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Evolution of crystallinity of PEEK and glass-fibre reinforced PEEK under tribological conditions using Raman spectroscopy

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ABSTRACT

A comparative study of PEEK and glass-fibre reinforced PEEK was performed to describes the degradation mechanisms in sliding conditions. Results were focused on Raman spectroscopy data in order to determine the local crystallinity rate of PEEK and to complete the scenario of degradation by taking into account the microstructure transformation during the wear tests. In the first period of the test, an amorphisation mechanism of both materials is identified. Then, during the second period of the test, these materials reach the glass transition temperature, and a cold crystallisation is detected in the wear track.

1. Introduction

Polyetheretherketone (PEEK) is a high performance semi crystalline polymer of the polyaryletherketone (PAEK) family introduced in 1978 by Imperial Chemical Industries [1]. It has high mechanical properties and resistance to chemical attack and thermal stability generally attributed to the strength of its aromatic backbone [2,3]. It is an exciting material for the aeronautical industry because it is light, easy to shape and flame retardant [4 6]. It is biocompatible, which makes it attractive in the medical industry as well [7,8].

Reinforcements were explored and led to numerous composite materials to increase these performances. Ceramics, such as fibreglass are interesting candidates for strengthening the properties of these polymers. Many studies have looked at the tribological properties of PEEK and glass filled PEEK [9 11]. These works described the friction and wear properties of these materials. The contact configurations varied from pin on disc [12,13], ball on flat [14] type or annular disc on plates [15]. Other studies involved in the effect of temperature [16,9] or humidity [11]. Lubrication with water or bovine serum is sometimes included in some research [15,10,8].

It is well known that the mechanical properties of PEEK are influenced by the microstructure and, in peculiar, the crystallinity rate. No work relates to the crystallinity change inside the wear, even less on the link with wear mechanisms.

Crystallinity is generally studied using X ray diffraction or differential scanning calorimetry. These techniques require significant portions of a specimen to estimate a macroscopic crystallinity rate (χ_c). Raman microspectroscopy is an appropriate technique to measure the local crystallinity rate inside a wear track through the submicrometre spot diameter.

The present study proposes to analyse the evolution of the crystallinity of PEEK and PEEK filled with glass fibre in the wear track after a tribological test. Spectroscopic analyses enhance the understanding of the degradation mechanisms of these materials.

2. Materials

PEEK granules (grade 450G) were supplied by Victrex (UK) and heat compression moulded at 380 °C, held there for 5 min and then cooled to 200 °C at 4 K/min. Fibreglass (30 vol%) reinforced PEEK composite (PEEK GF30) was purchased from Ensinger (Germany) and formed by extrusion. Fibre glass average length is 210 μm and their average diameter is 14 μm. The addition of glass fibre to the PEEK increases Young's modulus and thermal conductivity. The main mechanical properties of PEEK and PEEK GF30 are presented in Table 1. The glass transition temperature (T_g) remains unchanged between the PEEK and glass fibre composite at 145 °C. The crystallisation temperature (T_c) is 299 °C and 298 °C for PEEK and PEEK GF30 respectively. Finally, the melting temperature (T_m) increases with the addition of glass fibre. Tm corresponds to the maximum of the melting peak measured by DSC. T_m

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Table 1
Mechanical properties of materials.

Sample	Tensile modulus	Poisson's ratio	Thermal conductivity
PEEK	4 GPa	0.38	0.32 $W \cdot m^{-1} \cdot K^{-1}$
PEEK-GF30	6.4 GPa	0.32	0.35 $W \cdot m^{-1} \cdot K^{-1}$
Steel 440C	200 GPa	0.30	24.2 $W \cdot m^{-1} \cdot K^{-1}$

Table 2
Thermal properties of materials.

Sample	T_g	T_c	T_m
PEEK	145 °C	299 °C	328 °C
PEEK-GF30	145 °C	298 °C	340 °C

equals 328 °C for PEEK, and 340 °C for PEEK GF30 (Table 2).

Polymer (PEEK) and composite (PEEK GF30) samples are polished with SiC paper (grade P1000). The average roughness (Ra) then reaches 0.42 µm for both materials. The balls are 440C steel spheres supplied by RGPBalls (Italy) with a diameter of 9.5 mm. 440C steel contains 16 18% chromium and 0.4 0.8% molybdenum. The roughness of the balls equals 0.52 µm. The balls are used in their delivery state. All materials are cleaned with ethanol in an ultrasonic bath and then dried in an oven for one hour at 60 °C.

3. Methods

The crystallinity rate before friction testing is measured using differential scanning calorimetry (TA Instruments DSC, Q200) with a nitrogen flow rate of 50 mL/min. Hermetic aluminium pans encapsulate 10 mg samples. The samples were heated from 30° to 380°C at 10 $K \cdot min^{-1}$ in the aim to determine the melting and crystallisation temperatures. The temperature then is maintained for 1 min, and next, the sample is cooled from 380 °C to 30 °C at a speed of 10 $K \cdot min^{-1}$. The heating step is repeated once. The melting enthalpy used to determine the crystallinity χ_c is measured during the first melting cycle and divided by the melting enthalpy of an ideal crystal, i.e. $\Delta H_0^f = 130$ J/g [17].

Tribological experiments were performed in dry conditions using a TRIBOLAB tribometer (Bruker, USA) in a ball on flat configuration and reciprocating translation. The applied load was set to 25 N, giving an initial contact mean pressure of 119 MPa for PEEK and 156 MPa for PEEK GF30 in agreement with Hertz's theory. In these conditions, the initial contact radius is calculated to equal to 259 µm, and 226 µm for unfilled PEEK, and fibre glass reinforced PEEK, respectively.

The sliding stroke was 10 mm, and the frequency was 5 Hz. The tests were performed in ambient atmosphere (40 50% of relative humidity) and at ambient temperature (T = 24 °C). The tests are interrupted after 300, 600, 900, 900, 1200 and 1500 s, which is equivalent to the total sliding distances of $3 \cdot 10^7$, $6 \cdot 10^7$, $9 \cdot 10^7$, $1.2 \cdot 10^7$ and $1.5 \cdot 10^7$ µm respectively. The coefficient of friction, μ was recorded all along three tests to check the reproducibility of the tribological experiments.

The profiles on the wear tracks are recorded with an optical profilometer (Veeco, Wyko NT1100). The damaged volumes of the PEEK planes and the composite planes were represented as a function of the product of the total sliding distance (d) by the applied load (F_n). The average value of the five profiles measured on each wear track was used to calculate the damaged and worn volumes. A negative volume noted V^- and a positive volume, V^+, correspond to the quantity of material which is respectively below or above the average plane of the 3D profil of the track. The sum of the positive volume, V^+, and the negative volume, V^-, is used to calculate the damaged volume (V_{dam}). V_{wear} is the difference between the volumes V^+ and V^-, which corresponds to the ejected material of the contact.

After the tribological tests, the wear tracks, the counterparts and the wear debris were all observed by optical microscopy as well as environmental scanning electron microscopy (Zeiss, EVO HD 15 LS). In association with SEM imaging, the elementary analysis of the wear scars was studied by Energy Dispersive X ray Spectroscopy (Oxford). The settings for SEM and EDX are identical and as follows: accelerating voltage: 15 kV; working distance: 10 mm.

Raman micro spectroscopy using a Horiba LabRAM HR 800 Raman confocal spectrometer with a confocal hole of 35 µm, a 600 lines/mm holographic grating, an opacity filter and a helium neon laser emitting at 633 nm provided chemical and structural characterisations of the samples. The spot diameter was 0.858 µm, and the axial resolution was 3.125 µm using a ×100 magnifying lens with a numerical aperture of 0.9. On average, to obtain a Raman spectrum profile, 200 spectra were recorded on a transverse direction of the worn path from the centre to the unworn surfaces. It is allowed to get a statistical study on Raman peaks parameters such as the intensity of the major peaks. The surfaces were kept free from laser irradiation damage. Images of the analysed area were obtained after performing Raman spectroscopy and confirmed it.

4. Results

4.1. Coefficients of friction

The Fig. 1 shows the evolution of the coefficient of friction as a function of time. The coefficient of friction (μ) of the PEEK GF30 is higher than that of the PEEK during all the tests. Both compounds follow the same trend: at the very beginning, the coefficient of friction is around 0.25 whatever the material. After about 30 s, this value increases to 0.30 for PEEK and 0.34 for PEEK GF30. In the case of the PEEK, μ rises slowly until 0.35 until 1000 s, and finally, this value no longer changes until the end of the test.

For glass fibre reinforced PEEK, the coefficient of friction appears to evolve asymptotically to 0.45. The energy dissipation is, therefore, higher in the glass fibre reinforced PEEK and this dissipated energy must contribute to the increase of the contact temperature in the ball and the plane, as proposed by Davim [18]. Fibre glass has a negative effect on the coefficient of friction and its kinetics.

4.2. Wear

The tribological tests are interrupted at regular time intervals, then measured the width of the wear tracks and recorded the surface profiles

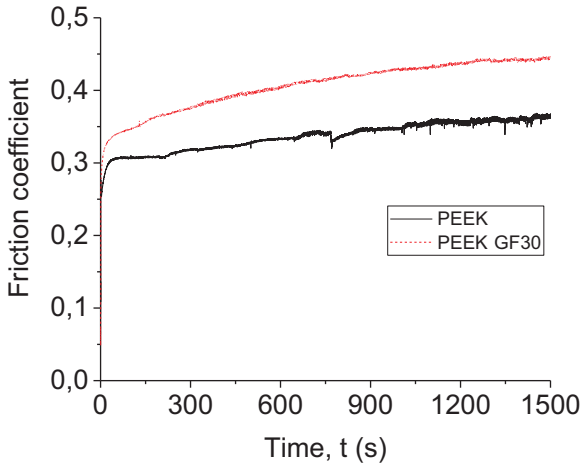


Fig. 1. Typical friction coefficient evolution for PEEK and PEEK-GF30 measured for a tribological test with a 440C steel ball in reciprocal translation during 1500 s (F_n = 25 N, f = 5 Hz).

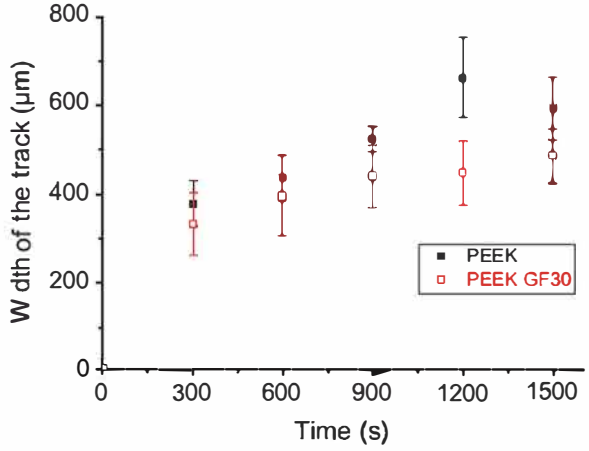


Fig. 2. Evolution of wear track width.

in 3 dimensions. The width of the track increases during tribological tests whatever the material (Fig. 2). However, the width measured on the track of PEEK is larger than that of PEEK containing glass fibres. After 300 s, the width of the track increases by about 0.17 µm/s for PEEK and 0.12 µm/s in the case of PEEK GF30.

The positive volume and the negative volume increase with the product of the applied force and the sliding distance, whatever the material considered (Fig. 3). Moreover, for a given material and identical experimental conditions, the values of V^+ are substantially equal to those of V^-. The volume variation is linear in the case of PEEK GF30. This linear evolution of volumes is also observed in the case of PEEK but, after 600 s, the slope changes considerably to follow a trend comparable to an exponential law.

While the V_{dam} of the PEEK GF30 follows a linear trend, the V_{dam} of the PEEK includes two periods: the first, between 0 and 600 s, where the volume variation remains linear, and the second, between 600 and 1500 s where the evolution of the V_{dam} is exponential. V_{wear} is ten times smaller than V_{dam}, whether it is PEEK or PEEK reinforced with glass fibres.

The material ejection is negligible compared to the material displaced by the sliding contact between the ball and the plane. Moreover, the plastic deformation of PEEK is thermally activated as suggested by the evolution of volumes. Indeed, the similarity between the exponential variation of the V_{dam} with a law of Arrhenius makes it possible to envisage an action of the thermal phenomena on the tribological mechanism of the PEEK. In the PEEK GF30, the fibreglass tends to reduce the enlargement of the wear track. The presence of fibreglass modify the degradation mechanisms and make PEEK GF30 less sensitive to plastic deformation. The reinforcement limits the deformation of the polymer matrix by providing more stiffness in the plane.

4.3. SEM and EDS

Optical profilometry of tracks and steel balls reveal clear differences between the 2 cases studied. Electron microscopy also provides more accurate images of these different zone (Fig. 4). On the one hand, the tracks on the pure PEEK plane are profound, clear and as soon as the tests exceed 1000 s, small polymer chips clumped to the extremities of the tracks. On the tracks produced with the PEEK (duration: 1500 s), the wear track shows streaks in the centre and wrinkles on the edges. Spaces regularly separate the wrinkles in the same way as the Schallamach waves. Polymer debris is found on the ball and is glued to the area in contact with the plane. The width of this track on the ball corresponds to the width of the track on the plane. On the other hand, the track on the glass fibre reinforced composite is narrow and dark. The wear tracks on the PEEK GF30 planes do not show any differences between the centre and the lateral part and are rather homogeneous. There is little debris at the end of the trail. Glass fibres are distinguished by the chemical contrast mode of SEM (electron backscatter detector) and EDS mapping (Fig. 5). Outside the track, the fibres are clear and regularly distributed. Zoom in the track show crushed fibres, their size has been reduced, and they take part in the debris bed with the polymer. The latter is also displaced and damaged, but the groove is not as thick as in the case of pure PEEK.

The steel balls that rubbed on the PEEK are intact, and polymer particles have adhered on the surface (Fig. 6.a). Debris with a roller shape is found on the ball outside the wear track. The balls that were used for tribological tests against PEEK GF30 are more damaged, and scratches are present (Fig. 6.b). A material cap is removed from the steel sphere, and a 500 µm diameter flat spot is scratched in the direction of sliding after a 1500 s tribological test. The EDS maps show that there is a transfer on both sides of the ball and the plane. Silicon elements are found on the steel ball, that origin is undoubtedly from crushed glass fibres embedded into the steel. The average size of these fragments is ten times smaller than the initial diameter of glass fibres. On the plane, iron and chromium elements are also detected and coupled with oxygen. These oxides are at the origin of the dark colour of the wear tracks.

4.4. Raman spectroscopy

The crystallinity rate of PEAK can be measured by Raman spectroscopy. The works of Agbenyega [19], Briscoe [20], Everall [21] and Stuart [22] highlight the changes in the spectra of PEEK for which crystallinity is different. Note that the more crystalline the PEEK is, the more modified the intensities of the vibration modes are. The 1146 cm^{-1} mode is the most intense of all. It is associated with symmetrical stretching of the C O C group. In general, spectrum should be normalised using this peak. However, the intensity of this vibration mode at 1146 cm^{-1} is strongly dependent in the rate of crystallinity. This

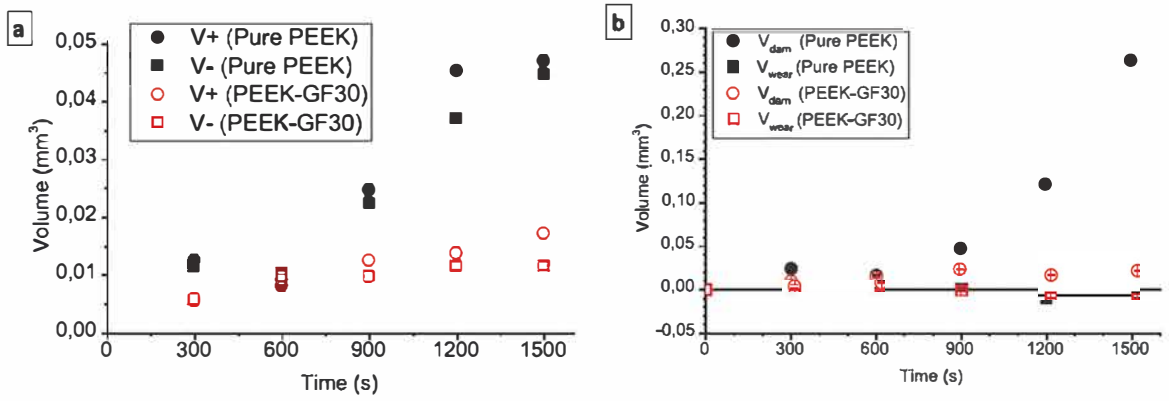


Fig. 3. Evolution for PEEK and PEEK-GF30 of a) V^+ and V^- and b)V_{dam} and V_{wear}.

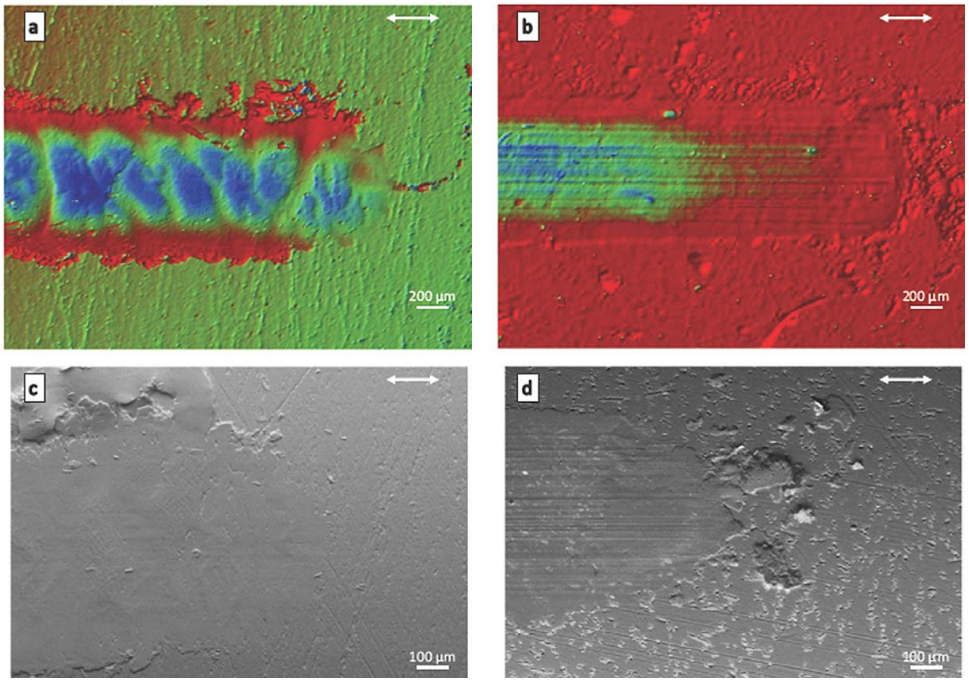


Fig. 4. Profilometry images (a and b) and SEM images (c and d) of worn surfaces for tests during 1500 s; pure PEEK (a and c), PEEK-GF30 (b and d). ⟷: sliding direction.

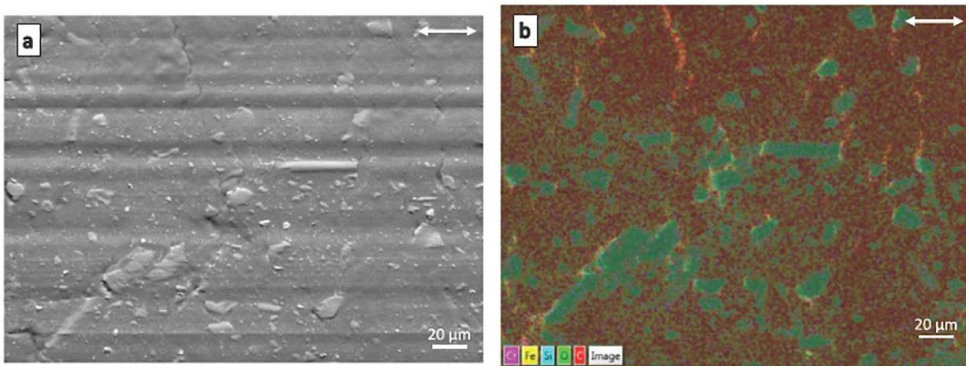


Fig. 5. Analysis of a PEEK-GF30 specimen for 1200 s tests; a) SEM images and b) EDS images.

sensitivity is used to study the change in crystallinity rate in the PEEK, but, as recommended by Briscoe et al. the spectra presented in this study are normalised to the second most intense peak [20]. This mode is located at 1598 cm^{-1} and is less sensitive to the degree of crystallinity. It corresponds to a vibration of the phenyl ring. The intensity of the modes at 1145 cm^{-1} and 1202 cm^{-1} which are related to the antisymmetric stretching of the C O C group increases when crystallinity decreases. The position of the stretching mode of the C=O bond is close to 1647 cm^{-1} when the PEEK is crystallised. This position translates to 1652 cm^{-1} with decreasing of crystallinity. Two other modes at 808 cm^{-1} (deformation of the C H bond outside the plane) and 3088 cm^{-1} (stretching of the C H bond) can also be detected. The information associated with the ratio between the modes at 1146 cm^{-1} and 1598 cm^{-1} are kept and note R_I to study the variation of crystallinity in the tracks resulting from tribological tests because their detection and the signal to noise ratio are generally good and thus allow fast acquisition of spectra.

Measurement campaigns with the Raman spectrometer are carried out as follows: First, two PEEK plates with different crystallinity levels are selected as a reference. Second, spectrum profiles in the transverse direction of the wear tracks are performed on PEEK samples that have undergone tribological tests at 300, 600, 900, 1200 and 1500s. Third, profiles similar to the previous ones are made on plates of PEEK GF30 composites.

Fig. 7 shows two spectra obtained for PEEKs with different crystallinity rates. The crystallinity rates are verified by the DSC and are 12% and 28%. The sample whose crystallinity is 12% has a ratio of R_I equal to 1.08, the one with the crystallinity rate of 28% at an intensity ratio equal to 1.35. These two values are used in the rest of the study to verify the evolution following tribological tests.

Raman spectra profiles are recorded in the transverse direction of the wear track on the PEEK. On average, 200 spectra are recorded on one profile. Figs. 8, 9 and 10 show the ratio of the intensities R_I as a function of the position in the wear track. The x = 0 abscissa represents the centre of the wear track. For clarity and after checking the symmetry of the results concerning the centre of the track, the R_I values are represented only a half width of the wear track, i.e. for positive values of x. The profiles are represented for tribological tests of 300, 600, 900, 1200 and 1500s. The grey area represents the average position of the edge of the wear scar for each test. The reference lines that indicate the crystallinity rate of the PEEK to 12% and 28% are also represented on the graph by a dotted line and a dashed line respectively.

After a tribological test of 300 s (Fig. 8.a), the half width of the wear scar is 190 µm. The profile reveals that in this track, the surface material is no longer homogeneous regarding crystallinity. At the centre of the track, between 0 and 100 µm, the crystallinity is lower than the outside of the wear track. The minimum R_I is measured on the lateral edge of the track between 100 and 190 µm. From 190 µm, the

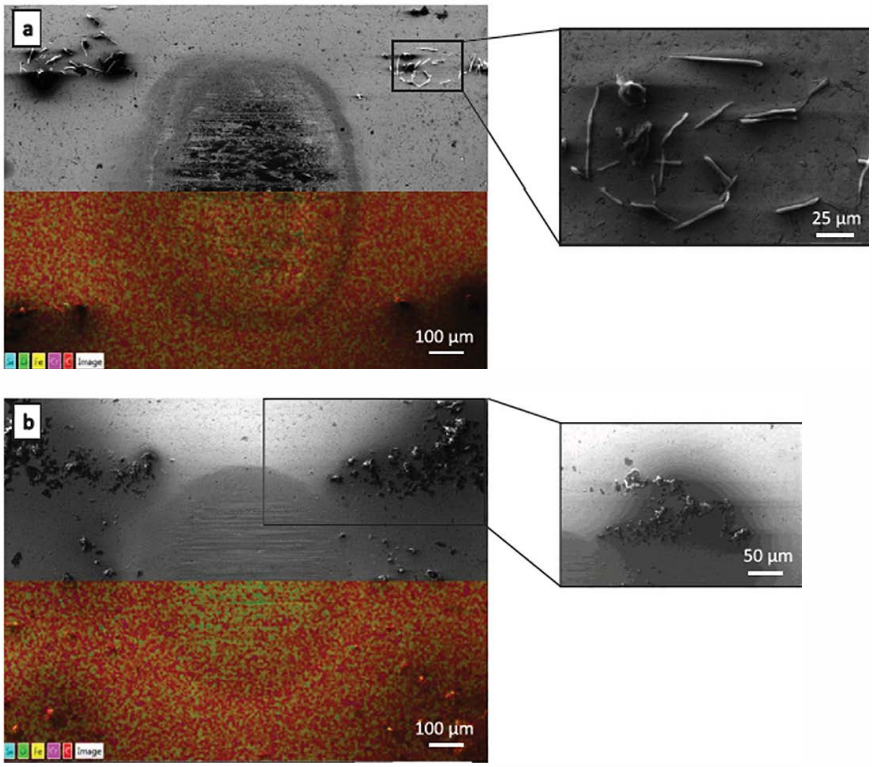


Fig. 6. SEM and EDS analysis of counterface against a) pure PEEK and b) PEEK-GF30.

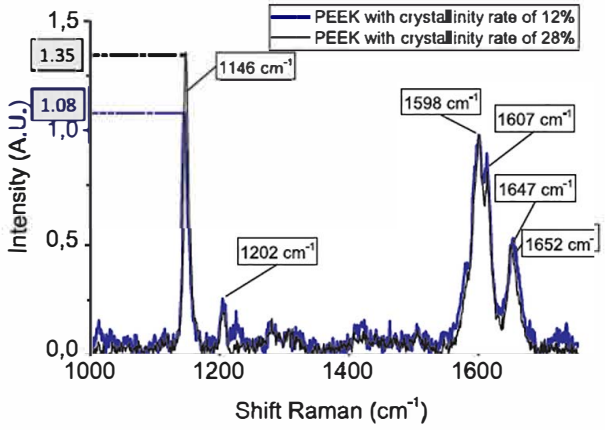


Fig. 7. Raman normalised spectra of 2 PEEKs with different crystallinity rates.

crystallinity rises to a maximum, which corresponds to the pure PEEK. In this case, the lowest crystallinity seems to correspond to the location of the Schallamach waves observed in microscopy and with the profilometer. It is in this lateral section of the wear scare that the most important phenomena of adhesion and plastic deformations occur and therefore where the disorder induced by friction on the polymer structure is the most important.

At 600 s, the half width of scar measures 215 µm (Fig. 8.b). R_I decreases; further, the material becomes more and more amorphous. In this case, too, the lateral area of the track is more amorphous than the central part.

At 900 s, 1200 s (Fig. 9.a and.b) and 1500 s (Fig. 10.a), the maximum crystallinity in the track is higher than our most crystallised reference (28%). This increase in crystallinity in the track breaks with the trend followed on tribological tests at 300 and 600 s. At the same time, the damaged volume grows exponentially. It is likely that a thermal effect led to these radical changes of microstructures in the track.

The Fig. 10.b shows the average crystallinity value as a function of the duration of the test and the sliding distance. At first, the crystallinity decreases. At 600 s, the PEEK has a crystallinity rate of about 12% on

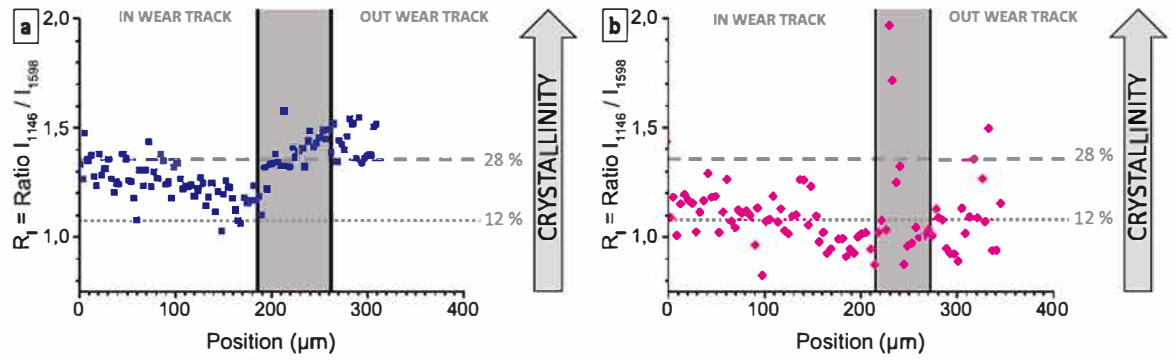


Fig. 8. Raman spectra profile recorded in the wear track of PEEK after 300 s (a) and after 600 s (b). The dotted and dashed lines represent a crystallinity rate of 12% and 28% respectively. The grey area represents the average position of the edge of the wear scar.

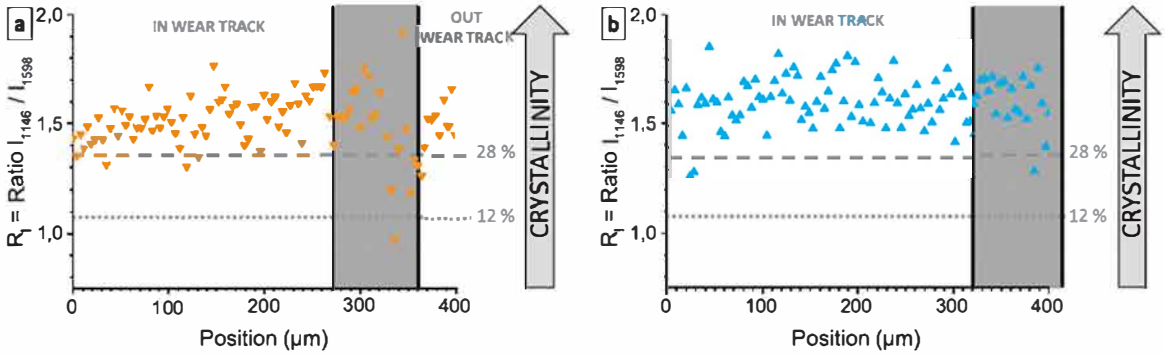


Fig. 9. Raman spectra profile recorded in the wear track of PEEK after 900 s (a) and after 1200 s (b).

average. After 900 s, the rate increases to more than 28%. This trend can also be observed outside the track.

When PEEK is reinforced with glass fibre, the fibres do not significantly affect the microstructure, and the crystallinity remains unchanged. DSC measurements confirm that the crystallinity rate of PEEK GF30 is about 28%. The intensity of the vibration modes of the PEEK matrix does not vary and the R_I reference values indicating crystallinity levels of 12% and 28% can be used with the PEEK GF30 plots.

Fig. 11 shows the evolution of R_I as a function of the position inside and outside the wear track of the PEEK GF30. The average R_I in the worn track is 1.70 while outside R_I is 1.77. These values indicate that the crystallinity rate is higher than 28% and significantly increased in all the area analysed by Raman spectroscopy.

Above 300 s tribological tests, the spectra recorded are strongly affected by the fluorescence of the glass fibre. This fluorescence does not allow reliable evaluation of the measurements. This fluorescence increases as the fibres are crushed and spread throughout the track by the steel ball during the sliding.

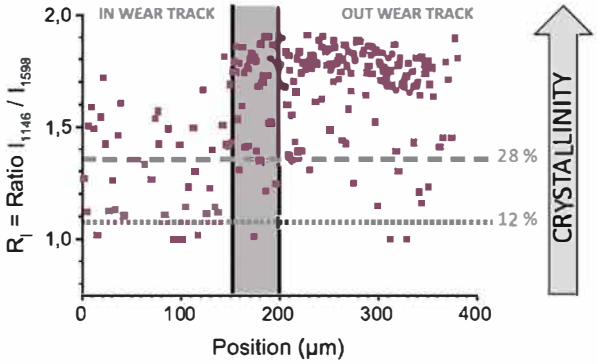


Fig. 11. Raman spectra profile recorded inside and outside the wear track of PEEK-GF30 after 300 s.

5. Discussion

The tribological analyses show that the degradation mechanisms of PEEK are mainly plastic deformation and adhesion. These mechanisms cause significant displacement of the polymer around the ball and amplify the dissipation of thermal energy in contact. The sliding of the ball causes a decrease in crystallinity in the contact and the appearance of a third interfacial body relaying the forces between the ball and the plane appears. Schallamach waves are formed in the transverse direction of the track, and polymer particles are detached, rolled in the interface. The polymer can adhere to the surface of the steel sphere. The contact temperature exceeds the glass transition temperature (T_g), and the PEEK starts crystallisation around 900 s. Bas et al. [23] in 1994 and Fougnies et al. [24] in 1999 reported the phenomenon of cold crystallisation of PEEK after exceeding the glass transition temperature. More recently, Martineau et al. [25] studied this phenomenon which leads to an organisation of macromolecular chains in an ordered structure above 143 °C. The mechanical sollicitation probably indices chains breakage. The shortest chains having more mobility to self organize, that could induce a higher level of organisation. During a tribological test, the mechanical energy is dissipated mainly in the form of heat and that this thermal energy is proportional to the friction coefficient. In our case, this thermal energy leads to the rise of the temperature in the contact and its immediate environment. Thus, in the case of PEEK, crystallisation occurs which starts between 600 and 900 s, continues until the end of the test and increase the order in the microstructure of the PEEK over the entire area analysed in Raman spectroscopy: inside and also outside the wear track.

The tribological behaviour of the PEEK GF30 is different. In these tests, the balls suffer greater damage than in the case of pure PEEK. There is a little transfer from the composite to the steel sphere. Thus, numerous debris of silica and polymer are detected in the flat formed at the extremities of the tracks. Particles detach from the ball and flow to the contact interface in the form of iron or chromium oxides. The fibre

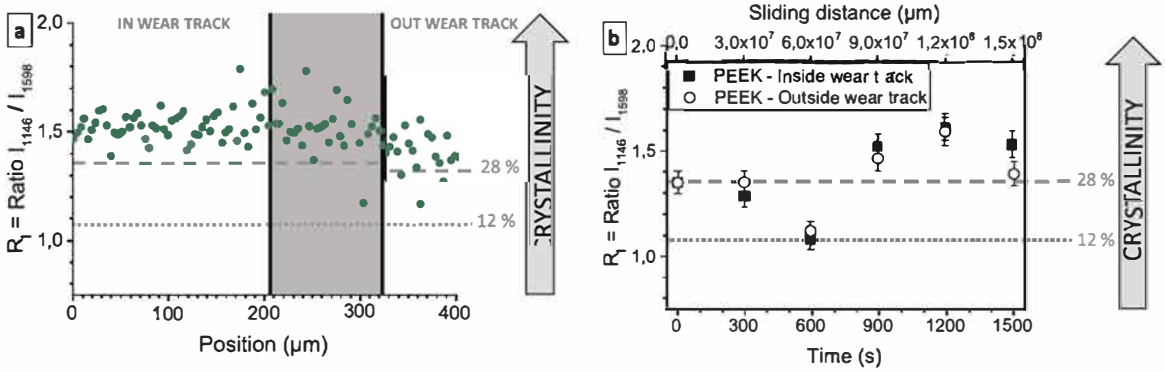


Fig. 10. Raman spectra profile recorded in the wear track of PEEK after 1500 s (a) and a graph of the R_I intensity ratio as a function of time and sliding distance. (b).

considerably rigidifies PEEK and reduces material displacement in the interface. It also reduces the mobility of the composite matrix by lim iting its plastic deformation. Abrasive and adhesive wear is responsible for the degradation of the material, and this wear is aggravated by the milling of the glass fibres which produces micrometre sized fragments in the contact. It promotes the appearance of scratches in the track and debris is trapped in the polymer, or the ball, or pushed out of the ball/ plane contact.

For glass fibre reinforced PEEK, this crystallisation phenomenon also occurs and happens earlier. Indeed, during tribological tests, the friction coefficient is higher than in the case of pure PEEK. The heat dissipated in the material is, therefore, higher. The glass transition temperature is then probably reached earlier. Thus, the microstructure becomes crystalline more quickly, and the crystallinity rate is more top than 28% from 300 s over the entire analysed area. Similarly, the in crease of crystallinity could stem from short macromolecular chains produced by the severe loading during the tribological test.

At present, the evolution of crystallinity cannot be detailed in the wear track beyond 300 s. Indeed, a high fluorescence is recorded in Raman spectra due to crushed glass debris.

6. Conclusions

A tribological test campaign was carried out with the sliding contact in a reciprocal translation of a steel ball on pure PEEK and a PEEK composite reinforced with glass fibre. Measurements of the friction coefficient and wear associated to microscopic observations have made possible to propose a degradation mechanism for these materials:

- Plastic deformation and adhesion are the main phenomena causing the appearance of Schallamach waves and wear on the PEEK;
- For PEEK GF30 composite, glass fibre milling and abrasion dom inate material degradation. Moreover, glass fibres, while increasing the stiffness of the material, reduce the mobility of the molecular chains and the plastic deformation of the polymer.
- The polymer crystallinity in the wear track changes during the ex periments in both materials. The heat generated in the interface allows the glass transition to be reached and then the increase of the crystallinity of PEEK and PEEK GF30 during tribological tests;

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