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# Analysis of cathodoluminescence behaviour of fluoropolymers

Guillaume Demol, Thierry Paulmier, Denis Payan

**Abstract**— This paper presents a study on cathodoluminescence (CL) of different space-used fluoropolymers, such as: Polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) and Ethylene tetrafluoroethylene (ETFE). This experimental technique allows highlighting radiative energy transitions under electron irradiation and degradation mechanisms under high radiation dose. Samples were irradiated with electron beam (10 keV – 1  $\mu$ A) under vacuum ( $10^{-6}$  mbar). A parametric study has been performed to analyse especially the effect of temperature and the injected radiation dose on the CL spectra of these different polymers. The CL spectrum for these three materials is composed of three elementary contributions at 2.2 eV, 2.4 eV and 3.75 eV, each of them being associated with specific processes in relation to different chromophores present in the materials or generated by electronic irradiation. A decline on the amplitude of the CL spectra with the increasing temperature or accumulated radiation dose has been observed on these fluoropolymers.

**Index Terms**— Charging, cathodoluminescence, defects, electron irradiation, material degradation, polymers, spacecraft.

## I. INTRODUCTION

Polymer materials are widely used on spacecraft for their thermal stability, high mechanical and electrical properties and relatively low specific weight. They are used on spacecraft as thermal control coatings, adhesives, seals, thermal insulations, electrical insulation or mechanical support. In this study, we will focus the attention on fluoropolymer films, such as FEP (Fluorinated ethylene-propylene), PTFE (polytetrafluoroethylene) and ETFE (ethylene-tetrafluoroethylene) used on spacecraft in OSR (Optical Solar reflector), multilayer insulation MLI, mechanical support or electrical-cable-jacketing.

In space environment, these polymers have to cope with irradiation by energetic particles, especially electrons, that can induce electrical charging and physico-chemical ageing processes. This charging phenomenon can lead to the initiation of electrostatic discharges and electrical arcs on different parts of the spacecraft (for instance solar arrays or electrical cables) that can induce significant damages or electromagnetic disturbances and generate strong risks for the spacecraft mission [1].

It has been shown previously [2]–[6], that charging effect is usually smoothed by ionization processes due to high-

energy electron irradiation that enhances significantly the bulk electric conductivity in these polymers through the creation of electron-holes pairs in the extended states: we speak about Radiation-Induced Conductivity (RIC).

Models based on solid-state physics have been developed at ONERA [7], [8] and other research groups [9]–[11] to describe and predict charge and ionization effects on space-used polymer materials. These models take into account different physical processes (ionization, trapping, detrapping and recombination) but some physical mechanisms are however not taken into account such as: energy transfer processes and ageing effect (by radical formation and structural modification). Previous results have indeed shown that the high radiation doses received by space used polymers may greatly alter their electrical properties (reduction of RIC and bulk conductivity on Teflon® FEP, PEEK, PEI and silicone with ageing [12]–[14]). This variation has been associated with a dramatic change of the structure of the materials, and band structure as well as formation of new deep traps that lead to an evolution of the traps energetic distribution profile [12], [15], [16].

It is therefore necessary to understand the physics steering charge transport, radiation/polymer interactions, and electrical ageing for a realistic predictions of spacecraft charging levels in space environment.

For this purpose, we have developed at ONERA, a cathodoluminescence spectroscopic technique (CL) for polymer analysis. CL corresponds to the emission of photon from materials irradiated, in our study, by energetic electrons (10 keV) that induce energy transfer in the bulk through different physical processes described in the following sections. This technique is relevant for the characterization of the different several physicochemical mechanisms (radical formation, recombination and de-excitation processes in relation with defect and impurities initially present in the material or generated by irradiation) occurring in irradiated materials and therefore to extract parameters related to the physics model used to describe charge transport in space materials (in particular the involved energies). This technique is widely used for the characterisation of inorganic materials [17], [18] but the application of this technique for polymer analysis is quite sparse [19]. The objective of this study is to use this technique on fluoropolymers to deepen our understanding of ageing, charge transfer and recombination

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effect in these irradiated materials. The major advantage of this technique is that it provides in-situ and instantaneous analysis of the irradiated polymer with no air exposure that could disturb the physico-chemical state of the materials and screen the ageing processes.

This paper presents the experimental characterization of different fluoropolymers by the CL technique. The attention has especially been focused on PTFE, FEP and ETFE polymers because they have a similar chemical structure but quite different charging behaviour under representative space environment [6]. The presence of tri-fluorinated side groups (for FEP) or the presence of ethylene groups within the monomer unit (for ETFE) can lead to very different degradation mechanisms [20], which could be characterized by CL measurements. In the first part, we compare the CL spectra of these three fluoropolymers in order to get a better understanding of the physico-chemical mechanisms steering cathodoluminescence in these materials. In the second part, we investigate the effect of material temperature and cumulative radiation dose (ageing) on the cathodoluminescence spectra of these polymer materials. This parametric study allows identifying the nature of the different emitted contributions and to assess the energy involved in the underlying processes.

## II. EXPERIMENTAL SETUP

### A. Experimental facility

Cathodoluminescence experiments have been performed with the MARCEL facility installed at ONERA (Toulouse, France). It is equipped (Figure 1) with a 10 keV (STAIB) electron gun. The axis of the gun is normal to the sample plane. The distance between electron gun exit and the sample is about 50 cm. It is possible to work in focused or defocused mode for the local or extended irradiation of the sample. A Faraday cup installed on the sample holder can measure the electron flux. The temperature of the sample holder (copper) can be controlled in the range 100 – 500 K allowing reproducing the temperature variations of materials on flight. A pumping system allows performing experiments at vacuum of  $10^{-6}$  mbar.

### B. Cathodoluminescence spectroscopy

A CL bench has been developed within the MARCEL facility. The experimental set-up is described in more detail in a previous paper [21]. A parabolic mirror has been used to enhance light collection. A UV-Vis-NIR spectrometer (StellarNet BLK-C-SR-50 model) was used to analyze the luminescence. The concave holographic grating spectrometer delivers high performance spectral analysis in the UV-Vis-NIR energy range covering 1.20 – 6.2 eV (200–1080 nm). The spectral resolution is determined by the grating and the slit width (50  $\mu\text{m}$ ) and is typically 0.5 nm. The SpectraWiz software is used for data acquisition. Integrated times of 10 s have been applied to avoid noisy spectra. The resulting spectra have been deconvoluted into Gaussian sub-bands using commercially available software (Origin 9.1, OriginLab Co., Northampton, MA, USA).

Fig. 1: Marcel facility

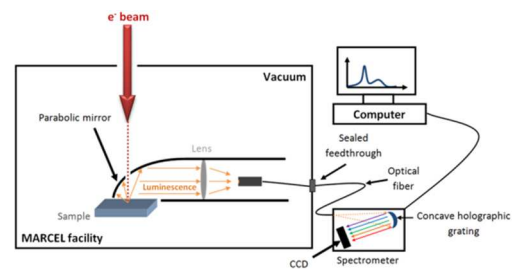
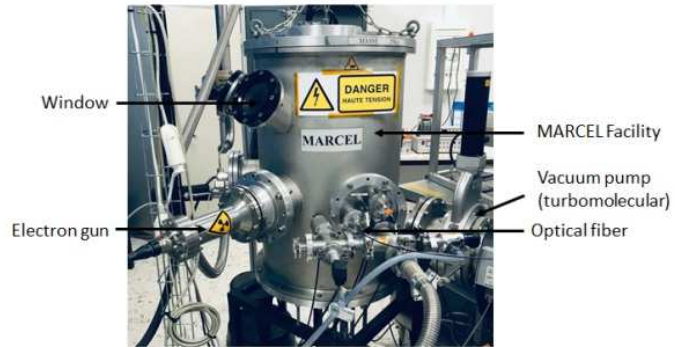


Fig. 2: Diagram of cathodoluminescence bench in the MARCEL Facility

### C. Sample preparation

In this study, we focused on three polymers belonging to the fluoropolymer family: PTFE, FEP and ETFE. PTFE and ETFE films have been purchased from Goodfellow. FEP films are Teflon® films from Dupont. The main interest is to understand the influence of the chemical structure on the luminescent properties of these polymers and to analyse possible common trends on the CL spectra due to identical chemical groups (chromophores). In addition, the advantage of cathodoluminescence is that it allows highlighting changes in the chemical structure (unsaturation for example) under electronic irradiation. All measurements have been carried out on 100  $\mu\text{m}$ -thick PTFE and FEP samples, and 125  $\mu\text{m}$ -thick ETFE films. 15 nm-thick semi-transparent silver electrodes have been deposited on both surfaces of samples for CL measurements. These electrodes have been connected to electrical ground during irradiation in order to get zero potential on the surface and then have a constant incident energy for the electrons along the irradiation. We demonstrated experimentally that the effect of this coating process on light intensity collected on the irradiated samples is very weak (light absorption by this thin metallic coating is very low).

### D. Irradiations conditions

Electrons beam (10 keV – 1  $\mu\text{A}$ ) in focused mode was used to irradiate the samples at room and low temperature (21°C to -100°C). Pt<sub>100</sub> thermistors with an accuracy of  $\pm 0.1^\circ\text{C}$  have been used to monitor the temperature of the material surface. The penetration depth of incident electrons (10 keV) has been estimated at  $\approx 1.3 \mu\text{m}$  for these materials using the Casino software [22]. Electron beam diameter is about 2.5 mm. The samples were exposed to very high radiation doses ( $3 \times 10^6$  to

$7.5 \times 10^7$  Gy). We analysed the influence of radiation doses and temperature ( $21^\circ\text{C}$ ,  $-50^\circ\text{C}$  and  $-100^\circ\text{C}$ ) on the profile and intensity of the CL spectra emitted by the three fluoropolymers (FEP, PTFE, ETFE).

### III. RESULTS

#### A. CL spectra of PTFE, FEP and ETFE

Figure 3 (a) compares the CL spectra at room temperature (RT) obtained on PTFE, FEP, and ETFE under electronic irradiation ( $10 \text{ keV} - 1 \mu\text{A}$ ). For sake of clarity, the spectra presented are normalised (Figure 3 (b)) in regard of the maximum intensity for each material. The CL spectra of these three fluoropolymers are very similar suggesting that the origin of cathodoluminescence processes is directly related to the chemical structure of these polymers. Two large emission peaks are present at  $\sim 2.2 \text{ eV}$  and  $\sim 3.7 \text{ eV}$ . The main difference between the three polymers is based on the absence of the  $\sim 3.7 \text{ eV}$  peak contribution for ETFE (Fig 3.a). We also note that the intense peak at  $\sim 2.2 \text{ eV}$  is shifted from one polymer to the other. In addition, this peak is asymmetric, which suggests that it contains two contributions. To identify them, each spectrum has been deconvoluted (Fig. 4), the parameters applied for this curve fit being presented in Table 1. The different energies, Full Width at Half Maximum “FWHM”, and maximum intensities involved in cathodoluminescence processes could be determined for each material. The spectral similarities (peak positions and FWHM) indicate that the physical processes involved in CL are certainly quite similar between the three materials. We will discuss in more detail the physical origin of these different peaks in section IV following the parametric study as a function of temperature (III.B) and irradiation time (III.C). To summarize, the analysis of the CL curves revealed 3 contributions  $P_1$ ,  $P_2$  and  $P_3$  present at the following respective energies:  $\sim 2.2 \text{ eV}$ ,  $\sim 2.4 \text{ eV}$  and  $\sim 3.7 \text{ eV}$ .

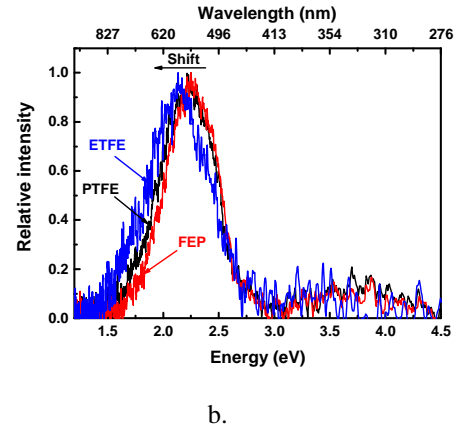
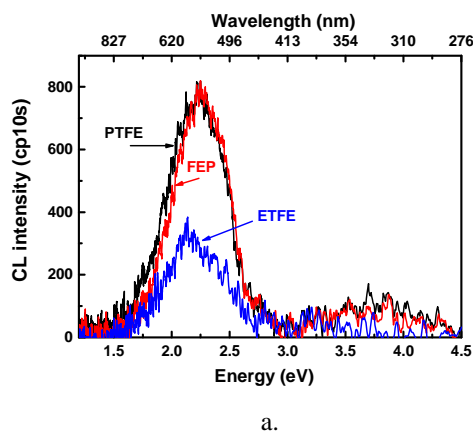
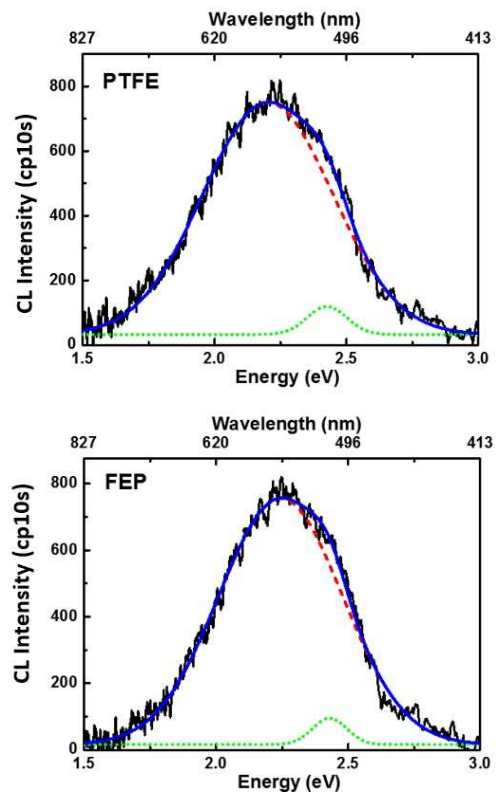


Fig. 3: (a) Comparison of the CL spectra of PTFE, ETFE and FEP at Room temperature. (b) Normalised spectra with respect to the peak at  $\sim 2.2 \text{ eV}$ .

#### B. Influence of temperature

In order to further understand the physico-chemical mechanisms steering the luminescence process from these three fluorine polymers, we analysed the temperature dependence on the CL spectra for these polymers. Experiments have been performed at  $-100^\circ\text{C}$ ,  $-50^\circ\text{C}$  and  $21^\circ\text{C}$ . The evolution of the CL spectra as a function of temperature is shown in Fig. 5. For all materials, we can observe mainly a decline of  $P_1$  at  $\sim 2.2 \text{ eV}$  and  $P_2$  at  $\sim 2.4 \text{ eV}$  with the increasing temperature (less pronounced on ETFE).  $P_3$  contribution at  $\sim 3.7 \text{ eV}$  is rather stable with temperature. No significant shift in the peak energy position was observed with temperature variations.



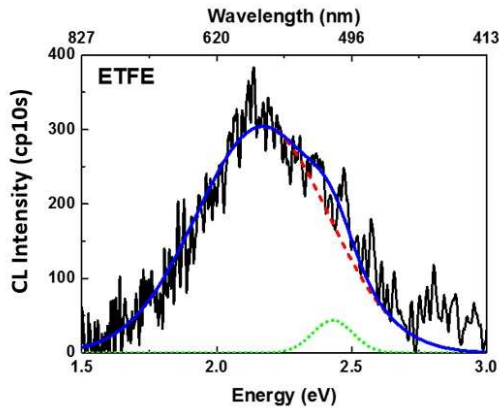


Fig. 4: Emission spectra of the irradiated film samples with the deconvolution process; P<sub>1</sub> (dash red) and P<sub>2</sub> (dot green curve); The solid blue curve indicates the summation of the components.

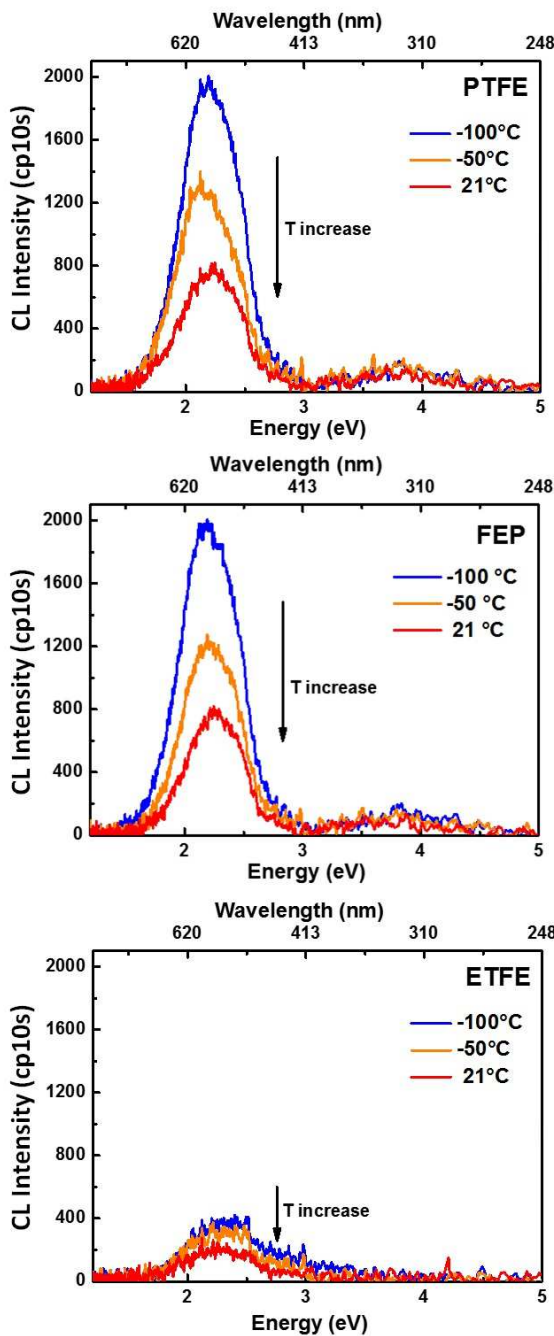


Fig. 5: Evolutions of the CL spectra of PTFE, FEP and ETFE at different temperatures (-100°C (blue); -50°C (orange) and 21°C (red)).

To complete these results, we also have examined the temporal/dose evolutions of the CL spectra at these 3 temperatures.

TABLE I:  
FIT PARAMETERS FOR THE DIFFERENT PEAKS OBSERVED ON  
THE CL SPECTRA FOR PTFE, FEP AND ETFE.

		Energy (eV)	Wavelength (nm)	FWHM (eV)	I <sub>Max</sub> (cps)
PTFE	P <sub>1</sub>	2,2	564	0,58	718
	P <sub>2</sub>	2,4	517	0,18	87
	P <sub>3</sub>	3,75	330	0,88	88
FEP	P <sub>1</sub>	2,25	551	0,55	739
	P <sub>2</sub>	2,45	506	0,15	80
	P <sub>3</sub>	3,7	335	0,88	80
ETFE	P <sub>1</sub>	2,15	577	0,58	304
	P <sub>2</sub>	2,45	506	0,17	43

### C. Influence of irradiation time / dose

Fig. 6 shows the irradiation time dependence of the CL emission spectra of PTFE and FEP at 21°C. In this section, we will focus only on the CL evolutions of PTFE and FEP because ETFE present very low luminescence efficiency. In general, all CL spectra decrease with irradiation dose. However, the decline in I<sub>CL</sub> for FEP is steeper than for PTFE. Indeed, after 250s of irradiation, I<sub>CL</sub><sup>PTFE</sup> (~ 2.2 eV) = 370 cps and I<sub>CL</sub><sup>FEP</sup> (~ 2.2 eV) = 230 cps which correspond to a decrease of about 53 % and 70 % respectively.

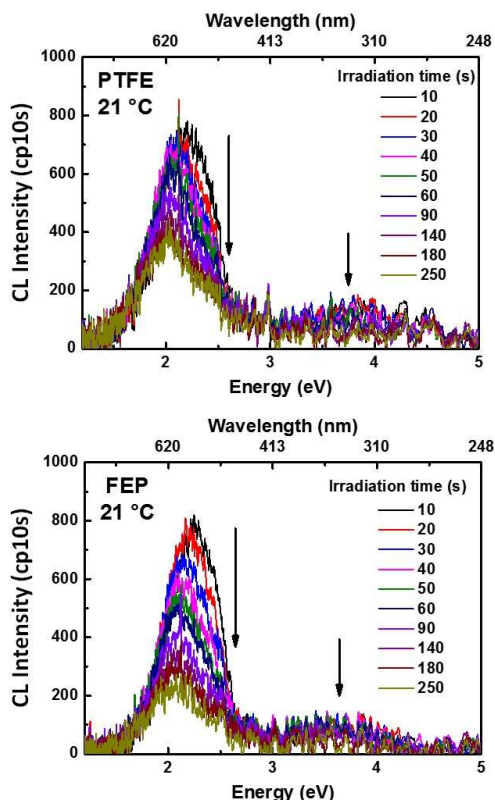


Fig. 6: The irradiation time dependence of the CL emission spectra (PTFE and FEP) at room temperature.

#### IV. DISCUSSION

The comparison of the CL spectra of the three fluorinated polymers (PTFE, FEP and ETFE) showed that the radiative transitions could be of the same nature. By deconvolution into Gaussian peaks, we suggested in this paper three contributions placed at  $\sim 2.2$  eV,  $\sim 2.4$  eV and 3.7 eV on the CL spectra. The slight differences in the position of the peaks from one material to another are probably due to differences in chemical conformation. This energy shift has already been observed in photoluminescence on ETFE and PTFE [23]. For a better understanding, the analysis will be detailed peak by peak.

The contribution at  $\sim 2.2$  eV is the most intense and present in these three materials. This peak cannot be explained by direct transitions  $\sigma^* \rightarrow \sigma$  (directly related to the C–F or C–C  $sp^3$  type single bonds present initially in the material). These transitions require excitation energy levels in the order of  $\sim 5$  eV, which is well beyond the incident energies involved in photoluminescence. Indeed, according to studies carried out on photoluminescence by Scanni et al [24] and other authors [25]–[27], this emission peak could be related to the electronic de-excitation corresponding to  $\pi^* \rightarrow \pi$  transition (from unsaturated bonds C=C mainly created by irradiation through chain-scission).

Many authors [20], [21], [24]–[27] have investigated the changes in the chemical structure of these three fluorinated polymers (PTFE, FEP and ETFE) under irradiation (gamma, ionic or electronic) and have demonstrated the creation of this type of unsaturated group (C=C) under irradiation. To

illustrate this point, we present in Fig. 7 potential reaction mechanisms that may lead to the formation of this type of chemical bond. The reaction mechanisms leading to the creation of C=C bonds in the three fluoropolymers are quite similar [30], [34], [35] given their close chemical structures. For this reason, we will only detail the degradation mechanisms induced by irradiation in ETFE.

The electronic irradiation of the macromolecular chain of the polymer can lead to two main processes [30]: 1. the splitting of the C–F and C–H lateral bonds for ETFE: we speak about dehydrofluorination processes. In the case of PTFE, we only observe cleavage of the C–F bond, whereas for the FEP copolymer, C–F or C–CF<sub>3</sub> bonds are involved in the cleavage process; 2. the homolytic cleavage of a C–C bond present on the main chain. These two cases will, in general, lead to different processes. Indeed, as shown in Figure 7, the process (1) corresponding to the phenomena of dehydrofluorination with the loss of fluorine (F) and hydrogen (H) atoms can lead to cross-linking mechanisms by radical recombination. For the second process (2), electrons beam irradiation leads to chain scission (C–C bonds breakage within the main chain), forming radical species (R–CF<sub>2</sub>–(C $\bullet$ )F<sub>2</sub> or R–CH<sub>2</sub>–(C $\bullet$ )H<sub>2</sub>). The interaction of these radical species with the main polymer chain will lead to the loss of a hydrogen or fluorine atom and the formation of unsaturated groups like R–CF=CF<sub>2</sub> or R–CH=CH<sub>2</sub>. Thus, the creation of this double bond could be at the origin of the fluorescence processes involved in  $\sim 2.2$  eV emission peak. Other mechanisms may of course lead to the creation of unsaturation within the macromolecular chain.

Depending on the irradiation conditions and the chemical structure, the polymers will therefore have either: (1) a tendency to cross-linking or (2) a preference for chain scission which can lead to the creation of unsaturation. This has been demonstrated by Rosenberg et al [37] who analysed the influence of the H/F atomic ratio on these competing mechanisms in several fluorinated polymers. It was found that the number of crosslinking nodes per dose unit increases with the increase of the H/F ratio: according to the authors, ETFE tends to crosslink more easily than FEP or PTFE. The hypothesis that has been suggested is that the presence of hydrogen atoms facilitates the formation of radicals leading to cross-linking. If it is therefore assumed that crosslinking processes in ETFE predominate in comparison with FEP, this could explain the low luminescence efficiency observed at  $\sim 2.2$  eV for ETFE (because fewer unsaturated groups like C=C would be observed in ETFE).

From different authors [24-27], this peak is therefore ascribed to fluorescence process induced by the C=C bonds. The evolution of the intensity of this peak with temperature is due to the fact that fluorescence is dependent on temperature variation.

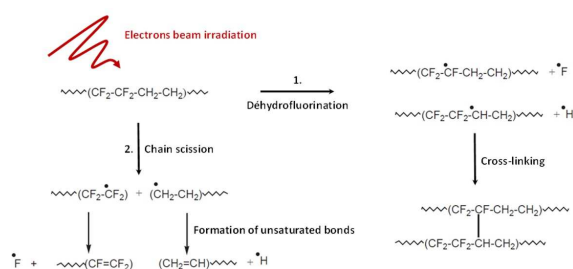


Fig. 7: Schematic representation of mechanism of electrons beam irradiation induced reactions in ETFE [36].

The weak peak at  $\sim 2.4$  eV can be ascribed to two processes. According to Khatipov et al [32, 40], the peak located at  $\sim 2.4$  eV could be attributed to the fluorescence of  $(\text{CF}=\text{CF})_n$  groups (with  $n = 4 - 7$ ) produced by chain scission induced by electron irradiation. The evolution of this peak with temperature is again not surprising since fluorescence can be affected by temperature with an increase of the fluorescence intensity when temperature drops down [29].

This peak could also be associated with radiative de-excitation mechanisms derived from carbonyl chromophore groups (C=O) [25], [38]. According to Charlesby et al [38], carbonyl group is present in fluoropolymers network in the form of impurities generated during material manufacturing. These groups would probably be located at the end of the macromolecular chain or a side chain. This carbonyl group can induce phosphorescence of the materials which increases with the decline of temperature. A diagram of this radiative de-excitation is illustrated in Fig. 8. This transition is a three-step process: First, electronic irradiation leads to the excitation of a chromophore center by energy absorption: from fundamental state to an excited state ( $S_0 \rightarrow S_1$ ). This step is followed by an energy inter-system crossing from the singlet state  $S_1$  to a metastable triplet state  $T_1$  in relation to the carbonyl group. Energy relaxation (transition from the triplet state to the fundamental state:  $T_1 \rightarrow S_0$ ) leads to phosphorescence phenomenon and therefore to the emission peak at  $\sim 2.4$  eV. Although this contribution has been attributed in the literature to carbonyl groups present under impurities form, it may well be possible that these species are also created during irradiation by the formation of hydroperoxide groups (R-OOH) [35] due to oxygen dissolved in the polymer (in the same way as polyethylene [39]).

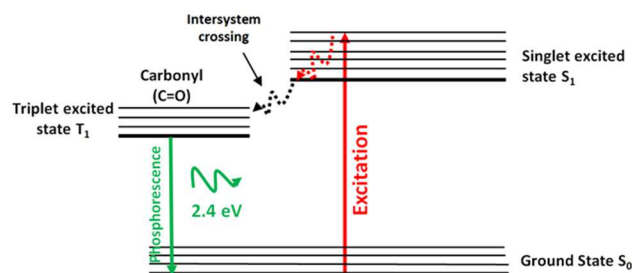


Fig. 8: A possible phosphorescence mechanism leading to the emission peak at around 2.4 eV.

The origin of the peak at  $\sim 3.75$  eV remains relatively uncertain, but could be related to other polyene  $(\text{CF}=\text{CF})_n$  chromophores generated by irradiation [27], as suggested by Khatipov et al [26].

Indeed, for ethylene-propylene-hexadiene terpolymer, ESR (electron spin resonance) measurements have also shown that the polyenyl radical  $-(\text{C}\cdot)\text{H}-(\text{CH}=\text{CH})_n-$  can be generated and detected for doses higher than 50 kGy [31] (which corresponds to the dose levels injected into the materials during the cathodoluminescence tests). This type of polyene group comes mainly from the prior creation of conjugated diene groups [31]. During irradiation, this chromophore would be excited from the fundamental state  $S_0$  to a singlet excited state  $S_1$ . The direct de-excitation of  $S_1 \rightarrow S_0$  leads to fluorescence phenomena.

Different trends observed experimentally allow us to better understand the involved processes. An interesting point concerns the strong differences in intensity observed between ETFE and the other two materials (PTFE and FEP) on this peak at  $\sim 3.75$  eV. Indeed, as we have seen in Figure 3, this peak does not appear on ETFE unlike PTFE and FEP. This can be explained by the important role, for luminescence, played by polyene structures of the  $-(\text{CF}=\text{CF})_n-$  type (with  $n$  between 4 and 7), these structures being generated by irradiation. In the case of PTFE and FEP, given their structure consisting essentially of C-F groups, the concentration of polyenes of this type ( $-(\text{CF}=\text{CF})_n-$  with  $n$  between 4 and 7) is high [40], which promotes cathodoluminescence processes. In the case of ETFE, on the other hand, the formation of short length polyene  $-(\text{CF}=\text{CF})_n-$  with values of  $n$  lower than 3 (limitation due to cross-linking phenomena) is furthered. According to Hudson et al [41], this type of structure has no luminescent properties, which explains why the intensity of the CL peak at  $\sim 3.75$  eV is very weak or even non-existent for ETFE. The same trend can be observed for the peak at  $\sim 2.2$  and  $\sim 2.4$  eV, likely to be attributed also to the fluorescence of polyene groups (with different  $n$  values): the intensity of these peaks is much lower for ETFE which could also be explained by a lower production of fluorescent polyene groups with  $n > 4$ .

The last point of analysis concerns the changes in the spectrum with the increasing dose: we were able to observe, for the three materials, a gradual decline in the intensity of the CL peaks with the increasing dose. This observation seems to contradict the physical origin proposed for these three peaks, which would be mainly due to the radiation effects and therefore to the dose. However, as mentioned by Khatipov et

al [26], irradiation induces also the production of optical centers (OC) that can absorb light emitted by the other fluorescent optical centers. The author mentioned, as demonstrated in this current paper, that different types of fluorescent optical centers can be produced by irradiation but also that the concentration of OC of absorption is higher than the concentration of OC producing fluorescence. The density of absorption OC increases with the radiation dose which hinders on the fluorescence process of the irradiated material leading to a gradual decline of the cathodoluminescence peaks. This process is confirmed by the fact that all materials samples presented a change of colour on the irradiated area.

As a summary, these tests show that the luminescence spectra of fluoropolymers are mainly governed by the large-structured polyenes and isolated double bonds generated by irradiation and by possible interaction processes with oxygen dissolved in the material (1. which partly promotes the formation of carbonyl groups, 2. which could interact with triplet states, particularly at room temperature, to inhibit the phosphorescence of the material). In other words, when the sample is irradiated by high-energy electrons, the absorption of energy leads to the excitation of electrons from the fundamental state ( $S_0$ ) to an excited state ( $S_1$ ) or higher excited states. Relaxation processes can take place within these states (rotational and vibrational) leading to the emission of phonons. The return of the electron present in the  $S_1$  state to the fundamental state  $S_0$  could generate the emission of photons at  $\sim 2.2$ ,  $\sim 2.4$  and  $\sim 3.75$  eV by fluorescence characteristic of the polyene groups formed during irradiation. However, excited electrons could also relax through the triplet states generated by carbonyl groups (C=O). The relaxation of these triplet states towards the fundamental state generates phosphorescence processes leading to the emission of energy photons at  $\sim 2.4$  eV. Table II summarizes the different luminescent processes involved in fluorinated polymers.

TABLE II.  
SUMMARY OF THE DIFFERENT POSSIBLE  
SPECTRAL CONTRIBUTIONS OF  
FLUOROPOLYMERS.

Energy (eV)	Natures	Groups	Luminescence transitions
$\sim 2,2$	Fluorescence	C=C	$S_1 \rightarrow S_0$
	Fluorescence	$-(CF=CF)_n-$ $4 < n < 7$	$S_1 \rightarrow S_0$
$\sim 2,4$	Fluorescence	$-(CF=CF)_n-$ $4 < n < 7$	$S_1 \rightarrow S_0$
	Phosphorescence	C=O	$T_1 \rightarrow S_0$
$\sim 3,75$	Fluorescence	$-(CF=CF)_n-$ $4 < n < 7$	$S_1 \rightarrow S_0$

## V. CONCLUSION

Cathodoluminescence analysis carried out on the various fluorinated polymers have highlighted the predominant role played by chemical processes on the luminescence of these materials. Irradiation leads to the formation of many unsaturated groups, such as the formation of polyene structures of the  $-(CF=CF)_n-$  type (with n between 4 and 7)

that mainly contribute to the fluorescence of these polymers under electron irradiation. Phosphorescence processes (induced by the luminescence of carbonyl groups (C=O)) could also contribute to cathodoluminescence. In addition, we highlight in this paper the different mechanisms that can lead to luminescence inhibition: formation (in the case of ETFE) of short length polyene groups ( $-(CF=CF)_n-$  type with  $n < 3$ ) which produces non-radiative transitions and the creation of color centers that can act as optical filters.

The analysis of polymers through cathodoluminescence spectroscopy is very important to get a better understanding of the physico-chemical ageing of these materials under irradiation. This CL technique is an interesting tool for in-situ characterization under vacuum and would avoid any air exposure that could induce recovery effects. Finally, as only few studies have been performed on cathodoluminescence of polymers, this paper provides new data and chemical information on the origin of CL spectra of fluorine based polymers.

## ACKNOWLEDGMENT

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