Stellingen behorende bij het proefschrift van J.A. Poulis

Stelling 1
Het is gewenst, alvorens de internationale temperatuurschaal van 1990 (ITS-90) te corrigeren voor de verwachte fout van ongeveer één millikelvin bij \( T = 0.65 \) kelvin, nieuwe metingen te verrichten in het temperatuur gebied tussen \( T = 0.3 \) kelvin en \( T = 2 \) kelvin.


Stelling 2
Gezien de levensduur van de huidige prothese-handschoenen (ongeveer 6 maanden) en vooral gezien hun gebruik binnenshuis, lijkt het testen van de invloed van UV-licht op het verouderingsproces onder hoge vochtigheidsgraad zinloos.


Stelling 3
Om een handprothese te realiseren met verminderd gewicht en veel bedieningsgemak, lijkt het ontwikkelen van een nieuwe kosmetische handschoen efficiënter, dan het ontwerpen van ingewikkelde compensatie mechanismen die het slechte mechanische gedrag van de huidige handschoenen moeten compenseren.

Stelling 4
De sociale vernieuwing heeft het daklozenprobleem vergroot.

Stelling 5
De bewering van fabrikanten dat meting van de concentratie van ATP geschikt is om micro-biologische verontreiniging te detecteren wordt niet gestaafd door de recente resultaten van J.A. vd Gugten - Poulis.

Stelling 6
De combinatie van ATP-Bioluminescentie en Urine stick lijkt de meest snelle en betrouwbare methode om de microbiologische verontreiniging van oppervlakken te bepalen.

*Int. Journal of Food Microbiology, (in press).*
Stelling 7
De relatie luchtvochtigheid heeft niet allen invloed op de hechting van lijmen aan een oppervlak, doch ook op capacitieve positionerings metingen.

Stelling 8
Lijminformatie dient gestandariseerd te worden.

Stelling 9
'Het verdrag van Straatsburg' dat televisie- en radiouitzendingen vanaf schepen of vliegtuigen voor de Nederlandse kust verbiedt, lijkt in tegenstelling tot wat gepropageerd werd, slechts geratificeerd om de greep van de regerende politieke partijen op de media te versterken.

Stelling 10
De brede maatschappelijke hang naar een schoner leefmilieu in Nederland is strijdig met het nog steeds groeiend aantal personenauto's.

Stelling 11
Nederland is meer gebaat met een "Derdewereldplicht" dan met de militaire dienstplicht.

Stelling 12
Het verdient aanbeveling om langs de drukke Griekse kustwegen, (als tussen de steden Kavála en Alexandroupoli), voorzieningen te treffen die het leven van de vele overstekende landschildpadden (Testudo Hermanni) kunnen redden.
Small Cylindrical Adhesive Bonds

Hans Poulis
CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Poulis, Hans
Small cylindrical adhesive bonds / Hans Poulis. - Delft:
Delft University of Technology, Faculty of Mechanical
Engineering and Marine Technology. - Ill.
Thesis Technische Universiteit Delft. - With ref.
ISBN 90-370-0082-7
Subject headings: UV/ozone cleaning / finite element analysis / agresssive environment.

Faculteit der Werktuigbouwkunde en Maritieme Techniek,
Technische Universiteit Delft,
Mekelweg 2,
2628 CD Delft,
Holland.

Gebruik of toepassing van de gegevens, methoden en/of resultaten enz., welke in dit rapport voorkomen
geschiedt geheel op eigen risico.

Any use or application of data, methods and/or results etc., occurring in this report will be at the user’s own risk.

2
Small Cylindrical Adhesive Bonds

Proefschrift

Ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. drs. P.A. Schenck,
in het openbaar te verdedigen ten overstaan van een commissie
aangewezen door het College van Dekanen
op dinsdag 18 mei 1993 te 16.00 uur
door

Johannes Aaldert Poulis,
geboren op 04-04-1959 te Leiden,
doctorandus in de wiskunde en natuurwetenschappen.
Dit proefschrift is goedgekeurd door de promotor:

Prof. ir J.C. Cool.
## Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>7</td>
</tr>
<tr>
<td>2. Adhesive selection</td>
<td>13</td>
</tr>
<tr>
<td>Three adhesives are selected for use during the experiments</td>
<td></td>
</tr>
<tr>
<td>3. Cleaning</td>
<td>37</td>
</tr>
<tr>
<td>Soap/water, Gas plasma and UV/ozone cleaning</td>
<td></td>
</tr>
<tr>
<td>4. Factors affecting the adhesion</td>
<td>63</td>
</tr>
<tr>
<td>Voids, heat treatment, relative humidity during bonding, surface exposure time</td>
<td></td>
</tr>
<tr>
<td>5. Design parameters</td>
<td>89</td>
</tr>
<tr>
<td>Optimum bond design using finite element analysis</td>
<td></td>
</tr>
<tr>
<td>6. Environmental effects</td>
<td>113</td>
</tr>
<tr>
<td>Influence of sweat and humidity on the adhesive bond strength</td>
<td></td>
</tr>
<tr>
<td>7. Summary</td>
<td>125</td>
</tr>
<tr>
<td>Appendices</td>
<td>129</td>
</tr>
</tbody>
</table>
Cover: A three dimensional impression of the researched adhesive bond
Chapter 1.

Introduction

1.1 Scope of the thesis

During the last few years, problems have arisen with regard to the adhesive bonding of very small cylindrical parts. The surface of these bonds was about 10 mm² or less (Fig 1.1). They were designed in order to make progress in a miniaturization process aimed at the construction of smaller and lighter orthoses as well as prostheses [7 - 9]. Other fastening methods (e.g. screw threads, soldering or shrink fits) were found to be disadvantageous compared with an adhesive bond, due to the very small dimensions and small tolerances of the parts. For example, some electro-pneumatic constructions with volumes of about 3 cm³ could contain as much as 50 separate parts which made the milling /turning of complicated forms a painstaking task, and the use of adhesive bonds seemed to bring solution.

![Adhesive](image)

*Figure 1.1 A cross section of the basic cylindrical adhesive joint used during the experiments.*

But the originally constructed adhesive bonds were found to be unreliable; for reasons unknown, the bond would break, sometimes so already in the first test cycle despite the fact that the bonded-surfaces were heavily oversized. Strangely enough, identical bonds would sometimes hold indefinitely. The aim of this thesis is to analyze and optimise the entire process of bonding, from bare metal up to the final use of small cylindrical bonds, and to determine the influence of the bonding parameters on the final adhesive bond strength. The surface morphology of the metal (stainless steel) and the adhesives selected (Chapter 2) are taken as a basis for the investigations and
Introduction

will be kept unchanged. The aim is to design a practical and basic guidance for engineers in order to optimise the design and facilitate the production of small cylindrical adhesive bonds with a minimum number of production steps, but in such a way, that the results are as reproducible as possible [16]. The suggestions with regard to an optimal bond strength and performance are based on a large number of experimental values as well as on finite element analyses which will be presented in the following chapters.

1.2 History of adhesives and adhesive bonds

In several museums in the world, wooden parts bonded together and dating back to 4000 B. Chr. and even earlier are to be found. The Egyptians already used some kind of starch in their preparation of papyrus. In the Middle Ages, there were several kinds of glue that were based on the cooking of a wide variety of animal remains. They were used for e.g.: book binding, the manufacturing of horse saddles and hats [10, 11, 12]. But professional adhesive bonding of metal parts has taken place only for the last few decades [13]. One of the reasons is that in later centuries metal parts could easily be soldered or welded. Adhesive bonding first became an interesting option in the mass production of airplanes around the time of World War 2. The first adhesively bonded metal structures had two different applications. In the first place, the viscous rubber vulcanized part functioned as a vibration damper. And secondly (almost at the same time) De Bruyne discovered that heated synthetic ‘joiner’s glue’ could be used to bond metals in the construction of airplanes. Right after the end of World War 2, the bonding of metal parts was applied by the Havilland aircraft company based on the work by De Bruyne.

In 1946, the Swiss company Ciba A.G. published the first article on the subject of epoxies as adhesives. This adhesive 'family' has been growing ever since. Epoxies are available both as cold and warm polymerizing liquids. What is typical of these adhesives is their high tensile strength (20 - 30 N/mm²) and good durability. A range of other adhesive families have been developed since then, such as polyurethanes and acrylics. As a result of
improvements of their performance, they are now able to compete with the epoxies (as will be explained in chapter 2) [1, 2].

1.3 Adhesives and mechanical fasteners

The basic advantages of using adhesives instead of the better known fastening techniques like set screws, pins, brazing, welding, press fits and shrink fits are generally known. This is particularly the case in the simplification of several fine-mechanical constructions. For this reason the use of adhesives in production processes has increased in recent years. The more so because of the increasing need for the accurate positioning of parts in production processes (e.g. the assembly of optical, electric and computer components [3, 14, 15]), and in view of the demand for lower manufacturing costs and an increased production rate (due to reduced tolerances). The most important advantages of using adhesives are listed below [4, 5, 6]:
- Reduction in weight as a result of a simplified construction (and often lesser parts).
- Reducing in space: simpler and/or smaller constructions are possible.
- New constructive possibilities which allow more accurate positioning.
- Cheaper assembly possibilities as a result of decreased tolerances on machined parts e.g. slip fits can replace press fits
- Good electric insulating properties.
- No extra retaining-parts are needed.
- Protective sealing against liquids and gasses
- Improved corrosion resistance (no metal-metal contacts)
- Enhanced structural appearance as protrusions punctures, and attachments are eliminated.
- Reduced manufacturing costs as a result of increased production speed.
- Parts that are very different chemically (e.g. plastics and metals) can be bonded.
- In case of a well designed adhesive bond, peak stresses as found in materials
bonded by rivets or pins are strongly reduced
- Higher flexibility and damping.

1.4 The adhesion process stepwise

From the selection of adhesive and the design of the bond up to the cured adhesive bond, five separate steps can be distinguished. A small change in one of the process variables may have a great influence on the final bond strength (or on its durability). For this reason, only one variable is allowed to change at the time. The five principal steps of the process are listed in Table 1.1 in relation to their variables. Basically, some of these variables should appear in more than one row, but for the sake of clarity they are mentioned only once.

\textit{Table 1.1 The adhesion process divided into five steps and related to the process variables.}\n
<table>
<thead>
<tr>
<th>Steps of process</th>
<th>Related variables</th>
</tr>
</thead>
</table>
| A search for the right adhesive and its intrinsic properties | * chemical nature  
* viscosity  
* pot life (see Chapter 2.) |
| Pre-adhesive application                              | * kind of adherents  
* design of the bond gap  
* method of adhesive application  
* surface treatment like cleaning, roughening  
* adhesive mixing (expelling of voids) |
| The adhesive application                              | * application pressure/time  
* relative humidity  
* creation of voids |
| Hardening of the adhesive                             | * curing temperature/pressure  
* curing time |
| The practical use or testing of the final bond strength | * impact/shear strength  
* temperature shock resistance  
* moisture resistance |
1.5 Limitations of adhesive bonds

It will be clear that the decision to use an adhesive bond instead of mechanical fasteners requires a basic knowledge of the physical and chemical processes involved. The process of adhesive bonding is influenced by a complex whole of interrelated variables playing a part before, during, and after the bonding process. Therefore its use requires a basic knowledge of the bonded surfaces (oxide layers, surface roughness), cleaning methods and adhesive viscosity in relation to the creation of voids and the design of the bond gap. Furthermore, knowledge of the characteristics of the performance of many kinds of adhesives is needed in order to choose the best one for the desired effect. This selection however, is made difficult and time-consuming by the fact that there are so many variations in the adhesive formulations and characteristics that are available. Experiments are often essential in choosing the right adhesive. This implies a time consuming study before the adhesive bond can finally be used in a production process. The most important practical disadvantages of the use of adhesives are
- Intensive cleaning of the bonded surfaces is often inevitable.
- The hardening of the adhesive may be time consuming. The optimal bond strength is obtained at least several hours later.
- It is necessary to keep all the physical and chemical process variables unchanged during the adhesion process
- There is especially an upper temperature limitation in the practical use of the bond.
- Possibilities of adhesive application are limited.
- The long term behaviour of the adhesive bond (if critically used) can be uncertain (due to elastic/plastic behaviour).
- The bond is sensitive to moisture.
- The stiffness of the construction can be reduced.
- The bond cannot be disassembled.
Introduction

References

7 M. de Boo, Wilmer ontwikkelt techniek om mensen een handje te helpen, Delft Integraal, maart 1989, pp 13-17.
Chapter 2

Adhesive selection

2.1 Definitions

2.1.1 Adhesion and Cohesion

An adhesive bond is constructed of two (metal) parts called adherents (or substrates) connected by an adhesive. In its basic form the adhesive bond very much resembles to a sandwich structure, compound of five distinctive parallel parts as can be seen in Fig. 2.1. Mechanically, this structure implies that (like in a chain) the strength of the whole (chain) will be as strong as its weakest part.

In connection with the above, two important terms have to be defined: cohesion and adhesion. Cohesion is defined as the forces between molecules in one and the same material, while adhesion is defined as the force between the molecules of two different materials. In the above example and the following, the force acting across the interface (between adherent and adhesive) is called: the adhesion [1, 82].

![Diagram of adhesive bond](image)

**Figure 2.1** A schematic representation of an adhesive bond and mechanical interlocking: metal-interface-adhesive-interface-metal.
2.1.2 Interface

The interface of the adhesive bond is the region in which a step gradient in the local properties is found. This may very well be a gradient in the intrinsic properties, such as the chemical composition or the molecular structure. In general, there will be a gradient across the interface of physical quantities such as the elastic modulus, thermal expansion coefficient, Poisson’s ratio, etc.

A necessary condition to obtain the optimum strength of an adhesive bond is based on an optimal contact between adhesive and adherent across the interface. Such an intimate contact requires a very clean surface [87, 88, 89]. Another condition is a mechanically stable thus crack-free adherent’s upper layer (or boundary zone).

The interface between the adhesive and its (metal) adherent’s counterpart is an important link in the final quality of the adhesive bond. This view will be the basis of all experiments described and carried out [2, 3, 76, 79, 81, 84].

2.2 Theories of adhesion

There is a lot of disagreement with regard to the basic reason for the adhesion between different materials. Roughly speaking, four major mechanisms of adhesion between a metal surface and an adhesive generally accepted:

- mechanical interlocking theory,
- electronic theory,
- adsorption theory,
- diffusion theory,

which will be briefly reviewed now [48, 49, 4, 5, 6, 70, 71, 85].

2.2.1 Mechanical interlocking theory

According to this theory, the adhesive interlocks with the irregularities or pores of the substrate (Fig. 2.1) thus increasing the bond strength of the adhesive bond. However, the adherent’s surface topography can, of course,
vary from ink-pot to pyramids or flat surfaces. Many authors demonstrate that increased surface roughness leads to an increase in the strength of the adhesive bond (which possibly also occurred at the used acrylic adhesives). Such an observation might indeed arise from increased mechanical interlocking at the interface.

But the surface pores can also function as collectors of dust and moisture that is difficult to remove. Besides, when a highly viscous adhesive is used, the rate of the wetting of the substrate will be slow, which often results in incomplete penetration of the adherent’s surface pores. Consequently, small voids are left on the interface and these might act as stress raisers thus reducing the durability of the bond to a value which may be lower when compared with a defect-free surface (Chapter 4) [6, 7, 8, 45, 80, 83, 92].

2.2.2 Electronic theory

If the adhesive and substrate have different physical and chemical properties, it is likely that some electron transfer will take place at the moment they make contact. The result can be imagined as a capacitor which is charged. This potential difference actually means that a double layer of electrical charge is formed at the interface and the electrostatic force resulting from this potential difference resists their separation [6, 9].

2.2.3 Adsorption theory

The adsorption theory of adhesion is the most generally applicable theory of adhesion and has been extensively discussed in literature [e.g. 6]. This theory proposes that -provided that sufficiently intimate intermolecular contact is achieved at the interface- the materials will adhere because of the surface forces acting between the atoms at the two surfaces. They are divided (in a somewhat arbitrary way) into primary and secondary bonds according to their relative bond strength (Table 2.1).

The primary bonds (Fig. 2.2) or chemisorption can be divided into ionic, covalent, and metallic bonds. Ionic binding arises when two atoms attract each other due to a difference in electrostatic charges. Covalent binding is a
state in which electrons are shared by two atoms and localised between them.

Table 2.1 The types of physical attractive forces that might play a role in the adhesion process, together with their typical bond energies.

<table>
<thead>
<tr>
<th>Type</th>
<th>Bond energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary bonds</strong></td>
<td></td>
</tr>
<tr>
<td>Ionic</td>
<td>590 - 1050</td>
</tr>
<tr>
<td>covalent</td>
<td>63 - 710</td>
</tr>
<tr>
<td>metallic</td>
<td>113 - 347</td>
</tr>
<tr>
<td><strong>Secondary bonds</strong></td>
<td></td>
</tr>
<tr>
<td>Hydrogen bonds</td>
<td>10 - 30</td>
</tr>
<tr>
<td><strong>Van der Waals bonds</strong></td>
<td></td>
</tr>
<tr>
<td>permanent dipole - dipole</td>
<td>10 - 42</td>
</tr>
<tr>
<td>dipole - induced dipole</td>
<td>4 - 21</td>
</tr>
<tr>
<td>London dispersion forces</td>
<td>0.08 - 42</td>
</tr>
</tbody>
</table>

![Ionic, Covalent, Metallic](image)

**Figure 2.2** Above: three simplified models of atomic binding. The inner circle represents the atomic centre, the outer circle the outer electron core and the black dots the electrons. The lower graphs show the principle of dipole-dipole interactions and hydrogen bonds.

16
Metallic binding is defined as a common share of electrons by the outer atom cores. Polymers are usually composed of covalently bonded C, H, O, N, S, etc atoms [25, 37].

Hydrogen bonds and the more common Van der Waals bonds are regarded as secondary bonds. Hydrogen bonds are characterised by the attractive forces which arise due to the existence of two different and unequal atomic cores and a small cloud of electrons. This kind of binding only exist between non-metals (like hydrogen and oxygen atoms) and is often only a special case of dipole-dipole interaction [41, 50, 86].

Van der Waals forces are divided into permanent dipole-dipole interaction, dipole-induced dipole interactions and London dispersion forces. This last interaction exists in materials without permanent dipoles moments, but possesses induced dipole-induced dipole interactions which results from the fact that the electrons in the molecules are in motion. The intermolecular forces are listed together with their energies in Table 2.1. It clearly shows the high electrostatic forces related to ionic bonds [6, 42].

2.2.4 Diffusion theory

This theory states that intrinsic adhesion of adhesive and substrate (both polymers) takes place by the mutual diffusion of polymer molecules across the interface. But because of the fact that the bonding discussed here takes place between steel (adherent) and a polymer (adhesive) this theory is not applicable and thus will not be discussed further [6].

2.2.5 Concluding remarks

It is evident that depending on the circumstances any of the three mechanisms of adhesion can be responsible for the intrinsic adhesion which enables an adhesive bond to resist separation under the application of a load. But whichever mechanism is responsible, thorough cleaning of the substrate surface is always a necessary condition. A lot of research has been carried out into the cleaning of the substrates and the adhesive bond strength. In Chapter 3 some relations will be shown between several cleaning methods
and their influence on the initial and the long-term behaviour of the bond strength [13, 14, 15, 16, 47].

![Normal stress](image1)

![Shear stress](image2)

![Cleavage stress](image3)

![Peel stress](image4)

**Figure 2.3** The four basically different types of loads that can be applied on an adhesive bond: (a) normal, (b) shear, (c) cleavage, and (d) peel forces.

### 2.3 Selecting the adhesive

Many factors have to be considered in selecting the adhesive that is best suited for a desired application. It has been explained before (Chapter 1) that design of the bond is a complex matter because of the interdependence of many (sometimes conflicting) properties. Selecting an adhesive only on the basis of its strength and durability characteristics can therefore lead to an improper choice.

Environmental resistance of the adhesive bond includes moisture resistance (especially at more elevated temperatures), to salt water, acids, and chemical solutions, but also biological inertness (particularly to fungi and bacteria). Some properties can be of importance for the design of the adhesive bond, like circumstances discussed in Chapter 1 its environmental resistance when used in prostheses or orthoses. However, most of the adhesive properties on comparable subjects found in literature (or data-sheets) are difficult to compare, because of the variety of test adherents, cleaning and measurement methods (often not mentioned). The design of a durable adhesive construction is not only the choice of the "right" adhesive, but a combined action of the selection of the adhesive, the cleaning of the substrate and an optimal construction, curing, application, etc (see also Chapters 3 and 5). The
Chapter 2

adhesive bond can be loaded by different forces (Fig. 2.3) which induce their stresses in the adhesive layer. Tensile (or direct) stresses for example, are exerted perpendicularly to the plane of the bond, while shear stress develops parallel to the substrates. Peel and cleavage stresses confine load contractions to small areas, and adhesive bonds subjected to these last two stresses are generally more prone to failure. Due to the fact that the modulus of elasticity (E) of adhesives is generally a factor 200 smaller than that of stainless steel, the stiffness of an adhesively bonded construction will largely be determined by the adhesive used. A more brittle adhesive will on the one hand increase the construction's stiffness, but on the other hand reduce it's service life due to increased stress peaks (Chapter 5).

The magnitude and the type of load on the bond further narrow the search for a suitable adhesive. Study of data sheets and literature demonstrated that most adhesives show their best performance under shear load, while only a few are well resistant to impact (or pulsed), peel or cleavage stresses. This means that in the design the peel and cleavage stresses in the adhesive layer of the final construction should be minimised. In the specific small cylindrical constructions as mentioned in chapter one, the load is largely restricted to shear stress [17, 18, 19, 78].

2.3.1 Primary selection criteria

This paragraph will describe the three most important criteria (sometimes called 'functional' or 'product criteria' in industrial environments) by which the three adhesives that have been used in the experiments are chosen. On the basis of the selection criteria described below [e.g 51- 60, 74, 75] two adhesive 'families' have been selected. Furthermore, several data sheets that were easily available have been studied [61- 67, 89, 90]. The three most important selection criteria out of a large number of sometimes conflicting or interrelated ones will be discussed below:
- the kind of adherent,
- environmental resistance,
- the shear and impact strength.
2.3.1.1 The adherent

The primary criterium in choosing the adhesive depends on the adherent(s) used: metal or plastic. In the prosthesis application mentioned above (Chapter 1), the adherent’s parts are constructed of 304 stainless steel. A classification which suits especially steel to steel bonding is made from a wide range of adhesives. This narrows the range of candidate adhesives considerably.

2.3.1.2 Environmental resistance

A good resistance to salt spray and weak acid solutions is necessary, because of the use that is made of the bond inside silicon hand gloves. Inside these closed (and water impermeable) gloves, there is often an aggressive atmosphere. This might cause an accelerated degradation of the interface and a weakening of the polymer. Years of practical experience in the maintenance of prostheses indicate that the atmosphere inside a glove is essentially a mixture of sweat, waste water, sand and dust. And due to the high humidity level of this internal ‘climate’ this often results in a growth of bacteria. A climate test has been developed to simulate this aggressive atmosphere (Chapter 6). Thus the second major selection criterium is the environmental resistance of the adhesive against moisture and salt water. Together with the aim of the investigations to use a minimum number of production steps, this criterium leads to the choice not to use a primer and makes several adhesive families like urethanes, less suitable for the final purpose.

2.3.1.3 Shear and impact strength

The third criterium by which the search for the most suitable adhesive is further narrowed, is the kind of stress to which the adhesive layer will be exposed. The most important stresses in the bond’s final use are: shear and impact (or pulsed) stresses.
2.3.2 Secondary selection criteria

Although the criteria mentioned above are indispensable for the selection of an adhesive, secondary criteria (or sometimes called 'process criteria' in industrial environments) have to be considered:
- the stiffness of the adhesive,
- the choice between a one or two part adhesive,
- the temperature range during application and use,
- the relation between viscosity and temperature,
- the relation between voids, viscosity and temperature,
- pot life,
- shelf life,
- toxicology,
- availability.

2.3.2.1 The stiffness adhesive of the adhesive

The results presented in Chapter 5 will show that the elasticity (defined by the E-modulus) of the adhesive is an important parameter when the stiffness and stresses in the construction of the adhesive bond are being considered. Generally, a brittle adhesive will be suited for use in a stiff construction. But on the other hand, a more flexible adhesive is often better resistant to pulsed loading. Therefore, it is of great importance that a new generation of adhesives with additives such as microscopic rubber particles has been developed [38 -40]. These toughened adhesives are strong and very well resistant to mechanical shocks. An example of two characteristic adhesive stress strain curves are shown in Fig 2.4 [37, 43, 44].

2.3.2.2 One or two part adhesives

A choice will have to be made between a one or two part adhesive. The first aspect to this choice is the difference in their characteristics. A two component adhesive presents more difficulties in use, like the determination of the weight of the two components before mixing them.
Adhesive selection

Another problem which arises during mixing is the possible creation of voids which might have a negative effect on the final bond strength, particularly on the small surfaces considered here (Chapter 4). For these reasons a two part adhesive clearly has some disadvantages for the use discussed.

![Graph](image)

Figure 2.4 Typical stress/strain characteristics of two toughened adhesives. A: a toughened one-part epoxy with a clearly delineated elastic limit (o). The second is a toughened acrylic for which the limit of the elastic zone is not clearly defined. Both adhesives fail at (*). The E-modulus of adhesive 'A' (E_A) is clearly higher, which indicates a higher brittleness.

2.3.2.3 Temperature range (application and use)

The temperature range of the adhesive constructions for the prostheses application considered here, lies in a range between -15°C and +35°C. This will meet most of the ordinary adhesive specifications. However, a restriction of temperature is needed during application and curing. Due to the presence of rubber O-rings and the small tolerances of the adherent's, the allowed temperature is restricted to a maximum of 80°C.

2.3.2.4 Viscosity and temperature.

Temperature influences the viscosity of the non cured adhesive. The higher the temperature, the lower its viscosity. The adhesive temperature is an
important factor in determining the adhesive’s pot life (see below). A higher temperature implies a faster curing (polymerising) of the adhesive and as such shortens the adhesive pot life. Regarding the construction of the substrate (Fig 2.5) medium viscous (around 1500 to 2000 mPa.s) adhesives will be suitable for the final purpose.

![Diagram](image)

*Figure 2.5 The investigated substrate with: d rod's diameter, W-d gap width, D cylinder diameter and h overlap length.*

### 2.3.2.5 Voids, viscosity and temperature

In view of the form of the bond gap and its dimensions:
- $1.00 \text{ mm} \leq \text{rod diameter } d \leq 3.00 \text{ mm}$
- $0.05 \text{ mm} \leq \text{adhesive gap width } W-d \leq 0.10 \text{ mm}$
- $0.05 \leq \text{overlap length } l \leq 3.00 \text{ mm}$

it is clear that the filling of such a blind, narrow and shallow gap is a difficult and painstaking task. There are clearly links between this filling problem and the adherent’s viscosity (Chapter 4). A low-viscous adhesive will easily fill the gap between two adherents with a low risk of creating voids, in contrast to a high-viscous one. Especially micro-voids, created at the irregularities (pores) on the adhesive/ adherent interface are filled more easily when a low-viscous one is used. It will take more energy to press a high viscous adhesive into the gap through the narrow supply tubes as used in the final design (Fig. 2.5). An increase in temperature during application will result into a reduced viscosity, but at the same time decreases the pot
Adhesive selection

life. Heating just the applied adhesive might solve this problem [77].

2.3.2.6 Pot life

In the case of a two part epoxy the pot life (processing time) is determined by the time between the mixing of the two components and the allowed application to the adherents. A short pot life implicates that the work will have to be done quickly, or imposes a restriction of the number of substrates that can be bonded within the same time span.

2.3.2.7 Shelf life

The shelf life of the adhesive is a less important aspect of the determination of the most suitable adhesive. All pre-selected adhesives keep their qualities (if stored cool) for at least 6 months up to a year.

2.3.2.8 Toxicology

With regard to the selection of a range of adhesives suitable for the final task, toxicology is found to play a minor role. All preselected adhesives were found to be unaggressive and not dangerous when handled in a normal way. However, standard precautions such as wearing hand gloves and safety glasses should be taken. The processing (i.e. mixing) of larger amounts of adhesive should be carried out in a fume cupboard [72].

2.3.3.9 Availability

As stated before, there is a large number of different adhesives but not all of them can easily be obtained. During the selection of an adhesive, one should make sure that the availability will not present any problem.
2.4 Types of adhesives

A selection of three adhesives from two adhesive ‘families’; the acrylics and epoxies which roughly possess the requirements mentioned above, are selected for further investigations, and will be briefly reviewed below.

2.4.1 Acrylics

The acrylics are the family of structural adhesives based upon acrylic resins; it includes a wide range of different acrylic resins and hardening reactions. One of the major advantages of modern acrylics is their improved tolerance to adhere to oily (metal) surfaces. They get this tolerance through added bonding agents in the primer or in the adhesive itself, which have the ability to penetrate through, or react with the surface contaminants. Some acrylics are sensitive to moisture [6]. Both cyanoacrylates and anaerobics (see below) belong to this wide range of acrylic adhesives.

2.4.1.1 Cyanoacrylates

These adhesives are true single component adhesives. The hardening reaction is initiated by alkaline surfaces (water vapour present on the surface is often sufficient to initiate the cure). The very low viscous cyanoacrylate polymer is able to form strong and durable bonds to almost any material because of its low viscosity and thus its good penetration of the pores of the adherent. The speed of curing is affected by the humidity, the nature and the condition of the surfaces and the film thickness or gap between the parts. The typical fixing time for close-fitting surfaces (0.05 mm gap width) at 20°C is about 5 minutes for 20% of the full strength. General limitations in the practical use of cyanoacrylates are the durability and application of their bond (because of their high curing speed the application is limited to small surfaces). Particularly exposing the cured adhesive to conditions of high humidity (at elevated temperatures >70°C) may cause bond failure. Cured cyanoacrylate bonds generally offer a limited resistance to impact and peel stresses. The hazard of rapid curing is that human skin can easily be bonded within a
fraction of a minute, precautions (eyes !) should therefore be taken when one is working with these adhesives [6].

2.4.1.2 Anaerobics

One of the acrylics is the so called anaerobic. This adhesive was first introduced in 1953 by the American chemist Dr. Vernon Kriebel. Since then an enormous growth in its performance and use has taken place. Basically, they consist of a wide range of different acrylic resins. They are in fluid form under atmospheric conditions but solidify when ambient air (oxygen) is expelled. These one-part adhesives are known as real mechanical jammers and are often used as a thread locking sealant or as fasteners in co-axial bonds by which the catalytic base influence of a metal initiates a polymerisation reaction. Anaerobics are available in several viscosities. Anaerobics are often used in thread-locking machinery assembly, other typical applications include the holding in place of locking keys and the sealing of bearings on shafts. In general, their moisture resistance is good [6, 73].

2.4.2 Epoxies

Epoxies come in many different forms and are available as liquid pastes, films, tapes, micro encapsulates and powders. They can be formulated for many individual characteristics such as different viscosities, high shear strength, good peel and impact strength, heat resistance, or high durability. In general they show outstanding characteristics, and compared to all other adhesives they are usually rigid, excellent gap fillers and protect against galvanic corrosion. Epoxies can be cured with or without heat, although most epoxies require a final heat cure of minimal 80°C to obtain their optimum strength. During the curing process they display only little shrinkage and do not emit volatiles. To obtain an optimal bond strength, the substrate parts should be thoroughly cleaned and dry [6, 20, 21].
# Adhesive selection

**Table 2.2** The three chosen adhesives and their properties [22, 23, 24].

<table>
<thead>
<tr>
<th>Properties/Adhesive</th>
<th>Epoxy: AW136/HY991</th>
<th>Anaerobic: Loctite 638</th>
<th>Cyano acrylate Black Max 380</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cure: Heat required?</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Two part</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Pot life</td>
<td>55-70 minutes at 25°C</td>
<td>5 minutes</td>
<td>2 - 3 minutes</td>
</tr>
<tr>
<td>Full cure</td>
<td>24 hours at 23°C 3 hours at 40°C</td>
<td>3 - 6 at 23°C</td>
<td>120 hours 23°C</td>
</tr>
<tr>
<td>Heat cure</td>
<td>For optimal strength: 1 hour at 80°C</td>
<td>20-50% higher strength with 24 hours at 85°C</td>
<td>For optimal strength: 1 hour at 80°C</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>20000-30000 at 25°C</td>
<td>2500</td>
<td>250</td>
</tr>
<tr>
<td>Shelf life</td>
<td>12 months</td>
<td>12 months</td>
<td>6 months (20°C)</td>
</tr>
<tr>
<td>Toxoid</td>
<td>moderate</td>
<td>Low</td>
<td>low if liquid, none if cured</td>
</tr>
<tr>
<td>Flammability (.C)</td>
<td>150 and 170</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Elasticity (N/mm²)</td>
<td>about 3000</td>
<td>about 5420</td>
<td>about 4960</td>
</tr>
<tr>
<td>Peel strength (N/mm)</td>
<td>Generally good</td>
<td>Generally good</td>
<td>5 on mild steel</td>
</tr>
<tr>
<td>impact strength (N/m)</td>
<td>Excellent</td>
<td>Good</td>
<td>excellent very high flexibility</td>
</tr>
<tr>
<td>Tensile shear strength (N/mm²)</td>
<td>20 (on R.V.S)</td>
<td>30 (static)</td>
<td>22 at grid-blasted steel</td>
</tr>
<tr>
<td>Oily substrate bonding:</td>
<td>Poor</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>Temperature range (°C)</td>
<td>-60 - &gt; +80</td>
<td>-55 - &gt; +120</td>
<td>-55 - &gt; +105</td>
</tr>
<tr>
<td>Acid solutions</td>
<td>Good</td>
<td>(generally good)</td>
<td>Good</td>
</tr>
<tr>
<td>Moisture resistance</td>
<td>excellent even at 90°C, and sea-water</td>
<td>Good</td>
<td>Good to very good</td>
</tr>
<tr>
<td>Gap limitation (mm)</td>
<td>0.05 - &gt; 0.10</td>
<td>&lt;0.25</td>
<td>0.05 - &gt; 0.1</td>
</tr>
</tbody>
</table>
2.5 Selected adhesives

Based upon the selection criteria mentioned above, the most suitable adhesive 'families' have been selected, and after a rough pre-selection three adhesives:
- A two part thermoplastic epoxy; HY991/AW136,
- Anaerobic; Loctite 638,
- Cyanoacrylate; Black Max 380,
have been chosen for use in the rest of the research program. The main properties of these adhesives are listed in Table 2.2. This does not necessarily mean that it is impossible to find adhesives with comparable characteristics. But for the said use in prostheses, the adhesives selected seemed to be a good choice for several reasons, which will be discussed below.

The two part epoxy has been chosen because of its excellent general characteristics such as a high shear strength, a very good impact strength, and what is more, an outstanding environmental resistance. Its viscosity (20000 - 30000 mPa.s) as well as its pot life (± 1 hour) are found to be very suitable for this purpose.

The selected anaerobic possesses a very good shear and impact strength together with reputedly excellent environmental properties such as moisture resistance. It had already proved to be very practical in mounting small cylindrical parts, with the practical advantage that a liberally dosed amount of adhesive can be easily removed after the enclosed adhesive has hardened. Its viscosity (2500 mPa.s) is moderate, which is found to be very practical.

Loctite 638 is a high strength retaining sealant which prevents corrosion. It is an adhesive with a very good shear (20 - 30 N/mm²) and impact strength particularly suitable for cylindrical bonds for dynamic use (like car gears). The cyanoacrylate Black Max 380 is a high performance modified ethyl cyanoacrylate, filled with an initially soluble rubber additive. This additive phase separates during the polymerization reaction creating small rubber particles with diameters of about a micron. This increases the toughness of the adhesive improving its resistance to extreme shock pulses (very good impact strength). Technical data sheets claim a flexibility that is ten times higher then other fast curing adhesives. A typical application of this adhesive is the bonding of loudspeaker parts. The manufacturer claims outstanding environmental resistance like when it is used in the adhesive sealing of
electronic underground switching boxes with surrounding corrosive soil acids. But high stresses at a high level of humidity has a negative effect on its physical properties.

2.6 Experiments

The most important experiments described in this thesis are listed in Table 2.3, and some will be discussed in more detail below. This choice of experiments has been based upon extensive study of literature a selection of which has already been mentioned above. The carrying out of their experiments required the construction of several instruments. For this reason a computer controlled tensile force testing machine [Appendix 1], an excentricity measuring instrument (Chapter 6), a climate room (Chapter 4) and sweat-test set up (Chapter 6) had to be designed and built. It has been proved that an optimal contact between polymer (adhesive) and metal (adherent) is the basis for good adhesion. For this reason, intensive cleaning of the adherent was expected to make a large contribution to the final bond strength (chapter 3). Most well known industrial methods of metal cleaning were found to be insufficiently reproducible for these experiments. Acid or base cleaning solutions which come in numerous different compositions are often used. They oxidize the surface pollution, activate and sometimes roughen the surface. In this way, different surface morphologies and roughnesses can be achieved. But again the problem of reproducibility arises because there are a lot of process variables involved. When such a method is used only occasionally in a workshop, this might very well influence the quality of the final product. And then the waste problem and the precautions are not even taken into account. Therefore research has been done to find a reliable, safe, cheap and easy-to-use cleaning method. Two advanced methods (UV/ozone and plasma cleaning) have been tested. Their influence on the -long term- bond strength has been compared by experiments. Research has been done into the UV/ozone cleaning method, to gain a better insight of the most important physical properties during this process. The experiments as well as the devices that were developed are described and discussed in Chapter 3. The durability of the adhesive bond is found to be influenced by environmental
Adhesive selection

loads such as moisture at elevated temperatures, and salt water (Chapter 6). The cured adhesive should possess appropriate mechanical properties (e.g. stiffness) and therefore adhesive bonds are often given a (short) heat treatment at 80°C. Tests will show that this might influence the -long term- bond strength (Chapter 4). Serious problems may arise when small voids are enclosed in the adhesive layer. They will generally make a minor contribution to the adhesive bond strength in case of large areas, but they are there in a small adhesive bond their contribution to the bond strength becomes detectable (Chapter 4).

Theoretical analysis by means of finite element analysis will support the experimental results. In particular with regard to several substrate dimensions, voids content, and eccentricity. The analyses are used in predicting the optimum stress (Chapter 6) distribution at different substrate dimensions and shapes. But also the influence of imperfections created by voids and eccentricity will be calculated. All these results will be compared with experimental values.

Table 2.3 The factors that are considered to be important during the adhesion process and which are experimentally investigated.

<table>
<thead>
<tr>
<th>The influence on bond strength of:</th>
<th>Experimentally investigated by:</th>
</tr>
</thead>
<tbody>
<tr>
<td>intrinsic adhesive parameters</td>
<td>* several curing tracks</td>
</tr>
<tr>
<td></td>
<td>* test of three adhesives</td>
</tr>
<tr>
<td>several cleaning methods and their influence on the long term behaviour of the bond strength</td>
<td>* no cleaning at all</td>
</tr>
<tr>
<td></td>
<td>* only a soap solution</td>
</tr>
<tr>
<td></td>
<td>* gas plasma cleaning</td>
</tr>
<tr>
<td></td>
<td>* UV/ozone cleaning</td>
</tr>
<tr>
<td>relative humidity during bonding</td>
<td>* bonding at high (95%), or low (≤5%) relative humidity</td>
</tr>
<tr>
<td>High humidity</td>
<td>* 0, 4,8 months: 95% RH/40°C</td>
</tr>
<tr>
<td></td>
<td>* salt spray tests/ temperature shocks</td>
</tr>
<tr>
<td>surface exposure time (SET)</td>
<td>*controlled environment</td>
</tr>
<tr>
<td>voids</td>
<td>* experimental tests</td>
</tr>
<tr>
<td></td>
<td>* finite element analysis</td>
</tr>
<tr>
<td>substrate dimensions</td>
<td>* several adhesive gap widths, overlap lengths, rod diameters</td>
</tr>
<tr>
<td></td>
<td>* finite element analysis</td>
</tr>
<tr>
<td>excentricity</td>
<td>* computer controlled measurements and finite element analysis</td>
</tr>
<tr>
<td></td>
<td>* relating the excentricity to the measured adhesive bond strength</td>
</tr>
</tbody>
</table>
2.7 Accuracy of the measured bond strength

The production of a reproducible adhesive bond strength is a complex matter embracing many factors, such as the accuracy with which the cylindrical parts have been manufactured. Figure 2.5 shows the substrate, with the drilled hole of the cylinder with a diameter accuracy of -0.00 / +0.04 mm, a surface roughness 1.6 ≤ Ra ≤ 3.0 and an overlap length: h ± 0.05 mm. The accuracy of the rod diameter (φ) is -0.01 ≤ φ ≤ +0.00 mm. Other quantities that influence the reproducibility of the adhesive bond strength are the accuracy of cleaning and the possibility of voids inclusion. This makes the measuring of the adhesive bond strength to a painstaking task. But intrinsic quantities are always involved, such as the time dependent behaviour (creep, stress relaxation, damping, and hysteresis) of adhesives. Structural defects in the adhesive bond might lead to an accelerated physical ageing which weakens the bond strength [25].

The physical and chemical quantities mentioned above are supposed to be responsible for the final bond strength for a greater or lesser degree. But they are often interrelated and as such it’s difficult to measure them separately. A small change in a quantity supposed to be constant may cause a larger influence onto the adhesive bond strength than the change that is supposed to be measured. For this reason it is difficult to compare the results of different workers in detail as it is likely that there are substantial differences in the experimental conditions [More reading on these subjects; 26-36].

References

1 J.Schweers, P.van Vianen, natuurkunde op corpusculaire grondslag, deel 1, 4e druk, ISBW 90-208-0991-1, pp 45-46.
5 E.H.P. Lochtenberg, J.J.G. Smits, Lijmen: theorie en toepassing, de constructeur,
Adhesive selection

22 Locitite data sheet nr. 5011, Viba, postbus 441, 2700 AK Zoetermeer, Holland.
34 A.J. Kinloch, *The science of adhesion*, part 1, Journ. of materials science 15,
Adhesive selection

61 Anonymous, Technical data sheet, Denka International b.v., Hanzeweg 1, 3771 Ng Barneveld, Holland: Uniloc for; anerobic/U.V.-curing/toughened acrylic/cyanoacrylate adhesives.
64 Anonymous, Laagland B.V. Postbus 9443, 3007 AK Rotterdam, Holland.
68 Anonymous, Ciba Geigy BV, Arnhem, P.O. Box 241, Arnhem, Holland.
79 D.E. Packham, *The adhesion of polymers to metals*, School of materials science, Univ. of Bath, Claverton Down, Bath BA2 7AY, UK.
Chapter 2

90  Anonymous, Henkel BV, Brugwal 11, 3432 NZ, Nieuwegein, Holland.
91  Anonymous, Stokvis Tapes en lijmen, P.O Box 4190, 2980 GD Ridderkerk, Holland.
Adhesive selection
Chapter 3

Cleaning

3.1 Introduction

Optimal adhesive bonding necessitates good and reproducible cleaning [1, 2, 3, 24, 32]. A cleaning method based on the interaction of UV-light and ozone gas has been developed and used. The UV-ozone cleaning method has been compared with gas plasma cleaning, soap cleaning and uncleaned samples. The cleaning efficiency is characterized by spectroscopic data, contact angle and tensile force measurements. The (short and long term) influence of these cleaning methods on the adhesive bond strength has also been experimentally tested and will be discussed. The aim of this part of the research program was to obtain an optimal adhesive strength and high reproducibility of small pin in hole cylindrical bonds as shown in Fig. 3.1.

![Adhesive](image)

Figure 3.1 A schematic drawing of the cylindrical stainless steel adhesive test-joint consisting of a rod (ϕ 2mm) and a cylinder. The small adhesive supply lines are also shown. During the experiments this object was used to test the adhesive strength.

3.2 The pre-cleaning process

The cleaning process is aimed at the removal of unwanted anorganic and
organic materials on the adherent’s surface (Fig.3.2) in order to obtain a reproducible purity [25]. The entire cleaning procedure consists of two successive cleaning processes: a pre-cleaning (or bulk-cleaning) followed by a final cleaning procedure such as UV/ozone or gas plasma cleaning [App. 2].

The major part of the organic and anorganic materials is removed by the bulk cleaning and it is only the very last layers of contamination that have to be removed during the final cleaning processes. The pre-cleaning process consists of five successive steps: soap cleaning [29], tap water washing, acid rinsing, tap water washing and distilled water washing.

Some preliminary experiments were performed in order to test several ordinary soap solutions, but no significant difference in their cleaning performance was found. An industrial type of liquid soap has been chosen for use in further experiments. The solution consists of a dilution of 2 vol.% of RBS 50 [4] concentrate in distilled water. Most of the oil and grease stuck onto the substrate’s surface is removed during this first cleaning step. The soap pre-cleaning takes place with continuous stirring and at a controlled temperature (40°C).

The substrates are removed from the soap solution after the liquid has cooled down to about 25°C in order to prevent a soap film from sticking onto their surfaces what would occur when the film of warm water quickly vaporises. In the second part of the pre-cleaning process the soap solution is washed away with running tap water during 15 minutes.

The last traces of soap are neutralized by placing the substrates in a 5 vol% acetic acid solution during two minutes. This weak acid solution is intensively stirred in order to provide an optimal contact between the solution and the substrates. In the next step, the acid solution is washed away with running tap water during 15 minutes.

Inorganic contaminants such as dust and salts cannot be removed by the UV/ozone cleaning procedure and should be removed during the pre-cleaning stage. Therefore, as a last cleaning step, the substrates are washed with double distilled (60mS) water, to remove inorganic materials such as salts which might still be on the surface after the fourth cleaning step.

It was experimentally found that all these cleaning steps should be performed in this order and within the given time-span in order to get the best reproducible adhesive bonding results.

38
3.3 UV/ozone cleaning

It has been known for some time that ultraviolet light to decompose organic molecules. But it is only during the past decade that the UV/ozone cleaning of surfaces has been explored [5, 6]. Sometimes the method is used in the production of integrated circuits to serve as a viable technique to keep materials clean following final processing [7, 31]. Since 1976 the use and application of diverse UV/ozone instruments has steadily increased (particularly in systems for the purification of drink/waste water, air sterilisation, clothes cleaning) [8, 9, 10, 37]. However, no articles have been found on the subject of UV/ozone cleaning as a surface treatment prior to adhesive bonding.

3.3.1 Instrument

The basic construction of the UV/ozone cleaning instrument that has been designed and built is shown in Fig. 3.3. It consists essentially of an aluminium cabinet with a folding door at the front side. The cubic content of the instrument is approximately 1.5 litres. Inside the cabinet, a lift table determines the distance of the substrate (A) with in relation to the UV tubes [26]. Possible types of UV sources are deuterium or xenon lamps. The shortest wavelength (184.9 nm) needed in the cleaning process is emitted
only by quartz enclosed fluorescent tubes. In this case the UV-light is obtained from two 4 Watt low pressure mercury UV-tubes (B) mounted in top of the cabinet. In this way, an uniform light intensity has been realised on the substrate level. On the back of the cleaning instrument there are connections for the oxygen gas input (D) and the ozone exhaust (E).

![Diagram](image_url)

**Figure 3.3** The schematic drawing of the UV/ozone cleaning box, with: (A) sample, (B) UV-source, (C) aluminium box, (D) the oxygen inlet, (E) exhaust.

### 3.3.2 The UV/ozone cleaning process

The high oxidation reactivity of ozone and the destructive effect of the UV-light is very effective in the removing of certain trace levels of organic material such as: human skin oils, cutting oil, mechanical vacuum pump oil, acid solder flux, cleaning solvent residues including acetone, ethanol, methanol and several others [27]. The cleaning rate depends on:

- the amount, kind and nature of surface contamination.
- the intensity of the UV source.
- the distance between the UV-source and the substrate.
- The reflectors used above the UV-source.
- The ozone concentration.
- presence of other inert gasses that function as a catalyst in the formation of ozone via the equation: \( \text{O}_2 + \text{O} + M \rightarrow \text{O}_3 + \text{M} \) (for which M is an inert body) [11].

40
Chapter 3

- the pressure of oxygen supply.
- the temperature of the substrate.

Particularly the combination of the two transmitted wavelengths 184.9 (which is responsible for the creation of ozone) and 253.7 nm of a quartz UV-source and ozone gas is found to be responsible for the effectiveness in the cleaning of the organic contaminated surfaces. Leaving out either the ozone or the UV-light components would reduce the cleaning rate as is illustrated in Table 3.1.

**Table 3.1** Exposure types vs. cleaning times using a separate ozone (O₃) generator [36] by J.R. Vig et al [16]

<table>
<thead>
<tr>
<th>Exposure type</th>
<th>Cleaning time</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Black light&quot; (&gt;300nm)</td>
<td>No cleaning</td>
</tr>
<tr>
<td>O₃, no UV</td>
<td>10 hours</td>
</tr>
<tr>
<td>253,7 nm, no O₃</td>
<td>1 hours</td>
</tr>
<tr>
<td>253,7 nm + O₃</td>
<td>90 seconds</td>
</tr>
<tr>
<td>253,7 nm + 184.9nm + O₃</td>
<td>20 seconds</td>
</tr>
</tbody>
</table>

The experimental results of J.R. Vig which are reprinted in Table 3.1 show that an extra dose of applied ozone gas gives a shorter cleaning time of the samples used. However, ozone has a broad absorption band centred at about 260 nm. At 253.7 nm the absorption coefficient is 130 cm⁻¹atm⁻¹. The intensity (I) of the 253.7 nm radiation reaching the sample therefore decreases from the source intensity (I₀) as

\[ I = I₀e^{-130pd} \]

where (p) is the average ozone pressure between the sample and the UV source in atmospheres at 0 °C, and (d) the distance between the sample and source in centimetres. This relation is in line with both the experimental results of J.R Vig [16], and some short experimental (unpublished) results found by the author. This means that in order to maximize the cleaning rate, the samples should be placed as close to the UV source as is possible at a
high ozone concentration.

3.3.3 Short chemical explanation

At high cleaning rates two wavelengths from the lower part of the UV light spectrum are of special importance (Fig. 3.4);
- 184.9 nm: This wavelength generates ozone and atomic oxygen out of oxygen gas. It is able to break contaminant molecular bonds.
- 253.7 nm: This wavelength is easily absorbed in the single (C-C) bonds of complex hydrocarbons, and used for the excitation and dissociation of these organic contaminant molecules on the substrate’s surface. The contaminant molecules and free radicals produced by this dissociation react together with the oxygen atoms through a series of complex photochemical reactions. But they can also react with other reactive free radicals (and the very reactive hydroxyl ion OH) produced during the process. The volatile molecules created, such as water and carbon dioxide will leave the process.

![Diagram](image)

Figure 3.4 A simplified model of the UV/ozone cleaning mechanism. The long molecular organic chains are broken into pieces by the UV-light, and ozone is both composed as well as decomposed during the exposure to ultraviolet light.

Oxygen gas has a high absorption peak at 184.9 nm. Ozone gas (O₃) can be created by exposing oxygen to this wavelength. Ozone gas is produced in a
two step endothermic photochemical process initiated by the photolysis of ambient oxygen ground state molecules at 184.9 nm. This causes the oxygen molecule to dissociate into two ground state atoms O(3P). These atoms might again react with oxygen to ozone (Fig. 3.5).

The destruction of ozone during the photolysis process takes place in two quite distinct stages. A very fast process (less than 50 µsec) followed by various slow processes lasting for many milliseconds. The direct result of this decomposition of ozone gas by the UV-source is the formation of atomic oxygen, a very strong oxidizing agent. Note that two kinds of oxygen are produced during this process; O(3P) and O(1D). These atomic oxygen atoms are partly responsible for the cleaning process. One of these oxygen atoms can be detached relatively easily due to its chemical structure. Nascent oxygen is one of the reaction products, which makes ozone practically the strongest oxidizing agent.

Ozone can also take part in inorganic reactions. This behaviour follows from its high redox potential (+2.07 Volt), exceeded only by that of gaseous fluorine (+2.85 Volt). It oxidizes metals (except gold, platinum and iridium) to their highest oxidation states, sulphide to sulphates, carbon to carbon dioxide, and ammonia into either the gas, dry or liquid state. In the majority of oxidation reactions ozone is reduced to molecular oxygen releasing only one oxygen atom [12, 13, 14].

![Diagram of ozone formation and destruction]

**Figure 3.5** A more detailed description of the way in which ozone is formed and destroyed during the UV/ozone cleaning process.
3.3.4 Oxygen input and ozone creation

The combination of ozone and 253.7 and 184.9 nm is known as the most practical for fast and efficient UV/ozone cleaning not in the least because of the high oxidation rate of ozone. Therefore its concentration during the cleaning process is expected to be important. Several experiments were carried out to investigate the effect that an increased concentration of ozone has on the cleaning rate.

In a first set of experiments the relation between the input of (medical) oxygen gas and the creation of ozone was measured. The ozone gas concentration created by the UV-lamps was measured by an ozone analyzer [15], but exceeded the maximum measurable value of 100 ppm and had to be diluted. In order to obtain a lower concentration of ozone at the input of the analyzer, the analyzed gas from the cleaning box had to be mixed with laboratory air, assuming no reaction would take place between the laboratory air and the ozone.

In Fig. 3.6 the experimental set up is shown; three glass flow meters (F1..F3) were used to measure the volume streams of the different gasses. The medical oxygen gas introduced into the cleaning box is measured by the F3 flow meter. The tubes transporting the highly diluted ozone gas are made of teflon. Every 10 seconds a volume of the mix of laboratory air and ozone gas from the cleaning instrument set by the F1 and F2 flow meters is sucked into the ozone analyzer. The experimental results were are shown in Figure 3.7. In view of these results with respectively one and two UV-tubes, at measuring times of 15 and 30 minutes, the following concluding remarks can be made:

- An increase in the concentration of oxygen gas leads to an increasing concentration of ozone gas dependent on the source intensity.
- An equilibrium ozone concentration arises in the case of constant introduction of oxygen gas.
- This equilibrium is reached faster in case of inputs of lower oxygen gas and a lower source power.
Figure 3.6 The experimental set up by which the concentration of oxygen during the UV/ozone cleaning process was controlled. The ozone concentration was diluted before it reached the ozone analyzer.

Figure 3.7 The influence of the UV-intensity and input of oxygen gas on the ozone gas concentration.
3.3.5 Temperature and cleaning rate

Experiments by other researchers like Vig et al [27] showed an increased cleaning rate at high temperatures. In order to have an indication of the temperature rise of the used substrates during cleaning, measurements were executed by an electronic sensor. This sensor was put on the lift (Fig. 3.3), exactly on the place of the substrate. The temperature was measured both with an oxygen input of 0.6 l/h oxygen, as well as without any input of oxygen. The experimental results reproduced in Figure 3.8 show that the temperature is largely determined by the heat of radiation of the UV/tubes and that is only slightly influenced by the oxygen flow.

![Figure 3.8 The change of temperature of the samples during the cleaning process, with and without oxygen input.](image)

3.4 Contact angle

Wetting can quantitatively be defined by the angle produced by a liquid drop in equilibrium on a (horizontal) solid surface [App. 6]. The surface tension is defined by Young’s equation which relates these terms to the equilibrium contact angle alpha (α). The measuring of the contact angle with water on a flat metal surface gives a good quantitative indication of the presence of (non-polar) organic surface contamination. The more contamination, the
larger the contact angle as is shown in Figure 3.9. Therefore, measured contact angles of substrates that have been cleaned in a reproducible way by means of different cleaning methods, will indicate the ultimate purity that can be obtained by each separate method [30]. This means that the contamination of the substrate can be related to the value of the contact angle. During all described experiments, double distilled water has been used as indicating liquid.

\[ \text{Heavily contaminated surface:} \]

\[ \text{Clean surface:} \]

\[ \text{Water} \]
\[ \text{Grease} \]
\[ \text{Metal} \]
\[ \alpha \]
\[ \text{Init. strength poor} \]
\[ \text{Durability poor} \]
\[ \text{a smaller} \]

\[ \text{Init. strength poor} \]
\[ \text{Durability poor} \]
\[ \text{a very small} \]

*Figure 3.9* The influence of the surface purity on the contact angle ($\alpha$). The cleaner the surface, the smaller the contact angle.

### 3.4.1 Cleaning method and contact angle

Several experiments have been carried out in order to investigate the relations between cleaning method, contact angle and adhesive strength. The contact angle has been measured after several (sometimes combined) cleaning steps [16, 17, 18].

These steps are schematically represented in Fig. 3.10. Flat (coin-like) 6 cm$^2$ 3µm diamond polished 304 stainless steel substrates were contaminated in a reproducible way by dipping them into stainless steel drilling oil [28]. First they were cleaned by means of tissue before the other processes of bulk-cleaning were carried out. Successive measurements of the contact angle were performed (represented in Figure 3.10 by "TEST"). The indicated pre-cleaning by means of soap and water included all five cleaning steps described in § 3.2.
3.5. Ozone concentration and cleaning rate

During the next set of experiments the cleaning rate in the UV/ozone box was measured using laboratory air. The measured data are drawn as crosses in Fig. 3.11. During a second set of experiments the cleaning rate was measured with an oxygen input of 0.6 litres/hour, its cleaning effect is presented by squares in Fig. 3.11. A slightly increased cleaning velocity as a result of the increased concentration of oxygen is observable.

The UV/ozone cleaning process functions only efficiently if both ozone gas and UV-light are present; however no upper limit of the ozone concentration or the UV-intensity and neither a relation between both with respect to the cleaning speed was found during various unpublished experiments. This observation indicates, that the ozone concentration is still a limiting factor in the cleaning rate. Thus the artificial increase of its concentration (e.g. by using an ozonizer) is expected to have a positive effect on the cleaning rate at a constant source intensity. This conclusion can also be drawn from Table 3.1 in which case a more powerful UV-source was used as in the here described experiments.
Figure 3.11 The effect of an increased concentration of oxygen gas on the cleaning speed.

3.6 UV/ozone cleaning inside blind holes

The UV/ozone cleaning effect is found to be an exponentially decreasing function of the distance between the UV-source and substrate (§ 3.3.2). Experiments have been carried out in order to determine the UV/ozone cleaning inside the cylinder shown in Fig. 3.1. As will be described below, a relation has been found between the cleaning effect of the UV source inside a blind hole on the one hand and both the hole diameter (1 to 3 mm) and depth (up to 10 mm) on the other. As it is impossible to measure contact angles inside a blind hole, a substrate as shown in Fig. 3.12 was designed and constructed. Instead of drilled holes, this two-part stainless steel substrate had milled grooves of different width and was composed of two identical counter pieces screwed together before cleaning and not taken apart until after the final cleaning stage in order to measure the contact angles ($\alpha$). Both parts were marked on top, and were always accurately positioned.

At the start of each pre-cleaning phase, the entire substrate was placed on the bottom of a cleaning dish, and the small holes were filled with water in order to replace the enclosed air. During the whole cleaning procedure (including pre-cleaning and principal UV/ozone cleaning) the marks were kept on top. Figure 3.13 shows the state of purity of the four notches by means of contact angle measurements after no cleaning had taken place. It can be clearly seen
that all measured contact angles are comparable and always far over 60 degrees. The values of the contact angles in the front, middle, and back of the grooves are randomly divided, and so is their variance. Knowing that the contact angle of soap cleaned samples can be as small as about 30° (§ 3.7.1) this means that the cleaning inside groves is clearly disturbed.

Now, when we compare Figure 3.13 which shows the contact angles of the uncleansed sample with Figure 3.14 after a pre-cleaning and successive UV/ozone cleaning time of 75 minutes with the UV tubes placed only 5 mm over the substrate holes, a different picture arises. The random situation of Figure 3.13 is changed into a situation that clearly shows the influence the opening diameter and hole-depth have on the cleaning. The reduced cleaning as a function of the diameter and depth of the groove can be explained in view of the knowledge that the investigated surfaces are mounted perpendicularly to the UV source. The cleaning speed as presented in the formula of § 3.3.2 should be multiplied by a factor cosθ (Lambert’s law of illumination) for which (θ) is the angle enclosed between the light beam and the normal of the surface. The cleaning effect as such dependents on the opening surface of the groove surfaces directed towards the light source (Fig. 3.15). A smaller diaphragm means that the groove’s surface is hit by fewer rays of UV-light, and that the penetration of this blind hole is reduced [19]. As a prove, the contact angle α has been drawn in Fig. 3.16 as a function of the proportion of the depth and diameter of the grooves: (l/d). This reveals clearly the highest cleaning effect at the upper exposed surface of the largest groove diameter, but the optimal cleaning effect (α = 8°) was not derived.

Figure 3.12 The substrate used to measure the cleaning of UV/Ozone inside small blind holes as a function of diameter and penetration depth. The top-marks are shown on the right sides.
Figure 3.13  The measured contact angle (α) inside 'blind' holes as a function of diameter and penetration depth. After no cleaning has taken place, the contact angles are all found to be comparatively large and random.

Figure 3.14  The measured contact angle (α) inside 'blind' holes after an additional cleaning with UV/ozone as a function of groove diameter and penetration depth.
Cleaning

Figure 3.15 The cleaning of vertically mounted surfaces is largely determined by the angle (θ) that the illuminating beams make with the normal of the surface. The smaller this angle, the higher the cleaning rate. So the larger the diaphragm of the blind hole (the drawing on the right), the deeper and more intense the illumination of the inside surface and thus the more intense the UV-cleaning.

Figure 3.16 The cleaning mechanism of UV-light inside blind holes is clearly dependent on the proportion of groove depth and its diafragma.
3.7 Several cleaning methods compared

![Cleaning Method Graph]

*Figure 3.17* The cleaning effect of several cleaning methods on stainless steel determined by contact angle measurements. The variance of the presented values is about ± 5%.

3.7.1 Contact angle and XPS

It is expected that there will be an inverse relation between the thickness of a layer of organic pollution on a metal sample on the one hand and the measured contact angle (α) of water on the other. Therefore, several contact angle measurements were done.

The contact angle of a drop of water on a flat 6 cm² 3μm diamond-polished 304 stainless steel sample was determined after each separate cleaning method had been used. The points shown in Figure 3.17 are the averaged values from at least 40 independent measurements. It is clearly visible that the contact angle (α) decreases when the sample purity increases. The measurements lead to the conclusion that UV/Ozone and plasma cleaning give the best cleaning results. In order to validate this conclusion substrate purities by UV/ozone and plasma cleaning have been investigated. The contact angle measurements executed only indicate the overall purity of the examined surface. With X-ray photon spectroscopy (XPS) the contaminating elements have been analyzed accurately.

Analyses by means of X-ray photon spectroscopy (XPS) [App. 5] have been
of soap stuck onto the substrate’s surface (identified by the Si\textsuperscript{2s}, Si\textsuperscript{2p}, Al\textsuperscript{2p} peaks) are better or even completely removed during the plasma cleaning (such as the Al\textsuperscript{2p} peak).

The peak intensity of several atoms of the stainless steel alloy (like Mo and Ni) becomes greater after the plasma cleaning (not included in Table 3.2). It looks as if the bombardment of (heavily) ionised atoms during the plasma cleaning has stripped off a surface (oxide)layer of the substrate.

From the XPS-measurements is concluded that the cleaning effects of UV/ozone and Plasma cleaning differ, even though not indicated by the contact angle measurements. The influence of the purity difference obtained by the two cleaning methods on adhesion is discussed in the next section.

Table 3.2 A comparison between UV/ozone cleaning and gas plasma cleaning on an atomic scale. It shows the relative decrease of several atomic elements to a soap cleaned stainless steel surface by means of the XPS measuring technique.

<table>
<thead>
<tr>
<th></th>
<th>UV/ozone</th>
<th>Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsuperscript{1s}</td>
<td>-0.6</td>
<td>-1.8</td>
</tr>
<tr>
<td>Si\textsuperscript{2s}</td>
<td>-0.2</td>
<td>-0.7</td>
</tr>
<tr>
<td>Zn\textsuperscript{2s} / P\textsuperscript{3p}</td>
<td>-0.1</td>
<td>-0.2</td>
</tr>
<tr>
<td>Al\textsuperscript{2s}</td>
<td>-1.4</td>
<td>-1.2</td>
</tr>
<tr>
<td>Si\textsuperscript{3p}</td>
<td>-0.3</td>
<td>-1.1</td>
</tr>
<tr>
<td>Fe\textsuperscript{2s} Zn\textsuperscript{3p}</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
<tr>
<td>Al\textsuperscript{3p}</td>
<td>-1.8</td>
<td>-5.6</td>
</tr>
<tr>
<td>Fe\textsuperscript{3p}</td>
<td>-0.3</td>
<td>-0.1</td>
</tr>
<tr>
<td>Cr\textsuperscript{3p}</td>
<td>0.0</td>
<td>0.6</td>
</tr>
<tr>
<td>O\textsuperscript{2s}</td>
<td>-0.3</td>
<td>-0.6</td>
</tr>
<tr>
<td>Zn\textsuperscript{3d}</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
</tbody>
</table>
Figure 3.18 Four cleaning methods and their effect on the adhesive bond strength.

3.7.2 Cleaning and adhesive strength

In this thesis substrate purity is found to be important by its influence on adhesive forces. For this reason the adhesive strength of small cylindrical substrates was measured as a function of four cleaning methods. The results are presented in Fig. 3.18 and Table 3.3. Several sets of cylindrical structures (rod diameter 2.0 mm, gap width 0.05 mm, overlap length 1.5 mm) made of 304 stainless steel were bonded with an anaerobic adhesive (Loctite 638). A release agent was applied to the bottom of the rods. After a pre-drying period of 12 hours at room temperature, they were subjected to a heat treatment of 2 hours at 80°C in order to increase the polymerisation (and thus the brittleness) of the adhesive. Each value presented in Figure 3.18 is found by averaging the adhesive forces of a set of 23 destructively tested parts. Again both UV/ozone and plasma cleaned surfaces produce the best (as well as comparable) results. They are in line with those of the first 2 rows of Table 3.3, which shows the percentage of adhesive stripped off the surface of the rod. This removed amount of adhesive was determined after destructive testing at the three cleaning stadia. The rod with the smallest of the two bonded stainless steel surfaces was found to be the most sensitive part of the cylindrical bond (see also Chapter 5). The more intense the cleaning, the higher the adhesive bond strength, and thus the more adhesive
Cleaning

was left on the rod's surface after the destructive test. Besides, the correspondence with Fig. 3.17, which shows the contact angle (α) as a function of the cleaning method is striking. This means that the adhesive strength clearly increases when the purity of the surface becomes greater.

Table 3.3 The percentage of adhesive failure on the rod after 0, 4 and 8 months of exposure to an aggressive environment. The values shown, are the visually estimated averaged values of adhesive stripped off the rod's surface after the tensile force test.

<table>
<thead>
<tr>
<th></th>
<th>0 months</th>
<th>4 months</th>
<th>8 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncleaned</td>
<td>95%</td>
<td>97.5%</td>
<td>100%</td>
</tr>
<tr>
<td>Water/Soap</td>
<td>75%</td>
<td>95%</td>
<td>90%</td>
</tr>
<tr>
<td>UV/Ozone</td>
<td>65%</td>
<td>90%</td>
<td>85%</td>
</tr>
<tr>
<td>Gas-Plasma</td>
<td>65%</td>
<td>85%</td>
<td>85%</td>
</tr>
</tbody>
</table>

3.8 Cleaning and humidity

In the foregoing the adhesive strength was determined immediately after bonding. But evidently often the adhesive strength after years of service life is of importance. For this reason, the adhesive strength of many cylindrical bonds was determined as a function of time when the substrates were exposed to a climate of high humidity. Because thorough cleaning was found to be important (see above) only three cleaning methods were tested. The parts (rod diameter 2 mm, gap width 0.05 mm, overlap length 1.5 mm) were bonded with Loctite 638 and their sensitivity to an aggressive environment of 90% relative humidity at a temperature of 40°C in a climate cabinet was determined.

The results of the measurements are presented in Figures 3.19A to 3.19C and in Table 3.3. They show that the adhesively bonded substrates that were uncleaned (Fig. 3.19C) display a weaker bond strength than those that were cleaned by means of the UV/ozone and plasma cleaning methods (Figures 3.19A and 3.19B). A general trend in the presented results is the decreasing long term bond adhesive bond strength. And again, the less thorough the
cleaning (compare Fig. 3.18), the higher the risk of failure of the bond. An unexpected effect is shown by the curves representing the adhesive strength of substrates that were cleaned by means of the UV/ozone and plasma cleaning substrates. The UV/ozone cleaned surfaces keep their adhesive strength much longer than those that were plasma cleaned. This contrasts with what would be expected on the basis of results obtained earlier from contact angle measurements. UV/ozone cleaning possibly affects (activates) the surface of the stainless steel in such a way that an interface is created which is more resistant to aggressive climates. When the results of the XPS experiments (§3.7.1) and the climate tests are compared the conclusion can be drawn that the measuring of the surface purity alone does not deliver enough information to predict the durability of an adhesive bond [21, 22]. For some organic/inorganic traces left on the stainless steel surface may improve the adhesive strength, as was observed in the case of described bonds in a humid environment.

Figure 3.19 A

Figure 3.19 B
Figure 3.19 A, B, C. The influence of an aggressive climate (40°C and 90% R.H.) on the adhesive bond strength of respectively UV/ozone-cleaned, plasma-cleaned, and uncleaned cylindrical joints, measured after 0, 4, and 8 months of exposure.

3.9 Cleaning speed of UV/ozone and gas plasma

Good cleaning is essential for high adhesive bond strength, however, like in all industrial activities the process time is important. Therefore, the purity (measured by the contact angle $\alpha$) of the flat diamond polished stainless steel substrates described above was determined as a function of the cleaning time, both by UV/ozone and plasma cleaning (Fig. 3.20). Every point is the average based on at least 20 measurements with a variance of $\pm 5\%$, which clearly shows that the time to achieve the ultimate cleaning, which corresponds with a contact angle of 8 degrees, differs by a factor five in favour of plasma cleaning. However, two comments have to be made: 
- the time that is needed to obtain the vacuum used during the process of plasma cleaning is not shown, as it mainly depends upon the vacuum system used and the potential voltage.
- the cleaning rate of the UV/ozone process can be increased by using a higher UV intensity, by reducing the distance between substrate and UV tubes, or by using inert gasses that will function as catalysts during the cleaning process.
In this chapter the UV/ozone cleaning process is shown to be a very useful and easy to use alternative to high quality stainless steel bonding preparation. UV/ozone cleaning proves to be comparable to the plasma cleaning, and superior to all other researched cleaning methods investigated in humid environments.

In Table 3.4 plasma and UV/ozone cleaning are compared. UV/ozone cleaning has proved to be a cheap, safe, and environmentally-friendly alternative to many laboratory and industrial cleaning processes and has been found to be useful at continuous as well as batch processes prior to coating [23]. A very simple alternative with only 20% reduced bond strength performance is soap cleaning.

It is generally accepted that material cleaning has a great influence on the adhesive bond strength. The relation between contact angle and adhesive strength on stainless steel was found to be only partially true. It has been proved experimentally, that the surface purity expressed by the contact angle more generally corresponds only to the initial adhesive bond strength. In contrast to UV/ozone cleaning, the high level of purity achieved by plasma cleaning in the long run does not benefit the high strength of the bonding in humid environments.

Most samples of the experiments described in this thesis have been carried
Cleaning

out by using plasma cleaning as a final cleaning method. This contrasts with what one should have expected on the basis of the experimental results described above. However, due to the low power UV-tubes used, the cleaning time is relatively long, and therefore unpractical.

Table 3.4 A more general comparison between the two best cleaning methods: gas plasma and UV/ozone cleaning.

<table>
<thead>
<tr>
<th></th>
<th>Gas plasma</th>
<th>UV/Ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial adhesive strength</td>
<td>Comparable</td>
<td></td>
</tr>
<tr>
<td>Contact angle</td>
<td>Comparable</td>
<td></td>
</tr>
<tr>
<td>Cleaning rate</td>
<td>Relatively fast, but total time span largely dependent on the time required to reach the vacuum</td>
<td>Comparable to gas plasma cleaning or faster, dependent on the power of the UV-tubes</td>
</tr>
<tr>
<td>Substrate’s form and material</td>
<td>Cleaning inside blind holes [34, 35]</td>
<td>Partially suitable for flat surfaces</td>
</tr>
<tr>
<td>Long term adhesive bond strength</td>
<td>Reasonable</td>
<td>Very good</td>
</tr>
<tr>
<td>Operation</td>
<td></td>
<td>Extremely simple: on/off</td>
</tr>
<tr>
<td>Initial investment</td>
<td></td>
<td>Low compared to plasma cleaning</td>
</tr>
</tbody>
</table>

References

4. RBS 50, Hicol postbus 1525, 3260 BA, Oud-Beijerland, Holland.
Chapter 3

13 H. Okabe, J.Wiley, Photochemistry of small molecules.
15 Ozone analyser model 8810, Monitor Labs, Envisco, Postbus 8, 2380 AA, Zoeterwoude, Holland.
26 Philips, Low pressure mercury lamp HUV5, lamps for special purposes, Philips Eindhoven, Holland.
28 Optima 172 drilling oil: Steenkist-Rooymans, Hurkestri 1/a, Eindhoven, Holland, DIN-Data Sheet: Firma Optima, Gmbh, 4800 Bielefeld 16, Germany.
30 M. Levine, Wettability of surface treated metals and the effect on lap shear adhesion, Adhesives Age, June 1964, pp 24-29.
Chapter 4

Factors affecting the adhesion

4.1 Introduction

A well known phenomenon in the science of adhesive bonding is the unpredictability of the final bond strength. A possible explanation may be the existence of singularities such as gas bubbles or voids. Voids are assumed to reduce the (long- and short-term) bond strength. For this reason, investigations have been carried out to trace their origins and experiments were executed in order to minimize their number and volume in the final adhesive layer. The presence of voids in the adhesive layer will be exposed from two points of view: voids created during the mixing of the adhesive and those created during its application.

The influence of voids on the stress distribution is supported by the finite element analysis of voids-resembling singularities (§ 4.2.2). It will be shown that the standard deviation of the destructively measured adhesive force can be reduced by removing voids out of the adhesive, as well as by improving the methods of the adhesive application [1].

Four different methods of adhesive application will be discussed together with experimental results. An instrument that reduces the number of intermediate steps before the adhesive application and which reduces the concentration of voids during mixing has been developed and tested (§ 4.3). The design of the basic form of the substrate shape (Fig 4.1 A) used in this thesis will be discussed and backed up by experiments (§ 4.4).

The general approach adopted in this section is to consider the adhesion from the point of view of imperfections, tracing the possible origins of (short- and long-term) reduced bond strength and increased standard deviation induced by chemical and/or physical changes of the adhesive or adherent. Besides the influence of voids on the adhesive bond strength, several other bonding parameters have been investigated, such as:

- a heat treatment (§ 4.5),
- the relative humidity (R.H.) during bonding (§ 4.6),
- the Surface Exposure Time (S.E.T., § 4.7),
- a combination of R.H., S.E.T. and cleaning on the quality of the bond.
Factors affecting the adhesion

![Diagram showing Adhesive layers in A and B]

*Figure 4.1 From A to B: the basic form of the substrate (A) is optimised to (B) in order to improve the adhesive’s gap-filling properties.*

### 4.2.1 Voids and adhesive bond strength

There is often a discrepancy between the calculated adhesive bond strength and the bond strength that is experimentally measured. Sometimes this can (partly) be attributed to adhesive defects such as voids [39, 18]. The uniformity of the adhesive film spreading on the adherent surface can have a significant effect on the final strength of the bond. Enclosed voids can act as stress raisers when the bond is loaded. This might cause rupture at stresses far below the expected bond strength particularly on the small areas involved where the effect of a relatively small void is expected to have a large influence [4, 5].

When the adhesive cannot penetrate into the adherent’s pores during the bonding process (Fig 4.2) small voids will be left on the interface and will decrease the net adhesive surface. They might also act as stress raisers, thus reducing the strength of the bond [6]. It has been calculated that this phenomena can reduce the adhesive bond strength to a value that is clearly lower than a defect-free interface [7]. A 30% decrease in the peel strength has been reported after comparison with defect-free surfaces [8]. These postulations predicting a reduced bond strength as a result of singularities in the adhesive layer (such as voids) are based upon Griffith’s crack theory [9] of 1910. This theory was reformulated by Irwin [10, 11] in 1948 and
proposed the term 'fracture mechanics'. It has only recently been applied to adhesive fractures [6].

(IN)COMPLETE WETTING:

![Diagram of incomplete (A) and complete (B) wetting of a solid by a fluid adhesive.]

*Figure 4.2 A visual simplification of incomplete (A), and complete (B) wetting of a solid by a fluid adhesive.*

### 4.2.2 Finite element analyses (F.E.A)

In order to investigate the stress effects that voids have on the small areas involved, two finite element models have been designed and analyzed. These models were based upon a small cylindrical adhesive bond (Fig. 4.1B) with the following dimensions: rod diameter: 2.0 mm, overlap length: 1.50 mm and gap width: 0.20 mm. One of the models contained three 'voids' with a diameter of 0.05 mm, located respectively in the middle, and at a distance of 0.01 mm from the top and bottom of the adhesive layer. These 'voids' are interpreted by the F.E.A-program as three horizontal air containing tubes (resembling the presence of a 'ring of voids'). Figure 4.3 shows the results of the finite element analyses of the axially symmetric models loaded by the rod, and grounded by the bottom of the cylinder. The lower graph shows the Von Misses stresses of the 'perfect' model on the inner and outer radius of the adhesive layer. The upper graph shows the effect of the same model containing the three 'voids'.

The lower figure clearly shows the place dependence of stress changes due to these singularities. The 'void' situated in the centre of the adhesive layer causes a small but clear distortion of the otherwise stable Von Misses stress.
Locally disturbed stress curves that are slightly decreased due to a decreased E-modulus can be found at the closed edge (a) of the adhesive layer [13, 14]. The only stress that has (slightly) increased due to a void's presence can be found at the outer open edge (b) of the adhesive layer.

Griffith's theory [15] states that failure of an adhesive bond may occur at a relatively small applied stress if there are any singularities in the adhesive layer or in case of surface defects. This will result in place-dependent stress concentrations that are much higher than the mean stress applied across the specimen. Highly increased stresses have not been noticed during the F.E.A. Considering the fact that the stress is generally higher at both edges of the adhesive layer than in its centre, it might still very well be that the presence of voids do have effect on the final bond strength but that this effect starts at a much smaller (microscopic) scale than can be detected by the finite element program.

Besides the effects mentioned, voids can also reduce the long-term behaviour of an adhesive bond in moist environments due to their function as a reservoir buffer for water [39, 43].

**Figure 4.3** The F.E.A. of three air voids in the adhesive layer (upper graph) of a cylindrical joint compared with a defect-free adhesive layer (lower graph).
4.3.1 General adhesive application

Adhesives are usually applied as liquids, pastes, or as supported films. In order to achieve a proper spreading, they are usually applied in liquid form or they are liquefied at some stage in the bonding process (like hot melts). Liquid adhesives lend themselves to being brushed, dipped, sprayed, or roller-coated (if they are low-viscous). In some adhesive bond designs it is possible to inject the adhesive into the bond gap. In this way, the intimate contact between adhesive and adherent is improved, particularly if the adhesive is pressurized into the micro-pores of the surface. Sometimes, adhesives must be applied to vertical surfaces. Particularly in that case, the adhesive’s tendency to flow downwards might be a serious problem. The use of a more thixotropic adhesive or a reduced bond gap (capillary force) might be a solution. A purpose-designed bond gap and the use of instruments improve the filling of the bond gap [2].

4.3.2 Adhesive mixing instrument

After the adhesive has been supplied (void-free) by the adhesive company, one of the first actions in which voids might be created is during the mixing of the two separately packed components, or the else in the intermediate steps before the adhesive application. For this reason, an instrument has been developed to weigh out, mix and apply a two-component adhesive with a reduced concentration of voids in one and the same disposable cartridge, which can be attached to several commercially available electro-pneumatically controlled dispensers.

4.3.3 Principle of operation

A commercially available 30 cc coaxial cartridge has been used as the basis of the design. It can be attached to an electro-pneumatic precision liquid dispenser [16] or vacuum pump by a flexible hose sealed to an up to 6 bar closed universal screw adaptor placed upon the cartidge’s top (Fig. 4.4). Before the adhesive can be dosed and weighed, the driving shaft/propeller (C
Factors affecting the adhesion

to $F$ in Fig. 4.5) has to be placed into the bottom of the cartridge (from the top down). The driving shaft ($E$) is supplied with an O-ring ($D$) in order to secure a liquid-proof fitting. The plastic propeller ($C$) is positioned on top of the driving shaft. It is designed to provide an optimal circular as well as a vertical mixing pattern without wasting adhesive to the walls of the cartridge [17]. After the driving shaft has been positioned, the cartridge is placed on a balance, and the adhesive parts can be dosed.

In order to mix the adhesive, the filled cartridge is put into a purpose-designed mixing instrument (not shown), which drives the propeller and holds the cartridge. The cartridge is closed by a screw adapter ($B$) which makes a connection to the vacuum pump through a flexible host. After about four minutes of both mixing and vacuum pumping (down to 150 mBarr), the adhesive is ready to be applied to the substrate.

The flexible host ($A$) is disconnected from the vacuum pump and attached to the automatic dispenser. The cartridge is taken out of the mixing instrument, and by screwing a (commercially available) dispensing tip onto its bottom, the driving shaft is pushed into the cartridge. In this way the outlet is opened, and the adhesive is ready to be applied to the adherents.

![Diagram](image)

**Figure 4.4** The developed dosing system: the adhesive is mixed under vacuum and applied to the substrate in the same cartridge by means of the electro-pneumatic dispenser.
Figure 4.5 A more detailed view of the cartridge; A: flexible host, B: screw adaptor, C: propeller, D: rubber O-ring, E: driving axis, F: temporary seal.

Substrate to determine the amount of voids
Top view:

Figure 4.6 The coin-like volume used to determine the amount of voids created during the various mixing processes.

4.3.4 Using the instrument

The following experiment describes the decrease in the concentration of voids in a two-component adhesive when use is made of the instrument described above. A substrate (Fig. 4.6) was designed and constructed to determine the voids concentration of the mixed adhesive. It was constructed of two (microscope) glass plates bound together by a (ϕ 24 mm, 1.5 mm high)
Factors affecting the adhesion

P.V.C. ring shaped spacer. In this way a small cylindrical and transparent coin-like volume was created. Two opposite drilled holes (Φ 0.4 mm) in the ring functioned as supply and eduction canals. These substrates were filled with the mixed two component (moderate-viscous) epoxy (Araldit AW 136/ HY 991) by use of the electro-pneumatic dispenser. After a 24 hours' cure at room temperature they were examined under a microscope and the number of voids sticking to the top glass plate was counted. The resulting data (Table 4.1) show the relative percentage of air voids (0.05mm < diameter < 0.2mm) counted inside a square of 1cm² centred in the middle of the substrate. The number of voids in the cured adhesive clearly decreases after a short vacuum treatment (in 4 minutes down to 50 Mbarr). But a vacuum treatment during the mixing of the adhesive in the mixing instrument described above clearly produces the best results. These experimental results show that the designed instrument is able to mix, weigh out, and apply a two-component adhesive to the adherent with a reduced concentration of voids.

<table>
<thead>
<tr>
<th>Relative percentage of voids</th>
<th>No vacuum treatment</th>
<th>Vacuum trtm. after mixing</th>
<th>Mixing + Vacuum trtm.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>70</td>
<td>60</td>
</tr>
</tbody>
</table>

**Table 4.1 The effect of different treatments on the relative percentage of voids in the adhesive.**

4.3.5 vacuum treatment and bond strength

In connection with the experiments described above, three vacuum treatments have been investigated to obtain information about their influence on the final adhesive bond strength. Three sets of 23 cylindrical stainless steel substrates with a rod diameter of 2.0 mm, a gap height of 1.5 mm and a gap width of 0.1 mm were cleaned with soap/water and gas plasma (Chapter 3) and bonded by the two component adhesive. In all three cases, the two-component adhesive was applied to the substrate by means of the electro-pneumatic dispenser. The investigated methods were:
- (1) adhesive application without any treatment.
- (2) vacuum treatment (in 5 minutes down to 150 Mbarr) together with mixing in the instrument described above.
- (3) a 5 minutes' vacuum treatment (in 5 minutes down to 50 mBarr) in a vacuum oven at 60°C immediately after the adhesive application.

The effects on the final bond strength are represented in Figure 4.7. They show that the vacuum treatment of the adhesive during mixing (method 2) results in an improved bond strength and reduced variance when compared with method 1, as a result of the lower voids concentration of the adhesive before its application. The third method (3) resulted in the highest average bond strength, but was found to be impractical, because the vacuum treatment caused the enclosed voids to rise, thus pushing the adhesive over the edge of the bond gap. This overflow of adhesive had to be removed before tensile force tests on the samples could be carried out.

Although method (3) resulted into the highest net bond strength, the standard deviation is clearly quite high. Possibly, because the more voids were enclosed, the less adhesive remained inside the bond gap. Thus a higher concentration of voids would lead to a lower adhesive bond strength. The variance is clearly the lowest when the vacuum treatment is carried out during mixing (method 2), most likely because in that case the number of (micro) voids has already been reduced before the adhesive application [17]. So method (2) seems to be the most practical one, producing the lowest standard deviation combined with a high bond strength. It has therefore been chosen for use in all other experiments in which the two-component adhesive is used.

**Figure 4.7** A comparison of three vacuum treatments and their influence on the adhesive bond strength.
Factors affecting the adhesion

4.4.1 Measuring the quality of adhesive bonds

In general, it is very difficult to determine the voids content of an adhesive bond in a non-destructive way. There are, however, a few exotic non-destructive measurement methods to indicate the quality of an adhesive bond [18, 19, 20, 21, 22, 38] such as: the Fokker bond tester, röntgen analysis, slow neutron analysis, and holographics. Of these instruments, only the Fokker bond tester [23] which measures the quality of an adhesive bond on the basis of ultrasonic sound reflections is easily commercial available. Unfortunately, it cannot be used for the small cylindrical surfaces discussed. And because the other methods mentioned are more rare and expensive, perspex dummies were used as an alternative in the experiments discussed below. This method of investigating the gap filling properties also had the advantage of producing quick results.

In the paragraphs below, the practical effects of the methods of adhesive application that have been investigated will be discussed. Different substrate forms have been investigated in order to get the optimally and most reproducibly filled adhesive gap. This was first done by using enlarged perspex substrates and then by using real-size perspex substrates. The last paragraph describes the adhesive application methods when they are tested on real-size stainless steel substrates.

4.4.2 Substrate construction

Figure 4.1A shows the shape of the adhesive substrate that was designed for the experiments and which had to be optimised. The reproducible filling of the adhesive gap widths of 0.05 mm was found to be difficult. After several different constructions had been tested, a compromise design as shown in Figure 4.1B was chosen as the definitive one. The bottom of the rod could be coated by a release agent (necessary for some experiments, like those in chapter 5) and small holes were drilled into the cylinder in order to optimise the adhesive application [3]. The positive effects that this optimised design of the cylinder had on the bond-gap-filling properties are visible in pictures 4.1 A/B.
4.4.3 Scale models: Enlarged perspex substrates

A practical problem in the science of bonding is the application of the adhesive in a reproducible way, with a minimum inclusion of voids. For this reason, several techniques of adhesive gap filling have been tested (using the instrument described above) on perspex cylinder models of different dimensions and structures, and a stainless steel rod. A set of these models was scaled up by a factor 6. The three adhesive application methods investigated are (Fig. 4.8):

(A) application of the adhesive onto both substrates and successively pushing them
   (e.g. screw-wise) together,
(B) putting the adhesive as a drop into the cylinder’s drilled hole, after which the rod is pushed (e.g. screw-wise) into the cylinder,
(C) using pre-centred substrate parts placed in purpose-designed racks (Fig. 5.1)

and supply the adhesive pressurised into its gap using the above described application instrument and the drilled channels in the cylinder.

Observations of the gap-filling methods A and B showed:
- The narrower the bond gap and the more viscous the adhesive, the more difficult it becomes to push the adhesive upwards, thus risking incomplete wetting. (Picture 4.1A)
- With either of these methods (A, B) it is very difficult to dose the adhesive accurately. Overdosed amounts of adhesive will flow over the edge of the cylinder, and an insufficient amount of adhesive results in incomplete wetting.
- There is always a large number of voids entrapped with the exception of the third method of bond gap filling (C) (Picture 4.1B).
- Method C showed a lower void inclusion as with this method the air is pushed ahead of the adhesive during the filling of the gap.
- Accurate dosing is possible with method (C) by means of the electro-pneumatic dispenser.
- Method (C) requires the design of the drilled adhesive supply lines and the use of substrate racks.
Factors affecting the adhesion

- The manufacturing of the more complex cylinder is time-consuming and more expensive than the one used in the (A) and (B) methods.

![Diagram of adhesion methods](image)

**Figure 4.8** Three different application methods: A: adhesive applied to both substrates, B: applied only to the cylinder, C: applied through the bottom of the cylinder using drilled pipes.

![Images of adhesion](image)

**Pictures 4.1 A/B** A: The stainless steel rod bonded in the blind hole of a perspex cylinder without adhesive supply pipes. B: Now adhesive supply pipes have been used. It is clearly visible that the number of voids is reduced with this improved method.
4.4.4 Scale models: real-size perspex substrates

The final design of the substrates discussed in this dissertation was mainly based on the results of the experiments described above with the enlarged models, as well as on experiments with the original-size substrates discussed below.

Despite the difference in dimensions of the experiments described above, the methods of bond gap filling were found to be applicable to small substrates as well. Again, these real-size test substrates were built up of a perspex (cylinder) and stainless steel (rod). In order to improve the reproducibility of the experiments, pre-centring substrate racks for 23 substrates were designed (Fig. 5.1). The adhesive application was further optimised by the use of the following experimental results:
- If the cylinder’s vertical supply line (l) is enlarged to 8 (mm), more voids are caught inside this volume. Unfortunately, a longer supply line results in an enlarged cylinder and higher material costs.
- Substrates from which sharp edges (2×45°) had been removed possessed the best gap-filling properties (Fig. 4.9).

The percentage of adhesive covering the walls of a real size perspex cylinder (with a stainless steel rod) was determined by means of the three different gap-filling methods (A, B, C). This allowed a qualitatively good interpretation of the used methods. The results can be found in Table 4.2. The methods A and B have been combined, because of their indistinguishable experimental results. The results reveal the gap filling superiority of method C, and support the values of the measured adhesive strengths of comparable stainless steel samples discussed below.

Figure 4.9 The removing of the sharp edges of the substrate parts improves the gap-filling properties, particularly with the methods A and B.
Factors affecting the adhesion

Table 4.2 The percentage of cylinder surface covered by adhesive (small perspex substrates)

<table>
<thead>
<tr>
<th>Percentage of surface covered</th>
<th>Method A/B</th>
<th>Method C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30-60</td>
<td>70-80</td>
</tr>
</tbody>
</table>

Table 4.3 The effect of two different methods of adhesive application methods on the bond strength.

<table>
<thead>
<tr>
<th>Disposing method</th>
<th>Average Force</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>droplet in cylinder (method B)</td>
<td>324</td>
<td>106</td>
</tr>
<tr>
<td>capillary filled (method C)</td>
<td>380</td>
<td>70</td>
</tr>
</tbody>
</table>

4.4.5 Adhesive application and bond strength

The gap-filling properties of a stainless steel cylinder and rod with rounded edges were further investigated. The adhesive force of real-size stainless steel substrates as a function of the three different application methods (A, B, C) has been experimentally determined, and their corresponding adhesive forces have been compared. The bond gap filling methods B and C that can be called best with regard to the adhesive bond strength were investigated once more, but now with stainless steel substrates. These cylindrical stainless steel substrates had a rod diameter: 2.0 mm, overlap length: 2.5 mm and gap width of 0.05 mm were soap/water and gas plasma cleaned (Chapter 3). They were bonded by Loctite 638; after 12 hours of curing at room temperature, they underwent a heat treatment of two hours at 80°C, before they were tested. The results displayed in Table 4.3 show that the purpose-designed adhesive gap for which the adhesive application system was used, leads to a higher bond strength. But what is also highly important, is the reduced standard deviation (STD) in the destructive force measured when the third method (C) is used. Probably because fewer voids are created during this improved
process of adhesive application. The results found in this paragraph are in line with the results found in the other paragraphs of this section which showed a superior performance of bond-gap-filling method (C). Gap filling method C results in a more than twofold increased load capacity and is thus highly recommended. It can therefore be concluded that a well-designed adhesive application method and gap have a positive influence on the adhesive bond strength. It can improve the bond strength, but what is more, it increases the reproducibility of the measured results.

4.5.1 Heat cure

It is generally known that a short heat treatment hardens an adhesive due to the increased polymerisation. This effect is often measured as an increased brittleness of the adhesive. It can also influence the durability of the adhesive bond (depending on the method of application) as will be shown below.

4.5.2 Effect of a heat cure on the polymeric structure

Two sets of cylindrical substrates (rod φ 2.0 mm, gap width 0.05 mm and overlap length 1.5 mm) were cleaned with soap/water and gas plasma (Chapter 3), a release agent [42] was applied to the bottom side of the rod, and then rod and cylinder were adhesively bonded with the anaerobic Loctite 638. After a pre-curing period of 12 hours at room temperature, one set of substrates underwent an extra heat treatment of two hours at 80°C. Figure 4.10 represents the two typical measured force/displacement curves measured, which clearly illustrate the increased modulus of elasticity (E), and the decreased value of the strain (ε) of a heat-cured adhesive compared with a non-treated one have been reproduced in Fig. 4.10. The suddenly very sharp transition at the fracture point as a result of the heat cure, indicates a higher degree of cross-linking within the polymeric structure. This was proved by Differential Scanning Calorimetry (DSC) measurements carried out on several adhesive samples as described below.
Factors affecting the adhesion

Figure 4.10 The typical effect of a heat treatment on the force-strain curve of an adhesive compared with that of a non-treated one.

4.5.3 Heat treatment and humidity

Six sets of cylindrical substrates (rod \( \phi \) 2.0 mm, gap width 0.05 mm, overlap length 1.5 mm) were cleaned with soap/water [Chapter 3], a release agent [42] was applied to the bottom side of the rod, and then they were adhesively bonded with the anaerobic Loctite 638. After a pre-curing period of 12 hours at room temperature, three sets underwent an extra heat treatment of two hours at 80°C. Then all sets were moved into a climate room of 95% relative humidity (R.H.) at 40°C.

The heat-treated bonds, which were exposed to this climate up to 8 months, showed a steady decrease in the adhesive bond strength (Fig. 4.11). This contrasts with the increase in the adhesive bond strength of non-heat-treated substrates (Fig. 4.12).

The force/displacement curves of all individual tensile force measurements were used to determine the average elongation at rupture (\( \epsilon = \Delta l/l \)) of the heat-treated and non-heat-treated sets. During the exposure to a high humidity environment, water will penetrate into the adhesive polymer. Three mechanisms that can affect the adhesive bond strength during such tests are:

- Weakening of the adhesive (depending on its chemical structure) leading to a reduced modulus of elasticity (E), an increased bond strength and elongation at rupture: (\( \epsilon \)).
As a result of the intake of water, the adhesive starts swelling; this improves its bond strength as a result of a better mechanical anchoring, which leads to an increased bond strength and enlarged strain (ε).

Water poured into the interface and oxidizes the adherent which decreases the adhesive bonding surface and with that the bond strength. While the adhesive bond is exposed to the high humidity at an elevated temperature (95%, 40 °C), the ε-value of the polymer starts slowly to decrease (Fig. 4.13). This could be the combined effect of three mechanisms: a decreased adhesive surface (as a result of water penetration and oxidation of the interface), the adhesive’s increased clamping to the metal due to its swelling, and reduced stress peaks because of an increased elasticity as a result of the increased flexibility of the adhesive. The ε-value of the non-heat-treated bonds seems to stabilize after 4 months of exposure and eventually becomes comparable to the heat-treated ones. However, the adhesive bond strength still increases as a result of the increasing flexibility, which compensates for the de-bonding. But it is expected that the effect of de-bonding will have an overruling effect resulting in a decreasing bond strength (see also §6.3.4).

**Figure 4.11** The effect of an aggressive climate on the adhesive strength of a set of heat treated substrates after 0, 4 and 8 months of exposure.

**Figure 4.12** The effect of an aggressive climate on the adhesive strength on a set of non heat treated substrates after 0, 4 and 8 months exposure.
Factors affecting the adhesion

![Graph showing effect of heat treatment on strain (ε) as a function of exposure to an aggressive climate.](image)

**Figure 4.13** The effect of a heat treatment on the strain (ε) as a function of the exposure to an aggressive climate.

4.5.4 Heat treatment, humidity and polymerisation

Differential scanning calorimetry (DSC) experiments [appendix 4] revealed that without an additional two hours’ heat treatment at 80°C, the anaerobic adhesive is only partly polymerised; this was determined by measuring the height of the exothermic peak.

After being stored for 7 days up to 4 weeks at room temperature (20°C, 35-40% R.H.), the exothermic peak of these adhesive samples was found to be at least four times higher than the exothermic peak of the ones that did undergo a heat treatment. This indicates that the adhesive was still not entirely polymerised due to the room temperature.

Samples stored inside the climate room (40°C, 95% R.H.) or during seven days or 4 weeks in a 40°C oven that was continuously washed with dried air (R.H. < 1%) still showed an exothermic peak of a value comparable with that of the samples that were stored at room temperature.

Also in view of the fact that the adhesive bond strength of three sets of substrates did not change during a period of 4 and 8 months in the oven at 40°C and <1% R.H., the conclusion is drawn, that the post-curing of the samples (due to temperature or humidity) inside the climate room (40°C, 95% R.H.) can be neglected.
4.6.1 Environmental humidity during adhesive bonding

Many adhesive bonds are constructed without any precautions with regard to air purity and particularly the relative humidity of the air (often 40% or more). Because of its high surface energy, a metal surface will always be coated with a few layers of contamination and water molecules (Fig. 3.2). Even when these layers have been removed after intensive cleaning and drying, the surface will soon be covered again by water molecules if no serious precautions are taken with regard to the air humidity. This layer of water may hinder optimal adhesion [25, 26, 27, 28, 37, 40]. In the experiments described below, the influence of the environmental relative humidity on the adhesive strength is determined. It was assumed, that in case of a higher relative humidity the water layer on the metal surface would be thicker, resulting in a lower adhesive strength. This effect was reproducibly confirmed by Zisman et al (Fig 4.14) by means of contact angle measurements of tetrabromomethane on glass [41]. These results showed that the adherent displayed a lowered critical surface tension of wetting (γc) at an increased RH. When it is assumed that there is a relation between the work of adhesion (W_A) and γc, a higher relative humidity could be correlated with a lowered adhesive bond strength.

![Figure 4.14 The effect of a changing ambient relative humidity on the contact angle [41].](image)

4.6.2 Experiment

Three sets of substrates were soap/water and subsequently plasma cleaned (Chapter 3). The substrate dimensions were: rod diameter: 2.0 mm, gap width: 0.05 mm and overlap length: 1.5 mm.
Factors affecting the adhesion

After the plasma cleaning the substrates were immediately moved into a small (0.2 m³) cabinet (Fig. 4.15). The substrates were adhesively bonded using Loctite 638 within 20 minutes’ time. The air in the cabinet was continuously refreshed by dried and activated carbon filtered air. During the measurements, both temperature and relative humidity were electronically verified [29]. The first set of 23 substrates was bonded in an atmosphere with a R.H. that was lower than 5%. During the second and third part of the experiment a venting closure was connected between the activated carbon filter and the cabinet. The venting closure was filled with distilled water and heated by a hot plate in order to obtain the desired relative humidity. In this controlled environment the two remaining sets of adhesive bonds were constructed at a R.H. of 45 and 75% respectively. After the adhesive application the bonds were moved into the laboratory air for a 12 hours’ post-curing and subsequently they underwent a heat treatment of 80°C during two hours. Then their adhesive strength was tested on the tensile force testing machine [App. 1].

The experimental results can be found in Figure 4.16, they show a decreasing bond strength as a function of an increasing relative humidity. This is in accordance with the results of the wettability experiments of R.A. Gledhill et al [25] (experimentally as well as theoretically). The physical effect of the adsorption of a thin film of water decreases the surface free energy of the stainless steel surface (γ). Additional water adsorption lowers this value even further, resulting in a decreased spreading of the adhesive across the surface, which results in a reduced bond strength (Chapter 2). Here again the overwhelming influence of humidity is demonstrated. A humid environment partly prevents heat curing to be advantageous and decreases bond strength, it also prohibits intimate contact and therewith reduces bond strength enormously.
4.7 Surface exposure time (S.E.T)

The surface exposure time (SET) is the time elapsing between the preparation of the surface and the actual bonding. When a cleaned object is exposed to the ambient air after it has been thoroughly cleaned, it will function as a "getter" and will readily adsorb water as well as organic contamination onto its surface (Fig. 3.2). Therefore, metal surfaces found in laboratories are generally of a hydrophobic nature [30]. Two major experiments have been done to investigate the effect of the SET.
on the adhesion [31, 32, 33, 35, 36]. They give some indication of the relation between the time elapsed between cleaning and bonding and the measured adhesive strength.

4.7.1 S.E.T and the contact angle

During the first experiment the effect of the surface exposure time was measured by means of contact angle measurements on flat and (6 μm) polished stainless steel substrates that had been cleaned with soap and subsequently with UV/ozone. The contact angles of water were measured (in laboratory air) several times and at several exposure times after the cleaning had taken place. The results are shown in Fig 4.17.

![Figure 4.17](image)

*Figure 4.17 The effect of exposure to laboratory air on the contact angle of an UV/ozone-cleaned stainless steel surface.*

4.7.2 S.E.T and the adhesive strength

The second experiment illustrates the influence of three surface exposure times on the adhesive strength of the cylindrical substrates. Three sets of cylindrical substrates (rod φ 2.0 mm, gap width 0.05 mm, overlap length 1.5 mm) were cleaned with soap/water and gas plasma [Chapter 3], and then adhesively bonded with the anaerobic Loctite 638. After a pre-curing period of 12 hours at room temperature, the substrates
underwent an extra heat treatment of two hours at 80°C. The adhesive was applied to the first set very quickly (within 5 minutes) in an atmosphere of a low R.H. (<5%) by means of the cabinet described above. The results displayed in Fig. 4.18 show that even a short surface exposure time of thirty minutes to laboratory air causes a decrease in the adhesive bond strength, and an increase in the variance. It is striking to see that the bond strength has not decreased after two hours of exposure to the same air compared with an exposure of half an hour. The reason of this phenomenon will be the high contaminating rate (dirt and humidity) of the cleaned surface during the first few minutes of being exposed. These results are well in line with the contact angle measurements of the exposed flat stainless steel substrates (above) which also showed that the value of the contact angle reached an asymptotic value as a function of the exposure time. However, the shown results should be interpreted carefully, for other impurities in the air will produce different contaminating rates, and consequently a difference in the measured adhesive bond strength after the same exposure time.

![Graph](image)

**Figure 4.18** The influence of an extended surface exposure time (SET) is correlated with a decreased adhesive bond strength.

### 4.8 Improved quality influenced by the S.E.T, R.H. and cleaning

The effect on the adhesive bond strength of the thorough plasma cleaning method and a combination of a short S.E.T and a low R.H. together with the
Values of uncleaned substrates are shown in a stacked diagram (Fig. 4.19) as well as in Table 4.4. Again, these results show very clearly the difference in the final quality of the gas plasma cleaning method compared to no cleaning at all. The gas plasma cleaned samples display a higher bond strength and a lower variance.

One of the aims of the investigations was to increase the reproducibility of the constructed bonds, as stated in Chapter 1. Moreover, the results of the experiments concerning the surface exposure time and relative humidity showed that during bonding the ambient air had great influence on the final value of the bond strength and its variance and therefore its quality. Figure 4.19 and Table 4.4 clearly illustrate the effects that cleaning and environmental surroundings during the adhesive application can have on the final bond strength. These presented data clearly show that a high-quality bond requires a well-defined environment during the adhesive application.

![Graph showing bond strength distribution](image)

**Figure 4.19** The influence on the quality of an adhesive bond as a result of a combined S.E.T. and a low R.H. (<5%) during the adhesive application of plasma-cleaned cylindrical substrates. The adhesive strength of non-cleaned substrates is used as a reference.

**Table 4.4** The illustration of the effects of: cleaning before, and the environment during the adhesive application on the final adhesive bond strength.

<table>
<thead>
<tr>
<th>Cleaning method:</th>
<th>Average</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>No cleaning</td>
<td>136</td>
<td>71</td>
</tr>
<tr>
<td>Plasma cleaning</td>
<td>260</td>
<td>56</td>
</tr>
<tr>
<td>Plasma + controlled R.H/S.E.T</td>
<td>401</td>
<td>30</td>
</tr>
</tbody>
</table>
References


15. A.A Griffith, Phil. Trans. R. Soc. Lond., A221, 163, 1920.

16. KD 30, Panacol-Elosol Gmb, Zeilweg 9, 6000 Frankfurt 50, W. Germany.


Factors affecting the adhesion

249.
Rotronic Hygroscop GT, Rotronic AG, Badener Strasse 435, PO box CH-8040, Zurich, Switzerland.

42  Lossing-B, Polyservice, Hoogeveenweg 83, 2913 LV Nieuwerkerk a/d IJssel, Holland.
Chapter 5

Design parameters

5.1 General introduction

This chapter gives a survey of the adhesive strength of the small cylindrical joints as a function of several form parameters. The first part of the chapter will discuss the influence of a small eccentricity on the measured adhesive strength. The second part will show the effects of changed dimensions of the substrate construction on the adhesive bond strength. All effects discussed will be backed up by experimental results as well as by finite element analysis (F.E.A).

![Image](image_url)

*Figure 5.1 A drawing of the substrate crate as used during the adhesive bonding in order to improve the quality of the bonded substrates.*

5.2.1 Eccentricity

During the experiments, utmost care was taken to obtain the best reproducible results. For this reason, three substrate crates as shown in Figure 5.1 were designed and built to make sure that all sets each containing 23 substrates, the axes of rod and cylinder would join during the adhesive bonding process. However, it is inevitable that a slight deviation of this ideal situation can
Design parameters

occur. The possible influence of a little eccentricity on the measured adhesive bond strength is discussed below.

An instrument has been designed and built to measure this eccentricity. Both the individual eccentricity and the strength of the bonds have been tested on the tensile force testing equipment [App. 1]. The influence of a deflection between the centre line axes of rod and cylinder on the final bond strength. In the two-dimensional space, the two centre lines can display four different positions;
(a) coincide \( \alpha = 0, \ \delta = 0 \)
(b) parallel \( \alpha = 0 \), but deflected \( \delta \neq 0 \)
(c) not parallel \( \alpha \neq 0 \), not deflected \( \delta = 0 \)
(d) intersect \( \alpha \neq 0, \ \delta \neq 0 \)
as can be seen in Figure 5.2. In three-dimensional space, they can also cross.

![Diagram showing four possible positions of rod and cylinder](image)

**Figure 5.2 (a-d)** The four possible positions of rod and cylinder when the principal axis of the cylinder can make an angle \( \alpha \) and/or can be shifted by a distance \( \delta \) in relation to that of the rod in a two-dimensional plane.

5.2.2 Stress caused by the eccentricity

A finite element program [Appendix5] has been used to detect the stress caused by eccentric centre line axes. A two-dimensional model as shown in Figure 5.2d with chosen values for \( \alpha \) and \( \delta \) \( \alpha = 0.07, \ \delta = 0.014 \) mm was
designed, and compared with the coinciding model (as Fig 5.2a). The results of the calculated Von Misses stress are visible in Figure 5.3. Due to the decreasing width of the adhesive layer when one looks from the closed edge (a) to the open edge (b) in the excentric model, the number of elements in the width of the adhesive layer decreases to just one column of analyzed elements (Fig. 5.3 top). It shows two increased stress peaks at both the closed (a) and open edge (b) of respectively about 60% and 45% compared to the symmetric model (Fig. 5.3 bottom). Moreover, the asymmetry in the Von Misses stress as a result of the eccentricity has increased. In general terms, this means that a less reliable bond has been created. This would imply that on the basis of the described analyses, the strength of an excentric adhesive bond could very well be inferior when compared with a symmetric one. It will be discussed below whether this is actually the case.

![Figure 5.3](image)

*Figure 5.3* The Von Misses stress on the inner and outer radius of the adhesive layer of an asymmetrically (top), and symmetrically bonded (bottom) rod and cylinder. The simplified drawing shows the closed (a) and open (b) edges.
5.2.3 The detection instrument

In order to distinguish the excentric states of the substrates (Fig. 5.2), an instrument with two electro-mechanical displacement detectors was designed and constructed.

The horizontal displacement of the cylinder is detected when the substrate is slowly turned around (Fig. 5.4). The rod of the substrate is pushed into a close fitting RVS tube perfectly centred into a driving wheel that lies in a V-shaped channel. By this makes the position of the rod’s centre line axis is known. The position of the cylinder’s centre line axis in relation to that of the rod axis is determined by two electronic displacement detectors. The centre lines of the detectors lie in the same plane as the centre line of the rod. The detectors scan the surface of the cylinder perpendicular to the rod axis at a distance (p) apart (Fig. 5.4). They are both connected to an analog-digital (A-D) converter of a computer as is schematically shown in Figure 5.5 [1]. A computer program was written to process the measured displacement data as a function of the rod’s rotation angle, resulting in measurements as shown in Figure 5.6. The relative resolution of the measured displacements was found to be better than 0.01 mm.

The displacement detectors were calibrated in such a way, that when a perfectly symmetric bonded rod was rotated, the amplitudes that measured by the detectors (U_{1,\varphi} and U_{2,\varphi}) as a function of the rotation angle (\varphi) were equal 0. They are represented in Figure 5.6 by two straight lines with a value of 0, without any superimposed oscillations caused by the eccentricity.

However if an excentric cylinder is rotated through the same axis, the measured amplitudes will show oscillations with values of: U_{1,\varphi} and U_{2,\varphi}, with maximum amplitudes of A_{1,\varphi} and A_{2,\varphi}.
A schematic representation of the asymmetry measuring instrument:

**Figure 5.4** A schematic representation of the functioning of the instrument measuring the eccentricity. With: 1. the cylinder, 2./3. electro-mechanical displacement detectors, 4. block with V-shaped channel.

**Figure 5.5** A schematic representation of the electronic set-up of the instrument measuring the eccentricity. With: 1. the rod, 2./3. electro-mechanical displacement detectors, 4. analog-digital and digital-analog convertor.
Design parameters

Figure 5.6 A typical measurement showing the measured amplitude oscillations ($U_{1,\varphi}$) and ($U_{2,\varphi}$) on the cylinder's radius $R_o$ due to its eccentricity as a function of the rotation angle ($\varphi$).

### 5.2.4 Definition of eccentricity

The most complicated situation of eccentricity in the two-dimensional space has been sketched in Fig. 5.2d with intersecting central axes of cylinder and rod. In three-dimensional space these two axes can cross due to a shift of the cylinder axis edges by vectors $s_1$ and $s_2$ (Fig 5.7). This figure shows the cylinder (dotted) together with the vectorial shifts of the upper and bottom planes: $s_1$ and $s_2$. The value of alpha ($\alpha$) determines the vertical angle between the centre axes of rod and cylinder. Delta ($\delta$) is the shortest distance in a horizontal plane between the cylinder's original centre line axis through (O) and its shifted centres ($s_1$ and $s_2$). Figure 5.8 shows the projection of the top surface onto the ground surface.

The values of alpha and delta have to be calculated in order to determine the cylinder's inclination in three dimensional space. When both the sine and the cosine rule are used in the triangle enclosed by O, $s_1$, $s_2$ and $x$, and when the expressions for sin $\alpha$ and $x$ are used, $\delta$ can be expressed as

$$\delta = s_2 \sin \gamma$$

94
\[
\delta = \frac{s_1 s_2 \sin \Delta \phi}{\sqrt{s_1^2 + s_2^2 - 2s_1 s_2 \cos \Delta \phi}}
\]

The distance between the detectors is known \((h)\). Because \(\Delta \phi\) is small, the angle \((\alpha)\) between the vectors \(s_1\) and \(s_2\) in the vertical plane can be found by

\[
\tan \alpha = \left( \frac{x}{p} \right)
\]

for which \(x\) is expressed by the cosine rule in the triangle \(O, s_1, s_2\) and \(x\);

\[
\alpha = \arctan \left( \frac{1}{p} \right) \sqrt{s_1^2 + s_2^2 - 2s_1 s_2 \cos \Delta \phi}
\]

This calculation shows that the values of both \(\delta\) and \(\alpha\) can be determined. Thus, an eccentricity can be expressed by means of two separate equations that are a function of respectively \((\delta)\) and \((\alpha)\). If the eccentricity has any influence on the adhesive force, there should be a relation between the measured adhesive force and the calculated \((\delta)\) or \((\alpha)\).

Figure 5.7 A three dimensional representation of the effect of the eccentricity of the original cylinder (dotted). It shows the cylinder’s new centre line axis in three-dimensional space in relation to the original axis.
5.2.5 Experiments

Sets of 23 substrates of several dimensions (rod φ: 2.00 mm, overlap length: h = 1.50 mm and adhesive gap width: t = 0.05 mm) were cleaned with water/soap and gas plasma (Chapter 3) and provided with a release agent. Then they were bonded with Loctite 638 and after a pre-curing period of 12 hours at room temperature they underwent a heat treatment of 2 hours at 80°C. They were all individually measured for their eccentricity by the instrument described in § 5.2.3 and subsequently for their adhesive strength by the tensile force testing machine [App. 1]. Figures 5.9 and 5.10 show the adhesive force as a function of the calculated (tanα) and (δ) of two sets of substrates. The results show that within the experimental measuring precision no evidence has been found for a relation between the adhesive force and (tanα) or (δ), nor, however, for a combination of both. This means that a
certain part of the spreading in the measured adhesive force cannot be directly attributed to the eccentricity.

Fig. 5.9  
*Figure 5.9* The relation between the measured values of the adhesive bond strength and the calculated rod inclination (tgα).

Fig. 5.10  
*Figure 5.10* The relation between the measured bond strength and the calculated values of horizontal shifting (δ).

### 5.3.1 Dimensional influences

It has been investigated what influence the dimensions have on the strength of the adhesive bond discussed. For this reason, experimental tests have been carried out with substrates of different dimensions, for instance with regard to their overlap lengths, rod diameters and adhesive layer thickness. The presented adhesive force is the value averaged from a set of twenty-three individually measured data. These results have been compared with the finite element analysis (F.E.A.) that was carried out [3]. On the basis of this combination, an optimal bond design will be proposed.
5.3.2 The construction's stiffness

The stiffness of the final construction will largely be determined by the modulus of elasticity (E) of the used adhesive for \( E_{\text{steel}} \approx 200 \times E_{\text{adhesive}} \). As an illustration the force-strain curves of the three chosen adhesives applied to the standard adhesive joint are represented in Fig. 5.11. The substrate dimensions: rod diameter 2.0 mm, gap width 0.050 mm and gap height 1.5 mm. The substrates were cleaned with soap and plasma (Chapter 2) and after a 12 hours' post-cure, they underwent a 2 hours' heat cure at 80°C. The presented curves have been measured on the tensile force testing machine [App. 1]. They clearly show the difference in the modulus of elasticity (E) of the used adhesives. The anaerobic adhesive was found to show the greatest modulus of elasticity, while the rubber filled cyanoacrylate shows to be the most flexible one.

![Force-strain curves of three different adhesives](image)

*Figure 5.11 The Force strain curves of three different adhesives, A: Loctite 638, B: Araldit AW123/HY991, C: Black Max 380.*

5.3.3 Experiments

Sets of adhesively bonded cylindrical parts were precleaned with soap and water and subsequently with gas plasma (Chapter 2). Before bonding, a release agent was applied onto the bottom of the rod to secure that only the side walls of the rod would determine the measured adhesive force. This
improved the final comparison with the results of the finite element analyses. The adhesive used in the described experiments was Loctite 638. The adhesive bonds were cured during 12 hours at room temperature and subsequently underwent a heat treatment of 2 hours at 80°C. Within 48 hours the sets were tested on the tensile force testing machine [App. 1.].

5.3.4 The finite element model

The F.E.A models discussed below are a two-dimensional $1/2\pi$ rotational symmetric slice simulation of the three-dimensional reality, giving typical deformations as shown in Fig. 5.12. In order to calculate the stresses, the drawn stainless steel and adhesive parts had to be divided into elements [App.5]. Those representing the adhesive were taken as squares of 0.125 mm$^2$ in all analyzed models. The areas of the elements representing the stainless steel parts were generally 25 to 100 times larger. This method secured the quickest and most reliable results for the analyses [4]. The rod length of the analyzed F.E. models was reduced to about a quarter of its real length in order to reduce the number of elements during the calculations. Its top was constructed of 'stainless steel' with a Youngs modulus (E) that was 100 times larger to conduct the applied force downwards in a fluent way. The Von Misses stress (the average value of the three principal stresses) is often used in analyzing adhesive bonds, because it generally has a close relation to the measured bond strength. But in cases of very small dimensions as discussed, local shear ($\tau$) and radial ($\sigma$) stresses are presented when needed.

A complex of interfacial bonding characteristics, non-homogeneity, fracture mechanics, environmental influences, and the elastic/plastic and time-dependent behaviour of the adhesive should be taken into account during calculations, when the aim is to predict the measured adhesive bond strength by computer analyses (Fig. 5.13) [17, 18, 19]. The presented F.E.A. are just calculations in the linear elastic region of the materials. Therefore, these results cannot be linearly coupled to expectations with regard to the bond strength; they can only be used as a rough guidance to optimise bond design
Design parameters

or to explain experimental results. In general, the durability of an adhesive bond increases when the stress in the adhesive layer is low [5-11].

Figure 5.12 A 5*10^7 times upscaled 2-dimensional diagonal outtake which sketches the displacements of the cylindrical parts as an effect of a force which is executed on the rod when the cylinder is grounded. The original shapes have been drawn by thick lines.

\[ \text{F.E.A} \]
\[ (\text{Finite Element Analyses}) \]

- Elastic/plastic behaviour
- Time dependent behaviour
- Fracture mechanics

Experimental results

Figure 5.13 Many influences should be taken into consideration when finite element analysis is used to calculate realistic values of adhesive bonds; a few are shown here.

Figure 5.14 The influence of rod diameter onto the radial stress distribution. The upper lines show the calculated stress of the \( \phi1 \) mm rod, the lower lines those of the \( \phi3 \) mm rod.

Figure 5.15 The shear stress
Chapter 5

Figure 5.14

Figure 5.15

101
5.3.5 Rod diameter (stiffness distribution)

The cylinders used in the experiments were manufactured of a φ 5 mm stainless steel rod. An adhesive gap was drilled into this cylinder, so that the adhesive gap width between rod and cylinder was 0.05 mm wide. When larger/smaller rod diameters were used, wider/smaller drilled holes in the cylinder were necessary, which reduced/increased its wall thickness. Particularly in the case of the smallest rod diameter this resulted in a considerable difference in the cross section areas of rod and cylinder, which is found to be responsible for the calculated adhesive stress peaks as will be discussed below.

With very small rod diameters (φ 1 mm) the stress distribution of both the radial (Fig. 5.14) and shear stress (Fig. 5.15) is highly asymmetric when compared with the calculated results of the φ 3 mm rod. In Figure 5.14, the very high radial stress peak on the inner open edge (b) of the adhesive is clearly visible. The existence of this peak is attributed to the unbalanced stiffness proportions of the rod (φ1 mm) and cylinder’s wall (1.95 mm thick). The stiffness of rod and cylinder can be related to their cross section areas (respectively πd²/4 and ~π(D²-d²)/4). When Hooke’s law is applied for a rod with a cross section area A = πr² and length (l₀), the application of a force (F) to both ends, will result into an elongation (Δl) as is shown in Figure 5.16:

\[\Delta l = \frac{F}{EA}l_0\]

\[F = AcE\]

\[\frac{l_0}{\Delta l} = A\]

102 Figure 5.16 The force (F) applied to a rod with cross section area (A) and length (l₀) which results into an elongation (Δl).
Table 5.1 The cross section area of the rod (diameter \(d\)), and cylinder wall width \(= (D-d)/2\) are related to their stiffness. The proportion in the last column shows that their stiffness becomes comparable with an increasing rod diameter at constant cylinder diameter.

<table>
<thead>
<tr>
<th>Rod diameter</th>
<th>((D^2-d^2)/d^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\phi 1) mm</td>
<td>24</td>
</tr>
<tr>
<td>(\phi 2) mm</td>
<td>(\approx 5.3)</td>
</tr>
<tr>
<td>(\phi 3) mm</td>
<td>(\approx 1.8)</td>
</tr>
</tbody>
</table>

This last equation shows, that the elongation (\(\Delta l\)) of a rod is inversely proportional to its cross section (A); thus a rod with a small diameter shows more elongation than one of the same material with a larger diameter at the same applied force.

When during a finite element analysis the wall thickness of the cylinder \(\pi(D^2-d^2)/4\) is reduced to a cross section area which is comparable to that of the rod with a diameter of 1 mm, the stress peak at the open edge is found to be highly reduced and becomes comparable to the one at the closed edge side.

The cross section area of the \(\phi 3\) mm rod and the corresponding cylinder’s wall area are found to be comparable in value. This thus results into two comparable stress peaks on the edges of the adhesive layer and a stabilising low-stressed bond centre. When the wall thickness of the cylinder is suddenly decreased to only 0.2 mm, stress peaks suddenly arise at the closed edge (a) (not shown). This proves that the position of the stress peaks at both edges (a) and (b) is primarily induced by the difference in stiffness of the used constructive parts (Fig. 5.17). The increasing adhesive bond strength (e.g. Fig. 5.22), is in accordance with the radial and shear stress calculated above, which fall in case of an increasing rod diameter. The measured adhesive bond strength strongly increases with an increasing rod diameter; thus it can be concluded, that in the case of axially loaded cylindrical bonded substrates the rod and axially loaded cylindrical bonded substrates the rod and the cylinder should be designed with equal local cross section areas, some constructive examples are given in Fig. 5.18.
Design parameters

Figure 5.17 The upper graph shows the radial stress in the adhesive cylindrical layer at a wall thickness of 1.95 mm. Decreasing this thickness to a value of 0.3 mm gives a spectacular decrease of the high peak at the open edge of the adhesive layer, and clearly has a balancing effect on the stress distribution.

Figure 5.18 a-d The first sketch (a) shows an unelegant construction to bond a rod into a massive body because of the induced stress peaks in the adhesive layer. Sketch b shows an improved design which locally decreases the body's stiffness. Especially sketch d is a nice example of tapering in order to reduce the stress peaks on both edges of the adhesive layer.
5.3.6 Overlap length

The Figures 5.19 and 5.20 show the F.E.A. of the radial and shear stresses as a function of overlap length at \( h = 0.50 \) and \( h = 3.0 \) mm. With the shortest overlap length of \( h = 0.050 \) mm, the radial stress (Fig. 5.19) shows a peak value at both adhesive edges and rapidly decreases (by 85% and 55%) when the overlap length is increased to \( h = 3.0 \) mm. This shows that an increase in the overlap length with one and the same rod diameter (\( \phi 2.0 \) mm) has a favourable influence on the stress distribution.

In case of the shortest overlap length of \( h = 0.50 \) mm (Fig. 5.19) no asymmetry is visible. Then the adhesive bond behaves as if it is entirely enclosed, showing a high shear stressed adhesive centre part, with -in comparison with the central area- two comparable (but high value) shear stress peaks at the edges, which quickly decrease when the overlap length is increased.

The stress peaks carry the heaviest load and may therefore very well be the origin of initial cracks. The most stable and fatigue-resistant adhesive bond construction is supposed to show a lightly loaded central area. This will reduce the stress peaks at the edges of the adhesive bond. This reduces hysteresis, resulting in a decreased relaxation behaviour, better known as creep, which leads to bond failure [10-12].

In line with the results of the F.E.A., a rapid increase in the experimentally measured adhesive joint strength is visible when the overlap length is increased. This effect can be found in Fig. 5.22. A sudden increase in the measured adhesive force, almost independent of the rod diameter, is visible after the overlap length has gone over about 2.0 (mm). It should be noticed, that the bond's load depends on the bonded area. A larger rod diameter means a proportional enlarged bonded area and thus a higher bond strength.

To study the influence of the bond length accurately Fig. 5.21 has to be transformed to a graph which shows \( F/D \) as a function of \( h \) as in Fig. 5.21. It shows clearly that an overlap length of only 2 mm is found to be very beneficial to the adhesive bond strength especially at small rod diameters. An overlap of at least 3 mm, independent of the rod diameter is highly recommended for cylindrical bonds.
Design parameters

Figure 5.19

Outer radius
Inner radius

Figure 5.20
Altogether, this means that the most simplified calculations that try to predict the adhesive bond strength as a linear function of the adhesive surface are wrong. Moreover, it supports the idea that the adhesive bond strength is strongly influenced by the value of the stress peaks on the edges as well as in the central area of the adhesive bond [13].

\[ F/\pi = \frac{N}{mm} \]

\[ h (mm) \]

**Figure 5.21** When an accurate effect of the overlap length and rod diameter on the adhesive bond strength is needed, the netto adhesively bonded surface should be taken into account. The measured adhesive bond strength must then be divided by the diameter of the rod. The numbers indicate the variance of the measured adhesive force.

**Figure 5.19** The influence of overlap length onto the radial stress distribution. The upper lines show the calculated stress at 0.5 mm overlap, the lower lines those of 3.0 mm.

**Figure 5.20** The shear stress

### 5.3.7 Adhesive layer thickness

The adhesive layer thickness is generally accepted to be an important parameter in adhesive bond design. The destructive experiments discussed below show that a thick adhesive layer generally results in a decreased bond
Design parameters

strength, which is in accordance with the results of other researchers [14, 15, 16].

The F.E.A. shows that in the model with the thicker layer (Fig. 5.22) the radial stress peaks at the inner open edge of the adhesive layer increases by almost 30% compared to the same peak in Fig. 5.23, as a result of the sharper bend of the adhesive at the substrate edges. The stress lines have to make a sharper turn from the one edge of the substrate to the other.
The shear stress (not shown) slightly decreases because there is a longer way available to cope with the strain difference between both substrate parts.
The Von Misses stress peaks (Fig. 5.23) are found to be influenced to a large extent by the value of the changed radial stress. The centre part of the Von Misses stress is found to be subdued by the shear stress, and shows an increased and very clear difference in stress between the inner and outer radius of the adhesive layer.
The experimental data (Fig. 5.24) which show the bond strength of substrates bonded with Loctite 638, that there is a relation between the adhesive bond strength and the gap width. The experimental obtained values suggest that even smaller gap widths should be advantageous. However, the realisation of smaller gap widths will be impeded by manufacturing tolerances (and thus costs) and adhesive application. But a wider gap reduces the stiffness of the adhesive bond construction and leads to an increased deformation of the adhesive layer, which induces an increased bending. The result is a higher peel stress, a killing stress for the adhesive bond. It may, therefore, be expected that the radial stress will have a comparatively strong influence on the experimentally measured bond strength.

**Figure 5.22** The influence of adhesive layer thickness onto the radial stress distribution.
The upper lines show the calculated stress at a $t = 0.050 \text{ mm}$ adhesive gap width, the lower lines those at $t = 0.20 \text{ mm}$.

**Figure 5.23** The von Misses stress.
Chapter 5

Figure 5.22

Outer radius

Inner radius

Figure 5.23
Design parameters

\[ F' \ (N) \]
\[ \text{Gap width (mm)} \]

**Figure 5.24** The effect of the layer thickness on the experimentally measured bond strength. (\( \phi \ 2.0 \ mm, \ h: \ 1.5 \ mm \)).

### 5.3.8 Conclusions

When Figure 5.25 is considered, being a compilation of 9 measurements of two different substrate dimensions; the overlap length (h) and rod diameter it can be concluded that the adhesive bonds involved get their optimal strength in case of a long overlap length (h = 3 mm) with a large (3 mm) rod diameter. Its comparison with the calculated Von Misses stress in the adhesive layer at the closed (a) and open edge (b) which are shown with inverse axes in respectively (Fig. 5.26) is striking. Because the highest measured bond strength corresponds to the lowest stress peaks, and inversely; the lowest adhesive bond strength corresponds to the highest stress peaks. But there is no one to one correspondance as stated before! It can thus be concluded, that during the design of a small cylindrical adhesive bond, the results presented above of the experiments that have been carried out as well as the obtained F.E.A. of the rod diameter, overlap length and adhesive layer thickness can be very useful. When the effectiveness of the adhesive force/(surface area) and the bond gap width are considered, the most effective design at a pre-determined surface, is to choose a bond gap of 0.05 (mm), with the smallest rod diameter at the largest overlap length.
Figure 5.25 The experimentally measured adhesive bond strength as a function of rod diameter and overlap length.

Figure 5.26 The Von Misses stress at the closed edge (A) and open edge (B) of the adhesive layer as a function of overlap length (h) and rod diameter (warning: the axis of the overlap length h and rod diameter have been inversed compared to Fig. 5.25).
References

1. A-D converter (TP5008) by Tie Pie engineering, PO box 115, 8900 AC Leeuwarden.
3. Algor Finite Element Analysis System, Algor, Inc. 260 Alpha Drive, Pittsburgh, Pennsylvania 15238, USA.
Chapter 6

Environmental effects

6.1 Introduction

It is difficult to predict the normal service life of an adhesive bond without any results of tests that predict its bond strength during practical use. Many accelerated environmental resistance tests for adhesive joints are known [1]. With regard to the special use in prostheses design, the effects of two simulations of service life conditions on the performance of adhesive bonds have been investigated. They consisted of a test with an elevated temperature at a high humidity, and a salt spray test with changing temperatures. A change in the adhesive bond strength was noticed after the bonds had been exposed to a high humidity environment, depending on whether it was heat-treated or not. The investigated time-dependent adhesive joint strength is found to decrease under accelerated test conditions. Its relationship with the real service-life joint strength is complicated. For this reason, the experimentally obtained results can be used only as a rough guidance in predicting the reduction of the adhesive bond strength, this due to the lack of comparable values under real-life conditions [2].

6.2 High humidity environment

6.2.1 Climate test on three adhesives

It has been investigated how the adhesive bond is influenced by the exposure to an aggressive environment for a long time. For this, three different adhesives have been used. The dimensions of the substrates used were: overlap length 1.5 mm, adhesive gap width 0.05 mm and rod diameter 2.0 mm. Before the adhesive was applied, the substrates were cleaned with soap and water. After a 12 hours' pre-curing period at room temperature, they were given a heat treatment of 2 hours at 80°C. One of the sets was immediately destructively tested on the tensile force testing machine [App. 1.]. The other two sets (consisting of 23 substrates each) were placed into a climate room in which they were exposed to a climate of 90% relative
Environmental effects

humidity (R.H.) and a temperature of 40°C. After 4 and 8 months respectively, these sets were also destructively tested. The obtained values of the adhesive bond strength are presented in Fig. 6.1 to 6.3. They show the influence of the climate on the adhesive bond strength of the three selected adhesives described in Chapter 2, namely:
- anaerobic; Loctite 638 (Fig. 6.1),
- cyano acrylate; Black Max 380 (Fig. 6.2),
- two component epoxy; Araldit AW136/HY991 (Fig. 6.3).

![Graph](image1)

**Figure 6.1** The effect of an aggressive climate of 40°C and 95% relative humidity on the strength of the adhesive bond when composed with Loctite 638.

![Graph](image2)

**Figure 6.2** The effect of an aggressive climate of 40°C and a 95% relative humidity on the adhesive bond strength when composed with Black Max 380.

![Graph](image3)

**Figure 6.3** The effect of an aggressive climate of 40°C and a 95% relative humidity on the adhesive bond strength when composed with Araldit AW 136/HY991.
6.2.2 Experimental results

Comparison of the Figures 6.1, 6.2 and 6.3 shows the experimental results of the nine sets of substrates bonded by the three different adhesives. Comparison of their bond strengths interpreted as a function of time shows a decrease in the bond strength of both the anaerobic and cyano acrylate adhesives, in contrast to a slight increase in the bond strength of the two-component epoxy. The increase in the bond strength of this last adhesive is in accordance with the data provided by its data sheet [3]. However, the decrease in the adhesive bond strength of the cyano acrylate was unexpected, for its manufacturer claimed that it is moisture-independent if kept unstressed, as was the case [4]. On the other hand, the moisture dependence of the cyanoacrylates is generally known [11, 12].

The two-component epoxy proved to produce the highest bond strength after a long exposure to the aggressive climate. But the mixing of this adhesive has the problem of voids being created in the adhesive layer leading to an increased variance of the adhesive strength (Chapter 4). For this reason, the experiments in the previous chapters were for the greater part carried out with the anaerobic adhesive.

6.3 The influence of sweat

The investigations described in this thesis have been carried out in order to make the production of adhesive bonds in prostheses and orthoses as reproducible as possible, as was stated in the first chapter. In order to get some information about the durability of the bonds in the environment in which they will eventually be used (prostheses and orthoses), literature about human sweat (rate and contents) has been consulted. On the basis of these data (§ 6.3.1), a sweat- resembling liquid has been composed and used in environmental experiments (§ 6.3.2).
Environmental effects

6.3.1 Sweat rate

A lack of ventilation of the human skin in f.i. a plastic glove (Chapter 1) makes the conditions of temperature and wetness in this enclosed area different from normal conditions in other parts of the body. Some investigators have found that when skin areas are enveloped in impermeable bags, the sweat produced is more concentrated than that from bare skin. Others, however, found no significant difference between such 'bag sweat' and normal body sweat.

Sweat is about 99 per cent water and is therefore well suitable for its part in the evaporative cooling of the skin surface. The most concentrated solute in sweat is NaCl; most of the water-soluble substances dissolved in human cellular plasma are found in sweat, some in higher and others in lower concentrations than in the human plasma. So sweat glands appear selectively to secrete some salts and to retain others. Besides, the sweat rate varies greatly from one part of the body to the other, according to the sweat gland density, age, water intake, skin temperature, vascular supply, acclimatization, etc. Methods for the measuring of sweating and techniques used in the sampling of sweat have been reviewed by Robinson after the different sampling techniques on men had been found to affect the concentration of sweat.

Present evidence indicates that water and NaCl are the principal substances found in sweat. The concentration of NaCl in thermal sweat is extremely variable, with low values of 3 - 5mMol/l. Study of literature shows that high concentrations of NaCl (above 80mMol/l.) are the most frequently found in sweat samples collected from local skin areas where the skin is enclosed in impermeable barriers (such as silicon gloves).

Potassium concentration in percussor sweat is isotonic to the human cellular plasma i.e. 5 mMol/l. In contrast with NaCl, the sweat K concentration is higher at low sweat rates (10 to 35 mMol/l) but approaches isotonicity (5mMol/l) as the sweat rate increases. In addition to the electrolytes Na and K mentioned above, sweat also contains magnesium, iodide, phosphorus, sulphate, and metals such as iron, zinc, cobalt, lead, manganese, molybdenen, tin, and mercury in trace amounts. When the sweat rate is low, the Ph of sweat is measured by values ranging from 4.0 to 6.8 [5, 6, 7].
6.3.2 Sweat experiment

An experiment was set up in order to find the influence of sweat on the adhesive bond strength. Three sets of substrates were prepared for the experiment (rod diameter 2.0 mm, overlap length 1.5 mm, gap width 0.05 mm). The sets were cleaned according to the standard procedure of soap/water and gas plasma cleaning as described in Chapter 3. Then the parts were bonded with Loctite 638 (anaerobic adhesive) and after 12 hours of curing at room temperature, they underwent a heat treatment of 2 hours at 80°C. They were mounted into the central part of the experiment: the glass desiccator (I.D. 150 mm), placed on a temperature controlled hot plate (Fig. 6.4). The bottom volume of the desiccator was filled with a sweat-resembling fluid (about 750 cc). The composition of the 'sweat' (used to imitate the aggressiveness of real sweat) was based on the articles mentioned above. Knowing the general corrosive effects of sea water (largely water and NaCl) [14], it was assumed that the adhesive joint would be sensitive to dissolved salts and acids in the liquid. This assumption was, however, in conflict with the adhesive's data sheet [10, 13]. The prepared solution consisted of 50 mMol/l NaCl, and 40 mMol/l KCl in distilled water. A drop of concentrated HCl was added to obtain a Ph of 3.5. The Ph-value of the sweat-resembling fluid was slightly decreased in order to accelerate the ageing process of the adhesive bond. The artificial sweat was circulated by a small pump, which sprayed the fluid through the desiccator chamber. The temperature was periodically changed from 25°C to 35°C and back (Fig. 6.5). The purpose of this rise in temperature was to increase the aggressive reactivity, and to imitate the 'real-life' temperature shocks of prostheses. To stabilise the temperature of the experimental set up, a cooling fan was placed on an upper sidewall of the desiccator.

One set of 23 substrates was immediately tested for its adhesive strength on the tensile force testing machine [App. 1], while the two remaining sets of substrates were placed in the desiccator (Fig. 6.4). After one and two months respectively, the sets of substrates were taken out of the desiccator and destructively tested.
Environmental effects

Figure 6.4  A schematic representation of the instrument which imitates the influence of artificial sweat onto the strength of the adhesive bond. A: substrates, B: desiccator, C: rotation pump, D: time controlled hot plate, E: air cooling.

Temperature changes during the sweat test:

Figure 6.5  The temperature changes of the sweat resembling fluid during the experiment.

6.3.3 Results

The experimental results are presented in Figure 6.6. In case of a longer exposure to 'sweat', the results resemble some of those of the climate tests. The destructively measured adhesive strength is temporarily higher due to the
absorption of water into the adhesive structure, which increases its flexibility (Fig. 6.7). This is followed by a decrease in the adhesive strength due to water perception onto the interface. It is important to notice that this fall in adhesive strength takes place faster (and much earlier) than was the case in the climate tests. Most likely because of the higher aggressiveness of the sweat-resembling fluid compared with the distilled water that was used in the climate tests. However, such sensitiveness had not been claimed by the adhesive manufacturer.

\[ \text{Force (N)} \]

\[ \text{Time (week)} \]

\[ \text{Figure 6.6 The effect of the sweat resembling fluid on the adhesive bond strength when composed with Loctite 638.} \]

\[ \varepsilon \]

\[ \text{Time (week)} \]

\[ \text{Figure 6.7 The effect of the sweat resembling fluid on the strain (\varepsilon).} \]
6.3.4 Explanation

When the two experiments discussed above (the effect of high relative humidity and sweat) and the effect of a heat treatment on the adhesive bond strength (Chapter 4) are considered, the following interpretation of the measured results is proposed. The cleaning procedure of all nine sets of substrates has taken place under the same circumstances. This narrows the risk that a difference in cleaning would be the factor responsible for the fall in the measured adhesive strength but leaves other possible explanations. The observed results can be explained when the adhesive layer is regarded as a semi-permeable wall as is the case with many organic coatings [8]. This means that the adhesive is more pervious to water molecules than to ions. When the bond is exposed to a high humidity environment, a high ion concentration on the metal side of the adhesive layer causes a flux of water to penetrate through the adhesive to the metal surface. Of course, this permeability is strongly dependent on the intrinsic polymer properties such as the polymer binder, additives and pigments.

During the time for which a coating is being exposed to an aqueous solution, water vapour and oxygen will diffuse into the adhesive film (Fig. 6.8). Subsequently, water may accumulate at the interface, forming a liquid film of at least some monolayers of water. At this stage, all ingredients for corrosion are there: anodic species (water and oxygen) and an aqueous film in which an electrochemical double layer is formed. After this situation has been reached, and depending on the specific materials and conditions, the formed blisters may grow as a result of anodic or cathodic delamination (Fig 6.9) or filiform corrosion.

The major mode of failure of coatings is blistering, which is caused by osmotic pressure through the adhesive layer as a result of e.g. surface contamination. The formation of blisters and the onset of underfill corrosion may be the result of a great number of different phenomena such as the swelling of the adhesive, the presence of voids or ions in the adhesive or contaminants such as salts like SO₂ that are present on the interface. But it can also be due to wet adhesion problems, poor adhesion properties, adhesion defects and so forth. Crosslinking of the polymer is very likely to occur as a result of a heat
treatment. In general, this decreases its permeability to gases, particularly when the permeant causes the polymer to swell. In several systems, however, the effect of crosslinking may not be of major influence and is overruled by the effect that functional groups may have on the water solubility. Besides, the possible evaporation of gases (like water) from the interface or inside the adhesive during the heat cure (as a result of expansion) leaves micro voids on the interface and in the polymer matrix. The accumulation of water at these spots can be the precursor of the increased corrosion process. This might explain the greater loss of adhesive strength compared to the sets of non-heat-treated substrates.

The higher ion concentration in the solution of the 'sweat' experiment gave rise to an increased electric conductivity of the liquid, thus increasing the observed debonding due to anodic and cathodic delamination. This offers an explanation for the increased deleterious effect of the heat treatment on the adhesive strength compared to the sets of non-heat-treated substrates [9, 16].

\[ \text{Chemical disbonding} \]

\[ \text{Mechanical disbonding} \]

\[ \text{Reduced adhesion} \]

**Figure 6.8** A simplified representation of the adhesive joint in contact with an aqueous electrolyte solution, showing the two possible hypotheses (chemical/mechanical disbonding) explaining the mechanism of the loss of adhesion due to water [15].
Environmental effects

\[ \text{Adhesive defect} \]

**Figure 6.9** Cathodic delamination under an intact or defective coating.

### References

1. Polytechnisch zakboek, Koninklijke PBNA BV, Postbus 9053, 6800 GS Arnhem, Holland.
Chapter 6


Chapter 7

Summary

The aim of the investigations described in this thesis was to optimise the design and production of small cylindrical bonds. The design of such a pin-in-hole bond has been analyzed in order to offer the engineer practical design rules to improve the strength of this bond. The production steps (such as the cleaning of the samples and the filling of the gap) have been planned for use in a workshop.

Some of the investigated parameters were found to have a considerably greater influence on the final bond strength than others. Cleaning turned out to be the most effective factor in the improvement of the final quality of the adhesive bond in comparison with all other factors investigated. The more intensively the substrates are cleaned, the higher will be their initial bond strength, durability and reproducibility. Contact angle measurements proved to be a reliable, quick and simple quantitative method of determining the purity of the metal samples with regard to organic (apolar) contamination. A contact angle of 8 degrees (by water) on a (flat) stainless steel surface gives a reliable indication for high quality bonds. The more advanced methods of gas-plasma and UV/ozone cleaning were found to produce the best results. A lot of attention has been paid to UV/ozone cleaning as it was found to be a quick method producing excellent cleaning results. However, the UV/ozone method is not very suitable for the cleaning inside small holes. It is found to be an ecologically sound method as well as an alternative or even a considerable improvement on several solvent-based cleaning methods. Because of its low price and simpliceness, several industrial applications of the method have been found, such as the cleaning of parts of hydraulic and marine engines.

Water in its fluid or gas phase is found to be disastrous to adhesive bonds in many aspects. A great improvement of the quality of the adhesive bond can be achieved when the adhesive is applied quickly and under controlled environmental conditions immediately after the cleaning has taken place. The favourable effect on both the adhesive strength and the reproducibility has been demonstrated. Finite element analyses showed that voids in the adhesive layer could only slightly affect the final adhesive bond strength. In real-life performance (moisture, vibration forces), however, they have a much greater effect than
Summary

this method predicts. Therefore, it is recommended that the adhesive gap is
designed in such a way that it can be filled without voids being trapped. An
instrument was designed and built that is able to weigh, mix and apply a two-
component adhesive in one and the same disposable cartridge with a
minimum number of voids being entrapped. The experimental evidence was
found which showed that the substrate’s bond strength is improved when the
bond gap is filled without voids being entrapped.

An important conclusion that can be drawn from the finite element analyses
as well as from the practical experiments, is that the width of the adhesive
layer in the analyzed models should be thin (about 0.05-0.1 mm, dependent
on the adhesive). It is advisable that the stiffness of the bonded parts (rod and
staff) is roughly comparable. As a result of this, stress peaks in the adhesive
layer will be reduced and equalised, thus improving the bond durability.

The climate and sweat tests that have been carried out determined the
influence of humidity and an aggressive environment on the adhesive bond
strength. The warm and humid environment clearly had a less disastrous
effect on the adhesive strength than the sweat-resembling fluid. Several
processes, such as the weakening of the adhesive and oxidation of the metal
surface, are found to determine the bond strength. The adhesive strength of
all adhesives tested (except the epoxy) decreased during the bond’s being
exposed to the high humidity environment. It was remarkable that, when the
anaerobic adhesive had had a 2 hours’ post-cure treatment at 80°C, its
physical and chemical properties had changed and its durability in a humid
environment decreased.

These observations of a decreasing bond strength during the exposure to
humid environments, together with the usually observed oxidation of metals
inside prostheses, make it advisable to isolate vulnerable parts from moisture.
Furthermore, the use of high-quality steel is expected to improve the
durability of adhesive bonds when these are subjected to humid environments.
Tests in which other people manufactured the adhesive bonds showed that the
final quality (reproducibility, average adhesive force) strongly depended on
the one by whom the adhesive bonds had been manufactured.

This leads to a final and general conclusion with regard to the investigations.
The art of bonding is a very serious and complex matter based upon a lot of
process parameters (that are sometimes difficult to measure). Therefore, the

126
Summary

final quality of the bond often reflects more the skills of the maker than the quality of the used materials. Automation of the entire bonding process (cleaning and adhesive application) with a minimum of human interference could therefore provide a solution.
The adhesive strength of the bonded objects (rod and cylinder) was experimentally tested on a computer-controlled tensile force testing machine, schematically drawn in Figure 1.

![Diagram of tensile force testing machine]

*Figure 1 Schematic representation of the tensile testing machine, 1: substrate, 2: force transducer, 3: amplifier connected to the computer by built-in A-D converter, M: computer controlled motor.*

This instrument has been designed to ensure a reproducible destruction facility [6,7] with a constant destruction rate. It measures the destructive force needed to separate the adhesively bonded rod and cylinder. Figure 2 shows the step motor (A) coupled to a sliding bar (D) by a low gear (G). The sliding bar is positioned by two steel conductors (B), and moves with a constant destruction rate of 37.5 mm/min.

During the destructive test, both sides of the substrate are fitted into a clamp. The rod is clamped to 'earth' through the force transducer (E) [4], while the backside of the cylinder is held by a clamping screw, so that it partly fits into the ball of a 'ball-and-socket joint' (F) with the adhesive bond centred in the ball (Fig. 3). The ball-and-socket joint was designed because it was found to be a solid and reliable construction which prevents that a momentum - depending on the angle between the rod and cylinder centre lines - would be applied to the adhesive bond during the destruction. Unfortunately, this
construction does not make any corrections for parallel displacements ($\delta$) between the rod and cylinder hart lines which will induce a (very small) bending moment during the destruction (see also Chapter 4). During the measurements, the tensile testing machine was placed in an upright position, together with the cylinder, which partly fitted into the ball. This resulted in the right positioning of the ball before each measurement. A computer program converts the measured signal of the force transducer into a force and regulates an external electronic power circuit which controls the electronic step motor [3].

![Diagram](image)

**Figure 2** The tensile force testing machine; A: motor, B: steel conductor, C: threaded rod, D: sliding bar, E: force transducer, F: the substrate, ball-and-socket joint and the two clamps shown in detail in Fig. 3.

Thus, the displacement of the sliding bar can be accurately measured. The actual measuring starts when the force transducer has passed a threshold value of 0.9 N and stops after the measured force has gone below the threshold value, or if the number of measurements gets over 360. The measured results are directly visualised on the computer screen and written on a disk, and/or printed.
Figure 3 The ball and socket joint with substrate (A). It keeps the rotation point in the centre of the adhesive bond, and the hart-line of the staff parallel to the destruction force. Both clamps are dotted.

References

1. TP5008 A/D D/A -converter, TiePie Engeneering, Postbus 115, 9800 AC Leeuwarden, Holland.
2. ROPLA Electronics, step motor controller, postbus 2506, 2500 VW Den Haag.
3. Superior Electronic, Type: MO61-FD-6120, Bristol CT, USA.
4. HBM zugkracht/ druck aufnehmer Q3, Hottinger Baldwin Messtechnik, Darmstadt, Germany.
5. Carrier frequency amplifier KWS/T-5, Hottinger Baldwin Messtechnik, Darmstadt, Germany.
Appendix 2.

Plasma cleaning

Introduction

Plasma chemistry is almost exclusively used for etching, cleaning and deposition processes in semiconductor device fabrication technology. Because of its well-known success in the cleaning of silicon wafers and its ability in the cleaning non-flat substrate forms, cleaning experiments have been done on the cylindrical stainless steel substrates.

The physical principle of plasma cleaning

Plasma is a state in which a gas at moderate vacuum (about $5 \times 10^2$Torr), is energised and excited typically by an electric field (Fig. 4). As a result of this, the gas breaks down into a variety

![Diagram of plasma cleaning instrument](image)

**Figure 4** The plasma cleaning instrument, A: Substrate, B: 1.5 KV Anode, C: vacuum wall, D: earthed ground plate, E: High tension transformer, F: Vacuum rotation pump.

of active species, ions and free radicals impinging on the surfaces of the workpiece (substrate) that has been placed inside the vacuum chamber. In principle, the cleaning process takes place in two different chemical reactions.
First by the bombardment of energetic ions whose momentum is sufficient mechanically to dislodge parts of the organic contaminants from the substrate's surface in an ionisation reaction such as: \( \text{Ar} + e^- \rightarrow \text{Ar}^+ + 2e^- \) 
This physical mechanism is particularly effective when one is working with "heavy" gases such as nitrogen or argon. This cleaning process is actually a mechanical one.

In contrast, a second mechanism is based upon a chemical reaction between the substrate's surface and the species generated by the plasma. The oxygen plasma used in this case is a chemical process in which oxygen radicals (O\(^\cdot\), atoms with one unpaired electron) are formed and organic contaminants are chemically oxidized.

\[
\text{O}_2 + e^- \rightarrow \text{O}^- + \text{O}^- + e^- [\text{+ organic}] \rightarrow \text{CO}_2 + \text{H}_2\text{O} + e^- 
\]

The compounds generated by either reaction are volatile and pumped away by the vacuum system and exhausted without leaving any traces.[8, 9, 10, 11]

References

10. R.N Booth, P.E Ongly, Plasma treatment in hybrid and conventional electric assemblies, I.V. Products, Limited, Abercarn, Newport, Gwent, NP1 5AR, UK.
11. S.L Buckles, Use of argon plasma for cleaning hybryd circuits prior to wire bonding, ISHM '87 Proceedings, pp 476.
Appendix 3.

X-ray photo electron spectroscopy (XPS)

In order to determine the composition of the contamination of stainless steel surfaces in several stages of the cleaning process, XPS measurements have been carried out. The principle of this measuring technique is based on the photo-electric effect. This means that light or short-wave electromagnetic beams are able to release electrons from their orbits of neutral atoms. XPS measurements are carried out at an ultra-high vacuum of $10^{-10} - 10^{-11}$ Torr. The used radiation comes from a monochromatic (e.g. aluminium) source. The kinetic energy of the electrons released from the specimen is accurately measured by an electron spectrometer (Fig. 5).

The binding energies of all electrons in the atomic cores (K, L, M, etc.) of each kind of atom are very strict and well-defined.

![Diagram](image)

**Figure 5.** The electron spectrometer, which measures the amount and kinetic energy of freed electrons from the specimen. By this method the kind and relative amount of specimen can be defined.

The principle of XPS measurements is based on this difference in electron binding energies. The electrons released from the specimen by the monochromatic X-ray beam are selected (scanned through the energy spectrum) by an electron spectrometer and counted by a detector. The peaks in the energy spectrum are identified, which reveals the chemical composition of the specimen. The relative intensity of the combinations on
the surface can be determined by comparing the heights of the separate peaks in the spectrum [12, 13, 14].

References
12 Fysisch-chemische methoden voor materiaalanalyse kollegedictaat (mt 45) 1979, diverse docenten, Laboratorium voor materiaalkunde, University of Delft, Holland.
Appendix 4.

Differential (heat flux) scanning calorimetry (DSC)

In order to determine the state of polymerisation of an adhesive sample after it has undergone several treatments, a research method called DSC has been used.

DSC is a technique that measures the difference between the heat fluxes of an investigated material (e.g. a polymer) and a reference material while both are subjected to the same (controlled) temperature program. The materials are locked up in a small aluminium sample can that is placed on a platter in a small oven.

(Left) Figure 6 The thermal analysis system, (S): sample (R): reference, and thermocouples.
(Right) Figure 7 A hypothetical presentation of a DSC thermogram.

This set up is shown in Figure 6. The measured voltages of the thermocouples are amplified by a differential amplifier, and written on a recorder as a function of heating. Figure 7 shows a simplified hypothetical presentation of the created graphs.

The measurements supply important data that can be used to determine the state of polymerisation of an investigated sample. Two of the phase transitions are detectable:
- The transition between amorphous and rubber-like behaviour of the polymer, the so-called glass transition temperature ($T_g$). On an atomic scale, this temperature indicates the freedom of the polymer chains to rotate around the head chains. The value of $T_g$ is dependent on the flexibility of the chain molecules. The less flexible, the higher $T_g$. Above $T_g$ the polymer will absorb more energy because of the rotation that has started. Consequently, the baseline in Figure 7 will start to fall.
The level of polymerisation of the adhesive indicated by the height of the second peak of Figure 7. This makes it possible to detect how much polymerisation has already taken place in the adhesive bond. It has been experimentally found that the results with regard to the adhesive’s $T_g$ and the surface below the exothermic peak were of special interest, because they reveal the state of polymerisation depending on e.g. heat treatment and storage circumstances [15, 16, 17, 18].

References

15 B.A. Schipper, Thermische analyses van polymeren, Techniek 34, Nr4, pp 200-212, 1979.
16 G. vd Plaats, H. Soons, Thermische analyse en enkele theoretische achtergronden, Lab Instrum., Nov. 1982, pp 97- e.v..
Appendix 5.

Finite element analysis

The optimal adhesive bond can only be constructed when small changes of the final bond strength caused by geometry and material parameters are known. Finite element analysis (FEA) can have a great influence on this design, as it can determine the stress in constructions as a function of applied forces and boundary conditions.

The analyzed structure is divided into elements in which the unknown variable (displacement, stress or strain) is expressed by the interpolation functions based upon its value in discrete points, called integration points. These points are defined inside each element. The values of these integration points determine together with the interpolation functions the global value of the variable throughout the structure. It will therefore be clear that the amount of integration points and thus the number and size of the elements ultimately determine the accurateness of the final solution.

The most important disadvantage of FEA is the influence of the size and shape of the element chosen on the final results. [19, 20, 21]

References

Appendix 6.

Elementary processes in adhesive bond formation.

The establishment of an intimate molecular contact is a necessary, though sometimes insufficient condition for the developing of strong adhesive joints. This means that the adhesive must be able to spread all over the solid surface. To meet this condition, a liquid adhesive must:
- display a zero or near-zero contact angle,
- have a viscosity that is relatively low,
- be brought into contact with the substrate in such a way that it assists in the displacement of any entrapped air.

The contact angle

Quantitatively, wetting can be defined by a liquid drop in equilibrium on a (horizontal) solid surface (Fig. 8).

![Surface wetting diagram]

Equilibrium: \( \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \alpha \)

**Figure 8 Determining the contact angle \( \alpha \).**

The surface tension at the three phases: the solid/liquid (S-L), solid/vapour (S-V), and liquid/vapour (L-V) points are defined by Young's equation [3, 4], which relates these terms to the equilibrium contact angle \( \alpha \) and can be written as:

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \alpha
\]

(1)
\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \alpha \]  

(1)

The term \( \gamma_{sv} \) represents the surface free energy of the solid substrate. When \( \alpha > 0 \) the liquid is non-spreading. If \( \alpha = 0 \) the liquid wets the solid entirely and spontaneously spreads over the surface at a rate depending on factors such as the liquid viscosity and the roughness of the solid surface. Therefore, for spontaneous wetting to occur:

\[ \gamma_{sv} \geq \gamma_{sl} + \gamma_{lv} (\alpha = 0, \cos \alpha = 1). \]  

(2)

The adhesion energy \( (W_A) \) is defined as the energy that is released when 1 cm\(^2\) of adherent surface and 1 cm\(^2\) of liquid (e.g. an adhesive) make contact:

\[ W_A = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \]  

(3)

Substituting equation 1 into equation 3, we find:

\[ W_A = \gamma_{lv}*(1 + \cos \alpha) \]  

(4)

This means that the adhesion energy is maximal when \( \cos \alpha = 1 \), or \( \alpha = 0^\circ \); then:

\[ W_A = 2\gamma_{lv} \]  

(5)

The measuring of the contact angle (e.g. with water) provides a good quantitative indication of the amount of organic surface contamination. The more surface contamination, the lower the surface free energy of the solid, and the higher the contact angle that is measured.

[22, 23]

References

Acknowledgements


Paranimf: Just Herder and Jan van Doorn with girl friends: Monika and Mieke.

At last but not least, my girlfriend Marianne Groot who has supported me during the last four and a half years, and who did the lay-out of this manuscript.

and all those others, without whom...
Curriculum Vitae


Hierna wilde ik geneeskunde gaan studeren, maar een loterij verhinderde dit. Als kind had maakte ik via mijn vader al vroeg kennis met de natuurkundige wereld van het Kamerlingh Onnes Laboratorium in Leiden alwaar ik uren lang voor muizen gaatjes doorbracht. Op later leeftijd ging de techniek zelf mij intresseren, hetgeen resulteerde dat ik mij uiteindelijk inschreef voor de studie natuurkunde (1978).

In 1985 studeerde ik af met als pre-kandidaat bijvak Biofysica, en postkandidaat bijvak vakdidactiek. Ik had inmiddels mijn twee en een half jaar stage bij Prof. Dr. G. Frossati in de cryogene techniek volbracht waar ik bijzonder veel praktische ervaring heb opgedaan.


Inmiddels was ik overeengekomen, om als A.I.O. (assistent in opleiding) onderzoek te gaan verrichten bij de vakgroep instrumenten, een onderafdeling van de faculteit Werktuigbouw / Maritieme techniek van de Technische Universiteit Delft. Ik werkte tussentijds tegelijk als adviseur bij Stork Product Engineering, tijdelijk als docent wiskunde op de Haagse Hogeschool voor Techniek, en s’zomers als reisbegeleider.
List of Publications

Articles:

UV/ozone cleaning a convenient alternative for high quality bonding preparation

Investigation of design parameters (in press)
The int. Journ. of Adhesion and Adhesives.

Lijm: de beste keuze (in press)
Mikroniek, Postbus 80.004, 3508 TA Utrecht, Holland.

UV/ozone als reinigings alternatief (in press)
Mikroniek, Postbus 80.004, 3508 TA Utrecht, Holland.

Optimalisatie van een cilindrische lijmverbinding (in press)
Mikroniek, Postbus 80.004, 3508 TA Utrecht, Holland.

Related articles:

Assistent in opleiding
M. de Boo, dinsdag 8-5-1990, NRC Handelsblad, Wetenschap & Onderwijs, pp4, Postbus 824, 3000DL Rotterdam, Holland.

UV-straling & ozon maakt oplosmiddelen overbodig
M. de Boo, Delft Integraal, 5/6-92, pp 21-24, Delft University of Technology, kamer 1011, Julianalaan 134, Postbus 5048, 2600GA Delft, Holland.

Solvents replaced by UV-radiation and ozone, (Adhesive bonding; good cleaning is half the battle) (in press)
M. de Boo, Delft Outlook, DO-93-2, Delft University of Technology, Postbus 5048, 2600GA Delft, Holland.