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Cross-Linking of Polytetrafluoroethylene During Room-Temperature Irradiation

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Exposure of polytetrafluoroethylene (PTFE) to α -radiation was investigated to determine the physical and chemical effects, as well as to compare and contrast the damage mechanisms with other radiation types (β , γ , or thermal neutron). A number of techniques were used to investigate the chemical and physical changes in PTFE after exposure to α -radiation. These techniques include: Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and fluorescence spectroscopy. Similar to other radiation types at low doses, the primary damage mechanism for the exposure of PTFE to α -radiation appears to be chain scission. Increased doses result in a change-over of the damage mechanism to cross-linking. This result is not observed for any radiation type other than α when irradiation is performed at room temperature. Finally, at high doses, PTFE undergoes mass-loss (via small-fluorocarbon species evolution) and defluorination. The amount and type of damage versus sample depth was also investigated. Other types of radiation yield damage at depths on the order of mm to cm into PTFE due to low linear energy transfer (LET) and the correspondingly large penetration depths. By contrast, the α -radiation employed in this study was shown to only induce damage to a depth of approximately 26 μm , except at very high doses.

Introduction

PTFE has superior chemical, electrical, and thermal properties when compared to most polymers. These favorable properties result in its use in many applications where chemical or thermal stability are important, including applications where exposure of polytetrafluoroethylene (PTFE) components to radiation is possible. For these reasons, as recent review articles illustrate^{1,2}, there have been numerous studies of the effects of exposing PTFE and other fluoropolymers to x-/γ-ray, β (electron beam), or neutron radiation.

Early studies of the radiation-induced chemistry of PTFE indicated that this material behaved quite poorly when compared to other types of polymers. Many of the mechanical properties of the polymer suffered when PTFE was dosed with γ-, β-, or neutron radiation.³⁻⁹ It was also reported that the polymer average molecular weight showed drastic decreases with radiation exposure. This behavior was attributed to radiation induced scission of the polymer backbone.¹⁰⁻¹³ A study on the subject of ion-implantation effects on PTFE concluded that it was not possible to cross-link PTFE because of the large fluorine pendant groups.¹⁴

More recent studies of PTFE irradiated at elevated temperatures found different results.^{4-6,9,15-17} Chain-scission induced degradation of PTFE's properties increased with increasing temperature up to the melting point. At and above the melting point, drastic differences were observed in the radiation chemistry. Many of the mechanical properties of the polymer either improved or did not significantly deteriorate when samples were irradiated while molten. This behavior was attributed to cross-link / chain-branch

formation enabled by much-higher polymer-chain mobility within the molten material as opposed to PTFE samples irradiated at temperatures below the melting point.

A recent study of the behavior of PTFE exposure to α -radiation indicated that the material behaved differently than what was expected from γ -, β -, or neutron radiation studies.¹⁸⁻¹⁹ Mechanical properties, such as hardness and elastic modulus, were observed to increase at moderate doses of α -radiation before falling off at high doses. It was conjectured that the most-likely explanation for the unusual behavior was a predominant damage mechanism of cross-linking for exposure of PTFE to α -radiation. This explanation is plausible because of the much higher linear energy transfer (LET) expected for α -radiation in comparison to other radiation types, which yields a higher reaction center density (i.e., a much shorter average distance between reaction centers) within the target material. For other radiation types, isolated reaction centers can only interact when their mobility within the polymer is very high, i.e. when the polymer is molten. The very high reaction center density generated by α -irradiation results in neighboring reaction sites that do not require significant mobility in order to interact. However, very little is known of the damage mechanism of PTFE exposed to α -radiation.

This paper represents the first in-depth study of the physical and chemical changes undergone by PTFE as a function of exposure to α -radiation. FTIR and DSC were used to monitor changes within PTFE samples after they were exposed to α -radiation. In addition to anticipated differences in radiation damage mechanisms, the high LET expected for α -radiation will lead to a much more shallow surface penetration than what is observed for other types of radiation, resulting in a different damage/depth

profile. The damage to the polymer as a function of depth into the sample was investigated with FTIR in conjunction with LET calculations.

Experimental

Sample Preparation: PTFE (Goodfellow), both 5 μm and 100 μm thick material, was used as received. Two sets of samples were prepared: One set, used for collection of FTIR data, that consisted of a stack of seven PTFE film-layers, each 5 μm thick, and another set, employed in the fluorescence and DSC studies, comprised of a single 100 μm thick layer. Both sample types were cut from the corresponding films to be approximately 1.0 cm in diameter and were irradiated in identical fashion, as discussed below.

Irradiation: Samples were irradiated using a tandem accelerator at the Los Alamos National Laboratory's Ion Beam Materials Laboratory. The accelerator was used to simulate the α -radiation from plutonium by generating a beam of 5.5 MeV He^{2+} ions. The PTFE samples, one 100 μm layer or seven stacked 5 μm layers, were loaded onto a stage, covered with a mask that confined the irradiated area to a 0.5 cm diameter circle in the center of the sample, and placed into a vacuum system. The samples were exposed to a scanned 0.3 cm^2 α -particle beam at currents of 0.2 nA for doses lower than 10^9 Rad and 5 nA for doses greater than 10^9 Rad. Samples exposed to 10^9 Rad of α -radiation were prepared at both beam currents and determined to be essentially identical with the methods employed in this study.

Fluorescence Spectroscopy: A ChemImage Condor Fluorescence Macroscope was used to obtain fluorescence images of each 100 μm thick irradiated sample. The

images were acquired using a 400 W xenon arc lamp with a 300-400 nm filter as the excitation source. A CCD camera and liquid-crystal tunable filter was used to collect the images. All images were corrected for possible variations in excitation intensity. Fluorescence spectra were obtained by adding the intensities from pixels within the irradiated area of each sample.

FTIR: In order to limit the number of bands in the spectrum which were totally absorbing, FTIR was performed in transmission mode through individual 5 μm sample layers. A mask similar to the one used for sample irradiation was employed to restrict data collection to the area which had been exposed to the α -radiation. Spectra collected were averaged for 128 scans at a resolution of 4 cm^{-1} and are presented as a ratio to background spectra, which were collected with identical experimental procedures to the sample spectra only with the absence of PTFE. The spectra from each layer of a given seven layer PTFE sample were averaged in order to obtain spectra representative of the entire thickness damaged by α -radiation. This was achieved by normalizing spectra to the intensity of the mode at 2366 cm^{-1} , which has previously been shown to be useful as an “internal standard” for FTIR spectra of PTFE.¹⁶

DSC: DSC was performed using a power compensated Perkin-Elmer Pyris-1 calorimeter. The 100 μm samples were trimmed such that the analyzed sample cross-sections were contained entirely within the irradiated regions, yielding samples weighing between 3.5 and 4.0 mg. During DSC data collection, the samples were heated through the melting point, to 375 $^{\circ}\text{C}$ and then allowed to cool. Both heating and cooling was performed at a rate of 20 $^{\circ}\text{C}/\text{min}$. The heats of melting and crystallization were determined from integrated peak intensities.

Results

Fluorescence Spectroscopy:

Figure 1 consists of the fluorescence spectra for samples exposed to a range of α -radiation doses, in addition to a virgin sample, as a function of emitted wavelength. What is observed in this figure is very similar to the results obtained for glass-fiber reinforced PTFE exposed to α -radiation in a previous study.¹⁸ The spectrum of virgin PTFE has a weak feature centered at about 580 nm. This feature was observed for all unirradiated samples that were analyzed, and is likely due to a minor impurity inherent to the manufacturing process. The fluorescence spectra of the 10^7 and 10^8 Rad samples do not show significant deviation from that seen for virgin PTFE. However, the 10^9 Rad sample shows a change in the fluorescence spectrum with an increase in intensity at wavelengths below 575 nm. A dramatic increase in intensity is observed in the spectrum of the 10^{10} Rad sample, which has been divided by 10 in this figure in order to be plotted with the lower dose sample spectra. The increase in fluorescence intensity that is observed for the high dose samples is likely explained by production of conjugated double-bond (C=C) species within the polymer during irradiation, as discussed in a previous study.¹⁸ Presence of conjugated double-bond moieties resulting in polymer fluorescence has also been observed during the thermal degradation of other polymers.²⁰⁻²⁴ Further evidence for the existence of C=C species is observed in the FTIR analysis of α -irradiated PTFE samples, and is discussed below.

FTIR:

The FTIR spectrum of virgin PTFE shows intense bands at 554.4 and 518.8 cm^{-1} due to CF_2 rocking modes, as well as bands at 641.2 and 627.3 cm^{-1} due to CF_2 wagging modes.²⁵ The present experimental setup also results in three totally absorbing bands in the 1250 to 1150 cm^{-1} region which are assigned to the symmetric and antisymmetric CF_2 stretching vibrations.²⁵ Full scale spectra are not shown, as the energies and peak shapes of the intense modes discussed above for virgin PTFE do not change significantly upon exposure to α -radiation. The most significant changes are observed in regions that contain relatively weak bands and are shown in Figures 2 and 3. These figures cover the 1075 to 675 cm^{-1} region and the 2000 to 1500 cm^{-1} region. The fundamental modes observed in the FTIR spectra of virgin and irradiated PTFE are assigned in Table 1. Combination and overtone bands are not reported in Table 1, as they do not show appreciable change upon irradiation and are very similar to what was reported for the FTIR spectrum of PTFE in a previous study.²⁵

The virgin PTFE spectrum shows several modes between 800 and 700 cm^{-1} , as seen in Figure 2. These features can be attributed to wagging and rocking modes of CF_2 groups that are located within amorphous regions of the PTFE solid.^{7,25} The intensity of these modes decreases upon exposure of PTFE to α -radiation, as observed in spectra of the 10^7 and 10^8 Rad samples shown in Figure 2, indicating a decrease in the number of CF_2 groups with an amorphous configuration. This result can be explained by assuming that chain scission is occurring in amorphous regions of PTFE, enabling the newly-formed chain-ends to crystallize, resulting in fewer CF_2 groups located in amorphously configured regions of polymer chains. Preferential scission of PTFE chains occurring in

amorphous regions of the solid has been reported previously during electron beam induced degradation of the polymer.^{26,27}

Increasing the α -radiation dose of PTFE to 10^9 and 10^{10} Rad (the 10^{10} Rad spectrum has been divided by 10) results in increasing intensities of features in the 800 to 700 cm^{-1} region. These modes at higher doses have been tentatively attributed to an increase in the number of CF_2 groups present in amorphous regions. However, it is possible that some of the intensity observed in this region is due to CF_3 groups.²⁸ In addition to the new modes in the 700 to 800 cm^{-1} region, a new mode can be observed at 985 cm^{-1} , first beginning to appear at 10^8 Rad and increasing in intensity with higher doses. A similar mode was observed in cross-linked PTFE and assigned to the presence of CF groups, more specifically a chain-backbone carbon atom that has lost a fluorine atom and gained a $-\text{CF}_3$ pendant group.^{16,29} The formation of CF and CF_3 groups is a result of the polymer chains undergoing cross-link / chain-branch formation reactions. While the formation of $-\text{CF}_3$ pendant groups is not a direct confirmation of cross-linking, the presence of this group has been shown to be a good indicator of cross-linking in radiation damaged PTFE.¹⁶ Polymer chain cross-linking and side-branch formation leads to lower crystallinity (and consequently a higher number of amorphous CF_2 groups as observed and discussed above) due to less efficient chain packing.

Figure 3 shows the $2000 - 1500\text{ cm}^{-1}$ FTIR spectral region for virgin PTFE and samples with increasing exposure to α -radiation. Several weak bands are observed in this spectral region for the virgin sample which appear to remain unchanged in irradiated samples. As seen in the figure, exposure of PTFE to α -radiation results in new bands in the $2000 - 1500\text{ cm}^{-1}$ spectral region which first begin to appear at a dose of 10^8 Rad.

The new bands are observed at 1882.2, 1810.9, 1784.8, 1776.1, 1730.8, 1716.4, and 1662.4 cm^{-1} . A previous study of electron beam irradiated PTFE revealed new bands at 1884, 1785, 1730, 1717, and 1671 cm^{-1} .¹⁶ The bands observed for electron beam irradiated PTFE closely resemble the new bands observed in Figure 3. These bands can be assigned to a variety of carbon – carbon and carbon – oxygen double bond species, as detailed in Table 1. The oxygen necessary to produce the oxidized species that are observed may originate as trace gasses in the vacuum system during irradiation or from oxygen species dissolved in the polymer. Presence of these carbon-carbon double bond species has been observed previously for PTFE samples that have undergone radiation-induced cross-linking.^{16,30}

To aid in the assignment of the remaining bands, the effects of exposing the 10^9 Rad sample to air for an extended period were studied and are shown in Figure 4. The 1910 – 1500 cm^{-1} FTIR spectral regions of the sample and the same sample after exposure to air for one month, as well as the difference of these spectra, are shown. The same spectral region for an unirradiated sample is included in the figure for comparison as a dashed line. The bands discussed and assigned above as being due to carbon – carbon double bond species do not show any significant change after the sample is exposed to air for one month. The intensity of the band at 1882.2 cm^{-1} decreases after the irradiated sample is exposed to air, indicating a decrease in the concentration of COF moieties in the sample. Concurrently, the intensity of the bands at 1810.9 and 1776.1 cm^{-1} increase. This behavior can be attributed to the hydrolysis of the COF groups by atmospheric water to form COOH groups.^{16,31} In a previous study of the exposure of

irradiated PTFE to air, new bands were observed at 1808 and 1776 cm^{-1} and were assigned to modes of free and hydrogen-bound COOH groups.

The FTIR data presented in Figures 2 and 3 indicate that all of the new moieties induced by α -radiation damage to PTFE increase in concentration up to an exposure of 10^9 Rad. However, increasing the dose to 10^{10} Rad does not result in a corresponding increase in the concentration of many of the new moieties. The concentrations of the oxidized species (COF and COOH) do not increase at all upon increasing the dose to 10^{10} Rad, as observed in Figure 3. This is similar to γ -irradiation of cross-linked PTFE, in which it was determined that the ability to generate carboxyl (COF and COOH) end groups decreased with increasing cross-link density.³⁰ This observation could also be due to insufficient amounts of oxygen for continued reaction at the highest doses, as irradiation was performed under vacuum in the present study.

One significant change that is observed is that the concentrations of the non-terminal carbon-carbon double bond species are observed to be approximately 15 to 20 times greater in the sample exposed to 10^{10} Rad than it is in the 10^9 Rad sample. These non-terminal species are the moieties observed with FTIR to most likely form conjugated carbon-carbon double bond sections within the polymer backbone. The increase in concentration of these double-bond species at an exposure of 10^{10} Rad is consistent with the fluorescence spectroscopy results discussed previously. These results will be discussed below, in conjunction with results obtained from DSC.

Radiation Damage Profile:

γ -, e^- beam-, and neutron- radiation can be assumed to pass entirely through most polymer targets because of its low LET. Conversely, α -radiation will only penetrate a finite distance into materials because of very high LET. This difference in damage vs. depth is an important piece of information in understanding how PTFE irradiation with α -particles is different than other radiation types. Quantification and interpretation of the DSC results presented below also requires this information. Light, high-energy particles, such as the He^{2+} ion of α -radiation, are known to deposit the majority of their energy through electronic mechanisms in the target material.¹⁴ These electronic mechanisms include processes such as electronic ionization or excitation. The program Stopping Range of Ions in Matter (SRIM)³² can be used to calculate the linear energy transfer (LET) via electronic mechanisms from the α -particles as a function of depth into the PTFE target. The results of a calculation for α -particles using experimental parameters from the irradiation process employed in the present study are shown as the dashed line in Figure 5. The electronic LET has moderate values at the surface of the PTFE, peaks at approximately 23 μm into the sample, and sharply falls off after that.

In addition to the calculated electronic LET of α -particles in a PTFE sample, Figure 5 also shows the x-axis divided into 5 μm intervals that represent the thickness of the PTFE layers used for this portion of the study. Presented within each “layer” in Figure 5 is the 900-1070 cm^{-1} FTIR spectral region taken from the spectrum of the corresponding layer in the PTFE sample stack exposed to a 10^9 Rad dose of α -radiation. This band has been attributed to the stretching of a C-F species as discussed earlier, and is indicative of damage (cross-linking) done to the sample. Virgin PTFE samples show no intensity in this spectral region, while layers from samples that have been sufficiently

damaged show this feature with an intensity that varies with depth into the sample. As can be seen in the figure, there seems to be good agreement between the relative intensities of this CF mode for PTFE layers within a stacked sample exposed to 10^9 Rad of α -radiation and the calculated electronic LET.

The integrated values of the CF band intensity and the calculated electronic LET for each layer of stacked PTFE samples exposed to 10^8 and 10^9 Rad of α -radiation are plotted against each other in Figure 6. The linearity of these plots reiterate the good agreement of the radiation damage to PTFE, as determined by the presence of C-F species, and the calculated electronic LET. In light of this experimental confirmation of the accuracy of SRIM at calculating depth of surface penetration for α -particles into PTFE, a value of 26.25 μm was used for quantification and interpretation of the DSC data presented and discussed below.

The fact that low or moderate doses of α -particles do not penetrate beyond 30 μm into PTFE is also shown in Figure 7, which displays FTIR spectra in the 1050 – 675 cm^{-1} region for a variety of samples. The bottom spectrum is that for virgin PTFE and represents the features expected in this region for undamaged PTFE, while the top spectrum is obtained from the 4th layer of a stacked PTFE sample (15 – 20 μm depth) exposed to 10^{10} Rad of α -radiation representing heavily radiation-damaged material. The four spectra in the middle are obtained from the 7th layers (representing 30 – 35 μm depth into the sample) of stacked PTFE samples exposed to 10^7 – 10^{10} Rad of α -radiation. These spectra illustrate that for samples exposed to 10^7 – 10^9 Rad of α -radiation, the particles have stopped before they reach a depth of 30 μm as no damage is observed in the spectra. The 7th layer of the sample exposed to 10^{10} Rad, in contrast to the lower dose

samples, shows extensive damage, indicating that the α -particles have traveled to a depth greater than 30 μm into this sample. This behavior can be explained by the onset of mass loss for doses nearing the 10^{10} Rad regime, as was shown by microscopy and gas evolution in a previous study.^{18,19}

DSC:

Previous studies of irradiated PTFE samples have shown that DSC is a very useful tool for determining the general mechanism of radiation damage (i.e. chain-scission vs. cross-linking) for a given set of experimental parameters.^{9,12} The heat of melting for α -irradiated samples could conceivably contain a variety of information; Including information on physical damage (i.e., disorder introduced into crystalline portions) and chemical damage (i.e., chain scission or cross-link / side branch production) caused by α -radiation. It can be difficult to discern the contributions to the heat of melting from each of these possible changes; however, some of this information is lost after a sample has melted, simplifying interpretation of data obtained during the recrystallization process. The heat of crystallization has been shown to be quite sensitive to the molecular weight of simple, straight-chained PTFE, and can be used to provide an estimate of the molecular weight of a given sample.³³ In the present study, if a sample undergoes chain-scission (i.e., a decrease in molecular weight), the heat of crystallization is expected to increase because the smaller chains can be more efficiently and effectively packed. If PTFE is cross-linked, adjacent chains cannot be as effectively packed, giving rise to a decrease in the heat of crystallization.

The DSC data, which has been normalized to sample weight, is shown in Figure 8. Figure 8a shows the melting endotherms obtained during heating of virgin and α -irradiated PTFE samples, while Figure 8b contains the crystallization exotherms obtained during cooling of the same samples. This data represents a combination of the ~26 % of the 100 μm thick sample that has been irradiated (26.25 μm calculated with SRIM and confirmed with FTIR) and the ~74 % that is virgin, as discussed above. The only differences between the virgin sample and the sample that has been exposed to 10^7 Rad of α -radiation is the appearance of a small shoulder on the low-temperature side of the melting endotherm and a moderate increase in intensity of the crystallization exotherm (i.e., higher heat of crystallization). Upon exposing PTFE to 10^8 Rad, the heating and cooling traces each exhibit two distinct, well-defined, features in addition to the appearance of a new shoulder during the melting of the sample. Exposure of the sample to 10^9 Rad results in well defined melting and crystallization peaks similar to those observed for the virgin material in addition to a very broad, low intensity crystallization feature beginning at about 275 $^{\circ}\text{C}$, also shown multiplied by a factor of five in Figure 8b. The 10^{10} Rad sample only shows the well-defined melting and crystallization features similar to those observed for the virgin material.

The heats of melting and crystallization for the radiation-damaged portion of the samples can be determined by several different methods in which different assumptions are made involving the procedure used to determine the contribution of the unirradiated portion (73.75 μm of the 100 μm total) of the samples to the total heat flow during melting or crystallization. The method used for reporting DSC data in the present study assumes that the heats of melting and crystallization for the unirradiated portions of the

samples are identical to those obtained for a virgin sample and that all of the remaining heat flow can be attributed to the irradiated portion. A second method assumes that the features with similar onset temperatures and peak shapes to those obtained for the unirradiated sample are due entirely to the melting/crystallization of the unirradiated portion of the samples. Additional features in the heat flow traces are then attributed to the irradiated portions of the samples. The lack of additional features in the ΔH_c and the significant increase in intensity of the “virgin-like” feature in the plots for the 10^7 Rad sample indicate that these features contain contributions from both the irradiated and unirradiated portions of the sample. Because of this, use of the first procedure described would be required for this sample. While there are small differences in the ΔH_m and ΔH_c values calculated from the data for the irradiated PTFE samples using the different methods described above, the data trends as a function of exposure are very similar.

The heat of melting, represented by squares connected with a solid line, and heat of crystallization, represented by circles connected with a dotted line, is reported as a function of exposure to α -radiation in Figure 9. The x-axis is broken to allow inclusion of the virgin PTFE sample, zero dose, data. The solid and dashed lines in the figure represent the heats of melting and crystallization, respectively, for the unirradiated PTFE sample, and are included for comparison purposes. It is interesting to note that the ΔH_m has a value that is approximately 160% of that observed for the ΔH_c . This behavior has been observed previously in a DSC study of PTFE³³, and can be attributed to a higher crystallinity in the as received polymer in comparison to the degree of crystallinity obtained during the relatively fast crystallization process (i.e., fast cooling rate) employed in DSC studies.

Significant increases in the values of the ΔH_m and ΔH_c are observed upon exposing PTFE to a 10^7 Rad dose of α -radiation. When the α -radiation dose is increased to 10^8 Rad the ΔH_m and ΔH_c both show further increases. The increase in the ΔH_c can be attributed to more efficient chain packing during crystallization due to smaller molecules, indicating that chain-scission results from α -irradiation at these relatively low doses. Much like what was observed in the FTIR data for low doses, the increase in the ΔH_m at low doses indicates that the majority of the scission is occurring within amorphous regions of the material, allowing the newly liberated chain-ends to more efficiently pack and increasing the overall crystallinity of the sample.

A further increase of the dose to 10^9 Rad results in a dramatic change, as ΔH_m shows a significant decrease from what was observed for samples exposed to lower doses of α -radiation, falling well below the value originally observed for the virgin material. The heat of crystallization also shows a significant decrease, although the value remains somewhat greater than that of the virgin material. At a dose of 10^{10} Rad the ΔH_m is similar to what was observed for the 10^9 Rad sample, while the ΔH_c has decreased to a value below that observed for the virgin material and similar in magnitude to the ΔH_m . The drop in the ΔH_c can be explained by a change in the dominant radiation damage mechanism from chain-scission to cross-linking and side-chain formation at doses between 10^8 and 10^9 Rad. The more significant decrease observed for ΔH_m can likely be attributed to both cross-linking/side-chain formation lowering the overall crystallinity as well as some disorder introduced into the crystalline sections of the sample by bombardment with this high dose of high-energy particles.

As mentioned above, the average molecular weight (M) of straight-chain fluoropolymers, such as the virgin PTFE samples and the samples exposed to relatively low doses of α -radiation, can be estimated from the ΔH_C obtained by DSC.³³ The unirradiated PTFE used in this study has an estimated average molecular weight of 3.9×10^6 amu which is equivalent to 77,000 CF_2 units per polymer chain. Exposure of this material to small doses of α -radiation results in a significant reduction in the average molecular weight. The heat of crystallization for the 10^7 Rad sample yields an average molecular weight of 1.6×10^5 amu, or 3,200 CF_2 units per molecule. The 10^8 Rad sample has an average molecular weight of approximately 3.2×10^4 amu or 640 CF_2 units per molecule. These numbers reiterate that at 10^8 Rad, a significant amount of chain-scission has occurred within the sample, and that up to this dose chain-scission is the predominant radiation damage mechanism. The average molecular weight was not estimated for the high-dose ($> 10^8$ Rad) samples, as the degree of cross-linking is likely to have a different effect on the ΔH_C than chain length does, possibly making the estimate inaccurate.

The estimates of the average molecular weight indicate a reduction of approximately two orders of magnitude in the polymer molecular weight when comparing a sample that has been exposed to 10^8 Rad of α -radiation to an unirradiated sample. A previous study of the α -irradiation of PTFE showed no reduction in the hardness or elastic modulus of a sample exposed to 10^8 Rad.^{18,19} Such a drastic reduction in molecular weight has been observed previously to not greatly affect mechanical properties such as the modulus in a study of the electron-beam induced chain-scission of PTFE.⁹

Discussion

Unlike other types of radiation, low temperature α -irradiation of PTFE results in cross-linking / side-branch formation. However, this is not the only damage mechanism observed. It appears from the loss of intensity in the amorphous CF_2 region shown in Figure 2 that at 10^7 Rad dose of α -radiation chain-scission is occurring within PTFE, resulting in higher sample crystallinity, in agreement with observations made with DSC. The FTIR and DSC data both clearly show that up to a dose of 10^8 Rad chain-scission continues to occur. Chain-scission of PTFE results in an increase in the concentration of end groups, which for the present system include $-\text{CF}_3$, $-\text{CF}=\text{CF}_2$, $-\text{COF}$, and $-\text{COOH}$. Bands that can be attributed to the presence of these end-groups begin to appear in the FTIR spectrum once PTFE has been exposed to 10^8 Rad. At this radiation dose, while chain-scission is the predominant damage mechanism, signs of cross-link / chain-branch formation begin to appear in the FTIR spectrum. It is not entirely unexpected that the damage induced in PTFE by α -irradiation consists of multiple mechanisms. In fact it is more common that the irradiation of a polymer sample yields several types of damage simultaneously, perhaps with one mechanism having a higher probability of occurring than another.³⁴

When the α -radiation dose that PTFE is exposed to is increased to 10^9 Rad, the predominant damage mechanism shifts to cross-linking / side-branch formation as indicated by the decrease in polymer crystallinity observed with FTIR and DSC. However, some chain-scission is still occurring at this dose, as indicated by the continued increase in end-group concentration. The majority of chain-scission occurring as the dose is increased to a value of 10^{10} Rad results in production of small, volatile molecules.

This is evident from the mass-loss indicated in Figure 7 as well as the negligible increase in the concentration of end-groups over what was observed for samples subjected to lower doses of radiation. It is also apparent from the DSC and FTIR data presented that cross-linking / chain-branch formation continues to occur between 10^9 and 10^{10} Rad exposure. The most significant change observed in this dose regime is a very large increase in the concentration of non-terminal carbon-carbon double bond moieties ($-\text{CF}=\text{CF}-$ and $-\text{CF}=\text{C}<$). The behavior observed for PTFE by an α -radiation dose of 10^{10} Rad is presumably explained by a structure that can no longer support new cross-link or chain-branch sites. Further irradiation of this structure results in chain-scission, mostly via small-molecule evolution, and defluorination to form sites of unsaturation.

Conclusions

The damage induced by exposure of PTFE at room temperature to α -radiation was investigated. The results are significantly different from what has previously been observed for other types of radiation in a number of aspects. Other types of radiation will yield damage at depths on the order of mm to cm into the PTFE target due to low LET and the correspondingly large penetration depths. By contrast, the α -radiation employed in this study was shown to only induce damage to a depth of approximately 26 μm , except at very high doses.

PTFE undergoes chain scission at all doses unless irradiated while in a molten state when exposed to other types of radiation. Similarly, PTFE samples exposed to 10^7 and 10^8 Rad of α -radiation at temperatures well below the melting point display chain scission, occurring primarily in amorphous regions, as the predominant damage

mechanism at these doses. However, unlike other types of irradiation, an α -exposure of 10^8 Rad produces a relatively small amount of cross-linking/side-branch formation, as indicated by the appearance of C-F and C=C species. Increasing the PTFE dose to 10^9 Rad results in a change of the dominant radiation-damage mechanism to cross-link / side-branch formation. Further exposure of PTFE to doses up to 10^{10} Rad results in further cross-link / side-branch formation. It is also apparent that at this high dose PTFE undergoes mass loss, most likely via small-molecule gas evolution. Increased defluorination is also apparent at 10^{10} Rad, resulting in a significant increase in the concentration of C=C species.

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Figure 1. Fluorescence spectra of virgin PTFE and samples exposed to a range of α - radiation doses. The virgin sample shows a fluorescence feature centered at approximately 580 nm, while a new feature grows in at high α - radiation doses.

Figure 2. 1075 to 675 cm^{-1} FTIR spectral region of virgin PTFE samples and samples exposed to a range of α - radiation doses. The data shows a decrease in concentration of the amorphous CF_2 units in the samples up to an exposure of 10^8 Rad, and an in-growth of new modes at and above the same exposure as detailed in the text.

Figure 3. 2000 to 1500 cm^{-1} FTIR spectral region of virgin PTFE samples and samples exposed to a range of α - radiation doses. This region indicates the production of a number of carbon, carbon and carbon, oxygen double-bond containing species, as outlined in the text.

Figure 4. 1900 to 1500 cm^{-1} FTIR spectral region showing the changes observed in a PTFE sample soon after exposure to 10^9 Rad α - radiation and the same sample exposed to room air for one month. a) PTFE sample exposed to 10^9 Rad α - radiation followed by room-air for one month. b) Same sample as a) before exposure to room-air. c) Difference spectrum between a) and b). The dashed line is the spectrum for the same spectral region of unirradiated PTFE.

Figure 5. The dashed line indicates the electronic linear energy transfer vs. α - particle depth into PTFE calculated with SRIM [32]. Included in each 5 μm PTFE thickness interval is the feature centered at 985.5 cm^{-1} in the FTIR spectrum of the corresponding layer from the stacked-layer PTFE samples dosed with 10^9 Rad of α - radiation. The data shows that the extent of polymer damage (in this case, CF group concentration) scales with the calculated electronic linear energy transfer, falling to zero at 26.25 μm .

Figure 6. Comparison of calculated electronic linear energy transfer, integrated at 5 μm intervals into PTFE and the observed intensity of the CF feature in the FTIR spectrum at 985.5 cm^{-1} . The square (circle) symbols represent data from a stacked-layer sample dosed with 10^8 (10^9) Rad of α - radiation. The lines correspond to the least-squares fit line through each set of data.

Figure 7. 1050 to 675 cm^{-1} FTIR spectral region of the 7th-layer (30 – 35 μm) of a virgin PTFE sample and samples exposed to a range of α - radiation doses. Included as reference, the top spectrum is from a very heavily irradiated/damaged sample. The data shows that at doses up to 10^9 Rad, changes attributed to α - particle induced damage are not present in the FTIR spectrum at 30 – 35 μm depth in the PTFE samples.

Figure 8. a) DSC data showing the melting endotherms obtained during heating of virgin and α - irradiated PTFE samples. b) DSC data showing the crystallization exotherms for the same samples. It should be noted that because of sample thickness, the samples consist of both irradiated and unirradiated portions, as detailed in the text.

Figure 9. The heats of melting (squares, solid line) and crystallization (circles, dotted line) of virgin PTFE and samples dosed with a range of α – radiation. The horizontal solid and dotted lines represent the values for the heat of melting and crystallization of virgin PTFE, respectively.

Table 1. Assignments of spectral features observed in FTIR data of virgin and α – irradiated PTFE. Previously determined assignments and corresponding observed energies in FTIR spectra are included.^{7,16,25,28,29,31}

Fluorescence Intensity (Arb. Units)

Virgin PTFE (cm ⁻¹)	α -irradiated PTFE (cm ⁻¹)	Assignment
518.8		CF ₂ rock (516)
554.4		CF ₂ deformation (553)
627.7		CF ₂ wag (625)
641.2		CF ₂ wag (638)
704.9		Amorphous CF ₂ (703)
719.3	723.2	Amorphous CF ₂ (718), CF ₃ deformation (727, 732, 737)
740.5	738.7	Amorphous CF ₂ (738), CF ₃ deformation (727, 732, 737)
774.3		Amorphous CF ₂ (778)
782.0		Amorphous CF ₂ (778)
854.3		Amorphous CF ₂ (850)
	985.5	CF mode (985)
1150-1250		CF ₂ stretch (1152, 1213, 1242)
	1350.0	CF ₃ stretch (1352)
	1370.2	CF ₃ stretch (1370)
	1663.3	-CF=C< (1671)
	1716.4	-CF=CF- (1717)
	1728.9	-CF=CF- (1730)
	1776.2	COOH _{free} (1776)
	1784.8	-CF=CF ₂ (1785)
	1810.9	COOH _{ass.} (1808)
	1884.1	COF (1884)
	3555.2	COOH _{free} (3580)