



Article Influence of Dry-Film Lubricants on Bond Strength and Corrosion Behaviour of 6xxx Aluminium Alloy Adhesive Joints for the Automotive Industry

Ralph Gruber ^{1,2,3,*}, Tanja Denise Singewald ³, Thomas Maximilian Bruckner ³, Laura Hader-Kregl ³, Martina Hafner ² and David Stifter ^{1,*}

- ¹ ZONA—Center for Surface and Nanoanalytics, Johannes Kepler University Linz, Altenberger Str. 69, 4040 Linz, Austria
- AMAG Rolling GmbH, Lamprechtshausener Str. 61, 5282 Ranshofen, Austria; martina.hafner@amag.at
 CEST—Centre for Electrochemistry and Surface Technology, Viktor-Kaplan Str. 2,
- 2700 Wiener Neustadt, Austria; tanja.singewald@cest.at (T.D.S.); thomas.bruckner@cest.at (T.M.B.); laura.hader-kregl@cest.at (L.H.-K.)
- * Correspondence: ralph.gruber@cest.at (R.G.); david.stifter@jku.at (D.S.)

Abstract: In the automotive industry, the application of dry lubricants on aluminium is indispensable for achieving a high-quality forming behaviour. To provide a short production time, these forming aids are not removed during the joining step. The aim of this study is the characterisation of the influence of dry lubricants on the bond strength and the corrosion resistance of a 6xxx aluminium alloy for automotive applications. For this purpose, samples with a well-defined surface were coated with 1 g/m^2 dry lubricant and joined with a commercial thermosetting 1K epoxy structural adhesive. The bond strength was measured with lap shear tests. To evaluate the corrosion resistance of the adhered aluminium samples, an immersion test in a 5 wt.% NaCl solution was used. Based on the fracture pattern analysis, the corrosion behaviour could be described, and the possible corrosion mechanisms are proposed. The influence of the load quantity of the dry lubricants is observed microscopically and mechanically. The environmentally induced degradation process of the adhesive is examined by an investigation of the volumetric change during the testing and with scanning electron microscopy. Using a simulation, the changes in the adhesive polymer matrix at the metal-adhesive interface caused by the dry lubricants are examined using polymer test procedures like dynamic mechanical analysis, differential scanning calorimetry and tensile tests. The results show a significant effect of the forming aid on the corrosion resistance of the adhered aluminium samples against the corrosive infiltration of the metal-adhesive interface.

Keywords: dry-film lubricant; aluminium metal sheet production; automotive industry; structural adhesive bonding; accelerated corrosion testing; corrosion mechanism; single-lap shear testing; polymer testing

1. Introduction

Dry lubricants are indispensable for achieving a high-quality forming behaviour of aluminium sheets for automotive applications [1]. To provide a short production time, these forming aids are not removed during the joining step [2]. Nowadays, structural adhesive bonding in car body production is among the standard joining processes and is widely applied in the automotive industry [3]. In addition to the conventional methods of joining automotive sheet metal, such as welding, riveting and bolting, adhesive bonding offers a number of advantages [4]. Bonding not only improves the rigidity of the car body, but it also protects against corrosion because of its sealing effect compared to welded joints [5]. It also provides the advantage of no substrate weakening during the joining procedure [6]. However, the long-life durability of bonded joints is seen as a crucial point [7].



Citation: Gruber, R.; Singewald, T.D.; Bruckner, T.M.; Hader-Kregl, L.; Hafner, M.; Stifter, D. Influence of Dry-Film Lubricants on Bond Strength and Corrosion Behaviour of 6xxx Aluminium Alloy Adhesive Joints for the Automotive Industry. *Lubricants* 2023, *11*, 437. https:// doi.org/10.3390/lubricants11100437

Received: 1 August 2023 Revised: 26 September 2023 Accepted: 9 October 2023 Published: 11 October 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The environmental influences that a car body is exposed to during its lifetime do promote degradation processes of the bonded joints [8]. These occur at the interface between the adhesive and the adherend and are caused by humid and corrosive environments [9,10]. But not only do environmental influences affect the long-life durability of bonded joints [11,12], other influencing factors, including contamination of the metal sheet surface or the lubricant load quantity, have an impact on the corrosion resistance of adhered joints [13,14].

Until now, the long-term durability of bonded joints has only been considered from the adhesive side, regardless of the substrate. Dry lubricants of any kind have not been considered. The influence of dry lubricants has been investigated in other contexts. Studies by Meiler and Jaschke looked at the effects of dry lubricants on the process chain in the manufacturing of automotive sheet metal and the associated compatibility with common adhesives [15]. The influence of lubricants on the corrosion resistance of alumina in NaCl solution was investigated by WU et al. using cryo-scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS); they showed a partial reduction of the corrosion properties by the dry lubricant [16]. By means of density functional theory (DFT) calculations, Blanck et al. investigated the wetting behaviour of dry-film lubricants on aluminium surfaces [17]. A combined view to elucidate the influence of dry lubricants on the long-term resistance of bonded aluminium joints is lacking in the literature.

To fill this gap in the research, the influence of dry-film lubricants (DFLs) on the bond strength and corrosion behaviour of adhesive joints of 6xxx aluminium alloys, as used in the automotive industry, was investigated in the current study.

For the simulation of the environmental influences, the adhesive joints with and without a DFL were subjected to an immersion test procedure and the effects on the bond strength and corrosion behaviour were investigated using single-lap shear tests and SEM characterisation. Based on the reproduceable results of this accelerated immersion and corrosion test, the possible corrosion processes were examined and identified.

The influence of the load quantity of the DFL during the immersion testing and the environmentally induced degradation process of the adhesive itself was also investigated microscopically and mechanically using SEM and tensile testing, respectively. In addition, the volumetric change of the adhesive during immersion was monitored and the changes in the adhesive polymer matrix at the metal–adhesive interface caused by the DFL were examined using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC).

2. Materials and Methods

2.1. Materials

As a representative for technical aluminium surface within the automotive industry, an AA 6016 AlMgSi alloy with a commercial surface finish was provided by AMAG Austria Metall AG (Ranshofen, Austria). The primary surface treatment was based on automotive standards and included acid pickling and a subsequent washing process to clean the substrate. The surface was then textured using electrical discharge texturing (EDT). The 1K epoxy structural adhesive in this study was BetamateTM 1630 (DuPont de Nemours Corporation, Wilmington, USA). This commercial variant is based on a standard epoxy resin with a corresponding hardener system and includes several additives and fillers. According to the manufacturer's data sheet, the curing temperature of the adhesive is 180 °C with a curing time of 0.5 h. The tensile modulus of the adhesive is 1500 MPa with a stress at break of 29 MPa and an elongation at break of 11%. To investigate the corrosion behaviour, the entire surface of the aluminium specimens was lubricated with a Multidraw Drylube E1 dry-film lubricant (DFL) (Zeller + Gmelin GmbH & Co. KG., Eislingen, Germany) in accordance with the standard industrial production process. This commercial hot melt that can be used for all types of metal (e.g., steel, zinc-coated steel, pre-phosphatised steel, stainless steel and aluminium) for coil coating. The dry lubricant met the requirements of the German Association of the Automotive Industry (VDA)'s performance specifications and is said to provide excellent formability and corrosion protection. The product's data

sheet describes Multidraw Drylube E1 as a water- and solvent-free dry lubricant based on mineral oils. It is said to contain hydrocarbons of a higher melting weight, which explains the processing temperature of the stated 70 °C. With a solidification point of approximately 40 °C, this dry lubricant is solid at room temperature. It is also resistant to ageing and is biodegradable, and its properties, as provided in its data sheet, are listed in Table 1.

Table 1. Characteristics of the dry-film lubricant Multidraw Drylube E1 [18].

Parameter	Value
Appearance/colour	solid/brown
Density at 15 °C	870 kg/m ³
Viscosity at 100 °C	11 mm ² /s
Flashpoint	>220 °C

2.2. Sample Preparation

The assembly of the single-lap shear specimens according to German Institute for Norms (DIN) European Norms (EN) 1465 consisted of two single aluminium panels with a size of $100 \times 25 \text{ mm}^2$, joined together with an overlap of 10 mm using the structural adhesive and a one-step curing at 180 °C. These curing conditions represent the curing conditions used in the industrial application. Half of the samples were lubricated in advance using the DFL at a load quantity of 1 g/m^2 . The uniform distribution of the dry-film lubricant was controlled using a coating thickness gauge (OFIS 2.0/AMEPA GmbH, Würselen, Germany). According to EN International Organisation for Norms (ISO) 527-2:2012, the dumbbell specimens (Figure 1) for the dynamic mechanical analyses (DMAs) and tensile tests were manufactured out of the adhesive. For this purpose, three different adhesive blends with DFL concentrations from 0 to 1 wt.% were prepared using a SpeedMixer (DAC150/FlackTek, Louisville, KA, USA) for 30 s at 3200 rpm. By means of a pneumatic cartridge press, the blends were separately injected in a 3 mm thick polytetrafluoroethylene (PTFE) mould and cured based on industrial application conditions at 180 °C for 30 min in a heating press. Silicon-coated release paper acted as a separating aid on both sides of the mould.



Figure 1. Preparation of adhesive dumbbell specimens according to EN ISO 527-2:2012.

2.3. Testing and Characterisation

2.3.1. Corrosion Test

According to the standard qualification procedures for adhered aluminium samples within the automotive industry, the immersion tests were carried out for 168 h in a 5 wt.% NaCl solution at 70 °C. To ensure comparability, every single test was conducted with

2 L of immersion solution in a closed test chamber. The samples were stored below the waterline for the entire duration of the test. After ageing, the samples were rinsed with deionised water and then subjected to a re-drying phase for 24 h under standard conditions. A summary of the experimental conditions can be found in Table 2. A schematic representation of the research content of this study is presented in Figure 2.

Corrosion Test	Parameters				
I	Exposure time	Temperature	Media	Description	Device
testing	168 h	70 °C	2 L of 5 wt.% NaCl	fully immersed	closed chamber

Table 2. Summary of the experimental conditions for the corrosion testing.



Figure 2. Schematic overview of the research content.

2.3.2. Tensile and Single-Lap Shear Test

Initially and also after each day of exposure to the immersion corrosion test, new samples from the testing batch were always mechanically tested to evaluate the influence of the DFL on the corrosion behaviour and the mechanical properties of the joints. Single-lap shear testing was performed on a tensile testing machine (Z250/Zwick, Ulm, Germany) with a 50 kN load capacity at 22 °C and 50% relative humidity (RH). The corrosion behaviour was described based on a fracture pattern analysis. An evaluation of the adhesive fracture patterns was carried out according to the German German Association for Welding and Allied Processes (DVS) guideline 3302 "Adhesive bonding in car body construction: Evaluation of fracture patterns" [19]. The same mechanical testing procedure was used to evaluate the influence of the DFL load quantity on the adhesion properties of the adhesive itself.

2.3.3. Dynamic Mechanical Analysis (DMA)

Interaction effects of the dry-film lubricant on the mechanical properties of the adhesive were investigated using DMA. The analysis was performed using a modular compact rheometer (MCR 502/Anton PAAR, Graz, Austria) in the torsion mode and the corresponding RheoCompass-Software 1.3 of the system supplier. The analyses were performed in a temperature range of -100 to 200 °C at a frequency of 1 Hz and a heating rate of 3 K min⁻¹.

2.3.4. Differential Scanning Calorimetry (DSC)

Changes in the thermal properties of the adhesive due to the DFL were evaluated using DSC (Q2000/TA Instruments, Eschborn, Germany) with an integrated autosampler and a cooling system. The measurements were executed in a temperature range of 30–250 °C in a protective nitrogen atmosphere with a 10 K min⁻¹ heating rate.

2.3.5. Scanning Electron Microscopy (SEM)

The effect of the forming aid on the corrosive infiltration of the metal–adhesive interface, as well as the morphological changes in the adhesive upon the immersion solution uptake, was investigated using a scanning electron microscope (EVO 40/Zeiss, Oberkochen, Germany) with an operating voltage of 10 kV. Before scanning, the specimen surface was coated with a thin gold layer by sputtering.

3. Results

In Figure 3, the results of the tensile tests are shown. The corrosion behaviours of the lubricated and unlubricated samples after the immersion corrosion testing are directly compared. The reference samples without DFL are highlighted in blue and the lubricated samples in brown. In addition to the tensile shear strengths, the diagram shows the residual forces as a function of the duration of the accelerated corrosion test. The results demonstrate the influence of the DFL on the corrosion behaviour of the joined aluminium samples when immersed in the NaCl solution over time.



Figure 3. Overview of the mechanical testing values as a function of the duration of the immersion testing. The corrosion resistances of the references without (blue) and samples with dry-film lubricant (brown) are directly compared.

After a small initial drop within the first 48 h, the samples without lubrication showed a relatively constant residual strength over the remaining test duration. In contrast, the samples with dry lubricant already showed a 7% deterioration of the bonding performance in the initial state. After 24 h of accelerated corrosion testing, there was already a 12%

decrease in the residual strength compared to the initial state. This corresponded to a deviation of 5% compared to the nonlubricated samples. This discrepancy increased as the corrosion test progressed. While the residual forces of the comparison samples remained relatively constant at approximately 90% over the entire test period, the values of the residual forces of the lubricated samples dropped rapidly. After only 4 days in the accelerated corrosion test, the remaining residual strength was only 53%. Towards the end of the test period, the samples only showed residual strength values of less than 10%, which is equivalent to a complete loss of the bond strength and would, therefore, result in a full component failure.

The influence of the DFL on the corrosion behaviour of the adhered aluminium samples can also be described based on the fracture pattern analysis. The samples without DFL, shown in Figure 4a–h, exhibited no corrosive attack of the metal–adhesive interface during the immersion testing. The fracture patterns constantly showed cohesive failure over the whole test period. It seems that the test duration and the associated infiltration of the adhesive joint with the corrosive medium was not sufficient to achieve a weakening of the adhesive bond caused by corrosion. By comparison, the samples that were lubricated with DFL in advance already showed a corrosive attack after the first 24 h of testing. It appears that the corrosion spread continuously from the edges of the tensile shear specimens over the entire width of the adhered joints as the corrosion test continued. With the increasing corrosive infiltration of the bondline through the ongoing corrosion test, as shown in Figure 4i–p, the residual strength of the single-lap shear specimen decreased. This behaviour can also be explained based on the fracture patterns shown. Corrosion in the bonded joint, also known as bondline corrosion, spreads continuously in a semicircle starting from the edges of the sample [20,21]. With the increasing test duration, the area of the corrosive infiltration also increased. This weakening of the bonded joint is equivalent to a decrease in the tensile shear strength, which was evident in the mechanical lap shear test, as depicted in Figure 4. After completion of the immersion testing, the fracture pattern of the lubricated samples showed laminar corrosive delamination over the whole bondline and a remaining residual strength of less than 10% compared to the initial state. The discolouration on the corresponding fracture patterns, as shown in Figure 4n–p, indicated the formation of corrosion products. In addition to a change in the surface composition, the products formed by the corrosion also influenced the adhesion of the adhesive to the surface of the Al substrate. Consequently, the formation of the corrosion products always corresponded to an excessive weakening of the adhesive bond.



increasing corrosive fracture pattern

Figure 4. Fracture pattern comparison between the lubricated–(**j**–**p**)–and nonlubricated–(**b**–**h**)– samples before–(**a**,**i**)–and after immersion testing.

In addition, cross-sections of the adhesive joints were characterised to gain more information about the lubricant-induced corrosion mechanism. Figure 5 shows cross-sectional images of an adhesive joint of a lubricated sample after five days of immersion taken using SEM. The adhesive is delaminated over the whole bondline and already shows degradation in the centre (Figure 5c). Measured by the thickness of the adhesive in the bondline, the adhesive in the centre of the sample seems to have already degraded by approximately half. This behaviour is the effect of crevice corrosion, with its corresponding concentration gradient of the corrosion products starting from the edges with increasing degradation towards the centre [22]. The result is delamination over the entire bondline accompanied by the loss of bond strength. Figure 5c also shows the corrosion products formed in the interphase between the Al substrate and the adhesive polymer. These corrosion products promote the weakening of the adhesive bond, as described above.



Figure 5. Cross-section (**a**) of a lubricated adhesive joint after 5 days of immersion showing bondline corrosion (**b**–**d**).

3.1. Displacement of DFL

Next to the effect on the corrosion behaviour, Figure 3 reveals an influence of DFL on the mechanical properties of the adhesive joints already in the initial state. The lubricated samples show a reduced tensile shear strength up to 7%. These findings indicate that the adhesive cannot absorb the DFL completely. Therefore, a single-lap shear test series with increasing DFL load quantities from zero to 5 g/m² was performed, with the results given in Figure 6.



Figure 6. Single-lap shear test results of specimens with ascending lubricant load quantities.

The results confirm that the DFL reduced the tensile shear strength of the adhered aluminium samples. The lubrication as commercially used, with an amount of 1 g/m^2 DFL, already led to a 7% decrease in the tensile shear strength compared to the initial value. The change became smaller with an increasing load quantity, which may be an indicator for the lubricant's displacement out of the adhesive joint. In the case of the saturation of the adhesive polymer with the DFL, displacement can occur during the curing of the adhesive joints. This process can be confirmed using the microscopic images shown in Figure 7. The top view of an adhesive joint from a lubricated specimen indicates an incomplete absorption of the DFL by the adhesive. The lubricant is literally squeezed out of the joint region and generates a wedge with a much larger open surface area that for allows an enhanced diffusion of the corrosive ingredients, like Cl⁻ or H₂O, of the immersion bath into the bondline. This, in turn, favours corrosion and leads to a significantly accelerated decrease in the bond strength.



Figure 7. Microscopic top view of the DFL's displacement out of the adhesive joint. Subfigure (**b**) shows magnified section of subfigure (**a**).

3.2. Swelling of the Adhesive

Structural epoxy adhesives like the one used in this study are not resistant against environmental conditions like humidity or water diffusion [7,10,12,23]. They are more inclined to take up the surrounding water, which leads to an increase in volume [24,25]. Table 3 shows the swelling and change in volume of an adhesive specimen according to DIN EN ISO 62:2008 during immersion in deionised water (DI) and in a 5 wt.% NaCl solution at 70 °C. The length, width and thickness of the 40 × 40 mm² samples were measured using a calliper gauge with an accuracy of 0.01 mm. The corresponding volumetric change was calculated using Equation (1), where V_1 and V_2 are the volumes before and after immersion, respectively.

$$\frac{\Delta V}{V_1} = \frac{V_2 - V_1}{V_1} \tag{1}$$

Table 3. Overview of the volumetric change after immersion.

Immersion Time (Days)	Volume Change in DI Water (vol.%)	Volume Change in NaCl Solution(vol.%)
7	17	12
14	18	14
21	19	15

The results indicate that immersion in DI water leads to a higher volumetric change than immersion in a 5 wt.% NaCl solution. This behaviour is the result of reverse osmosis and has already been reported in the literature [26]. It is also well known that water diffusion is a temperature-dependent process that proceeds many times faster at elevated temperatures and leads to the swelling of the polymer network [25]. Furthermore, it is reported that swelling of the adhesive forms cavities in the vicinity of inorganic fillers inside the polymer network due to the different expansion rates of both the polymer and inorganic ingredients. This creates considerable free volume into which water or immersion solution can enter [25]. At this point, it should also be noted that the water concentration inside the polymer is dependent on further swelling. As the absorption of water goes on, the size of the voids increases, which then leads to further diffusion [27,28]. Figure 8 confirms the presence of cavities in the vicinity of inorganic fillers inside the polymer network of the adhesive after immersion in a 5 wt.% NaCl solution for 7 days at 70 °C. Calcium oxide (CaO) and calcium carbonate (CaCO₃) are often used as inorganic fillers in commercial adhesive formulations to adjust certain properties, such as the mechanical and rheological properties and the sagging resistance [29]. CaO, for example, is a generally used adhesive additive because of its chemical water-binding ability, with the intention to minimise water deteriorative effects like the plasticisation of the adhesive. These particles can clearly be identified by their shape and appearance during a microscopic characterisation of the adhesive. Calcium carbonate is characteristically found in rectangular, layered particles, whereas calcium oxide is usually found in a spherical form in the adhesive [30]. During SEM characterisation, both particle shapes, associated to CaO and CaCO₃, can be found in the commercial adhesive polymer network. Furthermore, as already described above, cavities in the vicinity of these inorganic fillers, caused by swelling, can be detected. These voids favour the diffusion of immersion solution which promotes bondline corrosion at the aluminium–adhesive interface.



Figure 8. SEM image of the adhesive after 7 days of immersion. The polymer network shows cavities in the vicinity of organic fillers, as marked by the red arrows.

3.3. Change in the Polymer Matrix

At the aluminium–adhesive interface, the DFL is directly in contact with the adhesive and can interact. Therefore, three different polymer blends with DFL concentrations from 0 to 1 wt.% were prepared to simulate the interaction effect of a lubricant on the mechanical properties of the adhesive. The result of the tensile test of the pure adhesive dumbbell specimens with all three blends is shown in Figure 9 and indicates a change in the mechanical properties of the adhesive itself due to the DFL.

With an increasing lubricant concentration, the tensile modulus, as well as the breaking stress, decreased. The addition of 1 wt.% DFL to the adhesive resulted in a reduction of 7% for both the tensile modulus and the breaking stress. The increase in the breaking elongation with increasing DFL concentrations is the result of a lubricant-induced plasticisation of the adhesive [31]. The dry-film lubricant behaves as a plasticizer and creates spaces between the

epoxy polymer chains, reducing the intermolecular forces, like van der Waals and hydrogen bonds, allowing the polymer chains to move more freely [32]. This results in an increased elongation allowing the adhesive to stretch more before breaking. This behaviour might be useful in some applications when an improved flexibility due to temperature changes or mechanical forces is needed. However, there can also be drawbacks to this lubricantinduced plasticisation, such as a reduced cohesive strength, which was also observed during the tensile test of the adhesive dumbbell specimens. The observed decrease in the internal strength of the adhesive was caused by the DFL and may lead to weaker bonds in certain applications. Furthermore, plasticisers tend to migrate out of the adhesive over time, leading to a change in the properties and other potential issues.



Figure 9. Tensile test results of the adhesive blend dumbbell specimens with varying DFL concentrations. The black line corresponds to the tensile modulus, the red line to the breaking stress and the blue line to the breaking elongation.

This plasticisation was also observed in the DMA analysis. The loss factor tan δ is a measure of the dissipation energy of the sample and the peak maximum of its graph can be used for the determination of the glass transition temperature, T_g [33]. The glass transition temperature is the temperature range at which an amorphous material, like certain polymers, such as epoxies, undergoes a reversible transition from a rigid, glassy state to a softer, rubbery state upon heating or cooling. A change in the T_g is always associated with a change in the material properties [33–35]. As shown in Figure 10, the DFL reduces the glass transition temperature of the epoxy polymer by 2.5 degrees. This finding can, again, be explained by the lubricant-induced plasticisation of the adhesive polymer network. As mentioned above, the lubricant acts as a plasticiser, which can penetrate the molecular structure of the adhesive, and the spaces created between the polymer chains reduce the intermolecular forces, making the adhesive more flexible and rubberier. As a result, the T_g of the adhesive decreases because the glass transition occurs at a lower temperature. This finding confirms, once again, a DFL-induced change in the mechanical properties of the adhesive.

In addition to the actual modification of the mechanical properties of the adhesive due to the lubricant, a DSC analysis of the adhesive blends show an additional DFL-induced change in the thermal properties of the epoxy polymer. Basically, two peaks could be observed in the measurements. The small enthalpy peak at approximately 70 °C, as depicted in Figure 11, is attributed to the dissolution of the hardener inside the polymer network [36,37]. It was observed that the dry lubricant shifted the peak maximum by approximately 2.7 °C towards lower temperatures, which means that the hardener began to dissolve earlier due to the dry lubricant. The second and main peak is attributed to the curing reaction of the epoxy adhesive at about 182 °C. The lubricant reduces the on-set

temperature, which led to an earlier curing reaction. Additionally, the peak maximum of the heat flow graph was reduced by $5 \,^{\circ}$ C due to the DFL, as shown in Figure 11, and the polymer network's formation during the curing had in total a higher exothermicity.



Figure 10. DMA analysis plot showing a DFL-induced reduction of the Tg of the adhesive.



Figure 11. The DSC analysis reveals a change in the thermal properties after the interaction of the adhesive with the DFL.

3.4. Corrosion Mechanism

Based on the above findings, the responsible corrosion mechanism seems to be a combination of three processes based on different effects. The adhesive degradation during the accelerated corrosion testing is a normal process and occurs also on nonlubricated samples [7,12,20,26,38]. But in this case, the DFL promoted the degradation because of the incomplete absorption of the lubricant from the adhesive. The residual lubricant stands directly in contact with the adhesive at this interface (see Figure 12, number 1). This interaction led to a change in the epoxy polymer matrix and its mechanical and thermal properties. Additionally, the swelling of the adhesive, shown in Figure 12, number 2, caused by the reinforced diffusion of the immersion solution due to the larger contact

area of the DFL wedge, favoured further diffusion. The swelling of the adhesive created cavities in the vicinity of the inorganic fillers inside the polymer network. The increased free volume allowed the adhesive to absorb more immersion solution which promoted bondline corrosion at the aluminium–adhesive interface. The logical consequence of an incomplete absorption is, next to the already mentioned processes, a displacement out of the joint, which generated a wedge with a much larger open surface area for the enhanced diffusion of corrosive components (see Figure 12, number 3).



Figure 12. Overview of the responsible corrosion mechanisms. Number 1 represents the change in the polymer matrix itself; number 2 displays the swelling of the adhesive; and number 3 illustrates the displacement of the DFL, forming a wedge at the border.

4. Discussion and Conclusions

In this work, the influence of a DFL on the bond strength or the corrosion resistance of a 6xxx aluminium alloy adhesive joint was investigated. Environmental influences were simulated with an accelerated corrosion test, and the occurring corrosion mechanisms were examined and identified.

- In comparison with a nonlubricated reference, the DFL promoted a reinforced corrosive attack during a standardised immersion test procedure;
- The fracture pattern analysis indicated bondline corrosion already after 24 h of testing. A cross-section of a tested joint showed corrosive delamination of the adhesive, which led to loss of the mechanical strength of the joint;
- The load quantity of the dry lubricant already influenced the tensile shear strengths in the initial state. Microscopic characterisation showed a displacement out of the joint, which indicates an incomplete absorption of the DFL by the adhesive;
- Displacement favours the diffusion of corrosive media. This diffusion leads to a swelling of the adhesive and forms cavities in the vicinity of inorganic fillers inside the polymer network. These voids additionally favour the diffusion of immersion solution, which promote bondline corrosion at the aluminium–adhesive interface;
- At the interface, the dry lubricant is directly in contact with the adhesive. The interaction between both the DFL and the adhesive leads to a change in the mechanical and thermal properties of the adhesive. Tensile tests and a DMA revealed a lubricantinduced plasticisation with a decrease in the glass transition temperature;
- The dry lubricant also affects the curing behaviour, which was observed with DSC analysis.

Author Contributions: Conceptualisation, R.G. and D.S.; methodology, R.G. and M.H.; formal analysis, T.D.S. and T.M.B.; investigation, R.G.; resources, M.H. and D.S.; writing—original draft preparation, R.G.; writing—review and editing, L.H.-K., M.H. and D.S.; visualisation, R.G.; supervision, L.H.-K., M.H. and D.S.; project administration, L.H.-K., M.H. and D.S. All authors have read and agreed to the published version of the manuscript.

Funding: The Comet Centre CEST is funded within the framework of COMET—Competence Centers for Excellent Technologies by BMVIT and BMDW, as well as the Province of Lower Austria and Upper Austria. The COMET programme is run by FFG. This work originates from research in the Durabond and GreenMetalCoat (FFG 865864, Comet-Center (K1), 2019–2022; FFG 899594, Comet-Center (K1), 2023) projects.

Data Availability Statement: Not applicable.

Acknowledgments: Open Access Funding by the University of Linz.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. European Aluminium Association. *EAA Aluminium Automotive Manual—Joining*; The Aluminium Automotive Manual, European Aluminium Association: Ljubljana, Slovenia, 2015; pp. 1–5.
- Alfano, M.; Morano, C.; Moroni, F.; Musiari, F.; Spennacchio, G.D.; Di Lonardo, D. Fracture toughness of structural adhesives for the automotive industry. *Procedia Struct. Int.* 2018, *8*, 561–565. [CrossRef]
- Meschut, G.; Janzen, V.; Olfermann, T. Innovative and highly productive joining technologies for multi-material lightweight car body structures. J. Mater. Eng. Perform. 2014, 23, 1515–1523. [CrossRef]
- Barnes, T.; Pashby, I. Joining techniques for aluminium spaceframes used in automobiles. J. Mater. Process. Technol. 2002, 99, 72–79.
 [CrossRef]
- Chen, H.; Wang, D.; Na, J.; Chen, X. Effect of sealing treatment on mechanical properties of CFRP-Aluminum alloy single lap joints. *Int. J. Adhes.* 2022, 119, 103236. [CrossRef]
- 6. Cavezza, F.; Boehm, M.; Terryn, H.; Hauffman, T. A Review on Adhesively Bonded Aluminium Joints in the Automotive Industry. *Metals* **2020**, *10*, 730. [CrossRef]
- 7. Viana, G.M.S.O.; Costa, M.; Banea, M.D.; Da Silva, L.F.M. A review on the temperature and moisture degradation of adhesive joints. *Proc. Inst. Mech. Eng. Part L J. Mater. Des. Appl.* 2017, 231, 488–501. [CrossRef]
- 8. Goede, M.; Stehlin, M.; Rafflenbeul, L.; Kopp, G.; Beeh, E. Super light car-lightweight construction thanks to a multi-material design and function integration. *Eur. Transp. Res. Rev.* **2009**, *1*, 5–10. [CrossRef]
- 9. Mercier, D.; Rouchaud, J.-C.; Barthés-Labrousse, M.-G. Interaction of amines with native aluminium oxide layers in non-aqueous environment: Application to the understanding of the formation of epoxy-amine/metal Interphases. *Appl. Surf. Sci.* 2008, 254, 6495–6503. [CrossRef]
- 10. Lin, Y.; Chen, X. Moisture sorption-desorption-resorption characteristics and its effect on the mechanical behaviour of the epoxy system. *Polymer* **2005**, *46*, 11994–12003. [CrossRef]
- 11. Lörinci, G.; Matuschek, G.; Fekete, J.; Gebefügi, I.; Kettrup, A. Investigation of thermal degradation of some adhesives used in the automobile industry by thermal analysis/mass spectrometry and GC-MS. *Thermochim. Act.* **1995**, *263*, 73–86. [CrossRef]
- 12. Ocaña, R.; Arenas, J.; Alía, C.; Narbón, J. Evaluation of degradation of structural adhesive joints in functional automotive applications. *Procedia Eng.* 2015, 132, 716–723. [CrossRef]
- Hirsch, J. Recent development in aluminium for automotive applications. *Trans. Nonferrous Met. Soc. China* 2014, 24, 1995–2002. [CrossRef]
- 14. Gruber, R.; Singewald, T.D.; Bruckner, T.M.; Hader-Kregl, L.; Hafner, M.; Groiss, H.; Duchoslav, J.; Stifter, D. Investigation of oxide thickness on technical aluminium alloys-a comparison of characterization methods. *Metal* **2023**, *13*, 1322. [CrossRef]
- 15. Meiler, M.; Jaschke, H. Lubrication of aluminium sheet metal within the automotive industry. *Adv. Mater. Res.* **2005**, *6–8*, 551–558. [CrossRef]
- 16. Wu, D.; Ma, L.; Liu, B.; Zhang, D.; Minhas, B.; Qian, H.; Terryn, H.A.; Mol, J.M. Long-term deterioration of lubricant-infused nanoporous anodic aluminium oxide surface immersed in NaCl solution. *J. Mater. Sci. Tech.* **2021**, *64*, 57–65. [CrossRef]
- Blanck, S.; Loehlé, S.; Steinmann, S.N.; Michel, C. Adhesion of lubricant on aluminium through adsorption of additive head-groups on γ-alumina: A DFT study. *Tribol. Int.* 2020, 145, 106140. [CrossRef]
- Zeller+Gmelin Mulidraw Drylube E1. Available online: https://www.zeller-gmelin.de/zgSite/en/Lubricants/Forming/ Sheet-Metal-Forming/Multidraw-Drylube-E-1/p/22200?s=93A303F60CD8C34B29EFE69CA7585F7EFE92BF58 (accessed on 25 July 2023).
- 19. Richtlinie DVS 3302: Kleben im Karosseriebau: Bewertung von Bruchbildern. 2018. Available online: https://www.dvs-regelwerk.de/regelwerke/richtlinie-dvs-3302-09-2018 (accessed on 31 July 2023).
- 20. Abrahami, S.T.; Hauffman, T.; de Kok, J.M.; Terryn, H.; Mol, J.M. Adhesive bonding and corrosion performance investigated as a function of aluminum oxide chemistry and adhesives. *Corrosion* **2017**, *73*, 903–914. [CrossRef]
- 21. Nijemeisland, M.; Meteleva-Fischer, Y.V.; Garcia, S.J. Identifying interfacial failure mode in aerospace adhesive bonds by broadband dielectric spectroscopy. *Int. J. Adhes. Adhes.* **2022**, *118*, 103246. [CrossRef]
- LeBozec, N.; Thierry, D. Influence of test parameters in an automotive cyclic test on the corrosion and mechanical performance of joined materials. *Mater. Corros.* 2015, 66, 1051–1059. [CrossRef]

- Singewalda, T.D.; Brucknera, T.M.; Grubera, R.; Schimo-Aichhorna, G.; Hader-Kregla, L.; Poellerb, S.; Muellerb, M.; Kernc, C.; Luckenederc, G.; Stellnbergerc, K.-H.; et al. Water-uptake in hollow glass microspheres and their influence on cathodic and anodic delamination along the polymer/metal-Interface. *Corros. Sci.* 2022, 196, 110045. [CrossRef]
- Bruckner, T.M.; Singewald, T.D.; Gruber, R.; Hader-Kregl, L.; Klotz, M.; Müller, M.; Luckeneder, G.; Rosner, M.; Kern, C.; Hafner, M.; et al. Water absorption and leaching of a 1K structural model epoxy adhesive for the automotive industry. *Polym. Test.* 2023, 117, 107870. [CrossRef]
- Loh, W.; Crocombe, A.; Wahab, M.A.; Ashcroft, I. Modelling anomalous moisture uptake, swelling and thermal characteristics of a rubber toughened epoxy adhesive. *Int. J. Adhes. Adhes.* 2005, 25, 1–12. [CrossRef]
- Tai, R.C.L.; Szklarska-Smialowska, Z. Effect of fillers on the degradation of automotive epoxy adhesives in aqueous solutions: Part I Absorption of water by different fillers-incorporated automotive epoxy adhesives. J. Mater. Sci. 1993, 28, 6199–6204. [CrossRef]
- 27. Al-Harthi, M.; Kahraman, R.; Yilbas, B.; Sunar, M.; Aleem, B.J.A. Influence of water immersion on the single-lap shear strength of aluminum joints bonded with aluminum-powder-filled epoxy adhesive. *J. Adhes. Sci. Tech.* **2004**, *18*, 1699–1710. [CrossRef]
- 28. Han, X.; Jin, Y.; Zhang, W.; Hou, W.; Yu, Y. Characterisation of moisture diffusion and strength degradation in an epoxy-based structural adhesive considering a post-curing process. *J. Adhes. Sci. Tech.* **2018**, *32*, 1643–1657. [CrossRef]
- Sugiman, S.; Salman, S.; Maryudi, M. Effects of volume fraction on water uptake and tensile properties of epoxy filled with inorganic fillers having different reactivity to water. *Mater. T. Commun.* 2020, 24, 101360. [CrossRef]
- 30. Bruckner, T.; Singewald, T.; Gruber, R.; Hader-Kregl, L.; Müller, M.; Kern, C.; Hafner, M.; Paulik, C. Influence of hollow glass microspheres on 1K epoxy structural adhesive for the automotive industry. *Int. J. Adhes. Adhes. 2023*, *124*, 103396. [CrossRef]
- 31. Stuart, B. The application of Raman spectroscopy to the tribology of polymers. Tribol. Int. 1998, 31, 687–693. [CrossRef]
- 32. Doyle, G.; Pethrick, R.A. Environmental effects on the ageing of epoxy adhesive joints. *Int. J. Adhes. Adhes.* 2009, 29, 77–90. [CrossRef]
- 33. Chateauminois, A.; Chabert, B.; Soulier, J.P.; Vincent, L. Dynamic mechanical analysis of epoxy composites plasticized by water: Artifact and reality. *Polym. Compos.* **1995**, *16*, 288–296. [CrossRef]
- Carbas, R.J.C.; Marques, E.A.S.; da Silva, L.F.M.; Lopes, A.M. Effect of cure temperature on the glass transition temperature and mechanical properties of epoxy adhesives. *Adhesion* 2014, 90, 104–119. [CrossRef]
- 35. Zhou, J.; Lucas, J.P. Hygrothermal effects of epoxy resin. Part II: Variations of glass transition temperature. *Polymer* **1999**, 40, 5513–5522. [CrossRef]
- 36. Puentes, J.; Restrepo-Zapata, N.C.; Chaloupka, A.; Duddleston, L.J.L.; Rudolph, N.; Osswald, T.A. Quasi-isothermal DSC testing of epoxy adhesives using initial fast heating rates. *Appl. Poly.* **2017**, *134*, 45425. [CrossRef]
- 37. Maggiore, S.; Pedemonte, M.; Bazurro, A.; Stagnaro, P.; Utzeri, R.; Luciano, G. Characterization of the effect on an epoxy adhesive in hybrid FSW-bonding aluminium-steel joints for naval application. *Int. J. Adhes. Adhes.* **2020**, *103*, 102702. [CrossRef]
- Chen, Y.; Li, M.; Yang, X.; Wei, K. Durability and mechanical behavior of CFRP/Al structural joints in accelerated cyclic corrosion environments. *Int. J. Adhes. Adhes.* 2020, 102, 102695. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.