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Ageing of PEEK/Carbon Fibre composite under electronic irradiations: Influence on mechanical behaviour and charge transport

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ABSTRACT

Polymer used in satellite manufacturing are exposed to surface charging phenomenon due to electronic irradiations. This phenomenon can induce electrostatic discharges (ESD) which can lead to failures. In order to limit this phenomenon, we propose to develop PEEK composite reinforced with Short Carbon Fibres (SCF). We studied the behaviour of these composites in pristine state and after electronic irradiations compared to PEEK.

In pristine state, fibres induce a faster surface electron relaxation. This behaviour shows that SCF can reduce ESD risks in space which is a first validation of the concept. After irradiations, PEEK ageing mechanisms are not modified by the presence of fibres. However, SCF stabilise both the evolution of mechanical behaviour and surface potential relaxation compared to irradiated PEEK. This stabilisation comes from two contributions: fibres stabilise the ageing of the matrix and hides the influence of this ageing on composite mechanical and electrical behaviours.

1. Introduction

In geostationary earth orbit (GEO), materials used for spacecraft manufacturing are exposed to several environmental constraints like thermal cycling, micrometeorites and space debris impacts or irradiation by charged particles (e.g. protons, electrons). Especially for polymer materials, irradiation by electrons presents two main problematics for satellites.

The first problematic concerns the ageing of polymers. It results from the energy transferred by electrons passing through material volume. This energy transfer induces an ionisation of the polymer which leads to modifications of its physicochemical structure. Therefore, the polymer may no longer fulfil its main function and lead to satellite failures. Thus, it is essential to study polymer behaviour under electronic irradiations in order to better anticipate satellite lifetime in space environment. Recently, space industry started to use PolyEtherEtherKetone (PEEK), a high performance thermoplastic polymer, for structural applications in satellite manufacturing. This new polymer in space industry is intended to replace widely used thermoset matrices. Currently, PEEK is used in Carbon Fibre Reinforced Polymer as primary structure material for the articulated arm of the International Space Station [1] or as mechanical support for scientific instruments like the Search Coil Magnetometer that embarked on the Parker Solar Probe mission [2]. The use of this polymer results, among other properties, from its high tolerance to ionising radiations (electronic or γ irradiations). Indeed, many works studied the ageing of PEEK under ionising radiations and highlighted evolutions of its structure and properties. Nonetheless, these evolutions are observed for very high deposited energies compared to other polymers. Hegazy et al. studied gas emissions during γ and electronic irradiations [3,4]. They observed a release of CO and CO₂ for both irradiations and concluded that chain scissions occur mainly on ether and ketone functions. Moreover, they studied by Differential Scanning Calorimetry the influence of γ irradiations on PEEK thermal transitions [5]. They pointed out increase in glass transition temperature explained by a cross linking phenomenon and a decrease in both melting temperature and crystallinity ratio due to the formation of defects in crystalline structures. The influence of this ageing on the PEEK properties has also been studied. Under electronic irradiations, Sasuga et al. reported evolutions of PEEK mechanical properties [6,7]. For example, they observed a global degradation of its tensile properties like its elongation at break which decreases from 296% for pristine sample to 52% at 50 MGy due to cross linking. On its electrical behaviour, Shinyama et al. use Broadband Dielectric Spectroscopy to bring into evidence a wider relaxation time distribution explained by the increase in amorphous phase heterogeneity due to cross linking nodes [8,9]. However, these studies were carried out in

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the framework of nuclear applications and therefore, irradiations were performed under air which is not representative of space environment.

The second problematic concerns charging phenomena induced by low energy electrons. Due to the dielectric nature of polymers, these electrons accumulate at the polymer surface. This accumulation leads to an increase of electrical surface potential (voltage levels of several kilovolts can be reached) and induces electrostatic discharge (ESD) phenomena likely to degrade electronic systems. These ESDs are responsible for many spacecraft failures and anomalies in orbit [10]. Moreover, these charging phenomena are highly impacted by polymer ageing which can induces evolutions of its electrical properties and amplify electron accumulation. Optimisation of electrical properties of polymers is an important research axis for several application fields like anti static materials [11], flexible electronics [12,13] or aerospace industry [14,15]. One of the ways to optimise charge transport is to develop polymer composites loaded with electrically conductive fillers (e.g. metallic particles). Indeed, above a certain particle ratio named percolation threshold \(p_c\), the electrical conductivity brutally increases (about 10 15 decades) due to the formation of a conductive path between fillers. [16]. This percolation threshold is dependent of filler aspect ratio and the conductivity above \(p_c\) is dependent of filler nature (carbon or metallic fillers). This concept could be a good solution for limiting charging phenomena on polymers. However, most of the polymer applications on satellites require insulating materials. Therefore, it is necessary to work with filler ratio below \(p_c\).

In previous works, we investigated the influence of electronic irradiations, carried out in space representative conditions, to the physicochemical structure of PEEK [17,18]. We showed that electronic irradiations at room temperature induce cross linking of the amorphous phase and amorphisation of the crystalline phase. We observed that irradiations in the vicinity of glass transition temperature (165 °C) promotes cross linking phenomena due to a faster recombination rate of radicals in rubbery state, but does not modify crystalline phase ageing. This allowed us to highlight the significant influence of competition between amorphisation and cross linking on property evolutions. In this work, we aim to develop PEEK based composites reinforced with Short Carbon Fibres (SCF) in order to limit surface charging phenomena and to study their behaviour under electronic irradiations, a particular attention will be paid to the evolution of their mechanical and electrical properties. Moreover, these evolutions will be compared to those of the bulk matrix to study the influence of the fibres.

2. Materials and methods

2.1. Materials

For this study, PEEK films (Aptiv 1000 grade) were used in the form of semi-crystalline sheets having a thickness of 100 μm. PEEK/SCF composites were elaborated from the mixing of PEEK pellets (150G grade) and PEEK/SCF 30 weight% pellets (450CA30 grade). All materials (PEEK films and pellet batches) were supplied by Victrex.

The mixing of pellets was made with a laboratory twin screw extruder (Haake Minilab II from Thermo Scientific) at a temperature of 360 °C (i.e. 20 °C above melting temperature) and with a screw speed of 30 rpm. This speed value was chosen because it enables the mixture to be optimised while maintaining the integrity of the fibres (i.e. without damaging their aspect ratio) [19]. The mixing process consists to do a first pass in the extruder of the pellet blend at the desired SCF volumic ratio to obtain pre mixed extrusion rods. Thereafter, these rods are extruded again in order to homogenise the fibre dispersion. Fig. 1(a) and Fig. 1(b) show SEM images of cryocuts of the resulting extrusion rods, with a SCF ratio of 5 vol. % and 10 vol. % respectively.

These images do not show any fibre bundles or aggregates, this confirms that the mixing protocol used leads to a homogeneous fibre dispersion in composites. Moreover, they show that extrusion leads to a preferential orientation of fibres in the polymer melt flow direction. The analyse of multiple SEM images allowed us to measure an average fibre length of (57±8)μm and an average fibre diameter of (7.2±0.5)μm. The resulting aspect ratio is 7.9. Some empty areas (dark areas on images) are also observed and correspond to bubbles introduced in composites during extrusion process.

To determine the percolation threshold \(p_c\), composite samples were elaborated by hot pressing (360 °C, 20 min), in the form of cylinders with a diameter of 20 mm and a thickness between 1 mm and 2 mm, for several fibre ratios in the range [0 ; 16] vol. %. The real part of the dynamic conductivity \(\sigma'(\omega)\) was measured by Broadband Dielectric Spectroscopy at 10⁻² Hz and 25 °C for the different fibre ratios. In this way, \(p_c\) was determined at fibre ratio of 9 vol %. Percolation threshold is proportional to filler aspect ratio \(\xi\) according to Eq. (1) [20,21].

\[
p_c = \frac{0.7}{\xi}
\]

The aspect ratio of fibres calculated from this equation is about 7.8. This value is consistent with aspect ratio obtained from SEM image analysis.

However, as explained in introduction, PEEK space applications require electrical insulating materials. Therefore, studied PEEK/SCF composites have to be insulating: i.e. the fibre ratio need to be lower than \(p_c\). Thus, the ratio of 3 vol. % was selected to be studied in this work. At this fibre ratio, composite conductivity is about 10⁻¹³ S/m at 10⁻² Hz. Afterwards, to ensure that the ionising dose deposition is homogenous in our samples, PEEK/SCF 3 vol. % composites were elaborated in the form of 200 μm thick films.

2.2. Experimental irradiations

Samples (PEEK films and composites) were irradiated under high vacuum by a 350 keV mono energetic electron beam, thanks to SIRENE facility (ONERA, Toulouse, France). PEEK films were irradiated at two temperatures: room temperature and 165 °C, in continuity of our previous work, by using a heating sample holder (its design has been already described in [18]). Composites were irradiated only at room temperature to study how the fibres influence the ageing of PEEK. The use of high beam current densities (up to 60 nA/cm²) allowed us to achieve high ionising doses in less than 60 h. The resulting doses \(D (Gy) = \frac{1}{\rho} \int \frac{dE}{dx} \) were calculated using Eq. (2) (the detailed stopping power and dose calculations have been already explained in [17]). All doses mentioned afterwards correspond to mean dose in sample thickness.

\[
D (Gy) = 1.6 \times 10^{-9} \times \frac{1}{\rho} \int \frac{dE}{dx}
\]

With \(\Phi\) the total electronic fluence (electron/cm²), \(\rho\) the material density (g/cm³) and \(dE/dx\) the electronic stopping power of the material (keV/μm).

Two irradiation campaigns were carried out for each type of samples (i.e. PEEK films and composites). They lead to ionising doses of 1.2 x 10⁷ MGy and 3.4 x 10⁷ MGy. In these irradiation conditions, the ratios between back and front face doses are 1.5 and 2.1 for PEEK and composite respectively. The dose heterogeneity is higher in composites due to thicker samples (200 μm). However, this degree of heterogeneity is sufficiently low to consider a homogeneous dose deposition in composite thickness.

2.3. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) analyses were carried out on a DSC7 manufactured by PerkinElmer. Analyses were performed under nitrogen flow and consist of two heating runs and one cooling run between 50 °C and 400 °C at a rate of 10 °C/min. First order transition temperatures (melting temperature \(T_m\) and crystallisation temperature \(T_c\)) were measured at the maximum of the peaks while the glass transition temperature \(T_g\) was measured by the tangent method as well.
as the heat capacity jump $\Delta C_p$. Crystallinity ratio $\chi_c$ were determined using Eq. (3).

$$\chi_c = \frac{\Delta H_m}{\Delta H_m(1 - x_f)} \times 100$$

(3)

With $\Delta H_m$ the melting enthalpy (J/g), $\Delta H_m$ the theoretical melting enthalpy of a fully crystalline sample reported for PEEK at 130 J/g [22] and $x_f$ the weight fraction of fibres which is about 0.04 in PEEK/SCF 3 vol. %.

### 2.4. Dynamic Mechanical Analysis

Dynamic Mechanical Analyses (DMA) were performed on an ARES G2 strain controlled rheometer manufactured by TA Instruments. Sample dimensions are 35 mm × 10.5 mm. Due to their low thickness, samples were analysed in tensile geometry mode to ensure a good signal to noise ratio. Tests were carried out over the temperature range $[-130 \degree C; 250 \degree C]$ at a rate of 3 °C/min. Strain and frequency were fixed at 0.02% and 1 Hz respectively. In these conditions, samples are solicited in their linearity range allowing us to determine storage $E'_s(T)$ and loss $E''_s(T)$ moduli.

### 2.5. Broadband Dielectric Spectroscopy

Broadband Dielectric Spectroscopy (BDS) has been used to analyse electrical behaviour of polymers materials and has already been extensively described [23].

In this work, a Novocontrol BDS 4000 spectrometer associated with an Alpha A impedance analyser was used to determine DC conductivity and storage permittivity of samples. Samples were prepared in the form of 30 mm diameter film. Analysis were performed over a frequency range of $[10^{-2}; 10^6]$ Hz and for isotherms going from $-150 \degree C$ to $250 \degree C$ by 5 °C steps. The complex impedance $Z'(\omega)$ is used to determine the values of sample complex conductivity $\sigma'(\omega)$ and complex permittivity $\varepsilon'(\omega)$ using Eqs. (4) and (5) respectively.

$$\sigma' = \sigma' + i\sigma'' = \frac{e}{AZ'}$$

(4)

With $e$ the sample thickness (m) and $A$ its area (m²).

$$\varepsilon' = \varepsilon' - i\varepsilon'' = \frac{1}{i\omega C_0 Z'}$$

(5)

With $C_0 = \frac{e_0 A}{\varepsilon_0}$ where $\varepsilon_0$ is the vacuum permittivity.

By studying the real part of the conductivity $\sigma'(\omega)$, it is possible to determine a DC conductivity $\sigma_{DC}$ value versus temperature. According to the universal dielectric response formulated by Jonscher [24], the frequency dependence of $\sigma'(\omega)$ in a disordered solid can be describe at a given temperature by Eq. (6).

$$\sigma'(\omega) = \sigma_{DC} + A.\omega^\alpha$$

(6)

At low frequency, the term $A.\omega^\alpha$ becomes negligible in front of $\sigma_{DC}$ resulting in a frequency independent conductivity. This phenomena is characterised on $\sigma'(\omega)$ isotherms by the presence of a plateau at low frequency whose value is equal to $\sigma_{DC}$. Thus, the $\sigma_{DC}$ values reported in this work were extracted from these plateaux at a frequency of $10^{-2}$ Hz. For pristine PEEK and PEEK/SCF 3 vol. %, plateaux are observed above 205 °C and 195 °C respectively. Therefore, charge transport in samples can only be studied above the glass transition temperature by BDS.

### 2.6. Thermally Stimulated Surface Potential Decay

Thermally Stimulated Surface Potential Decay (TSSPD) is an original approach for studying charge transport in polymer materials. It consists of electrically charging the surface of a sample and following the decay of the resulting potential during a heating cycle. Initially, samples were charged with positive or negative potentials by using corona processes [25,26]. Recently, in order to better represent the space environment, Roggero et al. used low energy electrons to build surface charge under high vacuum [27]. This charging process was initially used for Isothermal Potential Decay tests [28].

Experimentally, the PHEDRE facility (ONERA, Toulouse, France) was used. Samples (40 mm) side square) were placed on a copper heating sample holder under high vacuum ($10^{-7}$ mbar). To ensure a good thermal transfer between samples and their support, a thermally and electrically conductive grease was used. Samples were then charged at room temperature by 20 keV electron beam using a Kim ball Physics EMG 4212 electron gun. In these conditions, the average electron implantation depth is about 4 μm. Once charged at $-4$ kV, a vibrating kelvin probe was used to measure the evolution of sample surface potential $U(T)$ during a heating run at a rate of 4 °C/min. The measurement principle of this vibrating kelvin probe is explained in an application note provided by the manufacturer [29]. In the rest of this work, only normalised potential $U(T)/U_0$ will be presented in order to allow the comparison between different assays.

From the evolution of $U(T)$, it is possible to calculate the current density resulting from potential relaxation. Indeed, the current $I(t)$ during relaxation can be calculated in a dielectric material using Eq. (7).

$$I(t) = C \frac{dU}{dt}$$

(7)
Where $C = e \varepsilon_0 \frac{U}{dt}$ is the sample capacity and $\frac{dU}{dt}$ the time derivative of surface potential. The current density $J(T)$ (A/m²) can be calculated using Eq. (8).

$$J(T) = \frac{e \varepsilon_0 \frac{10^{-2} \text{Hz}}{e} dEU}{\beta dt}$$

With $\varepsilon_0$ the real part of the permittivity obtained by BDS at a frequency of $10^{-2}$ Hz and $\beta$ the heating rate (°C/s).

### 3. Results and discussion

#### 3.1. Mechanical behaviour and charge transport in non irradiated samples

**Influence of fibres on mechanical behaviour**

Fig. 2(a) presents the DMA thermograms of pristine PEEK and PEEK/SCF 3 vol. %. For both samples, loss moduli thermograms show the storage (black) and loss (grey) moduli thermograms of pristine PEEK and pristine PEEK/SCF 3 vol. % (a). Evolution of $E_{\text{composite}}/E_{\text{matrix}}$ at 25°C as a function of SCF ratio (empty symbol data were extracted from [32]) compared to different mixing laws (b).

Fig. 2(b) presents the evolution of $E_{\text{composite}}/E_{\text{matrix}}$ as a function of fibre ratio. These data were compared to different mixing laws: parallel, series and Halpin Tsai models.

Parallel and series models consider continuous fibres with an uni directional orientation. For the parallel model, the mechanical stress is applied along fibre direction. For the series model, the mechanical stress is applied orthogonally to fibre direction. They are described by Eqs. (9) and (10) respectively.

$$E_{\text{c}} = E_{\text{m}}(1 - \Phi_f) + E_f \Phi_f$$

(9)

$$E_{\text{c}} = \left(1 - \frac{\Phi_f}{E_{\text{m}}} + \frac{\Phi_f}{E_f}\right)^{-1}$$

(10)

With $E_c$, the composite modulus, $E_m$ the matrix modulus, $E_f$ the fibre modulus and $\Phi_f$ the volumic ratio of fibres.

The third mixing law used is the Halpin Tsai model [35,36] which is described by Eq. (11). In this model, the parameter $\theta$ allows to take into account the influence of filler aspect ratio on the evolution of mechanical modulus. In case of a mechanical stress applied along fibre direction, $\theta = 2\nu$.

$$E_{\text{c}} = E_{\text{m}} \left(1 + \frac{\theta \Phi_f}{T - \nu \Phi_f}\right)$$

(11)

With $\nu = \frac{\nu_{\text{c}}}{\nu_{\text{m}}} \frac{1}{\nu_{\text{c}} + \theta}$

These three mixing laws are represented in Fig. 2(b) by considering $E_{\text{m}} = 2.8$ GPa, $E_f = 225$ GPa [37] et $\theta = 2\nu = 15.8$.

The figure shows that parallel and series models do not describe experimental data at all. This is explained by the hypothesis of the models which consider uni directionally oriented continuous fibres. Thus, in these conditions, parallel model overestimates modulus values while series model underestimates them. Nonetheless, Halpin Tsai model gives a good description of data by considering a fibre aspect ratio of 7.9 as calculated from the percolation threshold. This model assumes that stress is applied along fibre direction. Therefore, the fact that it well describes the evolution of glassy modulus with filler ratio indicates that there is a preferential orientation of fibres due to processing.

**Influence of fibres on charge transport**
The influence of Short Carbon Fibres on the charge transport in pristine samples was studied by Thermally Stimulated Surface Potential Decay below glass transition and by Broadband Dielectric Spectroscopy above glass transition.

Fig. 3 presents normalised potential thermograms and the corresponding Current Density obtained by TSSPD for pristine PEEK and PEEK/SCF 3 vol. %. The PEEK thermogram shows a potential decay which occurs in two steps associated with two relaxation phenomena. The first step is observed on the temperature range [60 °C; 140 °C] and corresponds to a slow potential decrease. It results in a slight increase of current density up to a plateau from 130 °C to a slow potential decrease. It results in a slight increase of current density up to a plateau from 130 °C to a slow potential decrease. It results in a slight increase of current density up to a plateau from 130 °C to a slow potential decrease. It results in a slight increase of current density up to a plateau from 130 °C to a slow potential decrease. It results in a slight increase of current density up to a plateau from 130 °C to a slow potential decrease.

In PEEK/SCF 3 vol. %, the presence of fibres induces significant changes of TSSPD thermogram compared to PEEK. On all the studied temperature range, the normalised potential is lower for composite than for PEEK. Thus, it appears that the first relaxation phenomenon leads to a faster potential decay, resulting in its total relaxation. This relaxation phenomenon being associated with charge transport in sample thickness, we can conclude that the presence of fibres increases electron conductivity in the composite even below percolation threshold. Moreover, the potential being totally relaxed before the glass transition manifestation, this second phenomenon is not observed. By looking at the current thermogram for composite, the absence of current peak around 160 °C confirms this observation. The figure also shows that during the first relaxation phenomenon, the current density is the same between PEEK and composite despite a faster relaxation process. This is explained by the fact that current density is also proportional to the electric field $E$ ($J = \sigma_{DC}E$). Indeed, despite a higher conductivity thanks to fibres, the electric field is lower: composites are charged with the same initial surface potential as PEEK samples ($U_0 \approx 4 \text{kV}$) while their thickness is twice greater.

In the literature, Das Gupta and Doughty were the first to study the charge transport in PEEK as a function of temperature [38]. They reported above glass transition temperature an activation energy of 2.1 eV (1 eV = 96 485 J/mol). This value is significant in regard to the activation energy measured for several other polymers (e.g. $\approx$0.6 eV for PET [39], $\approx$0.9 eV for PVDF [40] or $\approx$0.4 eV for PDMS [27]). They explained this value by the phenyl rings present on the backbone chain of PEEK which limit electron mobility. Afterwards, Kim and Ohki associated this high value with ionic charge carriers predominant above glass transition: ions being larger entities than electrons, the activation energy associated with their conductivity is higher [41]. Similar activation energy value has been already reported and associated with ionic charge carriers: for example Henri et al. reported an activation energy of 2.2 eV for a Polyimide [42].

However, for ionic conductive polymers, some studies reported that conductivity can be described by a Vogel Tamman Fulcher (VTF) equation above glass transition temperature [43,44]. This type of temperature behaviour indicates that ionic conductivity is activated by the free volume expansion in the polymer. This VTF behaviour is described by Eq. (12).

$$\sigma_{DC} = \sigma_\infty \exp \left( -\frac{1}{a_f(T - T_0)} \right)$$  

(12)

With $\sigma_\infty$ the pre exponential factor (S/m), $a_f$ a parameter related to free volume expansion coefficient (°C$^{-1}$) and $T_0$ the activation temperature of ionic conductivity (°C).

In this work, the VTF fit showed a better description of PEEK $\sigma_{DC}$ data than an Arrhenius fit on this temperature range. Therefore, we can conclude that the predominant charge carriers in PEEK above glass transition are ions whose transport is activated by the free volume expansion. It should be noted that the $a$ mobility in PEEK, corresponding to the glass transition manifestation, follows a VTF behaviour as well [18,45]. Thus, in PEEK, $a$ mobility and ionic conductivity above $T_g$ are both activated by the same process: the free volume expansion.

Fig. 4. Arrhenius diagram of DC conductivity above glass transition for pristine PEEK and PEEK/SCF 3 vol. %. VTF fit for each samples are represented in dashed lines.
In regards of PEEK chemical structure, it can be assumed that ions correspond to protons released from the aromatic rings due to temper ature increase; the resulting negative charge is stabilised by electron delocalisation. For composites, the same temperature dependence of conductivity is observed. This indicates that the main charge carriers above glass transition remain ions even in presence of carbon fibres. Thus, fit parameters obtained for pristine PEEK and PEEK/SCF 3 vol. % are reported in Table 2.

For PEEK, the $\alpha_f$ value is consistent with the one found in a previous study through the VTF fit of a relaxation ($\alpha_f = 4.4 \times 10^{-4} \, ^\circ\text{C}^{-1}$) [18]. A similar value is also found for composite. This confirms that the ion transport is activated by the same macromolecular process, i.e. the free volume expansion. However, a lower activation temperature is found for ionic conductivity than for $\alpha$ relaxation ($T_{\alpha} = 90 \, ^\circ\text{C}$), either in PEEK or PEEK/SCF 3 vol. %. In the literature, similar activation temperatures for this two process have been observed for a PolyEpoxy [43] and for a PolyThioPhene/PolyVinylAcetate composite [44]. In the free volume theory, this temperature is described as the temperature at which the free volume became higher than a critical volume above which the process is possible [46]. For both of the listed systems, the critical volume allowing the $\alpha$ relaxation process is the same than for the activation of ionic transport. However, the $\alpha$ relaxation of PEEK occurs at high temperatures due to the rigidity of the main chain. The ion size being small compared to $\alpha$ relaxing entities, the free critical volume associated with their transport is reached at lower temperatures: $T_\alpha < T_{\alpha}$.

Between PEEK and PEEK/SCF 3 vol. %, the $\sigma_{SC}$ values are very close. This is explain by the fact that carbon fibres are not ionic conductors and therefore, do not modify the ion conductivity. However, the fibre have an influence on the VTF fit parameters $T_m$ and $\alpha_f$. An increase in $T_m$ is observed in composite and indicates that in presence of fibres, the activation of conductivity by the free volume occurs at higher temperature. Nonetheless, once the activation temperature is reached, the free volume expansion is higher (i.e. increase in $\alpha_f$).

### 3.2. Influence of fibres on ageing mechanisms of PEEK under electronic irradiations

In previous studies, we showed by calorimetric analyses that amor phisation of crystallites and cross linking of amorphous phase occur in PEEK when irradiated by electrons [17,18]. The amorphisation process was highlighted by the decrease in melting temperature $T_m$ and in crystallinity ratio $\chi_c$. The cross linking was identified by the increase in glass transition temperature $T_g$ and by the irreversibility of modifications (e.g. the decrease in $T_m$ observed on first and second heating scan).

DSC analyses were also carried out on PEEK/SCF 3 vol. % com pOSites in order to identify the influence of fibres on the ageing of PEEK matrix. However, DSC thermograms are not presented here for the sake of clarity. Instead, data extracted from these thermograms are reported in Table 1 and their evolutions with dose in PEEK and PEEK/SCF 3 vol. % are compared in Fig. 5.

In presence of fibres, the evolutions of these thermal parameters follow the same trend than PEEK like described before. Thus, for this SCF ratio, fibres do not modify the ageing mechanisms of PEEK.

Specifically, Fig. 5 shows that the increase in $T_g$ during the second heating run is the same than for PEEK: the evolution of cross linking density with dose is not modified. The decrease in crystallisation temperature $T_m$ (shown in Table 1) is similar to the one observed in PEEK. This decrease is linked to the increase in cross linking and therefore is consistent with the increase in $T_m$ in the crystalline phase, a significant difference in crystallinity ratio is noticed between pristine samples: a higher $\chi_c$ is observed for the composite and explained by fibres which play the role of nucleation sites leading to a higher quantity of crystalline phase. After irradiations, a slightly lower decrease in $T_m$ is observed, especially fo the highest dose. Fibres seem to stabilise the crystallite ageing. This hypothesis is confirmed by the lower decrease in the crystallinity ratio of composite in front of PEEK samples. During the second heating run, $T_m$ is the same for PEEK and PEEK/SCF 3 vol. %: cross linking of amorphous phase limits the crystallite growth. However, the crystallinity ratio remains higher in irradiated composites. This is due to the fibres which still act as nucleation sites during cooling from melting state.

The influence of this physico chemical ageing on the mechanical behaviour of composites was studied by DMA. Storage $E'$ and loss $E''$ moduli thermograms are presented in Fig. 6 for pristine and irradiated PEEK/SCF 3 vol. %.

On the loss modulus thermograms, the $\gamma$ relaxation is not modified by ageing. This behaviour was also observed for PEEK samples and was linked to the fact that distance between cross linking nodes is larger than the size of involved relaxing entities. On the $\alpha$ relaxation, irradiations induce a shift of the peak to higher temperatures. This increase is similar in PEEK and is consistent with the increase in $T_g$. It is explained by the cross links which limit the mobility of chain sequences relaxing at $T_g$.

On the storage modulus thermograms, the presence of fibres has a significant influence on their evolution after irradiations. Contrary

<table>
<thead>
<tr>
<th>Dose (MGy)</th>
<th>$T_g$ (°C)</th>
<th>$\Delta C_p$ (J/g. °C)</th>
<th>$T_m$ (°C)</th>
<th>$\chi_c$ (%)</th>
<th>$T_{\alpha}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>151 147 0.13 0.11 341 342 35.8 40.1 299</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Dose 12 MGy</td>
<td>154 150 0.08 0.11 332 333 34.5 35.2 282</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Dose 34 MGy</td>
<td>159 153 0.10 0.13 323 320 30.9 29.7 265</td>
<td></td>
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to PEEK for which a significant increase in rubber modulus due to cross linking phenomenon was reported, no evolution either glassy modulus or rubber modulus is observed in irradiated composites. Thus, the presence of fibres stabilises the evolution of composite mechanical behaviour. This absence of evolution can be explained by two contributions. In one hand, fibres stabilise the ageing of the matrix under electronic irradiations and therefore, stabilise the evolution of mechanical behaviour. On the other hand, the presence of fibres hides the influence of matrix ageing on mechanical behaviour of the composite.

3.3. Evolution of charge transport in irradiated PEEK and PEEK / short carbon fibre composite

The influence of electronic irradiations on charge transport in PEEK and PEEK/SCF 3 vol. % composite was studied below and above glass transition temperature. In case of PEEK, the influence of irradiations in rubbery state ($T_{\text{irrad.}} = 165 ^\circ C$) was also investigated in the continuity of our previous work.

Charge transport below glass transition

Fig. 7 present the normalised potential thermograms for both matrix and for each irradiations conditions. For PEEK samples, room temperature irradiations induce a shift to lower temperatures of the first relaxation phenomena with increasing dose. It means that electronic transport occurs earlier after ageing. In PolyPropylene, Thysens showed that the decrease in crystallinity ratio leads to an earlier surface potential relaxation [47]: conductivity in polymers taking place in amorphous phase, the increase in amorphous quantity favours charge transport. In addition, this shift to lower temperature can also be partly explained by a decrease in the activation energy of this relaxation phenomenon. A decrease in the slope of the potential decay is observed as well (i.e. a decrease in the corresponding current density). Ageing induces a decrease in electronic conductivity which is explained by the increase in the quantity of charge traps. On the dipolar manifestation of the glass transition, we can denote a slight increase in the width of the potential drop. This is explained by the increase in charge traps associated with the increase in the number of cross linking nodes. This behaviour is totally opposite to the one observed after room temperature irradiations. This is due to the higher cross linking density whose effect becomes predominant in front of amorphisation effect. Similar trends have been observed in PEEK for other properties like penetrant diffusion [18]. These observations confirm that competition between amorphisation and cross linking has a significant influence on polymer property evolutions under electronic irradiations and more generally under ionising radiations.

For PEEK/SCF 3 vol. % composites, irradiated sample thermograms are very similar to the pristine one, regardless of the ionising dose. It shows that the presence of fibres tends to stabilise the surface relaxation process in front of electronic irradiations. This behaviour is analogous to the one observed through mechanical analysis and is explained in the same way by two contributions: a stabilisation of the matrix ageing and the hiding of ageing influence on electronic transport. This last part illustrates the fact that fibres tend to control the electronic conductivity, even below the percolation threshold.

Charge transport above glass transition

Fig. 8 presents the Arrhenius diagrams of $\sigma_{\text{DC}}$ above $T_g$ for pristine/irradiated PEEK (Fig. 8(a)), and for pristine/irradiated PEEK/SCF 3 vol. % (Fig. 8(b)). VTF fit are represented in dashed lines and fit parameters are reported in Table 2 for both PEEK and PEEK/SCF 3 vol. % composites.

For PEEK samples, room temperature irradiations lead to a decrease in $\sigma_{\text{DC}}$ with increasing dose on all the temperature range. A simultaneous decrease in $\sigma_{\text{DC}}$ is observed. For 165 °C irradiated PEEK, a greater decrease is observed: for the highest dose, this decrease is about one decade. These evolutions coincide with the increase in cross linking density in PEEK: a higher cross linking density induces a higher decrease in ionic conductivity. It is explained by cross linking nodes which limits ionic transport by decreasing amorphous phase mobility. Moreover, we observe that for 165 °C irradiations, PEEK $\sigma_{\text{DC}}$ tem perature behaviour tends to an Arrhenius behaviour. This change is observed as well through the significant decrease in $T_g$ for pristine samples. Indeed, when $T_g = 0 K$ the VTF equation becomes a typical Arrhenius equation. However, an opposite evolution is observed after room temperatur irradiations with an increase in $T_g$. In this case, the $T_g$ increase is associated with the increase in cross linking nodes which constrain the free volume and is coherent with the increase in $T_g$. For 165 °C irradiated samples, the change towards an Arrhenius behaviour indicates that ionic conductivity becomes less and less dependent on molecular mobility. To the authors’ knowledge, this trend has never been reported in literature. It can be supposed that the higher stiffening
of amorphous phase due to higher cross linking density limits the influence of molecular mobility on ionic transport.

On the $\alpha_f$ parameter, opposite evolutions between both irradiation temperatures are observed as well: an increase for 25°C irradiations and a decrease for 165°C irradiations. Again, this behaviour is explained by the competition between amorphisation and cross linking. For room temperature irradiations, the effect of amorphisation is predominant: the lower quantity of crystallites induces less constrains on amorphous phase and favours free volume expansion ($\alpha_f$ increase). For 165°C irradiations, the effect of cross linking becomes predominant and limits the free volume expansion ($\alpha_f$ decrease).

In PEEK/SCF 3 vol.% composites, a decrease in $\sigma_{DC}$ (along with a decrease in $\sigma_{\infty}$) with increasing dose is observed as well. This decrease is slightly higher than in room temperature irradiated PEEK. In contrast to electronic transport, the presence of carbon fibres does not stabilise the evolution of ionic conductivity under electronic irradiations. This is consistent with the observations made between pristine PEEK and PEEK/SCF 3 vol.% samples: since carbon fibres are not ionic conductors, ion transport stay driven by the matrix properties. Therefore, in pristine state, fibres have no influence on $\sigma_{DC}$ values while after irradiations, the matrix ageing leads to a decrease in $\sigma_{DC}$.

Some evolutions on fit parameters are observed. On the $T_0$ parameter, a tendency to increase is observed after 34 MGy. As for PEEK, cross links limit the free volume increase. However, no significant evolution of $\alpha_f$ is observed for irradiated PEEK/SCF 3 vol.% in contrast to PEEK.

4. Conclusion

The aim of this work was to elaborate PEEK/SCF composites in order to limit surface charging in space environment and to study their ageing under electronic irradiations (compared to the ageing of bulk
PEEK). The fibre percolation threshold was determined at 9 vol.%. PEEK space applications requiring insulator materials, the SCF ratio selected for this study is 3 vol. %.

In pristine state, fibres induce an increase in glassy and rubbery moduli compared to PEEK. This increase is higher in rubbery state because fibres play the role of additional entanglements. The influence of fibres on charge transport was studied above and below glass transition temperature. Below Tg fibre presence influences fibres of a higher density in the composite. Fibres show even below percolation threshold, this behaviour shows that SCF can reduce relaxation compared to PEEK. Fibres favour electronic transport, even below Tg.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>PEEK</th>
<th>PEEK/SCF 3 vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σ∞</td>
<td>α∞</td>
</tr>
<tr>
<td>Pristine</td>
<td>2.7 × 10⁻²</td>
<td>3.45 × 10⁻⁴</td>
</tr>
<tr>
<td>25 °C Irradiation</td>
<td>4.2 × 10⁻⁴</td>
<td>4.54 × 10⁻⁴</td>
</tr>
<tr>
<td>Dose 12 MGy</td>
<td>9.2 × 10⁻⁵</td>
<td>6.17 × 10⁻⁴</td>
</tr>
<tr>
<td>Dose 34 MGy</td>
<td>1.7 × 10⁻⁵</td>
<td>2.78 × 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>9.9 × 10⁻⁶</td>
<td>0.63 × 10⁻⁴</td>
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References


CRediT authorship contribution statement

Guilhem Rival: Conceptualization, Methodology, Validation, Inves tigation, Writing - original draft, Visualization. Éric Dantras: Con cepctualization, Methodology, Validation, Investigation, Writing re view & editing, Supervision. Thierry Paulmier: Conceptualization, Methodology, Validation, Investigation, Writing - review & editing, Supervision.

Declaration of competing interest

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