On the Influence of Polymer Surface Layer Thickness on the Adhesion of Composite Assembly. Differences between Initial State and Thermal Ageing

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Summary: Nowadays the interest of surface preparation in order to manufacture lighter bonded assemblies is well recognized. However only few study dealing with ageing of bonded composite assembly is described in the literature. The present paper mainly aims to compare the influence of the polymer surface thickness of carbon/epoxy composites on the adhesion behaviour at the initial state and after thermo-oxydative ageing. Conclusions show that contrary to the initial state, the reduction of the polymer surface layer thickness does not improve ageing behaviour. Indeed, the increase of polymer thickness provides a good protection of the degradation coming from micro/macro voids from the adhesive layer.

Keywords: adhesion; ageing; composites; epoxy

Introduction

Bonding of composite materials with an adhesive layer is one of the most promising alternatives to classical bonding techniques like bolting or welding. In order to increase the performance of composite assemblies different surface treatments have been developed.[1,2]

Then, as a consequence of efficient surface treatment, a composite assembly which initially owns adhesive failure, may be significantly improved and behave cohesively with a failure inside the material or the adhesive.[3,4] Once such cohesive failure reached there is no need to develop anymore the surface treatment as the material itself becomes the weak point of the assembly.

However presenting authors have already demonstrated that reducing the polymer surface layer thickness significantly increases adhesion performance, the highest performance corresponding to a direct bond between adhesive layer and fibre reinforcements.[5,6] These results clearly evidenced that reducing the polymer surface layer thickness appears necessary as it is the weak part of the assembly, at least at the initial state.

Unfortunately, as the role of the polymer surface layer thickness during thermal ageing of the assembly still remains unknown; the aim of the present study is to better understand the parameters governing the assembly behaviour over time when submitted to different ageing conditions.

Materials and Methods

Carbon/epoxy materials, surface treatments and assemblies as well as mechanical tests are described elsewhere.[3–5] Thermo-oxidative conditions were 140 °C, 160 °C and 180 °C under ambient air allowing to accelerate ageing but keeping the temperature far under the glass transition temperature (≈225 °C).

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Bonding Behavior at the Initial State

Hence at the initial state, the use of several surface treatments may increase adhesion performances of bonded composites. As an example presenting authors already demonstrated the effectiveness of peel ply treatment that provide rough and clean surfaces.[3] Then the variation of several surface treatment parameters, such as surface roughness (micro/macro roughness) or the nature of the peel ply (polyamide/ polyester) may influence adhesion performances (Table 1).

From Table 1, one can see that the variation of suitable surface parameters may progressively increase the bonding behaviour of the assembly. More than the single lap shear values, the failure mode also changed. Indeed P1 and P2 peel ply treatments get a complete adhesive failure and on the other hand P5 and P6 preparation own a nearly complete cohesive failure in the composite material between the fibre reinforcements and the polymer surface layer.

Once this cohesive failure inside the material reached, there's no need to enhance surface properties as the material itself becomes the "weak point" of the assembly. Then, one solution is to reduce the thickness of the polymer surface layer in order to bond directly the fibre reinforcement to the adhesive layer.

This result can be obtain with the use of excimer laser surface treatment, indeed if the fluence of the laser treatment is greater than the ablation threshold of the polymer matrix and below the one of the fire reinforcement, it's then possible to remove selectively the polymer matrix and leave the fibre reinforcement undamaged.[5] The use of suitable laser parameters may allow providing several surfaces which exhibit an increase area of fibre reinforcement (as visible on Figure 1).

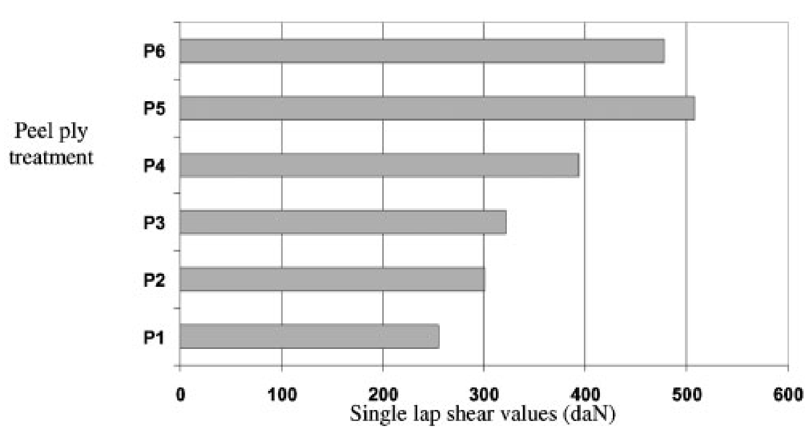
The performance of the composite assembly prepared with this laser ablation treatment in the medium ablation condition is over 800 daN, this result represents an increase of 30% compared to a classical surface treatment that lead to a cohesive failure inside the composite.

To sum up, at the initial state, the reduction of the polymer surface layer thickness may improve in a significant way the adhesion behaviour of the resulting composite assembly. However, the influence of this polymer surface layer during thermal ageing remains unknown.

Thermal Degradation of the Assembly

The most important degradation observed in such composite assemblies mainly comes from the micro/macro voids contained inside the adhesive layer.[7] Such voids are visible on transversal micro cuttings of

Table 1.
Single lap shear values (daN) from six several peel ply treatments.



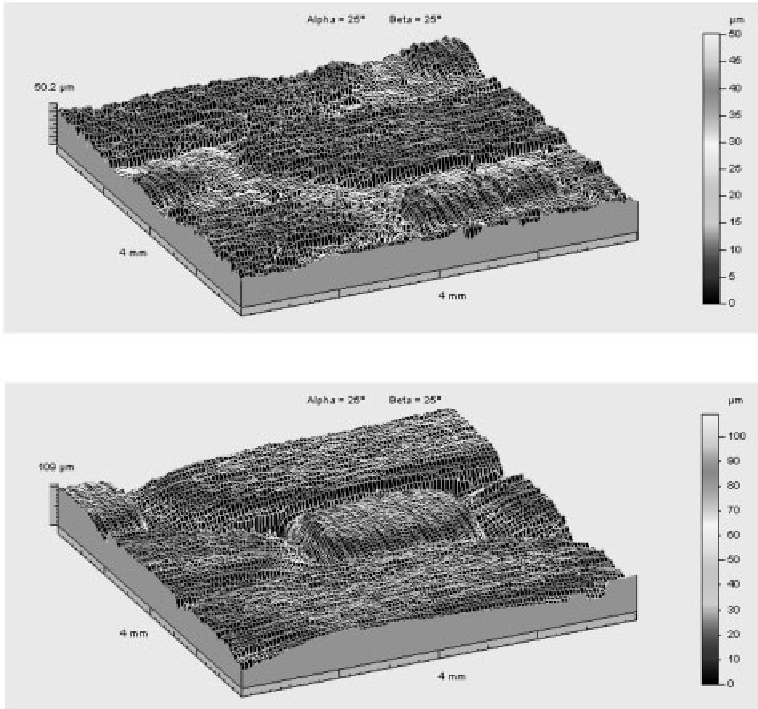


Figure 1.
Surface reconstitution of carbon/epoxy composite with two laser treatment (medium ablation at the top, complete ablation below).

bonded samples as viewed by optical microscopy (Figure 2).

Hence, the degradation of assembly under thermal ageing first initiates inside the micro/macro voids from the adhesive joint, propagates through the adhesive layer and then reaches the composite surface. As it can be seen on Figure 3 aluminium fillers (visible in white colour) of the adhesive may limit the degradation of

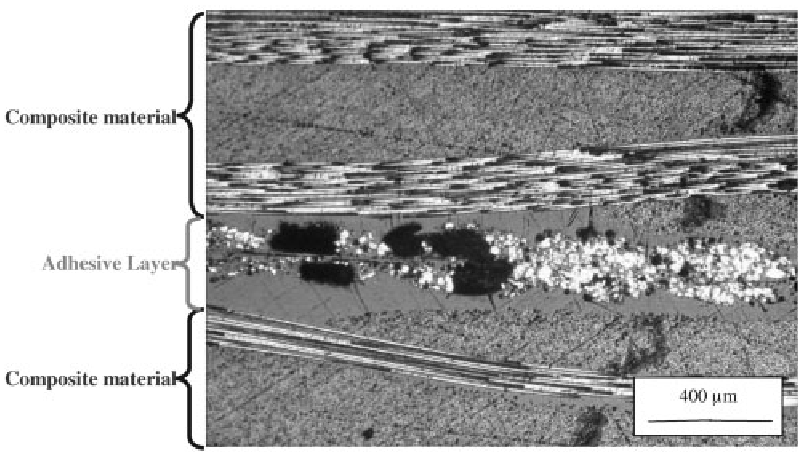


Figure 2.
Transversal micro cutting of non aged carbon/epoxy composite (micro/macro voids in the adhesive layer).

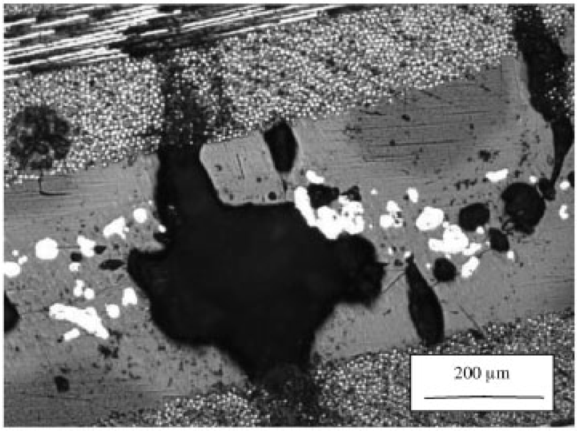


Figure 3.
Transversal micro cutting of aged samples (propagation of degradation, 1000 H 160 °C).

the adhesive layer by acting as a physical barrie, thus shifting the crack propagation from the adhesive to the composite ply.

As the polymer surface layer does not contain such ''large size'' fillers, the degradation then propagates rapidly in a large extend until it reaches the material fibre reinforcement (Figure 4) thus leading to the composite material degradation rather than the adhesive one.

To sum up, the degradation occurring in the adhesive mainly comes from defects that grow in both the adhesive and the polymeric material. Such degradation takes place in an easier way as there are no/few fillers (fibre reinforcement, metallic particles...). For this reason the use of surface treatments leading to an increase of the polymeric layer can significantly improve the thermal stability of the adhesive by favouring the propagation of polymer degradation inside the composite rather than in the adhesive one.

Increase of the Polymer Surface Layer Thickness

In the present study, two distinct ways of increasing the polymeric surface thickness

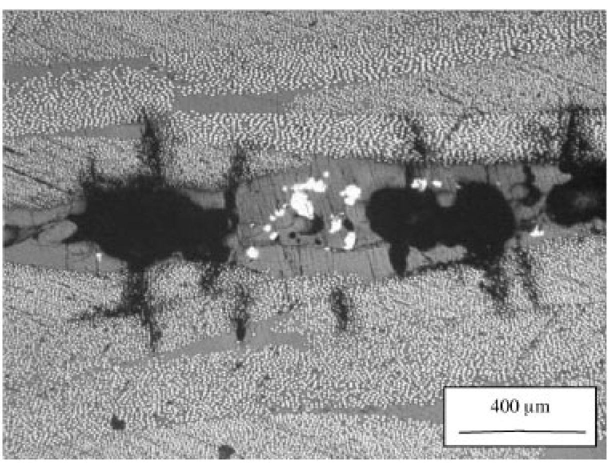


Figure 4.
Transversal micro cutting of aged samples (1000H –180 °C).

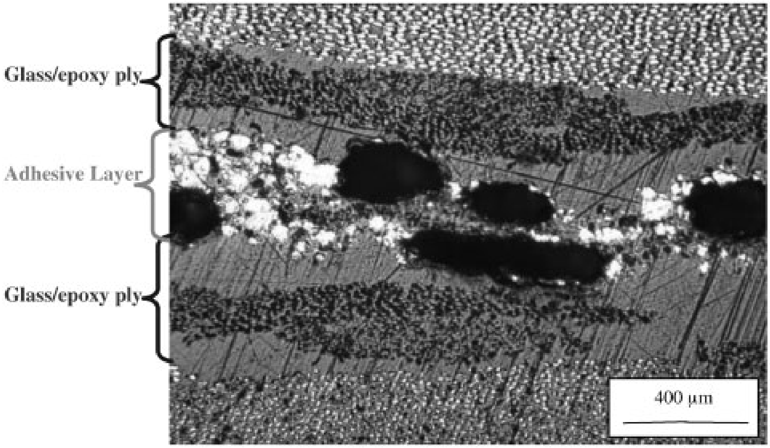


Figure 5.
Transversal micro cutting of non aged composite with an additional glass/epoxy ply.

have been investigated: the first one is performed with a pre-impregnate peel ply, while the second one uses an additional glass/epoxy ply on the surface inserted between the carbon/epoxy sample and the peel ply surface treatment (Figure 5).

These two methods are compared together with industrial peel ply treatment using single lap shear experiments. Results for corresponding assemblies are reported on Table 2 for specimen after 1000 hours ageing at 180 °C.

From these results, it clearly appears that increasing the polymer surface layer between fibre reinforcement and adhesive layer significantly increases the thermal stability of the composite assembly (preparation 2 and 3). In addition to lap shear values, observation of failed samples shows the "protection" provided by the increase of polymer layer thickness (results not shown).

Finally, the whole results clearly allow to state that thick polymeric surface layer contribute to the efficient protection of the adhesive bonding by acting as a "sacrificial layer".

Conclusion

The influence of polymer surface layer is clearly demonstrated as it completely governs the adhesion behaviour of composite assemblies both at the initial state and after thermal ageing.

At the initial the interest of reducing the polymer surface layer clearly appears as it allows to bond directly the fibre reinforcement onto the adhesive layer.

However during thermal ageing, as the degradation mainly comes from the micro/macro voids of the adhesive layer, the present study clearly indicates that both the degradation of adhesive material and the loss of assembly performances can be limited with the use of thicker polymeric material layer at the composite surface. Consequently, the interest of reducing the polymer surface layer thickness at the

Table 2.
Single lap shear values (daN) of bonded assemblies (1000 hours at 180 °C).

	Peel ply treatment (1)	Preimpregnate peel ply (2)	Additional glass/epoxy ply (3)
Initial state (non aged)	533 ± 32	495 ± 10	517 ± 21
1000 hours-180 °C	296 ± 10	429 ± 5	424 ± 27

initial state strongly limits the resistance of composite assembly when submitted to thermal ageing. In addition, more than the micro/macro voids effect, results also highlight the influence of adhesive aluminium fillers on the whole stability of the bonded assembly.

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