Characterization of the water–titanium interaction and its effect on the adhesion of titanium-C/PEKK joints

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This study investigates the mechanisms governing the degradation of co-consolidated titanium-C/PEKK interfaces. Atomic force microscopy was used to demonstrate that the titanium-oxide surface adsorbs moisture. Combined with the diffusion of water molecules through the composite tape material, this causes a severe deterioration of the co-consolidated titanium-C/PEKK interfacial toughness, as measured by means of a mandrel peel test on conditioned specimen. A partial recovery of the interfacial toughness after drying of the specimens indicates that the degradation is reversible, providing evidence that the interaction between titanium and C/PEKK is predominantly characterized by secondary bonds.

1. Introduction

The application of high-performance thermoplastic composites (TPCs) has significantly increased in the recent generation of aircraft. Thermoplastic-based composites present advantages over their thermoset counterparts, mostly deriving from the property of the thermoplastic matrix to soften when heated. From a manufacturing perspective, this property allows high production rates, for example through press forming [30], and cost-efficient assembly or joining by means of welding and co-consolidation [26]. Joining composites to other materials, primarily metals, is often required for structural interconnections [16]. In the case of Fibre Metal Laminates (FMLs), composites are combined with metals to obtain a material with superior properties compared to its constituents, having improved impact and fatigue resistance [8].

The present work focuses on co-consolidation, which is a joining method where TPCs can be directly bonded to metal parts during a typical composite consolidation or forming process [1]. At elevated temperatures, the thermoplastic matrix melts and acts as an adhesive, meanwhile the composite consolidation is also achieved. Hence, co-consolidation is an appealing alternative to the currently used joining methods, which are mechanical fastening and adhesive bonding [24]. Despite the reliability of these conventional methods, mechanical fastening leads to additional costs and weight to the structure, along with stress concentrations at the locations of the fasteners. The use of adhesives overcomes the issue of stress concentrations, but leads to additional challenges, since not only the metal surface, but also the TPC surface needs to be treated prior to bonding, as TPCs are generally characterized by a low surface energy [10]. In addition, using adhesive bonding leads to extra time and costs related to the curing step of the adhesive, while the co-consolidation is a one-step process.

Typically, the TPCs employed in aerospace applications are made of continuous carbon fibres in combination with high-performance thermoplastic matrices such as PEEK, PEKK or PEI [4]. It is well known that carbon fibres induce galvanic corrosion when joined to metals like aluminium or steel [29]. Consequently, in terms of material system, titanium alloys are often used in combination with both thermoplastic and thermoset-based composites with carbon fibres. Titanium and carbon fibres are galvanically compatible, hence avoiding any risk of corrosion.

In general, metal surface treatment is essential when bonding metal to polymers, as it promotes one or more bonding mechanisms [3]. Our previous research on co-consolidated titanium-C/PEKK joints showed that promoting mechanical interlocking, by increasing the roughness of the titanium surface prior to the co-consolidation, had a positive effect on the fracture toughness [19]. Treatments like laser ablation also promote mechanical interlocking with a consequent beneficial effect on the mechanical properties [12]. Moreover, etching and anodizing have a beneficial effect on the mechanical performance, as molecular interaction is promoted [21]. The effect of these surface treatments was mostly investigated in dry conditions. However, these joints are often exposed to harsh conditions during their lifetime, such as moisture and
elevated temperatures. Under these circumstances, the metal–polymer interface may undergo significant degradation, possibly leading to in-service failure. Therefore, to ultimately achieve reliable titanium–TPC joints, their durability in presence of moisture is a fundamental property that requires investigation.

The bond instability of titanium–thermoplastic interfaces in the presence of water is an issue addressed in several studies [2,20]. Until now, this aspect has been tackled by proposing different solutions in terms of different surface treatments. These solutions resulted in an improved bond stability. Nevertheless, to our best knowledge, the main cause of the bond degradation is not yet reported. The explanations provided for the improved bond stability are often limited and lead to different conclusions. For instance, according to Schulze et al. [28], there is a correlation between metal surface morphology and durability of the bond. Conversely, Ramani et al. [25] attributed the improved bond stability not to the surface morphology, but to the molecular interaction promoted between the two adherends.

The present work aims to find the root cause of the titanium–thermoplastic composite bond instability in the presence of moisture. First, AFM experiments were employed as a new experimental approach in the context of metal-composite adhesion, to investigate the interaction between water and the two adherend surfaces considered in this study, namely Ti6Al4V and C/PEKK. Second, the effect of these interactions on the adhesion of co-consolidated Ti6Al4V-C/PEKK joints was evaluated in terms of fracture toughness using a mandrel peel test. Combining AFM experiments with mechanical testing allowed to elucidate the nature of the molecular interaction between titanium and TPCs, and provided an understanding of the mechanisms that govern the bond instability in the presence of moisture. Comprehending both of these aspects is an essential step for finding reliable solutions that can ensure strong and durable titanium–TPC interfaces.

2. Experimental methods

2.1. Materials

The titanium alloy Ti6Al4V was selected in this study, as it is one of the most widely used in aerospace [21]. The titanium was provided in strips, with dimensions suitable for the mandrel peel test (120 × 10 × 2 mm²). The strips were supplied by Singeling B.V. and obtained via laser cutting.

The thermoplastic composite tape used was the Cetex® TC1320 material. It is a unidirectional (UD) C/PEKK prepreg manufactured by Toray Advanced Composites using AS4 carbon fibres and PEKK (poly ether ketone ketone) matrix. The tape is characterized by a nominal thickness of 0.15 mm and a fibre volume fraction of 59%. Additionally, this tape has a uniform fibre distribution and a rather smooth surface [19]. As a consequence, the amount of polymer at the surface is insufficient to fully wet the metal substrate, and thus to establish a reasonable bond. Therefore, the bond between the composite prepreg and the titanium substrate was ensured by placing an additional layer of PEKK film between the two adherends [19]. The PEKK film used was Kepstan® 7002 with a thickness of 50 μm.

2.2. AFM experiments

The interaction between water and the adherend surfaces was individually studied using Atomic Force Microscopy (AFM). The experiments were conducted with a Park XE-100 AFM from Park Systems. The measurements were performed in tapping mode using an ACTA AFM probe from AppNano. The probe spring constant was 26 Nm⁻¹ and it was determined with the thermal noise method [5]. The resonance frequency used was about 300 kHz, with a scan rate of 0.2 Hz. The free oscillation amplitude of the cantilever was set at 25 nm. All of the experiments were conducted at room temperature, in equilibrium with the water vapour at different conditions of relative humidity, whose value was monitored using a digital humidity sensor (Testo 174H), with an accuracy of ~ 3% RH. The first measurement was carried out at 5% RH to approximate a dry environment as much as possible. This low humidity level was achieved using an air dryer (super air dryer from Ter Horst B.V.). Subsequently, the environment in the AFM was modified to achieve high humidity conditions, obtained using a saturated KI aqueous solution [35]. Considering that the experiments conducted at high humidity implied the whole AFM to be conditioned with the humid air, a maximum value of 65% RH was used to avoid any potential damage of the instrument. The third test was conducted by reducing the humidity from 65% RH back to the initial condition of 5% RH using the air dryer. Overall, the objective of these three measurements was to gain a better understanding of the adsorption/desorption phenomena that occur at the titanium and C/PEKK surface, in that way providing more insight about their interaction with water. It should be noted that the measurements related to the interaction between titanium and water were performed on a mirror-polished titanium surface to specifically investigate the interaction between water and the titanium oxide that naturally forms on the surface, ruling out the effects that may be induced by the surface roughness [36]. For both metal and composite surfaces, a measuring window of 10 × 10 μm² was considered.

Phase images were recorded from these AFM experiments to detect changes in the tip–surface interaction. It has been reported that this method allows accurate probing and investigation of the water adsorption phenomenon, which is measured in terms of change in adhesion force between tip and sample surface [27,36]. In this work, this technique was adopted to investigate the water adsorption behaviour of titanium and C/PEKK. The water adsorption or desorption that may occur when increasing or decreasing the humidity of the AFM environment significantly changes the tip–sample adhesion via capillary forces due to the presence of water molecules between probe and tested surface. As the phase shift is directly related to the non-conservative tip–surface interactions, changes in the phase shift, when varying RH, can be associated with the presence of adsorbed water [36]. Therefore, if any water adsorption occurs because of the humidity increase, the resulting phase image is characterized by a shift (Δϕ) towards a higher adhesive material due to the water-AFM tip interaction, as schematically shown in Fig. 1.

Additional measurements were conducted in pinpoint mode to estimate the thickness of the water layer adsorbed at low (5% RH) and high (65% RH) humidity. Pinpoint mode allows the acquisition of force-displacement curves during scanning by applying a vertical oscillation
Fig. 2. Schematic representation of a force vs. distance curve, obtained by using the AFM in pinpoint mode. The resulting deformation for each point of the surface is related to the thickness of adsorbed water.}

well below the resonance frequencies of the probe [7]. Fig. 2 schematically illustrates the obtained data, from which the thickness of the water layer can be approximated as the deformation $d$. Measurements were performed in a grid of $10 \times 10 \mu m^2$, with each measuring point corresponding to an area of $40 \times 40 \text{nm}^2$. The average thickness of the absorbed water layer was estimated as the average of all measured deformations $d$.

2.3. TGA and mechanical characterization

2.3.1. Sample preparation and conditioning

After studying the titanium and C/PEKK surfaces with AFM, the two materials were bonded via an autoclave co-consolidation process. Subsequently, the fracture toughness was assessed using the mandrel peel test. The test samples consisted of titanium strips bonded to a single layer of UD C/PEKK prepreg, as schematically represented in Fig. 3(a). The samples were prepared by placing a single layer of C/PEKK tape on a flat mould, followed by a layer of PEKK film, and then by the titanium strips.

This study considers two different sets of samples prepared with two different titanium surface morphologies. First, the as-received surface was used to investigate the adhesion between a smooth and unmodified titanium surface (average roughness of $0.6 \mu m$) and C/PEKK. Second, a grit-blasted titanium surface was employed to investigate the adhesion between a rough titanium surface and C/PEKK. The grit-blasting treatment was carried out using particles of alumina oxide, whose dimensions were between $150 \mu m$ and $350 \mu m$. The grit-blasting pressure was 5 bar and the distance between nozzle and surface was $50 \text{mm}$, with which an average roughness of $2.5 \mu m$ was obtained. This titanium surface morphology was selected because it leads to a predominant cohesive failure of co-consolidated titanium-C/PEKK joints in dry conditions, and therefore to achieve the highest fracture toughness [19]. Using an optimized surface roughness allowed better understanding of the effect of grit-blasting on the bond stability between titanium and C/PEKK. Both types of titanium surfaces were cleaned prior to the bonding, using an ultrasonic bath of ethanol for 15 min. Afterwards, compressed air was applied to further remove contaminations introduced by the grit-blasting treatment [19].

The C/PEKK prepreg and the PEKK film were dried at $100 ^\circ C$ for $24 \text{h}$ prior to co-consolidation [31]. The alignment between the length of the strips and the fibre direction was ensured by placing the strips in a steel frame, as schematically depicted in Fig. 3(b). The mandrel peel test requires an initial pre-crack, which was created by applying a releasing agent (Marbocote 227-CEE) to the first $50 \text{mm}$ of the titanium strips. The same releasing agent was also applied to the steel frame to prevent any bonding between frame and PEKK. Fig. 4 shows the processing cycle used to co-consolidate the samples. Following the co-consolidation step, the first group of specimens was mechanically tested immediately after demoulding, and it was considered as the dry sample. The toughness of the second group of specimens was evaluated after storing them in a conditioning chamber kept at $70 ^\circ C$ and 80% RH (hot-wet environment). These specimens were identified as the wet-conditioned sample. The mandrel peel test was performed after $24 \text{h}$, $48 \text{h}$, $96 \text{h}$, $168 \text{h}$, $240 \text{h}$ and $480 \text{h}$ of exposure in the conditioning chamber. A third group of specimens was initially stored in the conditioning chamber, using the previously mentioned exposure times and then, before testing, it was stored in a vacuum oven set at $70 ^\circ C$ to dry for a week. These specimens were denoted as the re-dried sample. All of the samples investigated, meaning the dry sample along with the wet and re-dried samples having different exposure times in the conditioning chamber, consisted of five specimens.

2.3.2. TGA experiments

Considering that the geometry of the co-consolidated samples consists of a single layer of C/PEKK tape bonded to titanium, then the water may have access to the interface by diffusion through the composite.
Therefore, a water uptake study was conducted by performing thermogravimetric analysis (TGA) on the composite side of the co-consolidated samples using TGA 550 from TA instruments. The TGA specimens were obtained by first storing the co-consolidated titanium-C/PEKK samples in the conditioning chamber. Then, the composite ply was peeled from the titanium substrate, and a small area of 3 × 3 mm² was cut. Three specimens were tested for each conditioning time considered in this study (24 h, 48 h, 96 h, 168 h, 240 h and 480 h). The results were compared to the same TGA experiment performed on three dry C/PEKK specimens. All of the tests were conducted in a Nitrogen atmosphere, starting with a heating ramp from 25 °C to 100 °C at a rate of 10 °C/min. Then, an isothermal step was applied for a duration of 3 h. The water uptake, or weight fraction of water (w), was calculated as follows:

\[
w = \frac{m_f - m_i}{m_0} \times 100\%,
\]

where \(m_0\) is the mass of the TGA specimen at the beginning of the test and \(m_i\) is the mass detected at each time of the TGA test.

### 2.3.3 Mechanical characterisation

The mandrel peel test was used to evaluate the effect of exposure to high humidity on the fracture toughness. A schematic representation of the setup is provided in Fig. 5. For this material combination, the titanium strip is fixed to a sliding table, while the composite ply is bent around a mandrel. The test is similar to a standard 90° peel test, with the main difference that it makes use of a mandrel to prevent breakage of the peel arm. This solution is quite suitable for testing materials that have a tough matrix and a unidirectional reinforcement [33]. The mandrel used in this work had a radius of 10 mm.

The test setup was installed in a Zwick universal testing machine, where a tensile force \(F_p\) was applied to the composite ply to peel it from the titanium substrate, with a constant displacement rate of 15 mm/min. An alignment force \(F_a\) was applied to the sliding table, via a pneumatic actuator, to ensure that the peeling arm conformed to the mandrel. During testing, the two forces were measured with two 200 N load cells. The alignment force was kept constant at 60 N. The critical energy release rate \(G_c\) was then calculated as:

\[
G_c = \frac{1}{w} \left( F_p (1 - \mu) - F_a \right),
\]

where \(w\) represents the width of the specimen and \(\mu\) is the friction coefficient of the setup. Two steps were required to calculate \(G_c\). During the first step, the composite tape was peeled from the titanium substrate, while \(F_p\) and \(F_a\) were measured. During the second step, the test was performed on the same, now de-bonded, specimen where this time \(G_c\) was equal to 0. The two forces were again measured, from which the friction coefficient was calculated as:

\[
\mu = \frac{F_p - F_a}{F_p}.
\]

The mandrel peel test was also employed to further elucidate the water ingress mechanism, answering in particular the question of whether the water reached the interface by means of diffusion through the composite tape, or by means of diffusion through the edges of the specimen, which represent direct access to the titanium–composite interface. Two sets of samples (both having a grit-blasted titanium surface) were considered. The first one had the top of the composite ply sealed to block water access through the composite tape. The second had the edges sealed to block water access to the interface from the side of the sample. The sealing material used was an aluminium tape with a thickness of 0.1 mm. Both sets of samples were exposed for 24 h in the conditioning chamber before testing.

The mandrel peel test was followed by a crack surface analysis to determine the locus of failure. This analysis was conducted using a digital microscope (Keyence VHX-7000), a Scanning Electron Microscope (Jeol JSM-7200F) and a 3D optical profilometer (Sensofar S-Neox).

### 3. Results and discussion

#### 3.1 AFM results

Fig. 6 summarizes the phase images obtained by exposing the titanium surface to different humidity conditions. More specifically, Fig. 6(a) corresponds to the measurement carried out in a low humidity environment (5% RH) to approximate dry conditions. Fig. 6(b) depicts the phase image obtained in a high humidity environment (65% RH), and Fig. 6(c) shows the phase image obtained by subsequently lowering the humidity to the initial conditions (5% RH). Generally, a brighter colour (yellow) is associated with lower phase shifts, while a darker colour (blue) is associated with higher phase shifts.

A difference between the phase data obtained at low and high humidity conditions is noticeable from Fig. 6(a) and 6(b). Conducting the experiment in high humidity led to a darker phase image than the image at low humidity. This means that a higher humidity resulted in increased energy dissipation on the tip–surface interaction. Considering that all of the AFM measurements were conducted on the same 10 × 10 μm² region of the titanium surface, the observed differences in phase shift can be attributed to the AFM probe interacting primarily with the titanium surface in low humidity, and with water in high humidity. Therefore, the larger phase shift recorded in high humidity can be correlated to the accumulation of water on the titanium surface. From Fig. 6(a) and 6(c) it can be observed that re-drying the AFM environment resulted in a phase image comparable to the phase image measured with the initial (low humidity) conditions. Lowering the humidity led to a decrease in tip–surface interaction, thereby indicating that water desorption occurred. Fig. 7(a) and 7(b) summarize the phase images obtained for a C/PEKK tape subjected to low and high humidity conditions, respectively. Both of the images show the presence of bright regions (yellow) and dark regions (blue) in corresponding points. Generally, for semi-crystalline polymers, the bright colour indicates areas with higher modulus, associated with a high degree of crystallinity, while the dark colour indicates areas with lower modulus, associated with a highly amorphous polymer [6,13]. As a consequence, the corresponding phase distributions, also shown in Fig. 7, consist of two distinct peaks. The peak occurring at smaller phase shift values is associated with the crystalline regions, while the peak occurring at larger phase shift values is associated with the amorphous regions. Despite a minimal change of the phase shift between the two measurements, increasing the humidity of the environment altered neither the presence of the two peaks, nor the interval in which they occurred. This indicates that the AFM probe interacted with the same surface despite the different humidity conditions, thus denoting that there was no accumulation of water on the C/PEKK surface when increasing RH.

The titanium surface was further investigated with additional AFM experiments conducted in pinpoint mode. This method allows to have a rough estimate of the thickness of the adsorbed water layer as it can be directly correlated to the deformation value of each measuring point.
Fig. 6. AFM phase images of titanium surface in (a) low humidity environment (5% RH), (b) high humidity environment (65% RH), (c) re-dried environment (5% RH).

Fig. 7. AFM phase images of C/PEKK tape surface in (a) low humidity environment (5% RH), (b) high humidity environment (65% RH).

Fig. 8. Deformation distribution resulting from the AFM experiments carried out in pinpoint mode at (a) 5% RH after 24 h, (b) 65% RH after 3 h, (c) 65% RH after 72 h, (d) 65% RH after 96 h.

Fig. 9. Representative example of mass loss vs. time curves obtained from TGA experiments conducted on dry and conditioned C/PEKK tapes.

of the 10 × 10 μm² analysed surface, as described in Section 2.2 and illustrated in Fig. 2. The pinpoint mode results are depicted in Fig. 8

in terms of area fraction distribution as a function of the deformation \( d \). It can be noticed that an increase of the humidity is associated with an increase of the deformation from 0.5 nm in low humidity, up to a value of 1.3 nm in high humidity. This suggests that the thickness of the water layer also increases in a similar fashion. Moreover, it is evident that keeping the humidity at a constant value of 65% RH did not significantly alter the overall measured deformation after an exposure time of 72 h, thus indicating that the thickness of the water layer did not further increase over time.

The water adsorption phenomenon addressed in the present work using AFM experiments is in line with previous studies conducted on ideal titanium oxide surfaces. Kettler et al. [15] reported that residual vacancies of surface oxygen on rutile TiO\(_2\)(110) influence the adsorption properties by providing sites for hydrogen bonding to water molecules. Furthermore, it was shown that the layer of adsorbed water increases with increasing relative humidity. One of the typical properties of adsorbed water is that the closest water molecules to the oxide surface tend to form an ordered structure, due to the strong hydrogen bond interaction [34]. Concerning a titanium oxide surface, this phenomenon was observed by Dette et al. [9] on anatase TiO\(_2\)(110). This effect is dictated by a stronger interaction between water and titanium surface (730 meV) than water–water interaction (580 meV) [11].

3.2. TGA results

Another phenomenon that may occur and can also be detrimental to titanium-C/PEKK adhesion is water absorption and diffusion through the C/PEKK tape. This aspect was investigated using TGA experiments.
The effect of water diffusion through the C/PEKK tape, and subsequently adsorption on the titanium, on the fracture toughness of titanium-C/PEKK interfaces was investigated using the mandrel peel test. Fig. 10(a) depicts a typical example of the effective force, which is defined as the difference between the peel force ($F_p$) and the alignment force ($F_a$), measured during a peel test carried out on dry specimens. The black line corresponds to a specimen with a grit-blasted titanium surface, while the grey line corresponds to a specimen with an as-received titanium surface. The light-grey line corresponds to the effective forces measured during the step to determine the friction coefficient of the setup, which was found to be approximately 0.7% for all the samples. Fig. 10(b) shows the resulting resistance curves. It is evident that the toughness increases until a plateau is reached. The values in these plateau regions were averaged over five specimens for each sample, between displacement values of 10 mm and 30 mm, to determine the average fracture toughness.

Fig. 11(a) summarizes the obtained fracture toughness for all the samples having an as-received titanium surface. The highest fracture toughness of 0.5 kJ/m$^2$ was measured for the dry sample. The wet-conditioned samples show a significant decrease in fracture toughness to an average value of 0.2 kJ/m$^2$. Moreover, it can be seen that the highest drop of the toughness occurred after 24 h of exposure in the conditioning chamber. Increasing the exposure time did not have a significant effect on the toughness, whose average value reached 0.10 kJ/m$^2$ after a conditioning time of 480 h.

A similar consideration can be made for the samples having a grit-blasted titanium surface, whose toughness results are summarized in Fig. 11(b). The grit-blasted sample performed better than the as-received sample, showing an average toughness of 1.4 kJ/m$^2$ in dry conditions. However, the grit-blasting treatment did not improve the adhesion in wet conditions. A considerable drop in toughness, to a value of 0.2 kJ/m$^2$, was observed after 24 h of exposure in the conditioning chamber. Also in this case, the conditioning time did not significantly affect the toughness.

The toughness results of the samples, that were re-dried in vacuum after wet-conditioning, are also reported in Fig. 11(a) and 11(b). Overall, it is noticeable that the re-dried samples exhibit higher toughness values than the wet-conditioned samples. This result is an indication that the degradation of the titanium-C/PEKK bond is reversible. The re-drying process allowed the water molecules to desorb from the titanium surface, as previously observed in the AFM experiments discussed in Section 3.1. Consequently, the absence, or the significantly reduced amount, of water molecules at the interface, allowed the restoration of the interaction between titanium and C/PEKK, measured as a higher fracture toughness compared to the wet-conditioned samples. The reversibility of the titanium-C/PEKK adhesion is an important indication that the type of interaction between these two materials consists of secondary bonds, such as Van der Waals, electrostatic forces, or acid–base interaction [17], ruling out the hypothesis of any chemical interaction [32]. However, understanding the true nature of these secondary interactions still represents a challenging aspect that requires further research.

Additionally, both Fig. 11(a) and 11(b) demonstrate that the toughness did not fully recover to the value measured in dry conditions. In general, the highest toughness recovery occurred for the samples conditioned for 24 h before the re-drying step. Subsequently, the toughness that can be recovered did not further decrease after 96 h of exposure in the conditioning chamber. The AFM experiments conducted in pinpoint mode, and summarized in Fig. 8, appear to be in line with what was observed during mechanical testing. The AFM experiments provided an estimation of the thickness of the adsorbed water layer of about 1.3 nm. Our hypothesis is that water desorption causes a nano-scale gap
between the two adherends. Considering that secondary bonds, which characterize the titanium-C/PEKK interaction, are generally short-range forces, the incomplete recovery in toughness may be a macroscopic observation of the formation of this gap at the interface, previously caused by the presence of an adsorbed water layer. Moreover, it is evident that the grit-blasted samples exhibit a lower toughness recovery than the as-received samples. A possible explanation is that rough surfaces are characterized by crevices, which cause water condensation at higher humidity [36]. This phenomenon implies a larger amount of water adsorbed on the titanium. When water desorbs due to the re-drying step, it leaves a larger gap between the adherends than the gap between as-received titanium and C/PEKK. Considering that physical interactions are short-range forces, the lower toughness recovery may derive from the larger gap between a rough titanium surface and C/PEKK. Further research is required to verify this hypothesis. The use of the AFM experimental methodology proposed in this work shows the potential for also investigating the effect of surface morphology on water adsorption properties.

Fig. 12(a) and Fig. 12(b) show the results of the mandrel peel test conducted on the samples whose top and edges were sealed, respectively. It is evident that the top-sealed sample retained more toughness than the edge-sealed sample, thereby providing further evidence that the water accessed the interface by diffusing through the C/PEKK tape. This is an indication that this sample, characterized by a low toughness (0.5 kJ/m²), primarily exhibited interfacial failure. The crack no longer propagated along the titanium–composite interface, but it diverted into the composite ply. Observing the fracture surface on the composite side, it was possible to correlate the fracture toughness to the amount of matrix plastic deformation. Both crack surfaces were analysed in the region close to the crack initiation point, considering a window of 10 × 10 mm², as the transition from interfacial to intraply failure occurred within this region [19].

The fracture surfaces on the titanium side were analysed using SEM and optical microscopy. Fig. 15(a) and 15(c) show the fracture surface of a dry sample having an as-received surface. Largely, a clean titanium surface is observed, with small traces of matrix material from the composite tape. This is an indication that this sample, characterized by a low toughness (0.5 kJ/m²), primarily exhibited interfacial failure.

Fig. 15(b) and 15(d) show the fracture surface of a dry sample with a grit-blasted titanium surface. In this case, a combination of interfacial and intraply failure can be observed. The interfacial failure mostly occurred at the beginning of the crack propagation. The rough titanium surface caused a deflection of the crack path in the composite,
resulting in predominantly intraply failure [19], which is characterized by a failure at the fibre–matrix interface. This phenomenon explains the higher toughness measured for this sample, which is comparable to the interlaminar fracture toughness of UD C/PEKK laminates [19].

In the case of all of the wet-conditioned samples, characterized by a significantly lower toughness than the dry samples, the failure mostly occurred at the titanium–PEKK interface, similar to what was observed in Fig. 15(a) and 15(c).

A predominantly interfacial failure was also observed for the re-dried samples. From the results shown in Fig. 11(a) and in 11(b), it is evident that re-drying the samples led to a partial recovery of the fracture toughness. Extending the microscopy analysis to the fracture surface on the side of the composite tape allowed correlation between the difference in toughness and the extent of matrix plastic deformation. These fracture surfaces were analysed using the SEM and the 3D optical profilometer, and the resulting images and height maps of dry, wet-conditioned, and re-dried specimens are depicted in Fig. 16(a), 16(b) and 16(c). It can be noticed that the dry and re-dried specimens are characterized by a rough morphology, which is an indication that the matrix was plastically deformed. Conversely, the wet-conditioned specimen is characterized by a smoother tape surface, which suggests that almost no plastic deformation occurred during fracture. Even though interfacial failure was predominant for all of the re-dried samples, the recovery of toughness and matrix plastic deformation are two strong reasons that the interaction between titanium and PEKK matrix was restored when lowering the moisture content in the composite.

Overall, by analysing the interaction between water and adherends, the water diffusion mechanisms, and their effect on the mechanical performance of titanium-C/PEKK joints, our results provide insights on the type of molecular interaction between titanium and TPCs, and the mechanisms governing its instability. Understanding these two aspects is a fundamental step that will aid further research into suitable solutions to improve bond durability between titanium and thermoplastic-based composites. This may be achieved with the use of primers, which can offer a barrier against the diffusion of water, thereby delaying the bond degradation [14]. Another solution may be found in treatments focused on modifying the titanium surface. Titanium surface modification may lead to the formation of different surface oxide structures, characterized by different adsorption
Further research may be conducted using the AFM experimental methodology described in this work to investigate the effects of primers or chemical surface modifications on the adsorption properties of titanium. This will represent the next step towards finding suitable surface treatments that prevent or significantly delay the water adsorption on titanium. Additionally, modifying the titanium morphology to create anchoring features [22] may also result in an improvement to the grit-blasting treatment, whose interlocking effect, and consequent increase in toughness, is mostly provided by the alternating peaks and valleys that increase the slope of the resulting surface profile.

4. Conclusions

The present work investigated the mechanisms that govern the deterioration of co-consolidated titanium-C/PEKK interfaces in the presence of moisture. AFM experiments were conducted in different humidity conditions to understand the water adsorption properties of titanium and C/PEKK surfaces. The effect of water adsorption on the mechanical performance of titanium-C/PEKK interfaces was assessed using a mandrel peel test, by comparing the toughness of dry specimens to the toughness of specimens stored in a conditioning chamber prior to testing. Additionally, the toughness of specimens that were re-dried in vacuum was evaluated.

It was found that the nature of the titanium surface plays a major role in the bond degradation. The water molecules that diffuse through the composite ply when exposing the sample to hot-wet environment reach the interface and are mostly adsorbed by titanium. The presence of this adsorbed water layer causes a degradation of the pre-existing interaction between the two adherends, measured as a significant drop in the fracture toughness of the titanium-C/PEKK samples. Experiments conducted on re-dried specimens showed that titanium-C/PEKK bond degradation is reversible. Reducing the humidity of the environment led to water desorption and a consequent increase in fracture toughness. The recovery of the toughness is an important evidence that the adhesion between titanium and PEKK matrix mostly relies on physical bonding. This result clarifies why it is essential to treat the titanium surface prior to co-consolidation with suitable methods that prevent water adsorption. Promoting only mechanical interlocking with the grit-blasting treatment is not sufficient to ensure a strong adhesion in presence of moisture as it does not prevent or delay water adsorption.

CRediT authorship contribution statement

V.M. Marinosci: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. L. Chu: Writing – review & editing, Investigation, Formal analysis. W.J.B. Grouve: Supervision, Writing – review & editing, Conceptualization. S. Wijskamp: Writing – review & editing, Supervision, Conceptualization. R. Akkerman: Project administration, Writing – review & editing. M.B. de Rooij: Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] Ageorges C, Ye L, Hou M. Advances in fusion bonding techniques for joining thermoplastic matrix composites: a review. Composites A 2001;32(6):839–57.

[2] Baldan A. Adhesively-bonded joints in metallic alloys, polymers and composite materials: Mechanical and environmental durability performance. J Mater Proc Tech 2004;39(15):4729–97.

[3] Baldan A. Adhesion phenomena in bonded joints. Int J Adhes Adhes 2012;38:95–116.

[4] Beland S. High Performance Thermoplastic Resins and their Composites. William Andrew; 1990.

[5] Chu L, Bus M, Korobkov AV, Besseling NA. Calibrating lateral displacement sensitivity of AFM by stick-slip on stiff, amorphous surfaces. Ultramicroscopy 2019;205:1–4.

[6] Chu L, Grouve WJ, van Drongelen M, Guha Y, de Vries EG, Akkerman R, de Rooij MB. Influence of the polymer interphase structure on the interaction between metal and semicrystalline thermoplastics. Adv Energy Mater 2021;21(2):2000518.

[7] Chu L, Korobkov AV, Cao A, Schadeva S, Liu Z, de Smet LC, Soudhölter EJ, Picken SJ, Besseling NA. Mimicking an atomically thin “vacuum spacer” to measure the hamaker constant between graphene oxide and silica. Adv. Mater. Interfaces 2017;4(5):1600495.

[8] Cortes P, Cantwell W. The tensile and fatigue properties of carbon fiber-reinforced PEEK-titanium fiber-metal laminates. J Reinf Plast Compos 2004;23(15):1615–23.

[9] Dette C, Perez-Osorio MA, Mangel S, Giustino F, Jung SJ, Kern K. Atomic structure of water monolayer on anatase TiO2 (101) surface. J Phys Chem C 2008;112(22):11954–60.

[10] Escobar M, Henriques B, Fredel MC, Silva FS, Özcan M, Souza JC. Adhesion of CFRP/titanium hybrid material for improving fracture toughness of hybrid titanium-thermoplastic composite joints. Int J Adhes Adhes 2021;109:102893.

[11] Ketteler G, Gammel FJ, Kolb M, Rohr O, Kotte L, Tschiöcke S, Kaskel S, Krupp U. Investigation of surface pre-treatments for the structural bonding of titanium. Int J Adhes Adhes 2012;34:46–54.

[12] Molitor P, Barron V, Young T. Surface treatment of titanium for adhesive bonding to polymer composites: a review. Int J Adhes Adhes 2001;21(2):129–36.

[13] Molitor P, Barron V, Young T, Surface treatment of titanium for adhesive bonding to polymer composites: a review. Int J Adhes Adhes 2001;21(2):129–36.

[14] Nogate K, Yamaguchi T, Nakao M. Anchoring and chemical-bonding effects of anodic alumina microstructure on adhesion strength. CIRP Annals 2018;67(1):595–8.

[15] Pizzoni M, Lertora E, Mandolino C, Vincis S, Salerno M, Prato M. Comparative characterization of the surface state of Ti-6Al-4V substrates in different pre-bonding conditions. J. Adv. Joining Process. 2021;3:100058.

[16] Pramaniak A, Basak A, Dong Y, Sarker P, Uddin M, Littlefair G, Dixit A, Chattopadhyaya S. Joining of carbon fibre reinforced polymer (CFRP) composites and aluminium alloys–A review. Composites A 2017;101:1–29.

[17] Ramani K, Weidner WJ, Kumar G. Silicon sputtering as a surface treatment to titanium alloy for bonding with PEKEKK. Int J Adhes Adhes 1998;18(6):401–12.

[18] Schmitz I, Schreiner M, Friedbacher G, Grasserbauer M. Phase imaging as an extension to tapping mode AFM for the identification of material properties on humidity-sensitive surfaces. Appl Surf Sci 1997;115(2):190–8.

[19] Scholze K, Hausmann J, Wielage B. The stability of different titanium-PEEK interfaces against water. Procedia Mater. Sci. 2013;2:92–102.

[20] Shimizu K, Malmos K, Spiegelhauer S-A, Hinke J, Holm AH, Pedersen SU, Daasbjerg K, Hinge M. Durability of PEEK adhesive to stainless steel modified with aryl diazonium salts. Int J Adhes Adhes 2014;51:1–12.

[21] Slange TK, Grouve WJ, Warnet LL, Wijskamp S, Akkerman R. Towards the combination of automated lay-up and stamp forming for consolidation of tailored composite components. Composites A 2019;119:165–75.

[22] Slange T, Warnet L, Grouve W, Akkerman R. Deconsolidation of C/PEEK blanks: on the role of prepreg, blank manufacturing method and conditioning. Composites A 2018;111:389–99.

[23] Su Y, de Rooij M, Akkerman R. The effect of titanium surface treatment on the interfacial strength of titanium–thermoplastic composite joints. Int J Adhes Adhes 2017;72:98–108.

[24] Su Y, de Rooij M, Grouve W, Warnet L. Characterization of metal-thermoplastic composite hybrid joints by means of a mandrel peel test. Composites B 2016;85:293–300.

[25] Xiao C, Shi P, Yan W, Chen L, Qian L, Kim SH. Thickness and structure of adsorbed water layer and effects on adhesion and friction at nanoasperity contact. Colloids Interfaces 2019;3(3):55.

[26] Young JF. Humidity control in the laboratory using salt solutions—a review. J. Appl. Chem. 1967;17(9):241–5.

[27] Zarate NV, Harrison AJ, Littlefair G, Dixit A, Beaudoin SP. Effect of relative humidity on onset of capillary forces for rough surfaces. J Colloid Interface Sci 2013;411:265–72.