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Published version:

DOI:10.1016/j.wear.2018.05.005

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Abstract

Wear is among the main factors affecting the performance of artificial couplings in joint arthroplasty. In the attempt of investigating the applicability of PEEK and CFR PEEK in such applications, wear behavior of three medical grade PEEK formulations (unfilled PEEK, 30% wt. pitch carbon fibre reinforced PEEK and 30% wt. PAN carbon fibre reinforced PEEK) have been tested under dry and bovine serum lubricated conditions in a pin on flat test against Al_2O_3 1/8" spheres, replicating physiological conditions whereas possible. The crystallinity and the resulting mechanical properties of the three selected material were differentiated by annealing treatments performed at 200, 250, and 300°C. All the specimens were tested under both lubrication regimes.

The observed coefficient of friction variations, as well as the calculated volumetric wear rate, displayed an improved wear behavior of the reinforced formulations in both dry and bovine serum. Correlation among the modified material properties by annealing and the wear behavior was possible. The formation of a lubricating film was identified as responsible for an improved wear performance of PEEK and CFR PEEK formulations.

Introduction

Aging demographics and an increasing demand for an active life until later stages of life is continuously challenging the Total Joint Replacement (TJR) market [1]. Current solutions have often demonstrated to be subjected to failures and research in the field has been directed towards improving the characteristics of artificial replacements [2]. In particular, concerning the large joint applications, wear of Ultra-High-Molecular-Weight-Polyethylene (UHMWPE) is among the most significant factors affecting the long term duration of TJR [3].

Research clearly demonstrated that radiation-induced crosslinking can greatly improve UHMWPE wear resistance [4], but at the same time the involved chain scission creates active sites for potential oxidation of the material [5]. However, despite all the efforts to improve UHMWPE characteristics, including post-irradiation thermal treatments and anti-oxidant additivation [6, 7], the clinical performance of the newly developed formulations is still experiencing issues related to the loss of properties and wear [8].

In particular, specific applications such as knee and hip joints, where high conforming couplings and equally high applied loads induce a severe mechanical loading on the coupling components [9], it has been shown how crosslinked UHMWPE is prone to fracture [10, 11, 12, 13] as a result of its poor fatigue resistance, especially in its crossinked formulations as both the generated network of polymer chains and the post-irradiation thermal treatments decrease its capacity to withstand cyclic loading [14, 15].

As a result, despite the clear improvements in wear resistance, there is still concern in adopting crosslinked UHMWPE materials in high demanding applications, particularly in knee arthroplasty [9].

Alternative materials have been proposed to replace UHMWPE components for improving wear performance, and among those, Poly-Ether-Ether-Ketone (PEEK) and particular formulations of short Carbon Fibre Reinforced (CFR) PEEK are vastly studied [16].

PEEK is a high performances semicrystalline thermoplastic, whose repeating unit consists in three aromatic units connected by ketone and ether groups. Thanks to its chemical structure, PEEK has demonstrated superior mechanical properties, in particular to static and fatigue loading, and stability up to relatively high temperatures (300°C), as well as resistance to chemical and radiation damage [17]. These properties make the use of PEEK very attractive for highly demanding applications such as medical devices.

To date, its applications are mainly confined to spine and trauma devices, but the use of PEEK and its composites as a coupling material for joint replacement has been also proposed [18].

A large number of studies have been carried out aiming at investigating the wear performance of PEEK and its composites: both simplified wear tests and joint simulator studies have been carried out, with a great variety of couplings tested: predominantly, pin on flat and knee joint simulations against hard metals

(CoCr, Stainless Steels), ceramics (Alumina based), and even PEEK itself [19, 20]. However, the results provided are contrasting, either assessing a better, equal, or lower wear performance in comparison to the conventional UHMWPE reference [21]. Test conditions such as lubrication, applied load, and wear patterns, were greatly varied among those experiments, and might have affected the results to the point that there is still debate on whether those material can be successfully applied in large joint applications.

In fact, although it has been demonstrated that wear rates of CFR PEEK are lower than those of UHMWPE and its crosslinked formulations in numerous comparative studies [22, 23, 24, 25, 26, 27, 28], there is recent evidence supporting how more severe loading conditions and increased contact pressures can play a detrimental role in relation to CFR PEEK wear resistance [9, 29].

Additionally, debates on the biological response on PEEK and CFR PEEK have been raised. Despite carbon fibres are known to have excellent adhesion to the PEEK matrix and thus are unlikely to be responsible for the observed phenomena [30], contrasting results on inflammatory response following exposure to PEEK and CFR PEEK wear particles were observed [31, 32].

Therefore, especially in light of their potential to be used to replace UHMWPE in orthopaedic applications, there is great interest in better assessing the wear behavior of such materials.

As reported, a wide range of materials and conditions has already been investigated [22, 23, 24], however there are several aspects of PEEK and CFR PEEK that are still unexplored and require further attention.

As an example, it has been demonstrated that PEEK and CFR PEEK properties vary according to the crystallinity percentage and the processing conditions to obtain such materials [33].

Poor or little information is present correlating such variations, despite the large amount of papers investigating the wear behavior of PEEK and reinforced PEEK materials for a wide range of applications, from polymeric coatings for high temperature bearings to aerospace applications [34, 35]. As a result, the correlation between material characteristics in terms of crystallinity and mechanical properties and PEEK and CFR PEEK wear performance remains largely overlooked.

The aim of this study is therefore to provide data on the wear performance under two lubrication regimes of a range of PEEK and CFR PEEK formulations with different crystallinity and mechanical properties, in an attempt to widen the understanding of PEEK and CFR PEEK wear mechanisms.

By differentiating the material behavior, according to lubrications conditions and material formulation and processing, further support to the investigation on the applicability of these materials in total joint replacements will be provided.

Materials and Methods

Materials

Materials were supplied as granules by Invibio (Invibio Ltd, Lancashire, UK). Materials trade names were Ni1, Ni1CA30 and Motis- an unfilled PEEK, a 30% wt. PAN carbon fiber and a 30% wt. pitch carbon fibre reinforced PEEK composite, respectively. All materials were biomedical grade formulations with a well-known history of biocompatibility and biological safety [16, 18].

The carbon fibre of Ni1CA30 and Motis are different for mechanical properties and dimensions [36], and impart different mechanical properties to the two carbon fibre reinforced PEEK formulations [37]. It was also noticed that PAN and pitch carbon fibres differ in diameter, therefore the number of fibres within the two different CFR PEEK formulation has been shown to vary, influencing the material crystallization behavior and the final mechanical properties [38].

Sample preparation consisted of various steps: granules were preheated to 70°C to remove the residual moisture, and then injection molded into 250x25x2.5mm specimens. Nozzle temperature was maintained at 400°C, higher than the PEEK matrix melting temperature T_m (343°C), to facilitate material flow in the mold, which was maintained at 250°C.

The polymer flow and the friction between the molten material and the mould walls in the injection moulding process resulted in fibre dispersion and ultimately in a non uniform directionality of the reinforcement phase within the realized samples, with randomly oriented fibres for both PAN and pitch formulations as already shown elsewhere [36].

The crystallinity of the three PEEK injection molded samples formulations was then differentiated by annealing treatments. The chosen annealing temperatures were 200, 250, and 300°C, respectively. Specimens were heated up at a constant rate of 5°C/min in a programmable B180 oven (Nabertherm, D), held at the chosen temperature for 5h, and then air cooled to 20°C. Further details are reported elsewhere [33]. These treatments have shown to significantly differentiate crystallinity and the resulting mechanical properties for all the tested formulations [33], imparting microstructural changes that result in an increase of the overall polymer crystallinity and in a rise of mechanical properties and Elastic modulus, regardless the polymer formulation. An indication on relevant properties and their variation according to the annealing temperature for all the material formulations considered is provided in Table I.

Table I. List of the tested specimens and relative properties in function of the annealing conditions [33].

Material	Annealing T [ºC]	Crystallinity [%]	Flexural peak load [N]	E [GPa]	HV hardness
Unfilled PEEK (Ni1)	0	31.9±0.4	116	5.2±0.3	20.6±3.4
	200	32.8±0.1	121	5.4±0.2	21.3±3.7
	250	35.3±0.4	131	5.5±0.2	22.1±2.5
	300	40.5±0.6	136	5.5±0.1	23.2±1.2
30% pitch CFR PEEK (Motis)	0	31.5±0.1	327	5.8±1.3	28.3±0.6
	200	31.9±0.3	324	5.9±0.7	29.2±0.7
	250	34.9±0.1	354	6.1±0.6	30.8±1.8
	300	39.6±0.3	367	6.5±0.6	32.4±0.4
30% PAN CFR PEEK (Ni1CA30)	0	32.3±0.1	455	5.9±1.2	29.4±1.1
	200	33.7±0.7	462	6.0±0.3	29.5±0.8
	250	36.7±0.5	472	6.2±0.7	31.5±1.4

	300	42.1±0.5	497	6.7±0.6	33.8±2.2

After annealing, specimens were cut into 30x20mm plates from the injection molded samples. Water jet machining was used so as to limit any cutting stress to the material. A complete list of the tested specimens is reported in Table II. All samples exhibited the same surface roughness after machining, with Ra values ranging from 0.3 to 0.35µm.

Table II. List of the tested specimens and the annealing conditions.

Material	Fibre characteristics [20]	Annealing T [ºC]	Sample name
Unfilled PEEK (Ni1)	Unfilled	0	Ni1-0
		200	Ni1-200
		250	Ni1-250
		300	Ni1-300
30% pitch CFR PEEK (Motis)	Pitch (10±1µm diameter, 230±13 µm length)	0	Motis-0
		200	Motis -200
		250	Motis -250
		300	Motis -300
30% PAN CFR PEEK (Ni1CA30)	PAN (6±1µm diameter, 230±23 µm length)	0	Ni1CA30-0
		200	Ni1CA30-200
		250	Ni1CA30-250
		300	Ni1CA30-300

Wear testing

A CTER UMT-3 tribometer (Bruker, US) in a ball on flat configuration was used to perform the wear tests. The counterpart material consisted in an Al_2O_3 1/8" diameter sphere, as already experimented elsewhere [23, 24, 39]. The instrument has been equipped with a 2 axis load cell with a maximum payload of 10N in order to acquire the Fx and the Fn load simultaneously.

Ball-on-flat configuration has been chosen as it has already demonstrated to be a widely accepted method for screening and discrimination of wear properties among different materials [40]. Coupling with Al_2O_3 was chosen to replicate the well-known joint configuration and according to what already suggested in the literature for similar studies [23, 24, 41], since the use of hard metals in large joint couplings have raised concerns in terms of metal ions production and release, causing adverse tissue reactions up to, in some cases, the components recall [42].

Test was carried out at 37±2°C, in both dry conditions and in bovine serum lubrication regime. Bovine serum was additivated with 20mM of an EDTA solution (50% in ISO2 pure water), corresponding approximately to 7.5g/l, and with 0.2%vol Sodium Azide to prevent protein degradation, as prescribed by the reference standards [43]. The effect of bovine serum against dry conditions was evaluated, so as to investigate any potential in vivo scenario that might arise from the physiological ambient in terms of lubrication regime.

Indications from the literature on similar studies reported a broad range of applied loads for similar test configurations, with no clear indication on the optimal contact stress to be generated for accurately replicate the physiological conditions [44, 45, 46].

Physiological conditions are considered in wear simulation studies, however test conditions are device specific and therefore do not apply for the purpose of this study [47].

Moreover, in light of the considerations on the influence of the applied load on wear performance on PEEK and CFR PEEK [29, 48], it was decided to consider a more demanding test configuration for the performed comparisons.

This is considered to be in line of what already reported in the literature around PEEK and CFR PEEK wear under similar premises [39, 49, 50].

A 5N load was applied to the Al_2O_3 pin with a 10N calibrated load cell to induce an elasto-plastic damage of the polymer bearing surface, with the aim of obtaining a visible damage in the tested specimens by subjecting the material to non elastic conditions, replicating what already observed in orthopaedic joint polymer couplings [51, 52] and in similar studies [44, 45, 46]. Stroke length was 22mm (linear) with a frequency of 1Hz. Multi-directional sliding was not considered to be a discriminatory test condition given the much larger influence of the reinforcements orientation on the wear behavior of the tested materials, here randomly dispersed as already indicated [36, 53]. Test duration was initially 2h, for a sliding distance of 320m. A total amount of 5 specimens was used for each test configuration, so as to provide statistical significance to the obtained results. Some of the tested specimens were then further tested for a total time of 24h and a sliding distance of $3.8x10^6$mm, to simulate the long term performance of the selected coupling.

Coefficient of friction (COF), constantly monitored during the test, was determined by considering the normal load applied and the measured force for sliding motion between the sample and the Al_2O_3 counterpart, as the ratio

$$COF=Fx/Fn \quad (1)$$

Where COF is the coefficient of friction, F_n is the applied load, and F_x the measured sliding force. The data acquisition, for the whole test duration, was 2 points/sec.

The average COF has been calculated as the arithmetic mean between 1800s and 7200s. The 1800s time point has been selected because it is when all the specimens finished the initial run in time. Wear rate was determined by means of volumetric loss assessment obtained from stylus profilometry (Veeko Dektak 150, Veeko HK) measurements [19] after the test end (2h), and every 8h during the long term evaluation.

Six profilometer measurements were performed along the perpendicular direction in respect to the wear track every 3.2mm throughout the entire length of the damaged area. Profile variations indicated the material removal due to the sliding motion between the counterparts, and represented the worn area across the examined cross section. Volume loss has been calculated as the product between the average worn area, calculated by means of profilometer measurements, and the stroke length. An illustration of the measuring method is given in Figure 1.

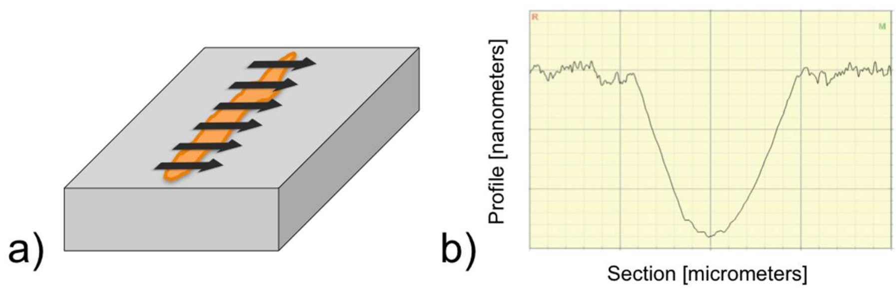


Figure 1. a), profilometry measurement scheme. The profilometry scan directions across the wear track are indicated by the arrows; b), recorded profile for the volumetric material loss calculation, as collected.

Wear rate was then calculated as

$$W = Va/(SxFn) \qquad (2)$$

where W is the wear rate, V_a is the removed material volume, S is the sliding distance and F_n is the applied load.

Scanning electron microscopy was performed with a Zeiss Evo 40 SEM (Zeiss, Oberkochen, D) and was used for evaluating the wear track for each tested specimen and also for the debris analysis, giving particular emphasis to the presence of naked carbon fibers within the generated debris that might enhance the adverse human body response [31, 54]. The SEM analyses have been performed using a secondary detector in order to better evidence the wear track morphology. Measurements have been carried out in high vacuum conditions.

At the end of the wear test, stereoscopic evaluation of the counter surface (Olympus SZX 7) has been performed as well, to investigate the effect of the sliding motion and assess any presence of marks, scratches and other forms of surface damage on the Al_2O_3 spheres.

Results

The measured friction coefficient (COF) values as a function of the wear test duration for each tested specimen is reported in Figure 2 and in Figure 3, for dry and lubricated (bovine serum) conditions, respectively.

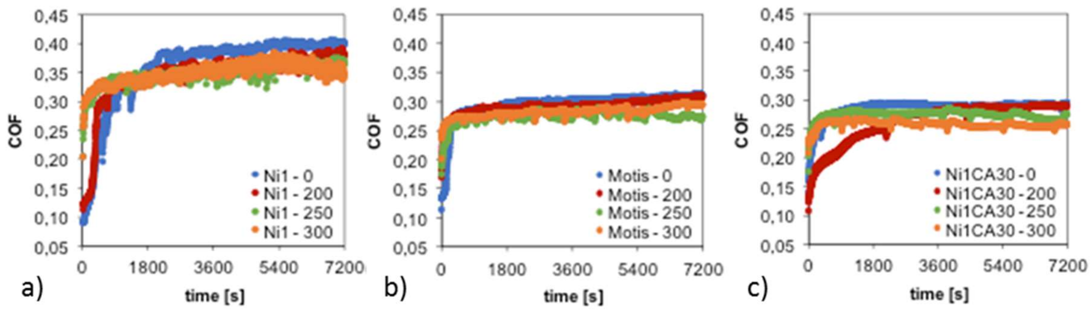


Figure 2. friction coefficient trend for Ni1 (a), Motis (b), and Ni1CA30 (c) in dry conditions for the entire wear test duration.

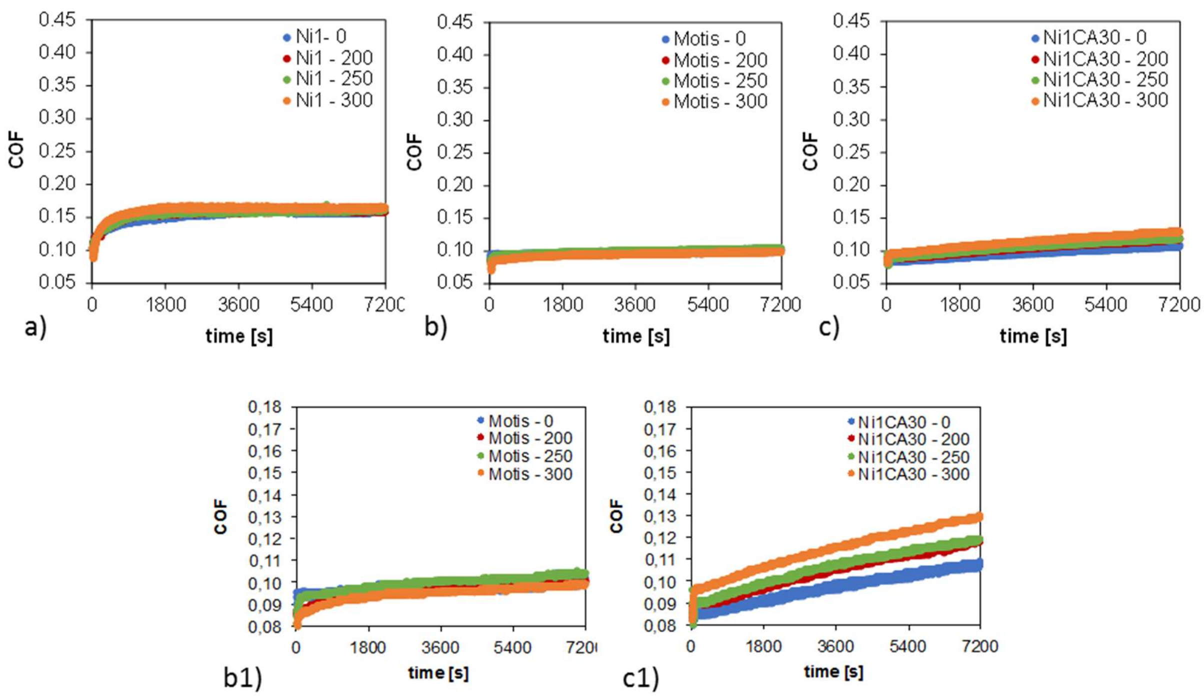


Figure 3. friction coefficient trend for Ni1 (a), Motis (b), and Ni1CA30 (c) in lubricated conditions (bovine serum) for the entire wear test duration; and magnification of Motis (b1) and Ni1CA30 (c1) data.

In dry conditions, COF increases within the first few cycles and reaches a plateau for each material considered. The reached value is lower for CFR PEEK when compared to Ni1.

On the contrary, in lubricated conditions COF differentiated among the three considered materials. In fact, while Ni1 unfilled PEEK friction coefficient trend did not vary compared to dry conditions, since it exhibited a plateau after the first run-in wear cycles, even if at halved values in respect to dry conditions, for Motis and Ni1CA30 CFR PEEK COF was found to raise steadily over time. Moreover, Motis CFR PEEK exhibits a slightly lower friction coefficient than Ni1CA30, which, in addition, showed a more pronounced increase with prolonged test durations. Ni1 unfilled PEEK registered the highest COF value among the three materials considered in both dry and lubricated conditions.

Under dry conditions, COF varied slightly according to the annealing treatment considered, from 0.389±0.010 to 0.356±0.010 for Ni1-0 and Ni1-300, from 0.389±0.010 to 0.286±0.006 for Motis-0 and Motis-300, and from 0.291±0.002 to 0.258±0.003 for Ni1CA30-0 and Ni1CA30-300, respectively.

COF variation in the lubricated regime observed was significantly lower: the measured friction coefficient ranged from 0.157±0.003 to 0.164±0.001 for Ni1-0 and Ni1-300, from 0.099±0.002 to 0.096±0.002 for Motis-0 and Motis-300, and from 0.100±0.004 to 0.118±0.006 for Ni1CA30-0 and Ni1CA30-300, respectively. Figure 4 reports the observed COF variations for all the tested materials as a function of the annealing temperature.

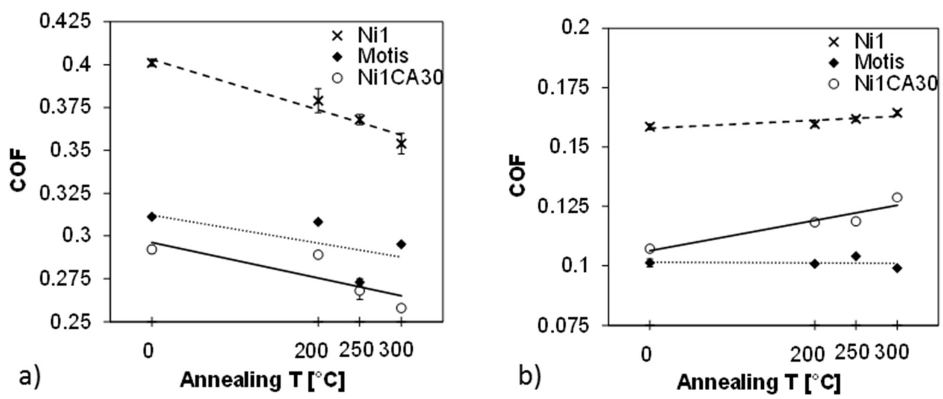


Figure 4. friction coefficient trend for Ni1, Motis, and Ni1CA30 in dry (a) and lubricated (b) conditions as a function of the annealing treatment temperature.

Under dry conditions, the wear rate of Ni1 unfilled PEEK ranged from 9.69±2.21 to 124.67±5.80mm^3/Nm for the untreated and the 300°C annealed conditions, respectively; while under bovine serum lubrication regime, the wear rate decreased to 5.84±1.04 and 7.89±0.70mm^3/Nm, respectively. For the CFR PEEK instead, wear rate under dry conditions varied from 2.23±0.57 to 6.92±0.96mm^3/Nm, and from 1.36±0.59 to 4.33±0.82mm^3/Nm, for Motis and Ni1CA30 materials in untreated and 300°C annealed conditions, respectively; while under bovine serum lubrication regime, wear ranged from 2.88±0.33 to 3.43±0.50mm^3/Nm, and from 1.85±0.18 to 4.16±1.00mm^3/Nm, respectively. Wear rates of the tested configurations are reported in Figure 5.

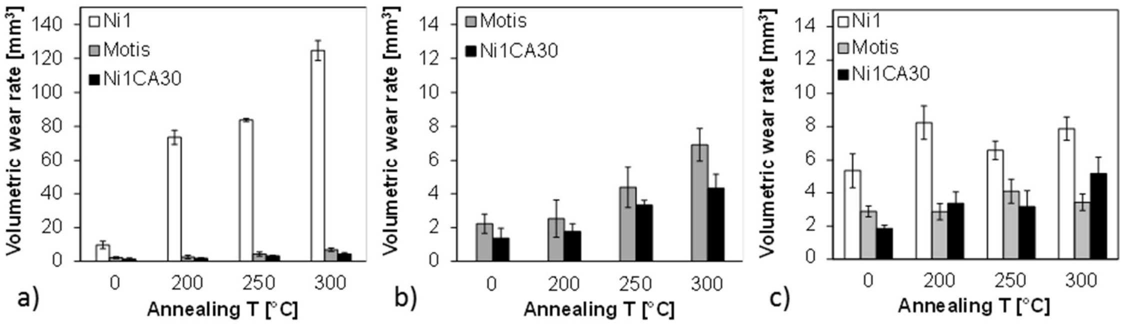


Figure 5. from left to right: calculated wear values for Ni1, Motis, and Ni1CA30 in dry conditions (a), and detailed magnification for Motis and Ni1CA30 (b); and wear values for Ni1, Motis, and Ni1CA30 in lubricated conditions (bovine serum, c).

Figure 6 reports the SEM images for each tested material after the wear test performed under dry conditions.

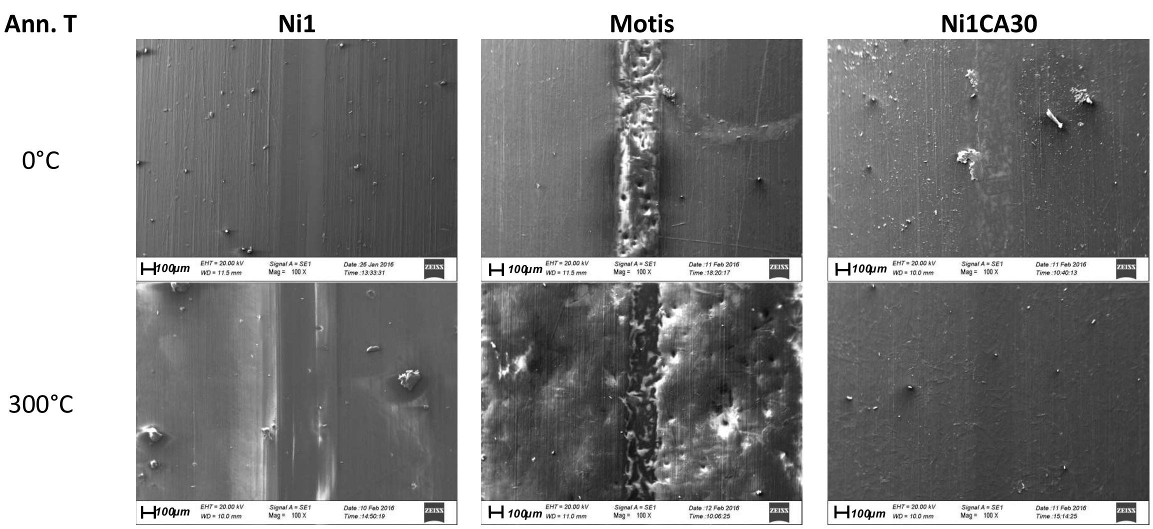


Figure 6. wear tracks of Ni1, Motis and Ni1CA30 at 0 and 300 C annealing temperatures under dry conditions at low magnification (100x).

Plastic deformation within the polymer matrix and a deep debris layer with material removal in the wear track was observed, and is detailed in Figure 7 and 8 where these phenomena are clearly visible. Higher magnification images for Ni1 material were used in order to better appreciate the phenomenon.

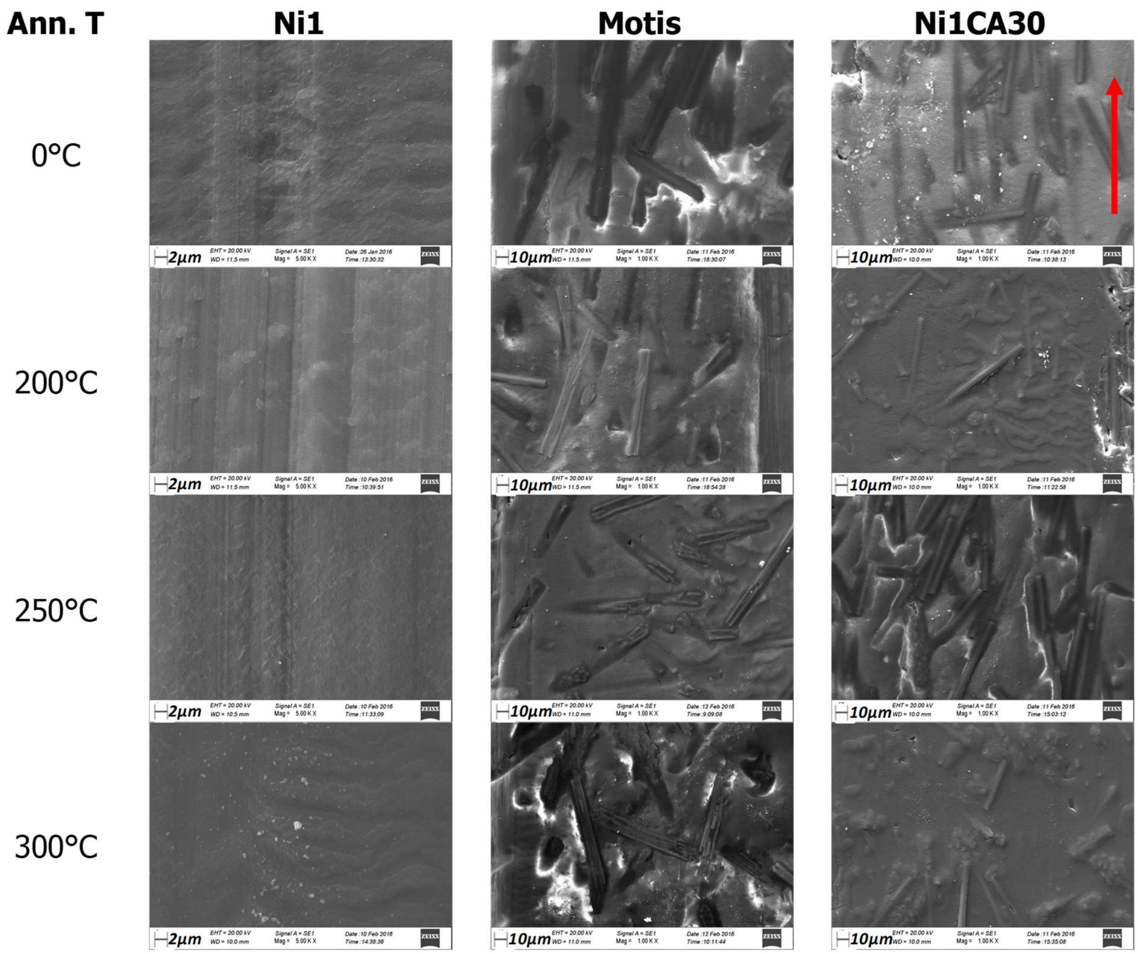


Figure 7. SEM micrographs of Ni1, Motis, and Ni1CA30 after the wear test under dry conditions, showing the wear tracks. The arrow indicates the sliding motion direction.

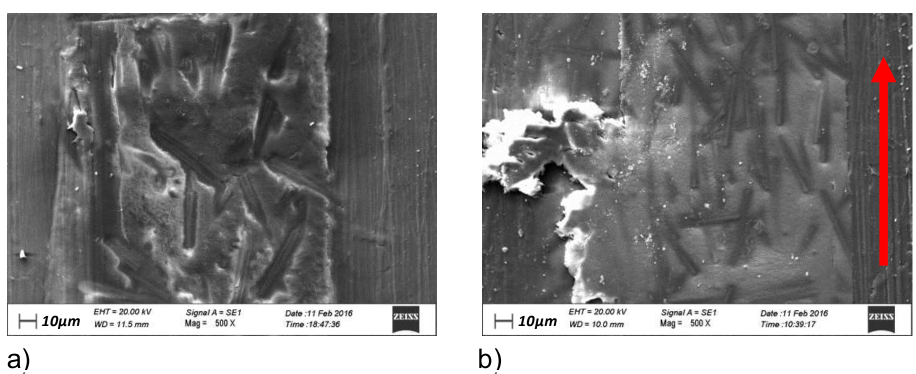


Figure 8. SEM micrographs showing material removal at the wear track border in Motis (a) and Ni1CA30 (b) after the wear test under dry conditions. The arrow indicates the sliding motion direction.

Under bovine serum conditions, instead, only debris formation and an early stage delamination effect can be observed. Moreover, in some areas of the CFR PEEK materials, fiber rupture has been individuated,

particularly for Ni1CA30. Nevertheless, fibres remained embedded within the polymer matrix for both CFR PEEK formulations, showing no significant evidence of detachment or removal.
Macroscopic wear tracks, images of each investigated material after the wear test performed under bovine serum conditions and the observed details of fiber appearance for the two CFR PEEK tested formulations are reported in Figure 9, 10 and 11, respectively.

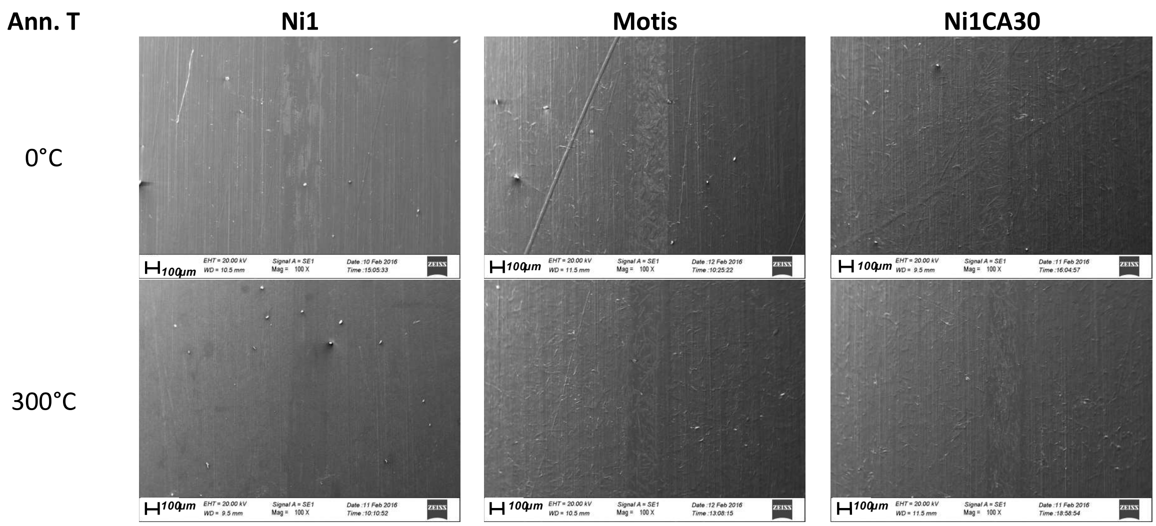


Figure 9. wear tracks of Ni1, Motis and Ni1CA30 at 0 and 300 C annealing temperatures under lubricated conditions at low magnification (100x)..

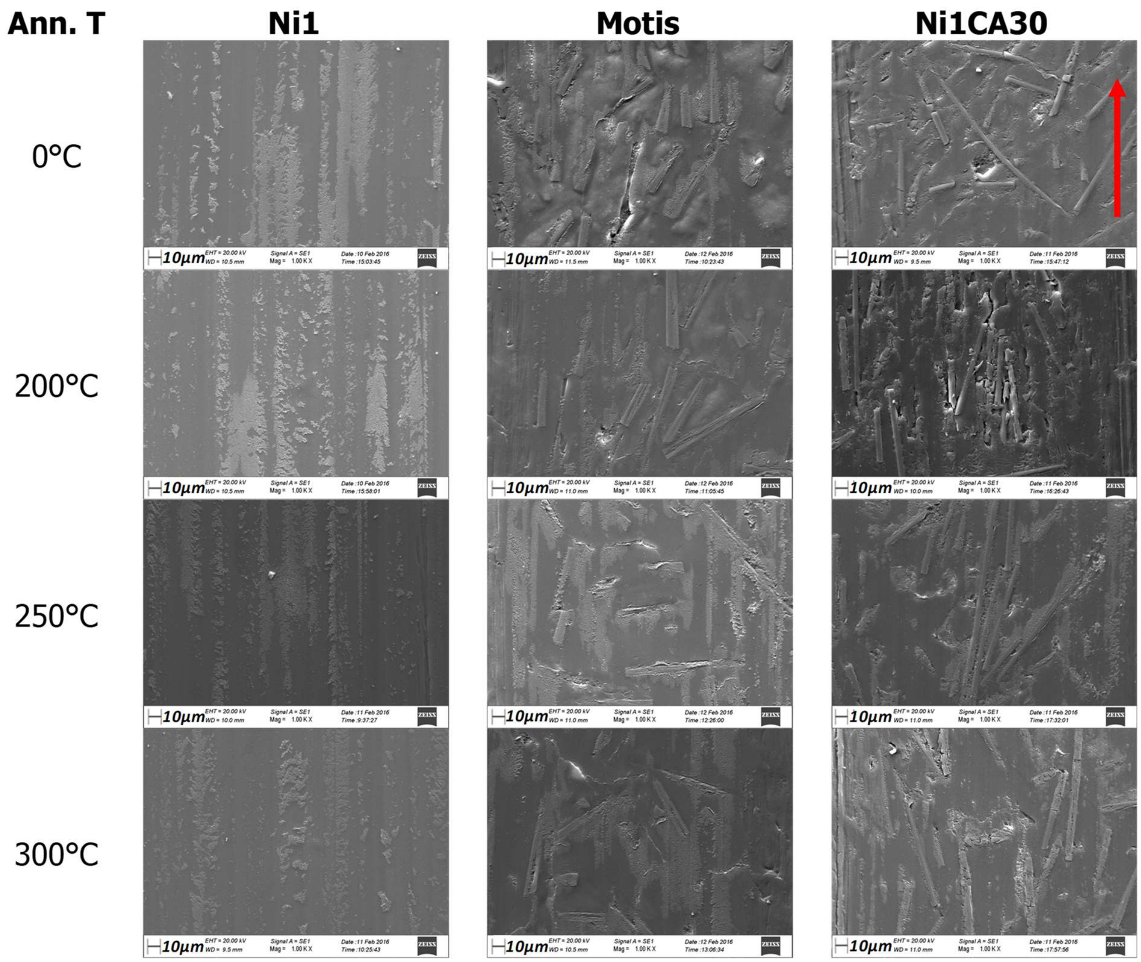
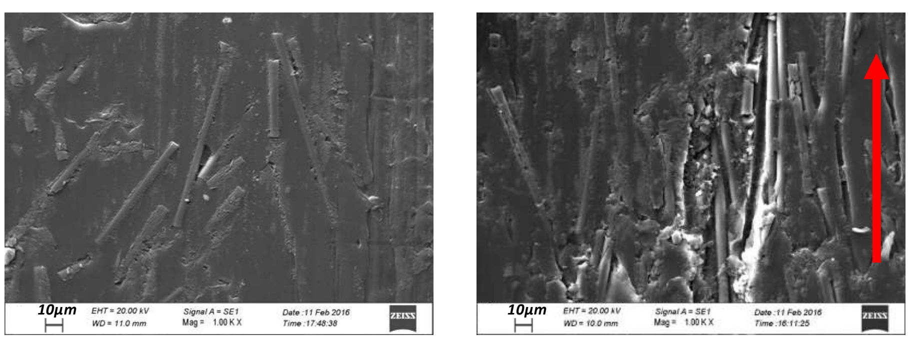


Figure 10. wear track images after wear test under bovine serum conditions for Ni1, Motis, and Ni1CA30 materials in all the tested formulations (untreated, 200, 250 and 300°C annealed). The arrow indicates the sliding motion direction.



a) b)

Figure 11. fiber appearance in Motis (a) and Ni1CA30 (b) samples, respectively, after the wear test in bovine serum. The arrow indicates the sliding motion direction.

Figure 12 and Figure 13 illustrate the Al_2O_3 counterpart and the typical debris observed after the wear test, respectively. Pins showed no sign of damages or scratches and no isolated carbon fiber within the analyzed debris collection were retrieved, indicating that the counterpart material, either PEEK of CFR PEEK, did not affect the surface appearance of the pin.

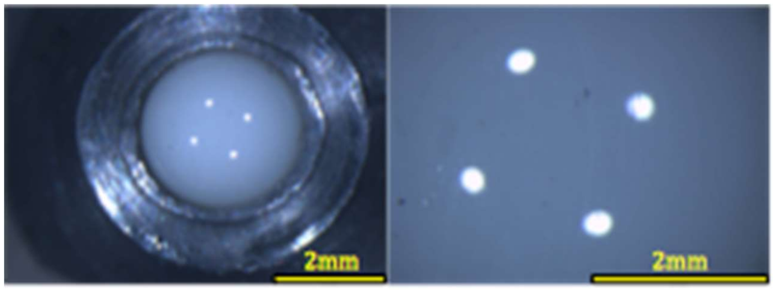


Figure 12. Al_2O_3 ball head after the wear test at different magnifications.

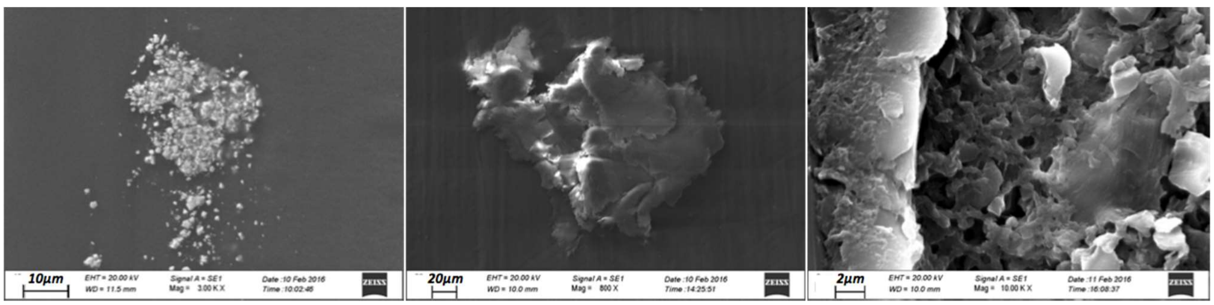


Figure 13. typical debris observed for each tested condition for unfilled (Ni1, left) and CFR PEEK (Ni1CA30, middle and right). No sign of fiber pull out could be observed.

Discussion

It has been reported in the literature that COF can give information about the wear mechanisms occurring during the tribological contact of two counterfaces [42]. Some authors further suggest that COF variation depends on three separate factors: the material roughness Ra and its evolution over time (i), the presence of third body particles (ii), and the formation of a boundary lubrication film between the two sliding counterfaces (iii) [55].

It has been shown that protein adsorption, boundary lubrication, and tribological properties are intimately connected [56]. Adsorption of proteins contained in the lubricant has been proposed as one of the main discriminant among differentiation of frictional and wear properties in orthopaedic bearings [57], by adhering on the materials' bearing surfaces and forming a solid like film interposing between the rubbing surfaces [57].

The formation of the solid like film can either hinder or facilitate the creation of a continuous lubricant film, contributing to increase or decrease tribological properties of the tested bearings, respectively [58].

The obtained results are in accordance to these theories: the higher COF observed in dry conditions in respect to bovine serum regime indicates that in the latter case a lubricant film formation occurs, reducing the tangential forces and ultimately, the measured friction coefficient (Figure 2 and 3).
The higher values recorded for the unfilled Ni1 PEEK confirm, as reported elsewhere [59], that the carbon fiber reinforcements can act as further lubricant. Differences in COF become more pronounced under bovine serum conditions (Figure 3) with 40% variations vs. 20% variation between Ni1 unfilled PEEK and the two CFR PEEK, indicating that the lubricant effect due to the carbon fiber becomes more important in wet conditions, where the lubricant film formation enhanced by the protein adsorption mechanism is the dominant factor.
Additionally, since COF does not reach a plateau for the CFR PEEK formulations tested under bovine serum conditions (Figure 3), it can be concluded that the boundary lubrication film formed in such conditions is not continuous, presumably due to (i) the own fiber reinforcement presence, that alters the tribological surface continuity, given the fiber-matrix interface asperities presence; and (ii) to the nature of the lubrication regime, presumably not supported by an uniform protein adsorption, resulting in an incomplete lubrication layer formation. In unfilled Ni1 PEEK instead, the steady state COF observed after the initial run in corresponds to the saturated absorption of bovine serum and the formation of a complete boundary lubricating layer, suggesting a difference in material wettability or in the protein substrate adhesion mechanism among the three PEEK formulations considered (Figure 2).
COF variations can give further indication on how surface morphology acts as an additional factor influencing the tribological properties of the tested material [60].
In fact, although all samples exhibited comparable Ra values, they differ in terms of crystallinity and consequently in terms of final mechanical properties (Table I). Material asperities, hardened as a result of the rise in the degree of crystallinity due to the annealing treatment , can decrease the resistance to sliding motion given by the polymer plasticity and the sample-antagonist surfaces interpenetration, leading, ultimately, to a COF reduction (Figure 4).
This occurs in a more pronounced way under dry conditions, where these material surface characteristics are considered to be more relevant since the absence of the boundary lubricating effect derived from the bovine serum medium presence and the resulting diminished interaction among the sliding surfaces [59].
COF variations under lubricated conditions are much less pronounced, with the exception of Ni1CA30, which showed on the contrary a COF increase, presumably due to the potential chemical degradation of the lubrication media under the tribological contact and the arising temperature and stress factors.
For all the considered material formulations, it was found that annealing treatment results in higher wear rate if compared to the untreated samples (Figure 5). This might be caused by the observed variation in the polymer properties, whose hardened structure (Table I) presumably enhanced the second body particle abrasion, implying debris formation as already reported elsewhere [19]. Wear rate under bovine serum conditions is lower than under dry sliding conditions for Ni1 unfilled PEEK, suggesting that the fluid film

formation has an impact in enhancing both the lubrication of the tribological contact and the heat transfer within the sliding surface, as already observed elsewhere [55], reducing the heat related damage in the polymer. In CFR PEEK formulations instead, the wear rate does not significantly change under dry and lubricated conditions, indicating that the graphite flakes generated from the reinforcement material abrasion play a role in the further lubrication of the contact surfaces [59]. Moreover, differences in the wear rate between the two CFR PEEK formulations and the unfilled PEEK are much larger (up to one order of magnitude) under dry conditions, further confirming that the formation of a lubricant boundary film is one of the key factors in PEEK tribology under the tested conditions [33], and that the formation of this layer is crucial for reducing not only the tangential forces created with the applied load, but also the wear phenomena occurring during the reciprocating motion applied.

Material characteristics such as hardness are also differentiating the wear rate among the three tested polymer formulations, as the lowest wear rates were displayed for the hardest material and vice versa (figure 5 and Table 1), and moreover, the differences in the measured wear rate observed between Motis and Ni1CA30 CFR PEEK are attributable to the different intrinsic characteristics of the two reinforcement materials as well. Under dry conditions, the higher fiber content (in number) of Ni1CA30 CFR PEEK [20], and its higher mechanical strength, result in a significantly lower wear rate when compared to Motis CFR PEEK ($p<0.005$). Conversely, under bovine serum lubrication regime, the differences are much less pronounced, up to the point that a lower wear rate for Motis CFR PEEK can be observed. This indicates presumably that the lubricant film formation is less prone to occur in Ni1CA30 in respect to Motis formulation, given the higher number of fibers and the related variations in surface asperity and liquid absorption, thus resulting in a higher debris generation and material loss, as also confirmed by the observed COF variation.

SEM images of the worn surfaces are in accordance with the above indications: in dry regime, it has been observed that in all the considered materials a certain amount of plastic deformation within the polymer matrix is present, with the formation of waves perpendicular to the sliding motion due to the material flow occurred as a consequence of the reciprocating sliding motion (Figure 7). This is considered to be typical of a fatigue regime derived from either thermal heating caused by the friction between the sliding components or high pressure generation given by high loads applications [60]. Both CFR PEEK material formulations show a deep debris layer with material removal in the wear track, and the beginning of delamination and debris production in the area at the border of the wear pattern, indicating severe material removal due to both the above mentioned effects of heat and load (Figure 8) and the loss of ductility resulting from the effect of the annealing treatment (Table I).

Under bovine serum conditions, instead, only debris formation and an early stage delamination effect can be observed (Figure 10). As previously noted, fiber rupture has been individuated, particularly for Ni1CA30, probably caused by the lack of continuity of the lubrication film formed during the wear test (Figure 11).

Overall, material removal and delamination appear to be more pronounced for Ni1CA30. For Motis CFR PEEK, these phenomena were less pronounced, despite present; additionally a certain amount of plastic deformation was observed in the surrounding polymer matrix, as well as some fiber thinning. However, despite the observed fiber damages, no sign of fiber detachment could be detected, indicating that debris production is always associated to a combined fiber-polymer matrix consumption, rather than to isolated fiber removal [61].

Conclusion

Overall, our findings indicate that a lubricant film formation seems to be the most relevant factor to take into consideration for the assessment of wear phenomena occurring within PEEK or CFR PEEK versus Al_2O_3 tribological coupling. CFR material exhibited the higher wear resistance compared to unfilled formulation, despite the observed differences were flattened in lubricated conditions. Under lubricated conditions in fact, wear rate reduction is much larger in unfilled material than for the two CFR PEEK formulations, to the point that no significant reduction of the wear rate could be assessed, presumably due to the incomplete lubricant film formation in reinforced materials.

Under dry conditions, annealing treatments affect negatively the wear resistance of all the tested PEEK formulations, indicating that material strength and crystallinity increase result in a detrimental effect for the wear rate. However, this effect is limited under bovine serum lubrication conditions for all the considered materials.

Additional improvements in wear resistance of the considered materials might be obtained through promoting the continuous lubrication film formation which is considered to be critical especially for CFR formulations, i.e. with the further optimization of the material roughness through surface texturing/modification techniques aiming at maximizing the polymer wettability and/or the surface interaction with the lubricant medium, so as to optimize the lubricant efficacy.

References

1. Crowninshield RD, Rosenberg AG, Sporer SM. Clin Orthop Relat Res. 2006 Feb;443:266-72
2. Revell PA. Joint replacement technology, Woodhead publishing, 2014
3. Kurtz SM. UHMWPE biomaterials Handbook, 2ed. Academic Press, 2009
4. Bracco P, Oral E. Clin Orthop Relat Res 2011; 469:2286-2293
5. Mc Kellop H, Shen FW, Lu B. JBJS Am 2000; 82A(12):1708-1725

6. Costa L, Bracco P, Brach del Prever EM, Kurtz SM, Gallinaro P. JBMR (B) 2006; 78:20-26
7. Oral E, Christensen SD, Malhi AS, Wannomae KK, Muratoglu OK. J Arthroplasty 2006; 21(4):580-591
8. Costa L, Carpentieri I, Bracco P. Polymer degradation and stability 2008, 93:1695-1703
9. Brockett CL, Carbone S, Fisher J, Jennings LM. 2017, Wear 374-375:86-91
10. Dalury DF, Pomeroy DL, Gorab RS, Adams MJ. 2013, J Arthroplasty 28 (8):120–121
11. Williams IR, Mayor MB, Collier JP. 1998, Clin Orthop Relat Res 356:170–180
12. Kurtz SM, Muratoglu OK, Evans M, Edidin AA. 1999, Biomaterials 20(18):1659–1688
13. Sathasivam S, Walker P. 1999, J Biomech, 32(3):239–247
14. Pruitt LA, Ansari F, Kury M, Mehdizah A, Patten EW, Huddlestein J, Mickelson D, Chang J, Hubert K, Ries MD. 2013, J Biomed Mater Res Part B: Appl Biomater 101(3):476–484
15. Atwood SA, Van Clitters DW, Patten EW, Furmanski J, Ries MD, Priutt LA. 2011, J Mech Behav Biomed Mater 4(7):1033–1045
16. Kurtz SM. PEEK biomaterials handbook, William Andrew Publishing, 2011
17. Stober EJ, Seferis JC, Keenan JD. Polymer, 1984; 25:1845-52
18. Kurtz SM, Devine JN, Biomat 2007, 28:4845–69
19. Geringer J, Tatkiewicz W, Rouchouse G. 2011, Wear 271:2793-2803
20. Kraft M, Koch DK, Bushelow M. 2012, The Spine Journal, 12:603-611
21. East RH, Briscoe A, Unsworth A. 2015, Proc IMechE Vol 229(3) Part H:187-193
22. Scholes S, Unsworth A. 2007, Proc Inst Mech Eng Part H: J Eng Med, 221(3):281–289
23. Scholes S, Unsworth A. 2009, J Mater Sci: Mater Med, 20(1):163–170
24. Brockett CL, John G, Williams S, Jin Z, Isaac GH, Fisher J. 2012, J Biomed Mater Res B Appl Biomater, 100(6):1459-65
25. Flanagan S, Jones E, Birkinshaw, C. 2010 Proc Inst Mech Eng Part H: J Eng Med, 224(7):853–864
26. Scholes SC, Inman IA, Unsworth A, Jones E. 2008, Proc Inst Mech Eng H, 222(3):273-83
27. Wang QQ, Wu JJ, Unsworth A, Briscoe A, Jarman-Smith M, Lowry C, Simpson D, Collins S, 2012. J Mat Sci: Mater Med, 23(6):1533–1542
28. Salah H, Fisher J, Tipper J, Williams S. 2016, Orthopaed Proc, 98-B(supp2):26-26
29. Evans A, Horton H, Unsworth A, Briscoe A. 2014, Proc Inst Mech Eng H, 228(6):587-592
30. Harris B. Engineering composite materials, Maney Materials Science, 1999
31. Lorber V, Paulus AC, Buschmann A, Schmitt B, Grupp TM, Jansson V, Utschneider S. 2014, J Mater Sci: Mater Med, 25:141-149
32. Utzschneider S, Becker F, Grupp TM, Sievers B, Paulus A, Gottschalk O, JanssonV. 2010, Acta Biomat, 6(11):4296-4304
33. Regis M, Bellare A, Pascolini T, Bracco P. 2017, Polym Degrad Stab, 136:121-130
34. Flock J, Friedrich K, Yuan Q. 1999, Wear, 225-229:304-311

35. Hanchi J, Eiss Jr NS. 1997, Wear, 203-204:380-386
36. M. Regis, S. Fusi, R. Favaloro, P. Bracco, Composite science and technology 2020-scientific and technical challenges, in: 9th Int. Conf. Compos. Sci. Technol, DEStech Publications Inc (USA), Sorrento, Italy, 2013, pp. 44-56.
37. M.C. Kuo, J.C. Huang, M. Chen. 2006, Mater. Chem. Phys. 99:258-268
38. Regis M, Bracco P, Zanetti M, Pressacco M. 2016, Mater Chem Phys, 179: 223-231
39. Scholes SC, Unsworth A. 2010, Wear, 268:380-387
40. AAOS. "Implant wear: the future of total joint replacement", Wright & Goodman ed. 1995
41. Lancaster JG, Dowson D, Fisher J. 1997, Proc. Instn. Mech. Engrs. Part H 211(H1):17-24
42. Biant LC, Warwick JM, Bruce FA, Van der Wall H, Walsh WR. 2010, J Arthrop, 25(2):11–16
43. ISO 14242, International Standard Organisation
44. Saikko V, Alhroos T. 1997, Wear, 207:86-91
45. Vincent J. Biomechanics-Materials. A practical approach, Oxford University Press, 1992.
46. Davidson J, Mishra A. 1992, in: Surface Modifications Technologies V (Sudarshan & Barza eds.) The Inst Mater, 1-14
47. ASTM F732. ASTM international, 2001
48. Laux KA, Schwartz CJ. 2013, Wear, 301(1-2):727-734
49. Song J, Xiang D, Wang S, Liao Z, Lu J, Liu Y, Liu W, Peng Z. 2018, Tribology International, 122:218-227
50. Lin L, Pei XQ, Bennewitz R, Schlarb AK. 2018, Tribology International, 122:108-113
51. Wang A, Sun D, Starck C, Dumbleton J. 1995, Wear 181-183(1):241-249
52. Seedhom B, Dowson S, Wright V. 1973, Wear 24:35-51
53. Sonntag R, Reinders J, Kretzer JP. 2012, Acta biomat. 8:2434-2441
54. Anderson J, Cook G, Costerton GB, Hanson SR, Hensten-Pettersen A, Jacobsen N et al. Host reactions to biomaterials and their evaluation, in: B.D. Ratner, et al. Biomaterials Science: An Introduction to Materials in Medicine, 2nd ed. Elsevier Academic Press, New York, 2004
55. Jia J, Chen J, Zhou H, Hu L. 2004, tribology letters, 17(2):231-238
56. Heuberger MP, Widmer MR, Zobeley E, Glockshuber R, Spencer ND. 2005 Biomaterials, 26:1165-1173
57. Scholes SC, Unsworth A. 2006, Proc. IMechE Vol 220 Part H:687-693.
58. Scholes SC, Unsworth A, Hall RM, Scott R. 2000, Wear 41:209-213.
59. Briscoe BJ, Sinha SK, in "Mechanism and Practice", G. Stachowiak ed., John Wiley and sons, 2005, UK
60. Ma N, Lin GM, Xie GY, sui GX, Yang R. 2012, J appl poly sci, 123:740-748
61. Davim JP, Cardoso R. 2009, Wear, 266:795-799