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Effects of Differing Radiation Methods on Charge Transport in Polymers

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***Abstract*—**Spacecraft charging issues are understood and mitigated through an understanding of material properties. Material properties are dynamic in the harsh environment of space. Approximations must be made to simulate the space environment in the laboratory. This paper reports on the investigation of the approximation that energy deposition causes the same aging effects in materials regardless of the radiation source. Samples of polytetrafluoroethylene (PTFE) and polyether-etherketone (PEEK) were irradiated with x-rays, γ-rays, or electrons at total ionizing dose (TID) of either 2 x 10^4, 2 x 10^5, or 2 x 10^6 rad. Charge was then injected in each sample with an 80 keV mono-energetic electron beam. The resulting charge distribution and charge transport properties were probed via pulsed electroacoustic measurements. Samples were measured in a parallel plate capacitor configuration where they were first grounded, a DC bias was applied, and then grounded again. Measurements of the thermal and structural properties were investigated via differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR) spectroscopy, respectively. The results indicate that there appear to be at least three distinct phases of charge transport characteristics in PTFE, while PEEK showed no substantial change at these TID. Measurable differences in the DSC and FTIR measurements were apparent for both PTFE and PEEK.

Index Terms*—*Spacecraft charging, accelerated aging, dose rate, polymer, radiation, pulsed electroacoustic

I. Motivation and Background

In order to understand and mitigate the deleterious effects of spacecraft charging, understanding of the charge transport properties of a material are paramount. However, the harsh environment of space induces substantial temporary and permanent effects in material properties. To study the long term aging effects of space, experiments are most often conducted in the laboratory. Due to the feasibility of experimentation, approximations are necessary in order to simulate the space environment on Earth. These approximations include both increased dose rates and differing sources of radiation. It is often not feasible to irradiate for years at a time nor to submit a sample to all space radiation sources simultaneously in the laboratory. This study aims to investigate the latter approximation that all energy deposition within a material is essentially equivalent regardless of the radiation source.

II. Approach

The following experimental approach was developed to investigate the potential differing aging effects of different dosing sources. Samples were aged at low, medium, and high total ionizing doses of approximately 2 x 10^4, 2 x 10^5, and 2 x 10^6 rad, respectively. The samples were aged with three different radiation sources: x-rays, γ-rays, and electrons. Once aged, a charge layer was deposited in the bulk of the samples with a mono-energetic electron beam. The resulting charge distributions were measured via the pulsed electroacoustic (PEA) method. During PEA measurements, the samples are first grounded, a small DC bias is applied, and then they are grounded again. This allows for observation of the effects of aging on charge transport properties of the materials. Additionally, measurements of differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR) spectroscopy were obtained to characterize the structural effects of aging on the materials.

The rest of this section will provide details of the materials as well as the irradiation and measurement methods.

A. *Materials*

The samples tested were polyether-etherketone (PEEK) and polytetrafluoroethylene (PTFE), both with nominal thicknesses of 125 µm. The PEEK samples (1000-125G) were obtained from Aptiv Victrex PEEK Film Technology [1]. The PTFE samples (MCVS005X12X3) were obtained from McMaster-Carr. Two samples per dosing scheme were prepared. That is, for each combination of material, dosing source, and total dose, two samples were prepared. Actual sample thicknesses were determined by averaging several measurements with a digital micrometer (Mitutoyo IP65; ±0.5 µm resolution). Samples underwent a vacuum bake out to remove any volatiles at 100 °C for 72+ hrs at approximately 10^{-4} Torr. Once baked, samples were stored in inert environments, either under vacuum or in plastic containers purged with dry N_2 or Ar.

B. *Radiation Sources*

The three radiation sources employed were x-rays, γ-rays, and electrons. The dose rates and TID achieved are summarized in Table 1.

The x-ray source was a Rad Source RS 2000 160 kV Biological Irradiator at Utah State University. The samples

TABLE I
DOSE RATES AND TOTAL IONIZING DOSES

Material		Low Dose			Medium Dose			High Dose	
		X-ray*	γ-ray*	Electron	X-ray*	γ –ray*	Electron	X-ray*	Electron
PEEK	Dose Rate (krad/hr)	50	0.24	0.2	50	0.24	1.5	131.9	13.4
	TID (Mrad)	0.02	0.02	0.0308	0.2	0.202	0.25	2	2.25
PTFE	Dose Rate (krad/hr)	50	0.24	0.1	50	0.24	0.9	131.9	8
	TID (Mrad)	0.02	0.02	0.0187	0.2	0.202	0.15	2	1.35

*Values are for equivalent dose in Si. Correction factor/error estimated to be ~5%.

were irradiated in plastic containers that were purged with Ar. The dosing was controlled by proximity to the source and user-selected calibrated source intensity.

The γ-ray irradiation was conducted with a Co^{60} source at Université de Montpellier. The samples were irradiated in plastic containers that were purged with either dry N_2 or Ar. The dosing was controlled via distance from the source.

The electron irradiation was conducted with a Sr^{90} source in the Materials Physics Group laboratory at Utah State University [2, 3]. The irradiation took place with a vacuum level of $<10^{-5}$ Torr. The dosing was controlled via distance from the source.

Deposition of charge was achieved via mono-energetic electron bombardment at the Université Toulouse III Paul Sabatier in France in the MATSPACE chamber [4] with a 100 keV electron gun (built at LAPLACE) at room temperature and a vacuum level of $<10^{-5}$ Torr. To deposit charge within the bulk of the samples after aging, they were irradiated with a 0.3 nA/cm^2, 80 keV electron beam for 2 min.

C. *Measurement Methods*

The measurement methods are described below.

Pulsed Electroacoustic Method

The pulsed electroacoustic method works by placing the sample in a parallel plate capacitor configuration. A pulsed voltage is then applied to the sample and any internal charge reacts via a coulombic force. This force results in an acoustic pressure wave that travels through the sample stack to a piezoelectric sensor on the backside of the ground electrode. Given the speed of sound and thickness of the material, simple time-of-flight allows for the determination of the internal charge distributions within the material [5]. Pulsed electroacoustic measurements were conducted at Université Toulouse III Paul Sabatier shortly after deposition of charge via mono-energetic electron beam irradiation. The PEA system used is described in detail in reference [6].

The samples were measured for a total of 30 minutes. They were first grounded for 10 minutes to measure the resulting charge distribution following the removal of the samples from the electron irradiation chamber. They were then submitted to a -16 kV/mm electric field for 10 minutes. Lastly, they are then grounded again for 10 minutes. This is labeled in each plot of Fig. 1. This allows for a probing of the charge transport properties of the material as the original distribution is captured and the response to an applied electric field is observed.

Differential Scanning Calorimetry

Differential scanning calorimetry measures the heat flow as a function of temperature of the sample, thereby characterizing the thermal response of the material. A TA Instruments Q2000 Differential Scanning Calorimeter was used with a protocol consisting of two successive cooling/heating scans. The temperature range was approximately -10 to +365 °C with a heating/cooling rate of 10 °C/min. The experiments were conducted with a dry N_2 environment to avoid any thermal degradation.

Fourier-Transform Infrared Spectroscopy

To investigate the changes in chemical structure, FTIR measurements were obtained for each sample with a VERTEX 70 fully digital IR spectrometer. The system acquires data in the mid-infrared region from 400 – 4000 cm^{-1} with a resolution of 2 cm^{-1}. The data were obtained in a transmission orientation of the FTIR system.

III. RESULTS

Representative PEA measurement results are plotted in Fig. 1. Note that the results were consistent across the duplicate sample measurements with the exception of the absolute magnitude of the charge density measured, which is typical [6]. The electron beam was incident at the sample surface identified on the plots as position zero. The deposited charge distributions for the pristine samples are peaked at approximately 50 μm and 70 μm for PEEK and PTFE, respectively.

PEEK did not show significant changes in the PEA results with dosing, so only the pristine sample is plotted for reference, see Fig. 1(a). However, interesting results can be seen in Fig. 1(i) where the PEA measurements were obtained too soon ($\lesssim$1 hr) after deposition of charge via the mono-energetic electron beam. This meant that the delayed radiation induced conductivity (DRIC) had not sufficiently decayed prior to the application of the electric field during the PEA measurements. The conductivity was temporarily increased via DRIC due to energy deposited in the region between the irradiated sample surface and embedded charge distribution. The effects of this increase in conductivity are observed for transitions both when the electric field is applied and when removed. This is observed as negative charge accumulation in the bulk near the sample surface by the ground electrode, and then positive charge accumulation at the same location, for voltage being applied and removed, respectively. Similar results were observed regardless of radiation source or TID and appear to only be

correlated with the time between mono-energetic electron irradiation and when the PEA measurements were taken, suggesting the observed effects are likely due to DRIC as explained above.

mobile within the PTFE material. With no electric field applied, the deposited negative charge appears to accumulate at the surfaces of the material near the electrodes, due to a combination of self-repulsion and attraction to induced charge

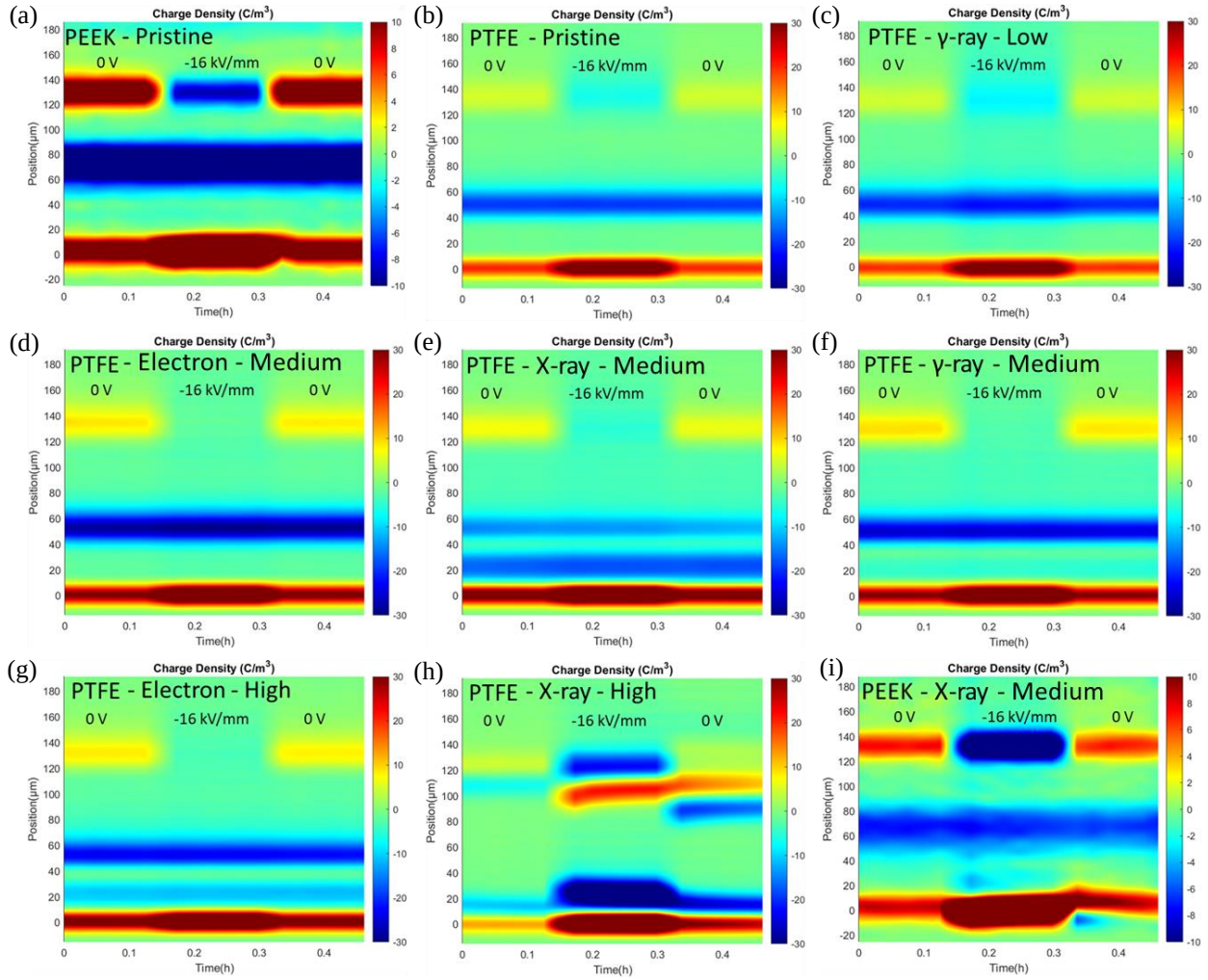

Fig. 1. PEA measurements of charge profiles are plotted as a function of time. Samples are grounded, -16 kV/mm applied, and then grounded again. Plots are measurements of (a) pristine PEEK, (b), pristine PTFE, (c) lowest TID γ-ray aged PTFE, medium TID PTFE aged by (d) electrons, (e) x-rays, (f) and γ-rays, highest TID PTFE aged by (g) electrons, and (h) x-rays. An example of complications from DRIC are shown in (i) with a PEEK measurement taken too soon after charge deposition.

The PTFE results appear to show three distinct phases of charge deposition and transport. The first is the typical single peaked charge distribution as seen in the pristine, γ-ray low dose, and electron medium dose (electron low dose was not measured via PEA), Figs. 1(b-d). The second phase is the appearance of multiple peaks. One of the charge distributions appears to be at the same position as in the first phase. The second charge distribution appears to be near the irradiated surface of the sample. This can be seen in the x-ray medium dose, γ-ray medium dose (very slight second peak near surface), and the electron high dose PEA measurements, Figs. 1(e-g). This double peak effect also appears to be observed in prior research with PTFE samples irradiated with 80 keV mono-energetic electrons [7]. However, at this stage the charge is still immobile upon application of the electric field. This changes in the third phase [Fig. 1(h)] where the charge appears to be on the electrodes. When the electric field is applied, a charge separation is observed. That is, negative charge accumulates at the ground electrode and positive charge accumulates at the high voltage electrode immediately, where no positive charge was previously observed. It is of note that the positive and negative charge is not observed to rapidly recombine (or screen their presence, as PEA depicts net charge) once the applied field is removed. Instead, there is a slow migration of some of the negative charge to the positive charge distribution. Measurements were not obtained sufficiently long to observe the dynamics until the sample reached equilibrium. It is worth noting that the mobile charge also appears to be bound within the material and did not discharge through the electrodes.

The DSC results are summarized in Table 2. Although PEEK did not show obvious change in the charge transport properties as measured by the PEA system, there were measurable

TABLE II
DIFFERENTIAL SCANNING CALORIMETRY RESULTS

Material		Pristine	Low Dose			Medium Dose			High Dose	
			X-ray	γ-ray	Electron	X-ray	γ –ray	Electron	X-ray	Electron
PEEK	ΔH_C (J/g)	44.50	45.87	43.18	45.67	41.51	43.92	45.35	50.05	49.29
	Crystallization (%)	54.27	55.94	52.65	55.70	50.62	53.56	55.31	61.04	60.11
PTFE	ΔH_C (J/g)	30.06	29.65	29.07	25.85	42.10	45.28	29.19	56.38	30.19
	Crystallization (%)	36.66	36.16	35.45	31.52	51.34	55.22	35.60	69.72	36.82

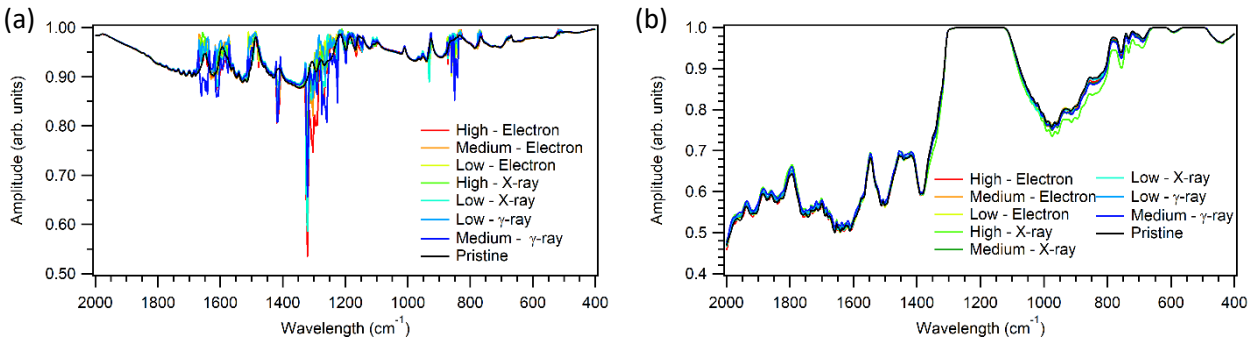

Fig. 2. FTIR results are plotted for (a) PEEK and (b) PTFE.

differences in both the heat of cold crystallization (ΔH_C) and the percent crystallization for the highest dose irradiations, with slightly larger changes for the x-ray high dose irradiation. PTFE also shows the largest change in both ΔH_C and percent crystallization for the x-ray high dose irradiation, but shows no significant change for the high dose electron irradiation, which may be due to the substantial difference in dose rates (refer to Table 1). There is a general trend of increased ΔH_C and percent crystallization with increased dose, regardless of irradiation source. However, there does appear to be an offset for the electron irradiated samples, where the low dose values are below the pristine sample measurements but still trend with increasing values for increased doses.

The FTIR results are plotted in Fig. 2. While there are assuredly changes in the spectra that depend upon irradiation, further work is necessary to more fully understand these changes. Some insight into the results may be gained by comparing the FTIR and DSC results to the discussions in the references [8, 9].

V. CONCLUSION

The differing effects of aging due to different dosing sources was investigated. The general trends of aging appear to mostly align, though more rapid aging was observed due to x-ray irradiation as compared to the slowest aging due to electron irradiation. This could also potentially be explained as a result of the differing dose rates, as the x-ray irradiations had the highest dose rate (particularly for the highest dose batch of samples) and the electron irradiations had the lowest dose rates. Further investigation is required to separate the effects of differing dosing sources and differing dose rates on the aging of polymeric materials.

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