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► **To cite this version:**

Romain Grangeat, Marion Girard, Silvio de Barros, Frédéric Jacquemin. An overview of interphase's formation and participation on water diffusion in epoxy/metal bonded assemblies. *The Journal of Adhesion*, In press, pp.1-21. 10.1080/00218464.2023.2206960 . hal-04093724

HAL Id: hal-04093724

<https://hal.science/hal-04093724>

Submitted on 10 May 2023

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An overview of interphase's formation and participation on water diffusion in epoxy/metal bonded assemblies

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Abstract

This overview aims at gathering the various existing works on interphases within epoxy/metal bonded assemblies. Indeed, this particular area plays an important role on the adhesion but also on the behavior in wet environment. Polymeric materials being hydrophilic, water diffusion occurs when they are in a humid environment. The water molecules then have an important impact on the mechanical and physical properties. The effect of water on the interfacial properties of adhesive joints is large discussed in literature. In this article, a complete interphase formation model is be proposed. This two-scenario model explain all the experimental results observed in the literature on the interfaces of a bonded joint. Moreover, hypotheses is made on the water diffusion mechanisms and the diffusive properties of the interface. This is allow explaining the change of the fracture surface observed during the wet aging of a bonded joint. A large number of studies have observed the transition from cohesive to adhesive failure.

Keywords: Bonded assembly; Interphase; Water diffusion; Adhesive materials.

1. Introduction

Bonding technique has become increasingly used in different industrial sectors such as the automobile, aeronautical and marine renewable energy (MRE). There are several types of adhesives, but for structural applications, two-component epoxy adhesives are the most commonly used. Indeed, their mechanical properties, their adhesion and their fatigue and ageing resistance make them ideal candidates. Although this type of adhesive has a good resistance in wet environments compared to other adhesives, a water diffusion can still occur from the presence of certain hydrophilic sites. This water diffusion can affect the mechanical properties and the lifetime of a bonded joint. The water content within the adhesive joint can then be used as an indicator of ageing ^[1]. Weitsman (2012) ^[2] has produced a book on this subject with a large number of studies, which shown how to determine the

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water diffusion properties of a polymer material for different diffusion kinetics. The same approach can be applied to adhesive materials, but these properties are only valid when the adhesive is in a free state. For the bonded assembly where the adhesive is confined between two substrates, it is important to look at the adhesive/substrate interface during ageing. The impact of this interface during ageing is large discussed in the works of Borges et al. (2021) ^[3]. Indeed, this review highlights the impact of interfaces on mechanical properties during wet ageing. It is important to note that the interface corresponds to the geometric boundary between the substrates and the adhesive. To obtain information, mechanical tests are usually carried out on unaged and ageing bonded assembly.

Bordes et al (2009) ^[4] performed Arcan tests on unaged and aged in seawater of epoxy/metal bonded assemblies. After ageing for 1 month, an adhesive failure was observed when tension and shear loading attributed to water molecules diffusing along the interface (**Fig. 1**).

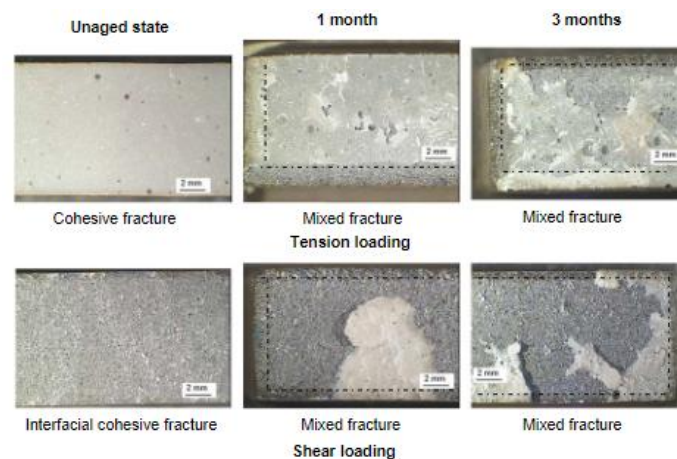


Fig. 1 - Failure surfaces of the Arcan specimen before and after ageing in seawater ^[4]

Equivalent results were observed in the work of Leger et al. (2013) ^[5] in tensile tests on single lap joints aged in immersion at 70 °C. After 14 days of ageing, the failure almost entirely occurs at the interface, resulting in a debonding of the substrate. This degradation is even more important when the temperature is high. Delozanne et al (2022) ^[6] have pointed out a possible thermal aging. Bellini et al (2020) ^[7] worked on single lap joints in composite material, they highlighted the difference in failure surfaces that can be observed between ageing in immersion and in air at the same temperatures. It was observed that air aged specimens showed slight fiber failures while water aged specimens showed fiber adhesive failures. This is probably due to greater degradation of the adhesives aged in water. Cura et al (2016) ^[8] proposed to assess the influence of different surface treatments and 6 months

water storage on the micro-tensile bond strength of composite resin onlays. This process is used in the field of health, for tooth repair. After 6 months in water environment more mixed failures was observed (predominantly between cement and composite resin onlay). They explained this change in failure surface by a higher hydrolytic degradation in the adhesive interface. Cavodeau et al (2020) ^[9] observed a decrease in adherence energy when studying the influence of water diffusion on an epoxy/steel bonded assembly. This decrease comes from the local hydrolysis progressively leads to the delamination.

In conclusion, during the wet ageing a change in the failure surface of a bonded assembly is observed ^[4, 5, 7, 8]. There is a passage from a cohesive failure (in the adhesive) to a mixed failure (a part occurs at the interface) after the humid ageing of a bonded assembly. The change of the failure surface shows that specific phenomena occur during the water diffusion within the interfacial area. In order to explain this, it is important to know the different adhesion theories. In order to achieve a successful and sustainable bond, it is important to have a good understanding of the adhesion phenomenon. There are three main theories to explain the bonding mechanisms: mechanical anchoring, physico-chemical models and the low cohesion layers. A brief overview of these theories is provided. However, none of them alone can explain the adhesion phenomenon. It is the results from the superposition of many elementary mechanisms.

First, mechanical anchoring is one of the first theories to justify adhesion, it has been proposed by McBain and Hopkins in 1925 ^[10]. It is based on the increase of the contact surface by adhesive penetration into the irregularities, microcavities and pores of the substrate. This penetration favors the physicochemical interactions, so it is necessary to have surfaces with a certain roughness. In this context, mechanical surface treatments can be interesting.

The other theory concerns the physico-chemical interactions (electrostatic attraction, chemical and thermodynamic bonds) between the adhesive and the substrate. Firstly, the electrostatic attraction model proposed by Derjaguin and Smilga in 1967 ^[11], this model considers a charge transfer when two materials of different natures are brought into contact. Secondly, the adhesion by chemical bonds proposed by Buchan in 1946 ^[12]. Sometimes it is possible to create covalent or ionic bonds at the interface between the adhesive and the substrate through chemical reactions. In this case, the adhesion

is attributed to the adsorption of the polymer on the substrate by chemisorption. Thirdly, the thermodynamic theory proposed by Schonhorn in 1963 ^[13]. This theory focuses on free interfacial energies and the wetting of the substrate by the adhesive. In this model, the wetting phenomenon reflects the ability of the adhesive to create Van-der-Waals or acid-base bonds with the substrate.

The last theory is not an adhesion model but concerns the rupture of interfaces, it considers the presence of a low cohesion layer. Indeed, in the case of a strong assembly cohesion, the failure does not take place in the interface, but on a neighboring layer. It is in this context that Bikerman (1967) ^[14] postulated the hypothesis of an interphase between two materials. Indeed, he considers a failure within the layer with the lowest cohesive strength, called interphase. This layer constitutes a transition area with properties gradients. It is therefore not necessary to confuse interface and interphase: the interface corresponds to the geometric area between the substrates and the adhesive, while the interphase can be considered as a layer of finite thickness with different properties of the substrates and the adhesive.

Gutowski (1999) ^[15] reviewed the principles of macromolecular design of polymer interface/interphase systems for obtaining maximum adhesion. The macromolecular reactions occurring in this area are complex and not fully understood. Montois et al. (2007) ^[16] consider that the formation of the interphase leads to an initial resistance weakening of the adhesive bonded joints. This has been shown by determining the fracture energies for different curing cycles, which results in different interphase thicknesses. Indeed, the interphase formation varies with the curing cycle, but also with the viscosity of the uncured adhesive. Aufray and Roche (2006) ^[17] works on this subject. They experimentally showed the dependence of the interphase thickness on the viscosity of the adhesive and the adhesive/substrate contact time. The formation of interphases leads to a decrease in the glass transition temperature and in residual stresses. A property gradient was highlighted in the work of Grangeat et al. (2019) ^[18]. For this purpose, optic fiber sensors were used to measure the optical index for different distances to the substrate. The index variation to the distance to the substrate shows the presence of a property gradient that was identified as coming from the interphases.

There are still a lot of questions about the interphases, both on formation and during wet ageing. This overview aims to highlight the different works done on interphases epoxy/metal, in order to understand how they are formed. By gathering the different works, a formation model based on

Coulaud's works ^[19] is proposed. Finally, the studies carried out on the diffusion of water within the bonded assemblies and especially at the level of the interphases make it possible to explain this change of failure surface observed during a wet ageing.

2. Interfacial area: interphase's creation place

2.1. Interphase: generality and introduction

Bikerman (1967) ^[14] was the first to put forward the hypothesis of layer presence with low cohesion between two materials. This lower cohesion would be due to the presence of imperfections coming from the implementation (air bubbles, contaminants, ...) and/or the discontinuity between the chemical phases present in the adhesive (**Fig. 2**). The interfacial area is the creation place of chemical or physical bonds between the polymer and the substrate, which leads to an important properties' gradient.

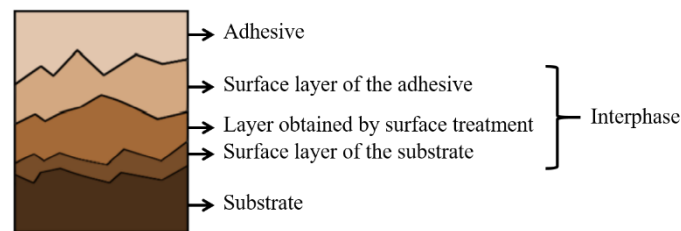


Fig. 2 - Interphase representation of an epoxy/metal bonded assembly ^[14]

As seen above, this particular area has been highlighted in a number of studies ^[15-18]. These different works highlight the interphases impact on the properties of the bonded assembly. It is possible to consider this area as a layer with heterogeneous properties of a fixed thickness. The value of this thickness depends on some factors that come in during the joint manufacturing. The main factors are the substrate type, the hardener type, the curing time, the curing temperature and the viscosity ^[16, 17, 20]. Aufray and Roche (2007) ^[20] shows the dependence of the interphase thickness on the epoxy/metal contact time at room temperature for two types of amine hardeners. They measured this thickness by infrared spectroscopy, it can be up to 300 μm . They consider that the interphase comes from a reaction of the hardener with the metal substrate.

The different reactions that can occur during the interphases formation are complex and poorly understood. The rest of this overview highlights the different phenomena that can occur within this

interfacial area. These different phenomena help to explain how interphases are formed between an epoxy/amine adhesive and a metal substrate.

2.2. Adsorptions reactions

First, after contact between the adhesive and the metal substrate, adsorption reactions can take place at the interface. These reactions can affect amine groups, epoxy groups and metal substrate.

Kelber and Brow (1992) ^[21] have shown that an amine protonation (addition of a $^1\text{H}^+$ proton) can occur when is in contact with copper and aluminum substrates. The reaction occurs when the substrates having surface hydroxides.

Turner et al. (1981) ^[22] worked on the chemisorption that can occur on the surface of an aluminum substrate. This work was carried out using inelastic electron tunneling spectroscopy. The chemisorption reaction leads to the formation of a chelate complex. Chelation is a physico-chemical process during which a complex is formed between a ligand and a metal ion. This reaction occurs between the epoxy/amine and the metal substrate by elimination of a water molecule between the hydroxide groups of the surface and the alcohol terminal of the adhesive.

Comyn et al. (1981) ^[23] shown a preferential adsorption of the hardener (the amine groups) which would block the interaction of the epoxide with the amine and with the substrate. This result has been obtained by using inelastic electron tunneling spectroscopy to epoxy/amine adhesive.

Kollek (1985) ^[24] worked on a model pre-polymer, DGEBA (DiGlycidyl Ether of Bisphenol A). He shows a possible chemisorption of the epoxide on a metal surface. This reaction occurs during the opening of the epoxy functional group by creating a covalent bond with the metal.

In some cases, the contact between the metal substrate and the air lead to a creation of an oxide layer on the surface. Bonds are created between the water molecules H_2O and the oxides, which polarize the metal surface. The polarized surface can then react with the polar groups of the epoxide and the amine molecules. These bonds lead to the hydroxide creation on the surface. For Schmidt (1986) ^[25] and Brockmann (1989) ^[26], adhesion occurs through a reaction between epoxies and amines with theses hydroxide groups.

These various reactions can lead to the inhibition of the epoxy/amine cross-linking. Indeed, as some amine or epoxy molecules have already reacted, they can no longer react to form the adhesive in its

final state. These absorption reactions could explain the formation of interphases. However, they are extremely local and do not justify the variation in properties that have been observed on macroscopic specimens in various works (fracture energy, glass transition temperature, elastic modulus...) [16-18]. It is therefore necessary to be interested in other reactions that may occur.

2.3. Interfacial area enrichment

In parallel to the adsorption reactions, amines migration can occur. Hong et al. (1992) [27] studied the interfacial region between a model adhesive (DGEBA) and a polyamide hardener on different steel substrates. XPS (X-Ray Photoelectron Spectrometry) measurements showed an enrichment of the interfacial area in amine. De Neve et al (1998) [28] studied the failure mode of an epoxy/steel bonded joint. For this purpose, they used XPS measurements that revealed in enrichment in hardener in the interface. This enrichment probably occurs during crosslinking by adsorption at the polymer/metal interface. Vries et al. (1989) [29] obtained similar results with the amines segregation near to the interfaces for another hardener. These works suggest a better chemical affinity of the amines groups with the metal substrate than with the epoxides functions.

However, there may also be an enrichment of this area by epoxides. Indeed, this result was highlighted by micro-FTIR (infrared spectroscopy) measurements in the work of Aufray and Roche (2007) [20]. They worked on two types of hardeners (DETA and IPDA) on an aluminum substrate. The results obtained are shown **Fig. 3**, epoxides functions for DETA and amine functions for IPDA are observed close to the metal substrate. There is, therefore, enrichment of this area by epoxides for DETA and by amines for IPDA.

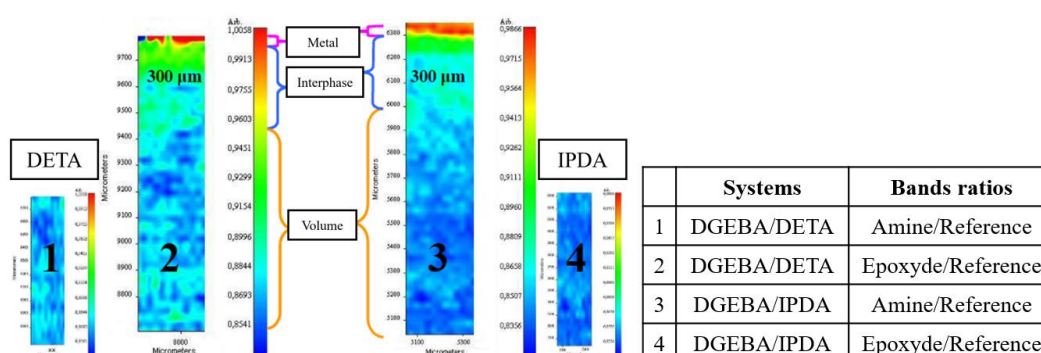


Fig. 3 - Micro-FTIR map of the interphase DGEBA/IPDA and DGEBA/DETA systems (Aufray and Roche (2007) [20])

In conclusion, these different studies show a chemical change in the interfacial area that occurs during the cross-linking of the adhesive. This chemical change could be the cause of the interphases formation by causing reactions with metal substrates.

2.4. Substrate dissolution

Amine hardeners have a basic character in their liquid forms ($10 < \text{pH} < 13$). Indeed, Roche et al. (2002) ^[30] measured a pH of 12 under ambient conditions for a DGEBA/IPDA aqueous solution with a stoichiometric ratio of 1. This ratio corresponds to a 20 % IPDA mass concentration. To do this, they also measured the variation in the dissolution potential of a titanium metal surface immersed in an IPDA solution (20 % mass concentration). The decrease of this potential is observed and comes from a partial oxidation of the surface oxides or hydroxides.

This oxidation leads to a dissolution of certain metal compounds such as surface oxides and hydroxides in the form of metal ions. Since they are no longer bound to the metal substrate, they are found within the epoxy/amine adhesive and can react with the organic compounds.

2.5. Organometallic complexes

Organometallic complexes can occur in the case of an epoxy/metal bonded assembly. An organometallic compound is a chemical compound with at least one covalent bond between a carbon atom and a metal.

In the case of epoxy/amine adhesive on metallic substrate, either two scenarios can explain the organometallic complexes formation, the reaction takes place on the surface of the substrate or the metal ions react within the adhesive.

Fauquet et al. (1994) ^[31] and Bentadjine et al. (2001) ^[32] have shown chemisorption of amine functions on a metal surface. In his thesis, Debontridder (2001) ^[33] then suggests the creation of a coordinative bond between the non-binding doublet of the amine and the metal. This would form organometallic complexes, which could migrate over several hundred microns (to create interphase).

Barthés-Labrousse (1996) ^[34] specifies that the mechanisms of reaction between amine and metal are multiple, and underlines that different surface treatments can lead to different reactions (for example by the variation of the surface acid-base, which changes with the surface treatment). It is important to

note that Schmidt and Bell ^[25] in their book proposed reaction mechanisms between epoxide groups and oxidized metal surfaces. This would explain the results obtained by Aufray and Roche (2007) ^[20] for the DGEBA/IPDA on an aluminum substrate.

The other possible scenario concerns the substrate dissolution, as seen previously the amine can dissolve the oxides or hydroxides layers. In this case, only the metal ions diffuse near to the substrate and a coordinative bond would be created between the non-binding doublet of the amine and the metal, forming the organometallic complexes. Roche et al. (2002) ^[30] assumed that the bond between amine groups and metallic ions results from the electron-rich nitrogen atom donating its lone pair to the electron-deficient metallic center. Thus, organometallic complexes were created by coordination bindings. This result is supported in the work of Kanzow et al. (2005) ^[35]. When the complexes concentration is higher than the solubility product, these complexes crystallize as sharp needles ^[30, 32] and play an important role on mechanical properties.

2.6. General model of interphases formation

Coulaud (2007) ^[19] proposed in his thesis a five-step model of interphase formation. This model was also adapted in the work of Borges et al. (2021) ^[3], but it does not explain the enrichment of the interfacial area in amines observed experimentally in the work of Aufray and Roche (2007) ^[20]. It also omits the absorptions effects that can occur by considering only an amines migration that leads to a dissolution of the substrate. Based on this model and knowing that the reactions can occur within the interface, a model of interphase formation is proposed with two scenarios (**Fig. 4**).

The first considers adsorption reactions on the surface of the substrate, which form organometallic complexes that can migrate over several hundred micrometers to create an interphase. This scenario can occur through a reaction of amines but also epoxides with metal oxides or hydroxides present on the surface of the metal substrate. The reaction favored will depend mainly on the nature of the epoxy/amine couple, the nature of the substrate and its surface treatment. The final interphase is composed of organometallic complexes, adhesive and unreacted epoxy functions (or amines).

The second scenario concerns the dissolution of metal oxides or hydroxides by the enrichment of the interface by amines. The oxides and hydroxides can then react with the amines to form organometallic

complexes that can migrate over several hundred micrometers. Unlike the first scenario, this one considers that within the interphase there are necessarily unreacted epoxy functions.

In both cases, the epoxy/amine reaction is not favored due to the formation of organometallic complexes.

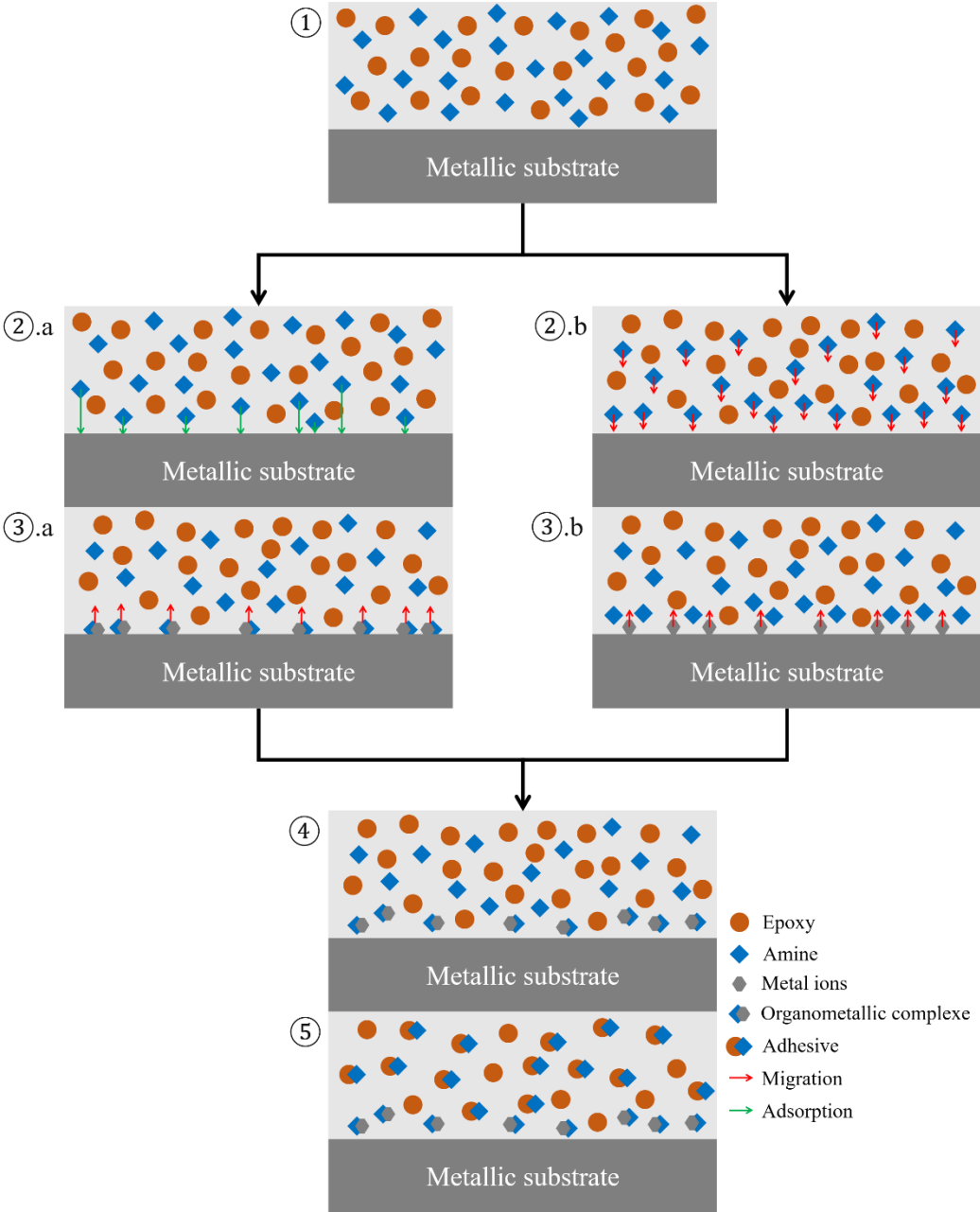


Fig. 4 - General model of interphases formation for epoxy/amine adhesive on metallic substrate (a: scenario with adsorption reactions, b: scenario with amine migration)

The steps of interphase formation represented by **Fig. 4** can be described. Step 1 is the manufacturing process of the adhesive by mixing the epoxy and amine molecules. Step 2 is an amines adsorption (or epoxies adsorption) in the first scenario (2.a) ^[31, 32], and amines migration in the second scenario (2.b)

^[27-29]. Step 3 is an organometallic complexes formation in the first scenario (3.a) ^[25, 33, 34] and oxides or hydroxides migration in the second scenario (3.b) ^[30, 35]. Step 4 is an organometallic complexes migration in the first scenario and formation in the second scenario. Finally, step 5 is the remaining epoxy/amine reaction to form the adhesive in its final state.

To support these results, Aufray and Roche (2007) ^[20] have highlighted the presence of residual epoxides (for DGEBA/DETA) and amines (for DGEBA/IPDA) in the interphase by micro-FTIR. Some compounds have not reacted which can lead to an under-crosslinking of this area. It would appear that the DGEBA/DETA system would follow the second scenario while the DGEBA/IPDA system would follow the first scenario considering epoxy adsorption in step 2.a. In his thesis, Aufray (2006) ^[36] showed the conversion rate variations a function of thickness for DGEBA/DETA and DGEBA/IPDA epoxy coatings on aluminum substrate. For small coating thicknesses of DGEBA/DETA, the conversion rate of the amine functions is close to 1, the compounds have all reacted, which is not the case for some epoxy functions. However, for the DGEBA/IPDA system certain amine functions have not reacted.

In conclusion, there is a competition between the adhesive cross-linking reaction and the organometallic complex formation. This is why the interphase thickness depends on the liquid/solid contact time and the adhesive viscosity. The chemical compounds gradient plays a role on the mechanical properties. There is a large work ^[16-18, 20, 32, 37] on the mechanical properties of the interphase and their impact on the macroscopic properties of a bonded assembly. This overview does not talk about it, but rather about its participation on the water diffusion, which is a subject that is still poorly understood.

3. Interphase's participation on the water diffusion

3.1. Water in interphases

Polymeric materials have the ability to uptake water. This water uptake leads to a drop in certain mechanical properties and affects the service life of the material. This can be seen in the case of bonded assemblies subjected to a humid environment. Water diffusion has a significant impact on the mechanical performance of the bonded assembly. When the adhesive is located in the core of a bonded assembly, the presence of interphases leads to a change in its diffusion behavior.

Zanni-Deffarges and Shanahan (1995) ^[38] worked on the water diffusion within an epoxy adhesive. They compared the behavior of the same epoxy adhesive in the case of a bulk specimen and in an epoxy/metal bonded assembly. They showed a faster water diffusion in bonded assembly, they explain this result by the interphase's participation. This result is supported in the work of Vine et al. (2001) ^[39], which considers that water diffusion weakens the interphases and reduces the life time of a bonded structure.

Chan and Yuen (2007) studied moisture diffusion of an epoxy/copper assembly by FTIR-MIR technique. They found an accumulation of water molecules in the interface. This would mean that the interface had a different absorption behavior against bulk epoxy; indicating that it requires a new model to describe the phenomenon. In his thesis O'Brien (2003) ^[40] also show this result for epoxy adhesives in different metallic substrates.

This water accumulation is also mentioned in the Cognard's work (1994) ^[41] who developed a model for the degradation of bonded assemblies by the accumulation of water molecules in the interface.

These different results can be explained by the presence of interphases, which have different water diffusion properties than the adhesive in a bulk. In his thesis, Bruneaux (2004) ^[42] outline the diffusion of water within a bonded assembly considering an inhomogeneous water diffusion front in the thickness (**Fig. 5**).

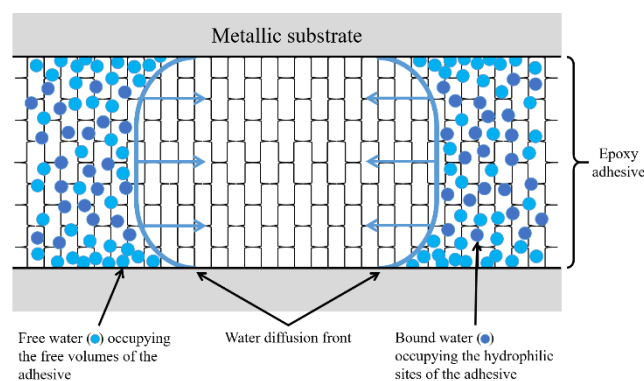


Fig. 5 - Summary diagram of the different water diffusion modes in a bonded assembly ^[42]

The water front diffusion front shows that molecules are more rapidly absorbed in the interphases. Moreover, they can accumulate in this area. These different results show the complexity of the water diffusion phenomenon in the bonded assembly. To explain these phenomena, the literature puts forward two hypotheses: the first one consists to take into account the capillarity effects along the

substrate and the second to consider an under-crosslinking of the interphases would accelerate the water diffusion.

3.2. Capillarity effect

Capillarity is the interaction that occurs at the interfaces between two immiscible liquids, between a liquid and air or between a liquid and a surface. In the case of water diffusion in epoxy/metal bonded assembly, the water molecules diffuse along the metallic substrate by capillarity effect.

In their works, Zanni-Deffarges and Shanahan ^[38, 43, 44] consider that the adhesive/substrate interface can constitute a preferential way of water diffusion. They propose a phenomenon of “capillary diffusion”. The diffusion front near the metal/polymer transition to be analogous to a wetting triple line (**Fig. 6**). Three phases are present: metallic substrate, wet adhesive and dry adhesive. Since the metal represents probably a high-energy surface, the interfacial free energy metal/dry adhesive could well be quite large and therefore a significant interfacial tension could help to advance the water diffusion front along the metallic substrate.

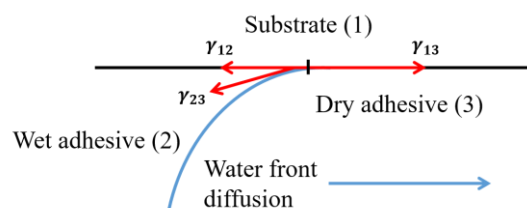


Fig. 6 - Model diffusion front near the metal/polymer transition. Terms γ_{12} , γ_{23} and γ_{13} represent interfacial tensions between phases metal, wet and dry adhesive

Cognard (1994) ^[41] and Bowditch (1996) ^[45] show that the capillarity effect can be amplified when the substrate has hydrophilic polar sites. The surface treatment can be modified the hydrophilic behavior of the substrate. The surface condition of the substrate, therefore, plays an important role in the water diffusion within the interphase.

3.3. Under-crosslinking area

Compared to the previously proposed model (**Fig. 4**), the interphases formation leads to the presence of residual unreacted amines (or epoxies) functions. These molecules are not involved in the formation of the macromolecular network. This can be interpreted as a change in the stoichiometry of the reaction. The network formed during a reaction between the amines and epoxies functions reaches its maximum molecular density when the stoichiometric ratio is optimal (equal to 1).

This interpretation is supported by several works in the literature ^[20, 32, 36, 37]. This work highlights the presence of residual amines (or epoxies) that have not reacted, resulting in under-crosslinking of the adhesive at the interphases. Obviously, it has consequences on the properties of the interphases, including the diffusive properties.

Krongauz (2010) ^[46] worked on dependence of solvent diffusion kinetics in cross-linked polyurethane acrylate networks. The dependence was monitored thermogravimetrically as a function of temperature and crosslink density. It was observed that the diffusion rate decreased with crosslink density increase.

Reinhart and Peppas (1983) ^[47] worked on the diffusion of solutes in swollen membranes. They showed a strong dependence of the diffusion rate with the cross-linking density. Equivalent results were obtained in the study of Robert et al. (1985) ^[48], who studied the effect of crosslinking degree on water transport in polymer micro particles.

De Parscau du Plessix et al. (2016) ^[49] conducted gravimetric tests on composites exposed to a wet environment. Tests were carried out on specimens with different cross-linking density. The results show a higher diffusion coefficient and water content at saturation for lower crosslinking density. Therefore, the crosslinking density of a polymer material plays an important role on the diffusive properties.

The physical explanation is as follows, when a material is not fully cross-linked, its molar mass is lower which leads to a lower density. The water molecules will thus have more facility to be absorbed and to diffuse within the material. The water diffusion is faster and more important when the crosslinking density is lower. Based on this result, diffusive properties of the interphases are higher.

In conclusion, it is necessary to take into account the interphases participation on water diffusion. The two hypotheses to accelerate water diffusion, capillarity effect or under-crosslinking, are not contradictory. The difference in diffusive behavior between the interphases and the bulk adhesive can be explained by the two hypotheses that may occur in parallel.

3.4. Interphase diffusive properties and modelling

The water uptake of a bonded assembly depends on the presence of the interphase. Indeed, its diffusive properties are different from the bulk adhesive and must be determined to model the water diffusion. This model is important in the study of structure ageing.

Joliff et al. ^[50, 51] worked on the water ageing of glass fiber composite material. They show the impact of fiber/matrix interphase, which modified the water diffusion kinetics. An experimental, analytical and numerical approach was carried out. In the interphase, they considered a diffusion coefficient ten times higher than the bulk resin. This coefficient was determined empirically by comparing the diffusion kinetics of the bulk resin and the composite. Reifsnider et al. (1988) ^[52] came to the same conclusion studying the water transport in fiber reinforced plastic. Zid et al. (2020) ^[53] carried out a numerical analysis by varying the ratio between the diffusion coefficient of the interphase and the matrix. They highlighted the impact that this can have on the local and barrier properties.

These different works evaluate the interphase participation on the diffusive coefficient. The other important parameter for the water diffusion is a water content at saturation.

Grangeat et al. ^[54, 55] deduced the water content at saturation of the epoxy/metal interphase using experimental tests with fiber optic sensors. It was shown that the smaller the distance to the substrate, the higher the water content at saturation. An increase of almost 50 % was obtained in the interphases. A similar results was obtained by Wu et al. (1995) ^[56] and Vogt et al. (2004) ^[57], which they highlighted an accumulation of water molecules respectively at the interface polyimide/silicon and in thin polymer films. Gibhardt et al. (2019) ^[58] worked on the effect of hygrothermal ageing on the interphase of glass fiber reinforced epoxy. They observed a fiber/matrix debonding and delamination, this failure cause to a plasticized interphase during the hygrothermal ageing. Only the interphases have plasticized because the water content in this area is higher than in the rest of the matrix. Krauklis et al. (2018) ^[59] showed the impact of fiber/matrix interphases on the macroscopic water uptake of a composite specimen, they also concluded that interphases lead to a higher water absorption.

In each case, the results lead to a higher diffusion coefficient and saturation water content. Using the water diffusion models listed in the Weistman's work ^[2], the local water content field can be modeled with the interphases diffusive properties.

Rocha et al. (2016) ^[60] modelled the water diffusion of a glass/epoxy composite taking into account the interphase presence between the fibers and the matrix. They considered that water diffusion in the matrix and in the interphase followed a Fickian behavior. The interphase thickness is set in accordance with the work of Joliff et al. ^[50, 51], and provides a reliable representation of the experimental results.

Grangeat et al. ^[54, 55] modelled the water absorption of an epoxy/metal bonded assembly taking into account the interphases presence. An analytical model was set up to represent the water content and the average diffusive properties of the interphases ^[55]. These diffusive properties were also measured experimentally using fiber optic sensors ^[54]. It was shown that it is necessary to take into account the interphases participation on water diffusion in local and macroscopic behavior.

3.5. Failure surface change

Water diffusion plays an important role in the lifetime of a bonded structure. Indeed, during water ageing the mechanical properties of the adhesive change. Crocombe et al (2016) ^[61] showed a drop in the elastic modulus of an epoxy adhesive as a function of its water content. They observed a 35 % drop in elastic modulus for a water content of 1 %. Park et al. (1997) ^[62] and Sharp et al. (2017) ^[63] showed a drop in glass transition temperature during water ageing of an epoxy adhesive. In the work of Park et al. (1997) ^[63] a drop of 35 °C was observed for 3 % water.

Another effect frequently observed during water diffusion is hygroscopic swelling. Loh et al (2005) ^[64] measured the volume change of an epoxy adhesive subjected to a humid environment. During hygroscopic swelling, in the case of an adhesive alone, the adhesive is free to deform. In the wet condition, when the steady state is reached and the material is uniformly saturated, the deformation field is homogeneous and the dimensions of the specimen have changed compared to the dry state. There is no longer a water content gradient and the stress field is zero. When the same adhesive is confined between two substrates, the hygroscopic swelling of the adhesive joint is stuck. The stuck deformation leads to the creation of internal stresses that can affect the structural integrity of the structure. In his thesis work, Mario (2007) ^[65] showed the creation of shear stresses in the interface of a bonded assembly subjected to a humid environment. These stresses result from the stuck hygroscopic swelling of the adhesive joint. This result was obtained by solving a hygromechanical model, which allows modelling the water diffusion, and to take into account the mechanical field induced by the hygroscopic swelling. Equivalent results have been obtained in the work ^[42, 66].

In addition to affecting the intrinsic mechanical properties of the adhesive and generating internal stresses, water diffusion can affect the interfacial area between the substrate and the adhesive. Cognard (1994) ^[41] proposes a four-phase damage mechanism (**Fig. 7**).

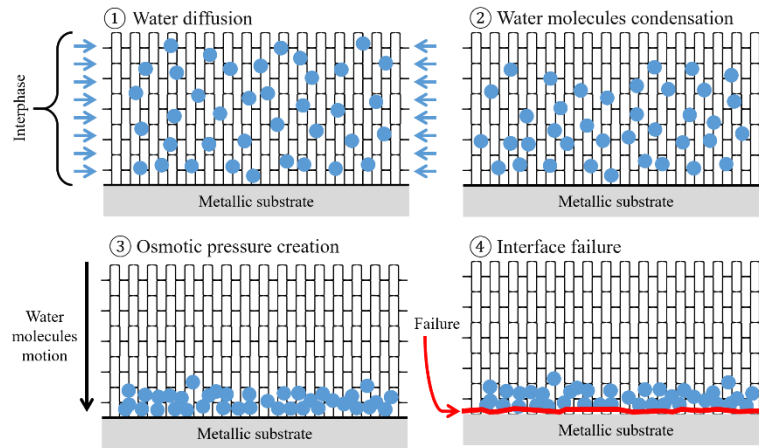


Fig. 7 - Damage mechanism by water molecules in bonded assembly inspired by Cognard (1994) ^[41]

First, the water molecules diffuse within the bonded joint. Then, they condense at the substrate and start to agglomerate near the interface. This leads to the creation of an osmotic pressure. This pressure is such that it can lead to the interface failure. This damage mechanism explains the transition from cohesive to adhesive failure that has been observed during the ageing of a bonded structure due to the interphases ^[4, 5, 7, 8].

4. Conclusion

This overview allows highlighting and gathering the various existing works on interphases within epoxy/metal bonded assemblies. The formation model proposed here allows understanding the different phenomena that lead to the interphases presence. They result from the reaction between amines and metal oxides (or hydroxides) which form organometallic complexes leading to the presence of property gradients. The interphases play an important role on the mechanical and physical properties of an assembly, mainly on the elastic modulus, the glass transition temperature and the conversion rate of this area. The second part of this work also shows the interphases participation on water diffusion. The literature puts forward two hypotheses to explain why the diffusion is faster and more important in this area: capillary effects and/or under-crosslinking. By characterizing the interphase diffusive properties, it is possible to model the water absorption of a bonded assembly. This modeling, coupled with the degradation model mentioned above, allows explaining the change of the failure surface observed during the bonded joint ageing in a wet environment.

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