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Relaxation of Radiation Effects in Polymers

Alexandra Hughlett Nelson
Utah State University

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Alexandra Hughlett Nelson

JR Dennison, Mentor Physics Department Utah State University

Abstract

Radiation can create atomic-scale defect states in polymers, leading to changes in their optical, electrical and mechanical properties. Recent studies of polymers have shown that these defect states are sensitive to oxygen or water exposure. It is believed that oxygen cause the number of defect states to decrease and the polymers to revert to their original states. However, the time scale of this regression is not known. This experiment quantified the time that it takes five polymers to recover and the extent of said recovery; polypropylene (PP), low density polyethylene (LDPE), fluorinated ethylene propylene (FEP), polymide (PI), and poly ether ether ketone (PEEK). In order to study the regression optical transmission data were taken using a StellarNet UV/VIS Spectrometer. Optical data were collected at different intervals of time and then compared in order to quantify the time frame of the regression. Failure to account for this time-dependent recovery in radiation studies may result in inaccurate results and has called into question previous studies involving radiation effects in polymers where exposure times were not recorded.

Introduction

The purpose of this experiment was to determine the effects of radiation on highly disordered polymers using optical transmission and investigate the recovery of these changes once exposed to atmosphere. Transmission curves were used to understand the nature, creation, and recovery of localized trap states in the polymers because these trap states are responsible for features in the transmission curves. Highly disordered polymers have a great deal of structural disorder compared to crystalline solids. Examples of highly disordered materials include: polyimide (PI), polypropylene (PP), low density polyethylene (LDPE), and fluorinated ethylene propylene (FEP). The high density of structural disorder leads to a high density of localized defects where electrons can be weakly bound. Trap states or defects, as depicted in Figure 1, are states electrons can visit with energies in between the valance and conductance band. There are two types of trap states, shallow trap (ST) states and deep trap (DT) states. These are caused by different types of defects in the material and result in the material absorbing different photon energies.

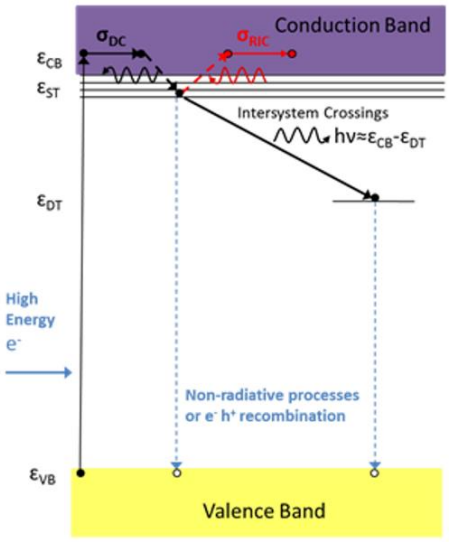

Figure 1. Energy level diagram of trap states in disordered materials and their corresponding energies [3].

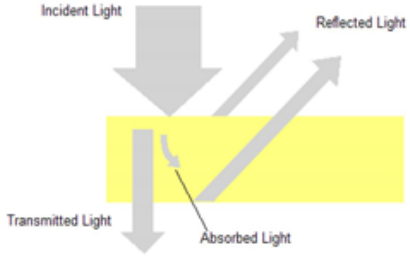

Figure 2. Incident light can be transmitted, reflected, or absorbed. [2].

Optical measurements provide one key method to explore the nature and distribution of these defect states. When light is shown on a material, it will either be reflected, transmitted, or absorbed (see Figure 2) depending on its energy [2]. Transmission spectra, like those shown in Figure 3, provide information about which energy photons are absorbed. The energies of these photons directly

correspond to the energy distribution of trap states. However, the transmission spectrums are not the only way to study trap states. The information for optical transmission and reflectance studies can be combined with other measurements made by the Material Physics Group including: conductivity [5], electrostatic breakdown [6], radiation induced conductivity, electron emission and cathode-luminescence. Together these may provide a synergistic model of the defect structure and transmission in highly disordered materials [3].

After transmission spectrum were taken, the features of the graphs were analyzed. Features and absorption edges in ~250 nm to 1000 nm (1.3 eV to 5.0 eV) UV to IR transmission spectra can be related to energies associated with various defects previously observed in highly disordered insulating materials [9]. The transmission spectrum, shown in Figure 3, shows two crystalline glasses, quartz and sapphire, and two polymers, polyimide (PI or Kapton) and polyester ether ketone (PEEK). Notice that quartz and sapphire both have very similar high transmission over the full spectra which reflects their high transparent nature. They do not have drastic dips like Kapton and PEEK. This is because the band gap energies, for quartz and sapphire, of ~8 eV and 9 eV are greater than the range of the spectrometer being used and therefore none of the photons tested can produce the quantized energy to excite an electron from the valance band to the conductance band to be absorbed.

Studying the transmission can allow us to determine the type of trap states found in the material, the energy distribution of these trap states, and the density of these trap states. For example, the slope and the intercept seen in Figure 4 can be used to understand the trap states found in Kapton. The intercept determines the minimum binding energy of the defect states. For

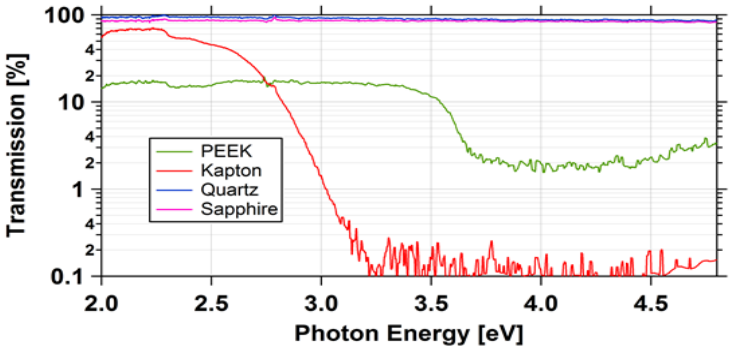

Figure 3. Transmission spectra for PEEK, Kapton, quartz, and sapphire [4].

Kapton this is ~3.2 eV, hence Kapton's orange color. For PEEK this is ~3.6 eV explaining its yellow color. The slope in the semilog plot is proportional to an exponential fall off of the energy density of defect states below the conductance band. Other highly disordered insulating polymers will have transmission spectrums similar to Kapton.

Research Objective

When a highly disordered polymer is exposed to in ionizing radiation additional defect states are created through processes including atomic displacement, band breaking or rotation, and crosslinking. Recent work has suggested that some of these defect states created by irradiation are sensitive to atmospheric exposure (more specifically oxygen, OH^-, or other reactive ions) [7]. It is proposed that after being exposed to atmosphere these defect states will relax and eventually recover. The nature and extent of the recovery time in not well known. The primary goal of this proposed project is to determine this time frame and understand the impact this has on transmission spectra and defect states. To do this data will be taken sequentially after irradiated polymers are exposed to atmospheric conditions.

It could take minutes, days, or weeks for the polymers to recover. Understanding the time and nature of the recovery is of critical importance. Depending on this time frame, previous experiments on properties related to the defect structures (*e.g,* conductance, transmission, etc.) involving irradiated polymers may be called into question as many experiments do not carefully document post-irradiation exposure to atmosphere. Often exposure to atmosphere was not noted or avoided.

Knowing whether atmosphere affects these defect states will have a profound effect on projects involving highly disorder irradiated polymers. Polymers used on equipment, including spacecraft, have been irradiated and tested. These tests were done assuming the polymer was behaving how it would after receiving a specific amount of radiation. In space this radiation would be continuous, and the

sample would be isolated from oxygen. Therefore, the sample would not be subject to recovery due to atmospheric exposure. However, on Earth the sample is typically removed from the radiation environment and exposed to atmosphere. If this exposure causes a relaxation in the defect states, the polymer under test conditions is no longer behaving how it would in space and the test could be inaccurate, perhaps even totally invalid.

Methods

A. Transmission Set Up

Two high-resolution spectrometers (StellarNet RED-Wave and Black-Comet; 200 nm to 1700 nm with 0.5 nm to 1.5 nm resolution) were connected to a UV/Vis/NIR light source using fiber optic cables to collect transmission data. The irradiated samples were then mounted to a card and placed in-between the fiber optics cables. The fiber optics cables then shine a light on the sample and the transmitted light is collected. The ratio of this transmitted light to incident light forms the transmission spectrum, which can be analyzed to determine the defect states found in the polymer.

B. Exposure to 5 kGy of Radiation

Initially, Kapton, PP, and LDPE were placed in the Space Survivability Test (SST) Chamber and exposed to 5 kGy of beta radiation. This radiation dosage was chosen because it mimics the dosage that a spacecraft in a geosynchronous orbit would receive over one year. The SST Chamber is a

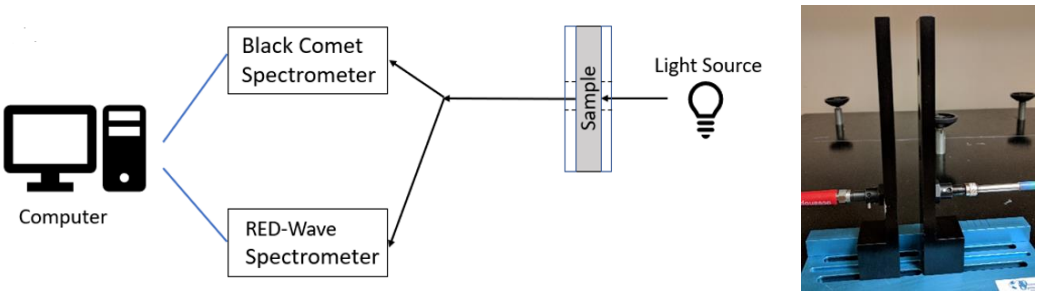

Figure 5. Left: Diagram of the optical transmission set up. Right: Picture of the transmission stand that holds the samples.

radiation chamber that allows samples to be exposed to beta radiation from a strontium 90 source. The SST chamber can simulate up to four times the electron and photon dose rate exposure in geosynchronous orbit or about 1-10 Gy/hr [1]. This allowed us to expose the polymers to dosages intended to mimic radiation dosages received by spacecraft in geosynchronous orbit on an accelerated basis (approx. 12-20 days). Such dosages have been shown to affect the optical and electric properties of these three polymers to varying degrees.

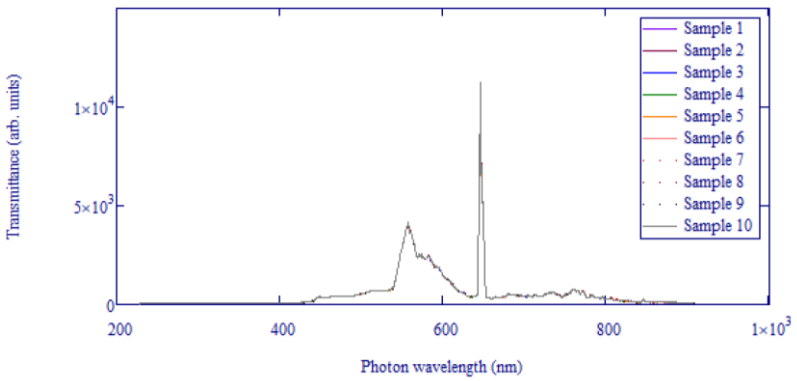

Figure 6. Raw intensity data of Kapton. The transmission spectrum is recorded ten times and is then averaged. This helps to eliminate background noise and tests the reproducibility if the spectrum measurements.

The radiation dosage is directly related to the distance the samples are placed from the source. For this radiation run the samples were placed 7.62 cm away from the source resulting in a dose rate of 13 Gy/hr. After being removed from the SST chamber the samples were immediately placed in an anerobic environment and remained there until transmission data were taken.

C. Exposure to 600 kGy of Radiation

After seeing the minimal changes in transmission results from exposing the samples to 5 kGy of radiation it was determined that a higher radiation dosage was needed. It was determined that PEEK would be exposed to 600 kGy of radiation. This was done over a period of three days using a high energy electron gun test chamber. The monochromatic electron beam used was at 80 keV with a dose rate of ~8 kGy/hr.

D. Collection and Analysis of Transmission Spectrum

After the samples were exposed to radiation, they were removed from the radiation source and mounted on cards. These cards where then slid into the transmission set up (see section A) and transmission spectrum were collected. The spectrometer measured the amount of transmitted light over the full wavelength range. Calculations were done at each wavelength using Eq. (1) to compute the transmission spectra of the sample.

$$\%\, Total\ Transmission = \left[\frac{I_{SR} - I_D}{I_N - I_D}\right] \cdot 100 \quad \textbf{(1)}$$

This relation compares the transmitted light from a radiated sample, I_{SR}, to the transmitted light from the system with no sample in place, I_N at each wavelength. The I_D term corrects for background light and is also known as the dark spectrum.

Typical raw intensity data from the spectrometer are shown in Figure 6. However, after it has been normalized to determine transmission using Eq. (1), the normalized transmission data look like that in Figure 4. Information related to the defect states can now be found from the transmission graph (see introduction). Finally, the corrected transmission spectra where compared to determine how the transmission curves change with radiation exposure and over what time scale the polymers returned to their original state. Computations where made using Eq. (2), where the transmitted light from a non-irradiated sample, I_S, is compared to the transmitted light from a radiated sample, I_{SR}, and the I_D term corrects for background light.

$$\%\, change\ in\ transmission = \frac{\left[\frac{I_{SR} - I_D}{I_N - I_D}\right]}{\left[\frac{I_S - I_{D'}}{I_{N'} - I_{D'}}\right]} \cdot 100 \quad \textbf{(2)}$$

Because the time that the relaxations occurs is of interest in this experiment, transmission spectrum were taken at varying intervals. In addition to collecting the transmission spectrum of the

irradiated samples, transmission spectrum for an unirradiated PEEK sample and glass witness samples were collected as controls.

Results

A. 5 kGy of Radiation

An initial exposure of 5 kGy did not result in a large enough change in transmission for the StellarNet RED-Wave and Black-Comet to detect. Figure 7 shows the transmission graphs of Kapton, LDPE, and PP after being exposed to 5 kGy of radiation. Notice that all three graphs have the same trend and that all three graphs consist of data that result in straight lines (except the noise at the high energy end of the Kapton graphs). The three samples used all have varying structures and react to radiation in different ways. Having the same trend on three graphs indicates that the samples did not receive a large enough radiation dosage to show a change in transmission. The trend that is observed is most likely the result of a change in an external factor and not a result of the radiation. This external factor may have been a shift in the detector, a shift in the sample, or another systematic error.

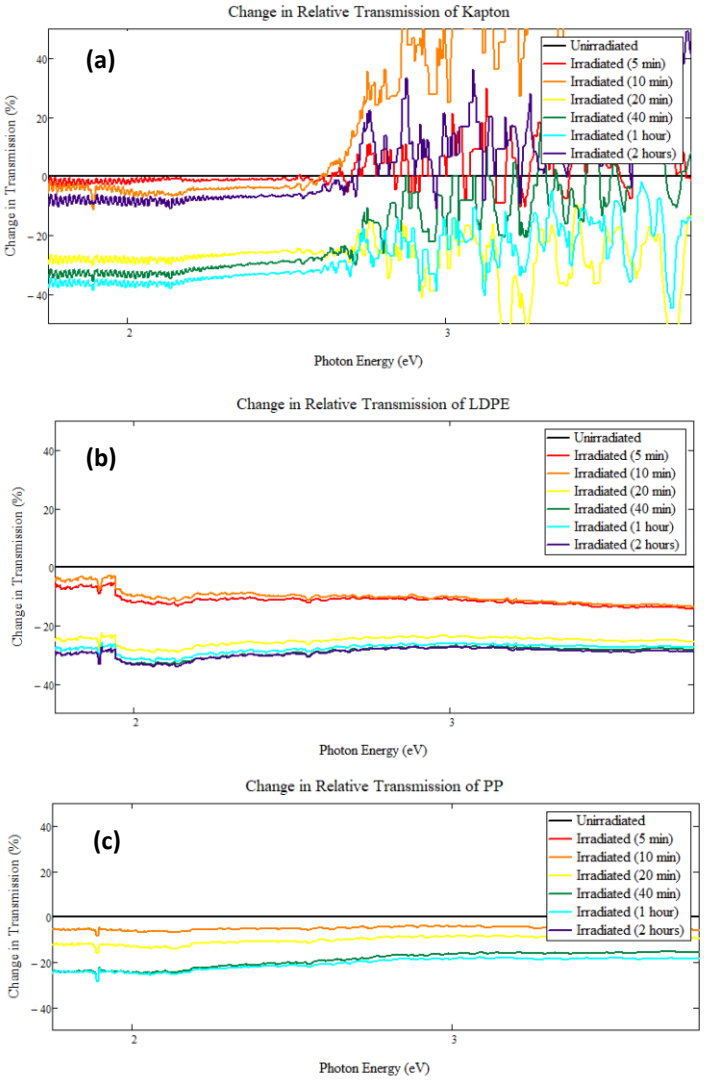

Figure 7. Relaxation of the change in relative optical transmission of (a) Kapton, (b) LDPE, and (c) PP after 5 kGy of irradiation.

B. 600 kGy of Radiation

An initial visual comparison of the samples immediately after being irradiated with 600 kGy and after being exposed to atmosphere, shows that there appears to be a significant change in transmission. Figure 8 shows the samples immediately after being removed from the radiation source and 230 hrs later. It appears like the yellow coloring, that resulted from the irradiation, lessens as time increases.

Figure 8. Visual comparison of irradiated samples at different times.

To confirm these qualitative visual results, transmission spectrum of all three PEEK samples and of the unirradiated PEEK sample were collected and compared. These results can be seen in Figure 9. The first three graphs all show the transmission results for the irradiated PEEK samples. However, these three samples all had slightly different radiation dosages. They were all placed in the radiation source for the same amount of time, but PEEK 1 was closest to the radiation source, with PEEK 2 in the middle, and PEEK 3 farthest from the radiation source. The closer the samples were to the source the more radiation is received as closer samples attenuated the incident radiation. The final graph is an unirradiated PEEK sample that can be used as a control for this experiment.

Despite the difference in radiation dosage, there are a few similarities between all four graphs. First, there is a discontinuity at approximately 2.4 eV. This energy corresponds to the point where the two separate spectrometers detector ranges overlap. Ideally, this discontinuity would not exist. However, its appearance in all four graphs indicates that there is a calibration issue. This calibration issue has been corrected in subsequent studies so raw transmission data can be compared.

Unfortunately, the data analyzed in this report cannot be adjusted. As a result, the data has been normalized using the unirradiated sample and the relative transmission is compared.

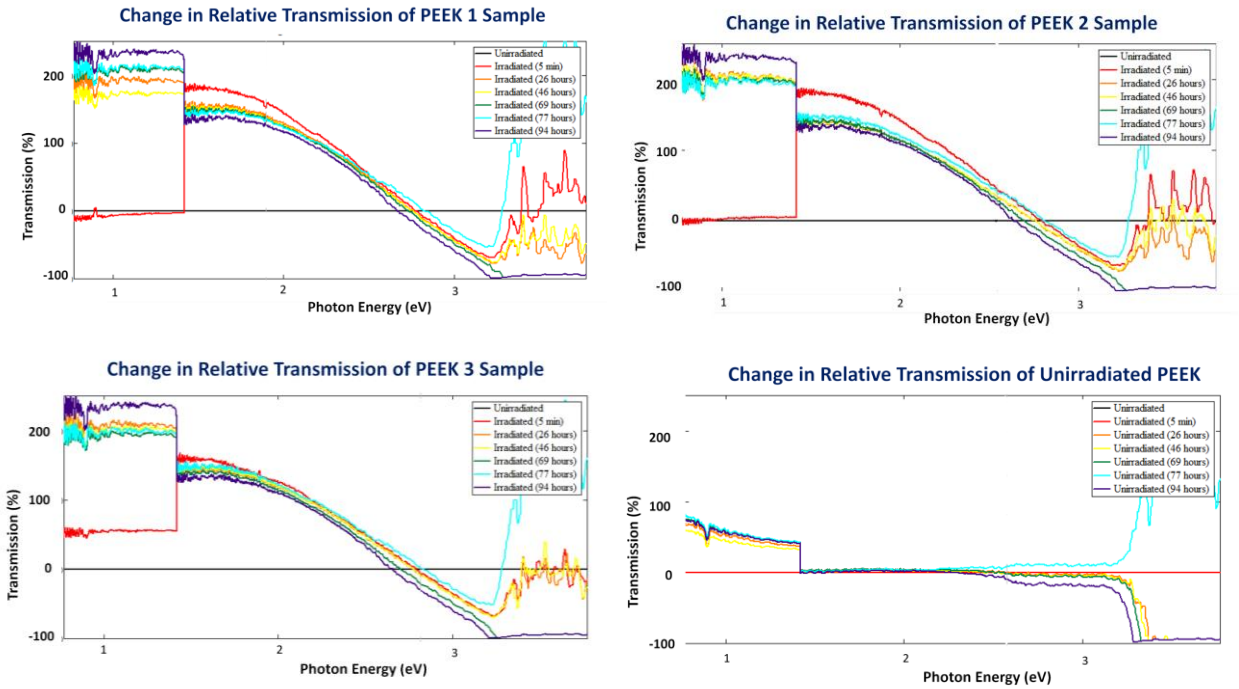

Figure 9. Relaxation in the relative optical transmission of the four PEEK samples after exposure to 600 kGy of irradiation and atmosphere.

The second similarity found in all four graphs is the noise present above approximately 4.25 eV. This noise is a result of the low intensity in the raw signal (see Fig, 6) above ~4.25 eV in the UV range. To eliminate this noise future data will be taken using a longer interval. This will create a smother curve and minimize the noise seen in the current graphs making the data above 4.24 eV usable.

Despite the calibration and noise error the data displayed in Figure 9, identifies some useful results. The data indicate that radiation does have a large effect on the transmission of PEEK. Changes in Figures 9 (a-c) show that the irradiated samples have >100% variations while the unirradiated samples seen in Figure 9 (d) shows <10% variations. This indicated that the large change in the transmission is a result of radiation and atmospheric exposure and not just atmospheric exposure.

Figures 9 (a-d) also show that different energies are affected in diverse ways with some energies decreasing in transmission and some energies increasing in transmission.

The graphs also show that time after irradiation influences the transmission. Each color on the graph correspond to a distinct time after irradiation with the colors being organized in rainbow order. The PEEK 1, 2 and 3 samples all show that as time continues the change in transmission begins to decrease and return to the transmission of the original unirradiated sample. This indicates a relaxation in the radiation effect. However, the current experiment did not determine if this relaxation was simply a result of elapsed time after irradiation, or if it corresponded to an exposure time to atmosphere after being irradiated. Future, experiments will try to determine which explanations of these is correct.

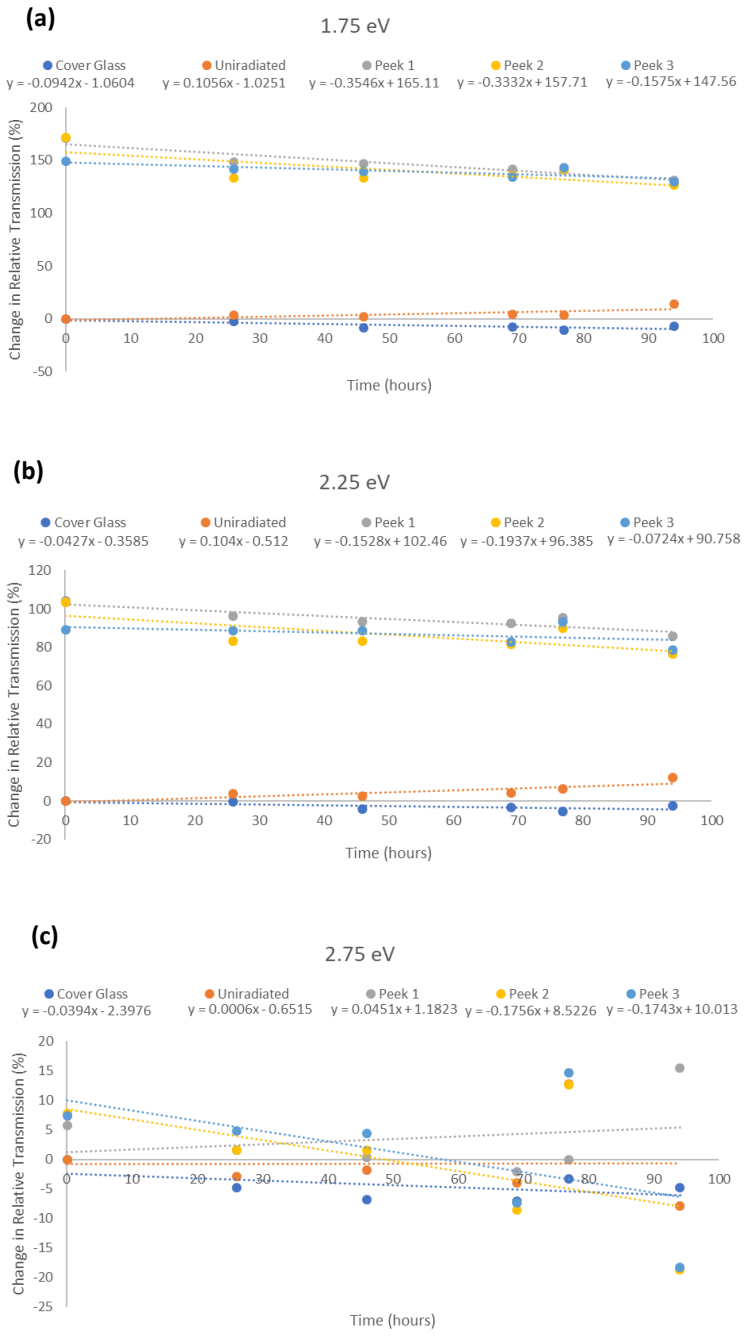

Figure 10. Change in relative transmission at (a) 1.75 eV, (b) 2.25 eV, and (c) 2.75 eV in all five samples and their respective best fit lines

$$\sigma_B = B\sqrt{\frac{1}{N-2}\left(\frac{1}{R^2}-1\right)} \quad \textbf{(3)}$$

In order to better understand the changes seen in Figure 9, the relative transmission of the samples at 1.75 eV, 2.25 eV and 2.75 eV were plotted over time (Fig. 10). After the data were plotted a linear fit was determined for each set of data. A visual inspection of these graphs shows that the irradiated peek samples have a negative slope indicating that the change in the transmission from the irradiated sample diminishes with exposure time and the samples irradiation effects are relaxing. The unirradiated peek and the cover glass appear to be flat. To confirm these visual results the uncertainty of the slope for each best fit line was calculated using Eq. (3). In Eq. (3) σ_B is the uncertainty in the slope, B is the slope, N is the number of samples and R^2 is the statistical r-squared value. The slopes and their associated uncertainties are listed in table 1.

Table 1. Slopes and corresponding uncertainties for the best fit lines in Fig. (10)

	Slope (% change in transmission per day)		
	1.75 eV	**2.25 eV**	**2.75 eV**
Peek 1	-9 ± 1.7	-4 ± 1.0	-1 ± 2.1
Peek 2	-8 ± 3.8	-5 ± 2.2	-4 ± 3.3
Peek 3	-4 ± 1.4	-2 ± 1.6	-4 ± 3.5
Unirradiated Peek	-3 ± 1.1	-2 ± 0.7	0 ± 2.5
Cover Glass	-2 ± 0.7	-1 ± 0.5	-1 ± 0.8

This table shows the slope of Unirradiated Peak and the Cover Glass are consistently less than the slope for the Peek 1, 2, and 3 samples. The Unirradiated Peek and Cover Glass are expected to have a slope of zero. Unfortunately, these results were not seen and are likely the result of a systematic error. However, the consistently larger slopes of Peek 1, 2, and 3 indicate that a relaxation of the radiation effects is occurring. The rate of relaxation is quantified by the slope of the best fit line. Another trend

that can be observed form table 1 is that the rate of relaxation is greater for the smaller eV values and decreases as you approach 2.75 eV.

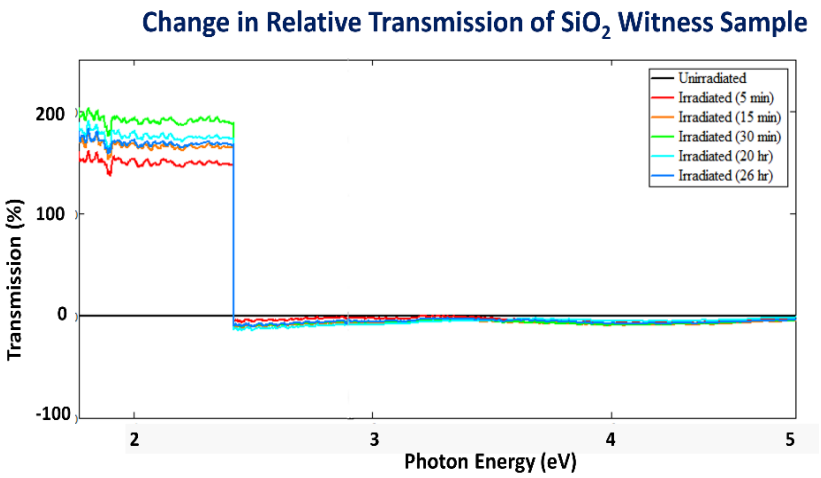

Figure 11. Relative in the relative optical transmission of SiO_2 after exposure to atmosphere

To quantify the magnitude of the uncertainty associated with each transmission spectra, transmission spectra of a SiO_2 cover glass slide were recorded at each time interval (Fig. 11). The hydrophobic SiO_2 glass is expected to be largely impervious to atmosphere and therefore not exhibit significant changes due to atmospheric exposure. Rather any observed changes would most likely be due to instrument drift or other systematic errors. Relatively small changes of <15% observed in the witness sample which are uncorrelated with exposure time confirms that instrumental drift is most likely not the cause of the much larger changes for irradiated PEEK of >100% seen in Fig. 9.

Conclusion and Future Work

The initial irradiation run showed that 5 kGy did not change the optical structure of Kapton, PP, and LDPE enough for the transmission spectrum to change appreciably. However, the second run with 600 kGy of irradiation demonstrated that radiation has a significant effect on the optical transmission spectra of PEEK. In the 1.25 eV to 2.75 eV energy range the relative transmission increased; the greatest increase, of 150%, occurs in the lower eV ranges and the smallest increase, 0%, occurs at approximately 2.75 eV. Additionally, a decrease in relative transmission can be seen in the 2.75 eV to 3.25 eV. The maximum decrease in transmission, -100%, occurs at 3.25 eV.

This change in transmission is hypothesized to be correlated with a change in the distribution of defect states. Over time the transmission spectra decrease, suggesting the radiation effects begin to recover with exposure to atmosphere. This may indicate that over time the number of radiation-induced defect states in the PEEK sample begin to decrease through chemical reactions with oxygen or OH^- radicals which repair radiation-induced damage.

Further analysis showed that the unirradiated PEEK samples did not change significantly with time. This indicates that radiation plays an important part in the changes that occur. It is hypothesized that both irradiation and exposure to atmosphere are required for the polymer to relax and begin to return to its original state.

After the large effect of radiation was confirmed an attempt was made to quantify the rate of the relaxation. The rate of relaxation at specific energies can be seen in table 1. It was also noted that the rate of relaxation is not consistent across all energies. The lower energies experience a faster relaxation and this rate decreases as the energies approach 2.75 eV.

Preliminary results found during this study are encouraging, but future work is necessary to determine further information about the nature and cause of the radiation induced defects. Additionally, the procedures of this experiment will be improved in an attempt to eliminate systematic errors. Additional samples will be tested to determine if all highly disordered polymers have a similar reduction in the radiation effects. The irradiation dosage will be varied to determine if this has an effect on the relaxation. All these things will then be combined to determine the rate of relaxation.

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