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ORIGINAL ARTICLE

Mechanical behaviour and failure modes of metal to composite adhesive joints for nautical applications

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Abstract In this paper, the influence of several parameters on the mechanical behaviour and failure modes of hybrid bonded joints aluminium/composite was investigated. Particularly, the effects of metallic surface condition, adhesive properties and thickness on single-lap joint resistance were analysed. To these aims, two adhesives were used and, for each adhesive, two different adhesive thicknesses (0.5 and 1.5 mm) have been investigated. Furthermore, two sets of joints for each adhesive kind and thickness were investigated: the former was obtained using aluminium blanks which were previously mechanically treated with sandpaper (P60) and the latter using aluminium treated with sandpaper and with presence of fillets in the ends of the overlap area. In order to improve the adhesion strength between polymeric adhesive and aluminium, two metal surface treatments have also been performed using a silane coupling agent, γ-glycidoxypropyltrimethoxysilane (γ-GPS). The mechanical performances and failure modes were found to be significantly increased using the chemical pre-treatments with γ-GPS silane coupling agent unlike other parameters investigated. As regard the thickness of the adhesive layer, the better value is found to be equal to 0.5 mm, for both adhesives investigated.

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1 Introduction

The implementation of composite materials in conjunction with metals into hybrid structural systems is currently developed in several key applications such as ships, aircraft, buildings, bridges, automobiles and other transportation vehicles [1–3]. As regard the nautical field, in the ship design, the topside structures show a critical stiffness and the hull structures show a critical strength. Consequently, the stability and the performance of the ships are enhanced by using a high-stiffness material (i.e. aluminium alloy or steel) for the topside structures and a high-strength material for the hull structures (i.e. glass fibre-reinforced plastic [GFRP] materials) [4], hence the necessity of a structural joining technology that could link a composite material and a metal structure.

Traditional joining technologies (i.e. riveting, clinching) are hardly applicable on composite materials as they induce critical stresses or since composite manufacturing technology does not allow their application. Moreover, for FRP structures, a drilling process to carry out bolt holes breaks fibres, causing several problems like peeling of the higher plies at the entry of the hole, resin degradation on the wall of the hole and delamination of the last plies in the laminate [5, 6]. These damages can initiate fatigue cracks and severely decrease fatigue strength of mechanical joints [7].

Furthermore, in mechanical fastening, the fasteners themselves are an important source of weight increase: in a weight-sensitive structure like aircraft and ship, the reduction of the number of fasteners is a research priority [8].

So the adhesive bonding can be considered as the best joining technology between composite materials and metal ones to obtain structures which do not require subsequent disassembly for maintenance and inspection.

Two kinds of bonding methods can be considered to carry out composite to metal adhesive joints: co-curing [7, 9, 10] and secondary bonding.

The co-cured joint utilises the same resin of the composite adherent as the adhesive, so that adhesive and FRP adherent are united. In this manner, both the curing and joining process can be achieved at the same time. Co-curing is usually preferred over secondary bonding because the manufacturing time and cost decrease and the number of parts is reduced.

However, co-cured assembly of large and complex composite structure requires large fabrication facility and complex tooling and, in this case, the secondary bonding is a useful process to replace the co-curing method [11].

Often metal–composite adhesive joints show low values of strength and limited durability as a consequence of poor adhesion degree between metallic adherent and polymer adhesive.

For this reason, a pre-treatment of the aluminium substrates is essential to promote one or several of the adhesion mechanisms (i.e. mechanical interlocking, physisorption and/or chemisorption) both improving the strength of the adhesive joints and influencing their failure mechanism.

In the literature, any number of papers can easily be found about the choice of the metallic surface pre-treatment and its influence on the joints' performances.

The simplest form of aluminium pre-treatments are based on solvent wiping, vapour degreasing or either of these methods combined with mechanical abrading (i.e. sandblasting) to remove the existing aluminium oxide surface layer and allows a new one to develop.

For low-to-moderate strength aluminium joints, vapour degreasing and alkaline cleaning are often used.

Chemical pre-treating processes, such as etching [12–14], produce higher reliability and longer service life in a bonded assembly. If the aluminium adherents are first cleaned, then sandblasted and finally chemically treated, the surface area is increased, the contaminants are removed and a new oxide layer forms, assuring excellent initial and long-term strengths [15].

Another chemical pre-treatment of the metal surface prior to bonding consists in the use of organosilane adhesion promoters. Kim et al. [16] evaluated the static and fatigue performance improvements of the silane-reinforced composite/steel adhesive co-cured joints.

A further consideration regards the attention that should also be given to the design of the shape of the ends of the overlap area of the joint where the transverse stresses tend to reach a maximum value.

The presence of spew fillet may greatly reduce the level of the transverse stresses increasing the bonding strength of the adhesive joints [17], influencing the failure mechanism of an adhesive joint. Consequently, the presence and shape of spew fillet is one of the most important parameters related to the bonding strength and the failure modes of this kind of joints.

When an adhesive joint is subjected to load, it can fail due to three different failure modes: adhesive, cohesive and mixed. The fracture is defined adhesive when the fracture occurs at the adhesive/adherent interface. It is defined cohesive when the crack propagates within the adhesive layer. In this case, the surfaces of both adherents after debonding are covered by fractured adhesive.

When both the failure modes occur, the failure is mixed. In this case, it is possible to define a ratio between adhesive and cohesive areas. Failure can also occur in the adherent if the adhesive is tougher than the adherent and the adhesive remains intact.

The aim of the present study is to analyse the performance of GFRP composite-to-aluminium alloy single-lap bonded joints. In particular, this work is focused on the failure modes and resistance of the joints depending on several parameters like the pre-treatments of the aluminium surface, the presence of the fillets, the kind of adhesive and the thickness of the adhesive layer. A total of 16 sets of joints (80 joint specimens) were produced and tested.

2 Experimental setup

2.1 Materials and manufacturing

GFRP laminate was fabricated by hand lay-up technique, cured at room temperature for 24 h and then post-cured at 60°C for 8 h. The stacking sequence of the composite structure was constituted of four layers of E-glass mat (randomly oriented fibres, with areal weight of 450 g/m^2) in a matrix of epoxy resin (SP 106 supplied by Resintex). The total average thickness of the laminates was 3.2 mm.

The aluminium alloy used was the AA2139-T4 received in 1×1 m panel of 3.2 mm thickness. The chemical composition of the alloy, as measured by energy-dispersive spectroscopy using a FEI QUANTA 200 F probe, is reported in Table 1.

Table 1 Chemical composition of the AA2139 alloy (in weight percent)

Cu	Mg	Mn	Ag	Al
4.73	1.3	0.44	0.61	Balance

Table 2 Epoxy adhesive: cost of each component and composition of the system

Resin	Hardener	Microballoons	Colloidal silica
100 g	18 g	20% by weight of R/H mix	5% by weight of R/H mix
11.3€/kg	19.1€/kg	15.5€/kg	21.8€/kg

Prismatic samples of 100 mm×25 mm dimension were cut with a saw from both aluminium alloy panel and composite laminate and then used to realise the joints.

In order to analyse the influence of the adhesive kind, two structural adhesives were used: a two-component methacrylate adhesive commercially known as Adekit A-310 and an epoxy adhesive. The latter is based on the same resin (SP 106) and hardener mix used as matrix of the composite laminates with adding of two filler powders: colloidal silica and microballoons.

The microballoons are hollow spheres of phenolic resin which are used to increase the volume of the resin/hardener system, achieving a light adhesive with excellent sanding characteristics. The colloidal silica is used to control the thixotropy of the resin system. The composition by weight of the epoxy adhesive system and the unitary cost (in Euros per kilogramme) of each component are reported in Table 2.

As regard the cost of raw materials associated to the adhesive solutions, the epoxy system (18.97€/kg, value obtained considering the cost per kilogramme of each component and the composition of the system) provides a cost savings of about 2€/kg compared to the methacrylate one (21€/kg).

Both the adhesive systems must be used carefully because of their high flammability (risk phrase R 11), irritability to eyes, respiratory system and skin (R 36/37/38) and tendency to cause sensitization by skin contact (R 43).

The influence of the adhesive thickness on the mechanical performances was analysed by producing two sets of joints, with adhesive thickness equal to 0.5 and 1.5 mm, respectively.

Furthermore, two sets of joints for each adhesive kind and thickness were investigated: the former was obtained using aluminium blanks which were previously mechanically treated with sandpaper (P60) and the latter with the presence of fillets at the ends of the overlap area and the aluminium surface treated with the same sandpaper.

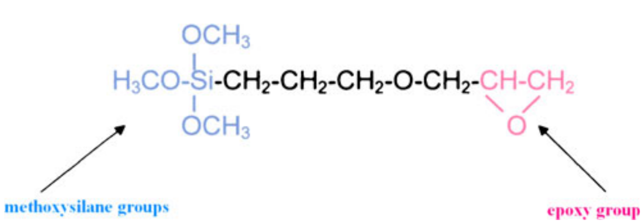

Fig. 1 Chemical structure of γ-GPS

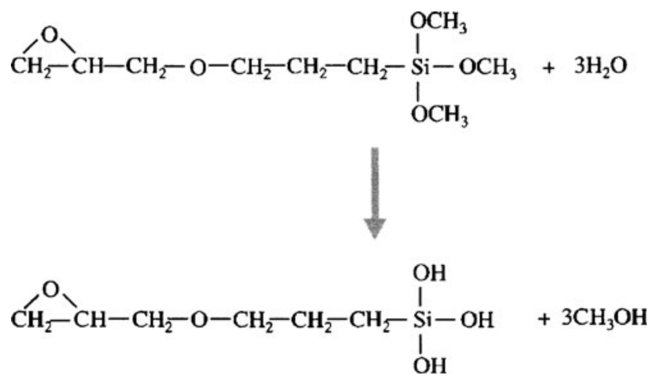

Fig. 2 Hydrolysis of silane coupling agent

Finally, to improve the adhesion strength between the polymeric adhesive and aluminium surface, two metal surface treatments were performed using a silane coupling agent, γ-glycidoxypropyltrimethoxysilane (γ-GPS) showed in Fig. 1.

γ-GPS was chosen because it has the epoxy organofunctional group which is compatible with the epoxy adhesive: it can react with both the curing agent and the non-reacted epoxy rings within the epoxy resin of the adhesive.

For this reason, the chemical pre-treatments were carried out only for the hybrid joints bonded with epoxy adhesive.

The first chemical pre-treatment (named 'S1') suggested by Kim et al. [16] consists in the immersion of aluminium

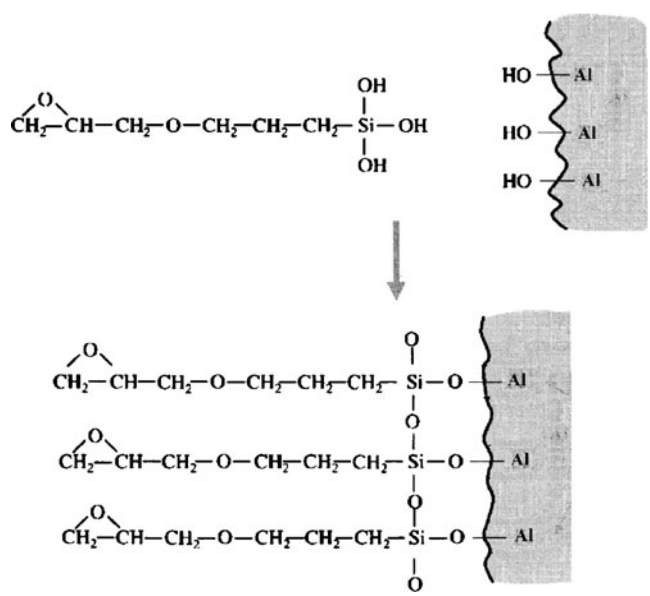

Fig. 3 Formation of covalent bonds via condensation

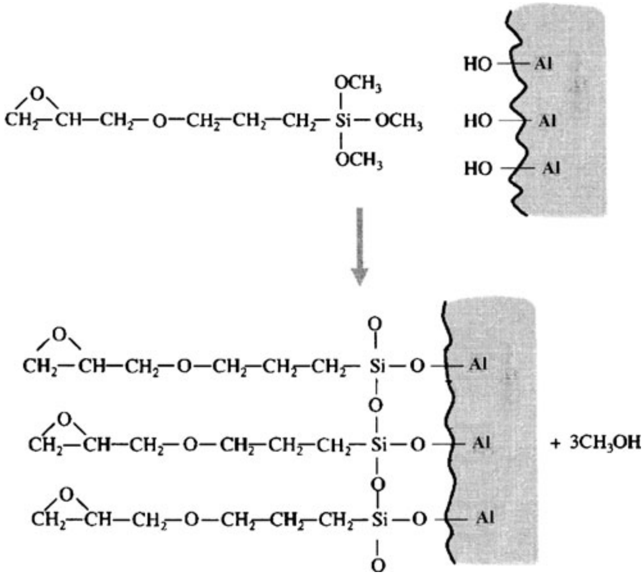

Fig. 4 Formation of covalent bonds through silane 2 chemical pre-treatment

alloy hydrated by warm water pre-immersion [18] in a aqueous solution of γ-GPS (1.0 wt.%) for 30 min.

The second chemical pre-treatment (named 'S2') is different from the first one because aluminium alloy was immersed in a toluene solution of γ-GPS (1.0 wt.%) for 30 min.

In the first case, the coupling agent diluted in water (1.0 wt.%) is hydrolysed to hydroxyl, producing methanol (Fig. 2), and then it reacts with hydrated aluminium via condensation with covalent bonds Si–O–Al (Fig. 3).

In the case of 'S2' chemical pre-treatment, diluting the coupling agent in a water-insoluble solvent, the methoxy group does not react in this first step. After this, by immersing the hydrated metal substrates into the solution, the methoxy groups of the silane coupling agent react with the hydroxyl ones of the metal surface, forming covalent bonds Si–O–Al (Fig. 4).

The details of all joints realised and tested in this work are reported in Table 3.

2.2 Mechanical testing

In order to evaluate the shear strength of the joints, the single-lap configuration (see Fig. 5), according to the standard ASTM D1002, was chosen.

Mechanical tests were carried out using a Universal Testing Machine model Galdabini Sun 5, equipped with a load cell of 50 kN. For each joint, five samples were tested with a cross-head speed equal to 2 mm/min.

The shear stress was simply calculated by the equation:

$$\tau = \frac{P}{A}$$

where P is the tensile load and A is the joint overlap region.

3 Results and discussion

3.1 Mechanical testing

3.1.1 Methacrylate adhesive

In Table 4, the measured average shear stresses of the joints produced using the adhesive Adekit A-310 are shown.

Table 3 Details of hybrid joints analysed

Adhesive	Adhesive thickness [mm]	Joint typology	Reference
Adekit A-310	0.5	No treatment	AD-0.5-NT
		Paper P60	AD-0.5-P60
		Paper P60 + fillets	AD-0.5-P60F
	1.5	No treatment	AD-1.5-NT
		Paper P60	AD-1.5-P60
		Paper P60 + fillets	AD-1.5-P60F
SP 106 system	0.5	No treatment	SP-0.5-NT
		Paper P60	SP-0.5-P60
		Paper P60 + fillets	SP-0.5-P60F
		Silane 1	SP-0.5-S1
		Silane 2	SP-0.5-S2
	1.5	No treatment	SP-1.5-NT
		Paper P60	SP-1.5-P60
		Paper P60 + fillets	SP-1.5-P60F
		Silane 1	SP-1.5-S1
		Silane 2	SP-1.5-S2

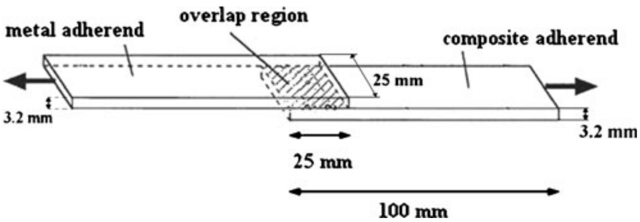

Fig. 5 Joint configuration

It can be observed that:

- ➢ the resistance of the joints increases at the decrease of the adhesive thickness;
- ➢ the resistance of the joints is not influenced neither by mechanical abrading nor by the presence of the fillets.

This can be explained considering that, for all samples, the occurred failures were adhesive at the interface between composite adherent and adhesive layer (adhesive GFRP). As shown in Fig. 6, in this case, the surfaces of composite appear 'clean', while the metal surface remains covered by fractured adhesive.

Consequently, it is evident that the methacrylate adhesive exhibit low compatibility with the composite adherent: both the mechanical treatment of the metal surface and the presence of the fillets are unable to modify the failure mode and, consequently, do not improve the shear stress.

Keeping into account that the only failure mode observed for the methacrylate-based joints is adhesive at the composite adherent/adhesive layer interface, the chemical pre-treatment was not carried out on this kind of joints. Indeed, the chemical pre-treatment allows improving the adhesion strength between the adhesive layer and the aluminium surface that, in this case, is not the weak point of the joint.

Table 4 Failure stress and mode of the hybrid joints

Joint	Failure stress [MPa]	Failure mode
AD-0.5-NT	7.47±0.47	Adhesive GFRP
AD-0.5-P60	7.56±0.23	Adhesive GFRP
AD-0.5-P60F	7.78±0.13	Adhesive GFRP
AD-1.5-NT	5.16±0.11	Adhesive GFRP
AD-1.5-P60	5.52±0.49	Adhesive GFRP
AD-1.5-P60F	5.97±0.18	Adhesive GFRP
SP-0.5-NT	1.81±0.22	Adhesive AL
SP-0.5-P60	2.10±0.29	Adhesive AL
SP-0.5-P60F	3.62±0.44	Partially cohesive
SP-0.5-S1	9.79±0.27	Cohesive
SP-0.5-S2	8.39±0.16	Cohesive
SP-1.5-NT	1.05±0.31	Adhesive AL
SP-1.5-P60	1.15±0.37	Adhesive AL
SP-1.5-P60F	1.82±0.37	Adhesive AL
SP-1.5-S1	8.67±0.20	Cohesive
SP-1.5-S2	8.03±0.14	Cohesive

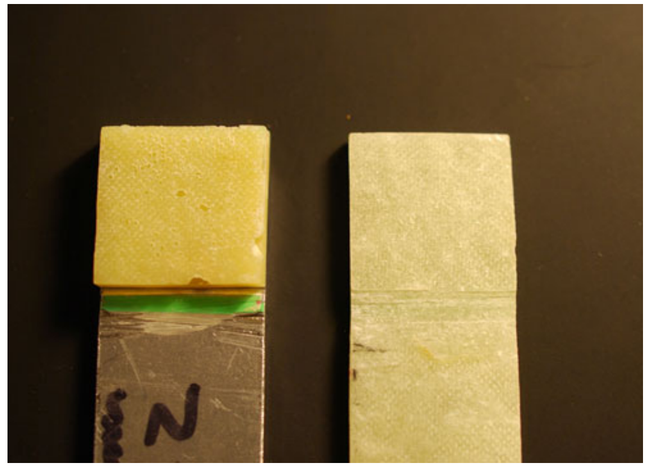

Fig. 6 Adhesive failure of the methacrylate hybrid joints

3.1.2 Epoxy adhesive

The average shear stresses of the epoxy-based hybrid joints (Table 4) show that:

- ➢ the resistance of the joints increases upon the decrease of adhesive thickness;
- ➢ the resistance of the joints is slightly influenced by mechanical abrading and presence of the fillets;
- ➢ by pre-treating the metal surface with silane coupling agent (γ-GPS), notable improvements in the failure stress of the adhesive hybrid joints are obtained.

In particular, the SP-0.5-S1 and SP-0.5-S2 joints show improvements in failure stress of about 441% and 363%, respectively, than those of the 'non-treated joints' (SP-0.5-NT).

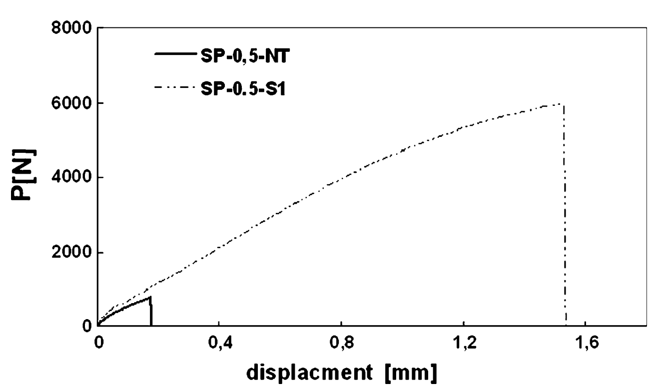

Fig. 7 Load–displacement curves of SP-0.5-S1 and SP-0.5-NT joints

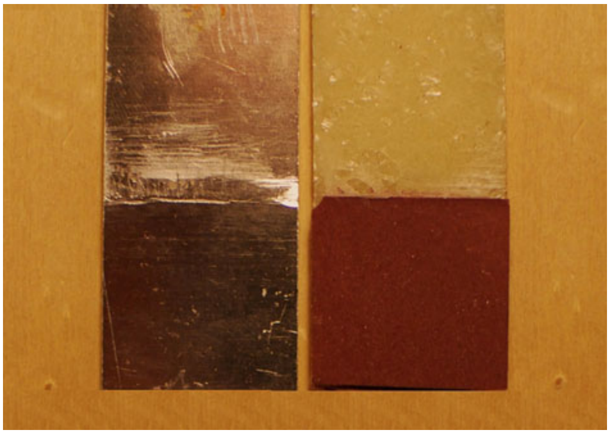

Fig. 8 Adhesive failure of the epoxy hybrid joints

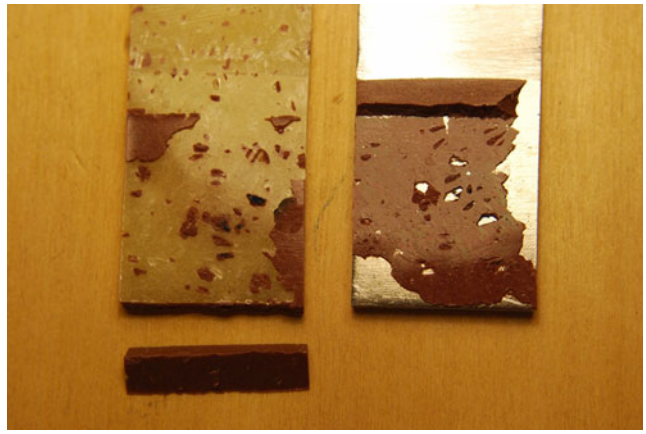

Fig. 10 Partially cohesive failure of epoxy hybrid joints

To better evidence the increases obtained using the chemical pre-treatments, the load–displacement trends for the SP-0.5-S1 and SP-0.5-NT joints are shown in Fig. 7.

As regard the joints with 1.5 mm adhesive thickness, the failure load increases to about 725% and 665% than those of the 'non-treated joints' for the joints with metal surface pre-treated with 'S1' and 'S2' procedures, respectively.

Consequently, it is evident that the chemical pre-treatment of the metal surface with γ-GPS silane coupling agent is an essential tool to improve the mechanical performances of metal to composite hybrid joints bonded with an epoxy adhesive.

The measured differences in the joints strength can be explained by taking into account the experimentally observed failure modes. The non-treated joints (for both adhesive thicknesses analysed) show only adhesive failure mode at the interface between aluminium surface and epoxy adhesive (adhesive AL) as shown in Fig. 8. On the other hand, the joints with metallic surface chemically pre-treated fail by cohesive failure mode (Fig. 9), which allows the evidenced resistance increase.

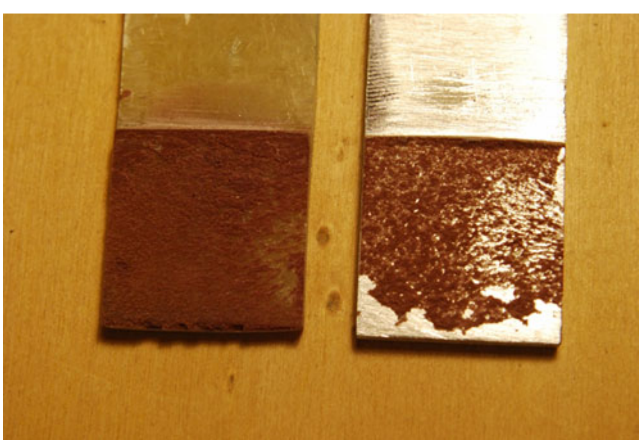

Fig. 9 Cohesive failure of the pre-treated epoxy hybrid joints

Unlike the methacrylate adhesive joints that fail adhesively between composite adherent and adhesive layer, the 'non-treated' epoxy joints show adhesive failure mode only at the interface between adhesive and metal. This means that the weakest part of the epoxy-based joints is the metal surface/adhesive layer interface. By pre-treating the metal surface with γ-GPS silane coupling agent, the strength adhesion enhances due to the formation of the covalent bond Al–O–Si between metal surface and epoxy adhesives. For this reason, the change of failure mode (adhesive to cohesive) happens and, consequently, the improvements of the joints resistance are found out.

Vice versa, the joint performances are slightly influenced by mechanical abrading and presence of the fillets because these parameters do not change the failure mode that

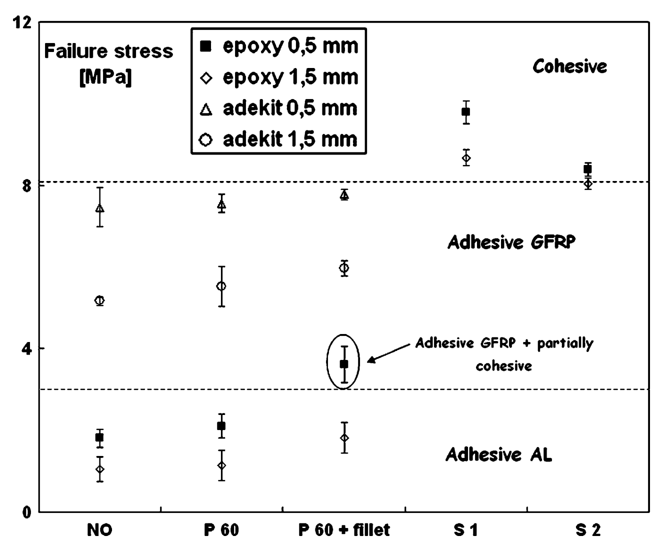

Fig. 11 Failure map

remains adhesive at the interface between aluminium alloy and adhesive layer.

Only the ‘SP-0.5-P60F’ shows partially cohesive failure mode (Fig. 10), and this leads to an increase in the failure load of 100%, compared to the ‘non-treated’ joints.

3.1.3 Failure map

The experiments clearly show how the parameters investigated in this work influence the failure mode and the resistance of the tested joints. For this reason, it is possible to draw an experimental failure map (Fig. 11), which shows the failure mode and the stress corresponding to each kind of joint (i.e. non-treated, P60, P60 + fillets, S1 and S2 pre-treatments).

In this map, three regions in which each experimental failure mode is dominant can be easily highlighted: for instance, if the stress failure is lower than about 3 MPa, only adhesive failures at the interface metal–adhesive occurred. Consequently, in this region of the map, this failure mode is the dominant mechanism.

For values of stress failure from 3 to about 8 MPa, adhesive failure at the interface GFRP–adhesive becomes dominant, while above 8 MPa, only cohesive failures occurred.

As discussed above, only ‘SP-0.5-P60F’ joints show a mixed failure mode: at the beginning, adhesive at the interface GFRP–adhesive, then cohesive on the fillet (Fig. 10).

4 Conclusions

In the marine field, the stability and performance of the ships are enhanced by using a high-stiffness material (i.e. aluminium alloy or steel) for the topside structures and a high-strength material for the hull structures (i.e. GFRP materials). For this reason, a structural joining technology that could link a composite structure with a metal one is essential.

In particular, a total of 16 sets of joints (80 joint specimens) were produced and characterized by single-lap shear tests according to the standard ASTM D1002.

The mechanical characterizations have shown that:

- ➢ the resistance of the methacrylate-based joints increases upon the decrease of the adhesive thickness but is not influenced neither by mechanical abrading nor by the presence of the fillets;
- ➢ all methacrylate-based joints were failed by totally adhesive failure mode at the interface between composite adherent and methacrylate adhesive;
- ➢ the resistance of the epoxy-based joints increases upon the decrease of the adhesive thickness and is slightly influenced by mechanical abrading and presence of the fillets because the failure mode remains adhesive at the metal–adhesive interface;
- ➢ by pre-treating the metal surface with silane coupling agent (γ-GPS), notable improvements in the failure stress of the epoxy-based joints are obtained;
- ➢ the non-treated joints (for both adhesive thickness analysed) show only adhesive failure mode at the interface between aluminium surface and epoxy adhesive, while by chemical pre-treating the metal surface, the joints realised fail by totally cohesive mode;
- ➢ among several parameters investigated, the chemical pre-treatments of the metal surface with γ-GPS silane coupling agent result to the best tools to improve the mechanical performances of metal to composite hybrid joints bonded with an epoxy adhesive.

From the experimental results, it is also possible create a failure map which shows the failure mode and stress corresponding to each kind of joint (i.e. non-treated, P60, P60 + fillets, S1 and S2 pre-treatments) that can be easily divided into three regions in which each experimental failure mode is dominant.

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