Effect of electronic irradiations on electrical properties of a high-performance space-used thermoplastic polymer

G. Rival[1,2], T. Paulmier[1], E. Dantras[2]

[1]ONERA / DPHY, Université de Toulouse, F-31055 Toulouse, France

[2]CIRIMAT / Physique des Polymères, Université Toulouse III Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

Abstract

Polymer materials used in satellite manufacturing are exposed to diverse environmental constraints. Since they are electrical insulator, electronic radiations can induce electrostatic discharge phenomena which can damage satellite electronic systems. Moreover, these charging issues are potentially amplified by radiation induced physico-chemical ageing. Thus, it is essential to investigate these modifications to anticipate the material behaviour once in orbit. PolyEtherEtherKetone (PEEK) being used recently in space industry for structural applications, it is necessary to study its behaviour regarding electronic radiations. This work aims to analyse the effects of experimental electronic irradiations on electrical properties of PEEK samples. In this context, semi-crystalline PEEK films were irradiated under high vacuum and at ambient temperature by a mono-energetic electron beam. Analysis of the electric and charge transport behaviours showed evolutions induced by radiative ageing. Especially, a DC conductivity decrease was observed which has been associated with more numerous charge traps.

1 Introduction

In space environment, satellites have to deal with many environmental constraints such as temperature cycling, micrometeorites and space debris impact, or irradiation by energetic particles (electrons, ions, ...) of high intensity. In the case of polymer materials, electronic irradiations are the source of two major issues. Since polymers are dielectric materials, low energy electrons will accumulate at their surface leading to an increasing surface potential and therefore to electrostatic discharge phenomena which are at the origin of many spacecraft failures [1]. Moreover, high energy electrons can induce physico-chemical ageing of the polymer which can modify the physical properties of the material. For example, Roggero et al. studied the effects of electronic irradiations on a silicone elastomer and showed undesirable modifications of electrical behaviour regarding charging issues [2]. Knowing that 45% of spacecraft failures are caused by electric malfunctions [3], it is essential to investigate the effects of electronic irradiations on newly space-used polymers in order to anticipate their behaviour once in orbit.

In this work, we focused on PolyEtherEtherKetone (PEEK) due to its increasing use in space industry. Since its first commercialisation by the Imperial Chemical Industries in 1978, numerous studies have investigated the behaviour of PEEK and its composites under different radiation sources like gamma rays [4], ultraviolet light [5] or under combined sources [6]. In the case of electronic irradiations, some research had focused on this topic like Hegazy et al. who analysed gas release during irradiation [7] or Sasuga et al. who studied the evolution of tensile properties of irradiated samples [8]. Recently, Paulmier et al. investigated the effect of irradiation on charging behaviour of PEEK [9]. They showed that irradiated PEEK had higher charging kinetics, therefore increasing electrostatic discharge risks in orbit. However, none of the article found studied the charge transport behaviour of irradiated PEEK.

In that way, this work aims to study the effects of experimental electronic irradiations on PEEK. This paper focuses especially on the ageing effects on the charge transport behaviour. Thus, PEEK samples were irradiated by an electron beam under high vacuum leading to a homogeneous ionizing dose. Dynamic Dielectric Spectroscopy (DDS) allows to study evolutions of DC conductivity temperature behaviour. In addition to DDS, Thermally Stimulated Surface Potential Decay (TSSPD) was used for the first time to investigate electron transport in PEEK, this technique allowing a good representativity of space environment.

2 Materials and methods

2.1 Material

For this study, PEEK samples were supplied by Victrex in the form of semi-crystalline sheets having a thickness of 100 μm. Its chemical structure is reminded in figure 1.
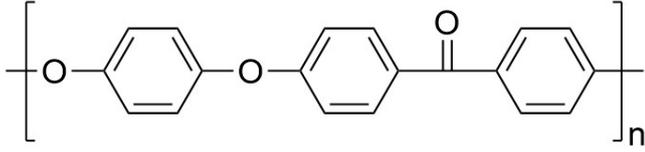
Figure 1: Chemical structure of PEEK

Physical structure analysis of neat samples was made using a Perkin Elmer DSC7 at a ramp rate of 10 °C.min⁻¹. Calorimetric glass transition temperature T_g was determined at 153 °C using tangent method and crystallinity ratio was calculated at 34 % using equation 1.

$$\chi_c = \frac{\Delta H_m}{\Delta H_\infty} \times 100 \tag{1}$$

Where ΔH_m is the sample melt enthalpy (J.g⁻¹) and ΔH_∞ is the theoretical melt enthalpy of a fully crystalline sample determined for PEEK at 130 J.g⁻¹ [10].

2.2 Experimental irradiations

To simulate the effects of electronic irradiations, samples were exposed at ambient temperature and under high vacuum to a mono-energetic electron beam of 350 keV, thanks to SIRENE facility (ONERA, Toulouse, France). The resulting ionizing dose of 3.4 10⁷ Gy was achieved in less than 60 h thanks to high beam currents (up to 60 nA.cm⁻²).

This experimental ionizing dose D (Gy) was calculated using equation 2.

$$D = \Phi \frac{1}{\rho} \left(\frac{dE}{dx} \right) \tag{2}$$

Where Φ is the total fluence measured during irradiation (cm⁻²), ρ the material density (g.cm⁻³) and dE/dx the stopping power (keV.μm⁻¹).

2.3 Dynamic dielectric spectroscopy

Dynamic Dielectric Spectroscopy (DDS) has been used many times to analyse electric behaviour of polymers and has already been extensively described [11].

For this study, a Novocontrol BDS 4000 spectrometer associated with an Alpha-A impedance analyser was used to determine DC conductivity of samples prepared in the form of 30 mm diameter film. Analysis were performed over a frequency range of [10⁻² Hz; 10⁶ Hz] and for isotherms going from -150 °C to 250 °C by 5 °C steps. The complex impedance $Z^*(\omega, T)$ measured over these ranges was used to determine the values of complex conductivity $\sigma^*(\omega, T)$

By studying the real part of the conductivity, it is possible to determine a DC conductivity value as a function of temperature. According to the universal dielectric response [12], the real part of the conductivity of a disordered solid can be describe by equation 3.

$$\sigma'(\omega) = \sigma_{DC} + A.\omega^s \tag{3}$$

At low frequency, the term $A.\omega^s$ becomes negligible 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 DC conductivity. Figure 2 illustrates the manifestation of this σ_{DC} plateau for a pristine PEEK sample.
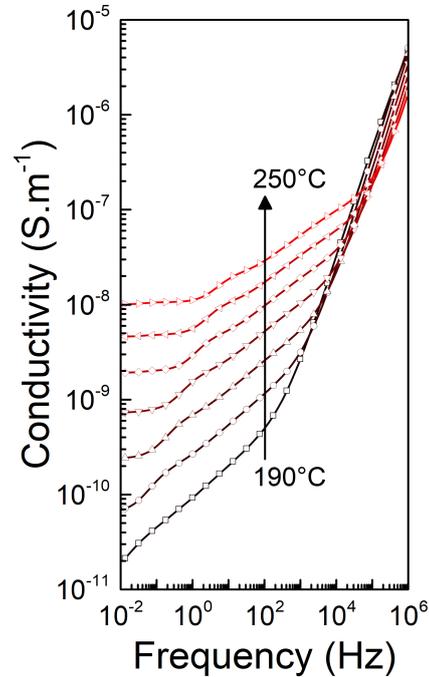

Figure 2: Frequency behaviour of the conductivity isotherms from 190 °C to 250 °C by 10 °C step for a pristine sample

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In practical, the σ_{DC} value was taken at 10^{-2} Hz for isotherms from 205 °C, temperature at which the first plateau is observed. The resulting $\sigma_{DC}(T)$ values were plotted on an Arrhenius diagram and fitted with equation 4.

$$\sigma_{DC}(T) = \sigma_{\infty} \exp\left(-\frac{E_a}{k_B T}\right) \qquad (4)$$

With σ_{∞} (S.m^{-1}) the pre-exponential factor and E_a (eV) the activation energy of the conductivity.

2.4 Thermally stimulated surface potential decay

Thermally Stimulated Surface Potential Decay (TSSPD) is an unusual method for studying electrical behaviour of polymers. It consists to electrically charge the surface of a sample and follow the decay of the resulting potential during a heating run. Initially, samples were charged with positive or negative potentials by using corona processes [13, 14]. Recently, in order to better represent the space environment, Roggero et al. used low-energy electrons to build surface charge [15], this process being initially used for Isothermal Potential Decay tests [16].

Since TSSPD is little known, no article were found concerning PEEK behaviour. Moreover, just few studies investigated its surface potential decay behaviour in isothermal conditions like Behrendt et al with corona charging [17] or Paulmier et al under space conditions [18].

Experimentally, the PHEDRE facility from the ONERA was used. Samples in the form of 40 mm side square, placed under high vacuum (10^{-7} mbar) at room temperature, were charged by 20 keV electrons using a Kimball Physics EMG-4212 electron gun. Once charged at around -4 kV, the evolution of surface potential was measured by a vibrating kelvin probe during heating at 4 °C.min^{-1}. Thereafter, in order to compare the assays, only normalised potentials $U(T)/U_0$ will be presented.

3   Results and discussion

3.1 DC conductivity behaviour

Figure 3 presents the Arrhenius plot of σ_{DC} for pristine and irradiated samples. Like described by equation 4, $\sigma_{DC}(T)$ shows a linear behaviour as a function of 1/T. Parameters obtained from these linear fits are reported for each samples in table 1.
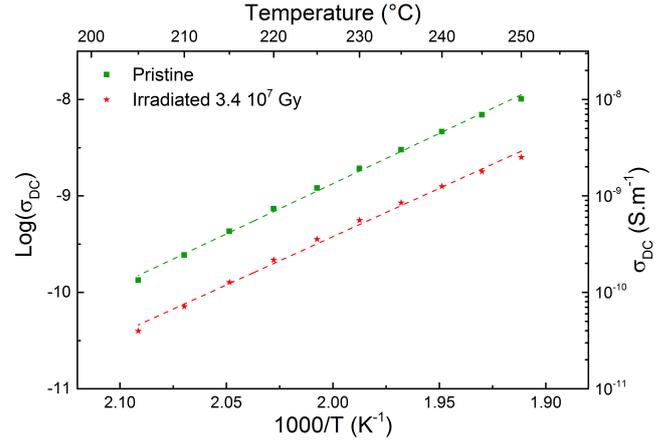

Figure 3: Arrhenius diagram of DC conductivity for the pristine and irradiated samples. Points represent experimental data while dashed lines represent fitted data

Figure 3 shows that conductivity of sample decreases with the ionizing dose. By looking at fitted parameters, pristine and irradiated samples show a high activation energy compared to other polymers ($\approx$0.3 eV for a silicon [2] or $\approx$0.9 eV for PVDF [19]). This high value for PEEK has already been reported and studied but not yet fully understood. Das Gupta and Doughty suggested that this value could be due to the presence of aromatic cycles leading to strongly bound electrons [20], while Kim and Ohki proposed that this value is associated with an ionic DC conductivity behaviour [21]. However, this activation energy E_a seems to be unchanged by irradiation. Regarding σ_{∞}, its decrease is consistent with the decrease of irradiated sample conductivity observed in figure 3. This lower value can be associated with an increasing number of traps limiting charge transport.

Table 1: Parameters obtained from the linear fit of σ_{DC} values

	E_a (eV)	σ_{∞} (S.m^{-1})
Pristine	2.1	9.2 10^{11}
3.4 10^7 Gy	2.0	4.1 10^{10}

3.2 Charge transport under space conditions

Figure 4 presents the TSSPD thermograms of pristine and irradiated PEEK samples. On pristine PEEK thermogram, two decay phenomena can be identified. A slow decay which extends over the temperature range [60 °C; 140 °C] and a much more intense and brief phenomenon at a temperature around 160 °C. This potential drop has been associated with

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the dielectric manifestation of the glass transition. Indeed, the orientation of dipoles in the electric field above calorimetric glass transition temperature T_g induces an opposite field which decreases the apparent surface potential [15]. Finally, the exact identification of the first decay phenomenon is more delicate. It can be assume that it correspond to electron transport in the sample. However, it is well known that polymer electrical conductivity is activated by the release of mobility above glass transition.
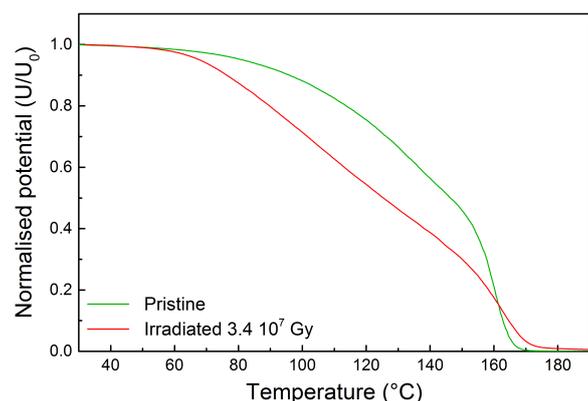

Figure 4: Normalised potential thermograms of pristine and irradiated samples

Irradiated sample thermogram reveals an important evolution of the first potential decay phenomenon. Indeed, it shows a start of potential decay at a temperature lower than for pristine sample. This shift can be associated with a decrease of its activation energy. Assuming it is a charge transport phenomenon, this decrease could be associated with shallower traps induced by irradiation. Moreover, even if this phenomenon starts at lower temperature, its kinetics seems to decrease with ionizing dose. This observation must be correlated with the conductivity decrease observed as well by DDS: a lower σ_{DC} value imply a limited charge transport. However, due to the lower activation energy, the phenomenon is more extended in temperature and lead to lower potential than for the pristine sample at the same temperature.

Finally, the TSSPD manifestation of the glass transition is also impacted by the irradiation. The potential drop seems to broaden with the ionizing dose indicating a larger distribution of relaxation times. This evolution suggests a much heterogeneous medium around relaxing entities which can be associated with defects created during irradiation.

4   Conclusion

This work aimed to analyse the effect of electronic irradiations on the charge transport behaviour of PEEK samples. The SIRENE facility from the ONERA allowed us to expose samples to high energy electrons (350 keV) with a high current beam (up to 60 nA.cm^{-2}), leading to an ionizing dose of $3.4 \, 10^7$ Gy.

Study of σ_{DC} behaviour displayed a decrease of conductivity. It has been assumed that this evolution is associated with more numerous traps created by irradiation which limit charge transport. TSSPD thermograms of PEEK showed two potential decay phenomena. The first ranging from 60 °C to 140 °C has been assumed to be due to electron leakage through sample. With an increasing ionizing dose, this phenomenon starts at lower temperature indicating a decrease of its activation energy. Moreover, irradiated sample shows a slower potential decay during this phenomena consistent with a limited charge transport. The potential drop observed at about 160 °C has been associated with the dipolar manifestation of the glass transition. It showed an increase of its temperature range for irradiated sample indicating a larger distribution of relaxation times and therefore, a much more heterogeneous medium. This increasing heterogeneity has been associated with defects created during irradiation. Moreover, it can be assumed that, by playing the role of new charge traps, these defects limit electron transport through sample and so, decrease its conductivity.

Finally, regarding electrostatic discharge risks, the effects of irradiation is more ambiguous. Indeed, the decrease of conductivity has a negative effect on charging kinetics and on potential relaxation. However, the charge transport phenomena observed below glass transition in TSSPD could minimize the effect of this decrease. Indeed, even if the charge transport is limited, the decrease of activation energy leads to a lower surface potential for the irradiated sample than for the pristine sample at the same temperature. For the future, it could be interesting to realise Isothermal Potential Decay above and below glass transition temperature in order to better understand the origin of this subglass phenomenon.

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