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Effect of relative humidity and full immersion in water on friction, wear and debonding of unidirectional carbon fiber reinforced epoxy under reciprocating sliding

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ABSTRACT

Unidirectional carbon fiber reinforced epoxy was tested in ambient air at three different levels of relative humidity and under full immersion in demineralized water. Reciprocating sliding tests were performed at 23 °C against either stainless steel or alumina balls moving in parallel or anti-parallel direction to the fibers. We demonstrate in this work that humidity and water immersion affect significantly the fiber debonding. Under sliding against stainless steel or alumina at low relative humidity, fiber debonding is more pronounced than at high relative humidity and at water immersion. The wear depth increases with increasing relative humidity when sliding against stainless steel, whereas it remains practically constant against alumina. For all test conditions, the wear depth is larger when tested against stainless steel than against alumina. It was found that the thin moisture film formed at the surface of the stainless steel counter body leads to a higher corrosive risk than water immersion. More precisely, we demonstrate that high humidity leads to the production of oxide debris originated from the stainless steel ball which increases markedly the wear by abrasion. These debris lead to a high fluctuation of the coefficient of friction measured on carbon fiber reinforced epoxy composite sliding against stainless steel at 85% RH, whereas a steady state coefficient of friction is noticed against alumina.

1. Introduction

Composite polymers are generally more resistant to aqueous and humid exposure than many metals. However, the mechanical strength of composite polymers usually degrades by water and humidity sorption [1,2]. Furthermore, debonding is one of the failure mechanisms in carbon fiber reinforced epoxy which can lead to untimely failure. In a detailed review on carbon fiber/epoxy interfaces, Hughes [3] explained that the weakest spot in debonding is usually the interface between the carbon fiber and the epoxy matrix. Such a debonding may originate from the composite fabrication process where differential thermal expansion stresses may be induced. More precisely, the resin contracts more than the fiber, and shrinkage stresses are induced on polymerization of the resin [3]. Arnold [4] described swelling effects and residual stresses in different epoxy composites. He concluded that the most significant origin of residual stresses in such composites is the differential shrinkage on curing or cooling. Most polymeric matrix materials shrink to a certain extent on curing, whereas the reinforcements tend to retain a constant volume. The matrix will then have a tendency to shrink onto the reinforcing fibers. This results in a better adhesion, but may also lead to a compressive stress on the fibers, and a tensile stress in the matrix.

Epoxy matrixes absorb atmospheric moisture causing a resin softening, swelling, and a loss of the mechanical performance of composites [5]. Adamson [6] detailed the transport steps of moisture in epoxy matrixes below the glass transition temperature (Tg). He proposed a three stage process in which at first the absorbed moisture occupies the free volume of epoxy, then in a second stage water becomes bound to network sites, and finally a swelling may take place because water enters the densely cross-linked regions. Another study showed that water or humidity sorption leads to

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delamination and void growth in carbon fiber reinforced epoxy [7]. Also, expansion due to water sorption was found to cause surface cracking in carbon fiber reinforced epoxy laminates [8]. Generally, the lowering of Tg due to water or humidity uptake reduces the bonding at the interface between matrix and fibers [9,10]. Akay [11] investigated epoxy immersed in water for 21 days at 70 °C. He recorded a lowering by 17% of the interlaminar shear, 10% of the compressive stress, and 7% of the flexural strength in unidirectional carbon fiber/epoxy laminates associated with a gain of 1.5% in laminate mass due to moisture uptake. Many studies on the effect of moisture on the interlaminar fracture toughness of composites [12] revealed that one of the most significant factors of fiber debonding is the swelling of the matrix which causes compressive stresses at the interface, followed by micro-crack formation and fiber debonding. This is particularly common in epoxy resin composites where the equilibrium water sorption content is higher than in other matrix materials [4].

On the other hand, extensive research showed that the relative humidity (RH) has a strong effect on the tribological behavior of composites. Generally, a high RH lowers the coefficient of friction and the wear rate [13]. Additionally, polytetrafluoroethylene (PTFE) reinforced by carbon fibers, polyimide (PI) reinforced by carbon fibers (CF) and PTFE, PI reinforced by CF and MoS_2, and polyetheretherketone (PEEK) reinforced by CF and PTFE composites maintain a lower coefficient of friction, and display a much higher wear resistance under sliding immersed in water against stainless steel than under dry sliding [14]. Komai et al. [15] found that water causes a reduction of the interfacial strength in several epoxy composites containing carbon and aramid fibers, especially under fatigue loadings. On the contrary, Walker and Zhi Hu [9] observed that the exposure to water increases the interfacial strength of short fiber interlaminar reinforcement layers in carbon fiber epoxy pre-impregnated composites. They also noticed that the bond strength to polyolefin reinforcement layers improved by exposure to water, possibly by a swelling mechanism [9]. In addition, it was found that water molecules improve the interfacial bond of epoxy reinforced with glass particles or fibers due to a combination of swelling stresses, and a water uptake that increases the matrix ductility due to plasticization [16].

Water can interact with epoxy resin in different ways. Apicella et al. [17] identified three possible modes of interaction: a) adsorption on hydrophilic centers on surfaces defining the void structure of the resin, b) condensation within the void structure, c) sorption and presumably bonding with the polymer network. Adamson [6] proposed that water first enters the void structure of epoxy resins and then migrates into the polymer network, but concluded that water is unable to disrupt the hydrogen bonding among polymer segments. Obviously, water affects mostly the resin and the interface on carbon fiber composites due to the good hydrolytic stability of carbon fibers. Similar results were found by Yamada and Tanaka [18] who studied the wear of various PTFE based composites against stainless steel under boundary lubrication with water. They assumed that the higher wear of the composites under water lubrication was due to the permeation of water molecules to the interface of the composites and the PTFE matrix, which results in the separation of fillers embedded in the PTFE matrix [18]. Lancaster [19] studied the wear behavior of various carbon fiber reinforced polymers sliding against metals in water, aqueous solutions, and organic fluids. He found that the wear of carbon fiber reinforced polymers as well as unfilled polymers under water lubrication is generally greater than under dry conditions. He concluded that the higher wear rate in water could not be attributed to a modification of the counter face by material transfer, because a transfer film on the counter face rubbed under water lubrication was not observed [19].

From the above discussion, it appears that the testing environment, and in particular the RH of ambient air can affect the mechanical and tribological performance of epoxy composite materials, and that these effects can be synergistic or antagonistic depending on the specific materials and properties studied. Plasticization of matrix materials by water can increase the resistance to crack formation, whereas in other cases, water uptake can enhance crack formation. Over the past three decades, the research in this area significantly increased aiming at a more reliable performance and lifetime assessment of composite polymers in different industrial applications. But, how failure processes are affected by environmental conditions under unidirectional or reciprocating sliding is still unclear.

In previous works [20,21], we examined the wear behavior of carbon fiber reinforced epoxy composite based on an in-depth analysis of the worn surfaces with reciprocating sliding in ambient air and with immersion in demineralized water. Immersion in water proved to be harmful to the wear resistance of the composite for sliding against stainless steel [21]. In the present study, environmental conditions of ambient air of different RH and a full immersion in water are considered and their effect on the friction and wear behavior of carbon fiber reinforced epoxy under reciprocating sliding against stainless steel or alumina balls is reported and discussed.

2. Experimental

A unidirectional carbon fiber reinforced epoxy was investigated. Its fabrication process is described in previous work [21]. Test samples of $5 \times 5\ mm^2$ were cut out of a mother plate of $20 \times 20\ cm^2$ using a diamond saw. The mother plate has a two layer structure consisting of an epoxy top layer of about 3 μm onto a fiber containing bulk material with epoxy as continuous phase [21]. Reciprocating sliding tests against either stainless steel or alumina balls with a diameter of 10 mm were performed in a test rig described earlier [20]. The sliding tests were carried out for 200,000 reciprocating sliding cycles in ambient air of 15, 50 or 85% RH, and immersed in demineralized water at 23 °C.

Reciprocating sliding tests were performed by putting the samples in an RH controlled tribotest chamber for about 15 min prior to the start of each test to stabilize the sorption onto the surface and subsurface of the test samples. The counter bodies were cleaned with acetone and subsequently with ethanol. Reciprocating sliding tests were performed at a normal load of 9 N and 7.3 N on using stainless steel and alumina ball respectively, to achieve the same maximum Hertzian contact pressure of around 100 MPa. A sliding frequency of 3 Hz and a peak-to-peak displacement amplitude of 600 μm were selected in order to achieve a gross slip sliding regime. Two different sliding directions, i.e. parallel and anti-parallel to the fiber orientation, were applied (Fig. 1). The repeatability was evaluated by performing a minimum of three replicate reciprocating sliding tests on each specimen for each set of testing conditions.

Focused ion beam (FIB) and scanning electron microscopy (SEM) (FEI NOVA NANOLAB 600) were used to prepare cross-sections through the worn areas in order to investigate the debonding and the outbreak of carbon fibers. White light interferometry (Wyko3300) was used to measure the maximum wear track depth.

The experimental sliding test conditions used can be grouped into three main divisions, namely one related to the sliding direction, another one related to the type of counter body ball, and finally one related to the environmental composition (see Fig. 2). The effect of each of these variables on the degradation of the carbon fiber reinforced epoxy was investigated in order to get a

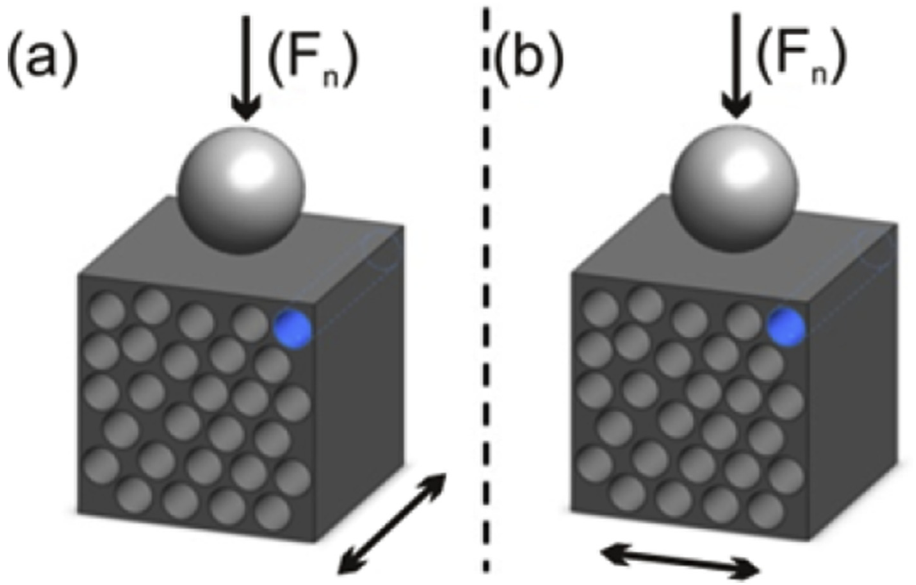


Fig. 1. Schematics of (a) parallel and (b) anti-parallel reciprocating sliding set up on unidirectional carbon fiber reinforced epoxy. The ball represents the counter body, and Fn the applied normal load. A single carbon fiber is indicated in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

better understanding on the role of the environment on the friction and wear behavior.

3. Results and discussion

3.1. In-situ information on the friction recorded at different RH

3.1.1. Sliding against stainless steel counter body

The evolution of the coefficient of friction (COF) recorded on carbon fiber reinforced epoxy composites sliding against stainless steel with the number of sliding cycles under different RH, is shown in Fig. 3. Humidity affects the COF of the polymer composites/stainless steel reciprocating sliding system. The initial COFs at low relative humidity ($\leq$50%) are relatively higher than at 85% RH. The COF starts at a value around 0.5 for both reciprocating sliding directions at 15% and 50% RH. It then decreases gradually before stabilizing at about 0.2 after a running-in stage of about 50,000 sliding cycles for both sliding directions. On the other hand, at 85% RH the initial COF is relatively low, namely 0.35, and even after 200,000 cycles the COF does not yet stabilize at a constant value. A remarkable fluctuation of the COF is recorded after 100,000 sliding cycles.

Lancaster [22] stated that epoxies are susceptible to the environment and tend to show different friction values in different humidity environments. The effect of humidity on the friction was explained by the fact that water molecules may modify the state of oxidation of the metal counter bodies [22]. He also proved that cross linked thermosets such as epoxies are rather more susceptible to the environment [22], and he reported that hydrogen bonding may play a part in increasing the friction of polymers containing OH groups in humid environments, when sliding against metal counter faces [22].

3.1.2. Sliding against alumina counter body

The COF recorded for the two reciprocating sliding directions against alumina counter body is presented in Fig. 4. The starting COF values are very similar to those recorded with the stainless steel counter body, namely 0.5 at 15% and 50% RH and only about 0.3 at 85% RH. The running-in phase extends to about 50,000 cycles. Under reciprocating sliding, the COF recorded in the alumina/composite sliding system does not depend much on the sliding direction relative to the fiber orientation.

At high humidity, the COF measured strongly depends on the counter body, whereas it is comparable in environments of relative

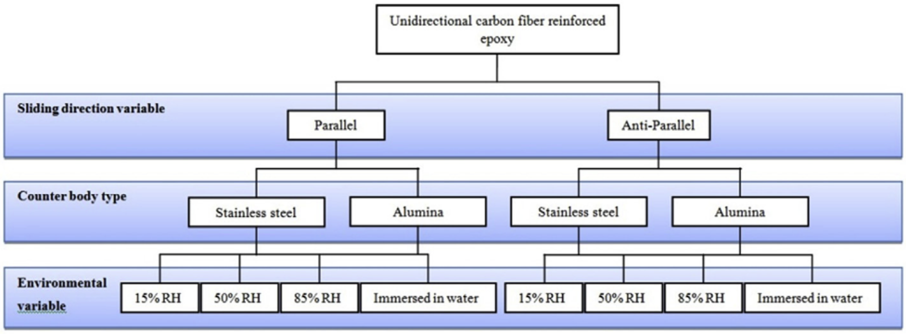


Fig. 2. Schematic of the experimental approach.

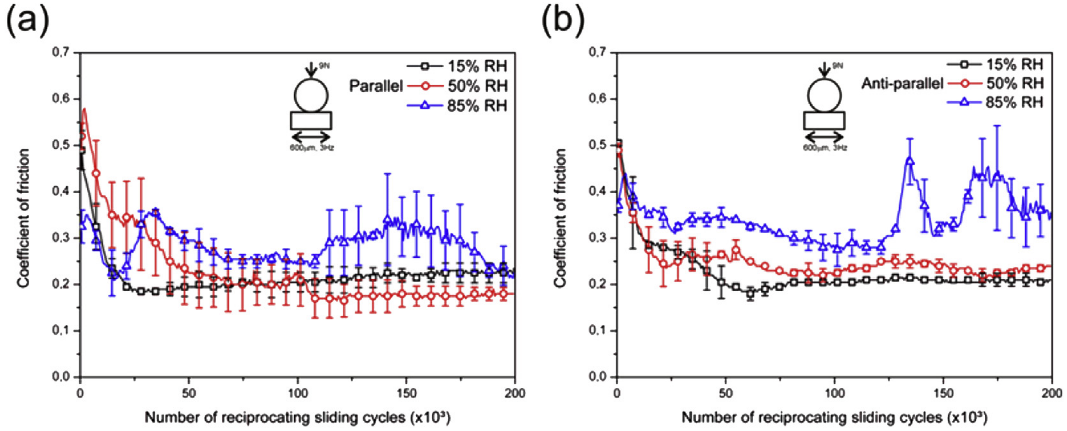


Fig. 3. Representative evolution of the COF recorded on carbon fiber reinforced epoxy sliding against stainless steel counter body in (a) parallel and (b) anti-parallel direction to the fiber orientation at RH values of 15%, 50% and 85%.

humidity up to 50%. No strong fluctuation of the COF is noticed on sliding against alumina.

3.2. In-situ information on the friction recorded at immersion of water

In this study, reciprocating sliding tests of stainless steel and alumina balls in demineralized water were also done (Fig. 5). The results of the three operated tests for each testing condition reveal a good repeatability. The running-in phase is absent in all the tests which can be due to the lubricant effect of water in the contact. Sliding under full immersion in demineralized water results in a coefficient of friction that starts relatively low, namely at around 0.16, and stabilizes at about 0.2 and 0.22 under anti-parallel and parallel sliding directions, respectively. Neither the counter body nor the reciprocating sliding direction shows an influence on the COF values in demineralized water. Cohen and Tabor [23] have shown that when water is added, there is an immediate reduction in friction as a result of absorbed water reducing the shear strength of the outermost surface. Wang et al. [24] revealed that distilled water reduces the COF recorded on nanometer Si_3N_4 filled PEEK but with the sacrifice of a large reduction in wear resistance. Tanaka [25] reported that the introduction of water into a polymer–metal sliding couple generally reduces the COF, but may increase the wear rate of the polymers.

3.3. Ex-situ characterization on tested samples

3.3.1. Surface and sub-surface characterization

3.3.1.1. Influence of relative humidity. Surface and sub-surface degradation of the unidirectional carbon fiber reinforced epoxy after reciprocating tests performed in parallel and anti-parallel sliding directions at the three RH values, were analyzed by top-view SEM and cross-section FIB–SEM. Corresponding SEM micrographs of the worn surfaces on the epoxy composites after 200,000 reciprocating sliding cycles against stainless steel balls are displayed in Fig. 6. The sliding directions are indicated by arrows, and the carbon fiber orientation is specified by three parallel lines. The grooves on the surface represent the replica of the mold texture. A clear increasing wear track size is noticed at increasing RH for both sliding directions. No significant difference in the wear track size is noticed between parallel and anti-parallel sliding at any of the three RH values. Under all sets of sliding conditions, debris formation took place. The largest wear tracks surrounded by a high amount of wear debris, are noticed at 85% RH for both reciprocating sliding directions.

Cross sections through wear tracks after 200,000 parallel or anti-parallel reciprocating sliding cycles against stainless steel balls, are shown in Fig. 7. Cracks along the interface between carbon fibers and polymeric matrix are detected with different intensities in the top 10 µm at the three RH conditions tested. The surface

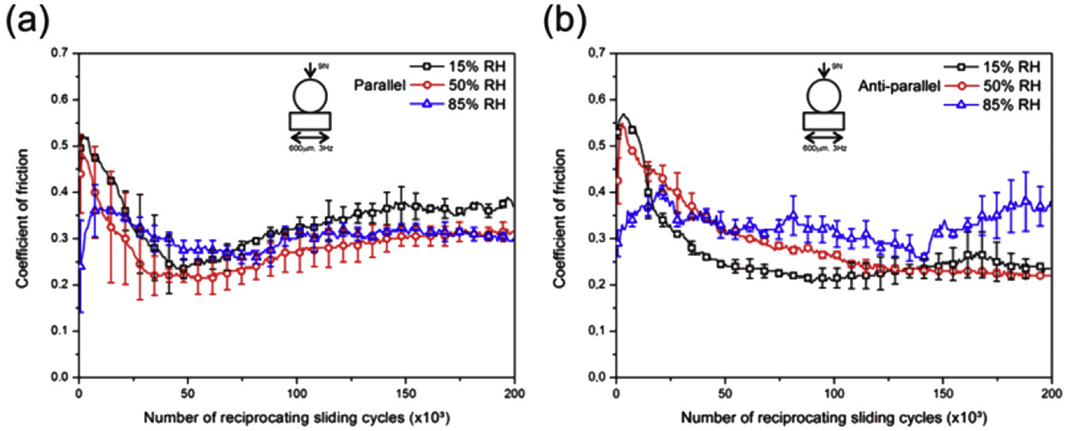


Fig. 4. Representative evolution of the COF recorded on carbon fiber reinforced epoxy sliding against alumina counter body in (a) parallel and (b) anti-parallel direction to the fiber orientation at RH values of 15%, 50% and 85%.

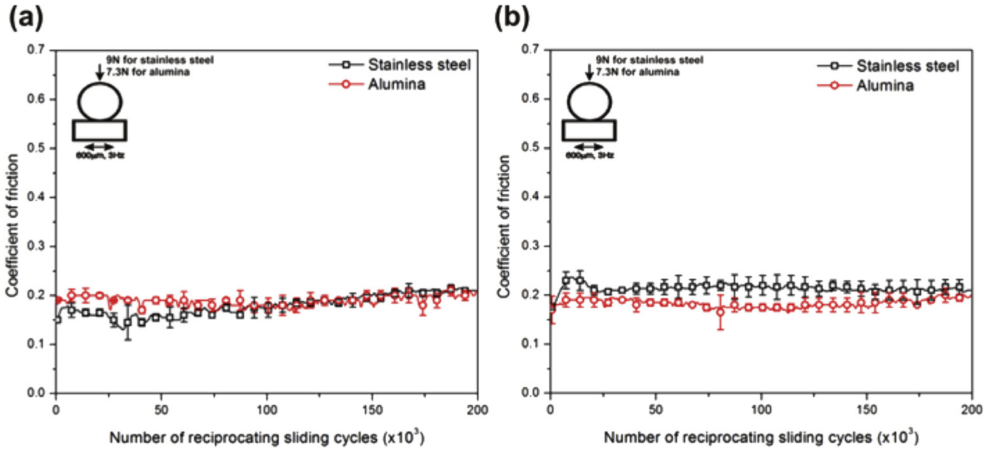


Fig. 5. Representative evolution of the COF recorded on carbon fiber reinforced epoxy sliding against alumina and stainless steel counter bodies in (a) parallel and (b) anti-parallel direction to the fiber orientation in demineralized water.

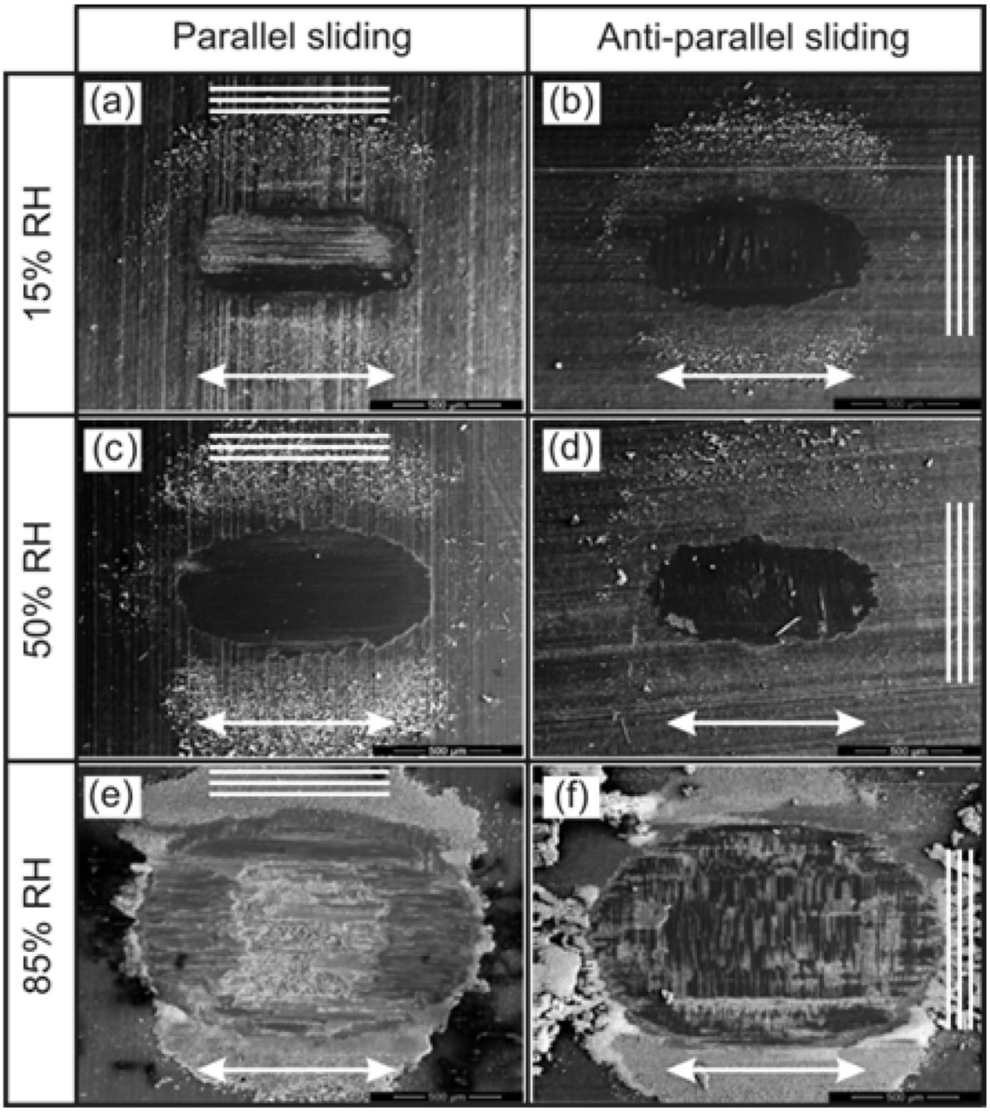


Fig. 6. Top-view SEM images of the wear tracks on carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles performed against stainless steel at different RH and sliding directions.

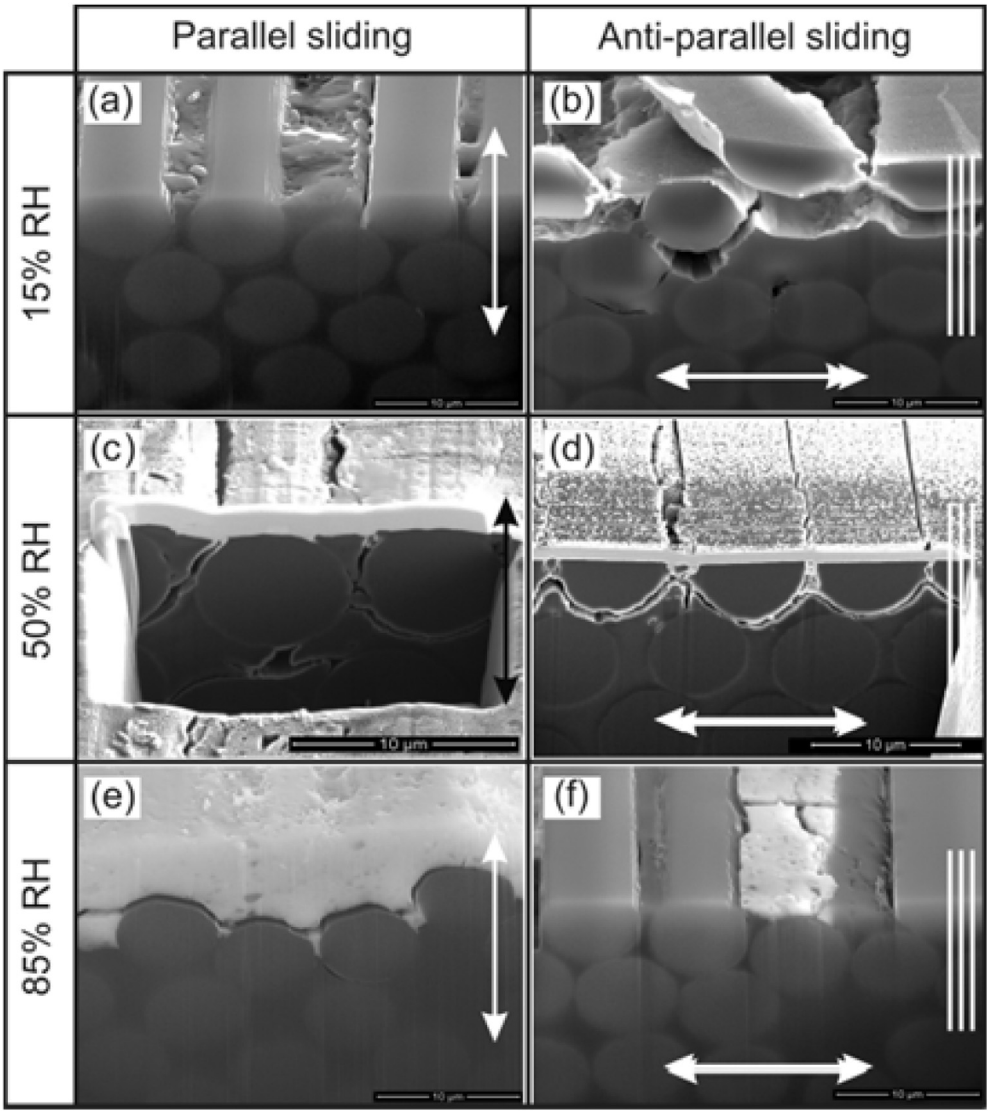


Fig. 7. FIB–SEM cross sections through wear tracks on carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles performed against stainless steel at different RH and sliding directions.

morphology of the carbon fiber reinforced epoxy after testing at RH ≤ 50% reveals clearly the carbon fibers and the epoxy matrix after the consumption of the epoxy top layer (Fig. 7a–d), whereas the samples after testing at 85% RH display debris traces (Fig. 7e and f). At 15% RH, the epoxy top layer is worn out and minor debonding at the interface fiber/matrix after parallel sliding is noticed (Fig. 7a), whereas after anti-parallel sliding (Fig. 7b) an extended debonding and a pull-out of the fibers are noticed. An extended debonding of the carbon fibers but no pull-out is noticed at 50% RH (Fig. 7c and d). The debonded surfaces between epoxy matrix and carbon fibers are rough due to the retention of epoxy material onto the carbon fiber surfaces.

The wear tracks on the carbon fiber reinforced epoxy tested against alumina ball at three RH values under parallel and anti-parallel reciprocating sliding, are shown in Fig. 8. The different wear tracks have approximately the same size, namely 1000 μm × 500 μm. Noticeable is that the sliding tests performed at 85% RH do not result in large wear tracks (Fig. 8e and f), as noticed on sliding against stainless steel (Fig. 6e and f).

FIB cross sections through the wear tracks on carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles performed against alumina in parallel and anti-parallel direction at different RH, are shown in Fig. 9. Fiber debonding occurs under sliding at 15% and 50% RH, but is very limited at 85% RH. In analogy with the stainless steel counter body, lesser debonding occurs under parallel sliding at 15% RH than under anti-parallel sliding (Fig. 9a and b, respectively). The debonding is more pronounced at 50% RH (Fig. 9c and d) and the top layer of carbon fibers becomes detached in the contact zone which facilitates the breaking and the subsequent pull-out of fibers from the matrix. At 85% RH, crack formation and debonding are markedly reduced (Fig. 9e and f). Moreover, the surface morphology after parallel sliding (Fig. 9e) is somewhat different from that after anti-parallel sliding (Fig. 9f). Indeed a consumption of the epoxy top layer and the carbon fibers is noticed under parallel sliding conditions whereas a connected surface of epoxy without any exposed carbon fibers is observed under anti-parallel sliding conditions. This might be due to the accumulation and blocking of epoxy debris in the wear track on top of the transversely aligned carbon fibers.

3.3.1.2. Influence of water immersion. Wear tracks formed on carbon fiber reinforced epoxy fully immersed in demineralized water

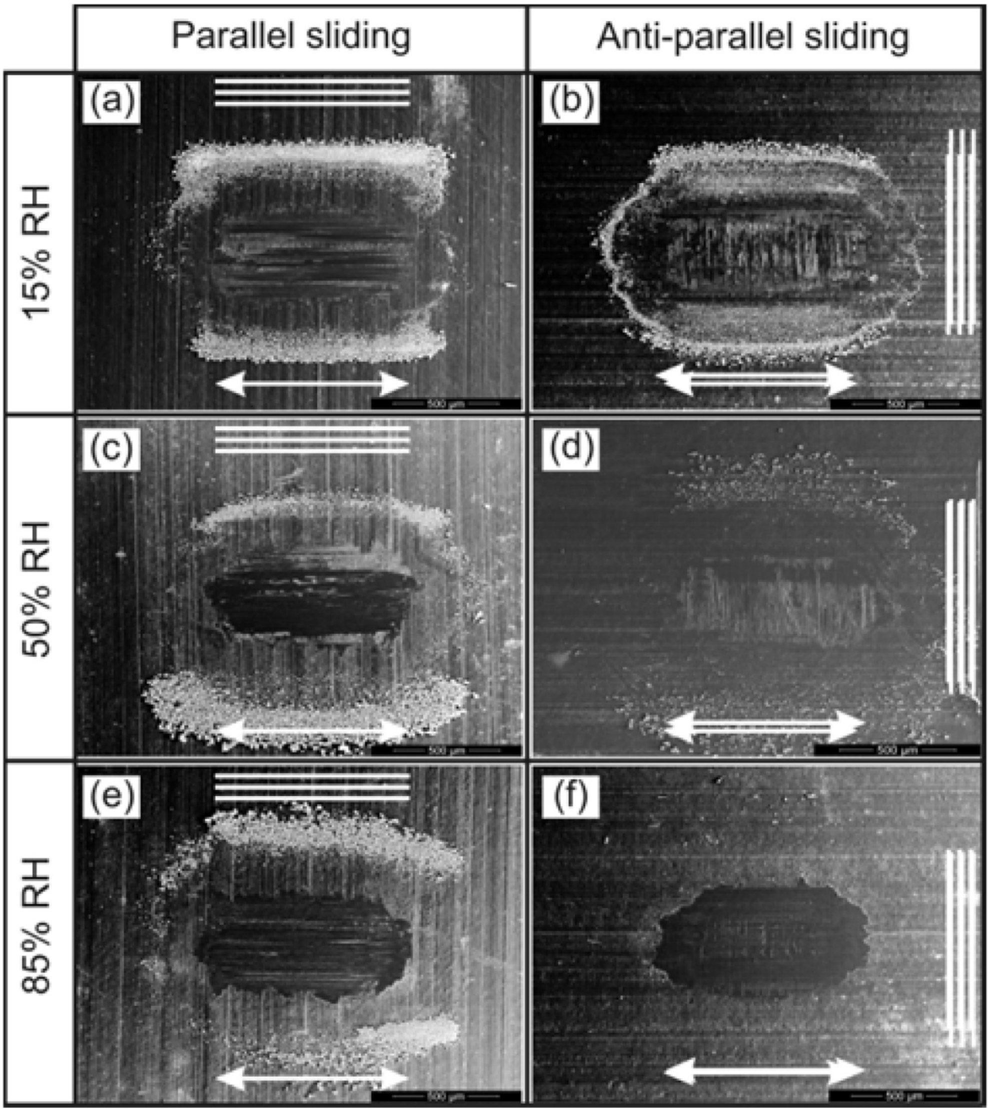


Fig. 8. Top-view SEM images of the wear tracks on carbon fiber reinforced epoxy after 200,000 cycles of reciprocating sliding performed against alumina at different RH and sliding directions.

under sliding against stainless steel and alumina counter body are shown in Fig. 10. Test samples were immersed in water just prior to the sliding tests. A reciprocating sliding against stainless steel (Fig. 10a and b) results in larger wear tracks than upon sliding against alumina (Fig. 10c and d), and debris were not noticed neither inside nor outside the wear tracks, notwithstanding that the maximum contact pressure was the same for both counter bodies. Moreover, water has the capability of washing away the debris from the rubbing region. Reciprocating sliding against stainless steel immersed in water ends up in larger wear tracks than in ambient air of different humidity values, whereas on sliding against an alumina counter body, the opposite is noticed.

Fig. 11 shows FIB cross sections through wear tracks formed on carbon fiber reinforced epoxy immersed in demineralized water after parallel and anti-parallel reciprocating sliding against stainless steel (Fig. 11a and b) and alumina (Fig. 11c and d). Neither debonding nor pull-out of fibers are detected. A complete wearing off of the epoxy top layer and a partial wearing off of the top layer of carbon fibers are observed on sliding against stainless steel ball (Fig. 11a and b). This explains the relatively large wear tracks noticed (Fig. 10a and b). The stainless steel counter body is wearing off the carbon fiber reinforced epoxy with very limited crack formation or debonding, whereas the epoxy top layer is not fully worn out on sliding against alumina, and no signs of either crack formation or debonding at the fiber/epoxy interface are noticed (Fig. 11c and d).

Interaction between carbon fiber reinforced epoxy and water may take place in different ways. The presence of water molecules at the sliding contact directly influences the wear behavior of the carbon fiber reinforced epoxy greatly [26]. Lu and Zhang [27] reported that immersion decreases the impact resistance of epoxy composites, and causes the fracture mode to change. More precisely, they recorded a 48% decrease of the composites mechanical strength after 60 days immersion at 80 °C, comparing to the original non-immersed samples. Water acts not only as a lubricant but also as a cooling agent, and thus lowers the friction-induced thermal heat dissipation into the composite. On the other hand, chemo-mechanical changes leading to enhanced softening and plastic deformation of the polymer matrix are expected. The different shear failure mechanisms observed on carbon fiber reinforced

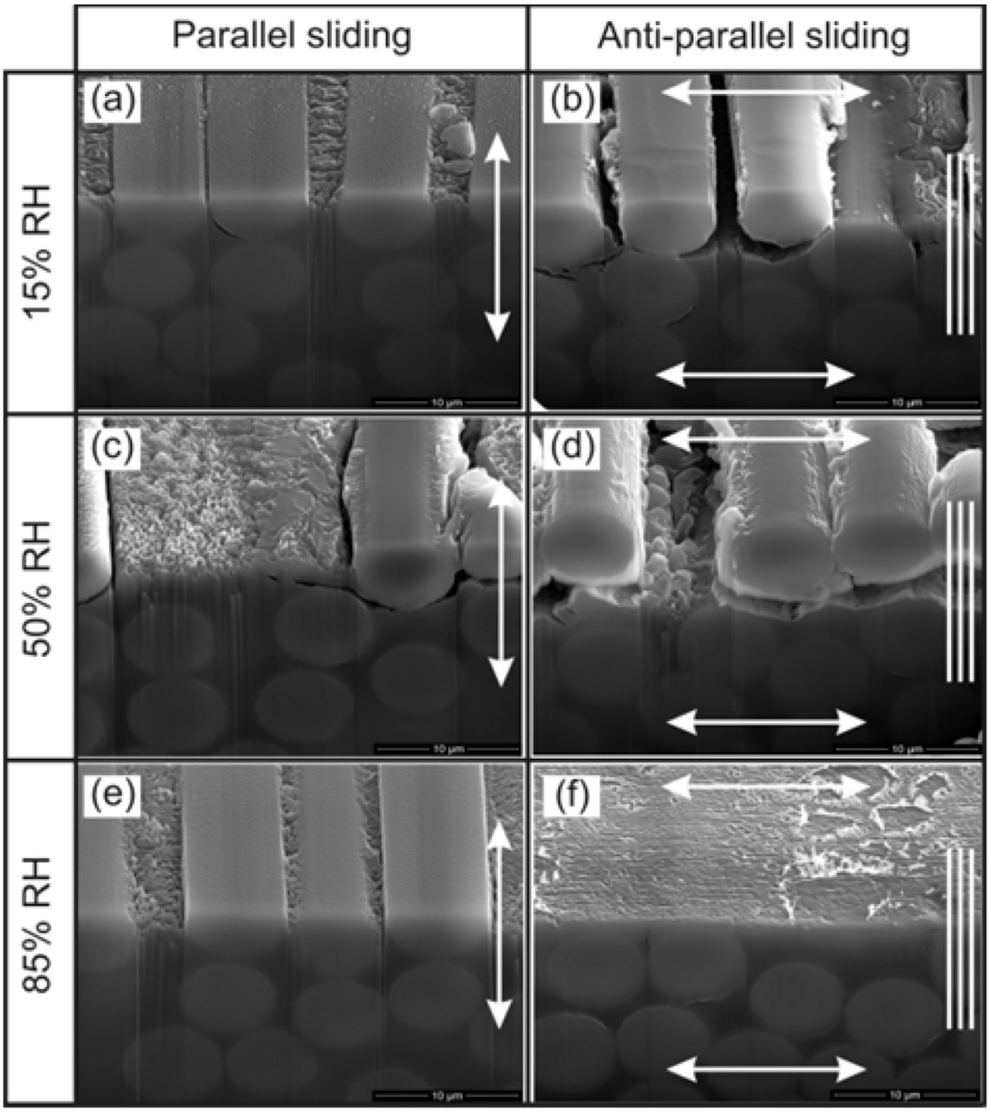


Fig. 9. FIB–SEM cross section through wear tracks on carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles performed against alumina at different RH and sliding directions.

epoxy may be explained by a combination of resin swelling and plasticization, and a lowering of the glass transition temperature of the epoxy resin when it absorbs water [28].

3.3.2. *Debris analyses*

EDX analyses of wear debris formed during anti-parallel sliding of carbon fiber reinforced epoxy against stainless steel at 15%, 50%, and 85% RH are reported in Fig. 12 as the ratio of iron to carbon and the ratio of chromium to carbon. The K-alpha peak of the elements Fe, Cr, and C was measured. At 85% RH, a relatively large amount of debris was noticed (Fig. 6e and f) of which the EDX spectrum shows intense Fe and Cr peaks. Therefore, it can be concluded that an atmospheric corrosion eventually enhanced by a mechanical wear of stainless steel in ambient air, took place in the sliding contact area. On the other hand, no metallic elements were detected in the debris generated at 15% and 50% RH. Thus, neither corrosion of the stainless steel counter body or formation of wear debris did occur at 15% and 50% RH. These facts can be linked to the fact that at 85% RH and 23 °C, there is a high probability of localized water condensation at the interface between the flat sample and the ball-shaped counter body due to the larger water contact angle and the higher average layer thickness of water molecules condensed from the vapor [29].

3.3.3. *Wear depth*

The maximum wear depth on the carbon fiber reinforced epoxy is plotted in Fig. 13 for reciprocating sliding up to 200,000 cycles against stainless steel. Measurements were done at three RH values under parallel and anti-parallel sliding directions.

Overall, the data in Fig. 13 show two different trends. First, the maximum wear track depths recorded in both sliding directions at 15% and 50% RH at any number of sliding cycles are relatively similar. A minor and almost linear increase in wear depth is noticed between 50,000 and 200,000 sliding cycles. Secondly, the maximum wear depths recorded at 85% RH are higher than at 15% and 50% RH.

The wear rate of polymers under sliding over the same track on the metal counter face has been reported to decrease in general with increasing number of sliding events until a limiting value is attained [30]. This reduction is frequently attributed to a

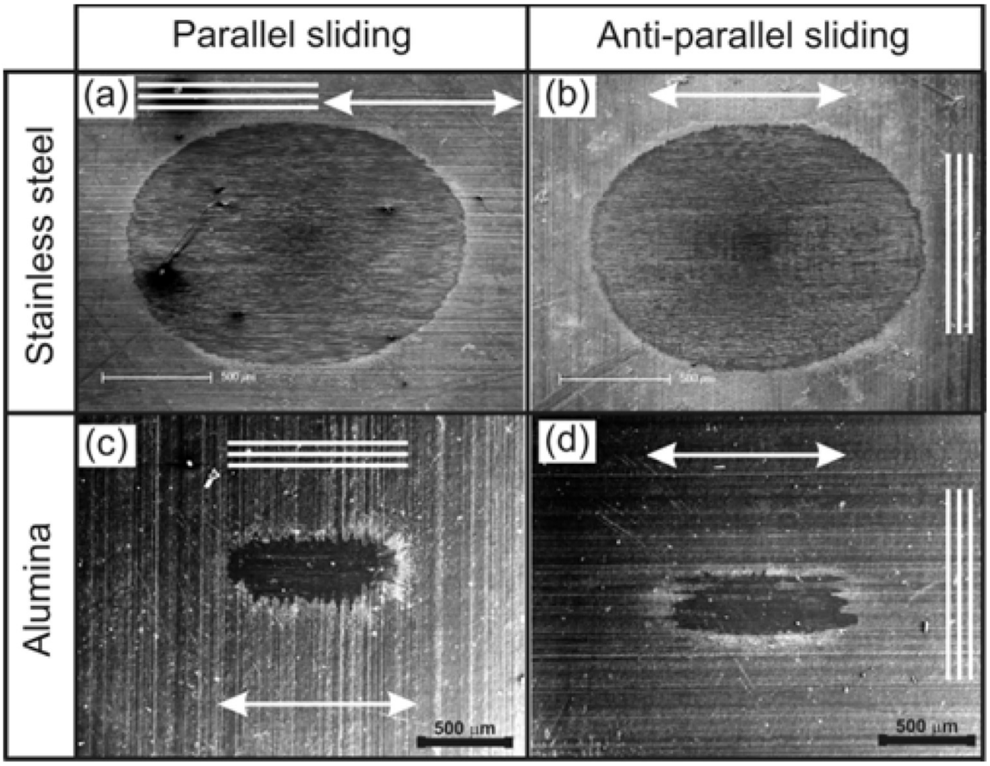


Fig. 10. Top-view SEM images of wear tracks on carbon fiber reinforced epoxy formed after 200,000 parallel and anti-parallel reciprocating sliding cycles in demineralized water against stainless steel and alumina balls.

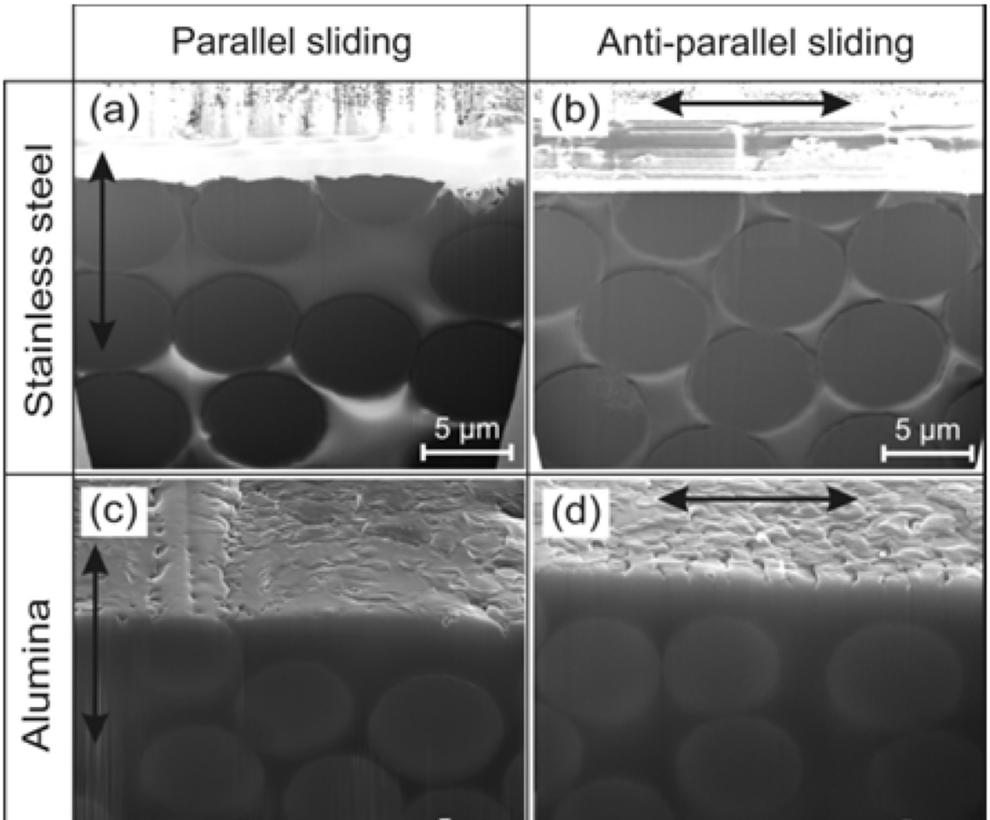


Fig. 11. FIB–SEM cross sections through wear tracks on carbon fiber reinforced epoxy obtained after 200,000 reciprocating sliding cycles performed in demineralized water against stainless steel and alumina balls.

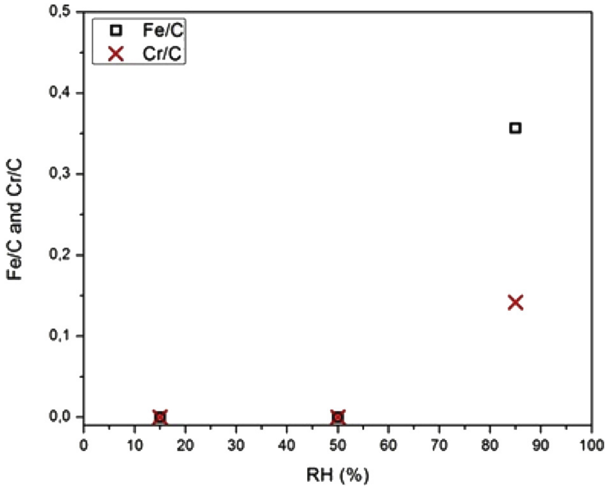


Fig. 12. EDX analyses of debris obtained after 200,000 reciprocating sliding cycles on carbon fiber reinforced epoxy sliding against stainless steel at 15%, 50%, and 85% RH.

modification of the topography of contacting surfaces by either environmental corrosion, a polishing or abrasion attributed to fillers incorporated in the polymers, or a growth of a film of transferred materials originating from the polymer and/or the fillers [30]. Carbon fiber reinforced polymers are reported to usually exhibit an initial high wear rate, called the running-in period, followed by an equilibrium or steady state period of much lower wear [31]. It can be concluded from Fig. 13 that the carbon fiber reinforced epoxy behaves in a similar way.

The maximum wear depth measured on carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles against either stainless steel or alumina for all the environmental test conditions selected is given in Table 1. The maximum wear track depths were measured in the center of the wear tracks after performing three single tests on the composite samples for each set of testing parameters. The given values of the maximum wear track depth in Table 1 are the average values of three wear track measurements and their average absolute errors. In the case of the stainless steel counter body, the maximum wear depth slightly increases by raising the RH from 15% to 50%, whereas it increases strongly at 85% RH at which the deepest wear tracks are measured under parallel and anti-parallel sliding.

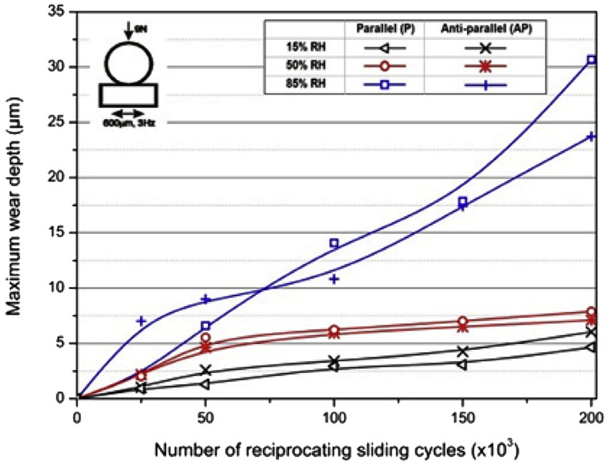


Fig. 13. Evolution of the maximum wear depth with number of sliding cycles on carbon fiber reinforced epoxy. Tests performed under parallel and anti-parallel reciprocating sliding against stainless steel at 15%, 50% and 85% RH. Line fits are guides to the eye only.

In the case of the alumina counter body, there is no significant influence of the RH. The sliding direction did not affect clearly the maximum wear track depth in most cases. No substantial wear depth could be measured after 200,000 cycles in demineralized water due to the low wear and the high roughness of the surface. In other words, the wear track is hardly detected.

Wear and fiber debonding as a function of test conditions, like counter body material, exposure to ambient air of different RH or immersed in water, sliding direction versus fiber orientation, are summarized in Table 2.

3.4. Discussion

3.4.1. Role of water condensate or water on sliding contact conditions

The stainless steel counter body can react in a humid environment by oxidation generating iron oxide. The presence of condensed water might have many undesired effects as it creates an aqueous medium that can act as an electrolyte. The rusting of iron is an electrochemical process involving the transfer of electrons from iron to oxygen [32]. Reaction between iron and oxygen can result in the formation of iron oxides Fe_2O_3 and Fe_3O_4 by:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \quad (1)$$

$$3Fe + 2O_2 \rightarrow Fe_3O_4 \quad (2)$$

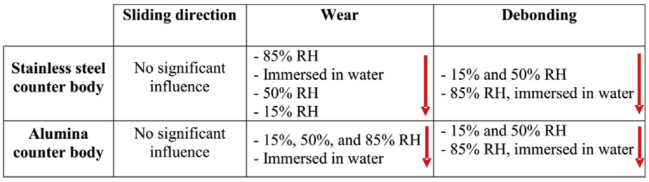
Oxygen usually enters the condensate by direct contact with ambient air which contains about 21% oxygen. Dissolved oxygen is present in demineralized water at a much lower concentration. Thus demineralized water is less corrosive than humid air since it contains only low levels (ppm) of oxygen as compared to 21% oxygen in air. Corrosion processes are divided into dry corrosion (Fig. 14c and b), damp corrosion (Fig. 14b), and wet corrosion (Fig. 14a) [33,34]. Syed [35] reported that damp moisture films or thin-film electrolytes tend to form on metallic surfaces under atmospheric exposure conditions if a certain humidity level is reached. Badea et al. [36] revealed that for iron the critical relative humidity is 70% in an atmosphere free of sulfur dioxide and in the absence of pollutants. This critical relative humidity level is not constant and depends on the material, the tendency of forming corrosion products, surface deposits to absorb moisture and the presence of atmospheric pollutants [35]. The contact angle which is the tangent angle between the composite surface and the counter body ball has also a crucial role in the formation of the moisture film. This angle is determined by the ball diameter. The moisture film starts to form by increasing the relative humidity till it reaches a specific thickness. In the presence of thin-film electrolytes in the contact edges, corrosion proceeds by balancing anodic and cathodic reactions which can lead to a galvanic coupling.

Syed [35] noted that corrosive contaminant concentration can reach relatively high values in the thin electrolyte films, especially under conditions of alternate wetting and drying. These alternative wetting and drying phenomena can be reached under reciprocating sliding conditions. Oxygen from the atmosphere is also readily supplied to the electrolyte under thin-film corrosion conditions. A diffusion transport mechanism for oxygen is applicable only to an electrolyte-layer thickness of approximately 30 μm and under strictly isothermal conditions [37]. The predicted theoretical limiting current density of oxygen reduction in an electrolyte layer of 30 μm significantly exceeds the practical observations on atmospheric corrosion rates [36]. Hosoya et al. [34] identified that the corrosion rate increases with the water film thickness. The

Table 1
Maximum wear depth on carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles against stainless steel and alumina at 15%, 50%, and 85% RH, and in demineralized water under parallel and anti-parallel sliding directions.

		15% RH (23 °C)	50% RH (23 °C)	85% RH (23 °C)	In demineralized water (23 °C)
Stainless steel counter body (9N)	Parallel (µm)	4.6 ± 1.9	7.8 ± 1.6	30.6 ± 2.8	17.9 ± 2.3
	Anti-parallel (µm)	6.1 ± 2.9	7.1 ± 2.8	23.7 ± 2.6	19.3 ± 2.1
Alumina counter body (7.3N)	Parallel (µm)	3.4 ± 1.8	2.1 ± 1.3	4.4 ± 2.1	~0
	Anti-parallel (µm)	5.1 ± 2.3	3.5 ± 1.7	5.2 ± 1.9	~0

Table 2
Summary of composite wear and fiber debonding (indicated by the arrows) of carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles as a function of test conditions and counter body material.



	Sliding direction	Wear	Debonding
Stainless steel counter body	No significant influence	- 85% RH - Immersed in water - 50% RH - 15% RH ↓	- 15% and 50% RH - 85% RH, immersed in water ↓
Alumina counter body	No significant influence	- 15%, 50%, and 85% RH - Immersed in water ↓	- 15% and 50% RH - 85% RH, immersed in water ↓

corrosion rate shows a maximum at the transition from moist to wet corrosion, and decreases when the water film thickens further under wet corrosion, controlled by the cathodic process, namely the diffusion of dissolved oxygen. Arnold [4] revealed that OH^- or H^+ ion concentrations originated from the presence of transition metal ions can significantly increase the corrosion. Carbon fibers are electrically conductive and electrochemically active and when they are in contact with a stainless steel counter body, they will take part in electrochemical reactions. As the electrochemical potential for oxidation of carbon is low, the carbon fibers tend to act as cathode, whereas stainless steel forms the anode and thereby corrodes preferentially [38]. The iron oxides formed at high RH may induce a large wear of the carbon fiber reinforced epoxy due to their abrasiveness. Higher humidity favors the oxidation of stainless steel, whereas upon water immersion oxides are not formed to such a large extent.

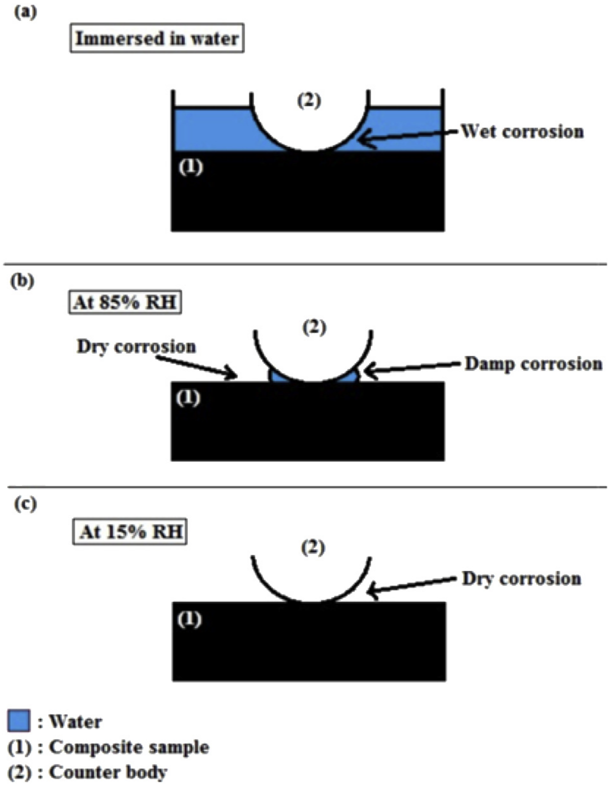


Fig. 14. Schematic illustration of carbon fiber reinforced epoxy sliding against stainless steel ball (a) immersed in water, (b) at 85% RH, (c) and at 15% RH.

3.4.2. Effect of water uptake on wear

The maximum wear depth against stainless steel is increased by around 3 times in demineralized water compared to at 15% and 50% RH for both sliding directions (Table 1). General observation of the surface of the wear tracks indicates that, when the polymer is wearing out, very small wear debris of polymer becomes detached and tends to accumulate between the asperities or within valleys between the carbon fibers (Figs. 6 and 7). This can lead to a smoothing of the sliding surfaces and decreases the wear. On the other hand, demineralized water can wash the sliding surfaces and cause a higher wear by preventing the composite debris to accumulate and to smoothen the contact surface.

3.4.3. Effect of water uptake on fiber debonding

The most frequently encountered functional groups in carbon fiber reinforced composite are −COH, −CO and −COOH. The adhesion to the polymeric matrix is stronger as the number of chemical bonds to the fiber is higher [3,39]. The bonding between the carbon fibers and the matrix is provided by the interface between the two components. This surface may have different properties than the bulk of the matrix, e.g. altered levels of crystallinity, cross linking, or chain orientation [4]. The situation is further complicated by the non-linear stress and strain response of both fiber and matrix. The bonding strength between the fiber and the matrix and the mechanical properties will affect the transverse breaking strength of the composites. Cracks will initiate as soon as the ultimate local stress and strain are reached. In other words, the initial cracking will occur when the local stress exceeds the local strength, and this is most likely at the interface. The presence of epoxy matrix at the surface of the carbon fibers after debonding (Fig. 7b–d) indicates a good adhesion due to the surface treatment of the carbon fibers [3]. The remaining traces of epoxy resin at the surface of the debonded fibers explain that the transverse fiber strength is low and that the fibers split near the aligned surface. The interface bonding was improved at high RH by either the enhancement of fiber/matrix adhesion due to the interaction of the composite samples with the environment or by the top layer ability to accommodate the stresses generated from the normal load and the shear forces.

A lowering of the glass transition temperature by 5 °C was recorded in the previous work on composite samples immersed in water for 20 h (the duration of the test) [21]. This reduction in Tg has been demonstrated by several different other researchers [40]. Some reported that the decrease in Tg of polymers is simply caused by water sorption, and stated that water can cause the resin to swell and to craze the surfaces [41,42]. Nanohardness measurements of carbon fiber reinforced epoxy composite done also after 20 h immersion in demineralized water showed a decrease of 15% in hardness and Young's modulus compared to composites in ambient air of 50% RH [21]. This increases the matrix flexibility and allows a better transfer of the normal and shear stresses to top layer fibers under the sliding contact and so retain strength. Walker and Zhi Hu [9] found that specimens immersed in water increase their ductility and this will lower the local stress concentration between fibers and matrix, thereby leading to a more uniform stress distribution. Joshi [28] revealed that a too strong bonding from an excessive surface treatment may induce a brittle failure of the composite, and that a too weak fiber bonding may not allow an adequate transfer of stress from the resin to the fiber. Water molecules soften the matrix and increase its energy sorption at the crack tip which enhances the crack nucleation resistance. Typically, the polymer swells when the composite absorbs water, whereas the reinforcement does not swell. If the epoxy matrix deforms elastically, the interfacial shear stresses reach a maximum value near the fiber ends, and then decay rapidly toward the center length of the fiber.

4. Conclusions

The influence of humidity and water immersion on the friction, wear, and debonding of unidirectional carbon fiber reinforced epoxy under reciprocating sliding against either stainless steel or alumina has been studied. Reciprocating sliding tests were done along a direction parallel and anti-parallel to the fiber orientation.

Under reciprocating sliding against stainless steel:

- The COF showed a running-in phase. A fluctuation of the COF was noticed in some cases which can be linked to the production of iron oxides originated from the metallic counter body. No fluctuation was noticed when no oxide debris was found (i.e., at 15% and 50% RH).
- The FIB cross sections revealed an extended cracking along the carbon fiber/epoxy interfaces, and a pull-out of carbon fibers at 15% RH. In ambient air of 50% RH, the debonding of carbon fibers occurs but not a fiber pull-out. Furthermore, at 85% RH the debonding almost disappears while an oxide top layer is present on the wear track.

Under reciprocating sliding against alumina:

- The recorded COF showed a similar evolution as the one noticed against stainless steel at all RH values expect 85% RH.
- A clear debonding at the interface between carbon fibers and epoxy matrix was observed at 15% and 50% RH, whereas no significant debonding took place at 85% RH and water immersion.

No clear influence of the sliding direction on the wear track size and maximum wear depth was noticed in the case of reciprocating sliding against either alumina or stainless steel. Fiber debonding and composite wear are the main failure processes noticed under reciprocating sliding. These two processes are greatly controlled by either RH or water immersion.

- In demineralized water, the debonding and cracking tendency is markedly lower than in tests performed at 15% and 50% RH, and sliding against alumina in particular ends up with very little wear.
- At low RH, the epoxy composite fails mostly by cracking, debonding followed by pull out of carbon fibers. On the other hand, at high RH values (i.e., 85%) the detected debonding significantly decreases under parallel and anti-parallel sliding.
- The maximum wear depth is slightly lower with alumina than with a stainless steel counter body. Important is the finding that the maximum wear depth is much larger on sliding against stainless steel at 85% RH due to the release of oxide debris which are abrasive.
- The RH and contact angle have a critical value for the formation of a moisture film which serves as an electrolyte in the galvanic coupling and leads the stainless steel counter body to corrode.

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