STUDY OF ADHERENT CONDITIONING ON THE FRACTURE TOUGHNESS OF BONDED JOINTS FOR COMPOSITE REPAIRS

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Abstract

In this study, two adhesive films are used to produce specimens of bonded joints between plain weave prepreg adherents (one adherent pre-cured and the other adherent co-bonded). A comparison is established between joints with the adherent in as-received conditions and joints in which the pre-cured adherent was conditioned in a climatic chamber in a humid environment until the moisture content reached saturation and then slightly dried. The specimens of bonded joints are tested in order to determine the fracture toughness under Mode I loading, as an indication of the bonding quality and strength. As a result of the study, the influence of moisture content and of the drying procedure of the moisture-saturated adherents on the mechanical performance of the bonding joints could be assessed.

1 Introduction

The introduction of carbon composites in aircraft structures encompasses the need to define robust methodologies to repair them. Adhesive films and laminating resins arise as potential bonding agents for repair patches; even, in the out-of-autoclave conditions imposed by in-field repair requirements. The performance of the repair is mainly related to the strength of its bonding to the structure, and the adhesion is highly dependent on the surface state of the adherents prior to the joining process (roughness, presence of chemical substances, moisture content, etc). Therefore, there is a clear interest to define repair procedures that could guarantee a proper adhesion with the patch. In particular, water content of the adherent prior bonding is of high concern. The amount of moisture uptake will depend on the environment and on the polymer acting as a composite matrix [1]. Most polymers will absorb atmospheric moisture to some extent and the more hydrophilic of these, e.g. nylon, may absorb up to 15 % by weight of water, %w/w. Carbon fibre reinforced epoxy composites will typically absorb 0.5-1.0 % w/w of atmospheric moisture [2].

In spite of the fact that structural design procedures take into account the detrimental effect of moisture on the mechanical properties of CFRP (carbon fiber reinforced polymers), its effect on repair interventions of damaged structures is unclear. For instance, moisture content of the damaged part has been found to have a significant effect on the performance of composite structural repairs. In previous published works it has been claimed that the presence of absorbed moisture in the adherent may be regarded as essentially the same as pre-bond moisture absorbed by the adhesive, since it will diffuse from the laminate into the adhesive during the heat and cure cycle [7]. Water in the surface of the adherent may act as contaminant, reducing the adhesion of the adhesive. Moreover, water in the adhesive may act as a polymer plasticizer, decreasing its glass transition temperature and favoring its ductile behavior (increasing its toughness). In summary, the pre-bond moisture of the structure to be repaired is expected to have an effect on the performance of the repair. It is therefore required to clarify both the effect of pre-bond moisture on the bond strength of the repair (given a particular set of adherent and repair materials and processing procedure) and, in view of that, to establish the convenient procedures to assure that the pre-bond moisture in the damaged structure is at the prescribed level that assures a resulting repair with the desired structural integrity.

A few studies have been reported on the pre-bond moisture effect and most of them concluded that the presence of moisture in the composite lead to the reduction in joint strength [2, 3, 4, 5, 8]. There are some unexpected results for certain adhesive joints according to which the strength increased as the moisture level increased [2, 6, 9]. Matrix ductility caused by the plasticization of the matrix [5, 12, 13] are the possible reasons for the increase in G_{IC}. For certain adhesives, no significant changes occurred with increasing pre-bond moisture content up to certain level, above which it decreased [5, 9, 10]. Some authors [4, 5, 6] have noticed that the presence of moisture in the adherent can change the locus of failure of joint from cohesive of adhesive to interfacial failure between adhesive-adherent interface. No single theory or model exists with sufficient experimental support to explain the generalized relation between pre-bond moisture and the mechanical properties of joints. Because of the uncertainty on the effect of pre-bond moisture, repair procedures tend to prescribe a drying step before bonding the patch.

The study reported here analyzes the potential use of two adhesive films as bonding agents for repairs in in-service conditions (precluding the use of the autoclave). It shows the effect of the pre-bond moisture on the fracture toughness of the adhesive joints by comparing specimens of joints bonded just after curing the adherents (no relevant moisture content is expected) to specimens where adherents have been immersed in water and then dried following different procedures.

2 **Experimental**

2.1 Materials

In order to determine the effect of pre-bond moisture in the adherents on the fracture behavior of bonded composites joints, an experimental study was carried out with two different adhesive films, F1 and F2. One of the adherents (a $[0, 90]_n$ plain weave carbon fabric epoxy prepreg,) was previously cured in autoclave conditions at 180ºC. The bonded joints with the pre-cured panel, the adhesive films (F1 and F2) and the fresh repair prepreg plies (also a plain weave carbon fabric epoxy prepreg, but 120ºC cured) were cured only under vacuum pressure. Time and temperature of the curing process was selected according to the manufacturer indications. A *teflon* insert was placed between the adherents so that an initial pre-crack of 60 mm was obtained. The dimensions of the panels were 350×300 mm and the specimens for Double Cantilever Beam fracture toughness tests were 25 mm in width and 145 mm in total length. Pre-cured panels were inspected by c-scan.

The bonded joints were also inspected to check that no flaws were present (zones with porosity). The pre-cured panels were conditioned before bonding following one of these procedures:

a) Pre-cured adherents with no further conditioning (type x_D: F1_D and F2_D)

b) The pre-cured panels where soaked by total immersion in water at 70±2 ºC for 336±12 hours and then, immediately after immersion, dried in an air circulated oven for 45 to 60 minutes at 80±5 ºC. (type x_1: F1_1, F2_1).

c) The pre-cured panels where soaked by total immersion in water at 70±2 ºC for 336±12 hours and then, immediately after immersion, dried in an air circulated oven for 24±0,5 hours at 80±5 ºC (type x_24: F1_24, F2_24).

Once the pre-cured panels were dried following one of these procedures the bonded joints were processed as described above.

2.2 Adherent Conditioning

During the adherent conditioning by immersion in distilled water for two weeks (336 hours), the moisture absorption as a function of time followed the trend shown in fig. 1. A final moisture content of 1.6 % was reached. Then, adherents were dried in an air circulated oven at constant temperature of 80°C. Weighing was performed on a balance with an accuracy of 0.0001 g. Adherents were removed from the oven at various time intervals of 1 hour and 24 hour for weight measurement. For the present study, the substrates were dried following two different procedures: during only 1 hour after immersion and dried for 24 hours after immersion. The resulting moisture content was 1.25 and 0.34 percent respectively.

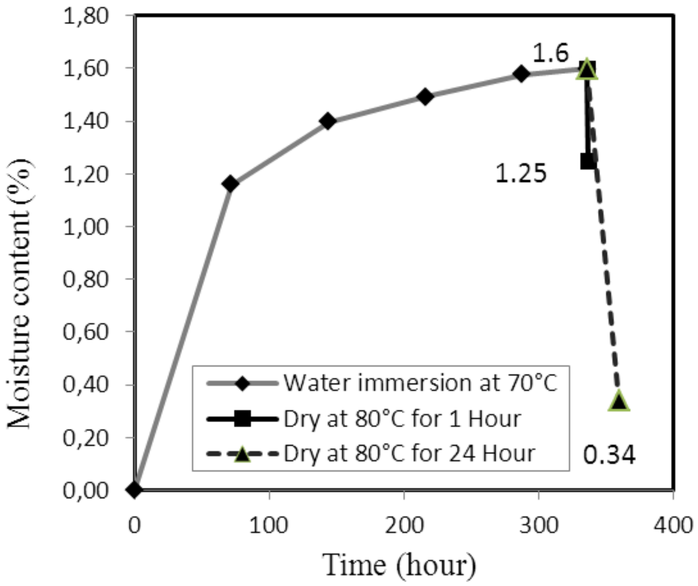

Figure 1. The moisture content of the pre-cured adherent after immersion in water at 70°C after and subsequent drying at 80ºC for 1 hour and 24 hours.

2.3 Mechanical Testing

Panels of bonded joints were cut to DCB (Double Cantilever Beam) specimens for the purpose of performing mode I tests and measure their fracture toughness energy, G_{IC}. The tests were performed according to ISO 15024 standard. All tests were performed in "As Received" state. A 100kN universal testing machine, MTS Insight, equipped with a 1 kN load cell, at a crosshead rate of 5 mm/min was used for the tests.

Tests were performed at room temperature in the composites laboratory of the University of Girona, with controlled environment (23±2°C, 50±5%HR). Each batch consisted of five specimens. The crack length during crack propagation was monitored optically at the specimen's edge by means of a long distance microscope Questar QM100. Values of load, displacement, and crack length were measured simultaneously for crack initiation and crack propagation data. These data was analyzed to enable for the calculation of the fracture toughness energy G_{IC} using several methods: Corrected Beam Theory and Modified Compliance Calibration for crack onset and propagation, and the Area Method for average propagation toughness. The data included in this report concerns the average of the propagation data as deduced by the Corrected Beam Theory and the Non-Linear point for the crack onset after pre-cracking the specimen in Mode I.

3 Results

Typical load-displacement curves for mode I delamination in DCB specimens are shown in fig. 2.

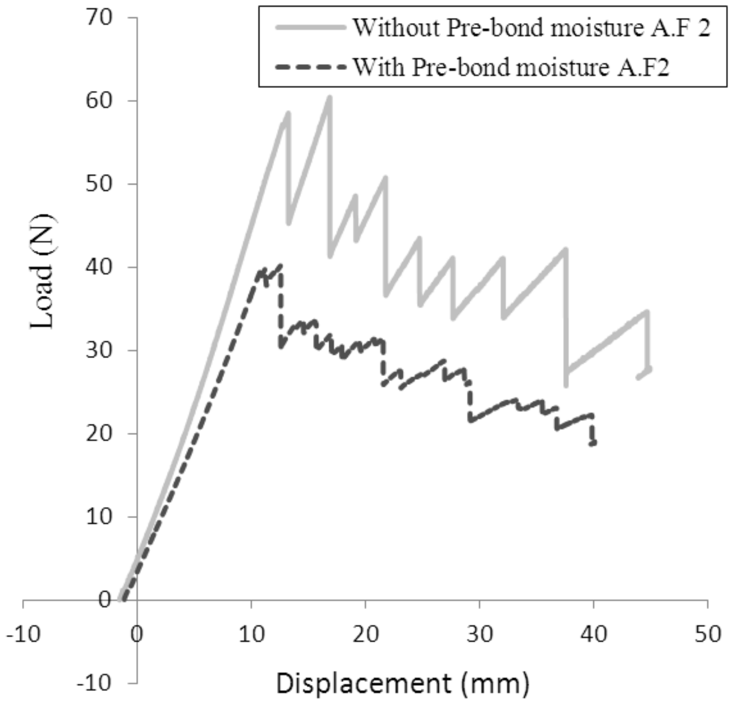

Figure 2. Load-displacement curves of Mode I DCB tests

The load showed nonlinearity from a relatively low load. Once the crack started to propagate, the alternating increasing and decreasing segments of this pattern corresponded to alternating phases of fast crack propagation and crack arrest. Crack growth was not monotonic but, instead, proceeds as a succession of rapid growth and arrest phases; this is commonly referred to *stick-slip* behavior. The most important fact for the bonded joint with as-received adherent, however, was that a multiplicity of cracks in the precured adherent were formed and propagated in different planes as shown in fig 3. That means that, in addition of the crack in the adhesive plane already existing (created in the precrack phase of the test), different cracks in the pre-cured adherent were formed and eventually progressed. This behavior was not observed in the specimen with pre-bond moisture conditioning (1.25%).

Due to the progression of multiple cracks in non-conditioned specimens, care should be taken when using the fracture toughness derived from these tests. It does not correspond to the fracture energy required to propagate a crack in the weaker interface of the bond (as is usually the case) but to the summation of the energy involved in the propagation of all existing cracks. Therefore, the obtained data should be understood as an overestimation of the strength of the bonded joint.

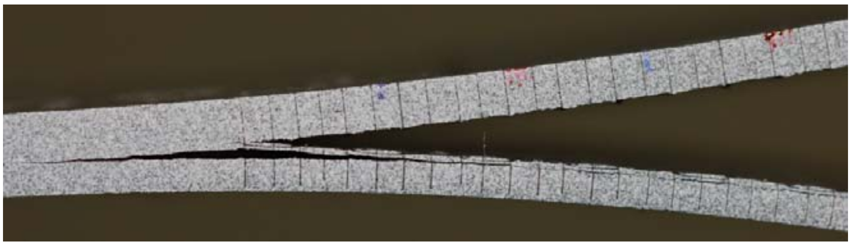

Figure 3. Failure mode of DCB joints bonded with adhesive films in absence of pre-bond moisture. This figure shows the progression of multiple cracks during testing.

Table 1 shows the average onset fracture toughness for crack initiation (Non-linear point, NL) from the *teflon* insert and from precrack. The onset results for the adhesive films F1 and F2 without moisture conditioning should be taken with caution due to the reasons explained in the previous section. There is an strong effect of the crack front state (insert or precrack) on the onset fracture toughness (more than 100% of increase in the precracked specimens).

Co-bonded joints NL onset from insert and precrack (CBT)	G_{IC} (J/m^2) without pre-bond moisture		G_{IC} (J/m^2) pre-bond moisture + + 1hr drying		G_{IC} (J/m^2) pre-bond moisture + + 24hr drying	
	Insert	Precrack	Insert	Precrack	Insert	Precrack
Film - F1	488	675	170	420	228	592
Film - F2	617	756	244	491	352	725

Table 1. Onset fracture toughness from the insert and from the precrack (NL point) resulting from the CBT data reduction method for the bonded joints with and without pre-bond moisture.

The mean propagation values of G_{IC} for joints manufactured using the two different adhesive films (F1, F2) are shown in table 2. The results show that the duration of the adherent drying process after water immersion (1 hour or 24 hour) has an important effect on the resulting fracture toughness of the joint. For both films, the fracture toughness increased around 50% in the longer drying process with respect to the value for 1 hour drying. It is also remarkable that the multiple crack propagation evidenced in the as-received specimens was not observed in these specimens with pre-bond moisture of the adherents. In any case, the fracture toughness values, $G_{IC,}$ for the joint bonded with adhesive films is four to five times higher than that of the joints bonded with the laminating resins [14] .

Adhesive	**Adherent condition**	**Test Condition**	**G_{IC} (J/m^2)**
Adhesive film A1 – A1_D	As Received	RT	790±32
Adhesive film A1 – A1_1	1,25%	RT	409±23
Adhesive film A1 – A1_24	0,34%	RT	629±58
Adhesive film A2 – A2_D	As Received	RT	804±102
Adhesive film A2 – A2_1	1,25%	RT	495±38
Adhesive film A2 – A2_24	0,34%	RT	751±59

Table 2. Average of the CBT propagation data of fracture toughness for the bonded joints without pre-bond moisture and with pre-bond moisture conditioning and drying for 1 hour and 24 hours.

4 Discussion

First, it should be discussed the observation that the specimens with adhesive films and non-conditioned adherents exhibit multiple crack propagation whereas the specimens with pre-bond moisture do not. The presence of multiple cracks is an indication that the interlaminar interfaces in the adherents are weaker (in terms of fracture toughness) than the interface created by the adhesive film. Fracture crack progresses through the path that requires less energy. Then, a crack in the adherent (delamination) is formed and progresses. Only when this delamination crack has grown enough it is energetically more favorable to propagate the adhesive crack. In the steady situation, both cracks grow at a different position (the delamination crack in front of the adhesive crack, see figure 3). In summary, the multiple crack propagation in an indication of a strong bond interface (the crack prefers to move to other weaker interfaces). The fact that specimens with pre-bond moisture do not exhibit it evidences that the bond interface is not as strong as it was in the non-conditioned specimens and the crack evolves without creating additional cracks elsewhere.

In the adhesive films, pre-bond moisture tend to decrease the bond strength as indicated by several evidences: i) the fracture does not involve several cracks in bonds with conditioned adherents; ii) there is a positive effect on fracture toughness of the duration of the drying stage after pre-bond immersion (drying for 24 hours lead to higher toughness than 1 hour drying, although it was not recovered the characteristic behavior of the non-conditioned specimens).

From these results it seems advisable that composite substrates should be dried prior to adhesive bonding, as observed by Sage and Tiu [13] and Parker [3].

5 Conclusions

Co-bonded joints with adhesive films acting as bonding agents for in service repair conditions have been produced. It has been analyzed the effect of the moisture uptake of the pre-cured adherent on the performance of the joint. For that purpose, the pre-cured adherent has been soaked in water and then dried. Fracture toughness for crack onset and propagation has been taken as an indicator of the joint quality.

For the samples with pre-bond moisture the fracture toughness of adhesive films (F1 and F2) was found to be almost six times higher than for laminating resins as published in ref. [14]. The fracture toughness of joints bonded with adhesive films and non-conditioned substrates indicates that the adherents are the weaker part of the bond. When pre-bond moisture is in the pre-cured adherent, the adhesive becomes the weaker part of the bond (to be confirmed, if the failure happened cohesively in the adhesive.). Extending the duration of the drying operation of the substrate with pre-bond moisture for the joints with adhesive films, F1 and F2, showed a positive increment in fracture toughness. To that purpose, more exhaustive drying processes might be necessary: while enlarging significantly the drying time might not be practical, increasing the drying temperature is still suitable.

References

[1] Wright W.W. The effect of diffusion of water into epoxy resins and their carbon-fibre reinforced composites. *Journal of composites,* **81**, pp. 201-205 (1981).

[2] Blackman B., Johnson B., Kinloch A., Teo W. The effect of pre-bond moisture on the fracture behaviour of adhesively bonded composite joints. *Journal of adhesion,* **84**, pp. 256-276 (2008).

[3] Parker B. The effect of composite pre-bond moisture on adhesive-bonded CFRP-CFRP joint. *Journal of composites,* **14**, pp. 226-232 (1983).

[4] Parker B. Some effects of moisture on adhesive bonded CFRP-CFRP joints” *Journals of composites,* **6**, pp. 123-139 (1986).

[5] Parker B. The strength of bonded carbon fibre composite joints exposed to high humidity. *Journal of adhesion and adhesives,* **10**, pp. 187-191 (1990).

[6] Armstrong K. Effects of absorbed water in CFRP composites on adhesive bonding *Journal of adhesion and adhesive,* **16**, pp. 21-28 (1996).

[7] Myhre S., Labor J., Aker S. Moisture problem in advanced composite structural repair. *Journal of composites,* **10**, pp. 289-297 (1982).

[8] Dodiuk H., Drori L., Miller J. Preconditioning of epoxy film adhesives for bond strength improvement. *Journal of adhesion and adhesive,* **4**, pp. 169-170 (1988).

[9] Robson J., Matthews F., Kinloch A. The bonded repair of fibre composites: effect of composite moisture content. *Journal of composite science and technology,* **52**, pp. 235-246 (1994).

[10] Selzer R., Fredrich K. Influence of water up take on interlaminar fracture properties of carbon-reinforced polymer composites. *Journal of materials science,* **30**, pp. 334-338 (1995).

[11] Garg A., ISHAI O. Hygrothermal influence on delamination behavior of graphite/epoxy laminates. *Journal of Engineering* Fracture *Mechanics,* **22**, pp. 413-427 (1985).

[12] Selzer R., Fredrich K. Mechanical properties and failure behaviour of carbon fibre-reinforced polymer composites under the influence of moisture. *Journal of Composites Part A,* **28A**, pp. 595-604 (1997).

[13] Sage G., Tiu. The effect of glue line voids and inclusions on the fatigue strength of bonded joints in composites. *Journal of composites,* **13**, pp. 228-232 (1982).

[14] Costa J., Renart J., Batista Y., Mahdi S., Rodriguez-Bellido A. *Detailed investigation of bonded joints for composite repairs* in Proceedings of *18th International Conference on Composite Materials,* Jeju, Korea (2011).