typically lend tensile strength to the material, while the matrix adds compressive properties. To change the material strength usually means changing the strength of the fibre/matrix interface. Similarly, the toughness is determined by the toughness of the polymer matrix. Changing the toughness can be done by adding modifiers [7] into the matrix as exemplified by Verrey et al. [8], where the modifiers are hyperbranched polymers and the observed increase in fracture toughness is about 60%.

The “fibre sizing” is a coating, which is added just after fibres are produced. The exact type of sizing depends on the application of the fibres [9]. The sizing protects the fibres and increases the compatibility with the underlying matrix. As reported by Feih et al. [10], who has investigated the relationship between sizing and the strength of the composite materials, the sizing also plays an important role for the “breaking” properties of the material. Atkinson and Kiely [11] has compared the commercial (electrochemical) treatment of carbon fibres with one using plasma modification; the authors found the air plasma treated fibres to perform better in case of composite materials.

The coating/surface modification of the fibres can be carried out in different ways [12]. Obviously, the choice of method depends on the planned use of the fibres. Three of the most commonly used methods are: (i) by self-assembled monolayers [13], (ii) by grafting to a surface, and (iii) by grafting from a surface.

When grafting to a surface the polymerisation is initially carried out in solution before the polymers are then attached to the surface, also from solution. As the polymerisation is done in solution the polymers are easy to characterise, and therefore this process including the functionalisation of the polymers may in principle be accurately controlled. On the other hand, it is not easy to control the density of the polymers attached to the surface in this manner, i.e. the number of reactive sites on the surface is generally higher than the number of attached polymer chains. Alternatively, when grafting from a surface the initiator of the polymerisation is first attached to the surface from a solution, before the actual polymerisation takes place [14, 15, 16, 17]. This allows for better control of the density of polymer chains on the surface. In this case the characterisation of the polymers is more complicated, i.e. due to the surface attachment, although methods like X-Ray Photoelectron Spectroscopy
(XPS) and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) may be used. Unfortunately, neither of these methods will tell us about the degree of polymerisation, though detailed characterisation of the polymers is possible if the polymers can be liberated from the surface e.g. by hydrolysis.

Using flat substrates as planar models of carbon fibres, Sidorenko et al. [18] have explored all three approaches. In this work all the specimens are checked for compression and shear strength with the hyperbranched polymers yielding the best results. Analogously, Tao et al. [19] obtain a functionalised surface with hyperbranched poly(acrylic acid), which is characterized in terms of stability and improved adhesion under different conditions. Tao finds the modified layer to be stable and the adhesion to increase 10 times compared to the unmodified surface.

Another type of surface modification employs silane coupling agents. This technique may be used to attach organic molecules to inorganic surfaces. An example can be found in Nakamura et al. [20] who concentrate on using silicon wafers with different coupling agents. Using this approach Nakamura finds that the adhesion is doubled.

Plasma modification (with a gas or with addition of a monomer) may also be used as means for surface modification. The influence of plasma modification on the surface chemistry of carbon fibres and the resulting strength of the composite material has been examined by Sherwood [21]. Likewise, Wade et al. [22] and Kusano et al. [23] have modified fibres by a plasma treatment to achieve an improvement in the strength of the fibre/ matrix interface. Lastly, Friedrich et al. [24] have used the plasma polymerisation technique for improving the interfacial strength of the materials, investigating the relationship between different functional groups on the surface and the interfacial strength.

1.3 Plasma polymerisation

To understand how plasma polymerisation (or luminous chemical vapour deposition, as Yasuda [25] claims is the better term) works, one must first understand what a plasma is. As illustrated on Figure 1 plasma is the fourth state of matter, the first three being the solid, liquid and gas phases. Arguably about 99% of matter in the Universe consists of plasma, e.g. the Sun. Essentially, plasma is a gas, where the constituents are ionized, that is electrons are stripped from molecules, and move around
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The ionized gas phase can be created in thermal or electric reactions or by light (ultraviolet or laser) [26, 27, 28]. Since a plasma is composed of free ions and electrons, it is susceptible to electrical and/or magnetic fields. The concept of plasma was discovered by Sir William Crookes in 1879 [29] and named by Dr. Irving Langmuir in 1929 [30].

![Figure 1. States of matter [31]](image)

In a plasma-initiated radical polymerisation – or plasma polymerisation for short – an ionized gas (which is usually a non-polymerisable gas) is formed, in the simplest case by applying an electric field between a pair of electrodes that form the walls in a plasma reactor (i.e. a plasma chamber). Some of the most frequently used (non-polymerisable) gases are Ar, H₂, He, N₂, and Ne. In the case of a glow discharge the ionized gas consists of an equal concentration of positive and negative charges (ions and electrons) in addition to a large number of neutral species. The pressure in the reactor can range from just a few Pa to atmospheric pressure. Electrons that are emitted from the cathode give rise to collisions with the gas atoms or molecules, creating excitations, ionizations, dissociations, etc. The excitation collisions give rise
to excited species that decay to lower energy levels by photon emission, e.g. using argon as an example,

\[
\text{Ar} + e^* \rightarrow \text{Ar}^* + e \\
\text{Ar}^* \rightarrow \text{Ar} + h\nu
\]

where \(\text{Ar}^*\) represents an excited argon species. This light-emitting process is responsible for the characteristic name of a glow discharge. The ionisation collisions simultaneously create ion-electron pairs, i.e.

\[
\text{Ar} + e^* \rightarrow \text{Ar}^* + 2e
\]

The ions are accelerated by the electric field towards the cathode, where secondary electrons may be produced, which again can give rise to more ionization collisions. In this way the combination of secondary electron emission at the cathode and ionization in the gas gives rise to a “self-sustained” plasma.

Due to the difficulties in controlling the polymerisation process in the gas phase, the plasma polymerisation typically takes place from a surface. The surface is first “pre-treated” with a flow of the ionized gas, e.g. Ar, to create free radicals on the surface. It is then treated with a constant gas flow which is a mix of the ionized gas and the monomer of choice. In free radical polymerisation of a vinyl monomer, i.e. conventional polymerisation, the monomer molecules react with free radicals to form covalent bonds. In this way a single layer of monomers is deposited on the surface, while new monomers react with those attached to grow polymer chains. As these chains continue to grow termination and recombination takes place. At the same time the continuous flow of ionized gas creates new radicals from the polymers that form the basis for new chains and leads to a three-dimensional cross-linked matrix. Since the flow of ionized gas and monomers is constant, the creation of free radicals from the polymers and the recombination of the free radicals is not kinetically coupled, leading to a “burying” of some of the free radicals in the plasma polymer [32]. The presence of un-reacted radicals is evidence that radical polymerisation takes place during plasma polymerisation [25].

In some cases the ionized gas can act directly as a sort of catalyst for the polymerisation [33]. By means of plasma polymerisation it is thus possible to polymerise a number of chemical substances that are not polymerisable by
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conventional methods, e.g. heptylamine and benzene. For example Ar$^+$ can react with the monomer M to create an excited species M$^*$

\[ \text{M} + \text{Ar}^+ \rightarrow \text{Ar} + \text{M}^* \]

which can dissociate into other chemically active species that may be polymerised.

Plasma polymerised films sometimes struggle with high internal stresses under which the coating may loose its properties and/or will crack. According to Yasuda [25] the internal stresses should be considered a characteristic of plasma polymerised films rather than a problem, though. Yasuda et al. [34] have developed a method for estimating the internal stresses in plasma films, where they calculate the internal stresses from a measure of the radius of a plasma surface, which “curls” as a result of internal stress. Further studies have been done by Shiga et al [35], Tamulevicius [36], Yu and Yasuda [37]. In summary the internal stresses in plasma polymerised films are found to be dependent on both the monomer structure as well as the plasma conditions during the modification. Furthermore, the internal stresses may be reduced by using thinner coatings (less than 100 μm) or by introducing a non-polymerisable gas [25]. In this work, since the thicknesses of the coatings are typically in the range of 100 nm, internal stresses were not expected to play a significant role for the analysis. For select specimens, however, the plasma coatings were clearly seen to break into flakes during hydrolysis, in particular in case of thicker coatings, suggesting that internal stresses do play a role, cf. Appendix B. In accordance with the authors cited above the internal stresses were found to be dependent on the plasma conditions (the plasma power).

1.4 Plasma polymerisation as a surface modification technique

Plasma polymerisation is widely used as a surface modification technique, for example in the production of bio-surfaces for different applications [38, 39, 40, 41, 42], in optical applications [43, 44, 45], and for improving interfacial strength [46, 47, 48]. One of the many advantages of plasma modification is that it can be used on a variety of different substrates and often yield quite good adhesion. It is also fast to perform and the range of monomers is nearly unlimited. Furthermore, it is a solvent free modification and samples do not need to be exposed to further surface modifications or cleaning, making it a rather “cheap technique” in terms of solvents.
Finally, it is generally “conformal” in the sense that plasma polymerisation do not change the surface topography in contrast to e.g. wet chemical treatments, where topographic features can give rise to uneven coating thicknesses.

The disadvantage, on the other hand, is that the physics of plasma polymerisation is very complicated, since a large number of species may be present in the glow discharge plasma, e.g. electrons, atoms, molecules, several kinds of radicals, several kinds of (positive and negative) ions, excited species, etc. These different species can all be interacting with each other, making the glow discharge plasma a complicated gas mixture. Consequently, the resulting polymers are in general also very difficult to analyse, i.e. requiring advanced high-resolution surface characterisation techniques. An in-depth discussion of the physics of plasma polymerisation can be found in the literature, see for example [49, 50].

There are several different types of plasma modification. If a continuous potential difference is applied between cathode and anode, giving rise to a constant current, the basic scheme described above is called continuous plasma polymerisation, or direct current (dc) glow discharge. In this case the formation of plasma is constant throughout the surface modification process. The performance of continuous plasma polymerisation as surface modification of fibre composites has been investigated by Marks and Jones [51], whereas Kruger et al. [52] compare the structure of films created with continuous and pulsed (see below) plasma polymerisation, respectively, by their thermoluminescence characteristics.

Probably the most used type of pulsed plasma modification is radio-frequency (rf) plasma polymerisation, where voltage is applied between the two electrodes, and where times “on” and “off” are introduced. Time “on” is when highly energetic ionized molecules are created. From the surface point of view “on” is when the surface is exposed to ionized gas, which creates radicals and often “destroys” the polymer structure. Conversely, during time “off” no ionization takes place, and the polymerisation goes on constructively. In radio-frequency plasma polymerisation the properties of the modified film depend on the “on” and “off” time.

Another kind of plasma modification is by atmospheric plasma. Since the gases are under normal pressure, this method does not require a vacuum system. Unfortunately, the treatment is also difficult to reproduce. The influence of atmospheric plasma
modification on the surface chemistry and surface topography has been discussed by Mortensen et al. [53].

### 1.5 Aims of this study

The goal of the present study is to investigate the strength of the interface between the carbon fibres and the polymer matrix using a suite of detailed surface characterisation techniques, in order to improve our understanding of what happens on the surface. For this purpose a number of different sample interfaces were created, e.g. representing interfaces with different characteristics.

Since working directly with carbon fibres is rather difficult, e.g. in terms of carrying out the surface modification, surface analysis and mechanical testing, a decision was made to use glassy carbon as a planar model of the carbon fibres, as glassy carbon has previously been found to be an adequate model of carbon fibres. For example by Launay et al. [54] who has compared the Hansen solubility parameters for different fibres, glassy carbon and epoxy resin. Glassy carbon is a mostly amorphous carbon with ribbon-like structures of highly ordered carbon sheets [55]. It is characterised by high strength, conductivity and high inertness to chemicals. For the project a special glassy carbon of type “Sigradur G” was chosen, since the temperature during processing of this type of glassy carbon is very similar to the treatment of carbon fibres.

For the surface modification plasma polymerisation using a low-power AC 2-phase plasma system was used [56]. The advantage of low power plasma polymerisation is that the amount of highly energetic species is quite low. Effectively the monomer molecules are not ionised in the gas phase and stay intact throughout the plasma process. The polymer growth is initiated as described above by active radicals present on the surface, creating covalent bonds between the polymer layer and the substrate, and then followed by conventional polymerisation. By changing the power of the plasma polymerisation, the properties of the modified layer, including the degree of cross-linking, was investigated and found to vary. Likewise, by varying time it was easy to manipulate the thickness of the created layer.
As mentioned previously high-resolution surface characterisation techniques are needed in order to probe the complex polymer coatings. A summary of the methods used in this study is given below.

The chemical composition of the modified layers was obtained mainly by X-Ray Photoelectron Spectroscopy (XPS) and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). XPS is a quantitative method, allowing us to investigate the elemental composition of the surface. ATR-FTIR, on the other hand, allows for a qualitative measure of the surface chemistry. Together these two complementary techniques were instrumental in order to understand the structure of the plasma polymerised films.

For quantification of the amount of carboxylic acid groups on the surface, e.g. after treatment under different conditions, the toluidine blue staining method was used.

Contact angle measurements were used to obtain an estimate of the surface energy.

Atomic Force Microscopy (AFM) was performed to image the topography of the surfaces on nanoscale.

A selection of the coated surfaces were tested for interfacial strength by a double cantilever beam method (Mode I), while “peel-off” tests were tried as a screening method. The mechanical tests were performed at the Material Research Department at Risø-DTU, by one of the collaborators in the project.

A detailed discussion of the above may be found in the following chapters.

1.6 Definition

Throughout this thesis the term surface is used extensively. The concept of a surface is widely used in many scientific fields, e.g. engineering, mathematics, chemistry, materials and polymer science, biology (implants, etc.), etc. As might be expected the meaning of the word “surface” is therefore often quite different. For a mathematician, for example, a surface might represent a two-dimensional plane in three-dimensional space, which may be described as having topography.

Within surface science the terminology of a surface is not equally well defined and very often does not mean only the surface. Here, the phrase surface also includes the probed thickness, which is otherwise usually omitted. In other words: the surface is
Introduction

actually not a surface but a *volume*. There are many different surface analysis techniques and they generally probe different such volumes. What is referred to as “bulk” using one technique may hence be part of the “surface” using another. In the following the term surface usually denotes a volume, though in the discussion of the contact angle measurements and the topography measured by AFM (Atomic Force Microscopy), the term will denote a two-dimensional structure.
Experimental methods used in the study

2 Experimental methods used in the study

This chapter provides supplementary technical details on each of the experimental methods used in these studies.

2.1 Low power plasma – “SoftPlasma”™

For surface modification a low power plasma set up was used. A detailed description of the plasma system can be found in Winther-Jensen [57, 58, 59]. The “SoftPlasma” technique has been developed by and is a trademark of Nanon A/S [60].

Figure 2 shows the plasma set up used at the Polymer Department, Risø-DTU, including an inside look into the chamber. The chamber itself is made from stainless steel (Figure 2a) and connected to two vacuum pumps. The set up is built in such a way that it has two separate lines, a chamber line and a monomer line (Figure 2b). Optionally, these lines can be connected. During the experiments described herein the system was supplied with Ar, a mixture of Ar and H₂ or air (between experiments).
For the pre-treatment/activation of the surface pure Ar or mixture of Ar and H₂ was used. The plasma pre-treatment is very important for the stability of the coating. If the conditions for the pre-treatment are set up wrongly, the resulting plasma coating has problems with stability, and so the activation conditions have to be carefully calibrated. The required time and plasma power depends on the substrate. For glassy carbon the activation time was set to 1 min with Ar, followed by 10 min with the Ar/H₂ mixture, before finishing with pure Ar for approx. 20 seconds (to remove the H₂). The activation current was set to 30 mA. More information on the plasma conditions may be found in Appendix A, Experimental Section.

During the polymerisation Ar was used exclusively as the non-polymerisable gas. Figure 2c shows a photo of the inside of the chamber with the plasma switched on. The colour of the plasma reveals the gas composition and can be used to detect impurities. The substrates of glassy carbon were mounted on double sticky tape on a
Experimental methods used in the study

glass tube, which was placed inside the chamber, while substrates of polyethylene (PE) were “hung” freely in the chamber. A quartz microbalance (QCM) crystal used to monitor the deposition rate on-line was also hung freely in the chamber. QCM measurements are discussed in section 2.4.

The working pressure of the chamber was as follows: the “standard” pressure, i.e. for a pure Ar flow, was 4.5–5 Pa; when using Ar and a single monomer the pressure was 9–9.5 Pa; when using Ar and a mixture of two monomers the pressure was about 10 Pa.

The low power plasma system is connected to an AC power supply. The two phases are connected to two electrodes, imposing a potential varying sinusoidal relative to the ground potential of the container. The potential of the two electrodes are out-of-phase by 180°. Due to the highly non-linear nature of the plasma, the current will vary in a non-sinusoidal fashion, where the ratio between the on and off times will be strongly dependent on the gas composition and the power introduced into the system.

2.2 Chemical surface characterisation

2.2.1 XPS

The principles of X-ray photoelectron spectroscopy are described in Watts and Wolstenholme [61] and Briggs [62]. For the XPS measurements two different machines were used: a SPECS Sage 100 instrument and a K-Alpha from Thermo Fisher Scientific.

The SPECS Sage 100, which was used for the majority of the measurements, is based on a non-monochromatic Mg Kα X-ray source having a power of 275 Watts (11 keV and 25 mA). During measurements the pressure in the sample chamber is always below 1 x 10⁻⁷ mbar.

Two kinds of spectra were obtained with the SPECS Sage 100: “survey” and “high” resolution spectra. The survey spectra were acquired at a “pass energy” (i.e. the width of the photon integration window) of 100 eV, probing binding energies in the range of 0 to 1100 eV. Afterwards, atomic concentrations were calculated from the intensities of the observed peaks in the spectra.
The high resolution spectra were acquired at 23 eV pass energy. The individual spectra were curve-fitted with a linear background and the full-width-at-half-maximum (FWHM) of the peaks constrained to 2 eV. Finally, the accurate binding energies were obtained using the C-C/C-H component in the C 1s spectrum at 285.0 eV as reference.

A smaller selection of the plasma modified surfaces were analysed with a new XPS instrument from Thermo Fisher Scientific. This XPS uses an Al K Alpha X-ray source and has an analysing spot size of 400 μm. For the acquisition of survey spectra the settings were as follows: 200 eV pass energy with an energy step size of 1 eV (10 scans). The probed range of kinetic energies in the survey scans was 0-1400 eV.

For the high resolution spectra of the chosen compounds the settings were: 25 eV pass energy with an energy step size of 0.1 eV (30 scans).

The spectra were analysed using ThermoAvantage v3.82 software from Thermo Fisher Scientific. The chemical shifts were cross-referenced using “The XPS of Polymers Database” by Beamson and Briggs [63].

2.2.2 ATR-FTIR

Attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR) was performed using a PerkinElmer Spectrum B instrument that was equipped with a Germanium (Ge) crystal. Spectra were collected within the range from 700 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and with averaging over 32 scans. The measurements were obtained at normal atmospheric pressure; where applicable measurements were performed both before and after water treatment. The ATR-FTIR vibrations were analysed using the “Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules” by Lin-Vien et al. [64].

2.2.3 Contact angle

Contact angle measurements were taken using OCA-15 equipment from Data Physics. The drop analysis was performed with SCA-20 (v. 3.11.6) software, where the drop volume was set to 4 μl for the automatic syringe.

Specimens were placed on an adjustable (x-y-z direction) stage that was cooled to 23°C. Using the automatic syringe a droplet was deposited on the surface, which is
Experimental methods used in the study

monitored by a camera mounted in such a way that the sharpness of the drop can be accurately corrected. Likewise, the brightness of the pictures can be regulated. The brightness is important, since the level of brightness depends on the type of surface. In the present case the contact angle was always measured using “the automatic mode” based on brightness levels.

2.2.4 Toluidine blue method

The toluidine blue staining method has been described by Sano et al. [65]. A detailed description of the method may also be found in Appendix B. Solutions, e.g. the fresh incubation dye and the acetic acid, were stored in distinct 30 ml flasks made of HDPE during the experiments.

In brief, a 2.0 \( 10^{-4} \) M solution of toluidine blue was prepared in 0.1 mM NaOH. Surfaces were then incubated in 5 ml of this dye solution for 1 hour in water bath at 40°C. Afterwards, they were carefully washed three times with 0.1 mM NaOH in order to remove the unreacted dye, before finally being dried with an Ar gun. Each of surfaces was now placed into a clean and dry HDPE flask, where 5 ml of acetic acid 50% v/v was added. The acid treatment lasted for 30 min at 40°C in water bath. Finally, 1 ml of the solution was taken out and placed in a 1.5 ml curvet, which was measured with a UV-VIS spectrometer (UV-1700 PharmaSpec, UV-visible Spectrophotometer, from Shimadzu). The spectrum was measured from 400 to 700 cm\(^{-1}\). The maximum absorption was at 630 cm\(^{-1}\). In conclusion, the amount of carboxylic acid groups was calculated by interpolation from a standard curve.

2.3 Topography of the surface – Atomic Force Microscopy

Two different instruments have been used for measuring the topography and thickness of the plasma coatings.

Most of the results presented in this thesis were obtained using a PSIA XE-150 state-of-the-art atomic force microscope using BS-Tap 300 tips, in tapping mode or intermittent contact mode. The BS-Tap 300 is a SiO\(_2\) symmetric probe with a length of 17 \( \mu \)m, which is produced by Budget Sensors. For thickness measurements the masking method of Hartley [66] was used. In brief, a droplet of a 5% poly-(D,L-lactide) (PDLLA) solution in acetone is pipetted onto the clean glassy carbon surface.
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and dried. This substrate is then subjected to plasma polymerisation. Next, the sample is placed in water for 24 hours to allow for the PDLLA to undergo hydrolysis. As a result of this procedure the PDLLA drop can be removed with a set of sharp tweezers, leaving a region on the substrate, which is free from the coating. The scan size for the thickness measurements was set-up for 20 μm and the scan rate to 0.5 Hz for determination of the cross-section picture. For topographical measurements the scan size was set-up for either 5 or 1 μm with a scan rate of 1 Hz. The data were analysed with the XEI software (version 1.5) from PSIA.

A few of the AFM measurements were performed using an older Dimension 3000 instrument from Digital Instruments. The same AFM cantilever was used as for the PSIA XE-150. The Dimension 3000 works only in tapping mode, and the topography scanning was performed on a 2.5 μm scale. The maximum scan size was 90 μm. For the surface analysis the NanoScope (R) III, version 5.12r3, software was used.

2.4 **QCM – Quartz Crystal Microbalance**

As mentioned in section 2.1 a quartz microbalance (QCM) crystal was used to monitor the rate of deposition during polymerisation. The QCM crystals used here were supplied by International Crystal Manufacturing Co., Inc., and had a working frequency of 10 MHz.

The QCM crystal was installed inside the plasma chamber and connected by copper wires through an impedance matching “PI-network” to an E5100A Network Analyzer from Agilent Technologies. The QCM was set up manually using dedicated software. The first step in the QCM analysis was to calibrate stray capacitances of the crystal assembly under measurement conditions, i.e. inside the plasma chamber. Afterwards, the chamber was pumped down to the working pressure, e.g. 4.5 Pa, and the polymerisation carried out as normal, with on-line monitoring of the crystal vibrations. The QCM measurements were carried out partly in collaboration with another Ph.D. student, Claus Højgård Nielsen.

2.5 **Mechanical tests**

Double Cantilever Beam (DCB) tests were used to assess the mechanical properties of the plasma treated model substrates. The DCB (Mode I) tests were carried out by Dr.
Experimental methods used in the study

Stergios Goutianos at the Materials Research Department, Risø-DTU. A brief description of this work is provided below, while further details are given in appendix D. A second, qualitative “peel-off” test was investigated by the author, assisted by technical staff from the Materials Research Department, and is also described below.

2.5.1 Double Beam Cantilever

The resin used for Double Cantilever Beam (DCB) sandwich specimens is an epoxy of type “Prime-20” from SP Systems. The resin and the hardener are mixed in a weight ratio of 4:1, then degassed for 2 times 5 min under vacuum, before the mix is finally injected into silicon rubber moulds between two plasma treated glassy carbon wafers (65x5x1 mm³). To keep the wafers apart and to create a “notch” of 20 mm in length Teflon films (0.5 mm in thickness) are used. The insert in Figure 3 shows an optical micrograph of the finished sandwich specimens.

The DCB specimens are first cured for 24 hours at room temperature and subsequently post-cured at 50°C for another 16 hours. Afterwards, the cured samples are ground and polished to facilitate optical observations of the crack growth (see below). The sandwich specimens are glued onto specially made stainless steel beams (6 mm in thickness) that could be mounted on the test fixture. A different epoxy adhesive (Scotch Weld) is used to glue the DCB specimens to the steel beams. This adhesive is left to cure for 24 hours at room temperature.

A special fixture [67], cf. Figure 3, is used to load the DCB specimens with force couples in order to create pure bending moments in the specimens. The loading of the specimens is performed at an approximately constant rotation rate of the beam ends. The particular specimen geometry and these loading conditions satisfy the condition for stable crack growth [68]. A comprehensive description of the geometry and how to calculate the plane strain energy release rate may be found in Appendix D.

The DCB tests are carried out either inside an environmental scanning electron microscope (Electroscan E3) or under an optical microscope. Specimens are monotonically loaded while recording the end-opening of the fixture and the applied moment, i.e. until a visible sharp crack has formed in the notched area, defining the fracture energy for crack initiation. At this point the DCB specimens are unloaded a little bit (to avoid time-dependent cracking), before continuing to load them until crack growth takes place. Again, the specimens are now unloaded partially, and the
crack length is measured. This procedure of loading and unloading continues repeatedly until the specimens fail.

The fracture resistance curve is obtained by plotting the measured fracture resistance as a function of the crack length. The behaviour of the fracture resistance curve is directly comparable to a typical R-curve, cf. Appendix D. The shape of an R-curve depends on the general material properties, e.g. the R-curve for brittle materials exhibits a monotonous linear behaviour (the longer the crack is, the more energy is needed), and so it is possible to characterise the material properties by comparison to a known type of R-curve [69, 70, 71, 72, 73]

Figure 3. Schematic illustration of the DCB specimen loaded with pure bending moments (not in scale, numbers given in mm); an optical micrograph is shown as insert.

2.5.2 Peel-off test

As an alternative to the DCB tests, a qualitative peel-off test [20] was examined, cf. section 7.3.

The preparation of glassy carbon samples for the peel-off test is shown schematically in Figure 4. In brief, two pieces of 40 μm metal foil are placed on top of a steel holder (a), creating a 17 mm wide rectangular interstice gap (b). The specimens are glued to the steel holder using a two-component epoxy adhesive (c), i.e. Epikote™ Resin
Experimental methods used in the study

MGS® RIM 135/H 137. The epoxy is mixed by hand (mixing ratio by weight 100:30) for 3 minutes before being placed in a vacuum oven in order to remove air bubbles. Afterwards, the epoxy is applied to the steel holder, which is already coated with a releasing agent, Multishield from Zyvax. The glassy carbon specimens are placed on top of the resin as shown in (d), the plasma treated side facing downwards, while another steel holder complete the sandwich (e). In this position the resin is cured for 24 hours at room temperature and then for another 15 hours at 60°C, followed by the detachment of the specimens from the steel holder (facilitated by the releasing agent). The epoxy layer is finally cut into 2x2 mm squares using a fine scalpel, and a Scotch 3M super-strength tape is attached to the “diced” surface.

By assumption the amount of epoxy squares that remain after peeling off the tape is a qualitative measure of the interfacial (epoxy-plasma coated surface) strength. Obviously, this yields no absolute information on how strong the interface is, however, it may be used to determine whether a particular interface is stronger or weaker than another treatment. In this study the tape is peeled off using an Instron 88 R 1362 machine, cf. Figure 5, which records time (which can readily be recalculated to distance) and load (in N). A load cell corresponding to a force of ±250 N (type: 2527-131; series no. 45082) was chosen. The “peel-off speed” was set at 5 mm/min. Variation of the peel-off speed show that the results may depend strongly on this setting.
Figure 4. Process of preparation of the samples for peel-off test.
Figure 5. Experimental set up for peel-off test and the sample view during the testing.
3 Plasma polymerised thin films of maleic anhydride and 1,2-methylenedioxybenzene for improving adhesion to carbon surfaces

This chapter summarizes the main results in the paper by Drews et al. published in Journal of Vacuum Science and Technology, 2007. The focus of the work is on plasma polymerisation and on chemical and topographical characterisation of plasma modified surfaces. The complete manuscript is reprinted in Appendix A.

3.1 Introduction

In this paper, plasma modification as means of improving adhesion to a planar carbon surface, i.e. the density of functional groups on the surface and its role on the interfacial adhesion strength, is investigated. Different concentrations of functional groups, i.e. carboxylic acid groups, are obtained by varying the plasma power as well as the choice of monomers. Here the discussion centres on the surface chemistry and topography of the modified surfaces. As mentioned in a preceding section glassy carbon is used as an experimental model of carbon fibres in reinforced composites.

For the plasma modification, the low-power 2-phase AC plasma system described in Chapter 2 with a power level less than 1 W/L was employed. One of the advantages of this system over other plasma systems is that the amount of free radicals is not very high. Hence, the polymerisation takes place mostly on the surface from radicals.
created during the pre-treatment, i.e. during the surface “activation”, while a constant flow of plasma keeps the polymerisation going. Maleic anhydride (MAH) and 1,2-methylenedioxy benzene (MDOB) are plasma deposited as homo-polymers and co-polymers in order to create layers with different surface compositions. In the case of maleic anhydride coatings, the surface chemistry may be changed by creation of carboxylic acid groups by hydrolysis in water. In the case of 1,2-methylenedioxy benzene the functional groups of carboxylic acid groups are created by plasma polymerisation as a result of the fragmentation of the monomer. All the surface modifications are made using the same treatment time while varying the plasma power. After the plasma treatment the surface chemistry is characterised using XPS and ATR-FTIR. Also, an AFM analysis is performed in order to probe the topography of the modified surfaces and study the relation between the surface topography and the plasma power. Finally, preliminary results of Mode I mechanical tests of the plasma modified specimens (Double Cantilever Beam method) are shown.

3.2 Results

From the AFM results, cf. Table 1, the surface roughness is found to grow with the plasma power. However, the thickness of the plasma polymerised layers also increases with the plasma power. Since plasma polymerisation process is a random process, it thus seems reasonable to assume that the observed increase in surface roughness should be attributed to the increase in thickness rather than the power level. Moreover, since the polymerisation time was kept constant, the changes in the thickness of the layers are probably related to the changes in the deposition rate of the plasma polymerisation.
Plasma polymerised thin films of maleic anhydride and 1,2-methylenedioxybenzene for improving adhesion to carbon surfaces

<table>
<thead>
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<th>Current (W/L)</th>
<th>Scan size (µm)</th>
<th>ppMAH Ra (nm)</th>
<th>ppMDOB Ra (nm)</th>
<th>ppMDOB/MAH Ra (nm)</th>
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<td>1</td>
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<td>0.79±0.42</td>
<td>1.98±1.90</td>
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<tr>
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<td>0.98±0.48</td>
<td>2.15±2.18</td>
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<tr>
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<td></td>
<td></td>
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<tr>
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<tr>
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<tr>
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<td>5</td>
<td>4.39±1.80</td>
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</tr>
</tbody>
</table>

Table 1. Roughness data for plasma modified layers on glassy carbon (reprint from Appendix A).

Despite the differences in the rate of film growth the XPS measurements show only insignificant changes in the surface chemistry as a function of the power level of the plasma polymerisation. The same is largely confirmed by the ATR-FTIR measurements, penetrating up to the first 1 µm of the surface. These observations are somewhat surprising as several authors report changes in the surface chemistry related to the plasma power. Arguably, the unchanged surface chemistry could be attributed
to the low power used during the polymerisation, e.g. which is found to preserve the ring structures and the functional groups of the monomers used. Alternatively, the XPS and ATR-FTIR analysis simply do not resolve the surface chemistry, as suggested by Figure 6, depicting the measured interfacial adhesion strength as function of the plasma power. In both cases the surfaces modified with a homo-polymer ppMAH and ppMDOB, respectively, show an obvious improvement in the interfacial adhesion strength with increasing plasma power, as compared to the untreated glassy carbon (Figure 6). This probably relates to changes in the surface chemistry. For ppMDOB the modified surfaces are at least twice as strong, and the strength increases with the plasma power level. For ppMAH the strength of the coatings exhibit a more complicated dependency on the plasma power level, although this coating was also investigated for the widest range of plasma powers as well as thicknesses of the plasma polymerised layer. For the co-polymer coating, on the other hand, only a marginal improvement in the interfacial adhesion strength is observed. Furthermore, the adhesion is very weak and therefore difficult to determine, since the specimens simply break during handling.
Plasma polymerised thin films of maleic anhydride and 1,2-methylenedioxybenzene for improving adhesion to carbon surfaces

Figure 6. Fracture toughness values for crack initiation as a function of power during polymerisation (time: 10 min – black and 3.2 min – grey). Open points represent experimental data whereas closed symbols represent the average value and the uncertainty for each treatment a) ppMAH, b) ppMDOB, c) ppMDOB/MAH, the solid line represents the fracture toughness of untreated glassy carbon, which is 7.5 J/m²; to guide the eye the dashed line represents the average value of initiation fracture toughness.

3.3 Summary

From the surface analysis of the plasma coatings, based on XPS and ATR-FTIR, observed changes in the surface chemistry of the plasma polymerised films as a function of the plasma power level are unexpectedly found to be insignificant. Conversely, the mechanical tests demonstrate a strong correlation between the plasma power level and the interfacial strength. This suggests that further investigations are required.
4 Stability and degradation of anhydride groups in pulsed plasma polymerised maleic anhydride coatings

In this chapter the stability and hydrolysis of surfaces modified with plasma polymerised maleic anhydride (ppMAH) is discussed. The chapter consists of three parts. The first part is a summary of manuscripts by Drews et al. to appear in Applied Surface Science, cf. Appendix B, and the proceedings of the 28th Risø International Symposium on Material Science, cf. Appendix C. The second part presents unpublished results of contact angle measurements complementary to both manuscripts, while the third discusses unpublished results on the stability of the ppMAH coatings under different thermal conditions based on AFM and XPS measurements. The chapter concludes with a brief summary of the results.

4.1 Hydrolysis of thin pulsed plasma polymerised maleic anhydride coatings

This chapter explores the hydrolysis and degradation/stability of coatings of ppMAH. Coatings made with different plasma parameters were exposed to aqueous hydrolysis media of different pH as a function of time and subsequently characterised using ATR-FTIR (structure analysis) and the toluidine blue staining method. The toluidine blue staining method yields a measure of the total number of carboxylic acid groups
in the coatings and provides quantitative results on the hydrolysis of anhydride groups to acid groups. Using the same experimental set up as described in Appendix A, i.e. a low power AC 2-phase plasma setup, coatings with constant thickness were deposited on glassy carbon or on polyethylene at different plasma powers, whereas coatings with varying thicknesses were obtained at constant plasma power by adjusting the polymerisation time.

The rate of the hydrolysis of the plasma polymerised coatings was found to be dependent on the pH of the hydrolysis media. In water, acid and weak alkaline solutions, the coatings appeared to be reasonably stable by visual inspection, while the observed degradation of the anhydride groups was slow. Likewise, the rate of hydrolysis of the anhydride groups in different solutions was similar. For stronger alkaline solutions, on the other hand, an acceleration of the reaction was observed as well as dissolution of the coating with extended treatment time.

In general the hydrolysis was found not to be dependent on the thickness of the polymerised layer. Three different thicknesses were tried, corresponding to 5, 10 and 20 minutes of polymerisation time. In all three cases 90% of anhydride groups are hydrolysed to carboxylic acid groups in 10 mM NaOH solution during the first 15 minutes. Conversely, the stability, i.e. from a mechanical point of view, was found to be highly dependant on the thickness of the coating. Films polymerised for 30 min that are placed in 10 mM NaOH were seen to break into flakes after 15 min, whereas films polymerised for shorter times (up to 20 min) do not experience this problem during hydrolysis.

As mentioned above coatings polymerised with different plasma powers and constant thicknesses were achieved by varying the polymerisation time. The observed trends of the hydrolysis of the coating in 10 mM NaOH are shown schematically in Figure 7. The hydrolysis of the coatings exhibit a strong dependence on the plasma power, i.e. those coatings created with low power have a tendency to dissolve more readily in sodium hydroxide solutions, while the coatings become progressively more stable with increasing plasma power. The resistance to hydrolysis can attributed to cross-linking during the plasma polymerisation (see next section). Increasing plasma power increases the time necessary to obtain the maximum concentration of carboxylic acid groups on the surface during hydrolysis, showing that the coating is therefore less able to swell because of the increased cross-linking.
Stability and degradation of anhydride groups in pulsed plasma polymerised maleic anhydride coatings

The number of carboxylic acid groups available on the surface, just after the samples are taken out of the plasma chamber, increases with decreasing plasma power. This is consistent with the suggested dependence of the cross-linking of ppMAH coatings as a function of the plasma power. Finally, the maximum number of carboxylic acid groups was found to be independent of the plasma power, cf. Figure 7 in Appendix B.

Figure 7. Schematic trends of the hydrolysis of plasma polymerised maleic anhydride coatings on PE. Coatings are produced with different plasma levels and the polymerisation time is varied to obtain the same thickness.

4.2 Pulsed plasma deposited maleic anhydride thin films as functionalised surfaces in composite materials

In this chapter, which is reprinted in Appendix C, the coatings of plasma polymerised MAH are reviewed. Furthermore, observed differences in interfacial fracture energy (measured by the double cantilever beam test, Appendix A), are discussed - based on analyses of the surface chemistry (measured by XPS, and the toluidine blue staining method) and the resistance to hydrolysis in alkaline solution (measured using the toluidine blue staining method, cf. Appendix B).
Recalling that results from XPS analysis (Appendix A) and the toluidine blue staining method (Figure 7, Appendix B) both consistently showed that changes in the surface chemistry were negligible, the time evolution of the hydrolysis was investigated (Figure 6 in Appendix B). As mentioned above the (slow) increase in the number of carboxylic acid groups observed for high and intermediate plasma powers may be attributed to cross-linked bonds, preventing the swelling of the ppMAH layers, where the different trends are related to the cross-link densities. Likewise, the dissolution of the coatings created with low plasma power levels would reflect an insufficient amount of cross-linking and a high content of oligomers. Alternatively, the bonds may be C-O bonds, which can be hydrolysed. In both cases the observed behaviour demonstrates a dependence on the plasma power level, as do the double cantilever beam tests (Figure 6(a); Figure 4 in Appendix C), which is not found in the surface analysis.

To explain these results it is necessary to consider the structure of the plasma polymerised thin films in terms of a strictly 2-D structure and as a bulk material. XPS is a surface sensitive method and only penetrates down to max. 10 nm regardless of the actual thickness and so this analysis is equivalent to the first view. As a bulk (3-D) material, on the other hand, there is a significant dependence on the plasma power level, i.e. as shown in case of the hydrolysis of the coating and through the mechanical tests. The behaviour of specimens created at a plasma power of 0.7 W/L are thus found to behave significantly different from specimens created at lower and higher plasma power, i.e. by showing a particular strong adhesion and “strong” (increasing) R-curve behaviour (R-curves are discussed in Appendix D). It is probable that the difference in the mechanical properties may also be related to the different cross-linking densities in the plasma polymerised layers; cf. Figure 4 in Appendix C. In case of weakly cross-linked plasma polymerised layers (low plasma power) the amount of oligomers is large and the cohesion low. Conversely, in case of highly cross-linked plasma polymerised layers (high plasma power) the linear polymers between the cross-links are short, and since cross-linked material cannot be stretched indefinitely, the cohesion is likewise expected to be low.

In conclusion, the present study fully demonstrates the importance of carefully optimising the conditions for creating the plasma coatings. Furthermore, it is shown that weak, intermediate and strong interfaces could easily be manufactured, and hence
Stability and degradation of anhydride groups in pulsed plasma polymerised maleic anhydride coatings

that plasma modification may play an important role in the design of composite materials.

4.3 Contact angle measurements of the hydrolysed coatings.

To elaborate on the hydrolysis of the ppMAH coatings discussed in the preceding section, a number of complementary contact angle measurements were carried out as a function of the hydrolysis time, e.g. in order to confirm the stability of the coatings. In all cases samples polymerised on PE substrates were used.

Contact angle measurement is a technique for analysing the surface energy and tension from the shape of a liquid drop deposited on a solid surface. The contact angle is defined as the angle between the surface and the tangent to the drop shape in the point where it touches the surface. This measure is extremely surface sensitive and has the ability to detect properties even on monolayers.

In the following water was used for the contact angle measurements, although it is generally best to use a liquid that does not interact with the underlying surface. In the present case, however, both the anhydride groups on the ppMAH surfaces as well as the hydrolysed carboxylic acid groups react chemically with water molecules, whether from the droplet or from the air (surfaces were only exposed to air after plasma polymerisation). Consequently, the contact angle measurement cannot be taken as a direct measure of the surface energy, but is used here as a measure of the interaction between the surface and water, i.e. as an expression of the changes in the surface chemistry and stability of the coating.

Figure 8 shows the amount of COOH created during hydrolysis (in black) and contact angle measurements (in grey), respectively, of (ppMAH 0.8 W/L; 10 min) surfaces hydrolysed in weak base (0.1 mM NaOH). The number of carboxylic acid groups has a peak value of approx. 20 nmol/cm². For comparison, in case of the hydrolysis in strong base (10 mM NaOH, results not shown), the density of carboxylic acids groups on the surface peaked at approx. 36 nmol/cm².
**Figure 8.** Surface behaviour during the hydrolysis in 0.1 mM NaOH over 3 hours for ppMAH 0.8 W/L, 10 min. The black circles represent the density of carboxylic acid groups created during hydrolysis of anhydride groups as a function of time, while the grey ones correspond to contact angle measurements. Corresponding contact angle measurements are shown in grey on Figure 8. Unlike the density of COOH the contact angle has constant high value of ~70°, suggesting that the ppMAH coatings are relatively stable in the mechanical sense, at least over the 2 hours of hydrolysis. As reported by Karin Bagger Stibius [74] unstable surfaces are typically characterised by small contact angles and high wetting.

Similar graphs picturing the hydrolysis of the plasma coatings created at high and low plasma power, respectively, are shown on Figure 9 along with the contact angle measurements. In case of films created at low plasma power (a) the observed dissolution is slow and continuous, i.e. as inferred by the toluidine blue staining method, while the corresponding contact angles are small, indicating near complete wetting of the surface. The dissolution and possible swelling of plasma polymerised layers have been discussed by Forch et al. [75]. In the present case only two contact angle measurements could be carried out, since in most cases the wetting was so high.
Stability and degradation of anhydride groups in pulsed plasma polymerised maleic anhydride coatings

that it was impossible to measure. Since the contact angle is found to be small even on surfaces unexposed to, e.g. aqueous solutions, it is assumed that the coatings created by low plasma power contain mainly oligomers and have a high content of monomer molecules.

Figure 9. Sessile contact angle measurements and hydrolysis of anhydride groups on surfaces modified with maleic anhydride of different plasma power levels; a) 0.12 W/L; b) 1.2 W/L as function of treatment time.
In case of films created at the highest plasma power, cf. Figure 9(b), the measurements indicate a slow hydrolysis (high hydrolysis resistance) with the number of carboxylic acid groups increasing throughout the full three hours of the hydrolysis. As mentioned above this behaviour may be assigned to an increase in the cross-linking density, related to the high plasma power level, and to swelling of the layers of plasma polymerised maleic anhydride during the hydrolysis [76]. Before the surfaces are exposed to the alkaline solution the contact angle measurements (in grey), on the other hand, show a high value of around 100°, which already after 15 minutes of hydrolysis drops to lower values similar to those of Figure 9(a). Based on the contact angle measurements the surface thus seems to become unstable, even though the hydrolysis data actually show an increase in the number of carboxylic acid groups during hydrolysis. Arguably, this could be interpreted as if the outer most layer of the coating is hydrolysed, and therefore a slow dissolution process is going on from the surface.

4.4 Stability under different thermal conditions

The stability of the plasma coatings of maleic anhydride on glassy carbon was investigated under different thermal conditions. The thermal conditions were chosen to resemble the conditions during preparation for mechanical tests. The motivation of this exercise was to characterise the response of the surface on different treatment conditions, e.g. in order to better understand the failure procedure. After plasma modification the glassy carbon substrates were cut into smaller pieces, which were analysed individually. The stability of the coatings was mainly tested for changes in the chemistry (by XPS) and the topography (by AFM).

Four experiments were set up as follows:

Specimens were heated up to 90°C in an oven for 24 hours.
Specimens were heated up to 90°C in water for 24 hours.
Specimens were kept at room temperature in water for 65.5 hours.
Specimens were kept at room temperature in water for 168 hours.

The topography, e.g. the surface roughness, and the surface chemistry were examined before and after the thermal treatments.
Stability and degradation of anhydride groups in pulsed plasma polymerised maleic anhydride coatings

Table 2 summarises the observed differences in the surface chemistry under different thermal conditions. The XPS results show almost no changes as compared to the unheated ppMAH.

<table>
<thead>
<tr>
<th>Sample treatment</th>
<th>O/C ratio</th>
<th>C-C, 285.0 eV</th>
<th>C-O, 286.5 eV</th>
<th>C=O, 288.0 eV</th>
<th>C(O)O, 289.2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppMAH</td>
<td>0.44±0.04</td>
<td>60.9±3.5%</td>
<td>17.1±2.2%</td>
<td>7.0±1.0%</td>
<td>17.2±2.3%</td>
</tr>
<tr>
<td>Water, at room temperature (65.5h)</td>
<td>0.43±0.01</td>
<td>61.5±0.9%</td>
<td>16.3±0.6%</td>
<td>6.0±0.8%</td>
<td>16.3±0.4%</td>
</tr>
<tr>
<td>Water, at room temperature (168h)</td>
<td>0.42±0.01</td>
<td>60.0±0.2%</td>
<td>18.8±1.7%</td>
<td>7.6±0.1%</td>
<td>13.7±1.7%</td>
</tr>
<tr>
<td>Water, heated up to 90°C</td>
<td>0.41±0.02</td>
<td>61.8±1.6%</td>
<td>18.4±1.6%</td>
<td>6.3±1.3%</td>
<td>13.6±1.8%</td>
</tr>
<tr>
<td>Heated up to 90°C</td>
<td>0.43±0.01</td>
<td>58.3±2.5%</td>
<td>20.0±0.4%</td>
<td>7.3±2.3%</td>
<td>14.6±0.5%</td>
</tr>
</tbody>
</table>

Table 2. Average chemical composition of the plasma maleic anhydride surfaces treated under different thermal conditions.

Table 3 shows the corresponding roughness’s of the modified glassy carbon surfaces before and after the different thermal treatments (measured by AFM).
<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>Clean glassy carbon; Roughness, nm</th>
<th>Before thermal treatment; Roughness, nm</th>
<th>After thermal treatment; Roughness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, at room temperature (65.5h)</td>
<td>0.90±0.02</td>
<td>4.74±0.02</td>
<td>3.07±0.05</td>
</tr>
<tr>
<td>Water, at room temperature (168h)</td>
<td>0.92±0.01</td>
<td>2.84±0.07</td>
<td>1.58±0.02</td>
</tr>
<tr>
<td>Water, heated up to 90°C</td>
<td>0.9±0.1</td>
<td>3.1±0.2</td>
<td>1.83±0.06</td>
</tr>
<tr>
<td>Heated up to 90°C</td>
<td>1.0±0.1</td>
<td>4.4±0.2</td>
<td>4.6±0.1</td>
</tr>
</tbody>
</table>

Table 3. Changes in topography after different thermal treatments; every value is an average of at least two AFM measurements; the scan size is 2.5x2.5 μm; tapping mode with Dimension 3000.

On average the roughness of clean glassy carbon is 0.93±0.08 nm. The roughness was found to increase, on average to 3.8±0.9 nm, after the plasma treatment with maleic anhydride (0.7 W/L; 10 min). The roughness of the untreated plasma coatings vary within uncertainty across the glassy carbon substrates. For those specimens heated in water significant roughness changes are observed as a result of the thermal treatments. In all three cases the roughness is seen to decrease, something that could be explained by collapsing of the film or by partial dissolution. Since the thickness of the film was not monitored, however, the degree of dissolution or delamination of the coating after the treatment is very difficult to assert. On the other hand, XPS did not show an increase in the carbon content, which might indicate that the coating is still thicker than the probing depth.

4.5 **Summary**

Coatings of plasma polymerised maleic anhydride have been analysed during hydrolysis and under different thermal conditions in order to study changes in the surface chemistry and topography. In general, XPS measurements show the surface chemistry to be unchanged under different treatment conditions, while AFM measurements show an increase in the surface roughness as a result of the plasma...
Stability and degradation of anhydride groups in pulsed plasma polymerised maleic anhydride coatings treatment, i.e. as compared to a clean glassy carbon surface. After hydrolysis the observed surface roughness is found to decrease. Similarly, the specimens heated to 90°C in water also exhibit a decrease in the surface roughness. This could be evidence of a possible dissolution of the film, however, the XPS results suggest that the coating remains thicker than the probing depth. Speculatively, if one assumes that the delamination of ppMAH layers has the same effect as the curing of the epoxy, the detached parts of the coating can therefore diffuse into the matrix.

The hydrolysis of ppMAH of different plasma power levels in 10 mM NaOH shows different trends of degradation of the anhydride groups on the surface. Possibly these differences may be assigned to different degrees of cross-linking during plasma polymerisation. In strong alkaline solutions the observed degradation of anhydride groups is fast and leads to delamination. The observed delamination is confirmed by contact angle measurements.
5 Surface characterisation of the fracture surfaces

This chapter discusses the analysis of the fracture surfaces after the double cantilever beam (DCB) tests, cf. section 2.5.1. A selection of representative specimens was analysed for changes in the surface chemistry and topography (using XPS and AFM, respectively) in order to obtain more information on the crack propagation and the failure mechanism. None of these results have previously been published.

5.1 Chemical analysis of the fracture surfaces

Chemical analysis of the fracture surfaces is important in order to improve our understanding of the crack propagation. Principally, the crack may propagate in four different ways: a) along the interface of glassy carbon and the plasma coating, b) in the plasma coating, c) along the interface between the plasma coating and epoxy resin, or d) in the epoxy resin.

As detailed in preceding chapter’s the surface chemistry of the plasma polymerised coatings on glassy carbon substrates has previously been investigated. The chemistry of the cured epoxy resin is well known from chemical fact sheets and was furthermore verified by dedicated XPS analysis (results not shown). Table 4 compiles the chemical composition of the fracture surfaces, as measured by XPS. Note that the glassy carbon (GC) and epoxy sides of the DCB sandwiches were analysed separately, to yield a more complete picture of the chemistry of the fracture surfaces.
<table>
<thead>
<tr>
<th>Sample name</th>
<th>Power, W/L</th>
<th>Time, min</th>
<th>Monomer</th>
<th>O 1s</th>
<th>C 1s</th>
<th>N</th>
<th>Si</th>
<th>Na 1s/ S 2p</th>
<th>Type of surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cured Epoxy</td>
<td></td>
<td></td>
<td></td>
<td>15.0</td>
<td>79.6</td>
<td>2.3</td>
<td></td>
<td>2.4%/</td>
<td></td>
</tr>
<tr>
<td>Glassy Carbon</td>
<td>5%</td>
<td>95%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.60%</td>
<td></td>
</tr>
<tr>
<td>ppMDOB Average, all treatments</td>
<td>19±2%</td>
<td>81±2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>050412 0.7 10 MDOB</td>
<td>18.8%</td>
<td>81.2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>050412</td>
<td>16.1%</td>
<td>83.9%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>ppMAH Average, all treatments</td>
<td>31±2%</td>
<td>69±2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060504b 0.7 3.2 MAH</td>
<td>23.5%</td>
<td>68.8%</td>
<td>7.70%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060504b</td>
<td>19.0%</td>
<td>77.9%</td>
<td>2.5%</td>
<td>0.60%</td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060704a_4</td>
<td>21.8%</td>
<td>75.1%</td>
<td>3.0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060704a_4 0.9 10 MAH</td>
<td>23.4%</td>
<td>73.4%</td>
<td>2.7%</td>
<td>0.60%</td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060704a_5</td>
<td>20.6%</td>
<td>75.1%</td>
<td>3.0%</td>
<td>1.30%</td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060703a_2</td>
<td>25.3%</td>
<td>71.0%</td>
<td>2.5%</td>
<td>1.30%</td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060703a_2 0.3 10 MAH</td>
<td>28.5%</td>
<td>68.4%</td>
<td>2.7%</td>
<td>0.40%</td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060703a_4</td>
<td>28.4%</td>
<td>69.2%</td>
<td>2.4%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060703a_4 0.3 10 MAH</td>
<td>26.6%</td>
<td>68.7%</td>
<td>3.7%</td>
<td>1.10%</td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060703a_5</td>
<td>25.1%</td>
<td>71.6%</td>
<td>3.0%</td>
<td>0.30%</td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060703a_5 0.3 10 MAH</td>
<td>29.4%</td>
<td>67.6%</td>
<td>2.9%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060703a_6</td>
<td>28.3%</td>
<td>68.8%</td>
<td>2.9%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060703a_6 0.3 10 MAH</td>
<td>25.6%</td>
<td>70.0%</td>
<td>3.3%</td>
<td>1.2%</td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060703a_7</td>
<td>25.1%</td>
<td>70.5%</td>
<td>3.7%</td>
<td>0.60%</td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060703a_7 0.3 10 MAH</td>
<td>28.7%</td>
<td>68.2%</td>
<td>3.1%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>060703a_8</td>
<td>25.0%</td>
<td>70.2%</td>
<td>3.9%</td>
<td>0.90%</td>
<td></td>
<td></td>
<td></td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>060703a_8 0.3 10 MAH</td>
<td>25.1%</td>
<td>69.8%</td>
<td>3.4%</td>
<td>1.10%</td>
<td>0.7%</td>
<td></td>
<td></td>
<td>Epoxy</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Chemical composition of surfaces before and after DCB mechanical tests. The rows labelled “ppMDOB” and “ppMAH”, respectively, are averaged over all plasma conditions before the fracture tests, cf. Appendix A, whereas rows labelled by a sample name (yymmdd#_speciment number) show the chemical composition of the fracture surfaces as a function of plasma conditions. For comparison the first two rows show the chemical compositions of cured epoxy and uncoated glassy carbon, respectively. An empty entry means “= 0%”. 

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Surface characterisation of the fracture surfaces

Before the mechanical tests the average surface composition for plasma polymerised maleic anhydride is found to be 31±2% oxygen and 69±2% carbon, whereas for plasma polymerised 1,2-methylenedioxy benzene the chemical composition is 19±2% oxygen and 81±2% carbon. For comparison the chemical composition of unmodified glassy carbon contains 5% oxygen and 95% carbon. Further details are given in Appendix A.

For surfaces modified with 1,2-methylenedioxy benzene (polymerised at a power of 0.7 W/L for 10 min) the coating thickness is about 100 nm, and the mechanical tests show an improvement in the interfacial strength corresponding approx. to a factor of 5. The chemical composition of the fracture surfaces (both sides of the specimen sandwich) are found to be practically identical to that of untested ppMDOB, suggesting that the crack propagates exclusively within the plasma coating. The lack of a nitrogen signal is further evidence of this, since the presence of nitrogen would also suggest a crack between the plasma coating and the epoxy resin.

As opposed to ppMDOB nitrogen is found on the fracture surfaces of all specimens polymerised with maleic anhydride, i.e. the XPS analysis show a nitrogen content of approx. 3% regardless of the plasma treatment. During the curing of the epoxy a chemical reaction takes place between the functional (carboxylic acid) groups of the coating and the functional (amino) groups of the hardener. The presence of nitrogen therefore signifies that the crack propagates along the interface between the plasma coating and the resin. The fact that the chemical surface compositions (O1s; C1s; N) from Table 4 seem to fall reasonably in-between those of cured epoxy (15%; 79.6%; 2.3%) and untested ppMAH (31%; 69%; 0%) would support this. In addition to nitrogen many of the specimens show further traces of silicium, sodium and sulphur. These are contaminations of the surface, which may have occurred during the sample preparation (i.e. at laboratory in the Materials Research Department), after the mechanical tests or during transportation. If the surfaces were contaminated during the processing, this might possibly explain some of the observed scatter in fracture energy (see Appendix A).

5.2 Topography of the fracture surfaces

In this study AFM measurements have primarily been employed as means to determine the thickness and roughness of the plasma polymerised layers, cf. section
2.3. Additionally, AFM was also used for inspection of the topography of the coatings after fracture mechanical tests, though only on an *ad hoc* basis. In case of fracture surfaces two ppMAH specimens were selected, based on chemical analysis, so that the chemical composition of the first (060703a_2) closely resembled that of the untested specimens, while the second specimen (060703a_5) differed significantly. Simple topographical analyses of these specimens are detailed below.

### 5.2.1 Introduction

Mandelbrot et al. [77] were the first to analyse the topography of (metallic) fracture surfaces, having investigated the surface morphology as a function of different processes taking place during strength testing. Typically, such analysis is carried out using either AFM (as in the present work) or SEM (Scanning Electron Microscopy). Although SEM allows for higher resolution, Daguier and co-workers [78] have compared the two methods, while examining the roughness of the fracture surface in an aluminium alloy as a function of crack velocity and stress intensity, and they find both techniques to yield similar results.

It is well established that fracture surfaces generally satisfy a scaling invariance known as *self-affinity* and exhibit scaling properties on two or three decades of length scales, e.g. as detailed by Daguier et al. [78]; Wunsche et al. [79]; and Bonamy et al. [80]. The determination of the scaling properties is often achieved using the roughness/ self-affine exponent, $\xi$, quantifying the scaling of the typical height (from the height profile) according to the power law, $h(t) \approx r^\xi$, where $r$ is a length. Reviewing the fracture surfaces of different materials, Bouchaud [81] have proposed that the roughness of the fracture surfaces does not depend on the material nor the method used for mechanical testing. Or in other words: that for most materials the associated roughness exponent takes on a seemingly *universal* value, $\xi \approx 0.8$, independent of the fracture mode and the material. While arguably most studies dedicated to the roughness of cracks have dealt with fracture surfaces close to this value, recent works, e.g. Ponson et al.’s [82] analysis of fractured Fontainebleau sandstone for which $\xi \approx 0.4-0.5$, have raised fundamental questions about the fracture physics, i.e. whether $\xi$ is actually a property of the material or the failure mechanism.

Polymeric fracture surfaces have previously been investigated by Mader et al. [83]. Mader et al. examined glass fibres that were surface modified with aminosilanes,
measuring the coverage of the polymer coating and its influence on a single fibre pull-out test. In brief they show that the amino groups on the surface react with the matrix, and that the roughness of the fracture surfaces increases the most, when the initial surface roughness is low. Other studies by Hinojosa et al. [84] and Gonzalez et al. [85] have probed the fracture surfaces of crystalline polymers. At the highest magnification the morphologies of the fracture surfaces are found to be similar to those for brittle materials with local plastic deformations. At lower magnification the fracture surfaces display crystalline features, which prove to be highly dependent on the sample preparation conditions. Interestingly, in both cases the roughness exponent for the fracture surfaces is found to be consistent with $\xi \approx 0.8$.

5.2.2 Results and discussion

Figure 10 shows fracture surfaces of two different ppMAH samples, chosen on the basis of the chemical analysis. From XPS analysis the chemical composition of the first specimen, (a)-(b), is found to be similar to that of an untested ppMAH surface, suggesting that the crack might propagate mainly inside the plasma polymerised layers as in the case of ppMDOB. Conversely, traces of nitrogen indicate crack growth along the interface between the plasma coating and the epoxy resin.

Figure 10 (a) illustrates the “fingerprint” left behind on the surface after the crack has formed. The image shows the “error function” measured by AFM. To measure the error function the position of the AFM tip is initially set to a particular value, and while scanning the topography is measured relative to this setting; even very weak structures can be asserted in this way. In Figure 10 (a) changes in the topography are clearly seen to grow from two round features. These are impurities in the glassy carbon, which obviously affects the overall fracture energy of the surface. It is, however, impossible to establish which layers are affected, since the error function only maps relative depth.

Figure 10 (b) magnifies a different part of the same specimen. This image pictures the absolute topography of the fracture surface. The part of the surface below the “boundary line” seems to be largely unfractured, whereas the regular “ripple pattern” dominating the upper part penetrates all the way to the glassy carbon substrate (approx. 80 nm). The latter indicates that in this region the crack propagates along the interface between the glassy carbon and the plasma coating. From Figure 10 (b) and
the chemical analysis it therefore seems likely that for this specimen cracks have occurred along both interfaces (glassy carbon-ppMAH, ppMAH-resin) and in the coating.

Figure 10. Topography of the fracture surfaces (ppMAH 0.3 W/L; 10 min). Images (a) and (b) picture the fracture surface of sample 060703a_2 (fracture energy of the interface: 23 J/m²), while images (c) and (d) are for sample 060703a_5 (fracture energy of the interface: 17 J/m²). Note that (a) shows the error function (see text) rather than absolute measures of the topography.

Figure 10 (c) and (d) shows analogous AFM pictures for different places on a second specimen, which was found to differ more strongly from the unfractured ppMAH
Surface charaterisation of the fracture surfaces

The surface structures in Figure 10 (c) have a height of approx. 70 nm, while the features shown in (d) are only a couple of nanometers.

Andrews [86] have defined three different regions or “zones” related to different types of morphologies, where the shapes of the zones are found to be related to the stress of the crack propagation in the material [87]. The first (very smooth) region of a brittle fracture surface is the “mirror zone”, which is associated with slow but accelerating crack growth. The second region of a brittle fracture surface is the “mist zone”, which has a cloudy look, and is caused by the crack propagating at up to the maximum velocity, but where insufficient energy is being released to cause crack branching. Finally, there is a rough and ridged “hackle zone”, where the crack branches while growing at maximum velocity, often resulting in a piece of material being ejected.

The observed morphologies, in particular Figure 10 (c), look similar to those reported by Guerrero et al. [88], who has studied the fracture surfaces of polymeric materials, i.e. polypropylene (PP) and amorphous polystyrene (PS), with AFM and SEM. Based on Guerrero’s work the morphology displayed by (c) is probably the transition from the mirror zone to the hackle zone, where the triangular region in the upper right represents the intermediate state. The “patch” morphology in the lower part of (c) and in Figure 10 (d), resulting from the removal of isolated patches of material from either side of the fracture surface, indicates the hackle zone. Arguably, the observed morphology, in particular Figure 10 (c), may be taken as additional evidence for crack growth along the interface between the coating and the resin.

5.3 Summary

The chemical compositions of ppMDOB and ppMAH fracture surfaces have been analysed with XPS in order to investigate the crack propagation. In case of ppMDOB the chemical composition of the fracture surfaces was found to be similar to that of the plasma treated coatings and practically identical on both sides of the sandwich specimens. Furthermore, XPS showed no traces of nitrogen or any contaminants, e.g. silicium. This suggests that the crack propagates exclusively within the plasma coating. In case of ppMAH the content of oxygen and carbon deviates slightly from unfractured specimens, and the fracture surfaces exhibit traces of nitrogen as well as contamination from silicium, sulphur and sodium. The presence of nitrogen suggests that anhydride groups or carboxylic acid groups have reacted with amino groups from
the hardener, creating chemical linkage between the plasma layer and the epoxy, and therefore that the crack propagates along the interface between the coating and the resin. Possibly, the contaminants contribute to the large spread observed in the fracture energies, cf. Appendix A.

Two of the ppMAH fracture surfaces were visualised with AFM in order to observe changes in the topography. AFM pictures of the first specimen indicate that the topography (e.g. defects) in the underlying substrate influences the crack propagation, and that for this specimen the crack even propagates into the interface between the coating and glassy carbon. On the other hand, the morphology in Figure 10 (b) can be taken as evidence that this specimen is a bad representative of the batch. Contrarily, the morphology of the second specimen is largely consistent with those found for similar polymeric materials, demonstrating that AFM can be used as a tool to obtain more information about the fracture surfaces.
This chapter presents unpublished results of reacting diamine compounds onto a plasma polymerised maleic anhydride surface. Two different diamine compounds both containing aliphatic carbon chains are examined: 1,2-ethylenediamine (EDA) and 1,6-hexanediameine (HDA). The chapter contains a brief summary of related work then concentrates on the experimental procedure and the chemical analysis of these reactions. Regrettably, complementary mechanical tests could not be carried out, as the test equipment at this point in the investigations proved to be in a state of permanent disrepair.

### 6.1 Introduction

As detailed in previous chapter’s the interfacial strength, i.e. between a glassy carbon surface and an epoxy layer, can be improved by functionalising the former with carboxylic acid groups, using a plasma treatment. The best adhesion was obtained after plasma modification with maleic anhydride. Alternatively, an epoxy layer may also react chemically with an amino group [89]. Carbon fibres having a functionalised coating of amino groups have previously been investigated, e.g. by Mader et al. [83], who found the fracture surface to be greatly influenced by the chemical linkage between the amino groups and epoxy resin. Similar promising results with amine groups on the surface were obtained by Westermann and Minzari [13].

Since amino-containing monomers are in general highly reactive towards rubber, such monomers can degrade the rubber air-sealing typically used in most plasma chambers. Also, the use of amino-containing monomers for plasma modification has another
Surface Polymerisation Methods for Optimised Adhesion, Joanna M. Drews

drawback, i.e. the surface chemistry (e.g. the relative content of oxygen, carbon and nitrogen) is well known from literature to change in a non-trivial manner over time (days) [90, 91, 92, 93].

Kettle et al. [94] have formerly examined the strength of the interface between carbon fibres and epoxy resin as a function of different functional groups, deposited by radio frequency plasma polymerisation. Kettle and his co-authors found the best results to be given by the carboxylic acid and amino groups, i.e. due to the chemical reaction with the epoxy layers. Similarly, using a peel-off test, Friedrich et al. [95] have assessed the interfacial strength between aluminium and plasma polymerised layers with varying concentrations of functional amino groups, carboxylic acid groups and hydroxyl groups. In this study, however, Friedrich finds the amino groups to yield the weakest interfaces. Other work by Lopattananon et al. [96] analyses different processes taking place on amino-coated surfaces during mechanical stress tests. Finally, ultra-high strength polyethylene fibres have been coated by means of plasma polymerised allylamine by Li and Netravali [97] for improved interfacial adhesion.

In the present study amino groups are reacted onto the surface after the plasma polymerisation of maleic anhydride, in order to avoid introducing amino-containing monomers directly into the plasma chamber. This approach has previously been described by Kluger and Hunt [98], who report the speed of the reaction in solution and under certain desirable conditions. Another study by Evenson and Badyal [99] have examined solvent-free surface functionalisation of anhydride copolymer films with different amides. Here, the authors find amide linkage to be formed with a high degree of conversion, while running to completion in less then 40 minutes. Evenson and Badyal have also shown that pulsed plasma polymerisation of maleic anhydride leads to the deposition of well-defined anhydride functionalised films, which readily undergo reaction with amine-terminated nucleophiles, i.e. to produce surface amide linkages; films that may be converted into cyclic imide groups upon heating [100]. Lastly, the modified specimens were tested for lap joint adhesion, and found to yield lower adhesion than that of the untreated surface.

Other work worth mentioning includes Fail et al. [101], who have looked at surface reactions involving amino compounds based on plasma polymerised maleic anhydride, in the context of producing packaging materials. Finally, Tseng et al. [102] have examined nanocomposites consisting of multi-walled carbon nanotubes treated
with plasma polymerised maleic anhydride and subsequently reacted with Jeffamine® - a range of commercial polyether amines. Tseng evaluates the tensile properties of the modified carbon nanotubes as well as the dispersion in the epoxy resin, finding the surface modification to improve the performance of the nanocomposites.

6.2 Reaction of the diamine molecules to the surface

The reaction of the anhydride groups on the surface with the diamine compounds was carried out just after the plasma polymerisation [99]. Both glassy carbon and PE substrates were used. Since amines are highly chemically reactive, the modified surface was taken out of the plasma chamber to avoid reactions with, e.g. the rubber sealings. The sample was then attached to the inside of a glass Petri dish that was placed upside down on top of another Petri dish containing a few hundreds of millilitres of the liquid diamine compound. As both diamine monomers have very high vapour pressures (ethylenediamine: 10 mmHg (20°C); hexanediamine: 1.5 mmHg (50°C)), a thin film of the unreacted monomers will immediately begin to form on the plasma treated surface. Hence, the surface (i.e. the top Petri dish), was heated to 50°C to create a downwards temperature gradient, which to some degree served to prevent the deposition of unreacted monomers. After exposure to the diamine vapour for approx. 1 hour, about half the specimens were analysed by XPS and ATR-FTIR, while the other half (only glassy carbon samples were heated, as PE would melt) was placed in vacuum and heated to 120°C for approx. 17 hours before XPS analysis. The intended chemical reaction of the anhydride groups with 1,2-ethylenediamine is detailed in Scheme 1.

Scheme 1. Reaction of 1,2-ethylenediamine with anhydride groups on the surface, cf. Evenson and Badyal [99]. The chemical reaction with 1,6-hexanediamine takes place under the same conditions and is carried out in the same way.
The heating after the aminolysis served two purposes. The first was to remove any unreacted remains of diamine molecules without the use of a solvent, the second to close the ring structure in order to obtain imide and amino groups on the surface, as described by Evenson and Badyal [100]. Both these functional groups are stable under normal atmospheric conditions.

As shown in Scheme 2 it is in principle possible for the second amino group of the diamine compound also to react with an anhydride group on the surface. This can only happen, however, if the relative positions of the anhydride groups (which are fixed to the surface) allow it. If both the amino groups of the compound react the result is similar to the cross-linking in the plasma coating. In the present study the aim was to prevent this reaction, if possible, since the resulting surface is less reactive towards the epoxy than if there are still free amino or anhydride groups.

Scheme 2. Possible reaction of 1,2-ethylenediamine with two anhydride groups. Since this reaction takes place on the surface, the reaction needs to meet special conditions for the placement of the anhydride groups.
Aminolysis of the anhydride groups on the surface

6.3 Surface characterisation

After the deposition of the diamine compounds, the surface chemistry was characterised. Changes in the surface chemistry were determined with ATR-FTIR, XPS and contact angle measurements. PE specimens were used only to characterise the surface (by ATR-FTIR and XPS) before being heated to 120°C in vacuum, while glassy carbon specimens were analysed (by XPS) before and after heating.

![Figure 11. ATR-FTIR spectra of PE specimens modified with: a) plasma deposited maleic anhydride (0.7 W/L 3min) for reference; b) plasma deposited maleic anhydride with evaporated 1,6-diaminehexane; c) plasma deposited maleic anhydride with evaporated 1,2-ethylenediamine. The evaporation of the diamines to the surface took place for 1 hour. All the spectra are normalised to the strongest PE peak (~2900 cm⁻¹).](image)

Figure 11 shows the ATR-FTIR spectra of the plasma deposited maleic anhydride surfaces after the diamine vapour reaction (b-c). For comparison, the spectrum of
ppMAH just after plasma polymerisation is also shown (a). Even though the substrate has been heated during the vapour deposition it seems apparent that a dominant film of 1,2-ethylenediamine is created on the modified surfaces as indicated by the observed changes in (c). On the other hand, the layer of diamines is not very thick, since the PE signal can still be clearly distinguished. Conversely, spectrum (b) from the reaction with 1,6-hexanediamine after reaction shows both signals from the plasma layer of maleic anhydride and the reacted compound. In both cases, after the reaction of plasma polymerised maleic anhydride with diamine compounds, new emerging peaks in the spectra indicate that the reaction took place. After the reaction the peak at 3340 cm$^{-1}$ has thus increased in its intensity, which is assigned to the amino groups. Furthermore, a new common peak appears at 1645 cm$^{-1}$ in the ppMAH and diamine compound spectra, which can be assigned to the Amide I band. Details of the ATR-FTIR analysis are summarised in Table 5.

<table>
<thead>
<tr>
<th>Wavelength, cm$^{-1}$</th>
<th>ppMAH</th>
<th>ppMAH + 1.2 EDA</th>
<th>ppMAH + 1.6 HDA</th>
<th>Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>3588</td>
<td>+</td>
<td></td>
<td></td>
<td>OH – O</td>
</tr>
<tr>
<td>3340</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-NH$_2$</td>
</tr>
<tr>
<td>1860</td>
<td>+</td>
<td></td>
<td>+</td>
<td>Anhydride groups</td>
</tr>
<tr>
<td>1780</td>
<td>+</td>
<td></td>
<td>+</td>
<td>Anhydride groups</td>
</tr>
<tr>
<td>1720</td>
<td>+</td>
<td></td>
<td>+</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1637</td>
<td>+</td>
<td></td>
<td></td>
<td>C=C</td>
</tr>
<tr>
<td>1645</td>
<td></td>
<td>+</td>
<td>+</td>
<td>Amide I band</td>
</tr>
<tr>
<td>1300</td>
<td>+</td>
<td></td>
<td></td>
<td>CH$_2$</td>
</tr>
<tr>
<td>920</td>
<td></td>
<td>+</td>
<td>+</td>
<td>COC stretch</td>
</tr>
</tbody>
</table>

*Table 5.* Chemical surface composition showing the observed frequencies and vibrations of the modified surfaces after attachment of the diamine compounds; values for plasma polymerised maleic anhydride are shown for comparison.
Aminolysis of the anhydride groups on the surface

As mentioned above the glassy carbon surfaces were analysed with XPS before and after the specimens were heated to 120°C in vacuum (i.e. after aminolysis). Results of the surface analysis are shown in Table 6. From XPS analysis it seems as if the surface still contain many unreacted species even after evaporation of the diamine compounds. This is expressed by a higher content of nitrogen being observed before heating (see Table 6). In both cases the loss of nitrogen is therefore found to be significant, most prominently in case of EDA. One possible interpretation would be that during the initial reaction the surfaces become saturated with the diamine monomer (see Figure 11 (c)). Speculatively, the heating process in vacuum not only closes the ring structure, cf. Scheme 1, creating imides on the surfaces, but also removes most of the unreacted molecules. It is, however, not strictly possible to conclude from XPS whether or not the reaction of anhydride with amino groups create imides, since the observed shifts in the high-resolution carbon spectra are very similar to those from plasma polymerised maleic anhydride. Furthermore, the shape of the high-resolution carbon spectrum remains the same.

<table>
<thead>
<tr>
<th>Sample treatment</th>
<th>C 1s</th>
<th>O 1s</th>
<th>N 1s</th>
<th>Si 2p</th>
<th>Br 3p3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppMAH (on GC)*</td>
<td>69±2%</td>
<td>31±2%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ppMAH + 1,2 EDA (on PE)</td>
<td>63.4%</td>
<td>13.3%</td>
<td>23.3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ppMAH + 1,2 EDA + heating (on GC)</td>
<td>74.4%</td>
<td>14.6%</td>
<td>10.1%</td>
<td>0.65%</td>
<td>0.25%</td>
</tr>
<tr>
<td>ppMAH + 1,6 HDA (on PE)</td>
<td>76.1%</td>
<td>12.6%</td>
<td>10.8%</td>
<td>0.5%</td>
<td></td>
</tr>
<tr>
<td>ppMAH + 1,6 HDA + heating (on GC)</td>
<td>75%</td>
<td>16.5%</td>
<td>8.3%</td>
<td>0.2%</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. XPS analysis of surfaces treated with diamine compounds. “GC” indicates a glassy carbon specimen. The row marked by an asterisk (*) has been averaged over different plasma powers.

Note that during the heating process in the vacuum oven, surfaces seem to have been contaminated, e.g. by Si and Br. The contaminations probably originate from the organic synthesis laboratory and the oven.
Finally, contact angle measurements were performed, cf. Table 7. The contact angle after aminolysis is found to be approximately $50^\circ$, which is distinctly lower than for the plasma polymerised maleic anhydride before aminolysis.

<table>
<thead>
<tr>
<th>Sample treatment</th>
<th>Advancing contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppMAH</td>
<td>$77^\circ$</td>
</tr>
<tr>
<td>ppMAH + 1,2 EDA after heating (on GC)</td>
<td>$49.7\pm3.2^\circ$</td>
</tr>
<tr>
<td>ppMAH + 1,6 HDA after heating (on GC)</td>
<td>$54.3\pm0.1^\circ$</td>
</tr>
</tbody>
</table>

*Table 7. Contact angle measurements of surfaces treated with diamine compounds. “GC” indicates a glassy carbon specimen.*

### 6.4 Summary

This chapter presents results of the aminolysis of the ppMAH surface. Based on observations it has been shown that it is possible to change the functional groups on the surface, and that the anhydride groups react with the diamine compounds under normal, ambient conditions. Moreover, it is demonstrated that heating of the surface during the aminolysis reaction makes it easy to purge the unreacted species left behind after the vapour reaction. By visual inspection it is further established that heating the specimens during the reaction facilitates the formation of a thin and reasonably uniform monomer layer on the surface; the former is supported by ATR-FTIR measurements, exhibiting a strong PE signal from the substrate. Conversely, more work obviously needs to be done in order to characterise the development of nitrogen on the surface than was allowed by time and resources in this study. Likewise, the complete lack of mechanical testing makes it impossible to assert whether the aminolysis and the attachment of aliphatic amine terminated carbon chains to the surface, has any significant influence on the interfacial adhesion of the composite material, as suggested by several authors.
The main part of this study involves plasma polymerised maleic anhydride. In addition, coatings of plasma polymerised 1,2-methylenedioxy benzene (ppMDOB) and co-polymer coatings of maleic anhydride and 1,2-methylenedioxy benzene (ppMDOB/MAH) were also investigated. The plasma polymers were created with different plasma powers and the coatings characterised using XPS and ATR-FTIR as described in preceding chapters. The observed changes in the surface chemistry as a function of different plasma powers have already been discussed in detail in Appendix A. The present chapter provides additional information and investigates the stability during hydrolysis in 10 mM NaOH. For the stability tests the toluidine blue staining method and contact angle measurements were used. Finally, the use of a peel-off test as a potential screening tool for the interfacial strength using ppMDOB surfaces as the test system was explored.

### 7.1 Plasma polymerisation of 1,2-methylenedioxybenzene

From previous studies by Winther-Jensen et al. [57] it is well known that 1,2-methylenedioxy benzene (MDOB) can produce carboxylic acid groups on the surface during low power plasma polymerisation. According to Winther-Jensen the carboxylic acid groups are created during the (low power) plasma polymerisation from the methylene bridge between two oxygen atoms. In the following, coatings of roughly the same thickness have been deposited with different plasma powers by varying the duration of the plasma polymerisation, as calculated from thickness measurements by AFM and polymerisation rates obtained by QCM.
### 7.1.1 Surface characterisation of the modified layers

Results of the chemical surface characterisation are summarised in Table 8 (XPS) and Figure 12 (ATR-FTIR). While most of these results are discussed in Appendix A, the analyses of a ppMDOB surface created with a plasma power of 1.2 W/L have not previously been published. Interestingly, XPS indicates that the high power plasma polymerised layers have a slightly different chemical composition than those created with lower plasma powers. In particular, there do not seem to be any traceable amounts of COOH groups on surfaces deposited at 1.2 W/L and the O/C ratio drops further to 0.18, following the same “trend” as suggested by previous results. Conversely, the observed discrepancies could be attributed to the use of different XPS instruments, cf. section 2.2.1. In case of lower plasma powers the SPECS Sage 100 system was used, having an analysing spot size of about 5 mm, which is exposed to x-rays for approx. 40 min. For the higher plasma power, on the other hand, measurements were carried out using the K-Alpha instrument with its smaller analysing spot of approx. 400 μm and an exposure time of just a few minutes. Moreover, only a single specimen could be measured in case of the highest plasma power, whereas for plasma powers of 0.3 and 0.7 W/L the values in Table 8 represent the means of about 10 samples. Unfortunately, it later proved impossible for technical reasons to repeat either of these XPS measurements.

<table>
<thead>
<tr>
<th>Plasma Power, W/L</th>
<th>O/C ratio</th>
<th>C-C, 285.0 eV</th>
<th>C-O, 286.5 eV</th>
<th>C=O, 288.0 eV</th>
<th>COO, 289.2 eV</th>
<th>π*-π &lt;290 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.24±0.04</td>
<td>65.0±4.4%</td>
<td>20.6±2.8%</td>
<td>8.2±1.7%</td>
<td>3.6±1.2%</td>
<td>2.5±0.5% 1.6±0.4%</td>
</tr>
<tr>
<td>0.7</td>
<td>0.23±0.03</td>
<td>68.1±1.8%</td>
<td>18.2±1.0%</td>
<td>7.8±1.0%</td>
<td>3.3±0.5%</td>
<td>2.2±0.3% 1.4±0.5%</td>
</tr>
<tr>
<td>1.2*</td>
<td>0.18</td>
<td>71.5%</td>
<td>15.5%</td>
<td>9.0%</td>
<td>------------</td>
<td>4.0%</td>
</tr>
</tbody>
</table>

Table 8. XPS results from ppMDOB. * = data was measured using K-Alpha instrument.

Complementary results of surface characterisation with ATR-FTIR are depicted in Figure 12. The figure shows the measured vibrations for specimens created with three
Other plasma coatings

different plasma powers, spanning the range from 800 – 2000 cm\(^{-1}\) and normalised to the 1600 cm\(^{-1}\) peak. The largest differences are found in the range of 1500 – 2000 cm\(^{-1}\), where the peaks assigned to carbonyl (C=O) stretch and C=C stretching, respectively, are observed at 1710 cm\(^{-1}\) and 1600 cm\(^{-1}\). From Figure 12 it would appear, as if the carbonyl peak at 1710 cm\(^{-1}\) decreases slightly in its intensity (e.g. compared to the peak at 1600 cm\(^{-1}\)) with increasing plasma power, consistent with the O/C ratio inferred from XPS. This can be assigned to processes taking place during the plasma modification, where more radicals are created at the higher plasma powers and subsequently more oxygen removed. Meanwhile the intensity originating from C=C remains largely unchanged, as can be expected, since it is difficult to activate the benzene ring in the monomer structure, and since the coatings have roughly the same thickness, i.e. the same content of carbon.

Figure 12. ATR-FTIR spectra for ppMDOB as a function of plasma power; a) 0.3 W/L; b) 0.7 W/L; c) 1.2 W/L. The spectra are normalised to the PE peak. For comparison, see Figure 3 in Appendix A.
Specimens modified by ppMDOB have been analysed with the toluidine blue staining method, cf. section 2.2.4, in order to determine the maximum number of carboxylic acids on the surface created during the plasma polymerisation at different plasma powers. For this purpose a dye incubation time of 6 hours is used; results are shown in Figure 13. As shown in the figure there is a dramatic decrease in the number of carboxylic acid groups on the surface, when the plasma power increases. Again, this is consistent with earlier observations from XPS and ATR-FTIR, suggesting a decrease in the surface content of COOH groups with increasing plasma power. Or in other words: significant amounts of carboxylic acid groups are only created on the surface during very low power plasma polymerisation, i.e. increasing power levels during plasma polymerisation lead to a reduction of oxygen in the plasma layer.

**Figure 13.** Samples ppMDOB as function of plasma polymerisation power, stored in the Petri dish after modification, were incubated with dye for 6 hours in 40°C.
Other plasma coatings

Based on the above and assuming that the amount of carboxylic acid groups influences the interfacial strength as is the case of ppMAH (through chemical linkage with epoxy resin), one would expect to see a decrease in the adhesion as a function of the plasma power. For ppMDOB, however, this is clearly not the case. Instead the mechanical tests from Appendix A show a small increase in the interfacial strength, which suggests that for ppMDOB the bulk properties are important.

7.1.2 Hydrolysis of ppMDOB

For comparison the resistance of ppMDOB coatings to hydrolysis have also been investigated using the toluidine blue staining method (section 2.2.4) and under the same conditions as ppMAH, cf. Chapter 4 and Appendix B. As mentioned above specimens coated with ppMDOB were created at different plasma power levels while keeping the thickness of the modified layer approx. the same. Aiming for a modified layer thickness of approx. 100 nm, ppMDOB coatings of three different plasma power levels were examined (the listed numbers refer to the plasma power and duration, respectively): (a) 0.3 W/L and 24 min 17 sec (10 mA); (b) 0.7 W/L and 10 min (20 mA); (c) 1.2 W/L and 6 min 28 sec (30 mA).

The effect of the hydrolysis in 10 mM NaOH was established after 0, 15 and 30 minutes, and after 1, 2 and 3 hours, respectively. Before being incubated with the dye for 1 hour, the hydrolysed surfaces were immediately rinsed with 0.1 mM NaOH to remove the hydrolysing solution and then dried with an Ar gun. During hydrolysis no carboxylic acid groups are created; these are instead created during the plasma modification and were found in the preceding section to depend strongly on the plasma power used in the polymerisation. Hence, the hydrolysis resistance can here be attributed to the differences in the chemistry of the plasma polymerised coatings, as severe chemical rearrangements must take place if MDOB is to be hydrolysed.

The response of ppMDOB coatings on PE to the hydrolysis are displayed in Figure 14, which shows observed changes in the density of carboxylic acid groups as a function of time exposed to the hydrolysing solution, i.e. the “hydrolysis time”.

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Figure 14. Density of carboxylic acid groups in ppMDOB layers deposited with different plasma power levels as a function of time exposed to a hydrolysing alkaline solution of 10 mM NaOH; ppMDOB a) 0.3 W/L, b) 0.7 W/L, c) 1.2 W/L. Differences with respect to Figure 13 are discussed in the text.
Other plasma coatings

From Figure 14 the plasma polymerised layers appear to be reasonably stable (within uncertainty) when exposed to the hydrolysing solution (10 mM NaOH) for a period of up to at least 3 hours, regardless of the plasma power. By comparison the hydrolysis resistance of the ppMAH layers exhibit a strong dependence on the plasma power (Chapter 4). The observed average number of carboxylic acid groups in the ppMDOB layers is (a) $0.22\pm0.02$ nmol/cm$^2$ for a plasma power of 0.3 W/L, (b) $0.27\pm0.3$ nmol/cm$^2$ for 0.7 W/L and (c) $0.21\pm0.02$ nmol/cm$^2$ for 1.2 W/L. The numbers are surprisingly low for 0.3 and 0.7 W/L, when compared to the observed numbers of carboxylic acid groups determined from a dye incubation time of 6 hours, cf. Figure 13. In case of the coating created with the highest plasma power (1.2 W/L), however, the number of carboxylic acid groups are in perfect agreement. A possible interpretation could be that during the shorter dye incubation, only the outermost carboxylic acid groups closest to the surface are detected, whereas in case of the extended dye incubation the probe penetrates the entire ppMDOB layers, resulting in the maximum number of carboxylic acid groups produced during plasma polymerisation. Alternatively, discrepancies could simply be assigned to the varying ages of the plasma polymerised specimens. A supplementary experiment involving 6 hours of hydrolysis followed by 1 hour of dye incubation should of course have been carried out to shed more light on these findings, but regrettably time constraints did not allow this.

ATR-FTIR spectra similar to those shown in Figure 12 were obtained during the hydrolysis of ppMDOB, cf. Figure 15. The surfaces were measured after they were taken out of the 10 mM NaOH solution, rinsed and dried with the Ar gun. Based on the ATR-FTIR analysis the exposure to a hydrolysing solution does not cause significant change in the surface chemistry. Observed minor variations in the intensities most likely reflect other factors, e.g. the way samples are placed in the plasma chamber or slight differences in the handling. Due to the geometry of the plasma chamber and the monomer flow the plasma thus varies more vertically than horizontally, which may give rise to the observed variations in the ATR-FTIR measurements. In case of ppMAH changes in the spectra owing to processes taking place during the hydrolysis dominate, and so such smaller variations are negligible.
Figure 15. ATR-FTIR of ppMDOB created with a plasma power 1.2 W/L. The spectra represent the surface during varying lengths of hydrolysis a) surface just after plasma polymerisation – f) surface after 3 hours of hydrolysis. The spectra are normalised to the PE peaks. For comparison see Figure 3 in Appendix A.

In addition to ATR-FTIR measurements, contact angle measurements (section 2.2.3) were also carried out as a function of the hydrolysis time. Results are shown in Figure 16, while comparable results for ppMAH may be found in section 4.3. For surfaces that were not exposed to the hydrolysing media the advancing and receding contact
Other plasma coatings

angles were found to be $70^\circ \pm 2^\circ$ and $29^\circ \pm 4^\circ$, respectively, regardless of the plasma power used.

**Figure 16.** Contact angle measurements on hydrolysed samples as a function of the hydrolysis time, ppMDOB: a) 0.3 W/L; b) 0.7 W/L; c) 1.2 W/L

During the hydrolysis of the surface the advancing contact angle clearly decreases for all plasma treatments, i.e. the hydrolysis makes the surfaces more and more hydrophilic. The receding contact angle on the other hand appears to be stable during
the hydrolysis and oscillates between 15-20°. Only for samples not exposed to the hydrolysing media the receding contact angle is higher. Similar behaviour for the advancing and receding contact angle have previously been reported for plasma coatings [74, 103, 104, 105]. Arguably, the observed increase in the degree of wetting of the surface as a function of the hydrolysis time seems to suggest that the outer most layer of plasma coating is not as resistant towards the hydrolysing media as proposed by, e.g. ATR-FTIR. Rather, during hydrolysis, the coating slowly swells and reacts with the hydrolysing solution until complete delamination finally takes place. Evidently, the delamination of the ppMDOB coating is significantly slower than that of ppMAH. The observed differences in the delamination rates arise from the structure of the monomer and reactions during the plasma polymerisation.

7.2 Coatings of plasma polymerised mixture of maleic anhydride and 1,2-methylenedioxybenzene

As described elsewhere the coatings of pure plasma polymerised maleic anhydride were found to hydrolyse fast under strong alkaline conditions, whereas coatings of plasma polymerised 1,2-methylenedioxy benzene (see above) demonstrated great resistance to the hydrolysis in alkaline solution. Based on these observations a mixture of the two monomers was also investigated in order to probe whether the resulting plasma co-polymer would share the favourable properties of both, i.e. improved adhesion and stability during hydrolysis.

7.2.1 Hydrolysis of ppMDOB/MAH

Since the co-plasma polymerised 1,2-methylenedioxy benzene/ maleic anhydride (ppMDOB/MAH) surface is used extensively for protein adsorption [56, 74], the stability of this coating towards hydrolysis is of high importance. In this section the hydrolysis of ppMDOB/MAH in 10 mM NaOH for two different sets of plasma conditions, corresponding to plasma powers of 0.5 and 0.7 W/L, respectively, is investigated. For comparison the effect of hydrolysis in aqueous media on these coatings is depicted in Figure 4 in Appendix A.

The hydrolysis in alkaline solution was monitored using the toluidine blue method for up to 3 hours, with measurements being taken after 15 and 30 minutes, and after 1, 2
Other plasma coatings

and 3 hours. After the hydrolysis the surfaces were rinsed with 0.1 mM NaOH and incubated with dye for 1 hour at 40°C. The results are summarised in Figure 17.

The results indicate clearly that the modified ppMDOB/MAH layers are not stable towards hydrolysis. In fact after just 30 minutes the hydrolysing solution visibly started to turn yellowish after the colour of the modified surface. In case of the coating created with a plasma power of 0.5 W/L, an almost immediate dissolution of the film is observed, similar to that of the coating of pure ppMAH created at a plasma power of 0.15 W/L, cf. section 4.1 (Appendix B). Conversely, in case of the coating created with 0.7 W/L, an increase in the number of carboxylic acid groups is first observed (originating from the hydrolysed anhydride groups), followed by a decrease after 15 minutes in the hydrolysing medium. Although the stability of the coating thus improved slightly with an increase in the plasma power, this improvement is not sufficient in order to merit more experiments with this particular co-polymer. Moreover, since the thicknesses of the modified layers are not the same, any comparison on basis of the number of carboxylic acids groups is rendered impossible.
Figure 17. Density of carboxylic acid groups in ppMDOB/MAH layers deposited with different plasma power levels as a function of time exposed to a hydrolysing media; ppMDOB/MAH a) 0.5 W/L, b) 0.7 W/L.

As in case of the ppMDOB and ppMAH surfaces, ppMDOB/MAH surfaces were analysed with ATR-FTIR and by contact angle measurements in order to characterise the surface chemistry.

Figure 18 and Figure 19 show the ATR-FTIR spectra of the modified co-polymer surfaces after different exposures to the hydrolysing media (see also Figure 4 in
Appendix A). Recalling that the duration of the plasma polymerisation was held constant, while the plasma power varied, it is not immediately possible to compare the results quantitatively, since the thicknesses of the modified layers were also different.

Figure 18. ATR-FTIR of ppMDOB/MAH created with a plasma power of 0.5 W/L. The spectra represent the surfaces during varying lengths of hydrolysis a) unexposed surfaces just after plasma polymerisation; b) – f) hydrolysed surfaces from 15 minutes to 3 hours. The spectra are normalised to the PE peaks.
The spectra labelled a) on Figure 18 and Figure 19 represents the samples just after plasma polymerisation, whereas b) and c) are the surfaces after hydrolysis for 15 and 30 minutes, respectively. The spectra show clearly the effect of the hydrolysis of the anhydride groups, i.e. signals from the anhydride groups (1860 and 1780 cm$^{-1}$) are seen to disappear after hydrolysis. There is also a strengthening of the peak at 1620 cm$^{-1}$, corresponding to carbonyl stretching, at least up to the first 30 min of hydrolysis. Lastly, almost complete dissolution is observed after 1 hour of hydrolysis in alkaline solution regardless of the plasma power.
Supplementary contact angle measurements were carried out, e.g. to determine whether or not there was some of the co-polymer left on the substrate, cf. Figure 20. For the co-polymer surface modified with a plasma power of 0.5 W/L the measured contact angle was around 45°, which decreased to below 10° (i.e. complete wetting of the surface; making the contact angle almost impossible to measure) after just 15
minutes of exposure to the hydrolysing media. For a prolonged hydrolysis time, the contact angle slowly increased again up to about 25°, which suggests that the modified layer is now completely removed from the surface, since what was measured is probably the plasma pre-treated PE.

Figure 20. Contact angle measurements on hydrolysed samples, ppMDOB/MAH: a) 0.5 W/L – after 15 min and 30 min in 10 mM NaOH complete wetting of the surface is observed; b) 0.7 W/L – after 30 min, 1, 2 and 3 hours complete wetting of the surface is observed, i.e. a contact angle below 10°.
Other plasma coatings

In case of the plasma treatment using a power of 0.7 W/L the contact angle on the surface just after plasma polymerisation (i.e. the surface is not yet exposed to the hydrolysing media) was found to be $60^\circ$, which decreased to only $16^\circ$ also after 15 minutes of hydrolysis. For prolonged exposure (up to 3 hours) to the alkaline solution, the surfaces demonstrated high wetting properties, which made it virtually impossible to do contact angle measurements (contact angles below $10^\circ$). This of course suggests that processes taking place on the surface during hydrolysis are very aggressive towards the plasma coating.

### 7.2.2 Mechanical tests of ppMDOB/MAH

In summary the surfaces modified with the ppMDOB/MAH co-polymer did not show any real resistance to the hydrolysis in an alkaline solution, i.e. complete dissolution of the coatings was observed after only 30 minutes regardless of the plasma power used.

As reported in Appendix A sandwich specimens consisting of plasma modified glassy carbon specimens and epoxy resin were subjected to interfacial strength tests. The DCB tests showed almost no adhesion between the plasma treated glassy carbon and the epoxy. Since the interfacial strength is not only affected by the number and species of functional groups but is also affected by the stability of the coating, these results are probably not surprising based on the observations above. Probably, mixing the two monomers during the plasma polymerisation causes the co-polymer layers to destabilise, which again leads to the poor adhesion.

### 7.3 Peel-off tests

In these studies the double cantilever beam (DCB) method described in section 3.1 has been used to carry out mechanical tests on the plasma modified substrates. To accommodate persistent technical problems an alternative qualitative peel-off method was developed to determine the strength of an interface [20]. The peel-off test, which is detailed in section 3.2, was tested on substrates of glassy carbon, plasma modified for 10 minutes with MDOB at different plasma powers (0.3 W/L, 0.7 W/L, 1.2 W/L). Preliminary results of the peel-off tests are shown in Figure 21.
Figure 21 displays three surfaces corresponding to different plasma powers after the peel-off test. The light and shiny coating is the epoxy, while the dark squares indicate areas, where the epoxy as well as the underlying ppMDOB layer has been removed from the glassy carbon substrate. The squares were cut through to the glassy carbon with a scalpel before the mechanical test. From the premise of the peel-off test the strength of the adhesion can be evaluated by the number of squares that are left on the surface. By this measure surface (c) presents the strongest interface and (a) the weakest, i.e. consistent with the DCB measurements, cf. Appendix A.

While performing the peel-off tests several sources of uncertainty were identified. First of all, the results were found to be strongly dependent on the thickness of the epoxy layer. If the epoxy was thicker than 100 μm or thinner then 40 μm, then the layer was difficult to remove. In case of the thick layers of epoxy it was also difficult to cut through. By trial and error the thickness of the epoxy on the plasma treated glassy carbon was eventually fixed at approx. 40 μm. Clearly, the layers of epoxy need to be exactly the same to allow inter-comparison between treatments.

Secondly, while cutting through the layers delamination was observed. The delamination arose between the glassy carbon and the plasma modified MDOB layer. This directly influenced the amount of squares removed from the surface by the peel-off, cf. Figure 21.

Thirdly, the depth of the cuts varied. Obviously, when cutting by hand it is impossible to apply the same exact strength on the scalpel every time. This was easily seen from
the varying depth of the cuts. In some places scratches had even been made in the
glassy carbon substrate, typically in these places where the epoxy had been
completely removed from the surface. Cutting with a scalpel has an additional
disadvantage, i.e. the blade pushes onto the sides of the cuts. In this way stresses are
transferred to the epoxy, which might be the source of the delamination. Since the tip
of a scalpel is formed more or less like a triangle, the stresses will depend on the
depths of the cuts, which as mentioned above are likely to vary. As a result the peel-
off test offers poor reproducibility in its current form.

In conclusion the peel-off test as it was used here needs more work. By virtue of it’s
relatively simplicity, however, this method has potential as a screening tool, before
more complex mechanical testing is carried out, e.g. DCB measurements.
8 Conclusion and outlook

In this study substrates of glassy carbon have been given a coating of functional chemical groups, e.g. carboxylic acid groups, using the plasma polymerisation technique. By adjusting the plasma conditions, i.e. the plasma power and the time of the polymerisation, coatings of reasonably well-defined thicknesses were achieved. In addition the rate of the polymerisation was found to depend on the monomer used.

Two different monomers have been investigated: maleic anhydride (MAH) and 1,2-methylenedioxybenzene (MDOB). Both monomers were plasma polymerised to create mono-polymer (ppMAH, ppMDOB) and co-polymer (ppMDOB/MAH) layers, respectively, while varying the plasma conditions. The stability performance of plasma coatings, deposited with different plasma power levels, was assessed as a function of time exposed to a hydrolysing alkaline media. In case of ppMAH the stability of the coatings was further examined for selected thermal conditions and for the pH of the hydrolysing media.

In case of ppMAH and ppMDOB/MAH the hydrolysis resistance has been found to depend strongly on the plasma power. The hydrolysis resistance thus increases significantly with the plasma power, whereas coatings created at the lowest energies exhibit a slow dissolution. It is proposed that this behaviour may be attributed to varying degrees of cross-linking within the films. This is supported by ATR-FTIR analysis, provided the coatings have roughly the same thickness. Likewise, the mechanical tests of ppMAH show a similar increase in the interfacial strength as a result of increasing plasma power, with an optimum value at 0.7 W/L. This may also be explained in parts by cross-linking layers. At the peak value the thickness of the ppMAH coating does not seem to influence the interfacial strength, however, to fully understand the relation between the thickness of the plasma polymerised layers and
the interfacial strength requires further investigations, e.g. in case of XPS the results were entirely inconclusive, showing no differences in the chemical surface composition as a function of plasma power.

In case of the ppMDOB/MAH co-polymer the mechanical tests show only marginal improvement in the adhesion, and the instability of the coating is found to pose serious problems for the analysis. Further work on the co-polymer was therefore abandoned.

Based on the DCB tests, ppMDOB offers a limited yet significant increase in the strength of the interface between the carbon substrate and the epoxy resin, as a function of increasing plasma power, although further measurements are needed in order to determine, e.g. the full mechanical properties. Meanwhile, consistent changes in the surface composition are found from both ATR-FTIR and XPS measurements, and also from the toluidine blue analysis. The number of functional carboxylic acid groups on the surface proves to depend inversely on the plasma power, i.e. the density decreases as a function of the plasma power level. Finally, the plasma polymerised layers of MDOB demonstrate remarkable resistance towards swelling and dissolution in a hydrolysing alkaline media. The results indicate that coatings of ppMDOB appear to be reasonably stable regardless of the plasma power.

Three preliminary studies have been carried out within the current scope. First of all, functional amino groups were reacted onto coatings of ppMAH under ambient conditions and subsequently characterised by chemical surface analysis. Since the mechanical properties of such specimens have not been tested in this study, future work should include supplementary mechanical (DCB) tests. Also, the topography of selected fracture surfaces has been investigated, using AFM, e.g. in order to obtain more insight on the nanostructure and the failure mechanism of the plasma polymerised substrates. To conclude a complementary peel-off method has been investigated, along with its potential as a possible tool for qualitative analysis of interfacial strength.
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Appendix A
Plasma polymerized thin films of maleic anhydride and 1,2-methylenedioxybenzene for improving adhesion to carbon surfaces

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Low power 2-phase AC plasma polymerization has been used to surface modify glassy carbon substrates that are used as an experimental model for carbon fibers in reinforced composites. In order to probe the role of carboxylic acid density on the interfacial adhesion strength a combination of different plasma powers and monomer compositions was used. Maleic anhydride (MAH) and 1,2-methylenedioxybenzene (MDOB) were plasma deposited separately and as mixtures to create layers with different surface compositions. In all cases the MAH was hydrolyzed to form carboxylic acid groups. Some carboxylic acid are present on the MDOB surface as a result of the fragmentation processes in the plasma. Chemical and physical changes were investigated as a function of plasma power at constant polymerization time. Surface chemistry analysis was performed with x-ray photoelectron spectroscopy and attenuated total reflectance Fourier transform infrared spectroscopy. Atomic force microscopy was used to measure the thickness of the plasma films and to monitor the surface roughness for the different polymerization conditions. Finally, preliminary results of fracture energy measurements of the plasma modified surfaces determined by a double cantilever method are presented. © 2007 American Vacuum Society. [DOI: 10.1116/1.2743653]

I. INTRODUCTION

The use of composite materials, e.g., glass or carbon fibers in a polymer matrix is becoming more widespread due to the improved performance that can be achieved by weight reduction. For example, structures such as wind turbine blades are getting even larger and carbon fibers thus become more interesting due to their high stiffness and strength to weight ratio." For structural purposes the fibers have to be combined with a matrix to form a composite material. For a certain relative amount and orientation of fibers in the composite, its mechanical properties (especially strength and fracture energy) depend on the level of adhesion between the fibers and the matrix. Furthermore, a strong interface does not necessarily result in improved mechanical properties.1

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Usually, under given loading conditions, there is an optimum adhesion to maximize the mechanical performance.2 Typically, wet chemistry is used to control the adhesion between the fibers and the matrix. Plasma treatment3 has been used for fiber surface activation in only few cases. With the increasing emphasis on environmental issues over the last few decades, however, there has been a growing focus on other, clean methods, e.g., plasma polymerization, for producing materials.4 Plasma polymerization is a solvent-free method, which makes it inexpensive in use. The technique further has the advantage of being easy to carry out, e.g., by allowing for easy handling of the monomers. The plasma process itself on the other hand involves complicated physical processes, requiring the optimization of a number of parameters including power, flow, time (on and off time) as well as placement of the sample, whether in the glow zone or beyond it. This study used a 2-phase pulsed AC plasma with samples placed in the glow zone. This plasma setup can be used with a power input no higher than 1 W/T in most cases. This is called a “soft” plasma. A special benefit of this tech-
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rique is that the power introduced to the system is enough to run the polymerization in a way comparable to conventional polymerization of the monomer but without plasma induced destruction of the monomer. Several studies already put special emphasis on preserving the chemical structure of the monomers—either the ring structure or the functional groups. The soft 2-phase AC plasma setup otherwise has all the advantages of conventional plasma polymerization.

The experimental investigation of the fiber-matrix adhesion often involves the use of model geometries such as the single fiber fragmentation test. In this study, planar specimens were chosen since they are easier to surface characterize, and since the analysis of the mechanical tests is straightforward. To mimic carbon fiber glassy carbon substrates were used as a planar model surface.

Glassy carbon consists of disordered domains of carbon bonded in a graphitlike manner without long range transition order. The size and amount of the graphite domains is dependent on the temperature treatment during processing. Due to unique nanostructure, glassy carbon is characterized by high hardness, high thermal stability, high electrical conductivity, and high mechanical strength. Some of these properties are higher than those of conventional graphite.

Glassy carbon has low surface reactivity, which allows surface modification to change it quite rapidly. This can be used to control the surface chemistry. Domingo-Cracia et al. have investigated oxygen rf plasma modification on glassy carbon. It was shown that even with extended use of plasma treatment, only the outermost surface was modified without interfering with the bulk properties. Other studies performed by Iwamoto et al. show that the oxygen plasma treatment influences different domains with graphitelike bonds and amorphous glassy carbon. Collard-Coet et al. report on the surface modification of carbon surfaces (graphite, glassy carbon, polymer surface) by plasma treatment with sulphur containing gases. The surface coverage with sulphur was shown to be dependent on the power and the pressure in the plasma chamber and also on the material that was used. Related work has been carried out by Tressaud et al. on carbon materials (graphitized and carbon blacks) which were plasma surface modified with fluorine gases. The interactions between the surface, the bulk material, and the gas penetration were investigated. The main application of this work was electrical conductivity.

Alexander et al. studied plasma polymers of acrylic acid deposited on aluminum substrates, and the interface between this treatment and epoxy resin. Also, Friedrich et al. reported on the adhesion of metal layers to polymer surfaces using a pulsed plasma system. Their work showed a dependence of the Al peel strength with different functional groups (carboxyl acid, hydroxyl, amino groups) on the surfaces used. These included polypropylene and polyethylene terephthalate. Both Alexander et al. and Friedrich et al. found that the carboxylic acid groups yield the strongest interfacial bonds.

Regarding the increase of the interfacial adhesion, Hindryckx et al. have shown increase in tensile strength, elongation, impact strength, and melt index of an interfacial system using maleic anhydride (MAH) grafted on high-density polyethylene-kaolin composites. Chiang and Ku reported on the grafting of maleic anhydride on Al plasma pretreated low density polyethylene for flame retardation using UV light. They observed an increase in the mechanical strength as a function of the amount of grafted maleic anhydride.

In the present study we explore the use of low-power plasma surface modification to improve the fiber-matrix adhesion. The study is limited to homo-pulsed plasma polymers of maleic anhydride (ppMAH) and 1,2-methylendioxybenzene (ppMDIO) and a co-pulsed-plasma polymer (ppMDIO/MAH) consisting of these two monomers. In the past the monomer maleic anhydride has been studied frequently using conventional polymerization and also with a pulsed or continuous plasma. Conversely, the monomer 1,2-methylendioxybenzene has rarely been studied. The focus of the present analysis is on the surface characterization of the modified layers. However, some preliminary results on the adhesion of the plasma treated glassy carbon substrates in an epoxy resin under nominal mode 1 conditions (normal separation) will be given for completeness.

II. EXPERIMENTAL SECTION

A. Materials

Plasma glassy carbon substrates (Sigradur G) were purchased from HTW Hochofenlehre, Germany in sizes of 50 × 20 × 1 and 65 × 5 × 1 mm. Polyethylene (PE) films were used as substrates for measuring the Fourier transform infrared (FTIR) spectra of plasma polymerized coatings. MAH was obtained from Sigma-Aldrich as briquettes. These were ground into fine powder in a hood and placed in a metal container under vacuum permanently. 1,2-Methylendioxy benzene (MDIO) was purchased from Fluka (purity 99.0%) and used without further purification. Ultrapure water was obtained using a Milli-Q system from Millipore. L-lactide) was received from Sigma-Aldrich in MW 90 000–120 000 and was stored in a freezer.

B. Substrate preparation

All the substrates were cleaned in an ultrasonic bath in different solvents, using dichloroform (5 min), acetone (twice: 2 × 5 min), and methanol (5 min), followed by drying with a jet of argon. The cleaned substrates were stored in polystyrene Petri dishes until use. This storage time was not longer than a few hours to two days prior to surface modification.

C. Plasma polymerization

The plasma polymerization apparatus using the 2-phase AC power supply plasma chamber has been described in details earlier. The glassy carbon pieces were mounted with double-sided tape on a glass tube for single sided coatings. A PE test substrate was used for attenuated total reflection (ATR)-FTIR measurements. The plasma polymerization was carried
Appendix A

out using either maleic anhydride or 1,2-
methylenedioxybenzene or mixtures of the two. The composi-
tion of the mixture was controlled by adjusting the gas
pressure of each component incrementally (from a basic
pressure below 5 Pa), starting with MOOIR (usually adding
2–3 Pa) and then adding MAH until the desired final pres-
sure is obtained, typically an additional 2–3 Pa. The total
pressure was about 10 Pa. In the case of pure monomer
synthesis, the basic pressure is below 5 Pa and the addition
of the monomer was up to 9–10 Pa. The polymerization proce-
dure consisted of two steps: surface activation followed by
the plasma polymerization. The surface activation step is a
spattering surface process to remove oxygen from the outer
layer of the surface. Without activation the modified layer
cannot properly attach to the surface. The activation time
was varied in order to determine a suitable value for use in
the experiment (data not shown here). For the activation step
Ar was allowed to flow through the chamber for 1 min (flow
rate of Ar 5 SCCM (SCCM denotes cubic centimeters per
minute at STP), followed by He for 10 min (50 SCCM), and
finally Ar for 20 s. During this time a plasma discharge was
maintained at a current of 30 mA (1.21±0.16 W/I). After
surface activation, the monomer was introduced to initiate
plasma polymerization. The initial plasma pressure of the Ar
carrier gas was set prior to activation. The plasma deposition
proceeded for 10 min, and in separate experiments the cur-
cent was varied from 10 to 30 mA (0.32±0.01–1.21
±0.05 W/I).

D. Water stability test

Some plasma coated samples were placed in water for
24 h in order to check the stability of the film. Both ATR-
FTIR measurements of the films deposited on PE and atomic
force microscopy (AFM) measurements on the glassy carbon
substrate were made. In all cases the surfaces were dried in a
fume hood in clean Petri dishes.

E. Surface analysis

ATR-FTIR was performed using a PerkinElmer Spectrum
B instrument that was equipped with a Germanium (Ge)
crystal. All spectra were collected within the range from
700 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and averaging
over 32 scans. The measurements were obtained at normal
atmospheric pressure. Measurements were performed both
before and after water treatment.

X-ray photoelectron spectroscopy (XPS) was performed
using a SPECS Bips h100 instrument with a mono-
microchromatic Mg \(K_α\) x-ray source at a power of 275 W
(11 keV and 25 mA). The pressure in the chamber was al-
ways below 1×10\(^{-9}\) mbar. Two kinds of spectra were ob-
tained: survey and high resolution. The survey spectra were
acquired at 100 eV pass energy in the range from
0 to 1100 eV. Atomic concentrations were calculated from
the intensities of the peaks in this spectrum. The high reso-


![Fig. 1. Schematic illustration of the DCB spectrum loaded with pair binding
moment (in set scale, numbers given in millimetre), an optical micro-
graph is shown as inset.](image)

and the full width at half maximum of the peaks was con-
strained to 2 eV. Accurate binding energies were obtained by
referring the C\(_{\text{C}}\)-C\(_{\text{C}}\)-H component in the C 1s spectrum to
285.0 eV.

Topographical and thickness measurements of the films were performed with a PSIA XII-150 AFM using BS-Tip
300 tips (SiO\(_2\) symmetric probe with length 17 µm) (Budget
Sensors) in tapping mode and intermittent contact mode. The
masking method of Hartley et al.\(^{22}\) was used for thickness
measurements of the plasma films. In brief, a droplet of a 5%
poly-(DL-lactide) (PDLA) solution in acetone was pipetted
onto the clean glassy carbon surface and dried. This substrate
is then subjected to plasma polymerization. Afterwards, the
sample was placed in water for 24 h to allow for the PDLA
to undergo hydrolysis. This was then removed with sharp
tweezers. As a result of this procedure there is a region on
the substrate which is free from the coating.

The scan size was set up for 20 µm and the scan rate to
0.5 Hz for determination of the cross-section picture. For
topographical measurements the scan size was set up for ei-
ther 5 or 1 µm with the scan rate 1 Hz. All data obtained
were analyzed with the pita, nxt software (version 1.5).

F. Fractography mechanics test

Double cantilever beam (DCB) sandwich specimens were
prepared using the plasma treated glassy carbon wafers (65
× 5.5 × 1 mm\(^2\)). The resin used was an epoxy system (Prime-
20, SP Systems, UK). The resin and the hardener were mixed
with a weight ratio of 4:1, degassed for 2.5 min under full
vacuum, and then injected into silicon rubber moulds be-
tween two glassy carbon wafers. Teflon films (0.5 mm in
thickness) were used to keep the wafers apart and to create a
notch of 20 mm in length. The DCB specimens were cured
for 24 h at room temperature and subsequently postcured at
50 °C for 16 h. The cured samples were ground and polished
to facilitate optical observation of the crack growth. An op-
tical micrograph of the prepared specimens where the glassy
carbon and the epoxy resin is shown in Fig. 1. Subsequently,
the sandwich specimens were glued on specially made stain-
less steel beams (6 mm in thickness) that could be mounted

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on the test fixture (see below). An epoxy adhesive (Scotch Weld) was used to glue the DCB specimens to the steel beams. The curing time for the adhesive was 24 h at room temperature.

A special fixture to provide stable crack growth was used to load the DCB specimens with force couples (Fig. 1). This creates pure bending moments in the specimen. This specimen geometry and the loading conditions satisfy the condition for stable crack growth. Additionally, this is one of the few testing methods where the energy release rate is independent of the crack length (the energy release rate is calculated from a J integral solution and is a function of the moment, geometry, and elastic properties of the materials). The loading was performed at an approximately constant rotation rate of the beam ends of the DCB specimens.

The experiments were conducted either inside an environmental scanning electron microscope (Electrosens E3) or under an optical microscope. During loading of the specimens, the end opening of the fixture and applied moment were recorded. The DCB specimens were subjected to monotonic loading until a sharp crack was formed in the notched area and then unloaded somewhat to avoid time-dependent cracking. In this way the fracture energy for crack initiation was obtained. Subsequently, the specimen was loaded again until crack growth took place. The specimen was again partially unloaded and the crack length was measured. This procedure was repeated until specimen failure to obtain fracture resistance curves (i.e., increasing J with increasing crack length also called R-curve behavior). Although a plastic zone may develop at the crack tip, the value for crack initiation is the intrinsic fracture energy of the interface (energy absorbed by the decohesion process itself). This is true because the J integral remains valid also for plasticity problems until unloading takes place. Under the assumption that the decohesion process is the same along the specimen length, any increase in fracture energy with crack extension (R-curve behavior) indicates the existence of extrinsic toughening mechanisms, i.e., plastic deformation near the crack tip. A strong interface results in significant R-curve behavior whereas its absence is indicative of a weak interface.

III. RESULTS AND DISCUSSION

As mentioned above extensive surface characterization was done on the different plasma polymer polymer surfaces made from ppMAH, ppMDMO, and ppMDMO/MAH. The aim was to elucidate the properties that influence the adhesion between the glassy carbon substrates and the epoxy. The techniques used included ATR-FTIR and XPS for investigating the surface chemistry, and AFM for topography and thickness measurements. Finally, fracture mechanics results for the different plasma treatments are given.

A. ATR-FTIR

All ATR-FTIR spectra were performed on plasma modified PE. High quality (e.g., where the peaks are intensive) ATR-FTIR spectra from clean glassy carbon are very difficult to obtain due to the high absorption of the laser by the substrate. Even though surfaces are modified by plasma treatment, the polymer layer is not sufficiently thick such that most of the ATR-FTIR signal is absorbed by the glassy carbon.

1. ppMAH surfaces

Representative ATR-FTIR spectra (bold line) of the plasma polymerized MAH films freshly deposited onto polyethylene (PE) at a plasma current of 20 mA (0.75 ± 0.05 W/f) are shown in Fig. 2(a). The saturated five-membered ring of anhydride groups absorbs near 1780 and 1780 cm⁻¹ region. There is also significant signal at 1730 and 1620 cm⁻¹. These belong to the carbonyl and ester groups.8 Moreover, signals attributed to monocyclic anhydrides and five-member ring anhydrides, respectively, are observed at 1700 and at 930 cm⁻¹.8,9 Additionally, in the ppMAH spectra a peak is found at 1230 cm⁻¹, this originates from ring stretching. The spectra in Fig. 2(a) show the effects of water treatment (dashed curve) on the chemistry of the ppMAH films. As expected the anhydride groups are hydrolyzed into carboxylic acid groups by the water treatment. This conversion is clearly observed in the difference spectrum between the hydrolyzed and polymerized samples [Fig. 2(b)]. The peaks from the anhydride groups at 1800, 1780, 1230, 1070 as well as 930 cm⁻¹ diminish, while the peak at 1730 cm⁻¹ increases in intensity.

2. ppMDMO surface

The ATR-FTIR spectrum of the ppMDMO surface (Fig. 3) shows a number of peaks including the C=O stretching (1710 cm⁻¹), stretching in C==C (1600 cm⁻¹) and in C-H
B. XPS analysis

1. Clean glassy carbon

As expected the atomic composition of controlled glassy carbon surface has 95% and 5% carbon and oxygen content, respectively (molar O/C ratio 0.05, Table I). The residual oxygen is most likely from surface oxidation that happens during or after processing of the substrates. The C 1s spectrum in Fig. 5(a) consists of peaks assigned to C–C/C–H/C=O=C (peak A) at 285.0 eV and a small peak assigned to C–O/C=O–OH at 286.5 eV (peak B). All the other peaks are n→π* shake-up peaks from unsaturated sp2 bonding of carbons (peaks C-G).

2. ppMAH surface

XPS measurements were performed on the ppMAH deposited on glassy carbon. Only carbon and oxygen should be present on the surface based on the monomer structure. The theoretical molar O/C ratio of the monomer is 0.75. However, there is significant loss of oxygen during the plasma polymerization since the molar O/C ratio for all plasma conditions (10–30 mA, 0.3<s, 0.01–1.21 ± 0.05 W/I) is ~0.5 (Table I). The molar O/C ratio does not change before and after the water treatment. Figure 5(b) shows the high resolution C 1s spectrum with peak fitted. All the C 1s spectra were fitted with four components [C–C, C–O, C=O, C=O] corresponding to the bonds expected on the modified substrate from the MAH monomer. Table I gives an overview of the curve fitting results which contribute to the C 1s spectra for all plasma conditions. There are no significant differences.
between the treatments with different power as well as before or after water treatment. The peak with the highest binding energy appears at 280.3 eV, and it can be assumed that the registered spectrum comes only from the plasma modified layer. If not, then there should be registered counts of higher binding energies from the substrate itself (from n > 0 shake up). Since the probe depth of XPS is ~10 nm the modified plasma layer is at least 10 nm thick.

![Diagram](image-url)  
**Fig. 5.** Representative XPS high resolution C 1s spectra for (a) clean glassy carbon surface; (b) pyPAH 20 nm surface; (c) pyMAH 20 nm surface; and (d) pyMAH/MDOB 20 nm surface.

**Table 1.** Summary of the XPS results for a pyMAH surface before and after water treatment samples. Due to insignificant changes before and after water treatment the data was averaged. The ratio O/C from the monomer is 0.75.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s (a)</th>
<th>O/C</th>
<th>C=O (%)</th>
<th>C=O=O (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy carbon</td>
<td>0.05</td>
<td>68.0%</td>
<td>13.9%</td>
<td>13.9%</td>
<td>11.2%</td>
</tr>
<tr>
<td>0.35V/0.01</td>
<td>0.43</td>
<td>61.8±3.4%</td>
<td>16.6±1.7%</td>
<td>16.6±1.7%</td>
<td>16.6±1.7%</td>
</tr>
<tr>
<td>0.55V/0.01</td>
<td>0.46±0.02</td>
<td>58.1±1.9%</td>
<td>18.1±1.6%</td>
<td>6.4±1.9%</td>
<td>18.1±1.6%</td>
</tr>
<tr>
<td>0.75V/0.05</td>
<td>0.46±0.04</td>
<td>60.9±3.5%</td>
<td>17.2±2.2%</td>
<td>7.1±1.0%</td>
<td>17.2±2.2%</td>
</tr>
<tr>
<td>0.99V/0.02</td>
<td>0.45±0.04</td>
<td>57.5±2.1%</td>
<td>19.8±1.6%</td>
<td>7.2±1.9%</td>
<td>16.7±1.5%</td>
</tr>
<tr>
<td>1.25V/0.05</td>
<td>0.42±0.01</td>
<td>58.7±2.2%</td>
<td>18.8±2.0%</td>
<td>7.1±1.4%</td>
<td>15.3±2.3%</td>
</tr>
</tbody>
</table>

*Summary of the curve fit for the glassy carbon not included. There are five peaks that are assigned to π → π* transitions. Refer to Fig. 5(a).*
3. ppMDOB surface

The ppMDOB coating on glassy carbon was also examined by XPS before and after water stability tests. The coatings tested were generated by two different plasma conditions: 10 mA (0.35x0.01 W/l) and 20 mA (0.78x0.02 W/l). The theoretical molar O/C ratio of monomer is 0.286, and during the plasma deposition process only a marginal loss of oxygen (the molar O/C ratio is 0.35-0.34, Table I) was observed compared to the ppMAH coating. Figure 5c) shows the O 1s spectrum for a representative sample. The ppMDOB is fitted with five different peaks assigned to C-H(C) at 285.0 eV, C—O—C—O at 286.5 eV, C—O O at 288.5 eV, O at 290.3 eV, and the last one corresponding to the unsaturated sp2 bonding (C=C=O) at approximately 291 eV. The peaks are in agreement with the monomer structure. Winter-Jensen et al. have previously argued that during soft plasma polymerization it is possible to get carboxylic acid groups from opening of the diradical.

4. ppMDOB/MAH copolymer surface

The ppMDOB/MAH samples were examined by XPS before and after the water treatment. In the C 1s spectra, there are not only peaks from C—C, C—O, C—O—C—O, C=O, and COO but also components with higher bonding energies; cf. Fig. 5d). The last of the fitted peaks is due to C=C=O shake up from the benzenoid ring in the MDOD monomer structure preserved in the polymerized film. The resulting fitted distributions, positions, and fracture percentages are shown in Table II. There are significant differences between the treatments. The molar O/C ratio is 0.37.

C. Film thickness

The thicknesses of the plasma deposited films were measured by cross sectioning the middle of the specimen after removal of the PDPAA film. Figure 6 shows the increasing film thickness as a function of the power used during plasma polymerization for all three coatings tested. From the data it can be seen that the ppMAH film thickness increases from 25 nm at 0.4 W/l to 100 nm at 1.2 W/l during the 10 min plasma polymerization time. With the ppMDOB film the same tendency is observed, although the deposition rate is higher than that of the ppMAH film. The ppMDOB film increases from 43 nm at 0.3 W/l to about 100 nm at 0.7 W/l. Interestingly, the co-plasma polymer MDDB/MAH has the greatest deposition rate and increases up to 125 nm at 0.8 W/l. Since the pressure during all three types of deposition is constant (at 10 Pa) the different deposition rates and thicknesses generated are a function of the plasma power and flow rate. The effect of increasing the deposition rate with increasing plasma power has previously been shown. This can be explained by the increase in the number of energetic electrons generating a higher population of energetic ions hitting the surface, particularly at low powers. Vaska et al. has shown that the polymer deposition rate (R) increases as the parameter, defined by the power (P) divided by the flow rate (F) and the molecular weight of the monomer (M), by R ∝ (P/FM). Figure 6 shows the deposition rate is smaller for “lighter” MAH than for MDDB for constant power and flow.

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Table II: Summary of the XPS results for a ppmDOB surface before and after water treatment samples. Due to insignificant changes before and after water treatment the data was averaged. The ratio O/C from the monomer is 0.286.

<table>
<thead>
<tr>
<th>Power (W/l)</th>
<th>O/C</th>
<th>C=O</th>
<th>C=O</th>
<th>C=O</th>
<th>C=O</th>
<th>C=O</th>
<th>C=O</th>
<th>C=O</th>
<th>C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35±0.01</td>
<td>0.37±0.02</td>
<td>55.9±1.0%</td>
<td>22.4±1.0%</td>
<td>0.6±2.0%</td>
<td>10.3±1.1%</td>
<td>2.7±0.1%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.78±0.02</td>
<td>0.37±0.03</td>
<td>54.7±4.0%</td>
<td>23.8±3.0%</td>
<td>0.7±3.10</td>
<td>10.0±1.8%</td>
<td>2.2±0.3%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
rate (i.e., the pressure is unchanged). This is not surprising as the Yasuda equation is only valid for homogeneous monomers. In the present study we compare monomers of very different chemistry natures. The dependence of single monomer polymerization is following the Yasuda parameters.

The results of roughness measurements of the plasma modified layers by AFM after water treatment are shown in Table IV. The roughness of the plasma modified layers are seen to generally increase with the polymerization power. Plasma polymerization is a random process. The roughness changes are due to polymer thickness. Even though that the plasma polymerization was performed for consistent period of time, the speed of polymerization has been changed.

### D. Fracture energy and fracture resistance

Figure 7 shows the fracture energy for crack initiation (intrinsick fractography energy) for the various plasma treatments tested. An increase in fracture energy for all the plasma modified substrates, despite the significant scatter in the results, can be seen when compared to the fracture energy of clean, non-treated glassy carbons (the fracture energy was between 5 and 7 J/m²). The degree of improvement in the fracture energy depends on the monomer used and on the time and power of the plasma as well. Specimens modified with ppMDOB show an increasing trend of fracture energy with increase of plasma power for the two different powers examined. The stronger interface regardless of the power is provided by the ppMAH modified surface. The fracture energy of ppMAH has an average maximum of 78.7 ± 2.4 J/m² at 0.7 W/l, the weakest (on average) of the interfaces has a fracture energy of around 20.4 ± 7.6 J/m² at 0.3 W/l. In Fig. 8 some representative fracture resistance curves are shown for a weak interface (ppMAH: 10 min, 0.3 W/l) and two strong interfaces (ppMAH: 10 min, 0.9 W/l and 3.2 min, 0.7 W/l). As expected for the strong interfaces, an increase in fracture energy with crack extension is observed. In contrast, for the weak interface, the fracture energy remains almost constant.

A study of the dependence of polymerization time on fracture energy was also made. In this case, a number of experiments were carried out using ppMAH deposited at 0.3 W/l for only 3.2 min. The interface was found to be as strong as the ppMAH surface deposited with the same power for 10 min.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Scan size (μm)</th>
<th>ppMAH</th>
<th>ppMDOR</th>
<th>ppMDOR-MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>1</td>
<td>0.71±0.01</td>
<td>0.79±0.02</td>
<td>1.98±0.09</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.93±0.03</td>
<td>0.98±0.04</td>
<td>2.15±0.10</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>0.78±0.01</td>
<td>0.81±0.01</td>
<td>1.37±0.10</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.37±0.10</td>
<td>1.37±0.10</td>
<td>2.32±0.23</td>
</tr>
<tr>
<td>0.7</td>
<td>1</td>
<td>0.81±0.01</td>
<td>2.28±0.75</td>
<td>21.1±12.78</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.5±0.45</td>
<td>2.54±0.55</td>
<td>22.7±9.44</td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>1.11±0.24</td>
<td>1.10±0.31</td>
<td>1.37±1.00</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.10±0.31</td>
<td>1.37±1.00</td>
<td>2.32±0.23</td>
</tr>
<tr>
<td>1.2</td>
<td>1</td>
<td>3.70±1.40</td>
<td>4.39±1.90</td>
<td>2.32±0.23</td>
</tr>
</tbody>
</table>
Appendix A

The following discussion concerns the ppMAH films since more data proves present for this treatment. The ppMAH films were found to be sensitive to the power used during plasma polymerization, whereas surface characterization did not reveal any significant difference in chemistry for the various treatments. The explanation for the difference in fracture energy for samples of similar surface chemistry is unknown. However, we speculate that there could be a subtle difference in cross-link density at the outer surface of the plasma polymer layer generated from the different treatments. This is not depicted in the XPS data. This could result in a different degree of diffusion of the epoxy resin during the curing process and a subsequent variation in the number of chemical links at the interface between the plasma polymer and the matrix. In addition, a different degree of cross linking results in films that have differences in cohesive strength. Perhaps both lateral bonds in the layer and maximum penetration of the resin into the film are desirable for a tougher interface. Another point that needs to be mentioned is the significant spread in fracture energy for crack initiation and fracture resistance curves among specimens of the same treatment. The different notch geometry from specimen to specimen could contribute to the scatter observed in the fracture energy for crack initiation but this cannot explain by itself the large differences experimentally observed. Surface contamination during specimen handling should also have an effect on the measured values. Furthermore, almost all experiments were terminated by the onset of unstable crack growth. Specimens show R-curve behavior being more prone to unstable crack growth. In some cases the interface crack kinked into the glassy carbon. The instability is characterized by a very high crack velocity and it is possible that there is a catastrophic or explosive effect of the epoxy resin. Pure epoxy specimens were also tested and the crack growth became unstable usually immediately after crack initiation. Similar results were reported by Du et al.13, who related this behavior to stick-slip fracture instabilities observed in polymers. Although, it was mentioned above that the experimental setup used here provided stable crack growth this is not necessarily the case for rate dependent materials. However, despite the significant scatter it has been shown that adhesion between glassy carbon substrates and an epoxy resin was altered by changing the parameters during plasma polymerization.

IV. CONCLUSIONS

Using a pulsed 2-phase AC plasma polymerization system it is possible to create thin polymer films with malonic acid and 1,2-methylene dioxybenzene on glassy carbon and on PC pieces with powers less than 1 W1. The deposition rate of the plasma polymer changes with the power used in the system as shown by thickness changes of the plasma polymer layer. Despite differences in the rate of film growth, the surface chemistry is somewhat surprisingly seen to remain the same. This is confirmed by XPS measurements that showed insignificant changes during plasma polymerization using different rates of power consumption. The XPS results were largely confirmed by ATR-FTIR measurements, although this technique penetrates up to the first 1 μm of the surface. These observations could perhaps be attributed to the low power (0.3–1.2 W/l) of the pulsed AC plasma system which was found to preserve the rigid structures and functional groups of the monomers used. Adhesive groups were still detected by ATR-FTIR.

ACKNOWLEDGMENTS

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Surface Polymerisation Methods for Optimised Adhesion, Joanna M. Drews


1117

Drews et al.: Plasma polymerized thin films of maleic anhydride

(2005).

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J. Sept A - Vacuum, Surfaces, and Films

1117
Appendix B
Hydrolysis and stability of thin pulsed plasma polymerised maleic anhydride coatings

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Abstract
The stability of plasma polymerised layers has become important because of their widespread use. This study explored the hydrolysis and degradation stability of coatings of plasma polymerised maleic anhydride. Coatings made with different plasma parameters were exposed to aqueous media of different pH as a function of time. ATR-FTIR was used for structure analysis and a toluidine blue staining method allowed quantitative analysis of the hydrolysis of anhydride groups to acid groups. Coatings with constant thickness were obtained at different plasma powers and layers with varying thickness were obtained at constant plasma power by adjusting the polymerisation time. The results show that the hydrolysis resistance of the modified layer is determined by the power used in the plasma polymerisation, while changes in the chemistry of the modified layer are insignificant.
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Keywords: Maleic anhydride; Coatings; AC plasma; Cross-linking; Swelling

1. Introduction
Plasma surface modification is a widely used technique for conveying specific surface properties that is applicable to a broad range of substrates [1,2]. One major advantage of plasma polymerisation is that it is a solvent-free process. A disadvantage is the complex nature of the deposited layer which is difficult to characterise in detail. The plasma power directly influences the chemistry of the deposited layer, since increasing fragmentation of monomers occurs with increasing plasma power. The plasma power that is used can thus change the nature of the deposited layer. This phenomenon was studied by Jenkins et al. [3]. Plasma modified layers have been applied to biosurfaces [4], to optical devices [5], to obtain metal–polymer interfaces [6], to improve adhesion [7], and to improve the biocompatibility of biomaterials [8,9].

Plasma polymerised maleic anhydride (ppMAH) has previously been deposited using pulsed radio frequency (rf) and continuous wave (CW) plasma systems [10,11]. The aim of studies by Ryan et al. [10] and Hu et al. [11] was to use pulsed plasma polymerisation to preserve the anhydride groups in the film. Surface chemistry characterisation was performed using XPS and FTIR. These studies showed that the number of anhydride groups decreased as a function of increasing plasma power. Complementary work by Søffer et al. [12] concentrates on the prediction of surface roughness, thickness, and the preservation of anhydride groups on the surface with pulsed plasma polymerisation using mathematical modelling to design surfaces.
The behaviour of pulsed plasma polymerised maleic anhydride in different solutions has been reported by Chu et al. [13]. The authors observed swelling and collapsing of the plasma coating in aqueous solutions with a dependency on pH. This process was found to be reversible.

In the reported work, AC 2 phase plasma system was used. This system uses power levels with the ability to preserve the functional groups. The present work reports the degradation and hydrolysis resistance of pulsed plasma polymerised maleic anhydride (PPMAH) films deposited on polyethylene (PE) films. Conversion of the anhydride groups to carboxylic groups was followed in particular. The basic surface chemistry of this type of film was reported along with the results of mechanical tests for interfacial adhesion to glassy carbon substrates by Drews et al. [14]. Even though the surface chemistry did not change with different plasma power levels, this strongly influenced the mechanical tests results. The reported improvement of the interfacial strength was from 5–7 J/m² (untreated glassy carbon) to 20 ± 7 J/m² at 0.3 W/L and with optimum strength 79 ± 3.6 J/m² at 0.7 W/L. The plasma power levels used to deposit the coatings are reported in the units Watt/Litre (W/L). The results of additional mechanical testing on this type of film have been reported by Gostasinos et al. [15].

The coatings that were studied were hydrolysed in different aqueous solutions. The hydrolysis was investigated both as a function of time and of plasma conditions, e.g. the power introduced to the system, and the deposition time, and the subsequent thickness of the deposited layer. The speed of the hydrolysis of pulsed plasma maleic anhydride was monitored using the toluidine blue staining method described in detail below. This provides a quantitative measure of the number of carboxylic acid groups produced. This method should be used with care in this material, though, as it was found to be very sensitive to variations in surface treatments. The toluidine blue staining method was found suitable for following the hydrolysis of anhydride groups to carboxylic acid groups on the surfaces under different hydrolysis conditions as well as for tracking the dissolution of the film.

2. Experimental

2.1. Materials

Polyethylene film (thickness 1 mm) was extruded in-house from BORDELIS PA 3220 granules. Toluidine blue O was obtained from Sigma Aldrich and stored at room temperature in the dark. Maleic anhydride (MAH) was obtained from Sigma Aldrich as barrettes. These were ground into a fine powder in a hood and placed in a metal container under permanent vacuum. Ultra-pure water was obtained using a MilliQ system from Millipore.

2.2. Substrate preparation

All the films were cleaned in an ultrasonic bath for 5 min in different solvents, including acetone, methanol and MilliQ water, followed by drying with a jet of argon. The cleaned films were stored in polystyrene Petri dishes until use. The films were stored for no longer than a few hours before the surface modification. The coated films were kept under vacuum in the plasma chamber until further use.

2.3. Plasma polymerisation

In order to obtain a uniform coating on both sides, the PE films were freely suspended at the centre of the plasma chamber. The plasma chamber set-up is described in detail by Winders-Jensen et al. [16–18] and Amdovici et al. [19]. The PE films were marked with a 10 mm wide border around the edges. The material near the edges was discarded after plasma polymerisation to eliminate edge effects. The process of plasma polymerisation is described in detail elsewhere [11]. In brief, a pre-treatment was applied before the actual plasma polymerisation. During this process the surface is treated with argon plasma for 1 min (5 Pa, 1.31 ± 0.07 W/L), a mixture of argon and hydrogen (10 min, 6 Pa, 1.2 ± 0.2 W/L), and finally argon (20 s). Immediately after the pre-treatment, gas-phase monomer mixed with argon was fed into the chamber, and the current was adjusted to the desired power (0.17–1.21 W/L). The polymerisation was carried out for designated periods of time, reported in minutes. The power of the plasma may be calculated from the equation $P = U^2/2Z$, where $U$ is the voltage across the chamber, $I$ is the current, and $V$ is the actual plasma volume (11.5 L).

2.4. Surface analysis

Attenuated total reflectance Fourier-transform infrared spectrometry (ATR-FTIR) was performed using a PerkinElmer Spectrum B, equipped with a Germanium (Ge) crystal. All spectra are collected within the range of 800–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and averaging over 32 scans. The measurements were obtained in ambient atmosphere. Measurements on the coatings were performed just after plasma polymerisation, after MilliQ water treatment, and after acid or alkaline solution treatment, respectively. The estimated penetration depth of ATR-FTIR is related to the wavelength of the light, and is around 1 μm. This is substantially thicker than the surface coating studied.

ATR-FTIR data were extracted as .asc files. The data were restricted to the region of 1500–2100 cm⁻¹. Peak fitting was done with the programme PeakFit [20] from Jandel Scientific Software. A linear background was applied to the analysed data. The peak area was fitted with 4 peaks (Pearson VII function [20]) with all parameters being set free.

2.5. Surface derivatisation

The toluidine blue surface derivatisation method of Sano [21] was used to determine the number of carboxylic acid groups in the volume of the coatings. In brief, a polyethylene piece with size 20 mm × 20 mm × 1 mm modified on both sides (the reactive area of the surface is
approximately 8 cm$^3$) was incubated with 5 mL of fresh toluidine blue solution ($2 \times 10^{-4}$ M) in 0.1 mM NaOH for 1 h at 40 °C in a water bath. Each carbonylic acid group was assumed to bind one molecule of toluidine blue (Scheme 1). Afterwards, the solution was removed and the surface rinsed 3 times with fresh 0.1 mM NaOH. The samples were placed in clean, dry HDPE flasks with 5 mL of 30% acetic acid for 30 min at 40 °C to release the bound toluidine blue into the solution. The absorbance of the solutions was measured with a UV-1700 Shimadzu spectrophotometer at a wavelength of 630 nm. The number of reactive carbonylic acid groups in the films was determined from a calibration curve of toluidine blue concentration versus absorbance.

The time of dye incubation was optimised on freshly deposited pulsed plasma polymerised maleic anhydride (ppMAH−0.7 W/L, 10 min) on the PE substrates. The optimal dye incubation time was established as 1 h after sequential measurements.

3. Results and discussion

The purpose of this study was to investigate the stability of the anhydride groups in plasma deposited films of maleic anhydride. The variables studied were: (i) exposure to different hydrolysis media, (ii) variations in the thickness of the surface coatings, and (iii) coatings that were prepared to the same thickness but that were polymerised using different plasma power levels. Since anhydride groups are sensitive to humidity, the study required freshly deposited films of polymerised maleic anhydride.

The toluidine blue method described above allows a quantitative estimate of the total number of acid groups in the coatings. Alternative high-resolution methods, e.g. XPS, probe only a limited part of the sample, and hence rely on the assumption of uniformity. Finally, the relationship between the concentration of carbonylic acid groups and the plasma power was determined as described below.

### 3.1. Plasma surface modification

ATR-FTIR measurements were performed on ppMAH films deposited on the PE films. The peaks from the PE substrate did not overlap with the characteristic peaks from the coatings. Changes in peak intensities thus provide a relative measure of the thickness of the given coating. The spectra of freshly deposited ppMAH were found to be in agreement with previously published results by Schiller [22] and Ryan [10]. The plasma modified surface showed a strong peak consistent with anhydride groups at 1780 cm$^{-1}$ that has a shoulder at 1860 cm$^{-1}$ [23]. These peaks are assigned to carbonyl stretch in the anhydride group. There are two additional peaks at 1370 and 1630 cm$^{-1}$, corresponding to ester and carbonyl groups [3].

Increased plasma power resulted in increased intensity of the ester and carbonyl peaks (1730 and 1630 cm$^{-1}$), relative to the anhydride peaks (1860 and 1780 cm$^{-1}$), as outlined in Fig. 1. The FTIR-spectrum of the maleic anhydride monomer has a line at 1627 cm$^{-1}$. This line which can be assigned to stretching vibration of the double bond C–C is sharp and with low extinction as compared to the absorptions at 1780 and 1860 cm$^{-1}$.

From the above observations it is thus unlikely that part of the intensity observed at 1630 cm$^{-1}$ in the plasma polymerised films is due to un-reacted maleic anhydride, although it cannot be strictly ruled out. The peak at 3300 cm$^{-1}$ also increases in intensity with an increase in plasma power. This peak is assigned to vibrations from carbonylic acid groups.

In an attempt to quantify the changes in surface chemistry with respect to the plasma power, the ATR-FTIR spectral region from 1500 to 2100 cm$^{-1}$ was analysed with a peak fitting algorithm. In this region there are two peaks assigned to carbonyl and ester groups (1630 and at 1730 cm$^{-1}$) and two peaks assigned to anhydride groups (at 1780 and 1860 cm$^{-1}$).

Changes in the ratios between the calculated areas under the carbonyl and ester peaks and the areas under the anhydride peaks (see Fig. 2) can be taken as an expression of changes in the chemistry of the polymerised layers, e.g. in the density of...
cross-linking. The amplitude varied with power in the fitting for the peaks associated with the anhydride group, whereas the peak position, the peak width, and the shape parameters were unchanged. The peak width and shape parameters were somewhat less robust for peaks associated with the carbonyl and esters groups. Fig. 2 indicates that the relative amount of the intact anhydride groups in the surface layer decreases with increasing plasma power.

There were no changes in the ATR-FTIR spectra for coatings deposited with the same power (0.7 W/L), but with different polymerisation times (10, 20, and 30 min) (Fig. 3). The ATR-FTIR registered the thickness changes of the plasma films by the changes of intensity of substrate PE peaks around 2820, 2850 and 1470 cm⁻¹.

3.2. Derivation of carboxylic acid groups

The PE films coated with ppMAH were removed from the chamber after polymerisation and placed into solutions for hydrolysis studies. Slow hydrolysis of anhydride groups starts in the coatings immediately after removal from the plasma chamber. The samples were therefore immediately analysed to minimise this effect.

A number of different solutions were tested in order to obtain full hydrolysis of ppMAH (polymerised with a plasma power of 0.7 W/L for 10 min). Initially, water treatment was attempted both at room temperature and at reflux (100 °C). The resulting hydrolysis was found to be rather slow regardless of the temperature. The number of carboxylic acid groups increased slowly with hydrolysis time (over a period of several days).

The hydrolysis media were changed in order to see whether the hydrolysis could be accelerated. Sulphuric acid (H₂SO₄) at a concentration of 1 M at room temperature was tested. ATR-FTIR spectra of the exposed samples were obtained after 30 min and 17 h, respectively (see Fig. 4). In both cases the hydrolysis rate was found to be comparable to that of the water treatment. Anhydride groups were still present in ATR-FTIR spectra after 30 min of strong acid treatment. Visual inspection confirmed that the coating was reasonably stable from a mechanical point of view.

Hydrolysis in alkaline solutions was investigated at 0.1, 0.5, and 100 mM, respectively. There was an acceleration of the reaction and the coating dissolved with extended treatment time when the molarity was increased. The influence of temperature on the hydrolysis rate was also investigated at the highest concentration. These results are presented in Table 1. After 24 h of hydrolysis under conditions of room temperature and reflux (100 °C), the surfaces were investigated. The number of carboxylic acid groups was 27 ± 2 and 3.2 ± 0.8 mmol/cm², respectively. The surfaces were examined again after 72 h and after 144 h at room temperature. This time, the staining method showed that the number of carboxylic acid groups on the surface was rather low (approximately 1 mmol/cm²) and that this did not depend on the treatment. A control experiment showed that there were 0.17 ± 0.04 mmol/cm² of carboxylic acid groups on a clean polyethylene piece that would indicate oxidation of the surface. Increasing the temperature increased the speed of the dissolution of the plasma layers. Even after an extended treatment, there was still some of the coatings.

![Image](image-url)
Appendix B

remaining which could be interpreted as a layer of ppMAH covalently bonded to the surface.

Surfaces modified with the same plasma power but coated with different thicknesses were investigated. Plasma polymerised coatings deposited for 5, 10, 20 and 30 min using a power rate of 0.7 W/L were all hydrolysed in 10 mM NaOH media. Samples were measured after 0 min, 15 min, 30 min, 1 h, 2 h and 3 h of hydrolysis. In all cases 90% of the hydrolysis of anhydride groups occurred in less than 15 min regardless of film thickness. The concentration of carboxylic acid groups in the film reached a plateau after 30 min of hydrolysis. The maximum surface density of carboxylic acid groups was as follows; 23 ± 1 mmol/cm² (5 min polymerisation), 37 ± 2 mmol/cm² (10 min polymerisation) and 59 ± 2 mmol/cm² (20 min polymerisation). These results are presented in Fig. 5. When the NaOH treatment time was extended to 72 h, the modified layer completely dissolved.

The number of accessible carboxylic acid groups on the surface decreased with hydrolysis time consistent with gradual dissolution of the film. The film polymerised for 30 min was not stable in the 10 mM NaOH solution. Flakes of the ppMAH were observed in the solution. In addition to gradual dissolution, thick ppMAH coatings were prone to delamination when exposed to the 10 mM NaOH solution evidenced by flakes of coatings floating in the solution. This instability probably originates from the high internal stresses in the coating created during the plasma process [24],

Fig. 6. Hydrolysis of anhydride groups to carboxylic acid groups measured with the toluidine blue staining method. The hydrolysis solution is 10 mM NaOH. A single film thickness of 20 nm was used for all samples. (a) ppMAH 0.17 W/L (5 min), 34 min; (b) ppMAH 0.3 W/L (10 min), 18 min; (c) ppMAH 0.7 W/L (20 min), 10 min; (d) ppMAH 1.2 W/L (30 min), 8 min.

augmented by volume changes due to hydrolysis. Such stresses are more easily accommodated in thin films.

Fig. 6 shows the results of the hydrolysis reaction as a function of time. Samples were prepared to obtain the same thickness of the deposited layer with different plasma powers by varying the polymerisation time. The course of the reaction is seen to depend on the polymerisation power, since the time required for hydrolysis and dissolution depends on this level. Coatings created with low plasma power (0.16 W/L–5 mA) show a maximum surface density of the carboxylic acid groups just after removal from the plasma chamber without exposure to a solution of NaOH. During these hydrolysis studies, there is a decrease in the amount of the carboxylic acid groups in the coating with time. Increasing power is thought to lead to both increased cross-linking in the film and increased rearrangement of the functional groups, e.g., formation of hydrolysable groups (ester, anhydride) in the main chain of the polymer. For films formed at low power with very little or no cross-linking, the hydrolysis of a few main chain bonds will lead to partial dissolution of the surface layer, and thereby to a decrease in the number of acid groups. On the other hand, for ppMAH coatings created with high power (1.2 W/L–30 mA) the density of carboxylic acids groups on the surface increased with hydrolysis time. In this case the hydrolysis rate was seen to be slow. This is in accordance with the higher cross-link
density, which, in turn, will inhibit the swelling, cf. Fig. 2. The number of carbonyl acid groups was found after 3 h of hydrolysis in 10 mM NaOH.

Coatings made with power levels of 0.3 and 0.7 W/L, respectively, were also investigated. In both cases the deposited layers of plasma polymerised maleic anhydride show three regimes: an increase, a plateau, and a decrease in the number of carbonyl acid groups on the surface. In terms of the above this may be interpreted as an initial swelling followed by hydrolysis of the linkage.

The number of carbonyl acid groups in films of the same thickness, but made with different plasma powers, are presented in Fig. 7. The maximum number of carbonyl acid groups in ppMAH films is not influenced by the plasma power introduced to the system.

4. Conclusions

The stability of plasma polymerised layers is particularly important due their widespread use. Plasma polymerised maleic anhydride coatings have been investigated to check their stability and the rate of hydrolysis of the anhydride groups. Studies were made of films polymerised with the same power and with different polymerisation times. This procedure gave different thicknesses of the coatings. The hydrolysis of these ppMAH coatings was found not to be dependent on the thickness of the layer. On the other hand, the stability of the coatings was found to be dependent on the thickness. Films polymerised for 30 min that were placed in 10 mM NaOH broke into flakes after 15 min whereas films polymerised for shorter times (up to 20 min) did not experience this problem during hydrolysis. A second kind of coating was polymerised with different plasma powers with the thickness being kept constant by varying the polymerisation time. The hydrolysis and stability of the coatings strongly depend on the plasma power. Coatings created with low power show a tendency to dissolve more readily in sodium hydroxide solutions, while the coatings became progressively more stable with increasing plasma power. It is thought that the resistance to hydrolysis is due to cross-linking during the plasma polymerisation.

Increasing plasma power increases the time necessary to obtain the maximum concentration of carbonyl acid groups on the surface during hydrolysis, and the coating is less able to swell because of the increased cross-linking. The maximum number of carbonyl acid groups was found to be independent of the plasma power. Moreover, the number of carbonyl acid groups available on the surface, just after the samples are taken out of the plasma chamber, increases with decreasing power (see Fig. 6). This is consistent with the proposed dependence of the cross-linking of ppMAH coatings as a function of the plasma power.

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References

Appendix C

PULSED PLASMA DEPOSITED MALEIC ANHYDRIDE THIN FILMS AS FUNCTIONALISED SURFACES IN COMPOSITE MATERIALS

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ABSTRACT

A low power AC 2-phase plasma setup was used for surface deposition of thin films of maleic anhydride (ppMAI) on glassy carbon or on polyethylene. The planar glassy carbon substrate models carbon fibres in composite materials. The substrates are treated with different plasma power levels. The present study focuses on the effect of plasma power on the surface chemistry, the properties of the modified layers and the adhesion between the substrates and an epoxy resin (interface properties). The discussion of the surface characteristics is based on surface chemistry analyses (XPS and toluidine blue staining method) and the interfacial fracture energy (measured by the double cantilever beam test method). To explain the observed differences in interfacial fracture energy, some of the samples were hydrolysed in alkaline solution. The hydrolysis ratio of preserved anhydride groups on the surface was monitored with the toluidine blue staining method.

1. INTRODUCTION

It is well known that the macroscopic properties of composite materials are strongly dependent on the integrity of the fibre-matrix interface. The optimisation of the fibre-matrix interface is essential for improved physical and in particular mechanical properties of fibre reinforced polymer composites. The adhesion between the fibres and the matrix is realised through bonds which play an essential role for the interface strength, especially in the case of polymeric
materials, which often consist of cross-linked constituents (Hansen (1999), Doi (1996), Launay et al. (2007)). The cross-links can be either covalent bonds or physical interactions, e.g. hydrogen bonds or dispersion and electrostatic forces. The Hansen solubility parameters can help in quantifying the physical affinities between the constituents.

Wet/solution chemistry is usually used to surface modify the fibres, whereas plasma treatment is mostly being used for cleaning (Keller et al (2005)). In this study the authors used the plasma polymerisation technique as a method of fibre surface modification by thin polymeric film deposition. The advantage of plasma polymerisation is that it is a solvent-free technique, which is rather easy and inexpensive to use. Post-treatment e.g. cleaning and purifying of the samples is not necessary unless further modifications are desired. The structure of plasma polymerised layers is usually very complex and thus difficult to understand and analyse. Properly understood and controlled, the complex structure can, however, be used in designing new high strength composite materials by tailoring the fibre/matrix interface or interphase.

The complex nature of layers modified with pulsed plasma comes from two processes taking place simultaneously, one is the polymerisation (time off – time for inactive plasma where addition of monomer molecules progress) and the other is creating radicals (mostly on the surface; time on – time for active plasma). The time on and off influences the chemistry and properties of polymerised layers (Schiller et al (2002)). Using the SoftPlasma™ technique the ratio between times on and off were controlled by the plasma power level – a higher plasma power level thus results in a more active (more radicals) polymerisation. The output of this process could be observed as an increase of the polymerisation rate (with constant flow of monomer and Ar). The plasma polymers created with low power are expected to have a high content of low molecular weight polymers. This could mean that the modified layer actually contained oligomers instead of polymers and was only weakly cross-linked. This material could often be easily dissolved. Hence, to obtain a stable layer of polymer, it is necessary that the power input to the system exceeds a minimum energy (Hegemann et al (2005)).

For the surface modification in the present study we used maleic anhydride (MAH). The layers of pulsed (rf) and continues (CW) plasma polymerised maleic anhydride (ppMAH) had previously been investigated and characterised using surface characterisation techniques (Ryan et al (1996)). It was concluded from their work that with manipulation of plasma power it is possible to preserve anhydride groups during the plasma polymerisation. The system of SoftPlasma™ used power less than 1 W/l. The distinct advantage of this plasma polymerisation method is that the required energy supplied into the system is low enough to run the polymerisation in a way very close to the conventional way (polymerisation in the solution).

In this paper we focus on the characterisation of the surface coatings made by soft plasma polymerisation of maleic anhydride. We also showed that the complex nature of the polymeric coating can be advantageous. The surface chemistry is analysed with X-ray photoelectron spectroscopy (XPS) and the toluidine blue staining method (Sano et al (1996)). The rate of hydrolysis of preserved anhydride groups, in the ppMAH films, during plasma surface modification as a function of plasma power levels was investigated. The hydrolysis ratio was monitored by toluidine blue staining. The fracture energy of the planar glassy carbon/epoxy interface was measured under nominal Mode I using the double cantilever beam method test method.

2. EXPERIMENTAL SECTION

Materials. Planar glassy carbon substrates (SIGURD GJ) were purchased from HTW
Appendix C

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Hochtemperatur, Germany in sizes of 20x20x1 mm$^3$ and 65x5x1 mm$^3$. Polyethylene (PE) foil (thickness 1 mm) was extruded in-house from BOREALIS FA 3220 granules. Toluidine Blue O was obtained from Sigma Aldrich and stored at room temperature in the dark. Maleic anhydride (MAH) was obtained from Sigma Aldrich as briquettes, which were ground into fine powder in a hood and placed in a metal container under vacuum. Ultra-pure water was obtained using a MilliQ system from Millipore.

**Substrate preparation.** The PE substrates were cleaned in an ultrasonic bath for 5 minutes in different solvents, including acetone, methanol and milliQ water. The glassy carbon substrates were cleaned in an ultrasonic bath in different solvents, using chloroform (5 minutes), acetone (twice – 2x5 minutes) and methanol (5 minutes). Finally, all substrates were dried with a jet of argon. The cleaned substrates were stored in polystyrene Petri dishes until use. The substrates were stored no longer than a few hours before the surface modification, after which they were kept under vacuum in the plasma chamber until further use.

**Plasma polymerisation.** The plasma chamber set-up is described in detail by Winther-Jensen et al. (2003; 2004) and Ademovic at al. (2005). This plasma coating technique, called SoftPlasma™. The process of plasma polymerisation is described in detail by Drews et al. (2007). The plasma polymerisation information is given in units of power per litre (W/L) and plasma polymerisation time (min). The power of the plasma may be calculated from the formula $P = U^2 / V I$, where $U$ is the voltage across the chamber, $I$ is the current during plasma polymerisation, and $Vol$ is the plasma volume equal to 11.5 l. In order to obtain a uniform coating on both sides, the PE substrates were suspended freely close to the centre of the plasma chamber and a 10 mm wide border around the edges was discarded. The glassy carbons for the mechanical tests were mounted on double sticky tape on a glass tube.

**Surface analysis.** X-ray photoelectron spectroscopy (XPS) was performed using a SPECS Sage 100 instrument with a non-monochromatic MgK$_x$ X-ray source at a power of 275 Watts (11 keV and 25 mA). The pressure in the chamber was always below 1 x 10$^{-6}$ mbar. Two kinds of spectra were obtained: survey and high resolution. Atomic concentration of the surface composition was calculated from the intensity of the peaks of survey spectra (0-1100 eV, 100 eV pass energy). The high resolution spectra (23 eV pass energy) of surface components was used to fit 4 peaks with full-width at half-maximum (FWHM) of 2.0 eV. The positions of the peaks was as follow: 285.0 eV for C-O, 286.5 eV for C-H, 288.0 eV for C=C-H (referencing peak), 289.4 eV for O=O.

**Fracture mechanics test.** Double Cantilever Beam (DCB) sandwich specimens were prepared using the plasma treated glassy carbon wafers (65x5x1 mm$^3$). The resin used was an epoxy system (Primer-20, SP Systems, UK). The resin and the hardener were mixed at a weight ratio of 4:1, degassed for 2x5 min under full vacuum, and then casted into silicon rubber moulds between two glassy carbon wafers. Teflon films (0.5 mm in thickness) were used to keep the wafers apart and to create a notch of 20 mm in length necessary to initiate a crack along the glassy carbon-epoxy interface. The DCB specimens were cured for 24 hours at room temperature and subsequently post-cured at 50°C for 16 hours. The cured samples were ground and polished to facilitate optical observations of the interface crack growth. Subsequently, the sandwich specimens were glued on specially made stainless steel beams (6 mm in thickness) that could be mounted on the test fixture. An epoxy adhesive (Scotch Weld) was used to glue the DCB specimens to the steel beams. The curing time for the adhesive was 24 hours at room temperature. More detailed description of the DCB method can be found in the following references: Bao et al (1992) and Sorensen et al. (1996)
Drews, Goutianos, West, Hvilsted, Almdal

**Surface derivatisation.** The toluidine blue surface derivatisation method of Sano et al (1993) was used to determine the number of carboxylic acid groups in the volume of the coatings. In brief, a polyethylene plate with size 20x20x1 mm³ modified on both sides (the reactive area of the surface is approximately 8 cm²) was incubated with 5 ml of fresh toluidine blue solution (2x10⁻⁴ M) in 0.1 mM NaOH for 1 hour at 40°C in a water bath. Each carboxylic acid group was assumed to bind one molecule of toluidine blue. Afterwards, the solution was removed and the surface rinsed 3 times with fresh 0.1 mM NaOH. The samples were placed in clean, dry HDPE flasks with 5 ml of 20% (v/v) acetic acid for 30 minutes at 40°C to release the bound toluidine blue into the solution. The absorbance of the solutions was measured with a UV-1700 Shimadzu spectrophotometer at a wavelength of 630 nm. The number of reactive carboxylic acid groups in the film was determined from a standard curve of toluidine blue.

RESULTS AND DISCUSSION

Surfaces were modified with pulsed plasma maleic anhydride (ppMAH) with different power levels (0.3, 0.7, 1.2 W/l) in such a way that the thickness of the films remained the same (approx. 80 nm). The freshly deposited layer of ppMAH on PE was placed into 0.1 mM NaOH for hydrolysis of the preserved anhydride groups on the surface. After hydrolysis of an anhydride group two carboxylic acid groups are obtained.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{WATER, BASE MEDIA} & \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

Hydrolysis of anhydride groups.

From XPS analysis we had previously shown that the surface chemistry was not influenced by plasma power level (Drews et al. (2007)). The XPS technique is a surface sensitive method, where about 70% of the signal comes from the first monolayer (approx. 1 nm). Only the last 30% comes from deeper layers (max. 10 nm). In other words, this analysis is equivalent to seeing the plasma modified layer (ppMAH) as a strictly 2-D structure, regardless of thickness. The average surface chemistry from XPS measurements for all plasma treatments yielded an oxygen content of 31.22% (O 1s) and a carbon content of 69.2% (C 1s).

Consistent results were found from the toluidine blue staining method, where the maximum number of carboxylic acid groups after full hydrolysis in the plasma layers was found to be the same within uncertainty, approx. 36 mmol/cm² (see Figure 1), i.e. it did not seem to be influenced by the plasma power level. We thus concluded that the changes of surface chemistry as a function of plasma power were negligible.
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Pulsed Plasma Deposited Maleic Anhydride Thin Films As Functionalised Surfaces In Composite Materials

Figure 1. Maximum number of carboxylic acid groups from toluidine blue staining method in the 80 nm thick films created with different power levels.

Figure 2. Hydrolysis of preserved anhydride groups in a 80 nm plasma film created with different power levels as function of hydrolysis time in 0.1 mM NaOH: a) 0.3 W/l, b)
As mentioned above, in order to investigate the hydrolysis, films were placed into a 0.1 mM NaOH hydrolysing medium. As shown in Figure 2, the time evolution of the hydrolysis of the plasma polymerised layers of maleic anhydride is found to be strongly dependent on the plasma power used. The hydrolysis of ppMAH prepared with low power (Figure 2(a)) shows a tendency of fast hydrolysis and slow constant dissolution, i.e. a fast initial increase of the number of carboxylic acid groups, followed by a gradual decrease after a short time in sodium hydroxide. A similar trend was observed for the ppMAH prepared with medium power (Figure 2(b)). The hydrolysis of ppMAH made with high power (Figure 2(c)) progressed slower with a gradual increase in the number of carboxylic acid groups on the surface over time.

The observed slow increase in the number of carboxylic acid groups could be attributed to the cross-linking of the layers. The bonds prevent the swelling of the ppMAH layers (Chui et al. (2006)), making it more difficult to hydrolyse the anhydride groups to carboxylic acid groups (Drews et al. (2007)). Similarly, the observed dissolution of the film could be an insufficient amount of cross-linking in the film and a high content of oligomers. An alternative explanation could be that the bands are not between C-C (covalent bonds), as we would expect, but between C-O which during NaOH treatment can be hydrolysed.

The effect of plasma power can also be seen in the mechanical tests of the planar glassy carbon specimens where ppMAH layers had been prior deposited on the glassy carbon surfaces. The substrates were plasma prepared with different plasma power levels from 0.3 W/l to 1.2 W/l. Figure 3 shows the dependence of interface fracture energy on the plasma power. The results show that there is an optimum plasma power value, 0.7 W/l, at which a very strong interface is obtained.

![Fracture energy vs. Power](image)

**Figure 3.** Fracture energy for crack initiation as a function of power level during ppMAH polymerisation (the polymerisation time is the same for all cases and equal to 10 min).

In Figure 4 the fracture resistance curves are shown for three different plasma treatments. For plasma power of 0.7 W/l the behaviour is significantly different from the other two treatments. Specimens prepared with a plasma power of 0.7 W/l exhibit a strong R-curve behaviour (increase of fracture energy with crack extension) and at some point unstable crack growth occurs. For the specimen shown in Figure 4 unstable fracture occurs after the crack has grown
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approximately 5 mm. On the other hand, specimens prepared with a plasma power of 0.3 W/l and 1.2 W/l show similar and stable crack growth up to approximately 10 and 15 mm, respectively. The former could be evidence an extrinsic toughening mechanism (i.e. plasticity), whereas the latter would be a sign of low cohesion.

![Graph](image)

Figure 4. Examples of fracture resistance curves of glassy carbon specimens prepared with different powers levels of ppMAH. The blue curve represents the value of untreated glassy carbon specimens (5.7 J/m²).

Arguably the reason for the different behavior of glassy carbon treated at different plasma levels could be the different amounts of cross-links in the plasma layers. If the plasma layers contain many oligomers, i.e. if they are weakly cross-linked – Figure 5(c), the material would be expected to show low cohesion. On the other hand, materials which exhibit a high amount of cross-links (Figure 5(a)) would also be expected to show low cohesion, since the linear polymers between cross-links are short. According to the theory of elasticity of rubber based on thermal motions of ideal chains, cross-linked material can be only fully stretched up to $\sqrt{N}$ times, where $N$ is the number of monomers (Doi, 1996).

![Schematic](image)

Figure 5. Schematic illustration of the plasma deposited ppMAH layers. a) highly cross-linked layer, b) intermediate cross-linked layer and c) weakly cross-linked layer.
CONCLUSIONS

Using AC 2-phase plasma polymerisation technique it is possible to create a thin layer of maleic anhydride on glassy carbon and polyethylene substrates. If one considers these thin films only as surfaces, the surface chemistry is not influenced by the plasma power. This is confirmed by the toluidine blue staining method and XPS results. If we consider, however, these films as bulk materials we can see that there is a significant dependence on plasma level. This was shown in the case of hydrolysis of the layer with the toluidine blue staining method and through the mechanical tests (interface fracture under nominal Mode I). The experiments show that it is important to carefully optimise the conditions of creating the plasma layers. On one side, we can obtain a layer with strong adhesion between substrate and coating and a strong R-curve behaviour. On the other side, we can obtain a highly cross-linked layer. In this case the adhesion is weak and quite probably problems of self cracking due to internal stresses are introduced (Yu and Yasuda, 1999). Finally it was shown (Figure 3) that it is possible, through the plasma polymerisation technique used, to obtain interfaces with unique properties. Weak, intermediate or strong interfaces could be easily manufactured giving the ability to design composites materials for specific applications.

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Appendix D
CONTROLLING INTERFACE ADHESION AND FRACTURE PROPERTIES IN COMPOSITE MATERIALS BY PLASMA POLYMERISATION

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ABSTRACT

The effect of plasma polymerization on the interface adhesion between carbon fibres and an epoxy matrix was investigated. This was done by loading with pure bending moments in nominal mode I planar glassy carbon/epoxy specimens. The glassy carbon was used to simulate the carbon fibres. The experiments demonstrated that significant increase in adhesion strength can be achieved although at the present there is considerable scatter in the results. A method was developed to experimentally derive the interface cohesive law by means of fracture energy, peak stress and critical interface crack opening.

1. INTRODUCTION

Composite materials (mainly in unidirectional lay-up) are used in wind turbine blades due to their high specific properties (strength and stiffness). A failure mode among others that can often occur in service is delamination because of their low properties in the transverse directions. Large scale fibre bridging can enhance the crack growth resistance (i.e. suppress delamination) during crack growth (Serensen and Jacobsen 1998). A number of micromechanical models have been developed to study the role of fibre bridging in the delamination resistance (i.e. Spearing and Evans 1992). The
bridging mechanism strongly depends on the interface fracture resistance (fibre pull-out or fibre sliding) and its value is usually assumed in modeling as it is a parameter difficult in general to be measured accurately. Characterization of the interface in terms of fracture energy implies use of linear elastic fracture mechanics. Considering that the fibre (i.e. carbon) diameter is of the order of 5-8 \( \mu \)m whereas the failure process zone is often less than 1\( \mu \)m and the inter-fibre distance is often less than one fibre diameter it can be argued that the interface failure should be treated as a large scale failure process zone problem. The interface is characterized by cohesive laws (stress-separation relations).

The interface properties depend on the compatibility between the (coated) fibres and the matrix. One function of the coating (or sizing) is to enable wetting and to create the physico-chemical link to the matrix during consolidation of the composite. Fibre sizing is mainly based on wet chemistry while in few cases plasma treatment (Moon and Jang 1999) is used for fibre surface activation. In this work a different approach, plasma polymerization (thin polymer film deposition on the fibre surface), was chosen to alter the fibre/matrix adhesion. Although the plasma process involves complicated physical processes it also offers a number of possibilities to obtain interfaces with different properties by varying i.e. the thickness of the deposited polymer film, the number of reactive groups, degree of molecule entanglement and cross-link. Additionally it is a clean process in comparison with wet chemistry.

The aim of current work is to use plasma polymerization to obtain interfaces with different properties (i.e. strong and weak interface) followed by mechanical characterization in terms of fracture energy, fracture resistance curves and cohesive laws. Experimental investigation of the fibre/matrix adhesion usually involves the use of model geometries such as the single fibre fragmentation test (Dralz and Madhukar 1993). However, planar specimens were chosen as they are easier to plasma treat and secondly the analysis of the mechanical tests is more straightforward. Glassy carbon was used to mimic carbon fibres, whereas the matrix was an epoxy resin. Double Cantilever Beam tests with pure bending moments were performed to obtain fracture resistance curves and interface laws under nominal mode I.

2. EXPERIMENTAL

2.1 Materials and plasma polymerization. Planar glassy carbon (9\( \times \)35 mm) substrates (SIGRADUR C, HTW Hochtemperatur, Germany) were used as an experimental model for carbon fibres. Two different monomers (MAH: maleic anhydride and MDQ: 1,2-(methyleneoxy) benzene) and a mixture of the two were used in a low power two-phase AC plasma polymerization (Ademovic et al. 2005; Winther-Jensen et al. 2005).

The polymerization procedure consisted of two steps: activation of the glassy carbon surface (creating radicals on the surface) and the actual polymerization. It is in the second step (in most cases the duration of this step was 10 min) that the polymer film is deposited on the glassy carbon surface (see Fig. 1(a)). The plasma discharge during this step was varied in separate experiments from 10 mA to 30 mA. A higher current leads to a thicker film (film thickness varies from 20 to 150 nm). The number of reactive
groups formed is also dependent on the current. The polymerization time also affects the film thickness and number of reactive groups. Fig. 1(b) shows an Atomic Force Microscope (AFM) picture of a polymerized film on glassy carbon. It can be seen that the deposited film has a finite thickness. X-ray photoelectron spectroscopy (XPS) was employed to confirm the modified layer. Fig. 2 shows XPS high-resolution Cls spectra for an untreated glassy carbon and for three treated glassy carbons. All spectra were fitted with four peaks (C-C 285.0 eV, O=O 286.3 eV, O=C=O 288.0 eV, O=O 289.2 eV) and for MDOB, MDOB/MAH there are additional peaks above 291.0 eV for π-π shake-up (coming from the aromatic structure). In brief, the peak 289.2 eV observed for all the plasma treated glassy carbons indicate the presence of O=C=O- (e.g., carboxylic acid groups or anhydride groups) and the intensity of the peak can be assigned to different amounts of reactive groups on the surface.

Fig. 1. (a) Schematic illustration of the 2-phase plasma polymerization. (b) AFM picture (units: μm) of a polymerized film (finite thickness) on glassy carbon substrate.

Fig. 2. High-resolution XPS carbon (Cls) spectra of: i) clean/untreated glassy carbon, ii) polymerized (MAH, MDOB, MAH/MDOB) glassy carbon. Polymerization time: 10 min, current during polymerization: 10mA.

The resin used was an epoxy system (Prime-20). The resin and the hardener were mixed at a ratio 4:1 by weight and degassed under full vacuum to remove air bubbles. The curing procedure was 24 hours at room temperature followed by 16 hrs at 50 °C.
mechanical properties are given in Fig. 3. In Fig. 3(a) the effect of loading rate can be seen, whereas from Fig. 3(b) it can be concluded that the resin’s behaviour is more close to a visco-elastic solid in the range of the strain levels examined. The specimen dimensions were in accordance to ASTM-D 638, specimen type I.

Fig. 3. (a) Epoxy (Prime-20) stress-strain curves at different loading rates, $\sigma$: strength in MPa, $\varepsilon$: failure strain (%). (b) Loading-unloading curves at different stress levels followed by a step of constant (zero) load for 2 hrs.

2.2 Double Beam Cantilever (DCB) specimen preparation and geometry. The epoxy resin (prepared as in 2.1) was poured in silicon rubber moulds between two plasma treated glassy carbon substrates (65 x 1 x 5 mm). Teflon films (0.2 mm in thickness) were used to keep the glassy carbon substrates apart. The DCB specimens were then cured for 24 hrs at room temperature and subsequently post-cured at 50°C for 16 hrs.

Fig. 4. (a) Specimen geometry (all dimensions in mm), (b) Detailed view of the specimen structure, and (c) Optical photograph showing the details of the specimen structure near the notch.

The cured samples were ground and polished to facilitate optical observations of the crack growth. Subsequently the sandwich specimens were glued on specially made stainless steel beams (6 mm in thickness), which could be mounted on the test fixture (see next Section). An epoxy adhesive (Scotch Weld) was used to glue the DCB specimens to
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the steel beams. The curing time was 24 hrs at room temperature. The geometry of the specimens can be seen in Fig. 4.

3. BASIC MECHANICS

3.1 Measurement of J. A special fixture (Sørensen et al. 1998) was used to load the DCB specimens with the force couples (Fig. 4(a)). This creates pure bending moments as shown in Fig. 5. The plane strain energy release rate can be determined by taking the J-integral (Rice 1968) along the boundaries of the specimen:

\[ J = \frac{1}{E_\upsilon} \frac{M^1}{B} \left( \frac{H}{H'} \right) \left( \frac{n}{n'} \right) \]  \hspace{1cm} (1)

where \( E_\upsilon \) and \( \nu \) are Young's modulus and Poisson's ratio of the steel, \( M \) is the applied moment, \( H \) the steel thickness and \( B \) the width. The definition of \( q \) and \( l \) are given in Appendix A. In Eq.1 the contribution from the epoxy is neglected as its stiffness is much lower than the steel and the glassy carbon. For this specimen crack growth is stable (Tsao et al. 1992; Sørensen 2002) and the J-integral is independent of the crack length \( a \).

Fig. 5. Schematic illustration of a DCB specimen loaded with pure bending moments. #1: glassy carbon and #2: steel.

3.2 Derivation of cohesive laws. The J-integral along a path just outside the failure process zone is (Rice 1968):

\[ J = \int_{\delta} \sigma(\delta) d\delta \]  \hspace{1cm} (2)

where \( \delta \) is the end-opening of the cohesive zone and \( \sigma \) are the cohesive stresses. Due to its path independence, the J-integral in Eq. 2 has the same value as in Eq. 1. Differentiation with respect to \( \delta \) gives (Tsao et al. 1992):

\[ \sigma(\delta') = \frac{\delta}{\delta\delta'} \]  \hspace{1cm} (3)

Thus, by recording \( J \) (function of \( M \) from Eq. 1) and the end-opening \( \delta \) simultaneously the cohesive law can be obtained from Eq. 3.

3.3 Test procedure. The loading was performed at an approximately constant rotation rate of the beams ends of the DCB specimens (Sørensen et al. 1998). The derivation of
the interface cohesive law requires the measurement of the crack opening during loading. Thus, the test fixture was placed under an optical microscope equipped with a video-recording system. A particle pattern was applied to the specimen surface prior to testing as shown in Fig. 6. The crack opening can be measured by following the displacement of a pair of particles such as 3-2 or 3-4 as shown in Fig. 6. A brief description of the method used to measure the crack opening is given in Appendix B.

Fig. 6. Particle pattern for crack opening measurements. (a) Specimen photograph prior to testing and (b) After crack initiation.

As soon as crack growth occurs the specimen is somewhat unloaded to avoid time-dependent cracking and the crack length is measured. This procedure is repeated until specimen failure. In this way fracture resistance curves could be obtained.

Fig. 7. (a) Fracture toughness values for crack initiation as a function of the current during polymerization (second step duration: 10 min). The monomers used were MAH and MDOD. (b) Fracture resistance curves for glassy carbons plasma treated with MAH at different currents and times.
Appendix D

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4. RESULTS

4.1 Cohesive law. To measure the intrinsic interface toughness (energy absorbed by the decohesion process itself) the cohesive law is measured at the notch root area (see Fig. 6). The example shown here corresponds to a plasma treatment with MAH for 3 min and current of 20 mA (the R-curve behaviour for this case is given in Fig. 7(b) with solid circles). The specimen is loaded as described in Section 3 up to point A (Fig. 7(b)). The J-integral as a function of the local end-opening is given in Fig. 8. Two different pairs of particles were used to measure δ: 1-2 and 3-4 (Fig. 6). The experimental data were fitted with an exponential and sigmoidal function.

![Fig. 8. J-integral as a function of the crack end-opening δ. The position of points 1-2 and 3-4 is shown in Fig. 6.](image)

![Fig. 9. Interface cohesive law. Points 1 and 2 used for measurement the end-opening δ.](image)

Following the procedure described in Section 3 the interface law can be obtained from Fig. 8. The results are presented in Fig. 9. Irrespective of the functions used to fit the
experimental data the peak stresses are very high and the crack opening at which the cohesive (interface) stresses vanish is less than 1 μm. This agrees well with the values (<800 nm) measured when performing the test inside the chamber on environmental scanning electron microscope.

4.2 Fracture toughness and fracture resistance curves. Fig. 7(a) shows the fracture toughness for crack initiation as a function of the current during polymerization. The polymerization time was equal to 10 min and two different monomers were used i.e. MAH and MDOR. Although there is considerable scatter in the results a trend can be seen especially for the case of MAH. There is an optimum current leading to better adhesion whereas an increase or decrease of the current results in weaker interfaces. In most cases a significant increase in fracture toughness was obtained in comparison with the case of untreated glassy carbons (fracture toughness 5-7 J/m²).

Fig. 7(b) displays the fracture resistance curves for glassy carbons plasma treated with MAH at different currents and times. A significant R-curve behaviour is observed for some interfaces (10 min - 25 mA and 3 min - 20 mA) whereas for some other treatments i.e. 10 min - 10 mA and 10 min - 30 mA do not have an R-curve type behaviour.

5. DISCUSSION

The scatter in the results presented above for fracture toughness (crack initiation) and fracture resistance curves (considerably different R-curve behaviour for the same plasma treatment from specimen to specimen) could be coming from the plasma treatment itself i.e. the plasma treated surfaces are very sensitive to contamination. Almost all experiments were terminated by the onset of unstable crack growth with specimens showing R-curve behaviour being more prone to unstable crack growth. In some cases the interface crack kinked into the glassy carbon. The instability characterized by a very high crack velocity and it is possible a visco-elastic effect of the epoxy resin (see Fig 3(b)). Pure epoxy specimens were also tested and the crack growth became unstable usually immediately after crack initiation. Similar results were reported by Du et al. (1998) who related this behaviour to stick-slip fracture instabilities commonly observed in polymers. In the DCB specimens loaded with pure moments the conditions $\Delta \mu < 0$ is always satisfied (a condition for stable crack growth for rate-independent materials). However the same condition is necessary for stick-slip fracture to occur in rate-dependent materials (Webb and Atlantis 1997a) and the form of the fracture resistance depends on the $\Delta \mu$ sign (Webb and Atlantis 1997b). The results presented here should be treated carefully as the crack growth resistance curves for the material systems tested are not only a function of the extent of crack growth but also a function of the crack tip velocity.

The peak cohesive (interface) stress was found to be very high for the example shown here. Although a simplified fitting procedure was used the peak stress should be in that range. This could also explain why sometimes the crack kinked into the glassy carbon (strength ~210 MPa according to the manufacturer) causing catastrophic failure. For the treatments giving low fracture toughness, the fracture resistance remains the
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same, whereas for the treatments giving higher fracture toughness, the fracture resistance increases with crack length (see Fig 7(b)). This suggests that for those specimens additional toughening occurs due to plasticity (Tvergaard and Hutchinson 1994). Crack growth could take still place (cohesive peak stress is much higher than the yield stress) if strain gradient effects are significant (Wei and Hutchinson 1997).

6. CONCLUSIONS

Planar plasma polymerized glassy carbon/epoxy specimens were used to study the effect of various plasma treatments on the adhesion between glassy carbon and epoxy under nominal mode I conditions. The selected material system is intended to mimic a carbon fibre/epoxy interface in composite materials. An increase in adhesion strength was found in comparison with the untreated specimens. A method to derive the interface cohesive law parameters (fracture toughness, peak stress and critical end-opening) was developed.

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REFERENCES


APPENDIX A

\[ \eta = \frac{h}{l} \]  
\[ I = \frac{1}{3} \left[ \frac{1}{\eta^3} + 3 \Delta \left( \frac{1}{\eta} - 1 \right) + \frac{2}{\eta^2} \left( \frac{1}{\eta} - 1 \right)^2 \left( \frac{1}{\eta} - 2 \right) \right] \]  
\[ \Delta = \frac{1 + 2 \psi + 3 \psi^2}{2(2 \psi + 1)} \]  
\[ \sum = \frac{E_b}{E} \frac{1-v^2}{1-v^2} \]  

APPENDIX B

A script for Image Pro software was developed to measure the distance between 2 particles as shown in Fig. 6. The position of its particle (a number of pixels) was defined as its area center. The resolution of the images was approximately 650 nm/pixel, whereas software's resolution was 1/10 of a pixel giving a final resolution of 65 nm which could be increased by using a higher magnification microscope. The main error source was defocusing during the experiments resulting in a wrong particle area calculation.
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