Analysis of the resistance of adhesively bonded joints with rigid-flexible substrates

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Abstract. Hydrogen, as an energy source, appears as a valid alternative to traditional fossil resources and supports the required reduction of CO₂ emissions. The most recent hyperbaric tanks built for hydrogen storage (type IV) are made of composite material. For the manufacturing of these tanks, an adhesive layer is being used to join the flexible internal polymeric core, the liner, with the external composite shell. This work aims to study the strength of the liner-composite joint using the Floating Roller Peel (FRP) test. To this purpose, finite element analyses of the peeling process are carried out using the cohesive model. In order to establish a framework for the investigation of the joint properties as a function of manufacturing parameters (e.g., adhesive type and surface preparation), this paper describes a potential procedure that can be used for the identification of joint properties.

1. Introduction
Hydrogen energy appears to be one of the solutions that can respond to the lack of fossil resources and face the problems of global warming by the reduction of CO₂ emissions. Hydrogen, together with an efficient system of conversion, as the fuel cells, represents a very promising solution to realize a more sustainable system of energy supply [1]. In this context, hydrogen storage plays a crucial role. Today the hyperbaric tanks, thanks to their combination of lightness and high mechanical strength, are considered the best choice for hydrogen storage, especially in the aeronautical and automotive fields. The fourth, i.e., the last, generation of these high-pressure tanks, called hyperbaric, is fabricated with a composite layup, i.e., carbon fibers with epoxy matrix [2]. Moreover, the interior surface of the vessel is coated with a polymeric layer, the liner, that is typically manufactured using polyethylene or polyamide. This layer is crucial to prevent leakages and to act as a thermal barrier against temperature fluctuations occurring during vessel filling-emptying cycles [3,4]. Since the reliability of the liner is crucial to achieve high performance, it is important to evaluate its mechanical properties [5–8]. Among the various research studies concerning the liner, Castagnet et al. [9] conducted mechanical tests on two semi-crystalline polymers in an environment saturated with hydrogen under controlled pressure (up to 3 MPa). Specifically, the tensile, creep and ductile fracture behavior of polyethylene and polyamide 11 was studied in conjunction with the exposure of these materials to hydrogen. It was found that the main
mechanical properties, e.g., creep deformation or yield stress, underwent a maximum decrease of 10%, which was deemed satisfactory for the intended purpose.

However, a much more severe limiting factor is represented by the occurrence of debonding at the composite/liner interface during service. In fact, despite many studies that are already present in the literature regarding the construction and reliability of these tanks [3,4,10–13], this issue received relatively less attention. More precisely, when the pressure inside the tank suddenly drops, the dissolved gases in the materials (liner, composite, glue) generate bubbles that can lead to the formation of large cracks at the composite-liner interface that could lead to the phenomenon known as “explosive decompression”. The subsequent filling phases exacerbate the phenomenon by promoting further separation and crack propagation, facilitated by the deformation of the liner.

Recent works have demonstrated that explosive decompression can be mitigated by enhancing the adhesion at the composite/liner interface [14–16]. Improving interfacial strength will increase the lifetime of the structure and so, the efficiency of the energy storage. This is a challenging issue hampering the use of hydrogen as an energy source, and that is currently tackled within the framework of an EU-level research collaborative by the authors and co-workers [17].

The project aims to understand the phenomenon of the explosive decompression, through experiments and modeling. However, the present study is focused on the analysis of debonding at liner/composite interfaces using experiments and numerical simulations. In particular, a model material system comprising a flexible polymeric layer bonded to a composite substrate using an epoxy adhesive is analyzed using the floating roller peel test [18,19]. The sample is representative of the actual materials and manufacturing methods that have been selected for the vessels. Mechanical tests are carried out using a benchtop testing machine fitted with a high-resolution CCD camera. By using the available experimental data in conjunction with finite element simulations, the study describes a potential approach for the determination of the mechanical properties of the joint. The proposed method can be valuable for the refinement of the manufacturing process of the composite/liner interface, which includes the selection of an appropriate adhesive and surface preparation method.

2. Experimental

2.1. Materials

The pre-pregs employed for the manufacture of composite plates is the HexPly® M77, produced by the Hexcel Corporation (Stamford, USA). The main mechanical properties of the material are given in [20]. The composite is obtained using an epoxy matrix formulation that is specifically designed for prepreg applications and short curing cycles. The matrix is very versatile and can be cured in a wide range of temperatures ranging from 80 °C up to 160 °C. HexPly® M77 is based on modified epoxy resin. It can be pre-impregnated with various types of fibers (glass, carbon, aramid) and can remain for long periods at room temperature without losing its workability properties.

The liner is a thin layer of polymeric material, i.e., polyamide 6 (PA6), also known as Nylon. It is a semi-crystalline thermoplastic material, purchased, under the trade name of SUSTAMID® 6, from the Röchling company (Mannheim, Germany). Information about the material is reported in the datasheet [21].

A very important aspect of the project concerns the research and development of a new formulation for the adhesive that allows reaching a satisfactory level of resistance against the explosive decompression and decohesion of the composite/liner interface. Various epoxy adhesives are currently under examination, whose differences are mostly due to distinct Young’s modulus and strain at failure. The proprietary formulation that has been assessed in this work features the lowest available Young’s modulus.
2.2. Floating roller peel test
The configuration chosen for the peel test, i.e., the Floating Roller, has been fabricated as suggested by standard ASTM D3167 [18]. The tensile tests were performed using an electromechanical machine, the MTS Criterion Model 42, equipped with a load cell with a capacity of 100 N, connected to a control unit.

A high-resolution camera (Prosilica GT2450, Allied Vision) was positioned in front of the test machine for image acquisition, connected to another control unit as shown in Figure 1 (a). The camera was interfaced with commercial software (Vic-Snap, Correlated Solutions) to capture images through an acquisition card (DAQ-STD-8D, National Instruments). This card was connected directly to the test machine thus allowing the acquisition of images at a specific delta displacement of the crosshead, in particular, equal to 1 mm.

The fixture proposed in the standard has been slightly modified as shown in Figure 1(b). This was deemed necessary to have access to the delamination area and to be able to view the deformation mechanism of the liner during the entire peeling phase. The tests were performed under displacement control using a crosshead displacement speed of 152 mm/min [18].

![Figure 1](image1.png)

**Figure 1.** Set-up employed for the mechanical tests. (a) Benchtop electro-mechanical testing machine fitted with a high-resolution CCD camera. (b) Modified floating roller peel fixture that allows access to a region of interest around the peeling front.

3. Finite element modeling
In support of the experimental analysis, the chosen peel test has been reproduced in a numerical environment. The proposed model aims to represent, in a simplified but reliable way, the floating roller peel test. The analysis of the joint mechanical behavior can greatly benefit from the use of numerical techniques such as finite element analyses (FEA) with cohesive zone models (CZM). The CZM is rooted in the cohesive approach by Dugdale [22] and Barenblatt [23], and is based on the assumption that the damage mechanisms leading to the fracture are located in a thin layer of material in front of the crack tip, i.e., the so-called process zone. The damage depends on the progressive separation of the fracture surfaces and occurs following a predefined Traction-Separation Law (TSL).

Several models are reported in literature [24]. This work employed the bilinear model, as shown in Figure 2. Following an initial separation of the crack surfaces \( \delta \), cohesive stress \( T \) increases linearly with a slope \( K_\delta \), that is the stiffness of the cohesive element. The stress then reaches a maximum \( T_c \) (critical stress) at the displacement \( \delta_0 \), after which it begins to decrease until it gets to zero at the...
maximum displacement $\delta_f$, which corresponds to complete decohesion and to the consequent advancement of the fracture.

**Figure 2.** The triangular cohesive model employed in the finite element simulations.

The equations that describe this model are given as follows:

$$
T = \begin{cases} 
K_n \cdot \delta & \text{if } \delta < \delta_0 \\
\frac{T_n \cdot (\delta_f - \delta)}{\delta_f - \delta_0} & \text{if } \delta_0 < \delta < \delta_f \\
0 & \text{if } \delta > \delta_f
\end{cases}
$$

(1)

The energy dissipated during the fracture process, given by the area under the curve of the TSL, is known as the critical fracture energy $G_C$. For a bilinear TSL the critical fracture energy can be calculated as:

$$
G_C = \frac{T_n \cdot \delta_f}{2}
$$

(2)

The finite element model of the joint is shown in Figure 3. The specimen is constrained to slide obliquely with a slope of 25 degrees. The joint is made up of a rigid and a flexible substrate, with a thickness of 1.63 mm and 0.63 mm, respectively, selected based on the ASTM standard dimensions [18]. The adhesive layer has a thickness equal to 0.1 mm. The roller was modeled as a frictionless rigid body.
The joined materials have been modeled using 2D continuum elements assuming plane strain deformation, while the adhesive layer is replaced by a single row of cohesive elements. Cohesive stress and energy have been varied in the FE simulations, while the stiffness of cohesive elements, $K_n$ (or $K_s$) was set equal to 100 N/mm$^3$ both in the normal and shear direction. This value was obtained by dividing Young's modulus of the adhesive employed in preliminary experiments (10 MPa) by the thickness, $t$, of the adhesive layer (0.1 mm). By replacing the entire adhesive layer by a single row of cohesive elements the macroscopic response of the adhesive is represented by the cohesive zone. In this way, the fracture process of the adhesive and the inelastic deformations in the bulk are directly embodied within the traction-separation relation. In Table 1 the parameters used for the cohesive elements are summarized.

### Table 1. Cohesive parameters.

| Adhesive | $T_n$ | $G_C$ | $K_n$ | $K_s$ | $t$ |
|----------|-------|-------|-------|-------|-----|
|          | 5 ÷ 25 MPa | 0.2 ÷ 1.8 N/mm | 100 N/mm$^3$ | 100 N/mm$^3$ | 0.1 mm |

Notice that a mode independent formulation has been assumed whereby the fracture energy of the interface is set being equal to $G_C$, while the cohesive strength of the interface in shear has been set equal to twice the normal traction. The boundary conditions are described in Figure 3, and the simulations have been carried out under displacement control, with a maximum applied displacement of about 60 mm. The maximum number of iterations within each increment and the number of allowable cutbacks were both set equal to 50 since, given the geometric nonlinearity of the problem, higher values than the standard ones are recommended [24]. The required output is the load/displacement plot, whose point data have been determined at the point of load application. The parametric analyses have been fed using the available data extracted from literature for both the composite [12,13,25,26] and the cohesive [27–30] properties.
4. Results

4.1. Preliminary floating roller peel tests

Peel tests were performed using the floating roller peel test configuration described earlier. A typical load/displacement curve obtained from the experiments is shown in Figure 4. The highlighted green regions represent the values that were excluded from the analysis, i.e., those corresponding to displacement less than 25.4 mm (as suggested by the standard) and greater than 180 mm. In fact, these values are generally influenced by edge effects and are not representative of the strength of the joint [18]. The orange dashed line indicates the steady-state value of the peeling load obtained averaging the results of ten samples. The high-frequency fluctuations in the recorded peel load can be associated with variations of interfacial adhesion across the fracture plane. This point was further confirmed by the analysis of fractured surfaces.

![Figure 4](image)

**Figure 4.** The average value and standard deviation of the load recorded during the peel tests.

At visual inspection, the fracture was always adhesive (near interfacial), as shown in Figure 5. The surface of the composite was free from any trace of adhesive, that indeed was entirely located at the liner surface. Alternative surface preparation methods and adhesive formulations are currently being investigated to assess potential improvements in the manufacturing methods.

![Figure 5](image)

**Figure 5.** Adhesive failure of the joint. In yellow the adhesive attached to the PA6.

In Figure 6 the deformed shape of the liner is shown as recorded during mechanical tests. The deformed configuration and the load-displacement response of the sample will be used as suitable input
variables for the determination of cohesive strength and fracture energy from finite element simulations. This point is discussed further in the subsequent section.

![Figure 6. (a) Deformed shape of the liner during the peel and (b) detail around the roller.](image)

4.2. Sensitivity analysis using finite element modeling

A sensitivity analysis of the finite element model to the variation of the cohesive parameters was conducted. In particular, it was verified how the load-displacement response and the deformed configuration of the sample vary when the characteristic values of the TSL are varied, i.e., the initiation damage normal stress ($T_n$) and the critical fracture energy ($G_c$). The stiffness $K$ of the cohesive elements, as already mentioned, was set equal to $100 \text{ N/mm}^3$, a value obtained as the elastic modulus of the adhesive divided by the thickness of the cohesive elements. The behavior of the liner was modeled as perfect elasto-plastic, with Young’s modulus of 3200 MPa and yield stress of 80 MPa, data taken from the material datasheet (PA6) [21]. Mechanical tests are ongoing in order to determine accurately the stress-strain response of the material.

![Load/Displacement graphs](image)
Simulations were performed by setting the critical normal stress at 10 MPa and varying the fracture energy $G_C$ between 0.2, 0.6, 1.0, 1.4, and 1.8 N/mm. The resulting load/displacement curves and the deformed shape of the liner in a region of interest located near the crack front are shown in Figure 7. As expected, increasing the energy implicates a higher value of load necessary for the peeling and also a greater curvature of the liner. Five more tests were then performed, by keeping constant fracture energy $G_C$ and varying the critical stress, in order to evaluate the model sensitivity. For conciseness, the results are not reported herein, however, similar to the previous case, increasing $T_n$ led to higher peel loads and greater deformations.

4.3. Potential inverse procedure for identifying cohesive parameters

In order to evaluate the properties of the adhesively bonded joints, an iterative procedure is currently being developed where the input cohesive properties are varied until there is a match between experiments and simulations. The procedure is developed along similar lines of what is reported in [31]. Considering the modeling assumption discussed earlier, there are only two parameters that need to be determined, that is the cohesive energy and the normal stress.

To get an estimation of these values, the average load and the deformation of the liner around the roller will be used as an input variable to build an objective function ($\phi$, phi). To this end, the following equation has been used:

$$\phi(G_C, T_n) = \ln(\alpha_{LOAD} \cdot \phi_{LOAD} + \alpha_{HUMP} \cdot \phi_{HUMP})$$

where

$$0 \leq \alpha_{LOAD}, \alpha_{HUMP} \leq 1$$

The two-weight coefficients $\alpha_{LOAD}$ and $\alpha_{HUMP}$ have admissible values between 0 and 1. The functions $\phi_{LOAD}$ and $\phi_{HUMP}$, are described as follows. $\phi_{LOAD}$ represents a residual between the average peel load extracted from experiments and simulations. In FE analyses it depends on the combination of the parameters $G_C$ and $T_n$. Note that these quantities are represented by vectors, and as such, they have been treated in the calculations. In particular $\phi_{LOAD}$ consists of the sum of the squared differences between
the values of a load curve taken as a reference ($P_{REFERENCE}$) and the values of a load curve obtained from a numerical simulation ($P_{COMPUTED}$). The whole is normalized by dividing by the sum of the square of the reference values.

$$\varphi_{LOAD}(G_C, T_n) = \frac{\sum (P_{REFERENCE} - P_{COMPUTED}(G_C, T_n))^2}{\sum P_{REFERENCE}^2}$$  \hspace{1cm} (5)

$\varphi_{HUMP}$ is similar in both form and meaning to the previous one. In this case, the quantities involved are the ordinates of the profiles of the deformation of the liner. The used reference system originates in the center of the roller. The interval on the x-axis in which to consider the values has been set between -5 mm and 10 mm. The function is defined as:

$$\varphi_{HUMP}(G_C, T_n) = \frac{\sum (\gamma_{REFERENCE} - \gamma_{COMPUTED}(G_C, T_n))^2}{\sum (\gamma_{REFERENCE} - \gamma_{ROLLER})^2}$$  \hspace{1cm} (6)

The numerator contains the sum of the square of the difference between the y-coordinates of the deformed profile of the liner ($\gamma_{REFERENCE}$) and the ordinates of the profile obtained from a single simulation ($\gamma_{COMPUTED}$). In the denominator, instead, in order to normalize, we find the sum of the square of the ordinate difference between the reference and the roller profile ($\gamma_{ROLLER}$).

At this point, it was necessary to have an automatic procedure that would allow running various numerical simulations by changing each time the pair of parameters to be identified, i.e., the critical stress $T_n$ and the critical energy $G_C$. For this purpose, scripts have been used, which connect a numerical computing environment with the FEA software. Once all the simulations are completed, another script processes the output data returning the values of the function $\varphi (G_C, T_n)$. Finally, contour plots are generated with these values. Isolines help to highlight any areas where the combinations of input cohesive properties provide peeling load and deformed configuration similar to those extracted from the experiments.

Preliminary validation tests have been carried out using pseudo-experimental data generated using finite element models and $G_C = 1$ N/mm and $T_n = 15$ MPa. The result reported in Figure 8 refers to $\alpha_{LOAD} = \alpha_{HUMP} = 0.5$. This combination considers in equal measure the influence of liner deformation and average peel load. It is shown that the minimum value of the objective function is indeed located at $G_C = 1$ N/mm and $T_n = 15$ MPa. However, these simulations account for deterministic values of the inputs, while some extent of variation is expected from the experiments, therefore the robustness of the method must be also proven against noisy pseudo-experimental data.
Figure 8. Contours for the Phi function. The minimum area is in dark blue.

5. Conclusions
The floating roller peel test has been used to characterize adhesively bonded joints, representing the structure of a hyperbaric tank. The test has been reproduced in a numerical environment for supporting experimental observations. An inverse identification procedure has been proposed and implemented for the determination of joint properties. Preliminary validation has been carried out using pseudo-experimental data. Further work is currently ongoing to refine the model and assess the method's robustness against noisy experimental data retrieved from mechanical tests.

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