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Development of new surface treatments for the adhesive bonding of aluminum surfaces

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ABSTRACT

Bi-functional water-soluble polymers have been investigated as bonding layers (BL) on aluminum surfaces to promote the adhesion of adhesives for structural bonding applications in the automotive sector. The BLs are located at the interface between two parts: the aluminum substrate and the adhesive (an epoxy-dicyandiamide). The formation and the morphology are studied mainly by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Many process parameters have been investigated such as: i) long or short immersion time in the treatment baths containing the polymers, ii) formulation using three different concentrations. The performances of the BLs under these different operating conditions are evaluated via several mechanical tests: micro-scratch, three-point bending, single lap shear. Results were compared with results obtained with already existing products, launched for the same application, surface treament prior to structural adhesive bonding of aluminum in transportation.

1. Introduction

Adhesive bonding is one out of many joining technologies [1,2], along with welding and riveting to name a few. It produces a continuous and homogeneous joint line or joint surface rather than localized contact points. This continuous joint surface presents several advantages versus welding and riveting: i) more uniform stress distribution over the bonded surface [2–4], ii) good damping properties for noise and vibrations, which therefore improves the comfort of drivers and passengers [2,5], iii) an increased stiffness (improved safety in the case of car bodies), iv) no galvanic corrosion issue (metal-to-polymer contacts instead of metal-to-rivet contacts), v) a weight reduction [6] (adhesives have a much lower density than mechanical fasteners). However, regarding light weighting, the largest gain comes from the replacement of steel by aluminum, which was actually enabled by adhesive bonding. Indeed, aluminum, easier to recycle and lighter than steel, is an attractive alternative to steel but its drawback is a lower aptitude to welding. Aluminum started to be massively used in the automotive industry [7], and especially for the body-in-white, when surface treatment technologies yielding durable adhesive joints and applicable at large scale were developed. Several automotive manufacturers embarked on the design of so called "aluminum-intensive cars" [5,8,9], which allowed them to reduce the fuel consumption [10]. As a matter of fact, adhesive bonding as method of assembly allows to limit the CO_2 emissions of vehicles into the atmosphere by reducing their weight (about 30%) [6], by replacing steel with lighter aluminum [5,7,11]. The bonding assembly method was set up as well as the preparation and surface treatments in order to promote the joint durability and the adhesion of compounds to an aluminum surface [12–15]. It is precisely the aim and development of these surface treatments, also called bonding layer (BL).

For decades, surface treatments prior to bonding relied on inorganic technologies (anodization, titanium and/or zirconium hexafluorides, titanium and/or zirconium hexafluorides combined with organic polymeric adhesion promotors). Very recently, BLs exclusively consisting in organic molecules and especially organic polymers, were developed [16,17]. These polymers contain different bonding functions with, on one hand, the aluminum substrate and, on the other hand, with the adhesive. Thus, the transition from inorganic to organic treatments, by varying the nature of the anchoring functions (the lateral functions) within the polymers to optimize their role as bridging agent between two different

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types of compounds to ensure efficient and durable structural bonding, constitutes a novelty in the field of surface treatments for adhesive bonding. For this, polymers having different functions such as, phosphonic acids and carboxylic acids have been developed. These functions will form covalent bonds with the aluminum hydroxides of the substrate and the functions present in the adhesive, such as epoxy and amine functions. Different reaction mechanisms have been determined, a dehydration reaction between the phosphonic acid function and the aluminum hydroxides [18–21] and an esterification reaction between the acrylic acid functions and the epoxides of the adhesive [22,23]. The bonds formed as a result of these reactions were demonstrated by XPS, ATR-IR and ^{13}C NMR analyzes. Also, Nitowski et al. [24] also put in evidence nucleophilic additions between the vinyl groups (when present in the surface treatment formulation) and amine functions of the adhesive [25,26].

This kind of BL has been developed to be convenient for various applications and different application methods, including spraying and dipping processes (for parts and coil processes). This work focuses on one hand on the nature of polymers and on the other hand on the impact of the polymer concentration in the surface treatment bath and immersion time in these treatment baths. In this study, immersion times of 120 or 3 s (to approach contact times typical of parts immersion processes and coil processes, respectively) were investigated, and correlated to the morphology of BLs and on their adherence performance using various mechanical tests.

2. Experimental

2.1. Materials and sample preparation

The aluminum grade AA5754 is an alloy widely used in the automotive industry. We used AA5754 supplied by FBCG (Al: 94.9%, Mg: 2.6–3.6%, Fe: 0.4%, Si: 0.4%, Mn: 0.5%, Cr: 0.3%, Zn: 0.2%, Cu: 0.1%, Ti: 0.03%). The treated coupons are 100 mm long 25 mm wide and 3 mm thick.

The adhesive used for the micro-scratch and the single lap shear tests is a commercial epoxy-dicyandiamide, Betamate 1496 F from Dupont company. The curing step is carried out in an oven at 180 °C during 40 min.

The second adhesive used for the three-point bending test is a two-component epoxy-amine at low viscosity, Araldite AY103 with HY991 from Gaches supplier. The curing cycle is 1 h at 130 °C in oven.

The two systems used in this study are described in the following table (Table 1). The first one consists in a poly (vinyl phosphonic acid-*co*-acrylic acid) supplied by Solvay (Addibond 021), while the second system (Addibond 275) contains the same polymer plus the vinyl phosphonic acid monomere itself (VPA). They are compared with a commercial formulation, which is composed of a polymeric adhesion promotor and an inorganic $H_2(Ti, Zr)F_6$ part which forms a conversion layer. This product was selected as reference because it is already on the market and is used in aluminum surface treatment for structural bonding applications.

All treated substrates undergo the same surface preparation, as well as the same method of deposition of BL. This takes place via successive immersions in different baths placed on a heated orbital table (Fig. 1) set at 45 rpm and at 80 °C so that the solutions reach a temperature of 50 °C ± 3 °C.

The very first step consists in immersing the aluminum surfaces in a commercial solution of DBT Alu 200 from Chemtec, which is a "two-in-one" solution, cleaning and etching (c/e), to save time compared to conventional processes which involve first an alkaline degreasing step, followed by an acidic step. The sheets of aluminum were produced by rolling processes, the near surface deformed layer (NSDL) resulting from this process contains lubricant residues on the surface and in inclusions, as well as particles of fragmented intermetallics and oxides. This step (c/e) aims at removing this NSDL and also at activating the surface by removing and replacing native alumina with controlled aluminum hydroxides groups, to generate a surface adequate for surface treatments. According to the recommendations of the technical data sheet, the substrates are dipped for 3 min (at 50 °C) in a concentrated bath at 50 g/L. This is followed by two successive rinses by immersion in two separate baths of distilled water (also at 50 °C) for 1 min each.

The c/e reference is obtained after the rinsing and drying steps, coarsely with compressed air at first and then in an oven for 10 min at 80 °C to remove traces of water. All the other samples, after the rinsing steps, are directly immersed in the BL baths (at 50 °C), either for 120 or for 3 s, then rinsed again, but this time under distilled running water for 1 min and finally dried exactly the same way as described above.

2.2. Materials characterization

2.2.1. TEM analysis

To characterize the morphology of BLs and more precisely the thickness of the BL, cross-sectional observations were made with a transmission electron microscope (TEM) for BL Addibond 021 and Addibond 275 on AA5754.

First of all, the samples were metallized with gold (200 nm thick layer) using a Cressington 118 Auto metallizer (England), and secondly with platinum (2–3 μm thick layer) inside the FIB in order to protect the BL before slicing the sample using a focused ionic beam (FIB).

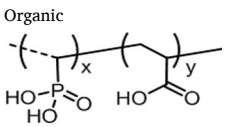
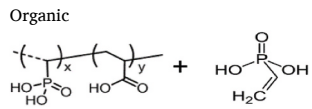
A focused ion beam coupled with a scanning electron microscope was therefore used because this method makes it possible to cut and observe a sample slice with very high cutting precision. The region of interest is therefore observed to determine the thickness of the BL on the aluminum substrate.

Taking into account the scales observed and analyzed, the observation of the morphology of the BLs was carried out under a transmission electron microscope using a JEOL JEM 2100 F device (Japan). The source is field emission with an acceleration speed of 200 kV and a resolution of 2.3 Å.

2.2.2. XPS analysis

X-Ray photoelectron spectroscopy (XPS) analyses were carried out on Addibond 021 and Addibond 275 at two immersion times respectively 120 and 3 s, as well as at three different concentrations, low, medium and high, as well as on a raw reference. These analyses made it

Table 1
Nature of polymers forming BL.

	Addibond 021	Addibond 275	Commercial formulation
Nature of the BL	Organic 	Organic 	Mixed organic/inorganic
Lateral function (%mol)	Phosphonic acid (30%) Acrylic acid (70%)	Phosphonic acid (82.5%) Acrylic acid (17.5%)	Organic part + Conversion coating H2(Ti,Zr)F6

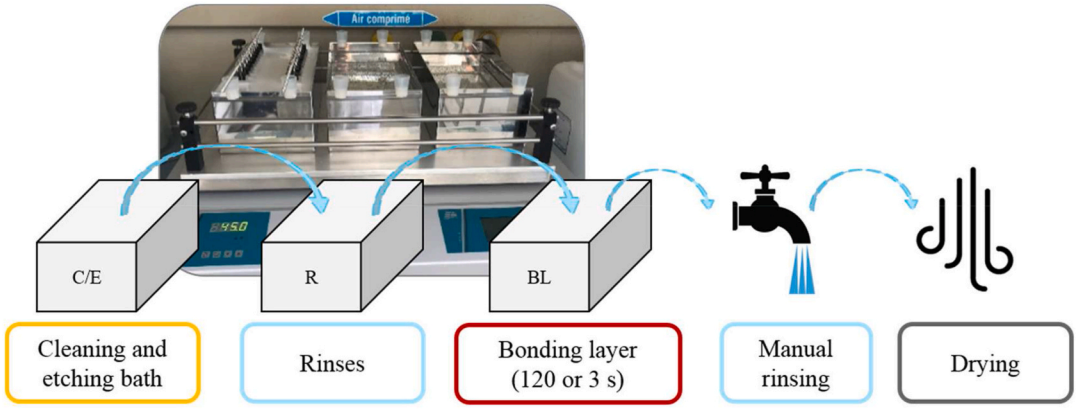


Fig. 1. General process of depositing bond layers on AA5754 substrates.

possible to determine on one hand the binding energies between the BL and the aluminum substrate and on the other hand the elemental composition in atomic percentage of the BL at the extreme surface.

A ThermoFisher Scientific K-ALPHA spectrometer (United States of America) was used for XPS surface analysis with a monochromatized AlKα source (hν 1486.6 eV) and a 200 µm X-Ray spot size. A pressure of 10^{-7} Pa was reached in the chamber when transferring the raw, Addibond 021 and Addibond 275 samples. The full spectra (0–1320 eV) were recorded with a constant pass energy of 200 eV and high resolution spectra with a constant pass energy of 40 eV. Charge neutralization was applied during analysis and depth profiles were fulfilled with an Ar^+ ion gun (500 eV energy). The depth sequence was divided into 14 levels (0, 8, 16, 24, 39, 55, 70, 86, 117, 148, 179, 211, 242, 289 nm) in order to finely probe the extreme surface of the material. High resolution spectra (i.e. C1s, O1s, N1s, P2p, P2s, Al2p, Cu2p, Mg1s, and F1s) were quantified through Scofield sensitivity factors using the AVANTAGE software provided by ThermoFisher Scientific.

2.2.3. *Model reaction with the adhesive and related analyses*

The reaction between the Addibond 021 and the epoxide adhesive was investigated with glycidyl ether 4-methoxylphenyl, model for the epoxide adhesive. The Addibond 021 was dried as a very thin film at room temperature on a glass panel, further dried in an oven at 80 °C for 10 mn. On the resulting thin film was then added an excess of glycidyl ether 4-methoxylphenyl, and the blend was heated till 50 °C, to melt down the epoxide. Both were then mixed with a spatula and heated to 180 °C for 40 mn, conditions typically used to cure the structural epoxide adhesives. The resulting product was then combined with both water and chloroform, to solubilize unreacted polymer (in the water phase) and the unreacted epoxide (in the chloroform phase). The whole product was recovered after filtration of the water phase: there was no product found i) in the chloroform phase after chloroform evaporation, ii) in the water phase while all the product was recovered as being insoluble in the water phase. This insoluble matter was analyzed by solid NMR and ATR-IR. A blank experiment was done with the polymer alone (Addibond 021, no added epoxide): the film was prepared in the very same conditions and then submitted to the same temperature profile. The objective was to get reference NMR spectra and ATR-IR chromatograms.

2.2.3.1. Solid NMR analysis. ^{13}C Experiments were performed on a Neo Avance Solid 400 MHz Bruker spectrometer (9,4 T) equipped with a 4 mm probe (France). For the high power decoupling (HPDEC) the length of the P90 pulse was 3.8 µs and the recycling delay was set to 30 s. The proton was decoupled at 80 KHz and MAS frequency was set to 6 KHz. Adamantane was used as the ^{13}C chemical shift reference (δ 38,5 ppm for the left peak).

2.2.3.2. ATR-IR analysis. The product prepared as described above was also analyzed by ATR-IR. Products were analyzed by ATR-IR (Attenuated Total Reflection - Infrared) on a Bruker spectrometer (France), Tensor 27, with the adequate ATR-diamond set. Wave lengths were varied from 650 to 4000 cm^{-1}, with a 4 cm^{-1} resolution and 35 scans were performed for each sample.

2.2.4. *Micro-scratch test*

The scratch resistance of the systems was evaluated using a micro-scratch test with increasing normal loading, with normal forces in the Newton range. This technique is based on the comparison of the critical normal forces values, leading to typical damages of the studied systems (plastic deformation, ductile/brittle transition with cracking of the layer or of the substrate itself, lateral displacement of material, chipping or delamination of the layer, etc.).

A semi-complete system was produced for this test: a treated aluminum coupon is coated with the adhesive (Betamate 1496 F) on its tip and a Teflon coupon is then placed on top so that a 25 mm wide by 12.5 mm long overlap is obtained. After the adhesive curing cycle, the Teflon coupon is removed to obtain the sample to be scratched (Fig. 2). The thickness of the adhesive is heterogeneous, but lies around 200 µm, and contains small air bubbles due to the non-adhesion of the Teflon coupon.

The scratches are performed with a Scratch-Test REVETEST equipment from CSM Instrument (Switzerland) by applying a progressively increasing normal force from 55 to 100 N over a total distance of 4 mm with a scratch speed of 1 mm/min. For each sample, three scratches were made to evaluate the repeatability.

To compare BLs to each other, the normal force of adhesive delamination, corresponding to the aluminum substrate baring, was chosen (full black cross on Fig. 3), which corresponds to the normal applied force at which the interface between adhesive and treated substrate

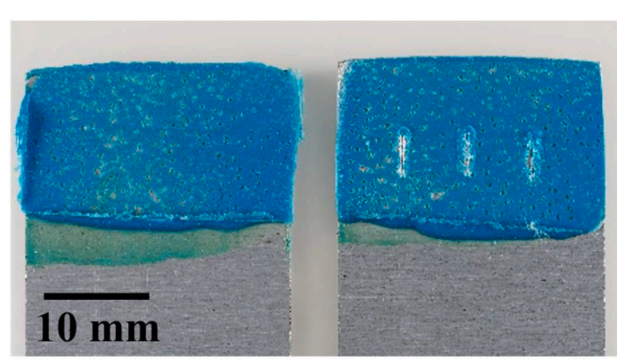


Fig. 2. Sample before and after scratched on treated AA5754 with Betamate 1496 F adhesive.

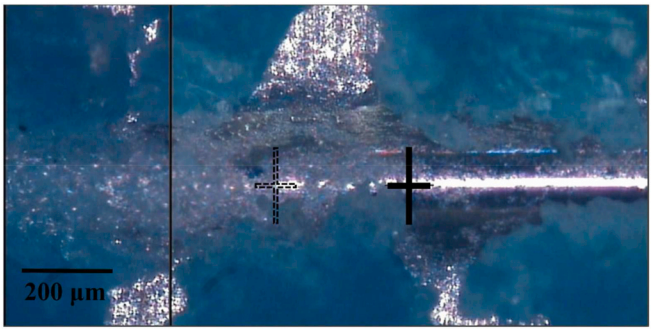


Fig. 3. Example of a micro scratch with represented by the dotted cross the start of exposure of the substrate and by the full cross the complete exposure of the substrate.

failed, leading to further damage within the substrate if the loading continues to increase (the track of the indenter in the aluminum can clearly be seen).

2.2.5. Three-point bending test

For this mechanical test was operated according to the ISO 14679-1997 standard, which specifies the use of substrates 50 mm long, 10 mm wide and 1.5 mm thick. An adhesive cube is made using a three-part mold (Fig. 4) to form 25 mm long, 5 mm wide and 4 mm thick cube by applying 0.5 mL of adhesive using a 1 mL syringe.

The test is conducted by an INSTRON traction machine (model 3369, France) equipped with a 500 N load sensor and a jaws system suitable for the three-point bending where the distance between supporting pins is 35 mm. The speed of the test is 0.5 mm/min. The force at break (N) is obtained from the graph showing the force values (N) as a function of the displacement (mm).

While the standard recommends at least 6 samples per series, 24 samples were performed per series and the Dean and Dixon statistical test [28] was used to rule out the most aberrant results. One sample per series (in average) was discarded, with a percentage of 5%.

2.2.6. Single lap shear test

The single lap shear (SLS) is a very widespread and mastered test in the industry, it is also easy to implement, which is why it is very often used as a routine test, especially in automotive applications.

The treated coupons are glued together with a 25 mm by 12.5 mm overlap and the bond line (adhesive film thickness) is 200 µm, controlled by the presence of glass beads (with a diameter between 150 and 250 µm) within the adhesive itself.

The test is carried out on the same traction machine as the three-point bending test, but equipped with a 30 kN load sensor. The assembly is placed such that the jaws (of 30 kN) grasp the coupon tips over 50 mm. The pulling speed is set at 10 mm/min. The load at break (N) was retained, as well as the stress at break (MPa) which corresponds to the force required to break the adhesive joint. Five samples are tested per series to obtain average values.

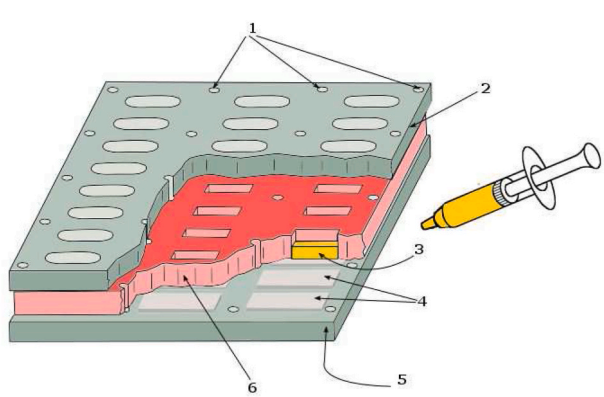


Fig. 4. Preparation of samples according to ISO standard 14,679–1997 [27]
1: Fastening (20 bolts), 2: Fastening plate, 3: Silicone spacer, 4: Adhesive block, 5: Substrates, 6: Lower plate.

For this test, assemblies were tested "fresh" and after ageing. "Fresh" means the SLS assemblies are tested shortly after their production. "Ageing" means that assemblies are placed in a corrosion chamber and submitted to 500 cycles at 49 °C, each 2 h-long, consisting in an acetic acid salt spray for 30 mn followed by 1h30 at 98% relative humidity, according to the ASTM G85-A3 standard. The solution used in the corrosion chamber consists of sodium chloride (42 g/L) and acetic acid (10 mL/L) to reach a pH between 2.8 and 3.0. Total ageing time is 1000 h.

3. Results and discussion

3.1. Characterization of the bonding layer – aluminum substrate interface

3.1.1. Adsorption mechanisms of the bond layer

The BL is located between the aluminum substrate and the adhesive (epoxy-dicyandiamide). For effective bonding this BL should be strongly linked to both parts. This guided the design of the polymers tested here, that is why the Addibond polymers have several reactive functions with the aim of reacting covalently with the species present on the one hand on the aluminum substrate and on the other hand in the adhesive.

First of all, it has been shown by X-Ray photoelectron spectrometry analyses [18], that the phosphonic acid functions present in Addibond 021 and Addibond 275 react covalently with aluminum oxides by a dehydration reaction described in Fig. 5.

Esterification reactions between the carboxylic acid functions of polymers and the epoxide functions of the adhesive according to the following mechanism (Fig. 6) also take place. These reactions were evidenced by ^{13}C solid NMR and ATR-IR.

Starting from peaks typical of carboxylic acids, a new peak appears at 175 ppm in ^{13}C solid NMR (Fig. 7), while a new signal appears at 1700 cm^{-1} in ATR-IR (Fig. 8). These new signals are typical of ester functions, in line with the reaction shown Fig. 6.

Also, by mechanisms less known but shown in the work of Nitowski [24], there is a nucleophilic addition reaction (Michael addition) between the vinyl functions (of the vinyl phosphonic acid monomer) and the amine functions of the adhesive (Fig. 9), [25,26].

Finally, all these mechanisms make it possible to ensure a chemisorption of the polymers constituting the BLs with respect to the substrate and the adhesive.

3.1.2. Bond layer morphology

By TEM observations with FIB preparation, it was possible to distinguish in Fig. 10 a thin layer between 5 and 10 nm thick which would represent the BL of Addibond 021 (the same observations has been seen on Addibond 275 sample). The thin 5–10 nm layer appears on images of clear contrast between the aluminum (light grey) and the gold layer (black).

It was noted on the sample of Addibond 021 areas where the BL appears to be denser and more porous areas (dotted black circles) where the gold from the metallization diffuses into the BL. This phenomenon seems to indicate that the polymers of the BL do not organize themselves in the same way over the entire surface of the substrate, and perhaps testifies to an inhomogeneity in the reactions between the aluminum hydroxides and the phosphonic acid and carboxylic acid functions of polymers.

It was possible to observe the layer thicknesses (between 5 and 10 nm) on all Addibond samples, in both cases of 120 or 3 s immersion times (see Table 2), which means that this time is not a key parameter on the formation and therefore on the morphology of the layer.

However, for the commercial formulation, the immersion time is

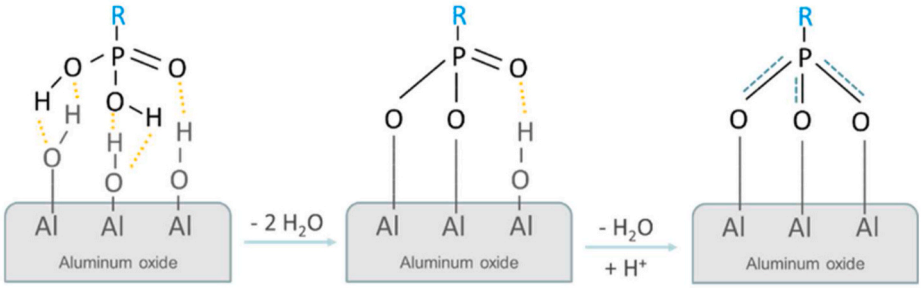


Fig. 5. Reaction mechanism between phosphonic acid functions and aluminum oxides.

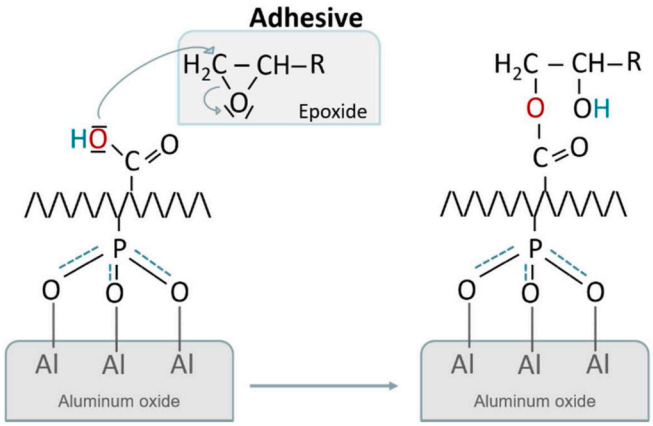


Fig. 6. Reaction mechanism between carboxylic acid function and epoxide functions.

clearly impacting because for short immersion times, the layers are around 50 nm while for long times the layers are between 150 and 250 nm thick. This is explained by the nature of this layer which is in part a conversion layer. The formation of a conversion layer based on zirconium and/or titanium is initiated by the dissolution of the native aluminum oxide layer present at the surface by the fluoride ions, then by the precipitation of the zirconium and/or titanium caused by a local increase in pH at the surface due to dissolved oxygen reduction reactions. This precipitation corresponds to the formation and thickening of the conversion layer, which is a function of the immersion time in the treatment bath, and preferably occurs around the cathode intermetallic particles present on the surface of the aluminum alloy. This phenomenon therefore causes variations in thickness, as the layer is more irregular close to the intermetallic particles [29].

3.1.3. *Surface analysis with XPS*

To confirm the chemisorption of Addibond to aluminum surfaces, previously discussed, XPS analyses were performed at the extreme surface of the aluminum substrate, between 0 and 5 nm thick, which corresponds to the thickness of the BL. It was possible to note on the spectra of interest, aluminum, oxygen and phosphorus binding energies (Table 3). Indeed, Al (2p) was identified between 75.1 and 73.3 eV, between 532.1 and 532.3 eV for O (1s), between 190.7 and 191.3 eV for P (2s) and finally between 133.7 and 133.9 eV for P (2p) corresponding all to Al–*O*–P bonds. These binding energies demonstrate the formation of a covalent bond between the aluminum substrate and the phosphonic acid functions of the polymers [18]. We can illustrate this covalent bond according to the previous reaction mechanism of dehydration (Fig. 5).

We can specify that beyond the thickness of 5 nm analyzed (at the extreme surface), we no longer find the energies at 75.3 eV for Al (2p), and no energy peaks for P (2s) and P (2p). This means that the constituent polymers of the BLs are no longer present and that the bulk of the aluminum has therefore been reached. Indeed, over an analyzed thickness of 5–289 nm, binding energies were identified at 72.9 eV for Al (2p), corresponding to Al-metal bonds, characterizing the aluminum alloy.

The phosphorus rate in atomic percentage at the extreme surface of the substrate (always between 0 and 5 nm thick) were checked to confirm the presence of polymers at different concentrations (low, medium and high) and immersion times (120 and 3 s) in Fig. 11.

As expected Addibond 275 contains a little more phosphorus than Addibond 021 thanks to the presence of the VPA monomer which provides more phosphorus. In addition, it is noted that at constant concentration the immersion time has no significant effect, especially for Addibond 275. Thus the formation and the morphology of the BL seem to be similar for short or long immersion times, which means that the

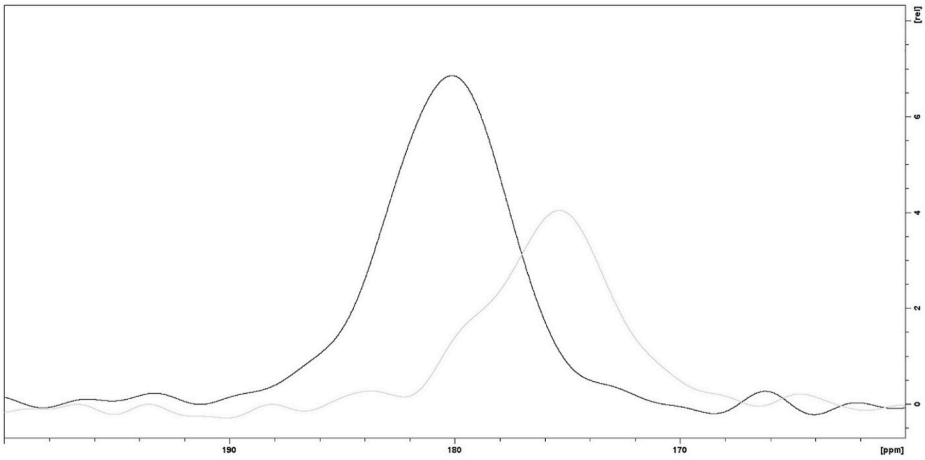


Fig. 7. Solid ^{13}C NMR spectrum, black spectrum: Addibond 021 alone, grey spectrum: Addibond 021 with 4-methoxyphenyl glycidyl ether (epoxy adhesive model).

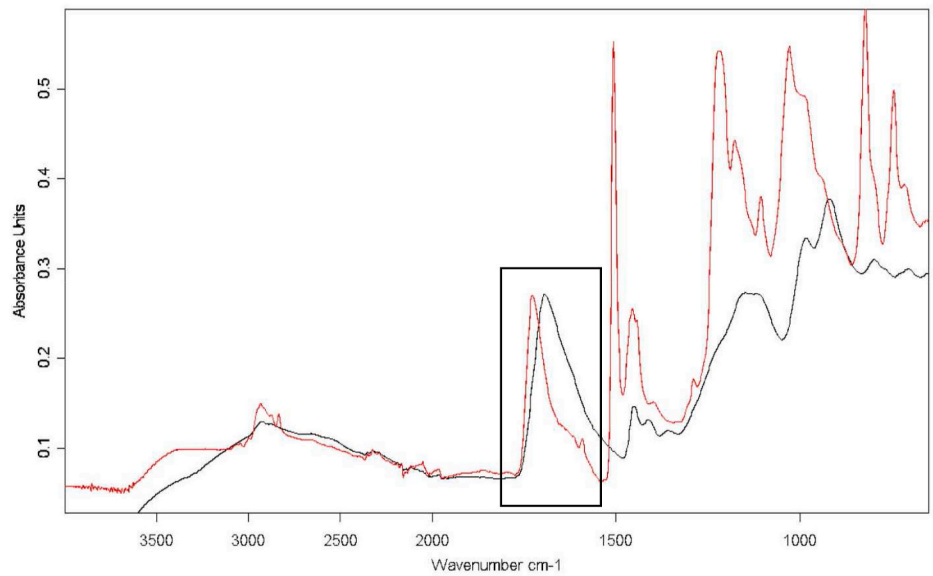


Fig. 8. ATR infrared spectrum, black spectrum: Addibond 021 alone, red spectrum: Addibond 021 with 4-methoxyphenyl glycidyl ether (epoxy adhesive model). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

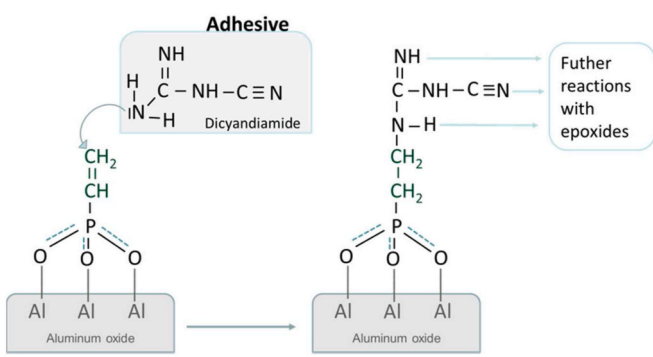


Fig. 9. Reaction mechanism between vinyl functions and amine functions [24].

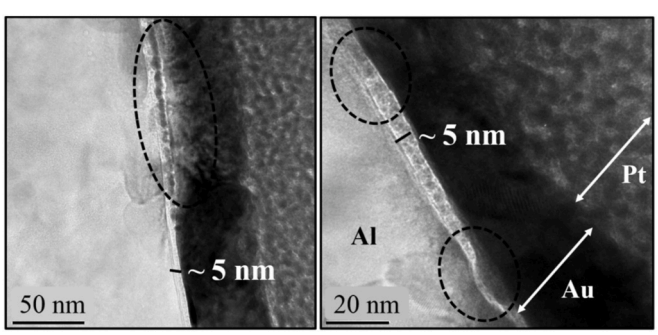


Fig. 10. Thickness of Addibond 021 at 120 s of immersion time on AA5754 observed with TEM.

Table 2
Final thickness of BLs (nm).

	Addibond 021		Addibond 275		Commercial formulation	
Immersion time (s)	3	120	3	120	3	120
Final thickness (nm)	5–10		5–10		50	150–250

Table 3
Binding energy (eV) by XPS of Addibond 021 and 275 between 0 and 5 nm thick on AA5754 substrate.

	Spectra	Addibond 021 and 275 (120 and 3 s)
Binding energy (eV)	Al (2p)	75.1–73.3
	O (1s)	532.1–532.3
	P (2s)	190.7–191.3
	P (2p)	133.7–133.9
Characteristic bonds		Al–*O*–P

polymers are chemisorbed in the first seconds of immersion. But concentration seems to be a critical parameter, and in our conditions, the optimal solution is generally observed at medium concentration (except for Addibond 021 immersion 120 s). At lower concentrations the quantity of polymer is probably not sufficient to ensure a maximum of bonds with the substrate. At higher concentrations it would appear that the polymers adsorb less to the surface because the surface is probably already saturated, and that potentially there would be residual non-chemisorbed polymers on the surface that would not be taken into account during the XPS analysis.

3.2. *Characterizations of the bond layer – adhesive interface*

To characterize the performance of the bonding layers at the aluminum bond layer substrate interface, several mechanical tests, such as micro-scratch test, three-point bending test and single lap shear test, were carried out and compared.

3.2.1. *Micro-scratch test*

This test was carried out on the raw substrates and at each step of the process (cleaned and etched (c/e), Addibond 021 deposition on c/e, Addibond 275 deposition on c/e and commercial formulation on c/e, at two immersion times (120 and 3 s) at a concentration called « medium », which is of about 1500 ppm for Addibond.

First, on Fig. 12, we can notice the benefit of surface preparation over a raw substrate can be noticed. Indeed, the normal force of the raw reference (X symbol) is 7 N lower than that of the reference having undergone a surface preparation c/e (right cross symbol). This confirms the interest of carrying out a surface preparation to promote and improve the mechanical anchoring of the adhesive and/or the

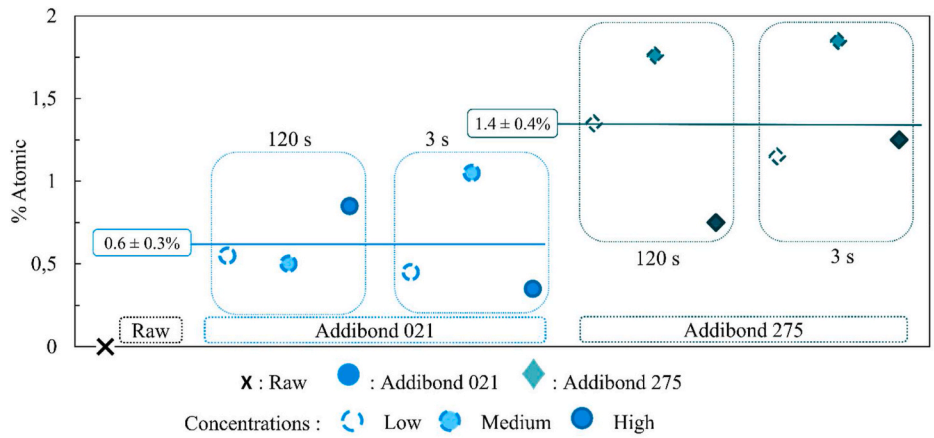


Fig. 11. Atomic percentage of phosphorus at the extreme surface, between 0 and 5 nm thick, of Addibond 021 and Addibond 275 at two immersion times (120 and 3 s) and three concentrations (low, medium and high concentration) on AA5754 substrate.

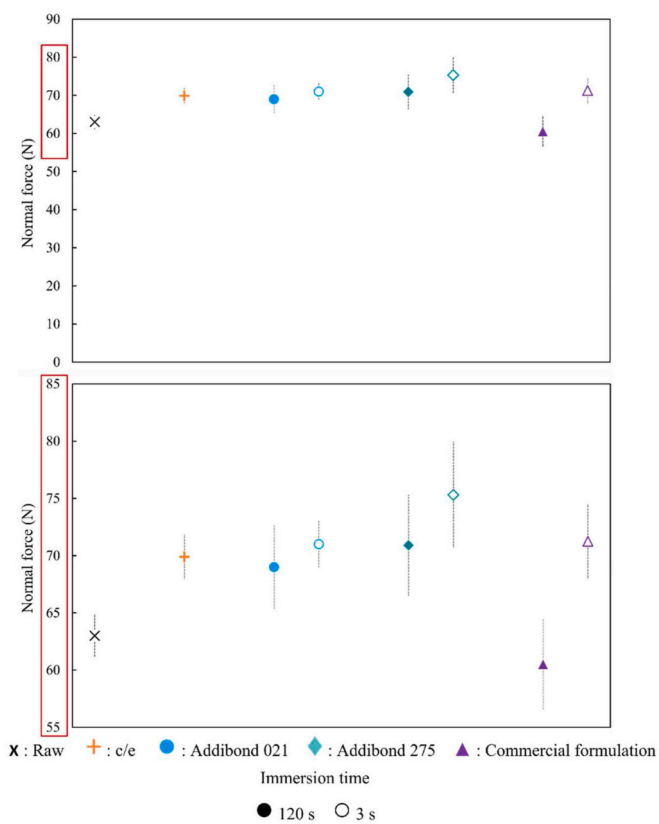


Fig. 12. Normal force of delamination (N) obtained by micro-scratch for Addibond 021, Addibond 275 and the commercial formulation systems, at 120 and 3 s of immersion time for each, on AA5754 substrate with the adhesive Betamate 1496 F.

physicochemical phenomena such as the controlled formation of aluminum hydroxides with respect to a "raw" substrate.

The normal delamination force of the reference c/e sample is similar to that of the samples with the surface treatments. For these samples, the failure being always cohesive for SLS test (in the adhesive used for the test), the value corresponds to the cohesive force of the adhesive, and these similar values for the different samples shows both the high performances of the surface treatments as well as the validity of the testing set-up. Moreover, the micro-scratch test depends on several factors including the surface roughness, but it has been seen by measurements of roughness with the interferometer that the value of roughness Sa is of the order of 0.3 µm, for the c/e reference as well as for those with BLs references, which could explain that these samples have similar results in normal force of delamination (N).

Nevertheless, we can compare the results of the normal force leading to delamination for the Addibond 021 and Addibond 275 systems. First, we can notice that Addibond 275, which contains more phosphonic acid functions (82.5% versus 30% for Addibond 021), shows the highest normal force results (75 versus 70 for Addibond 021), especially for the 3 s sample. Thus, the possibility to generate more covalent bonding with the substrate for Addibond 275 [18], seems favorable to the increase of the critical normal force of delamination.

In addition, we find that the immersion time moderately impacts Addibond systems compared to the commercial formulation. This means that the Addibond systems can also be used as a spray or in immersion systems. This versatility in application processes is an advantage for these products. On the contrary, commercial formulation is impacted by short or long immersion time: for the sample at 120 s Of immersion the force of exposure of the substrate is clearly lowered, becoming even lower than that of the raw substrate. This phenomenon could be explained by the presence of the inorganic part which forms an $H_2(Zr, Ti)F_6$ conversion layer. For this type of compound, the longer the immersion time, the thicker the conversion layer [29], as discussed previously.

Thus the formation of a thick BL is harmful to the adhesion, and this according to the theory of the layers of weak cohesion [30] which describes that the interfacial forces are always stronger than the force of cohesion of the thicker layer component of the assembly, here the BL. It follows that the failure will always take place in the layer with the weakest cohesive force.

Consequently, these two different types of chemistry (organic for Addibonds, organic and inorganic for the commercial formulation) intended for the same application, which is structural bonding, present different performances, with greater robustness for Addibonds.

3.2.2. *Three-point bending test*

As the micro-scratch test, the three-bending test was conducted on the same references namely: raw, c/e, Addibond 021, Addibond 275 and commercial formulation, for all samples at two immersion times (120 and 3 s) at a medium concentration.

In this test, Araldite AY103 with HY991 adhesive, with a formula very similar to that of Betamate 1496 F, was used to evaluate the universal side of BL against different adhesives.

According to the results of force at break (N) (Fig. 13) it is observed a very similar tendency as that obtained with the micro-scratch test. Indeed, it appears once again that the cleaning-etching is beneficial for

improving adhesion phenomena, and that BL Addibonds are moderately impacted by the immersion time. On the other hand, the commercial formulation is again influenced by the formation of a thick BL, which considerably lowers the force at break. So, both mechanical tests are very well correlated.

3.2.3. Single lap shear test

The following graph (Fig. 14) summarizes the single lap shear results in stress at break (MPa) before and after ageing of raw sample, c/e, Addibond 021, Addibond 275 and the commercial formulation at two immersion times (120 and 3 s) and three different concentrations (low, medium and high).

It was also noted the fracture facies of the samples, cohesive or adhesive. For similar stress at break, it is preferable to obtain cohesive rupture because this means that the weak point is the adhesive and not the interface of interest, BL - adhesive.

As previously on both three-point bending and micro-scratch test, the results of stress at break (MPa) before ageing (full bar) show better results after cleaning etching (second bar on the left) as compared to a raw sample (first bar on the left), it is determined a gain of almost 50%. Also, for Addibonds, the effect of concentration affects the results in stress at break more than the immersion time, taking into account the error bars. Indeed, it is observed that at a medium concentration the breaking forces are higher than for low and high concentrations (particularly for Addibond 021). This can be compared with the XPS analyses where it was observed that at this same medium concentration there was a higher atomic percentage of phosphorus at the extreme surface, which translates more chemisorbed polymers at the surface and therefore an improvement in the adhesion phenomena on either side of adherents, substrate and adhesive.

For commercial formulation before ageing, the reverse phenomenon operates. Indeed, the long immersion time (120 s) forms thicker, brittle layers according to the theory of weak boundary layers, and therefore the breaking force results are lower, in good agreement with the previous mechanical tests. However, at short immersion time (3 s), the results are at the same level as the Addibonds, because the BL is thinner (around 50 nm), this therefore confirms the hypothesis of weak boundary layers for thicker layers. On the other hand, the effect of the concentration for the samples at 3 s is clearly null. This can be explained by the fact that it is a precisely formulated solution (containing additives, adhesion promoters, etc.) which visibly allows the effects of concentration to be controlled. For the samples at 120 s, the effect of the BL

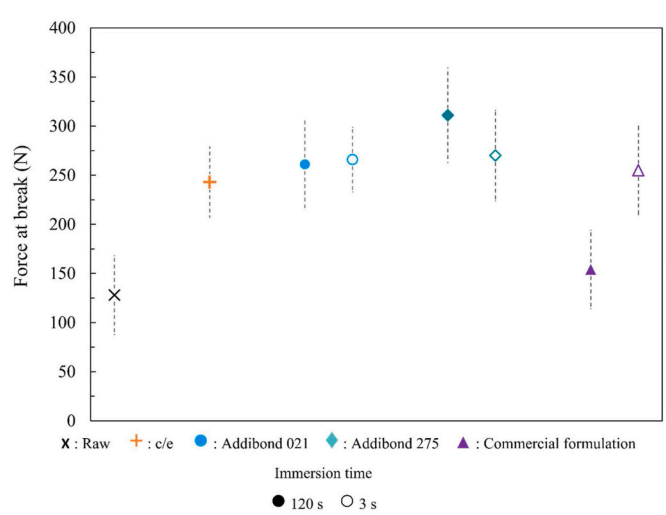


Fig. 13. Force at break (N) obtained by three-bending point for Addibond 021, Addibond 275 and the commercial formulation, at 120 and 3 s of immersion time for each, on AA5754 substrate with the adhesive Araldite AY103 and HY991.

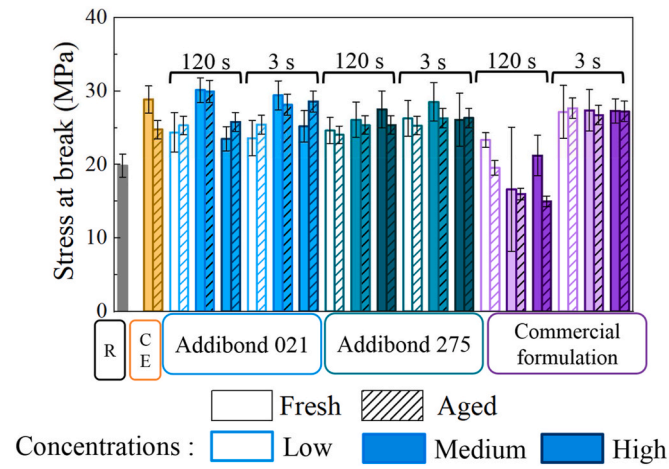


Fig. 14. Stress at break (MPa) obtained by single lap shear, before and after ageing, for Addibond 021, Addibond 275 and the commercial formulation, at 120 and 3 s of immersion time for each, on A5754 substrate with the adhesive Betamate 1496 F

thickness is too predominant on the results to conclude on the effect of the concentration.

We can also discuss the fracture facies of the samples. It is possible to correlate the highest breaking stress results with cohesive breaks (Fig. 15), notably for c/e, Addibond 021, Addibond 275 (120 and 3 s for both), as well as the commercial formulation at 3 s. For the lowest results, a distinction is made between adhesive ruptures (raw sample and the commercial formulation at 120 s) which testifies to a fragility at the BL - adhesive interface.

Then for the results after ageing (hatched bars), it is noted exactly the same tendency as before ageing, that it is on the level of the results of stresses at break or of the facies of fracture (Fig. 16). We can note that there are no results for the raw references because the five samples broke during the salt spray ageing cycle, the same for the commercial formulation at 120 s at medium and high concentration. That is why only 1 sample has could be tested for each (that is why there are no error bars in Fig. 17).

As the trend of the results is the same before and after ageing, it is interesting to calculate the percentage of retention rate, which corresponds to the ratio of the stress at break after aging to that before ageing according to equation (1).

$$R\% \quad \frac{\textit{Stress at break after ageing}}{\textit{Stress at break before ageing}} \times 100 \tag{1}$$

If we look at the retention rates on Fig. 17, we see that those of Addibond 021, Addibond 275, and the commercial solution at 3 s are between 92 and 100%, or even more than 100% (which means in this case, the samples after ageing have higher breaking stresses than before ageing), while the c/e reference is at 86%. It can then be confirmed that Addibond products provide a better resistance to ageing than a simple cleaning-etching as a surface preparation and that the performances of the BLs are well improved.

It is also noted the commercial formulation at 120 s which exhibited low stresses at break and cohesive fracture facies does not exceed the retention rate of the c/e reference. This means that the weak results before ageing remain after ageing, and that there is not the phenomenon of exacerbated performance after ageing as observed for the other samples. As reported in the work of Otto Lunder [31], it is during the ageing step of the samples (in a salt spray for example) that the performances of bonding layers are exacerbated.

Thus, as it was seen previously, the three types of mechanical tests are well correlated. Indeed, the surface preparation (c/e) is always seen to be beneficial as compared to a raw sample, and the BLs, always have

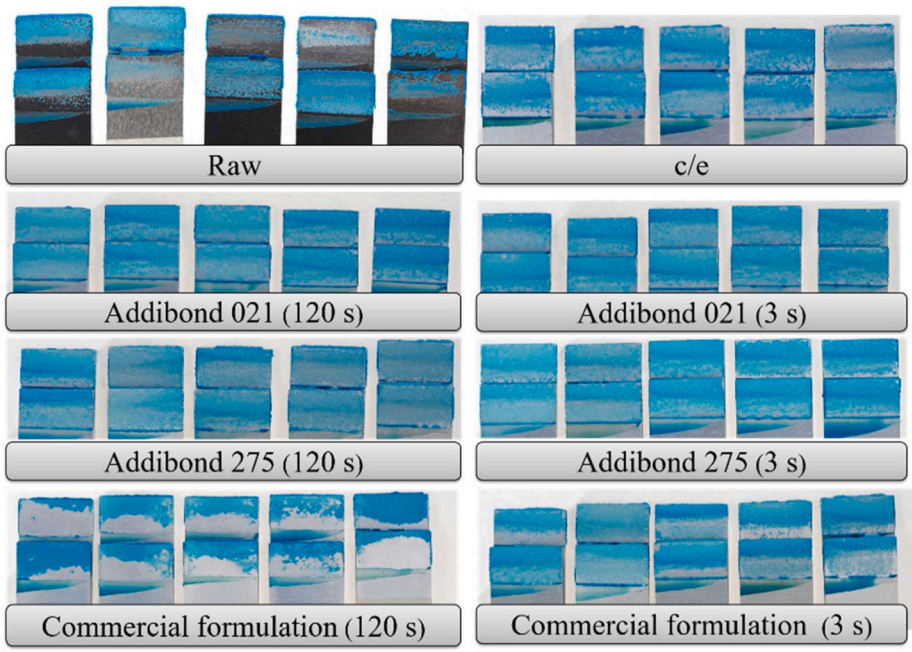


Fig. 15. Fracture facies obtained by single lap shear of raw, c/e, Addibond 021, Addibond 275 and commercial formulation samples, on AA5754 substrates with the adhesive Betamate 1496 F, before ageing.

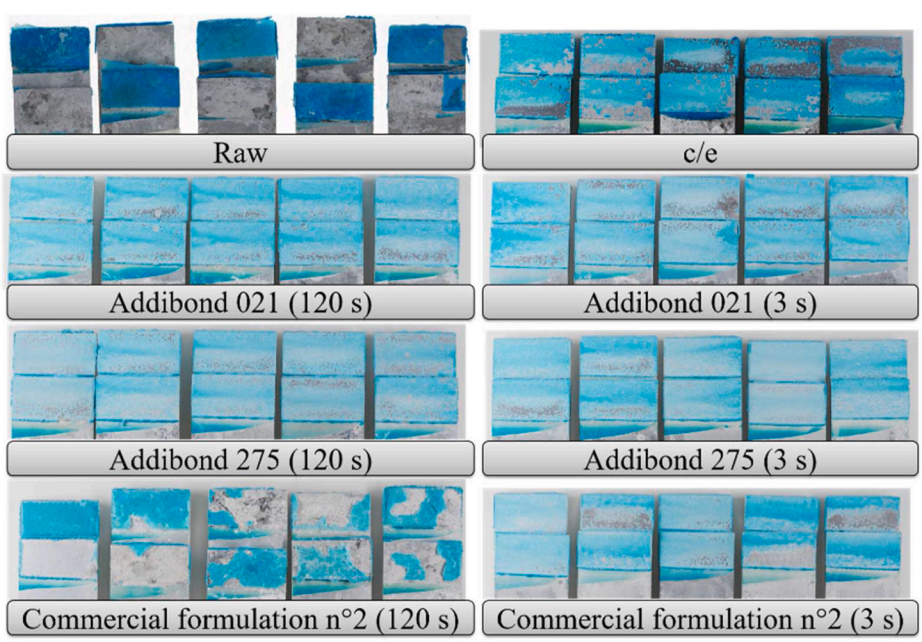


Fig. 16. Fracture facies obtained by single lap shear of raw, c/e, Addibond 021, Addibond 275 and commercial formulation samples, on AA5754 substrates with the adhesive Betamate 1496 F, after ageing.

the same effect whatever the immersion time and the concentration in the tested range.

4. Conclusions

The morphology and reactions of BL Addibond systems were determined: the Addibond BLs are effectively chemisorbed on each side of the adherents, the aluminum substrate and the epoxy-dicyandiamide adhesive, by dehydration reactions, esterification or even nucleophilic addition. The Addibond polymers appear to organize into a 5–10 nm thick polymeric monolayer to form BL. This layer does not vary in thickness despite the immersion time (120 or 3 s) in the treatment bath containing the polymers, since the polymers will be chemisorbed at the surface of the aluminum in the early stages of immersion.

The thickness of the commercial BL seems to be very decisive subsequently in the mechanical tests since it was shown in tests of micro-scratch, three-point bending and single lap shear (before and after ageing), that Addibond 021 and Addibond 275 products which form thin BLs (5–10 nm) and commercial BL of 50 nm thick showed higher results in terms of strength or stress at break than thicker BLs (150–250 nm) formed by commercial formulation at 120 s of immersion.

In addition, it was seen in the three types of mechanical tests

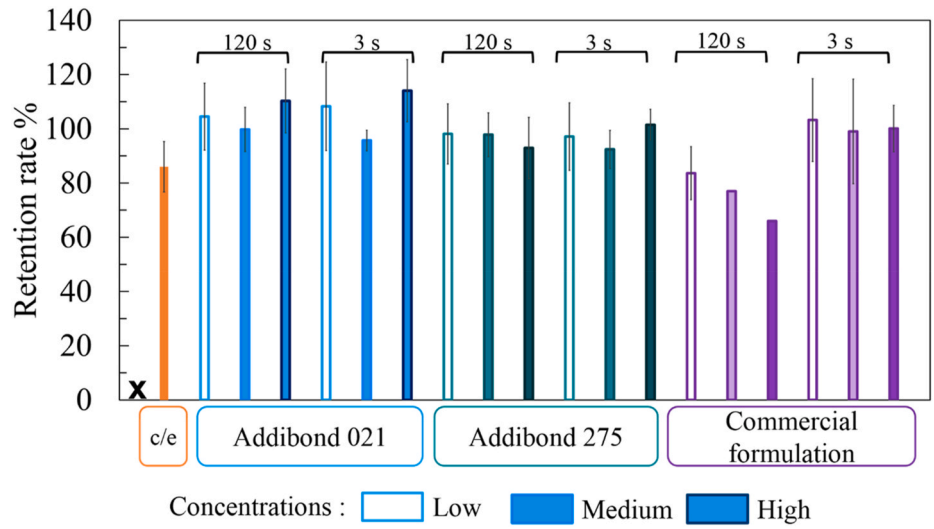


Fig. 17. Retention rate in percentage of stress at break obtained by single lap shear for Addibond 021, Addibond 275 and the commercial formulation, at 120 and 3 s of immersion time for each, on a substrate AA5754 with the adhesive Betamate 1496 F

conducted, that the results exhibited the same trends and are very well correlated. This means that despite different stresses, scratching, bending or shearing, the same behavior operated.

Finally, through single lap shear tests, it was observed, after an aging process (1000 h), that the stress and break results of Addibond products approach those of the c/e reference. The calculation of the retention rate could effectively demonstrate the advantage of BLs compared to a simple cleaning-etching (c/e) since the retention rate of Addibond products is at least greater than or equal to 92%, while the c/e reference is around 86%.

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