CATHODOLUMINESCENCE & ELECTRICAL ANALYSIS OF SPACE USED POLYMERS

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ABSTRACT

Polymer materials have been tested in the dedicated experimental facility SIRENE (ONERA, Toulouse, France) to perform electric analysis by a new characterisation technique named Thermal-Stimulated Current (TSC). An experimental approach shall as well be presented, which allowed bringing into evidence the shallow charge trap levels in polymers. A cathodoluminescence technique has also been developed, in MARCEL facility installed at ONERA, for the investigation of optical and electrical properties of materials. This analysis is interesting for the characterization of defects / impurities present in materials. These two test benches are complementary and make it possible to extract physical parameters. The implementation of these parameters in physics models developed at ONERA will allow us to improve our understanding and prediction of charging behaviour and radiation-induced conductivity evolution of these polymers under space conditions.

INTRODUCTION

Polymers are widely used on spacecraft for mechanical, thermal, optical, or electrical application. These materials used on spacecraft are submitted to a large spectrum of electron which induce the implantation of charged particles in their overall thickness. This charging process can lead to important potential gradient which may trigger electrostatic discharges and electrical arcs. In previous studies 1,2, it has been shown that the charging behaviour in these space conditions differs significantly from one material to the other. Kapton tends to become more and more conductive while FEP exhibits non-montonous behaviour. These behaviours are explained by radiation-induced conductivity due to high-energy electron irradiation which, through ionization processes, increases the bulk conductivity in these materials. For a better prediction of these charging phenomena, it is necessary to understand the physics steering charge transport and radiation / polymer interactions. A specific model has been developed at ONERA 3 taking into account ionization, trapping / detrapping and recombination effects. Charge traps are due to physical defects and chemical imperfections (impurities) in materials. These defects act as traps and/or recombination center for the implanted charges which strongly modify dielectric properties and charge transport in material. The energy and spatial distributions of these traps depend on the nature of the defects. A better understanding of these trapping / recombination mechanisms is needed to improve the physical models describing charge transport in space used dielectric materials. This paper presents both the development of the two test benches as well as the experimental characterization results on some space polymers.

EXPERIMENTAL SETUP AND PROTOCOL

1. Thermal Stimulated Current

The Thermal-Stimulated Current (TSC) method is a non-isothermal technique for investigation of trap levels in semiconductor / insulator materials. In principle, this method consists in filling the traps through irradiation after cooling down the material to low temperature and then heating up the material at a constant rate. The measured conduction current (ITSC) will depend on the different trap levels present in material bulk. The energy level (activation energy) within the band gap of a specific trapping center is related to the temperature at which it is emptied. Furthermore, the number of traps contributing to the observed current peak depends on the amount of trapped charges, which are released. Generally, a TSC curve is represented by a current as a function of temperature. If the trapped charge carriers (electrons/holes) are thermally released to the conduction band (electrons) or valence band (holes) on heating the material, the TSC would present a peak in the curve. In the case of a discrete distribution of traps, TSC curve may consist of several peaks (each originating from distinct trap energy). The schematic diagram of the TSC method is shown in Fig. 1.

1.1. SIRENE irradiation Facility

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The experiments have been performed in the unique irradiation test facility (SIRENE), funded by CNES and installed at ONERA (Toulouse, France). This facility simulates the charging effects produced by electrons in space environment (geostationary orbit). This is achieved by the use of three monoenergetic electron beams (20 and 400 keV). The initial beams being diffused in order to get a space like electron radiation configuration. The electron beam spectral characteristics of the SIRENE facility with an energy spectrum approaching that of the geostationary charging environment is shown in Fig. 2.

1.2. Experimental procedure

Investigated polymers included commercial films of the low density polyethylene “LDPE” (100 µm thick), Kapton (50 µm), as well as Fluorinated ethylene propylene “FEP” (100 µm). In this paper, we present only the results corresponding to LDPE. The dimensions of the samples were 5 x 5 cm². All specimens (25 mm in diameter) were metallized on both sides with semi-transparent nanoscale layers of silver. A guard electrode was also deposited to avoid surface leakage on rear face. During all the tests, a negative polarization of -200 V or -1000 V was applied (corresponding to electric field respectively equal to 2.10⁶ and 1.10⁷ V/m). Irradiation have been done with monoenergetic electron beam with high energy electrons (400 keV), inside a vacuum chamber at low temperature (-150 °C). At these temperatures, the electron/hole pairs created by ionization processes are quickly trapped in the bulk of material. The duration of the irradiation was 1 hour. A Faraday cup installed on the sample holder allows to measure the electron flux during tests (8 pA.cm⁻²). A 30-minute relaxation phase took place before the temperature increase. TSC were recorded from -150°C to about 120 °C at a constant heating rate of about 1°C/min.

2. Cathodoluminescence

Cathodoluminescence (CL) is the emission of light in response to electron radiation. The emitted photons correspond to energy transitions located between the conduction and valence bands. The CL technique is relevant to characterize the defects and impurities present in different materials, especially for the extraction of characteristic energies involved in trapping and recombination processes. In addition, CL measurement allows analyzing the evolution of chemical structure of the material along the irradiation process (aging phenomena).

2.1. MARCEL irradiation Facility

The irradiation test chamber MARCEL (Fig.3) installed at ONERA (Toulouse, France) has been used in this study. It has been developed for the characterization of space used materials under electron irradiation. It is equipped with a 10 keV (STAIB) electron gun and a non-contact Kelvin Probe (TREK model 341B). A pumping system allows performing experiments at vacuum of 1.10⁻⁶ mbar. A Faraday cup installed on the sample holder can measure the electron flux before tests. The temperature of the sample holder (copper) can
be controlled in the range (100 K to 500 K) allowing reproducing the temperature variations of materials on flight.

This facility has been amended to perform cathodoluminescence spectrometry. Fig. 4, provides a general schematic of the experimental system. A parabolic mirror (light collector) has been designed to enhance light collection. A hole with a diameter of 3 mm allows the path of the incident electrons to the sample. The focal point of the parabola is set on the specimen. A lens was attached to the probe to drive the luminescence towards the fiber inlet.

A sealed feedthrough on the fiber allows the passage from the vacuum to the ambient atmosphere without loss of luminescence up to the UV-Vis-NIR spectrometer (StellarNet BLK-C-SR-50 model). The concave holographic grating spectrometers deliver high performance spectral analysis in the UV-Vis-NIR wavelength range covering 1.20 eV to 6.2 eV (200-1080 nm). The spectral resolution is determined by the grating and the slit width (50 µm) and is typically 0.5 nm. This grating is aberration corrected and has no mirrors to minimize stray light. The SpectraWiz software is used for data acquisition. Integrated times of 5 seconds (s) were chosen to avoid noisy spectra. The obtained spectra have been deconvoluted into Gaussian sub-bands using commercially available software (Origin 9.1, OriginLab Co., Northampton, MA, USA).

CL spectra can be expressed in energy (electron volt, eV) (bottom axis) or in wavelength (nm) (top axis) by the relation:

\[ E(\text{eV}) = \frac{hc}{\lambda(\text{nm})} = \frac{1239.85}{\lambda(\text{nm})} \]

Where \( h \) is the Planck constant and \( c \) the light velocity. The Y-axis represents the intensity and is expressed in photon counts.

**EXPERIMENTAL RESULTS**

1. **Thermal Stimulated Current**

In order to extract the trapping / detrapping processes parameters, we shall focus in the following on the discharging process under thermal stimulation of LDPE sample. The TSC technique is often used to determine the trapping parameters of polymers. The TSC spectra obtained from LDPE with and without irradiation are shown in Fig. 5. The blue TSC spectrum shows three peaks designated \( P_1 \), \( P_2 \), and \( P_3 \) in ascending order of temperature. These three peaks correspond to three kinds of trapping level in this insulating material. On the other hand, the second TSC (curve II) has no peak except the steady state conduction current greater than 110°C. Since the big difference between both TSC spectra is due to prior irradiation, these three TSC peaks are related to the charge introduced by the irradiation as mentioned in the previous section. The first TSC spectrum can be used to evaluate the depth energy (or Activation Energy \( E_a \)) of the traps. Several methods can be used for extracting parameters. In our case, this energy is calculated by using the initial rise method introduced by Garlick and Gibson.
TSC current as a function of temperature can be approximated by the following Arrhenius equation:

$$I_{TSC}(T) \propto \exp \left( -\frac{E_a}{kT} \right)$$

For which, $k$ is the Boltzmann constant, $T$ is the absolute temperature and $E_a$ is the activation energy. The activation energy can be determined from the slope of an Arrhenius plot of $\ln(I_{TSC}(T))$ versus $1/T$. The calculated activation energies are gathered in Table 1. This “initial rise” method is very interesting for parameter extraction for isolated traps. The overlap of the peak $P_3$ with the peak $P_2$ does not allow the extraction of the activation energy with this method. In general, the TSC technique makes it possible to highlight shallow traps (<1 eV).

Table 1. Characteristics of LDPE samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak</th>
<th>Temperature (°C)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE (100 µm)</td>
<td>1</td>
<td>40</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>70</td>
<td>0.67</td>
</tr>
</tbody>
</table>

2. Cathodoluminescence

We compare in this study the differences in cathodoluminescence (CL) spectra of different space-used polymers (PEEK, PEKK, see Fig.6). In order to understand the underlying physics, we carried out a parametric study (chemical structure, dose, and temperature).

2.1. Chemical structure

We have compared the CL spectra of PEEK and PEKK in Fig. 7. An example of the deconvolution of the PEEK is presented in Fig. 8. The spectra differ from one material to another but the position of each peak is similar for both materials. These similarities suggest that these peaks are probably related to the chemical structure of both materials. By comparing the ratio of intensities of each peak for the two polymers, we are able to get a first idea on the nature of these contributions. Peaks $P_1$ to $P_4$ can be assigned to:

- $P_1$: Ether group
- $P_2$: Other
- $P_3$: Aromatic group
- $P_4$: Ketone group

$P_3$ and $P_4$ peaks are in line with the results of Bo Qiao et al, where they showed with photoluminescence measurements (photon excitation), the presence of two peaks at 443 nm and 490 nm (2.80 eV and 2.53 eV respectively). Although these results are not interpreted, we are able, by comparing the two materials with a similar chemical structure, to associate $P_3$ and $P_4$ peaks.
with mechanisms of radiative de-excitation of the phenyl and ketone groups by fluorescence or phosphorescence phenomena. 
P2 peak is the same for both materials, which could be associated with degradation / oxidation products formed during irradiation.
To improve our understanding of the origin of the contributions and more particularly for P2, we carried out additional tests (dose and temperature effect).

2.2. Dose effect

Fig. 9. shows the evolution of each contributions (P1 to P4) of PEKK and PEEK as a function of dose. Peaks evolutions show similarities between both polymers. 
We can see that peaks P1, P3 and P4 decrease with the increasing dose while the P2 contribution increases. The decline of P1, P3, and P4 (in relation to the chemical structure) is the result of scission of the main chain or bonding (C-O, C-H and C=O respectively). This dose-dependent decrease in intensity has already been observed on other types of polymers 9. The P1 peak decline (previously attributed to ether groups) is more pronounced for PEEK. This difference in decay kinetics could be related to cross-linking mechanisms. Additional tests must be carried out to improve our understanding on the nature of this peak. The increase of P2 with dose is more pronounced for PEKK. The most likely hypothesis would be the creation of a new chemical group following chain scission (radical recombination processes). In order to identify and assess the chemical degradation of materials, we have performed XPS tests. These experiments were carried out in the same conditions performed for CL and showed a spectral evolution as a function of dose (not shown here). A widening of the bands has been seen and can confirm the change in the chemical structure (by scission / cross-linking processes) of the polymers. In addition, deconvolution of the XPS spectra at high doses demonstrated the creation of an ester (O=C-O) group. The formation of this group is the result of a recombination between ketone and ether radicals (reaction 4) causing photon emission by chemiluminescence. A decrease in O1s surface peaks with the increasing dose was observed, which could be attributed to a loss of surface oxygen (O2, CO2 degassing...) supporting the hypothesis of degradation of the chemical structure. Potential reactions to bond scission are presented below:

Reactions (1) show the cleavage of the C-H bond. Reactions (2) and (3) respectively represent the scission between the phenyl and ketone/ether groups 10. Reaction (4) corresponds to the creation of a new chemical group(ester) by recombination between ether and ketone radicals

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**Fig. 8. CL spectra acquired from PEEK and reconstruction of the CL spectrum on the basis of four elementary components**

**Fig. 9. Evolution of each contributions as a function of dose (PEKK / PEEK)**
2.3. Temperature effect

The CL spectra clearly show a decrease in contributions as the temperature decreases. Lowering the temperature leads to a decrease in carrier mobility and molecular motion. This decrease could be associated with a decrease in recombination mechanisms between radicals (less of: cross-linking, creation of new groups by chemiluminescence mechanisms...). A diagram illustrating potential mechanisms is illustrated in Fig. 11. At low temperatures, the charge carriers are quickly trapped and participate at a lower level to recombination mechanisms. When temperature increases, the carriers can get detrapped (by thermal activation) and recombine between charges of opposite sign.

CONCLUSION

In this paper, we have presented some results obtained using two characterization methods (TSC and Cathodoluminescence). We were able to show that low temperature irradiation allowed charge trapping. The rise in temperature allowed possible identification of three trap levels in the LDPE (according to the literature). The cathodoluminescence technique has made it possible to highlight deep traps and radical formation through a parametric study. Spectral similarities were observed between PEKK and PEEK which were attributed to their chemical structure and degradation products. Scission / cross-linking mechanisms have been proposed in relation to CL and XPS results. The complementarity of these two techniques makes it possible to probe shallow and deep trap levels. The parameters thus extracted will be used in the models developed at ONERA.

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