



**KTH Chemical Science  
and Engineering**

# Electrically Induced Adhesive Debonding

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## Abstract

Electrically induced adhesive debonding is a process where an adhesive can be debonded at command with help of an applied voltage. To make this process function, the adhesive is bonded between two metal substrates. In this study an epoxy adhesive is adhered between two aluminium foils forming a laminate structure. The adhesive is made ionically conductive by an addition of an ionic liquid before the curing. This arrangement forms an electrochemical cell, where the metal substrates act as the electrodes while the ionically conductive adhesive acts as the electrolyte. When a voltage is applied over the laminate, a current passes due to electrochemical reactions at the electrode interfaces and ionic transport in the adhesive.

This type of material can potentially be used in a wide range of applications. This includes making adhesive joints in automotives to both reduce the total weight but also to simplify the disassembly after end-of-life, enabling an inexpensive recycling process. Another potential use for debondable adhesives is within consumer packaging. Here it could be possible to pack and transport goods using less packaging material as well as making the handling easier.

The aim of this study was to increase the understanding about the processes leading to debonding. This knowledge is important in the development of new types of debonding adhesives. In this study, the commercial laminate Sinuate® was used as a model system. The experiments were focused on the electrochemical behavior and were performed mainly using galvanostatic polarization and electrochemical impedance spectroscopy. Information about the chemistry of debonding was collected with techniques such as scanning electron microscopy (SEM), mass spectrometry (MS) and Raman spectroscopy. The debonding did always take place at the anodic interface, separating the adhesive and the anode aluminium foil. It was found that the total cell resistance increased drastically during polarization, and that essentially all of this increase originated within the anodic half of the laminate. Examining the resistance behavior with EIS, it was found that the increase in total resistance was reversible.

The anodic electrochemical reaction during polarization was determined to consist mainly of an oxidation of aluminium, while the major reaction at the cathodic interface was reduction of water into hydrogen. The debonding process, which took place at the anodic interface, could be related to reaction products formed in the polarization process. These products grew out from the anodic aluminium surface into the adhesive. A debonding mechanism is proposed where these products induce an increase in the adhesive volume, causing stresses at the interface which ultimately result in debonding.

## Sammanfattning

Elektriskt framkallad delaminering är en process som gör att en limfog kan fås att släppa på kommando med hjälp av en pålagd elektrisk spänning. För att processen ska fungera måste limmet vara bundet till två metallytor. I den här studien används ett epoxylim, bundet mellan två folier av aluminium, vilket bildar en laminatstruktur. Limmet gjordes jonledande genom en tillsats av en jonvätska innan härdningen. Detta laminat bildar en elektrokemisk cell, där metallytorna agerar som elektroder och limmet som elektrolyt. När en elektrisk spänning läggs över laminatet, uppstår en elektrisk ström till följd av elektrokemiska reaktioner vid elektrodytorna och jontransport i limmet.

Dessa material skulle kunna användas inom ett brett spektrum av användningsområden. Exempel på detta är användandet av limmade fogar i fordon, vilket skulle både minska fordonens vikt och underlätta demonteringen efter livscykelns slut. En förenklad demontering skulle resultera i en billig återvinningsprocess. Andra exempel på användningsområden för elektriskt släppbara limmer är konsumentförpackningar. Inom detta område skulle varor kunna packas med mindre mängd förpackningsmaterial och hanteringen under transport och uppackning skulle kunna förenklas.

Målet med det här arbetet var att öka förståelsen kring processerna som leder till delaminering. Dessa kunskaper är viktiga för utvecklande av nya sorter av elektriskt släppande limmer. Det kommersiella laminatet Sinuate® användes som ett modellsystem. Experimenten fokuserades kring elektrokemin och utfördes främst med galvanostatisk polarisering och elektrokemisk impedansspektroskopi (EIS). Information om släppprocessens kemi inhämtades med tekniker som svepelektronmikroskopi (SEM), masspektrometri (MS) och Raman-spektroskopi. Det upptäcktes att delamineringen alltid skedde i det anodiska gränsskiktet, på så sätt att aluminiumfolien och limytan separerades. Polarisationsprocessen ledde till en drastisk ökning av den totala cellresistansen och större delen av denna härrörde sig från den anodiska delen av laminatet. Denna ökning i resistans fanns vara reversibel genom att använda EIS. Den elektrokemiska reaktionen vid anoden bestod till största delen av en oxidation av aluminium, medan den katodiska reaktionen bestod av en reduktion av vatten till vätegas. Processerna som ledde till släpp i det anodiska gränsskiktet kunde härledas till SEM-resultaten, där reaktionsprodukter observerades. Dessa produkter växte ut från aluminiumytan och in i limmet. En släppmekanism föreslås, där de bildade produkterna orsakar en volymsökning i limmet, vilket leder till spänningar i gränsskiktet som i sin tur gör att limmet släpper.

## List of papers

- I.    **Experimental Investigation of Electrically Induced Debonding of Adhesive**  
S. Leijonmarck, A. Cornell, C.-O. Danielsson, T. Åkermark, B. Brandner and  
G. Lindbergh  
Manuscript, submitted to *Journal of Applied Electrochemistry*
  
- II.   **Electrochemical Characterization of Electrically Induced Adhesive Debonding**  
S. Leijonmarck, A. Cornell, C.-O. Danielsson and G. Lindbergh  
Manuscript

### Division of work between authors

In paper I, the mass spectrometry measurements, calculations and part of the interpretation were made by T. Åkermark. The measurements using Raman spectroscopy were carried out by B. Brandner. All other experiment and the writing were performed by me. For both papers, A. Cornell, G. Lindbergh and C.-O. Danielsson acted as supervisors.



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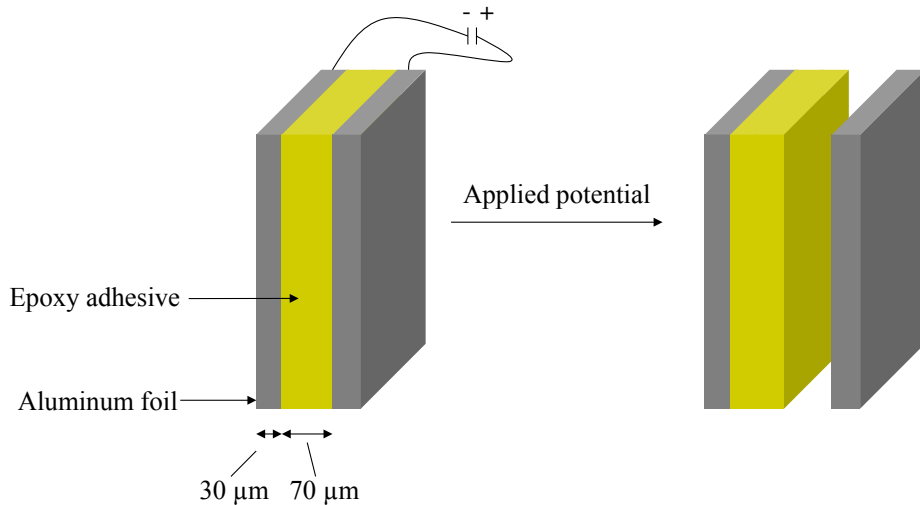


# 1. Introduction

## 1.1 Electrically induced debonding of adhesives

The background story to debonding adhesives with electricity starts with a problem that US Air Force (USAF) had. They wanted to attach monitoring devices on the hull of aircrafts, use the devices during flight and then remove them without damaging the aircraft. All technical solutions up to then fell off when the aircraft flew faster than Mach 2. EIC Laboratories, a research company in the US, was confronted with the problem by USAF and the result was a functional adhesive. This adhesive was strong enough to allow flying above Mach 2 with the measuring device still attached and when the measurements were done, the device could easily be removed with help of an electric voltage over the adhesive [1]. Since then, EIC Laboratories has patented a number of formulations for functional adhesives [2-6]. Two of those formulations are marketed, at the time of publication, as E4 and M4, which both are epoxy-based [7]. Following this, Stora Enso, a Finnish-Swedish paper, wood and packaging company, developed a laminate product, based on an epoxy adhesive, named Sinuate®, with a release functionality suited for packaging applications.

The typical set-up for this technique is a laminate structure, where two aluminium foils are joined by an epoxy adhesive-mixture containing additives creating ionic conductivity. The laminate thereby comprises an electrochemical cell where the foils work as electrodes and the adhesive as electrolyte (fig. 1). When a potential is applied over the laminate, a current passes through the adhesive, causing a debonding at either the anodic, for Sinuate®, or the cathodic interface. The debonding process works for a number of metals, including aluminium, steel, low alloy steel, stainless steel, copper and titanium [1].



**Figure 1 – The debonding process**

## **1.2 iPack**

This study was performed within the framework of iPack Vinn Excellence center. The general goal of iPack is to develop the field of intelligent packaging. An important aid to reach this intelligence is by using radio frequency identification (RFID). RFID is a wireless communication system, based on tags which are remotely read by a reader through radio waves. In a passive system, the tag is powered by the incoming radio waves emitted from the reader, while an active system has a battery included in the tag [8]. The RFID technique can thus be a part of a packaging system that can communicate with the surroundings. This, in combination with a debonding adhesive, is among the features studied within iPack. A package is constructed so that it can be opened remotely when a correct identification is sent to the included passive RFID tag. Since a voltage over 30 V is desired for fast debonding of the Sinuate® adhesive, many standard batteries in series are needed. This is, however, unfeasible due to the large increase in the size and weight of the opening device. Instead, a charge pump is used. This pump is a DC-DC converter, where an incoming voltage of 2.5 to 10 V is converted to a 30 V output. Such a device can, as an example, be used in a secure medicine dispenser, where only the desired number of pills is dispensed according to ordination. [9]

## **1.3 Applications**

Using debonding adhesives in the area of packaging could possibly reduce the amount of packaging material as well as make the handling of consumer products easier during shipping and unpacking. This can be made by adhering the products to each other, rather than packing them in boxes. The products can then be handled as a bulk instead of individually, saving time during unpacking. At the given store shelf, a current makes the products available for purchase.

Debondable adhesives also find potential applications in a number of different fields outside the packaging field. The general use of adhesives has increased in the automotive industry, due to the introduction of lightweight composite materials, which are difficult to bond with traditional techniques, such as welding. [10-11] ‘Design for disassembly’ is an important topic in the automotive industry where not only the design for functionality is considered, but also the possibility for an uncomplicated deconstruction of the automobiles [12]. At the same time, regulations regarding end-of-life material recycling are to be introduced. An example of this is the EU End of Life Directive 2000/53/EC, which demands that vehicles produced must be recyclable to 85 % by weight [13]. This altogether opens up a huge market for debonding adhesives.

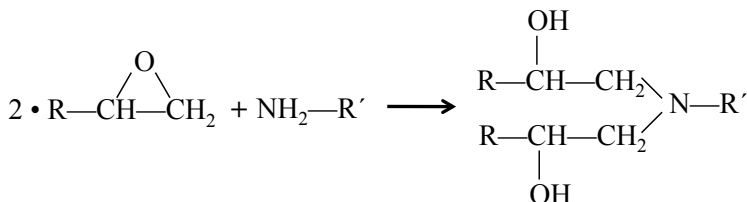
Using debondable adhesives to fasten collars for animal tracking in the wild enables a robust holder for tracking equipment. When the tracking is finished, a signal to the attached power source makes a current pass through the adhesive and the animal is freed from the collar without any need for sedation [14]. These are only a few examples, since stable bonding coupled by debonding at command could be used in a multitude of applications.

## 1.4 Adhesion

Adhesion is a complex phenomenon, describing the bonding between two different substances. The origin of the adhesion forces can roughly be described by three theories, summarized below. Mechanical interlocking is an adhesion theory which addresses the bonding as due to purely mechanical forces. These mechanical forces stem from the locking that takes place when the adhesive penetrates a substrate surface. This type of bonding demands a rough substrate surface to be significant. The second adhesive theory is based on molecular bonding between the adhesive and the substrate. This theory sum up the influence of both intramolecular forces, such as ionic, covalent and metallic bonding, and intermolecular forces, such as dipole-dipole and van der Waal bonding. These forces need short distances and close contact between the adhesive and substrate. The third theory is based on thermodynamic interactions at the interface between adhesive and substrate. The adhesion is formed by a minimization of the surface energy and not by actual bonding at the interface. The molecular bonding theory is the most accepted way of describing adhesion, even though the area is debated. [15-16]

## 1.5 Epoxy adhesive

The epoxy adhesive is a thermosetting polymer and is usually a mixture of polymer chains containing epoxy groups and a hardener containing an amine group. The curing process (fig. 2) creates a heavily crosslinked matrix [17].



*Figure 2 – The curing process of epoxy adhesives*

## 1.6 Delamination techniques

Electrochemistry is not the only technique for debonding adhesive. The other methods can be divided in mechanical, thermal and chemical debonding. Mechanical debonding means that a mechanical force is applied to the adhesive, leading to adhesive or cohesive rupture. The key issue is to design a system where a relatively small force is needed to debond, without losing the mechanical properties during use of the product. An example of such a debonding solution is Roll Out 2000 [18], where car windscreens are easily removable due to a metal wire inserted between the window frame and the window itself. Another example of mechanical debonding is 3M's Post-It notes, which stick to a given surface but are easy to remove by hand [19].

Thermal debonding is based on the concept that adhesives may lose their adhesion or cohesion when heated. Two examples illustrate the technique. Microspheres filled with gas, exploding material or other volatile compounds, added to the adhesive before curing, swell/explode when subjected to heat. This causes the adhesive to crack and therefore release [20]. Another approach is the incorporation of electrically conductive materials into the

adhesive. When a current passes through these materials, heat is produced from the electrical resistance causing the adhesive to fail. The conductive materials can be anything from powders to nets or sheets [21]. Reworkable adhesive systems, i.e. with adhesive reattachment to substrate after debonding, have been also been developed using thermal debonding. An example of this is a thermoplastic polymer covalently bonded to a thermoset polymer network. Below the glass temperature,  $T_g$ , of the system the polymer is a hard material which shows good adhesive properties. Going above  $T_g$ , the material softens and loses its adhesive properties. But, upon cooling, the material regains the previous adhesive properties [22].

An example of chemical debonding of adhesives relies on a mixture of an organic adhesive and an oxidizer, such as ammonium perchlorate. Once the already-applied adhesive is heated above the ignition point of the system, the destruction of the adhesive causes a debonding. [10]

Comparing these techniques with electrochemical debonding is not straightforward. It is difficult to claim that a given technique is better than another, there just are applications that fit the technique better. This is exemplified by a customer packaging in need of a controlled debonding solution. In this case, an electrochemical debonding might be the best solution, since a current can be passed in a controlled fashion, without damaging the goods inside. Thermal debonding might, on the other hand, destroy the packaged goods.

### **1.7 Previous work on electrically debonding adhesives**

Some studies concerning the processes behind the debonding have been performed at Stora Enso. A diploma work at master level was aimed at investigating a debonding adhesive produced by EIC Laboratories with Auger electron spectroscopy (AES) [23]. This study found elevated concentrations of phosphorous and fluorine on the anodic aluminium substrate surface after polarization. The penetration into the bulk aluminium of said elements was also higher than for the unpolarized case. The phosphorous and fluorine arise from the salt used to increase the conductivity in the adhesive, ammonium hexafluorophosphate. When examining the anodic epoxy surface after polarization, traces of aluminium were found. Höglblad presents the theory that the electrochemically formed aluminium ions form salts with the free fluorine ions in the adhesive. This undermines the surface and leads to debonding. The electrochemistry of the EIC adhesive and to some extent Sinuate® was studied. It was found that the anodic interface was changing from alkaline to acidic during polarization, for both types of adhesives. It was also found that samples stored in 0 % relative humidity (RH) showed no signs of delamination after polarization. For the EIC adhesive, it was determined that aluminium fluoride was formed following the polarization [24]. No heating during polarization of EIC adhesives has been detected [1] so, as a starting point, a debonding caused by an increase in temperature was not expected. Instead, electrochemistry seems to be very important for the debonding process.

The mechanical properties of unpolarized Sinuate® laminates have been examined at Stora Enso [25]. The tensile strength (ASTM 2095) was 8 MPa, the shear strength (ASTM D1002) was 3.5 MPa and the peel strength (Y-peel) was 8 N/cm.

## **1.8 Aim of the work**

The main aim of this work is to understand the mechanisms behind the processes, in which an adhesive is debonded with help of an electric current. This understanding is essential for the further development of the electrically debondable adhesives. For widespread use, the adhesives need to be tailored to meet the demands of different applications. Some applications may rely on adhesives capable of withstanding outdoor conditions with large variation in temperature and humidity. Other applications may need an adhesive with food-grade classification or an adhesive of a specific kind of chemistry. It would also be beneficial to be able to perform fast debonding at lower voltages, such as a few volts instead of the 30 to 50 volts that are used today.

The written material covering electrically induced debonding of adhesives [1-6] presents information about the functionality but no open literature, besides the mentioned work at Stora Enso, on the mechanisms leading to debonding has been found. Furthermore, few studies on electrically induced delamination of polymers from metals are found in the open literature. One example reports on removal of paint from metal bridges, using an external electrolyte and an applied potential over the electrolyte and the paint. The cause for that debonding is believed to be an increase in pH together with hydrogen evolution [35].

With this as background, a fundamental study of the debonding was needed, covering all from electrochemical to mechanical aspects of the processes.

## 2. Materials and methods

### 2.1 Materials and equipment

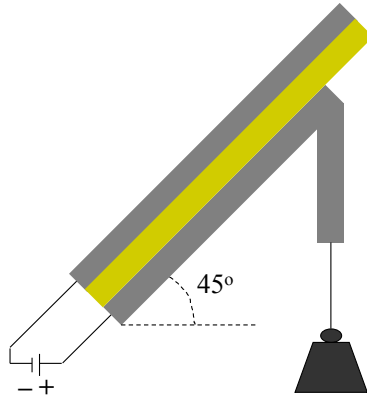
As a model system for debonding adhesives, Sinuate® laminates from Stora Enso were used. Sinuate® sheets are premade laminates, consisting of two aluminium foils (30  $\mu\text{m}$  each) joined by a 70  $\mu\text{m}$  layer of epoxy adhesive. These laminates are based on the ElectRelease technology described in the introduction. The laminates were prepared by dipping a fiberglass net (1080 style fabric, 23 % void area) in an adhesive mixture (73.4 wt% D.E.R. 652 from DOW as epoxy component, 2.3 % dicyandiamide as curing agent, 0.125 % 2-methylimidazole as accelerator, 18.5 % 1-ethyl-3-methylimidazolium ethyl sulfate (EMIM-ES) as ionic liquid, 5.5 % polyethylene glycol 400 aiding the conductivity and 0.5 % Gransurf 77 from Grant Industries as emulsion agent) and then pressed and heated during curing.

To achieve a range of adhesive water content, laminates were stored above the liquid surface in beakers with saturated salt solutions at room temperature (LiCl 11 % RH (relative humidity),  $\text{CaCl}_2$  29 % RH and  $\text{Mg}(\text{NO}_3)_2$  53 % RH) as well as in a desiccator (0 % RH), leading to different water contents in the cured adhesive [13].

The galvanostatic polarization experiments, where a potential is measured while a constant current is passed through the cell, were performed using a PAR 273A potentiostat, EG&G Princeton Applied Research and the electrochemical impedance spectroscopy (EIS) experiments were performed using an AUTOLAB 302N potentiostat. The frequency range used for all EIS experiments was 100 mHz – 100 kHz.

### 2.2 Controlled debonding – Fall rig

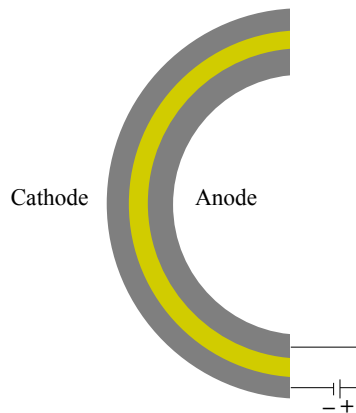
The debonding process is gradual, so the adhesive strength decreases over time with no defined point of debonding. A small mechanical force is always needed to achieve total debonding. One of two methods to achieve a well-defined and complete adhesive debonding was a set-up where a weight was applied to the laminate (fig. 3). The laminate, with a width of 1 cm, was fixed to a surface at 45° inclination. A part of the anodic aluminium foil was peeled off and a weight of 200 g was added to this loose end. This weight is equivalent to  $\sim 2 \text{ N/cm}$ , leading to a debonding at approximately a quarter of the bond strength at 8 N/cm [25]. The laminate was then polarized continuously, resulting in a release at the anodic interface when the adhesive forces were lower than the force acting by the added weight. This set-up was used for laminates stored in 29 % RH at current densities of 0.050  $\text{mA/cm}^2$  and 2  $\text{mA/cm}^2$ .



**Figure 3** – The rig set-up for measurements with controlled debonding

### 2.3 Controlled debonding – Laminate bending

A second way of realizing debonding was to bend the laminates prior to polarization. By forcing a free-standing laminate into a half-cylinder shape, the anodic interface released during polarization. However, this release only takes place if the anode faces inwards the center of the cylindrical arrangement (fig. 4). The bent laminates were photographed over a graded paper to determine the sample circle diameter, followed by polarization with  $0.050 \text{ mA/cm}^2$  until the first signs of debonding. This debonding then starts at an edge of the laminates.

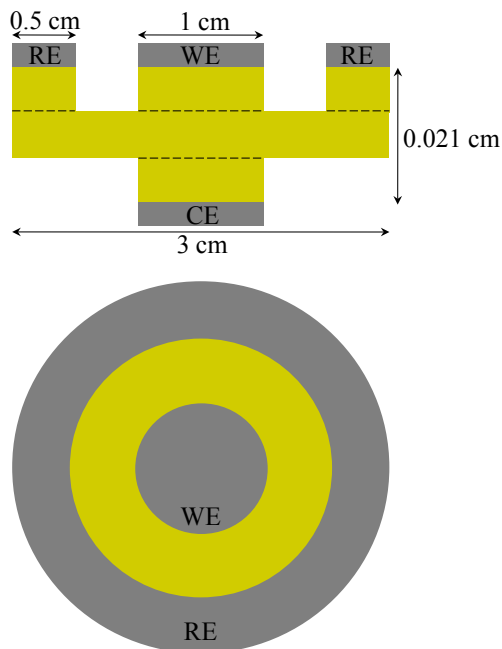


**Figure 4** – The set-up for controlled debonding of bent laminates

### 2.4 The three-electrode cell

Setting up a three-electrode cell where the electrolyte is solid is not straight-forward, and when the electrolyte also has high resistance, problems with especially reference electrode placement arise [26-30]. An acceptable solution to this problem, which uses a circular quasi-reference electrode surrounding the working electrode, is shown in figure 5 [28-29]. This

solution was analyzed for the present system by modeling a three-dimensional system with primary current distribution. The cell was assembled with circular pieces punched out from a Sinuate® laminate. A piece with a diameter of 3 cm had both aluminium foils peeled off, so that only the adhesive remained. The working and counter electrodes were then created by two identical pieces, where one of the foils was removed from each piece. These pieces, with 1 cm in diameter, were then placed centered on both sides of the adhesive surface. The key part of the placement is to ensure that the working electrode is not misplaced in relation to the counter one. The quasi-reference electrode was then punched and placed to surround the working electrode. Prior to measurements, a weight was added on top of the cell to assure good physical contact at the adhesive-to-adhesive interfaces.



**Figure 5** – The three-electrode set-up (not to scale). Dashed lines indicate two joined adhesive surfaces. RE – reference electrode, WE – working electrode, CE – counter electrode. Top: Cross-section of the set-up. Bottom: Top-view of the set-up

## 2.5 Other experimental methods

Besides the techniques described above, a number of experimental methods were used to characterize the debonding process, including scanning electron microscopy (SEM) together with an appended energy-dispersive spectroscopy (EDS) detector, in-situ mass spectrometry and Raman spectroscopy. Further details about the use of these methods can be found in the attached manuscripts.



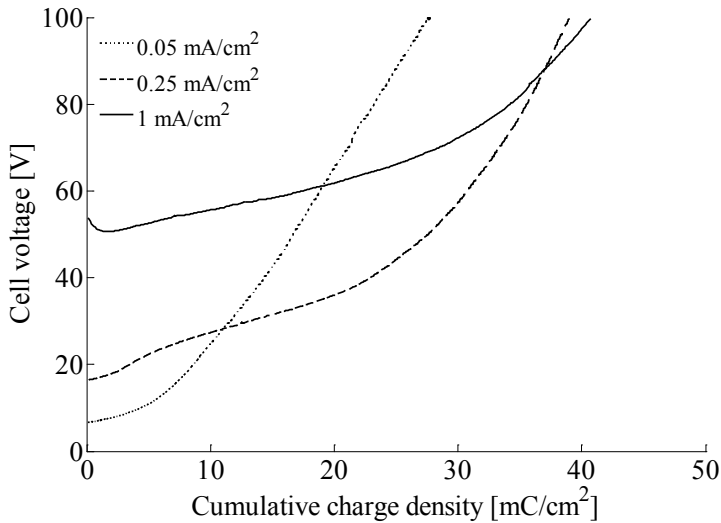
### 3. Results and discussion

#### 3.1 Electrochemical characterization

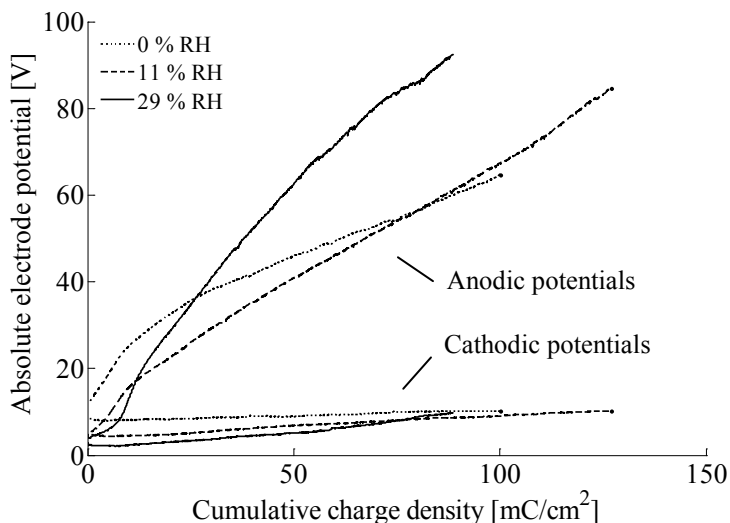
Galvanostatic measurements make it possible to track the potential over both time and charge during polarization. Using this electrochemical tool together with a three-electrode set-up, information about potential changes at individual electrodes can be harvested, instead of information from the whole cell.

Both three-electrode (fig. 5) and two-electrode set-ups (the unaltered laminate) were used, to measure the galvanostatic potential response during polarization of the adhesive laminates. The galvanostatic measurements showed that the cell potential increased (figs. 6-7) as a constant current was passed through the laminate. This increase was shown to be located almost entirely in the anodic half of the laminate (fig. 7), meaning that the electrochemical reactions at the anodic interface result in a resistance increase.

The potential/charge curves consist of two regions, differentiated by a difference in  $dE/dQ$  (fig. 6). The transition from one  $dE/dQ$  to the other took place at a higher charge density when using a higher current density. The second slope is believed to be related to a rupture between adhesive and aluminium, so it seems that not only charge but also time is important to the debonding process.

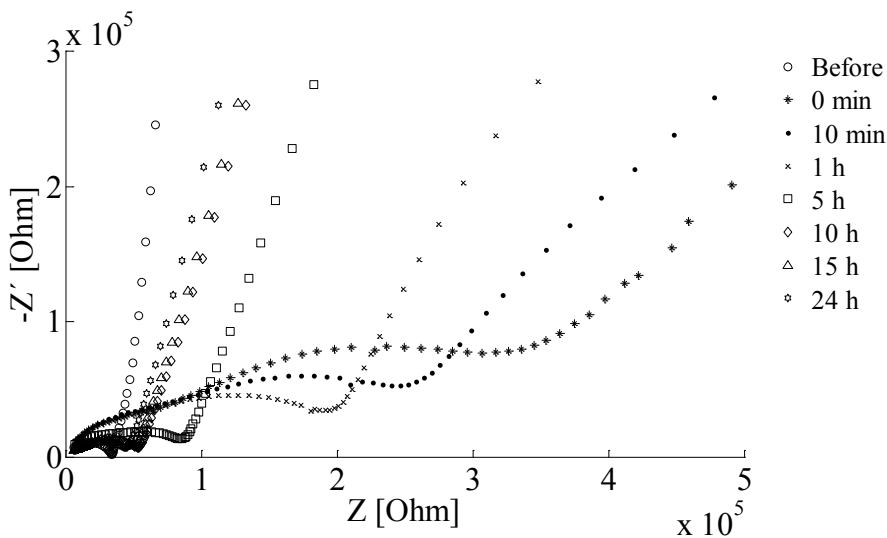


**Figure 6** – Galvanostatic two-electrode measurement at different current densities. Samples stored at 29 % RH

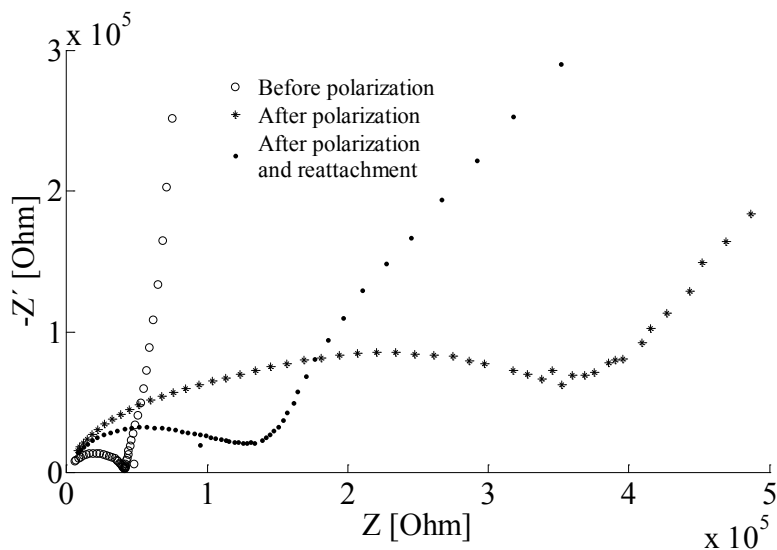


**Figure 7** – Galvanostatic three-electrode measurement of samples stored at various air humidities. The current density was  $0.050 \text{ mA/cm}^2$

Electrochemical impedance spectroscopy (EIS) was used to examine the laminates after polarization of  $50 \text{ mC/cm}^2$  using  $1 \text{ mA/cm}^2$  (fig. 8). EIS was performed directly after polarization and then in steps up to 24 hours. The measurements immediately subsequent to polarization showed, in accordance with the galvanostatic measurements (fig. 6), that the impedance increases drastically compared to the impedance before polarization. The following measurements show a gradual relaxation in impedance behavior over time. After 24 hours, the EIS characteristics had reverted back close to the pre-polarization ones. That is, the processes leading to the large increase in impedance during polarization appear to be almost completely reversible. It was, however, difficult to assess the origin of this reversibility based on these measurements. But, by performing an EIS experiment where the anode was removed and immediately reattached after polarization (fig. 9), it could be seen that a large part of the impedance reversibility could be created almost instantaneously. Since this reversibility was formed both over time in contact with the anode and immediately without contact with the anode, it was likely that the impedance increase was formed by a mechanical phenomenon, such as a change of the adhesive volume.

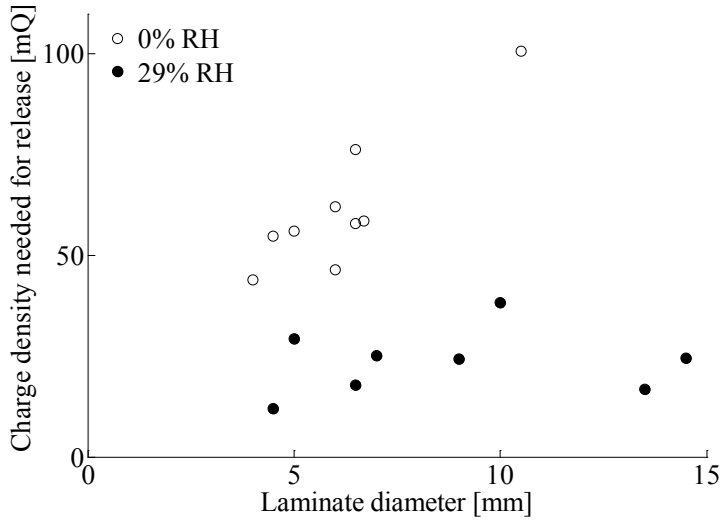


**Figure 8** – EIS before and after polarization of  $50 \text{ mC/cm}^2$  using  $1 \text{ mA/cm}^2$  followed by a range of relaxation periods.



**Figure 9** – EIS before and after polarization of  $50 \text{ mC/cm}^2$  using  $1 \text{ mA/cm}^2$  followed by a measurement where the anodic aluminium foil had been removed and immediately reattached

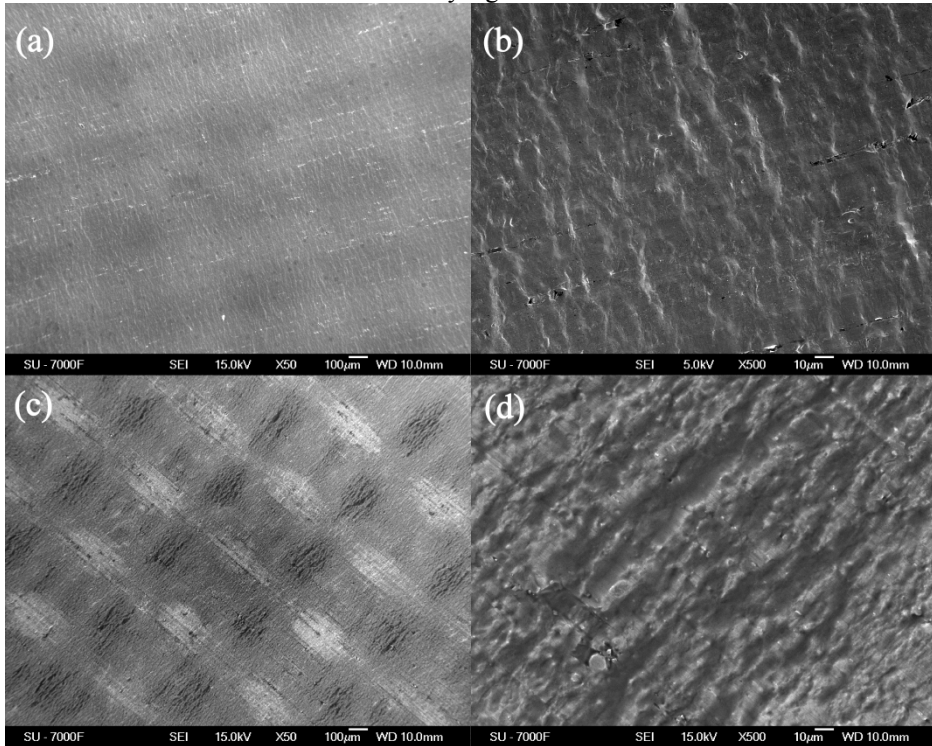
The debonding process progresses gradually during polarization. To achieve total debonding after polarization, a small mechanical force is always needed for a flat laminate. This behavior makes it hard to correlate debonding with other parameters. Two methods were therefore used to create a well-defined debonding with only polarization as stimulus; a weight applied to the laminate and bending of the laminate. The experiments with an applied weight were performed at two current densities,  $0.05 \text{ mA/cm}^2$  and  $2 \text{ mA/cm}^2$ . The resulting charge densities needed for debonding were  $2\text{-}2.5 \text{ mC/cm}^2$  when applying  $0.05 \text{ mA/cm}^2$  and  $6\text{-}7.5 \text{ mC/cm}^2$  when applying  $2 \text{ mA/cm}^2$ . However, when a charge density of only  $2.5 \text{ mC/cm}^2$  was passed through a laminate at  $2 \text{ mA/cm}^2$ , delamination still occurred but it happened 20 seconds after the current interruption. It is then evident that the electrochemical reactions, by themselves, are not responsible for the debonding, but the debonding is a multi-step process, where the latter steps are delayed at high current densities above  $2 \text{ mA/cm}^2$ . These findings do also correlate with the findings in figure 6, where the shift in the  $dE/dQ$  took place at a higher charge density when using a higher current density. Using the second debonding technique, laminate bending, the effect of air humidity during storage was examined. The bending of a laminate into a free-standing curved shape is believed to introduce enough stresses at the interfaces, especially at the inside one, for a complete debonding to occur without additional external mechanical force. It was found that the charge density needed for debonding depended on the water content of the adhesive (fig. 10). Laminates stored at higher humidity debonded at a lower charge density than drier laminates. That is, an increased amount of water in the laminate seems to aid the processes leading to debonding.



**Figure 10** – Charge density needed for self-debonding with the anodic side bent inwards at different diameters. Current density:  $0.050 \text{ mA/cm}^2$ .

### 3.2 Chemical characterization

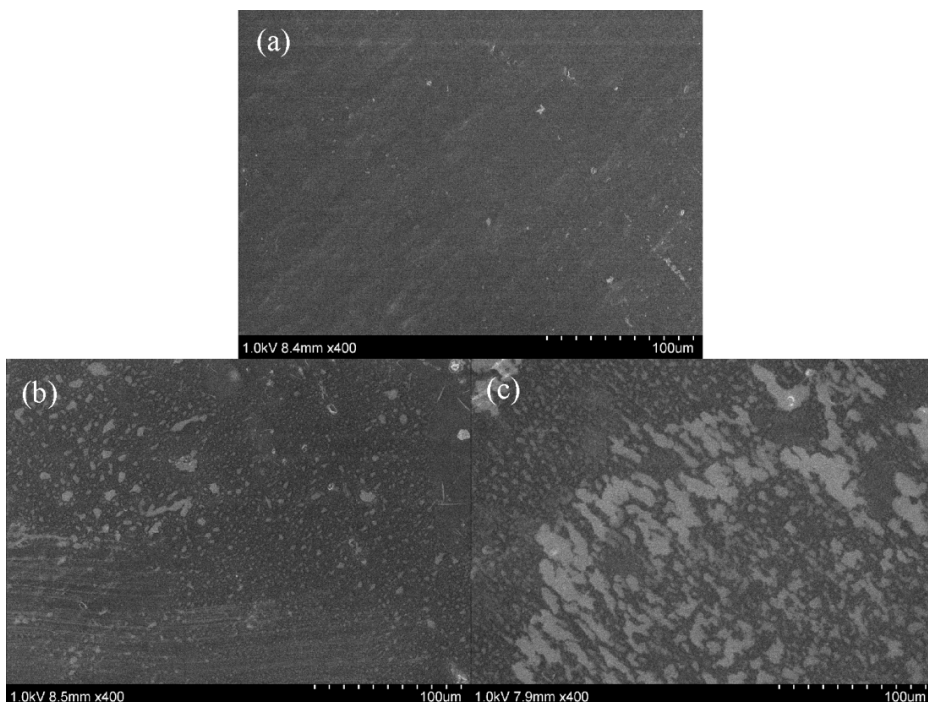
To get a better understanding of the debonding process, the electrochemical measurements were complemented by chemical and spectroscopic techniques. A SEM study was made in attempt to obtain more insight to the processes behind debonding, starting with a polarized anodic aluminium surface. An unpolarized aluminium surface (fig. 11a-b), torn from the adhesive, showed a uniform composition. Comparing this with a polarized anodic aluminium surface (fig. 11c-d), a well developed mesh structure was found, formed by the electrochemical reactions on the surface. A pattern is visible since the fiber glass net in the adhesive affects the current distribution. The formed reaction products contained carbon, oxygen and sulfur besides the aluminium. These SEM results lead to the idea that the anodic electrode reaction is an oxidation of the aluminium metal. Noteworthy is that the oxygen content of the surface, not counting the patchy reaction products, increased up to  $7.5 \text{ mC/cm}^2$ , but then remained at the same level also at higher charge densities, up to  $50 \text{ mC/cm}^2$ . This formed oxide layer is very thin. Assuming a formation of  $\text{Al}_2\text{O}_3$  with a charge density of  $7.5 \text{ mC/cm}^2$ , the resulting layer would be approximately 3 nm thick, making it implausible that the increase in cell resistance is caused by a growth of aluminium oxide.



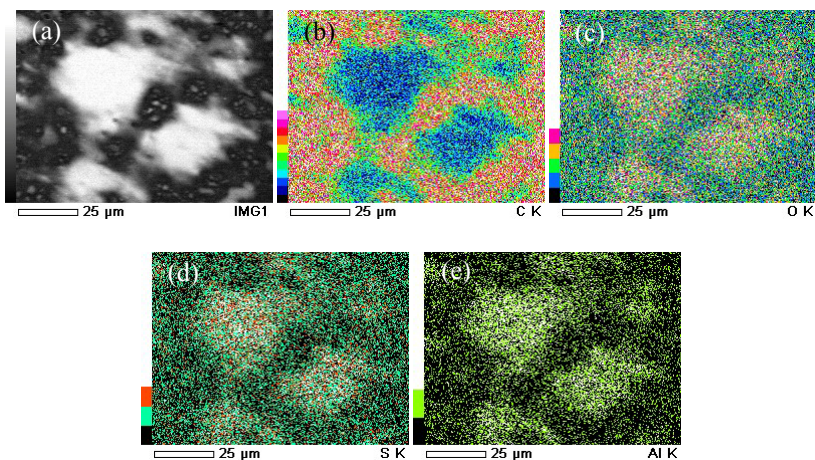
**Figure 11** – Aluminium foils removed from laminates. (a) – Reference aluminium foil (no current passed). (b) – Magnification of (a). (c) –  $50 \text{ mC/cm}^2$  passed, anodic side. The darker spots were located under void areas in the fiberglass net which allowed a high amount of material to react in this part of the interface. (d) - Magnification of a dark spot in (c).

The other side of the anodic interface, the adhesive surface, was also examined with SEM. Here it was seen that the reaction products formed at the anodic interface protruded into the adhesive phase (fig. 12a-c). The amount of material that had penetrated the adhesive was higher for the samples stored in higher air humidity than for those stored in lower. These results display, just as the experiments with bent laminates, a distinct difference between the 0 and 29 % RH samples. It is then likely that the release characteristics and formation of these phases are linked. The formation of the aluminium complexes would also most likely cause a volume increase in the adhesive, creating a volume mismatch with the rigid aluminium surface. This penetration of reaction products, into the adhesive, could then be the cause of the volume increase discussed concerning the EIS results.

An EDS analysis mapping of samples stored in 29 % RH (fig. 13) showed that the heavier domains contain less carbon, but more oxygen, sulfur and aluminium than the surrounding adhesive material. The formed products in the adhesive are believed to consist of aluminium ethyl sulfate, as the only sulfur source is the ethyl sulfate anion, and aluminium oxide/hydroxide. This fits the elemental analysis and is further strengthened by the fact that ethyl sulfate is electrochemically very stable. The electrochemical stability against oxidation of ethyl sulfate, where the equilibrium potential in pure EMIM-ES is 1.55 V vs. standard hydrogen electrode (SHE) [31], is higher than for both aluminium, with a standard potential of -1.662 V vs. SHE [32], and water, with a standard potential of 1.229 V vs. SHE in alkaline environment [32], which are both present at the anodic interface. As in the study of the EIC laminate [23-24], the mobile anions interact with the anodic aluminium metal due to the polarization. Another similarity lies in the traces of aluminium found on the anodic EIC adhesive surface after polarization.



**Figure 12** – SEM images, where secondary electrons were detected using a detector positioned to produce compositional contrast. (a) Unpolarized adhesive surface stored at 29 % RH (b) Anodic adhesive surface stored at 0 % RH polarized with 50 mC/cm<sup>2</sup> (c) Anodic adhesive surface stored at 29 % RH polarized with 50 mC/cm<sup>2</sup>



**Figure 13** – EDS mapping of an adhesive surface, pre-stored at 29 % RH, after polarization with 0.050 mA/cm<sup>2</sup> up to 50 mC/cm<sup>2</sup>. The brighter the area, the higher the concentration of the element in question. (a) SEM image of the area analyzed; (b) Elemental map of carbon; (c) Elemental map of oxygen; (d) Elemental map of sulfur; (e) Elemental map of aluminium

Using in-situ mass spectrometry (MS) during polarization, it was possible to make both a qualitative and a quantitative analysis of the volatile species produced during polarization. Comparing laminates debonded with and without polarization, the differences lie in the released amount of hydrogen and to some extent water. The amount of hydrogen detected was proportional to the charge density passed through the laminates. This production of hydrogen most likely arose from the reduction of water at the cathodic interface. The difference in water emission, from the anode, occurred only at higher charge density, above  $50 \text{ mC/cm}^2$ , and led to a lower rate of water emission. This change is believed to arise from a change in the water transport properties in the adhesive. The water transport is likely partly blocked by the adhesive-penetrating reaction products formed during polarization. Since no further differences between the polarized and unpolarized samples were observed during these measurements, it can be determined that no volatile species are formed during polarization. Also, no changes in the polymer chemistry on the anodic adhesive surface after polarization were detected by Raman spectroscopy. It is then likely that the only reactions at the anodic interface during polarization, is the observed thickening of the aluminium oxide layer and the growth of adhesive-penetrating products.

### **3.3 The debonding mechanism**

Starting with the electrochemical reactions on the anode, it is clear that the major reaction, caused by polarization, is oxidation of the aluminium metal. This can be understood by looking at the SEM/EDS results where both a thickening of the aluminium oxide/hydroxide layer as well as a growth of the aluminium-containing penetrating substances were observed after polarization. Added to these findings are the MS results showing that no volatile species were formed on the anode and the Raman spectroscopy results, where no changes were found in the polymer chemistry on the anodic surface of the adhesive. This oxidation would fit the proposed idea about the debonding as a multi-step process, since only the oxidation of aluminium should not in itself cause a debonding. The electrochemically formed aluminium(III) ions do, in a second step, associate with surrounding species. The SEM/EDS reveals that both aluminium oxides/hydroxides as well as a product likely to be aluminium ethyl sulfate are formed. This formation is divided into two geometrically separated domains: a thickening of the oxide/hydroxide layer and, more important, a growth of the compound protruding from the aluminium surface, likely consisting of a mix of aluminum oxide/hydroxide and aluminium ethyl-sulfate. This compound grows outwards from the aluminium surface, penetrating the adhesive phase. This penetration introduces stresses at the interface since the increase in volume in the adhesive is not accompanied by a growth of aluminium volume. The formed stresses should then eventually lead to a loss-of-contact between the adhesive and the aluminium surfaces. This process can be demonstrated using the EIS results. Polarizing a laminate leads to increased total cell resistance. When leaving the polarized laminate under pressure, it was seen that this increase in resistance gradually disappeared over 24 hours. This decrease in resistance is likely brought about by a relaxation of the described stresses, probably by plastic deformation in the adhesive bulk. When the stresses revert, the anodic surfaces can again make contact and the total resistance thus reverts. This phenomenon can, however, be explained by other processes, such as dissolution of the formed reaction products. But further results from EIS, where a large drop in total resistance was observed when the anode of a polarized laminate was removed and immediately repositioned, makes the situation clearer. In this case, the interfacial volume



mismatch between adhesive and aluminium could be relaxed by the removal of the anode. At the repositioning of the anode, good contact could be established once again resulting in a decreased resistance. The validity of the suggested debonding mechanism can be further strengthened with the connection found between the growth of the adhesive-penetrating reaction products and the debonding characteristics. Comparing laminates stored in 29 % RH with those stored in 0 % RH, it was clear that the laminates stored in a more humid environment both debonded at a lower charge density and had a larger amount of penetrated compounds in the adhesive. Thus, it is then likely that the formed products promote the debonding (fig. 14).



**Figure 14** – A schematic representation of the proposed debonding mechanism. The reaction products penetrate the adhesive, causing an increase in volume, which leads to interfacial collapse.

To summarize, the proposed debonding mechanism comprises a volume increase at the anodic interface, leading to a rupture at the interface between aluminium and adhesive (fig. 14). The volume increase is caused by the growth of electrochemically formed reaction products into the adhesive causing swelling. It is also possible that an additional weakening of the bond is brought about both by the earlier described decrease in pH [24, Paper I], causing anodic undermining, as well as the growth of the low-cohesion partial layer of aluminium ethyl sulfate/oxide/hydroxide between the aluminium and the adhesive.

## 4. Conclusions

The study on electrically induced adhesive debonding aimed at obtaining a deeper understanding of the processes leading to debonding. For the Sinuate® laminate, the debonding took place at the anodic interface. The debonding was, however, not a sudden event, but the adhesive strength decreased gradually over time.

The electrochemical parts of the study showed first of all that the cell potential during galvanostatic polarization increased with time. Further studies with a three-electrode set-up determined that almost all of this potential increase arose from the anodic side of the laminate. It was also seen that the electrochemical processes were affected by the water content of the adhesive, since an adhesive stored at higher humidity had lower resistance than one stored in a drier.

MS and SEM proved to be useful techniques for the study of the debonding chemistry. The MS studies gave useful information about the anodic half-cell reactions as no gaseous oxidation products were found during polarization. The cathodic process, on the other hand, produced hydrogen, which most likely was formed from reduction of water. Using SEM, it was seen that a reaction product was formed on the anodic aluminium surface during polarization. This product contained carbon, oxygen, sulfur and aluminium and grew outwards from the aluminium surface, penetrating the adhesive phase. The amount of these penetrating phases was larger for a laminate stored at high humidity than for one stored in a drier.

Examining the release characteristics, the debonding was determined to be a multi-step process. The actual process leading to debonding was thus not the electrochemical oxidation at the anodic interface. A relation between this debonding process and the formation of the penetrating reaction products could be seen. From this it was possible to propose a debonding mechanism, where a volume increase in the adhesive, at the anode, leads to internal stresses at the interface, leading to adhesive failure.

## 5. Future

Even though functional and accessible adhesive laminate products are available, the usage is very scarce. Today, essentially all electrically debondable adhesives are epoxy-based. The epoxy adhesives are thermosetting polymers, which cure at either mixing of epoxy and hardener or at heating of single-component composition of epoxy and a thermally activated hardener. These curing processes often need time, pressure and heat to form a strong bond, making it undesirable from a production point-of-view. When the high adhesive strength of thermosets is not needed, other types of adhesive should be examined. A preferred debondable adhesive would be a thermoplastic adhesive. This adhesive, if kept at a temperature above the glass temperature, behaves in a liquid-like fashion. When the polymer is applied to a substrate it cools below the glass temperature and solidifies into an adhering specie. This joint can then be debonded with an electric current at command. Adding heat would soften the adhesive and perhaps allow it to bond once again. It is also important to achieve lightweight and low-cost integrated power sources for the debonding process, for widespread use of. Inexpensive and robust wiring is also essential for this purpose.

However, overcoming these obstacles would create a product of immense potential. It could reshape the concept of automobile design, creating light-weight and recyclable products. This is especially important due to the legislative processes, which enforce recyclability. Production of safe and easy-to-open consumer packaging, built on debonding adhesive, could also be a huge market. The problem with hard-to-open consumer packaging has over the last years been acknowledged in the popular press, where terms such as ‘wrap rage’ has been used to cover the phenomenon [33-34], so there is no doubt about the potential market for debonding adhesives in this case. Further use of the technology can be found as an integral part of a new packaging-solution system. Produced goods, adhered to each other with a debondable adhesive, could be shipped with a minimum of packaging materials. These package bulks could then conveniently be separated by an electric current in the destination store-shelf. All in all, debonding adhesives could find application in a huge spectrum, ranging from high-technology product such as the secure medicine dispenser to easy removal of wallpapers.

Future studies of debonding adhesives could be focused within several areas. From a scientific point of view, it would be rewarding to study the debonding characteristics of various metals and other conducting materials. It would also be rewarding to study the effect of different concentrations of the hardener. The stiffness of the cured adhesive should affect the amount of mechanical stresses during polarization and therefore lead to variations in debonding characteristics. From an industrial perspective, it would be good to have a wide range of debondable adhesive chemistries, able to suit any application. Furthermore, an incorporated power source eliminates the need for external electrical connections. This could be achieved by either an attached battery or a construction whereby the adhesive laminate is a galvanic cell. It would also be an improvement if the debonding could be made independent from the surrounding air humidity, for a more controlled process.

The debonding process of the adhesive is functional, but a number of matters could be improved. The main issue of the process is the large potential needed for rapid debonding. A

lowered adhesive resistance would take care of part of this problem. Another aspect is the increase in resistance, created by the polarization. This increase seems to be related to a gradual debonding process, according to the present work. Therefore, it would be advantageous if the debonding were to take place more suddenly, thereby avoiding the resistance increase.

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