

Surface and sub-surface degradation of unidirectional carbon fiber reinforced epoxy composites under dry and wet reciprocating sliding

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ABSTRACT

In this paper, the effect of water on the friction and wear of a carbon fiber reinforced epoxy tested under reciprocating sliding against a stainless steel counter body is reported. The tribological behavior of unidirectional carbon fiber reinforced epoxy composite was investigated in ambient air and in demineralized water, and the role of water on the (sub-) surface degradation is discussed. The effect of sliding direction relative to the fiber orientation has been studied. The correlation between the debonding of carbon fibers at the fiber-epoxy interface, and the wear behavior of the carbon fiber composite are discussed based on an in-depth analysis of the worn surfaces done by environmental scanning electron microscopy, white light interferometry, atomic force microscopy, and focused ion beam. We demonstrate that the carbon fiber reinforcement greatly improves the tribological properties of epoxy under sliding in both dry environment and demineralized water. A reciprocating sliding performed along an anti-parallel direction to the fiber orientation under dry conditions results in a large degradation by debonding and breaking of the carbon fibers compared to sliding in

parallel and perpendicular directions. Immersion in water has a harmful effect on the wear resistance of the carbon fiber reinforced epoxy composite. The competition between crack growth and the wear rate of epoxy matrix and/or carbon fibers in the sliding track determines the level of material loss of the composite in both test environments.

KEYWORDS: A. Carbon fiber, B. Adhesion, B. Debonding, B. Interface

1. INTRODUCTION

Epoxy composite materials are widely used in engineering applications, however, when they are used in water, their mechanical properties are strongly affected by water sorption, which usually causes plasticization and diminishes the mechanical strength [1, 2]. In general, water reduces the coefficient of friction by acting e.g. like either a lubricant [3] or as a washing agent for some composite materials [4]. The greatest advantage of carbon fiber reinforcement in epoxy composites is the high corrosion resistance due to the chemical inertness of both constituents. Moreover, carbon fiber reinforced epoxy composites are light in weight, and have a high stiffness and toughness [4]. In tribological applications, these composite materials can suffer from different surface damages in both dry and water environments. It is well known that the interface between the reinforcement fibers and the matrix plays a crucial role in the degradation and the failure of reinforced composites [5-7]. Recently, detailed studies have been dedicated to link the interface adhesion with the mechanical properties of different reinforced composites [8-10]. The tribological properties namely friction and wear of carbon fiber reinforced carbon matrix composite were studied under different environmental and experimental conditions. A higher abrasive wear was reported with larger difference between the hardness of the carbon fiber and the carbon matrix [ref??]. Moreover, it was shown that moisture inhibits the high wear at low speed displacement [11]. The positive impact of sea-

water on the fatigue resistance of glass fiber reinforced polyester or vinylester resin systems has been reported [12]. In previous work [13], the friction and wear behavior of carbon fiber reinforced epoxy under ambient air conditions were evaluated, which showed that both friction and wear depend strongly on the carbon fiber orientation relative to the sliding direction. Shim *et al.* showed that the presence of water molecules in the sliding contact greatly influences the wear behavior of carbon fiber composites [14]. Nogueira *et al.* showed that the water diffusivity is related to the availability of molecular sized holes in the polymer structure [15]. The presence of such holes depends on the polymer structure, surface morphology, and crosslinking density. The water affinity of the polymer has been related to the presence of hydrogen bonding sites along the polymer chains, which create attractive forces between the polymer and water molecules [15]. Water absorption by epoxy resins has been extensively studied because of its impact on the structure properties of such resins. However, no attention was given in literature up to now on the subsurface behavior in fiber reinforced epoxy composites under sliding conditions with respect to the sliding parameters and the environmental test conditions.

In this work, the surface and subsurface degradation and the fibre/epoxy interface adhesion of unidirectional carbon fiber reinforced epoxy were investigated under reciprocating sliding against stainless steel counter bodies in demineralized water and in ambient air. Friction and wear values recorded in both environments are compared for sliding tests performed in different directions relative to the fiber orientation. Main degradation processes are identified.

2. EXPERIMENTAL

The materials used in this study are bulk epoxy and a carbon fiber reinforced epoxy composite. The carbon fibers used are of type STS-24 K having the following specific

properties: 24,000 filaments, 4,000 MPa tensile strength, 240 GPa tensile modulus, 1.7% elongation, 7 μm diameter, and 1.75 g/cm^3 density. For the production of the bulk epoxy, standard di-glycidyl ether of bisphenol A (DGEBA, Epikote 828) and Aradur 3486 (aliphatic polyamine) as a hardener (ratio epikote/hardener 100/30) were used. Carbon fiber reinforced samples were obtained as follows: the resin was mixed, poured in a mould and cured at room temperature followed by an oven treatment. The cycle to cure those samples was 24 hrs at room temperature plus 8 hrs at 80 °C. The stack of pre-impregnated fibers was placed on a polytetrafluoroethylene (PTFE) sheet on an aluminium base plate. It was covered with another PTFE layer and a 10 mm thick aluminium plate was put on top. The assembly was covered with bleeder fabric and a vacuum bag. Vacuum was applied through a tube that was incorporated in the sealing of the bag. A vacuum of 0.095 MPa was then applied for 15 min at room temperature to de-bulk. Following, the assembly was placed in an oven (while maintaining the vacuum) and heated up to 90 °C for 60 min and finally heated at 130 °C for 90 min. After that, the assembly was taken out of the oven and the vacuum was released.

The friction and wear behavior of the carbon fiber reinforced epoxy samples of 5x5x5 mm^3 were tested under reciprocating sliding against stainless steel ball counter bodies in a fretting mode I machine [16]. The reciprocating sliding tests were carried out in two different environments, namely in ambient air of 50% relative humidity at 23 °C, and immersed in demineralized water at 23 °C. Sliding tests in demineralized water were performed by putting the composite samples just prior to the start of the test in a container filled with demineralized water to avoid water sorption prior to testing. All tests were performed for 200,000 sliding cycles against stainless steel (AISI 316) balls with a diameter of 10 mm and G20 grade (ISO 3290). The balls were cleaned prior to the reciprocating sliding tests with acetone and subsequently with ethanol. A normal load of 9 N, a sliding frequency of 3 Hz, and a peak-to-peak displacement amplitude of 600 μm were used in all tests. The sliding tests were

performed along a sliding axis either parallel to the fiber orientation or perpendicular but in-plane with the fiber orientation, but also with the sliding axis perpendicular and off-plane to the fiber orientation. The repeatability was tested by performing a minimum of three tests for each sample and set of testing conditions.

White light interferometry (Wyko3300) was used to measure the maximum wear track depth, and environmental scanning electron microscopy (FEI ESEM XL 30) was used to image the worn surfaces on the composites. The focused ion beam (FIB) technique (FEI NOVA NANOLAB 600) was used to prepare cross-sections through the worn areas in order to investigate the (sub-) surface degradation by visualizing the debonding and breaking of carbon fibers. A thin layer of gold (about 150 nm) was sputtered on the whole sample surface, while a subsequent platinum sputtering (for about 2 μm thickness) was done on the edge of the cross section in order to prevent etching. It was assumed that the FIB technique did not cause any delamination within the composite samples. A DSC 2920 thermogravimetric analyzer was used to determine the glass transition temperature by performing a heat cycle starting from room temperature up to 300 °C at 10°C/min. Atomic Force Microscopy (AFM) data were obtained with two different equipments, namely, a Nanoscope IIIa (Bruker) and an Agilent 5500. The images were obtained in ambient air with either silicon (force constant close to 40 N/m) or silicon nitride (force constant close to 0.1 N/m) cantilevers operating in contact mode or in dynamic mode but in this latter case only with silicon cantilevers. In order to discard artifacts, several cantilevers were used. In addition, in order to better assess the differences between the surface morphology of samples tested under ambient air and demineralized water conditions, both kind of samples were imaged with the same tip. The mechanical properties of the composite samples were determined by nano-indentation measurements using a CSM Instrument equipment, operated with a Berkovich diamond indenter tip at maximum normal loads of 25 and 50 mN with a dwell time of 5 s. Average

values of the Young's modulus and hardness were calculated from 5 duplicated measurements of each of the chosen indentation loads by using the Oliver-Pharr method [17].

3. RESULTS AND DISCUSSION

3.1. Composite structure

The FIB-SEM technique was used to analyze the surface and sub-surface down to about 25 microns in depth of the pristine and worn composite samples. The two components of the pristine composite, namely carbon fibers and epoxy polymer matrix, are clearly distinguishable in Figure 1. The top layer of epoxy has a non-uniform thickness in the range of 1.5 to 6.0 μm which covers the underlying composite structure. The carbon fibers reinforcement (volume fraction of 67%) is distributed inhomogeneously throughout the composite.

3.2. Wear track depths

The wear rate of graphite reinforced polymer composites commonly increases with increasing humidity or on changing the test environment from dry to wet [4]. Presently, a detrimental effect of an immersion in demineralized water on the wear behavior of both unfilled epoxy and carbon fiber reinforced epoxy is found as well (Table 1), and that for composites tested along three different sliding directions as well as for bulk epoxy. Maximum wear track depths were measured in the center of the wear tracks after performing three single tests on the epoxy and 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 these three measurements and their average absolute errors. Overall, the deepest wear tracks are recorded on bulk epoxy where the addition of water increases the wear track depth by a factor of 3.5 compared to ambient air sliding, i.e. from about 21.4 μm up to 74.7 μm . For the reinforced epoxy composite, the wear tracks produced in parallel direction are significantly less deep than those formed by sliding in

anti-parallel direction under both demineralized water and ambient air sliding conditions. This can be explained by the non-continuous contact of the counter body ball with the fibers for anti-parallel sliding, whereas for parallel sliding the contact of the carbon fibers with the counter body is continuous. Important to note is that under sliding in the perpendicular direction the effect of water is strongest, since the wear track depth increases from about 3.4 μm for sliding in ambient air up to 21.5 μm for sliding in demineralized water.

The composite structure influences greatly the wear depth in both ambient air and demineralized water. Under ambient air sliding, the wear depths after 200,000 sliding cycles are about 3-4 μm for parallel and perpendicular sliding tests. SEM analyses revealed the removal of the epoxy top layer and only a slight wear of the first fiber layer in the case of parallel sliding tests. On the contrary, insignificant wear of the composite took place under perpendicular sliding compared to the other two ambient air sliding conditions due to a better wear resistance of the carbon fibers in vertical direction, whereas in anti-parallel sliding the wear depth of 7 microns indicates that the epoxy top layer and nearly one complete fiber layer have been worn down. In demineralized water condition, the wear depths are remarkably higher. About 2.5 fiber layers plus the epoxy top layer were consumed for parallel and anti-parallel sliding. In the same condition, the wear depth is significantly higher in perpendicular sliding direction.

In summary, the values of the wear tracks depths (Table 1) show that, whatever is the orientation of the carbon fibers, demineralized water decreases the wear resistance of the carbon fiber reinforced epoxy composite when sliding against a stainless steel counter body.

3.3. Dissipated energy

The evolution with sliding cycles of the tangential force versus displacement loops corresponding to the anti-parallel sliding direction under ambient air and demineralized water sliding is shown in Figure 2. The corresponding amount of dissipated energy is represented by

the area of the loops. Three stages are distinguished: the first 10,000 cycles corresponding to the running-in stage, the middle stage between 10,000 and 50,000 cycles, and the final stage covering the last 150,000 cycles corresponding to the steady state region. The rectangular shape of the loops in Figure 2 indicates that sliding was performed under gross slip conditions. A striking feature is noticed at the turning points in the loops when sliding is done in ambient air. The tangential force locally increases at the four extremities of the sliding movement where start/stop conditions prevail. The shear stress is expected to reach its maximum at these two ends of the wear track. Halfway the sliding test, a decrease of the dissipated energy per cycle is noticed. It might be due to a lubrication effect resulting from the wearing out of the carbon fibers or due to a smoothing of the sliding contact [4].

In demineralized water, the tangential force decreases by about the half for the anti-parallel sliding direction (Figure 2b) at the start of the displacement. It is possibly due to the lubrication effect of demineralized water. Overall, the drastic changes in shape and size of the loops in Figure 2 clearly demonstrate the high sensitivity of the carbon fiber epoxy reinforced epoxy to the test environment, such as a reciprocating sliding contact in demineralized water.

According to Godet's model of the surface degradation of metallic, ceramic, and plastic materials the rapid increase of the dissipated energy in the first few cycles is controlled by the elimination of the initial surface [18]. The increase might be due to an increase of the roughness by an epoxy debris abrasion effect. The ball counter body starts sliding against the top epoxy layer (Figure 1) and the dissipated energy increases rapidly due to the adhesive behavior of epoxy. So, in the first stage only epoxy will interact with the steel counter body and a transition from a two-body to three-body contact will be established by debris formation. The epoxy/stainless steel sliding contact generates mostly epoxy debris. In our previous work [13], two types of debris were identified for this situation: a) debris expelled from the contact near the edges of the wear track as a result of the high contact pressure and

the reciprocating sliding displacement, and b) debris detached from the epoxy matrix but entrapped in the contact by the repetitive sliding movement. The decrease of the dissipated energy starting at about 1,500 cycles can be due to a smoothing of the two contact surfaces as well as a change in chemical composition of the composite surface at the contact when reaching the initially buried carbon fibers (Figure 2a). After removal of the epoxy top layer, a mixture of epoxy and carbon fibers is exposed in the sliding track. It is well known that carbon fibers act as lubricating agents due to their ability to form graphitic tribofilms [13]. Finally, a steady-state phase is reached after about 50,000 sliding cycles where a much lower tangential force is maintained under reciprocating sliding in both ambient air and in demineralized water. A slight change in the dissipated energy is noticed during the last stage of our sliding tests under both ambient air and demineralized water conditions which can be due to the increase of the wear track concavity. The same evolution of the dissipated energy was noticed for the parallel sliding direction.

3.4. Coefficient of friction

The coefficient of friction recorded on bulk epoxy is plotted in Figure 3 as a function of sliding cycles performed in ambient air and immersed in demineralized water. The coefficient of friction in ambient air remains stable at 0.56. On the other hand, in demineralized water the initial coefficient of friction is relatively low, namely 0.33, and increases gradually with increasing sliding cycles up to a value fluctuating between 0.45 and 0.55.

The coefficient of friction recorded under ambient air and demineralized water sliding in parallel and anti-parallel directions for the composite material is presented in Figure 4. In ambient air, the coefficient of friction under anti-parallel sliding stabilizes at about 0.25 after 25,000 cycles (Figure 4a), whereas the steady state is reached at 0.20 under parallel sliding at about 50,000 cycles (Figure 4b). In both directions in ambient air, a similar evolution of the coefficient of friction with sliding cycles is observed. The coefficient of friction starts at a

relatively high value of 0.5, decreases rapidly during the first 2,000 running-in cycles, and then remains quite constant. The onset of a steady state friction value after an identical number of sliding cycles was also noticed by Ohmae *et al.* for the case of unidirectional carbon fiber reinforced epoxy sliding against steel with relative slip [19].

A significant influence of the demineralized water is noticed during the running-in stage. In ambient air parallel sliding, the coefficient of friction quickly increases from an initial value of around 0.5 to a value below 0.6 whereas in demineralized water, the coefficient of friction remains at a value close to 0.2 (Figure 4b). The coefficient of friction starts relatively low, namely at around 0.16, then reaches a peak value of only 0.23 at around 10,000 cycles and stabilizes at a value of about 0.2 for demineralized water sliding in anti-parallel direction and 0.22 for demineralized water sliding in parallel direction. In the case of demineralized water parallel sliding, the coefficient of friction gradually increases after a subsequent drop to about 0.16 around 25,000 cycles.

Water has the capability of washing the surface [20]. In other words, one effect of water is the removal of any surface film or wear debris formed in the sliding contact. Lancaster reported that water and aqueous solution inhibit the formation of a transfer film on the counter body [21]. This film can be formed by the accumulation of epoxy debris [22] or by the accumulation of graphitic flakes originating from the carbon fibers [13]. These researches showed that the lubricating films formed on the wear track reduce the contact surface roughness, and also improve the wear resistance of the composite. Thermosets such as epoxies are rather more susceptible to the environment [4]. The cross linked thermosets containing OH groups may be influenced by hydrogen bonding. In other words, hydrogen bonds with water molecules are formed at the expense of cross links, which causes increased plasticity of the composite.

3.5. Surface degradation

3.5.1. Sliding in parallel and anti-parallel direction

The (sub-) surface degradation on the composite material after reciprocating sliding tests in the three different directions, namely parallel, anti-parallel, and perpendicular, was analyzed by ESEM and FIB-SEM.

Cross section images obtained by FIB after anti-parallel sliding in ambient air are shown in Figure 5. Cracks which propagate along the carbon fibers interface are detected in the surface and subsurface. Likely, the cracking starts in the epoxy matrix at a point where the carbon fibers are proximately underneath and the layer of epoxy is less thick than in other areas. The stress is localized and not released to elastic deformation knowing that the elastic deformation of the carbon fibers is very limited compared to the epoxy matrix. The resulting debonding starts before the counter body touches the carbon fibers, and even starts during the very beginning of the sliding tests, even before 50 sliding cycles (Figure 5a) (white arrow). The composite surface starts to fail by crack nucleation followed by crack propagation caused by the repeated sliding motion. Some epoxy material remains present on the carbon fiber surrounding the debonding zones (Figure 5c). A complete debonding along a carbon fiber is shown in Figure 5d proving that the interface is the weakest point in the composite mechanical integrity under reciprocating sliding, and that the debonding can take place fiber after fiber due to the non-homogeneous ordering of the carbon fibers. In more details, the carbon fibers are not positioned within the same horizontal plane which leads the counter body to be in contact first with the higher fibers, then to the lower positioned ones. It was shown that the highest contact pressure appears at the rear edge of each fiber within the contact area [23] because of the discontinuous stress distribution. The stress is absorbed mostly by the matrix through the depth until countering the carbon fibers which are brittle and limited to absorb the stress. The accumulation of the stress in that region will create debonding of the carbon fibers.

For both sliding directions a serious degradation and debonding of the carbon fibers is detected in the central contact area (Figure 6). The composite surface after testing in the anti-parallel direction (Figure 6b) shows a higher wear on the carbon fibers than is the case of parallel sliding (Figure 6a), and with the cracks generally surrounding the interface of the reinforcement fibers with the epoxy but being restricted to the top carbon fiber layer.

ESEM micrographs of the wear track surfaces on composite samples tested in ambient air in parallel and anti-parallel directions are shown in Figure 7. The alignment of the carbon fibers and the sliding directions are indicated by parallel lines and arrows, respectively. It is clear that the number of broken fibers produced during parallel sliding (Figure 7a) is very limited as compared to the one produced during anti-parallel sliding (Figure 7b). The material damage in the case of anti-parallel sliding is significantly larger in terms of density of cracks and the pull out of carbon fibers.

During reciprocating sliding tests, the samples are subjected to different stresses: compressive stresses resulting from the applied normal load and shear stresses caused by the combination of the lateral displacement and the normal loading. In addition, the composite material suffers differently depending on the reciprocating sliding direction. Specifically, the parallel and anti-parallel sliding directions accommodate the stress by bending and shear.

In the case of sliding in the parallel direction (Figure 7a), the dominant stress in the composite is shear stress along the fiber axes. The sliding of the stainless steel ball counter body produces a surface wear causing a progressive thinning of the carbon fibers.

In the case of anti-parallel sliding (Figure 7b), the dominant deformation is caused by torsion associated with bending and shear stresses. Partially broken fibers are located mostly at the sliding ends of the wear track. This can be explained by the varying sliding speed of the counter body during sliding. The start-up and stop-down of the counter body at the turning points of the sliding track in each cycle are probably at the origin of this localized damage.

They precisely increase the shear stress as appearing from the dissipated energy hysteresis loops. The shear stress is associated with a torsion load due to the transverse movement of the fibers, thus yielding a higher probability of carbon fibers breakage. In other words, after fiber debonding due to crack propagation, the relative displacement of the carbon fibers increases with sliding cycles till they exceed the ultimate shear strength, and the fibers break.

ESEM images of the wear tracks formed on carbon fiber reinforced epoxy after 200,000 sliding cycles in demineralized water did not reveal any significant degradation (not shown). This indicates that under demineralized water sliding cracks and fiber pull out occur much lesser than under ambient air sliding. Cross section FIB-SEM images of wear tracks obtained after parallel and anti-parallel sliding in demineralized water are shown in Figure 8. The debonding of the carbon fibers located close to the surface is very limited.

3.5.2. Sliding in parallel direction on bulk carbon fibers

In this study, reciprocating parallel sliding tests were also done on a bundle of the pristine carbon fibers, which was fixed onto a metallic plate holder. In order to reduce the rolling of the carbon fibers, the exposed fibers distance was minimized by gluing the extremities. The effect of water on the coefficient of friction recorded for reciprocating sliding on carbon fibers in ambient air and in demineralized water is shown in Figure 9. The coefficient of friction decreases from around 0.35 under sliding in ambient air down to 0.20 in demineralized water. So, demineralized water reduces the interaction between the stainless steel counter body and the carbon fibers.

3.5.3. Sliding in perpendicular direction

Considering an elliptical shape of the wear tracks, the total number of carbon fibers in contact with the counter body in the case of parallel and anti-parallel sliding can be calculated as:

$$N = \frac{a}{d} \quad (1)$$

With N the estimated number of carbon fibers in contact with the counter body, a is the width or length of the wear track, d the diameter of one carbon fiber ($= 7 \mu\text{m}$). In the case of parallel sliding, the wear track width is $500 \mu\text{m}$ and N is about 70 fibers, while in the case of anti-parallel sliding, the length of the wear track is $1000 \mu\text{m}$ and N is about 143 fibers.

A correction can be applied to the perpendicular direction on the four corners of the wear track due to the elliptical form:

$$N = \frac{67(ab - 2a'b')}{100\pi r^2} \approx 7615 \text{ fibers} \quad (2)$$

with r the radius of the carbon fiber ($= 3.5 \mu\text{m}$), a' ($= 120 \mu\text{m}$) and b' ($= 260 \mu\text{m}$) are respectively the width and the length of the area where no contact is happening.

These calculations show that under sliding in perpendicular direction the shear loading will be taken up by a much higher number of carbon fibers than under parallel and anti-parallel sliding, and that the stress will be distributed more homogeneously. As a consequence, the damage at interfacial regions is less. The compressive and shear stresses induced by the reciprocating sliding lead to a fiber bending under forward and backward motion of the counter body in the sliding contact. This resembles a “toothbrush” type of movement of the fibers. The stress is transferred from a certain but relatively high number of fibers to another large set of fibers. Sliding in a perpendicular direction will thus be accommodated discontinuously by repeated compression-tension [23]. In this case, some cracks also grow within the fiber and propagate parallel to the surface, as can be seen in Figure 12a.

The carbon fibers consist of ribbons of carbon atoms aligned parallel to the axis of the fibers. Since they are essentially amorphous in nature they have less long range ordering of carbon atoms than the hexagonal planes of carbon atoms present in graphite. The ribbons are essentially parallel to the surface of the carbon fibers and the layered planes along the axis of the carbon fiber are interlinked in a complex way. The high strength of these carbon fibers

results from the interlocking and folding of ribbons, so the sheets of carbon atoms cannot slide past each other as in graphite [24].

The evolution of the coefficient of friction on carbon fiber reinforced epoxy tested in perpendicular direction under either ambient air or demineralized water condition revealed a non-significant difference between both test conditions (Figure 10). In ambient air, the initial coefficient of friction is 0.25 and much lower compared to the ones recorded in the other two sliding directions, namely about 0.50. This lowering can be explained by the difference in the nature of the sliding area. Under perpendicular sliding, the counter body is in direct contact with a mixture of carbon fibers and epoxy right from the start of the sliding tests, whereas under parallel and anti-parallel sliding a running-in period is needed to wear off the epoxy top layer and to reach the carbon fibers. The perpendicular sliding displays a similar steady state value (about 0.20) of the coefficient of friction as recorded under parallel and anti-parallel sliding, although a gradual but minor increase is recorded throughout the major part of the sliding test starting from about 30,000 sliding cycles. This increase in friction is likely the result of the gradual increase of the wear track depth with the number of sliding cycles.

FIB cross sections of the wear tracks formed on carbon fiber reinforced composite after 200,000 sliding cycles in perpendicular direction are presented in Figure 11. Crack formation and pull-out of carbon fibers as well as debonding at the fiber/epoxy interface are very limited. From a geometrical point of view, and based on the previous calculations, the number of fibers per unit of surface area in contact with the stainless steel counter body is much higher for the perpendicular orientation than in parallel and anti-parallel directions. In fact, a simple estimation (see Equations (1-2)) based on the area of the sliding contact indicates that the number of affected fibers differs by about 2 orders of magnitude between parallel and anti-parallel sliding whereas it is very much higher under perpendicular sliding.

The AFM results (Figure 12) show a significant difference in the topography of the wear tracks, although the values of the root-mean-square surface roughness corresponding to the AFM images are very similar, i.e. 113 nm and 121 nm in the case of sliding in ambient air and in demineralized water, respectively. Under ambient air sliding, a clear variation of the relative height of the two components in the composite appears (Figure 12a). After releasing the normal load and due to the load bearing capacity of the matrix and the carbon fibers, the elastic recovery is dissimilar. The surface of the carbon fibers appears flat and smooth, whereas under demineralized water sliding (Figure 12b) it is hard to distinguish the composite components from the profile of the wear track. The non-distinguishable profile characterized by a larger number of height fluctuations can be explained by the scratch effect of the stainless steel counter body ball or by a thin and non-homogeneous transfer film on the contact surface. It is also expected that the fiber orientation influences the entrapping behavior of wear debris occurring on the sliding interface in parallel and anti-parallel sliding directions and thereby it might affect the formation of a transfer film.

3.6. Effect of demineralized water on composite plasticity

The effect of water immersion on the structural changes of the carbon fiber reinforced epoxy composite was done by DSC. Typical DSC scans of the composite material exposed to ambient air and after immersion in demineralized water for 20 hours (i.e., equal to the total duration of the reciprocating sliding tests) are shown in Figure 13. It is concluded that the glass temperature (T_g) diminishes from 125 °C to 120 °C after an immersion for 20 hours in demineralized water. De'Nève and Shanahan concluded that a 1% uptake of water in epoxy resin corresponds to a reduction of 8 °C in T_g [2]. Even in the case of exposure to ambient air, the ordinary water sorption in the free volume of the epoxy network can increase the chain mobility and an overall reduction in T_g is expected.

Nano-indentation tests have been done on the surface of the composite samples in ambient air and after 20 hours of immersion in demineralized water. It is noticed that the immersion in demineralized water reduces the Young's modulus and the nanohardness of the composite material with about 10% and 15 %, respectively (Table 2).

The results obtained in this work are in good agreement with results reported by Tanaka [25] and Lancaster [21]. The wear of carbon fibre-reinforced polymers in water, sea water, or aqueous solutions is generally greater than that obtained under dry wear test conditions. The introduction of water into a polymer/metal sliding contact generally reduces the coefficient of friction, but may increase the wear rate of the polymer. The increase of wear under water immersion is most likely due to a modification of the surface structure of the polymer by water. Two interplaying phenomena are responsible for the surface degradation of the composite, namely the absorption of water and the wear of the top layer. After a number of sliding cycles, the wearing out of the surface by a few nanometers allows water molecules to penetrate into the sample. This accelerates the degradation of the composite material, firstly by plasticization of the epoxy material due to a mixed mechanical and chemical effect, and secondly by loosening the interface between epoxy matrix and carbon fibers. The decrease of the wear resistance of the carbon fiber composite is therefore related to the continuous degradation of the mechanical properties of the material exposed at the surface of the sample due to the infiltration and interaction of water with the epoxy resin. In this respect, Powers reported on a crazing effect onto the epoxy resin caused by a local swelling up on water uptake [26]. Water can also diffuse into the top surface layers by the unoccupied molecular volume of the epoxy resin and the water-polymer affinity due to the hydrophilic centers of the network [15]. Indeed, water is more acidic than the secondary hydroxyl groups and it has a higher electron density than the functional centers of the polymer network. It has been reported that the formation of the bond between OH groups from the polymer network and

water requires breaking of the intramolecular hydrogen bonds between the polar groups of the resin [15]. The hydrogen bonds between water molecules and polar hydroxyl groups of the epoxy network will disrupt the inter-chain hydrogen bonding. A network of fine cracks on the surface of the composite material is then formed, which weakens the top surface of the composite [26]. The rupture of the interchain hydrogen bonding by water molecules would produce an increment of the chain mobility during the glass transition region and a reduction in the effective crosslink density of the material. This reduction weakens the epoxy matrix which may wear off more easily. The immersion of demineralized water can be influenced by either time or/and temperature. The chemical nature of the resin matrix controlled by the curing process will primarily influence the amount of water absorption [27].

The uptake of water, particularly in the case of water immersion, decreases the impact resistance of the composites, and causes a change in fracture characteristics [28]. Water immersion induces a change in fracture mode from a dominant fiber fracture into a dominant fiber delamination. Demineralized water causes an effective loss of the elastic modulus and increases the plasticity of the epoxy resin, which will exhibit visco-elastic behavior. Obviously, the cross sections made in the wear tracks after sliding in demineralized water indicate a less debonding for all sliding directions. In this respect, it has been reported that the interlaminar shear strength of carbon fiber composites increases slightly with a small amount of moisture or water uptake [29-31]. On the other hand, Tanaka [25] suggested that an increase in wear rate can be attributed to the penetration of water into the amorphous regions of semi-crystalline polymers leading to plasticization and enabling polymer fibrils to be detached more easily. Concerning the wear resistance of the composites, a decrease is noticed on sliding in a demineralized water environment (see Table 1). In presence of water, the wear rate is higher than the crack propagation rate and, therefore, the crack propagation is not expressed (Figures 8 and 11b). Different to metals, the crack propagation rate of carbon fiber

reinforced epoxy is then limited. Crack propagation appears after nucleation caused by sliding movement. Once cracks nucleate, the repeated shear stresses lead the cracks to propagate into the weakest regions of the composite whereas in demineralized water, as is shown in Table 1, the wear is higher than in ambient air and it does not let cracks to propagate. The failure mechanism of the composite sample is limited to crack nucleation and high wear: crack nucleation followed by limited crack propagation, crack removal by the high material loss, and (re-) nucleation of cracks at different locations due to the repetitive sliding movements.

Under demineralized water reciprocating sliding in perpendicular direction, water can more easily penetrate into the composite in depth along the fibers via flaws and micro-cracks in the wear track due to a toothbrush effect on the fibers caused by their forward-backward movements. This could explain the higher wear rate for sliding in demineralized water in perpendicular direction as compared to the parallel and anti-parallel orientations.

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CONCLUSIONS

The behavior of unidirectional carbon fiber reinforced epoxy composites under reciprocating sliding has been studied in ambient air or in demineralized water. Reciprocating sliding tests were done along a direction parallel, anti-parallel, and perpendicular to the fiber orientation.

Under sliding in demineralized water, the most severe degradation was observed on sliding in the anti-parallel direction. The sub-surface degradation consisted of a cracking along the fiber/epoxy interfaces, and a partial pull out of carbon fibers. On sliding in parallel direction, a more limited cracking along the fiber/epoxy interfaces was noticed which resulted in a lower wear compared to anti-parallel sliding tests. On sliding perpendicular and off-plane to the fiber orientation, the sub-surface debonding of fibers was most limited. In ambient air, the coefficient of friction varies significantly with the carbon fiber orientation vs. the sliding direction what is linked to the extent that delamination and de-bonding under shearing take place.

In demineralized water, the sliding behavior differs significantly from the one in ambient air. The wear increases for all the three sliding directions. A lowering of the mechanical properties of the epoxy matrix in the presence of water and the resulting increased plasticization explain that. A competition between wearing out and crack growth controls the degradation of the carbon fiber epoxy composites. The lowest sub-surface cracking tendency is noticed under perpendicular sliding. On the contrary, the sliding direction does not significantly affect the coefficient of friction in demineralized water.

The surface and sub-surface degradation of carbon fiber reinforced epoxy under reciprocating sliding in ambient air depends greatly on the sliding directions vs. the fiber orientation. Cracking is the main degradation process under sliding in ambient air, and the sliding behavior is then affected by the rate at which nucleation and propagation of cracks, as well as debonding and pull out of fibers, take place. On the other hand, in demineralized water the level of overall material loss results from the competition between sub-surface crack growth and the wear rate of epoxy matrix and/or carbon fibers at the surface in the sliding track.

REFERENCES

- [1] Pantelakis SG, Katsiropoulos CV, Tserpes KI, Felgeyrolles T. Effect of Water Absorption on Strength of the Aeronautical Composite Material Fiberdux HTA/6376. In: Aliabadi MH, Abela S, Baragetti S, Guagliano M, Lee HS, editors. *Advances in Fracture and Damage Mechanics VIII*. Stafa-Zurich: Trans Tech Publications Ltd; **2010**. p. 457-60.
- [2] De'Nève B, Shanahan MER. Water absorption by an epoxy resin and its effect on the mechanical properties and infra-red spectra. *Polymer*. 1993;34(24):5099-105.
- [3] Hughes JDH. The carbon fibre/epoxy interface—A review. *Compos Sci Technol*. 1991;41(1):13-45.
- [4] Lancaster JK. A review of the influence of environmental humidity and water on friction, lubrication and wear. *Tribology International*. 1990;23(6):371-89.
- [5] Peacuterez-Pacheco E, Moreno-Chulim MV, Valadez-Gonzaacutetelez A, Rios-Soberanis CR, Herrera-Franco PJ. Effect of the interphase microstructure on the behavior of carbon fiber/epoxy resin model composite in a thermal environment. *Journal of materials science*. 2011;46(11):4026-33.
- [6] Moon CW, Jung G, Im SS, Nah C, Park SJ. Effect of Anodic Oxidation of H₂SO₄/HNO₃ Ratio for Improving Interfacial Adhesion between Carbon Fibers and Epoxy Matrix Resins. *Polym-Korea*. 2013;37(1):61-5.
- [7] Peng QY, Li YB, He XD, Lv HZ, Hu PA, Shang YY, et al. Interfacial enhancement of carbon fiber composites by poly(amido amine) functionalization. *Compos Sci Technol*. 2013;74:37-42.
- [8] Varley RJ, Tian W, Leong KH, Leong AY, Fredo F, Quaresimin M. The effect of surface treatments on the mechanical properties of basalt-reinforced epoxy composites. *Polym Compos*. 2013;34(3):320-9.

- [9] Liu P, Guan QB, Gu AJ, Liang GZ, Yuan L, Chang JF. Interface and its effect on the interlaminar shear strength of novel glass fiber/hyperbranched polysiloxane modified maleimide-triazine resin composites. *Appl Surf Sci.* 2011;258(1):572-9.
- [10] Ma KM, Chen P, Wang BC, Cui GL, Xu XM. A Study of the Effect of Oxygen Plasma Treatment on the Interfacial Properties of Carbon Fiber/Epoxy Composites. *J Appl Polym Sci.* 2010;118(3):1606-14.
- [11] Ozcan S, Filip P. Wear Of Carbon Fiber Reinforced Carbon Matrix Composites: Study of Abrasive, Oxidative Wear and Influence of Humidity. *Carbon.* DOI: 10.1016/j.carbon.2013.05.061
- [12] Poodts E, Minak G, Zucchelli A. Impact of sea-water on the quasi static and fatigue flexural properties of GFRP. *Composite Structures.* 2013;97(0):222-30.
- [13] Dhieb H, Buijnsters JG, Eddoumy F, Celis JP. Surface damage of unidirectional carbon fiber reinforced epoxy composites under reciprocating sliding in ambient air. *Compos Sci Technol.* 2011;71(15):1769-76.
- [14] Shim HH, Kwon OK, Youn JR. Effects of fiber orientation and humidity on friction and wear properties of graphite fiber composites. *Wear.* 1992;157(1):141-9.
- [15] Nogueira P, Ramirez C, Torres A, Abad MJ, Cano J, Lopez J, et al. Effect of water sorption on the structure and mechanical properties of an epoxy resin system. *J Appl Polym Sci.* 2001;80(1):71-80.
- [16] Mohrbacher H, Celis JP, Roos JR. Laboratory testing of displacement and load induced fretting. *Tribology International.* 1995;28(5):269-78.
- [17] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic-modulus using load and displacement sensing indentation experiments. *J Mater Res.* 1992;7(6):1564-83.
- [18] Godet M. Third-bodies in tribology. *Wear.* 1990;136(1):29-45.

- [19] Ohmae N, Kobayashi K, Tsukizoe T. Characteristics of fretting of carbon fibre reinforced plastics. *Wear*. 1974;29(3):345-53.
- [20] Jia J, Chen J, Zhou H, Hu L, Chen L. Comparative investigation on the wear and transfer behaviors of carbon fiber reinforced polymer composites under dry sliding and water lubrication. *Compos Sci Technol*. 2005;65(7-8):1139-47.
- [21] Lancaster JK. Lubrication of carbon fibre-reinforced polymers part I—Water and aqueous solutions. *Wear*. 1972;20(3):315-33.
- [22] Clarke CG, Allen C. The water lubricated, sliding wear behaviour of polymeric materials against steel. *Tribology International*. 1991;24(2):109-18.
- [23] Goda T, Váradi K, Friedrich K. Fe micro-models to study contact states, stresses and failure mechanisms in a polymer composite subjected to a sliding steel asperity. *Wear*. 2001;251(1-12):1584-90.
- [24] Harris PJF. New Perspectives on the Structure of Graphitic Carbons. *Critical Reviews in Solid State and Materials Sciences*. 2005;30(4):235-53.
- [25] Tanaka K. Friction and wear of semicrystalline polymers sliding against steel under water lubrication. *Transactions of the ASME Journal of Lubrication Technology*. 1980;102(4).
- [26] Powers DA. Interaction of water with epoxy Sandia report. SAND2009-4405.
- [27] Wright WW. The effect of diffusion of water into epoxy resins and their carbon-fibre reinforced composites. *Composites*. 1981;12(3):201-5.
- [28] Xiao-jun L, Qi Z. Effect of Water Absorption on the Impact Properties of Carbon Fiber/Epoxy Composites. *Chinese Journal of Aeronautics*. 2006;19:14-8. .
- [29] Joshi OK. The effect of moisture on the shear properties of carbon fibre composites. *Composites*. 1983;14(3):196-200.

[30] Selzer R, Friedrich K. Mechanical properties and failure behaviour of carbon fibre-reinforced polymer composites under the influence of moisture. *Composites Part A: Applied Science and Manufacturing*. 1997;28(6):595-604.

[31] Peacuterez Pacheco E, Cauich Cupul JI, Valadez Gonzaacutetez A, Herrera Franco PJ. Effect of moisture absorption on the mechanical behavior of carbon fiber/epoxy matrix composites. *Journal of materials science*. 2013;48(5):1873-82.

FIGURE CAPTIONS

Figure 1. FIB-SEM cross section image perpendicular to a pristine carbon fiber reinforced epoxy sample.

Figure 2. Dissipated energy loops recorded under reciprocating sliding on carbon fiber reinforced epoxy in anti-parallel orientation in (a) ambient air and (b) in water.

Figure 3. Evolution of the coefficient of friction with reciprocating sliding cycles recorded on bulk epoxy in ambient air (dry) and on immersion in demineralized water (wet).

Figure 4. Relative evolution of the coefficient of friction recorded on carbon fiber reinforced epoxy in anti-parallel (a) and parallel (b) orientation in ambient air (dry) and immersed in demineralized water (wet).

Figure 5. FIB cross section images of the wear tracks on carbon fiber reinforced epoxy for anti-parallel sliding in ambient air after (a) 50 cycles (b) 300 cycles (c) 10,000 cycles and (d) 50,000 cycles.

Figure 6. FIB cross sections of wear tracks on carbon fiber reinforced epoxy obtained after 200,000 reciprocating sliding cycles in (a) parallel and (b) anti-parallel direction in ambient air.

Figure 7. ESEM images of the wear tracks on carbon fiber reinforced epoxy obtained after 200,000 reciprocating sliding cycles in ambient air in (a) parallel and (b) anti-parallel direction.

Figure 8. FIB cross sections at the wear tracks obtained on carbon fiber reinforced epoxy after 200,000 reciprocating sliding cycles done in (a) parallel and (b) anti-parallel directions in demineralized water.

Figure 9. Evolution of the coefficient of friction recorded on bulk carbon fibers with reciprocating sliding cycles performed under demineralized water and ambient air sliding in parallel orientation.

Figure 10. Evolution of the coefficient of friction recorded on carbon fiber reinforced epoxy under perpendicular sliding in ambient air (dry) and immersed in demineralized water (wet).

Figure 11. FIB cross section of wear tracks on carbon fiber reinforced epoxy after 200,000 sliding cycles in perpendicular direction performed (a) in ambient air (dry) and (b) in demineralized water (wet).

Figure 12. AFM images and surface height profiles taken from the wear tracks on carbon fiber reinforced epoxy after perpendicular sliding after 200,000 cycles (a) in ambient air (dry), and (b) in demineralized water (wet).

Figure 13. A typical DSC scan of carbon fiber reinforced epoxy after exposure to ambient air of 50% RH and after immersion in demineralized water for 20 hours.

Table 1. Maximum wear track depth (in μm) on bulk epoxy and reinforced epoxy composite for sliding in anti-parallel, parallel and perpendicular directions in ambient air and in demineralized water after 200,000 sliding cycles

Sliding direction	Epoxy	Anti-parallel	Parallel	Perpendicular
Test condition				
In ambient air condition (50% RH, 23°C)	21.4 \pm 3.1	7.1 \pm 2.8	3.9 \pm 1.6	3.4 \pm 1.9
In demineralized water (23°C)	74.7 \pm 4.1	19.3 \pm 3.6	17.9 \pm 2.8	21.5 \pm 3.8

Table 2. Young's modulus and nanohardness of the carbon fiber reinforced epoxy composite top surface in ambient air and after 20 hours immersion in demineralized water

Mechanical properties	Young's modulus	Nanohardness
Test condition	(GPa)	(MPa)
In ambient air condition (50% RH, 23°C)	18.1 \pm 2.1	1476 \pm 171
After 20 hours immersion in demineralized water (23°C)	16.5 \pm 2.4	1250 \pm 169

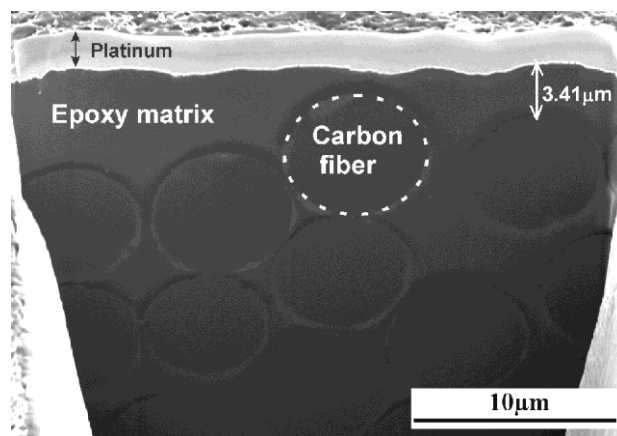


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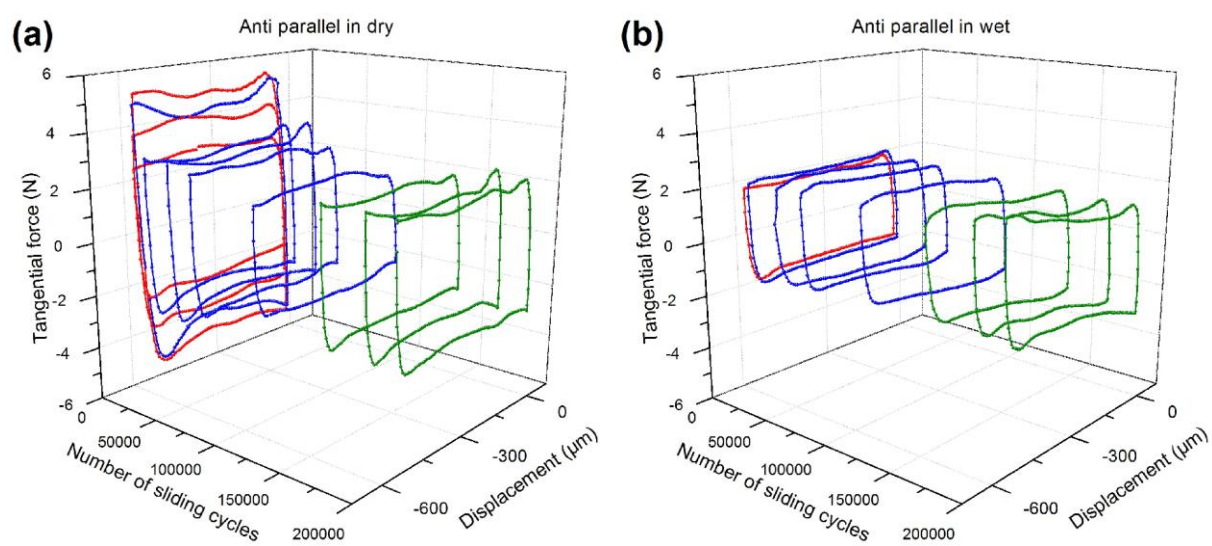


Figure 2.

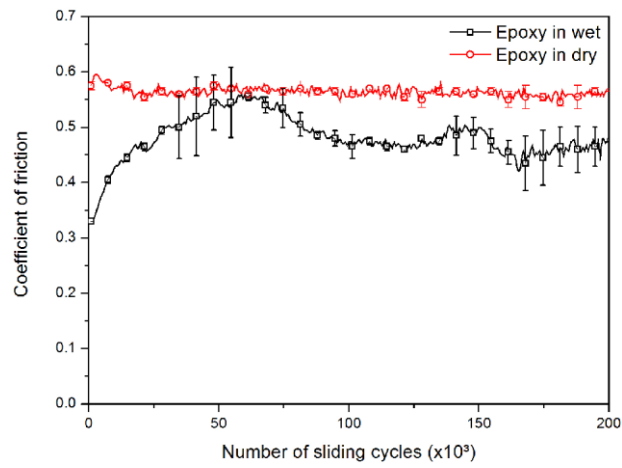


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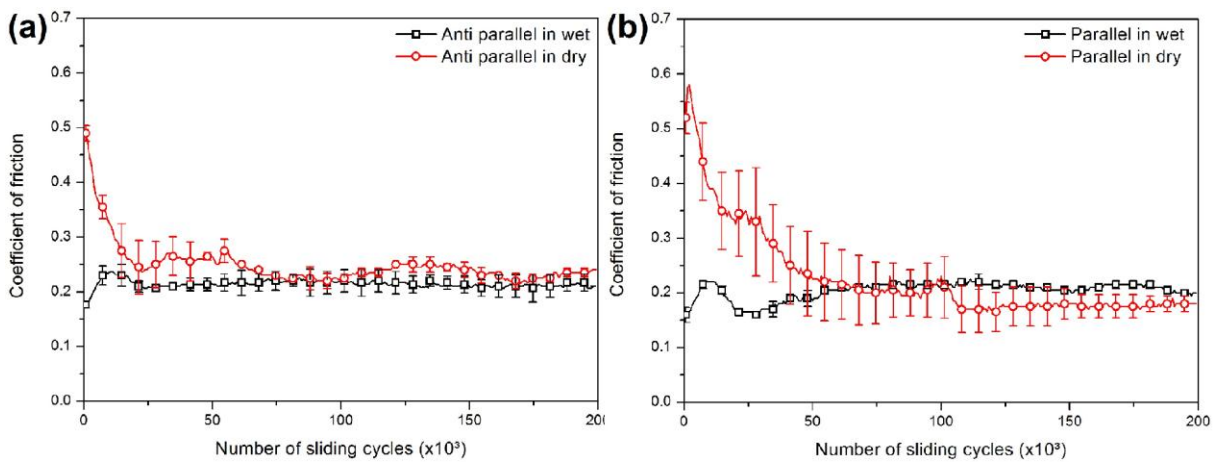


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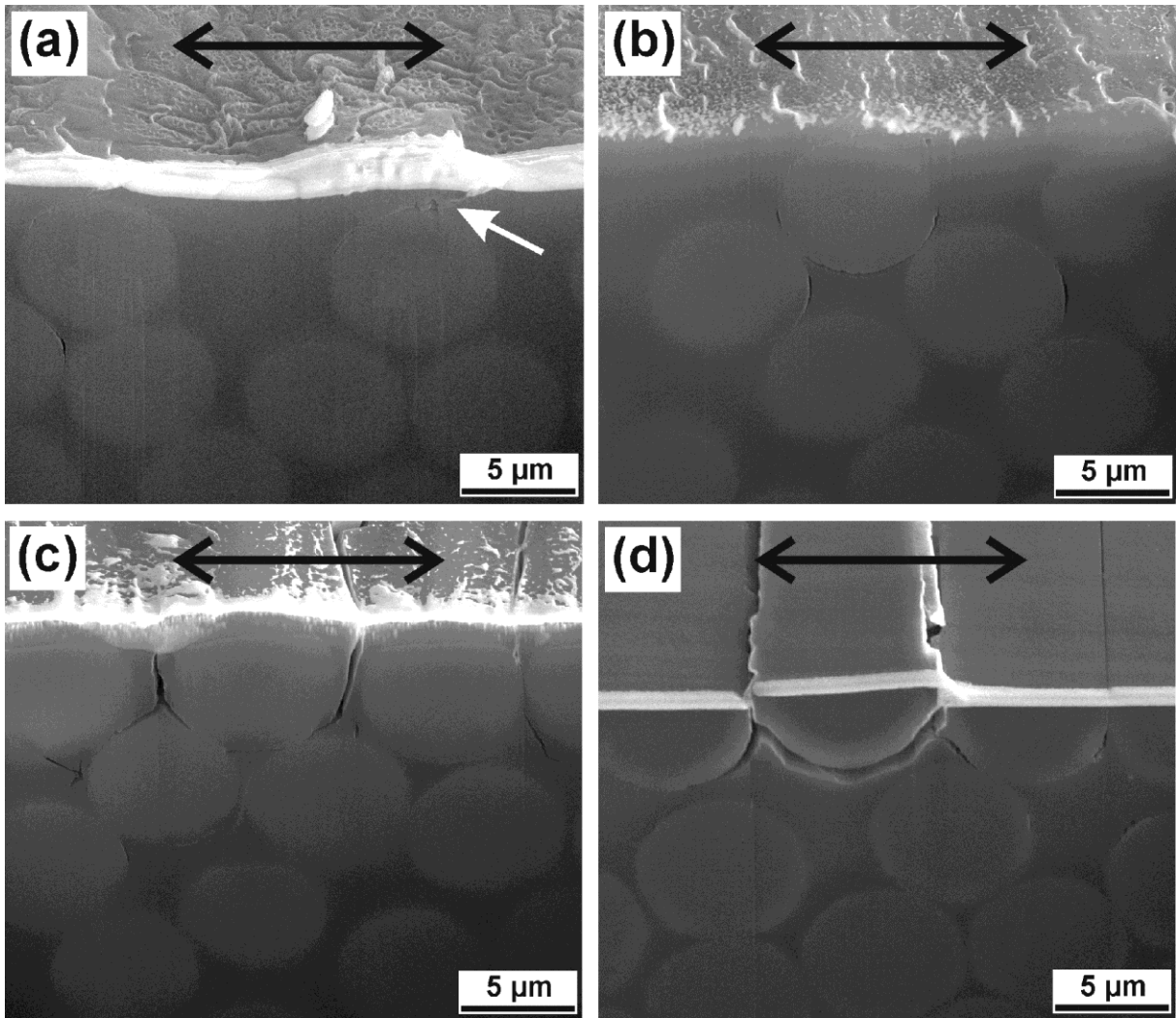


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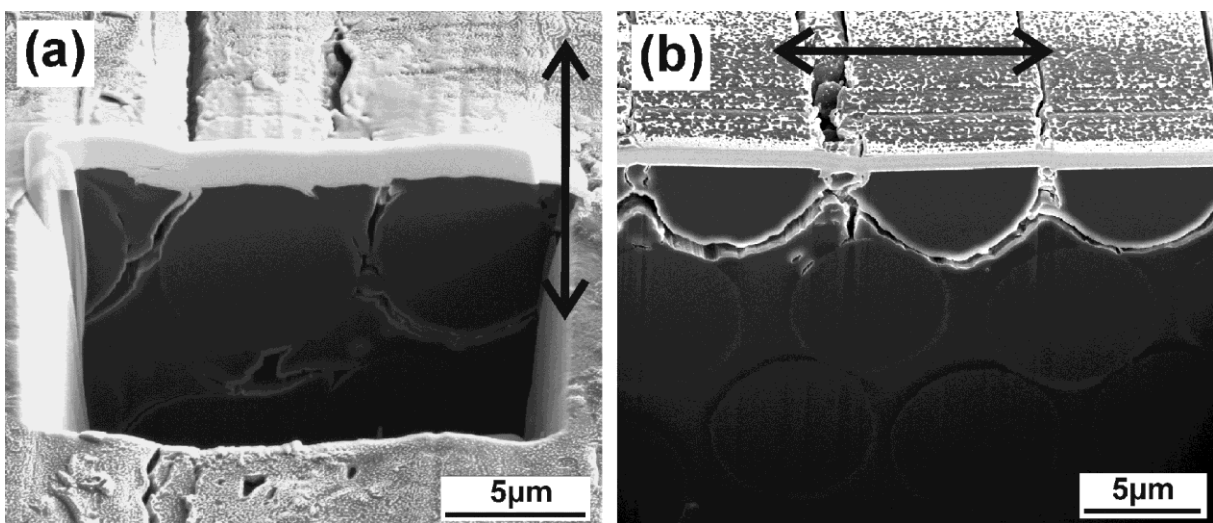


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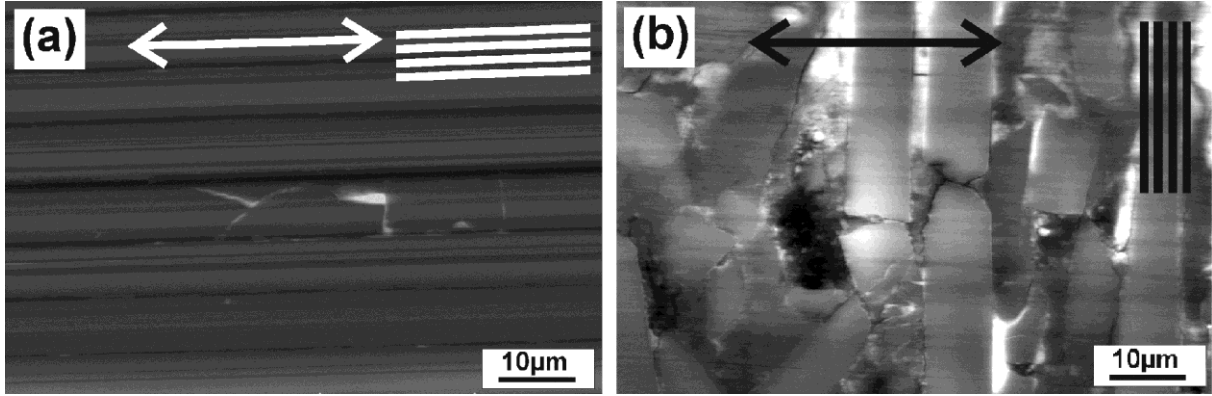


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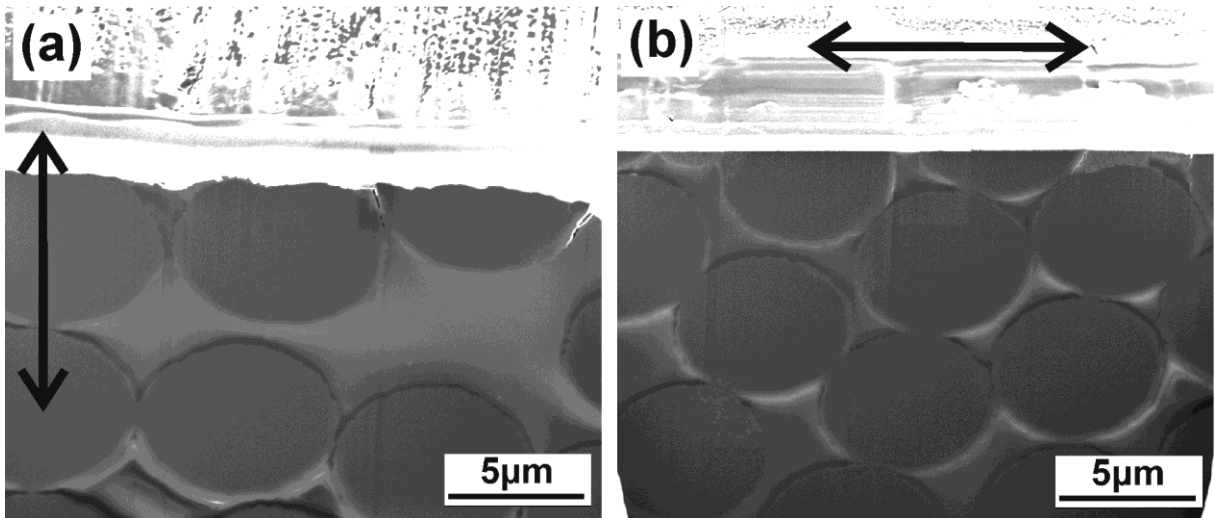


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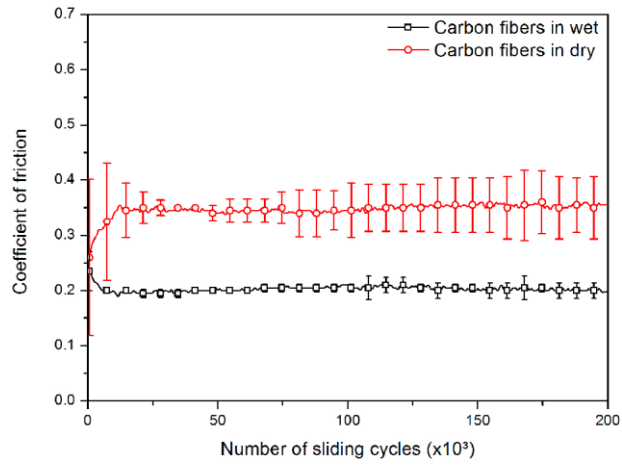


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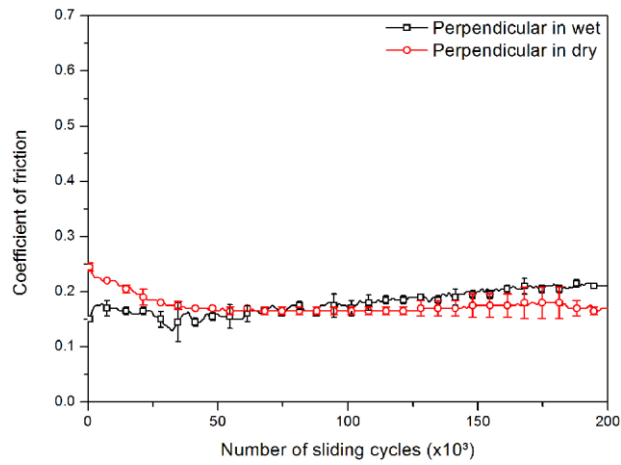


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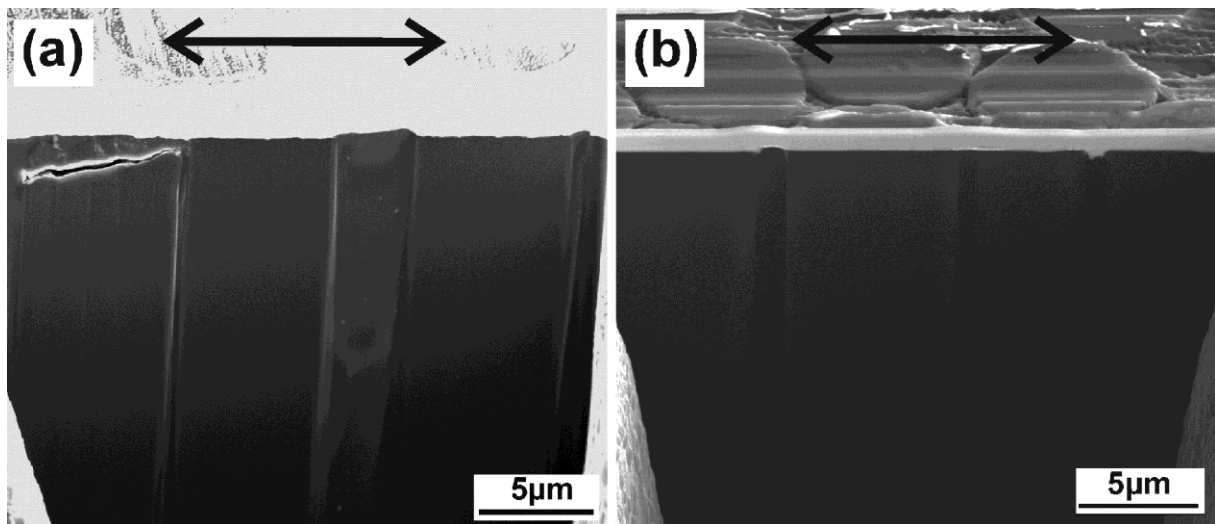


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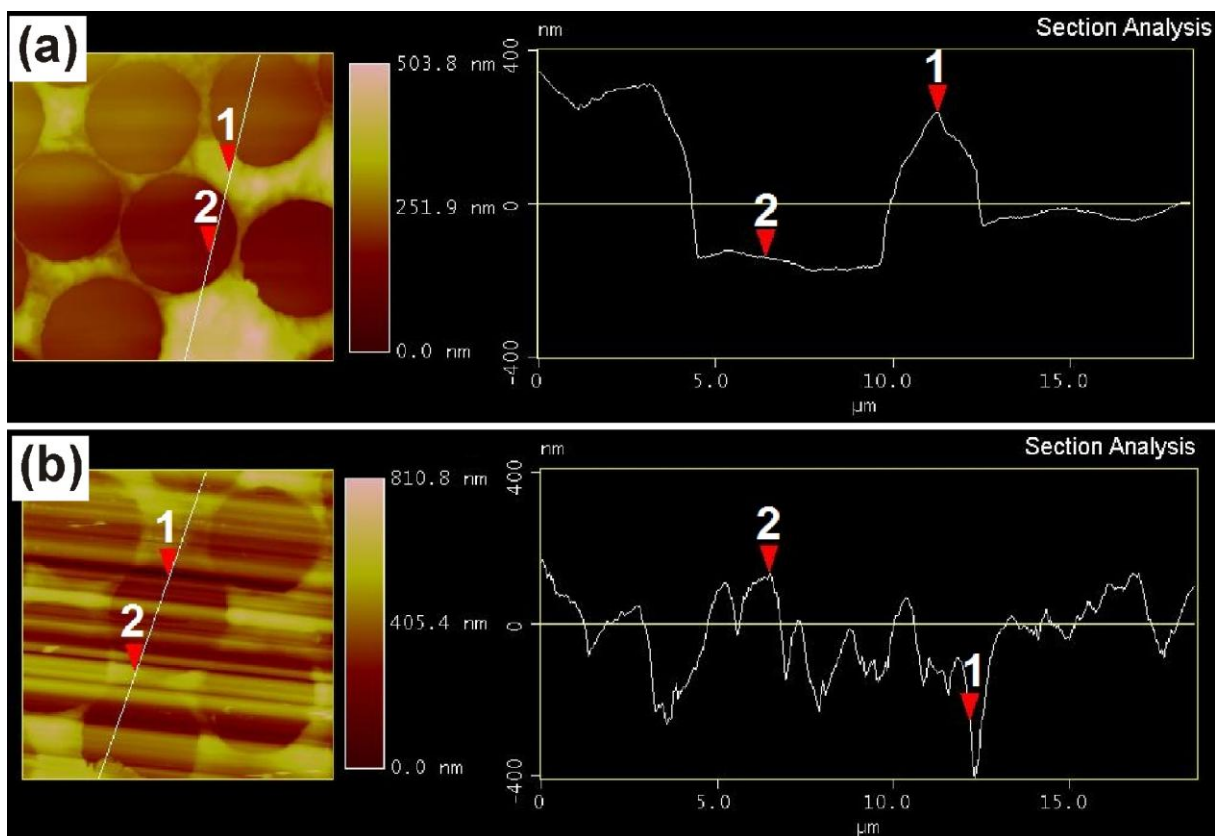


Figure 12.

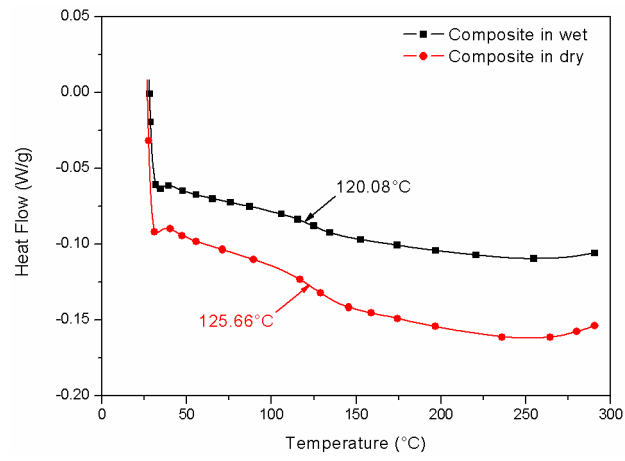


Figure 13.