Macromolecules **2003,** *36,* 7132−7137

An Investigation of the Thermal and Tensile Properties of PFA Following γ-Radiolysis

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Received April 17, 2003

ABSTRACT: For some applications for fluoropolymers they must be subjected to high-energy radiation, e.g., when they are grafted with styrene using an irradiation method to produce fuel cell membranes or matrix supports for combinatorial chemistry. In some of these applications they may be subjected to mechanical stress or elevated temperature, so it is important to elucidate the effects of the radiolysis on these properties. In the present work the effect of γ-radiolysis on the glass transition, melting behavior, and thermal stability of PFA has been studied as well as the effect of the radiolysis on the tensile properties of the polymer.

Introduction

The thermal properties of poly(tetrafluoroethylene), PTFE, indicate that it is a linear, nonbranched, non-cross-linked polymer.[1] When polymerized, PTFE has a high degree of crystallinity and melts at high temperature over a narrow temperature range. The polymer is stable up to 723 K, but when heated further, a single step weight-loss profile is observed by thermal gravimetric analysis.[2] If PTFE is cross-linked by exposure to radiation while in the molten form, the melting temperature and crystallinity drop due to hindrance of chain packing in the network structure.[3] The polymer is also less thermally stable after cross-linking and decomposes in two steps as a result of the low molecular weight component which is a product of concomitant radiation-induced scission.[4]

When TFE is copolymerized with hexafluoropropylene, HFP, to form the copolymer, FEP, or with perfluoropropyl vinyl ether, PPVE, to form PFA, the melting temperatures and crystallinity of the resulting copolymers are lower than for PTFE. FEP with 12% HFP melts at 535 K while PFA has a slightly higher melting temperature due to the lower concentration of the comonomer used.[5]

At temperatures close to room temperature PTFE undergoes two crystal−crystal transitions, corresponding to the triclinic−hexagonal and hexagonal−pseudohexagonal transitions. FEP and PFA exhibit just one transition in this low-temperature region, although in the case of FEP, the transition becomes broad and difficult to detect if the comonomer concentration is high.[5,6]

Thermal analysis of FEP and the poly(tetrafluoroethylene-*co*-perfluorinated vinyl ether)s has been used to examine the incorporation of comonomer side chains into the crystallites. Pucciariello and co-workers observed that the melting temperatures of FEP copolymers quenched from the melt were higher than the melting temperatures of perfluormethyl vinyl ether, PMVE, copolymers with a similar amount of comonomer. They considered this as evidence for the incorporation of HFP side chains into the PTFE crystal lattice as point defects, but the exclusion of the larger perfluoroalkoxy side chains.[7−11] X-ray diffraction studies also support these finding.[13−16]

While the thermal properties, particularly the melting transitions, of PTFE and cross-linked PTFE have been widely studied, the same is not true for PFA. In this paper the thermal properties of unirradiated PFA and PFA irradiated over a wide temperature range are examined. The mechanical properties of PFA irradiated at 303 K are also examined with the view to determining the maximum allowable limits of radiation exposure for subsequent grafting applications.

Experimental Section

Sample Radiolysis. The samples PFA (DuPont, code TE 7132 pellets), except for the samples irradiated at 633 K, were placed in Pyrex tubes and evacuated at 1×10^{-2} Pa for 24 h. The tubes were sealed by melting a narrow neck in the glass, and then the samples were irradiated either at the Australian Nuclear Science and Technology Organisation (ANSTO) in a pond facility (dose rate 1.5 kGy h^{-1}) or at the University of Queensland using a 220 Nordian Gammacell (dose rate 5.9 kGy h^{-1}). After irradiation, the tubes containing the samples were heated at 473 K for 2 h to remove the remaining radicals before being opened in a nitrogen atmosphere. The tensile measurements were made immediately after the samples were removed from the sample tube. This was done to minimize any reaction of the irradiated PFA with air.

The samples irradiated at 633 K were irradiated in a specially designed vacuum vessel using an electron beam accelerator (ELV-2, Budker Institute of Nuclear Physics, Novosibirsk, Russia). The temperature of the samples could be controlled during exposure, and the electron energy was 1.5 MeV with a beam current of 2 mA. The total irradiation dose was built up in steps with a dose of 50 kGy per step at an average dose rate of 14.7 kGy min^{-1}.

Thermal Analysis. Dynamic mechanical analysis (DMA) was performed using a Perkin-Elmer DMA 7 over the temperature range 303−473 K. The PFA sample was cut from a lantern designed for solid-phase organic chemistry, SPOC, and

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10.1021/ma0302309 CCC: $25.00

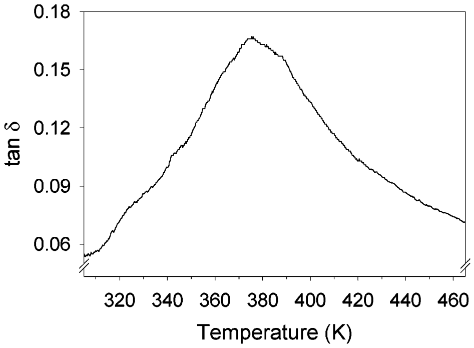

Figure 1. DMA of unirradiated PFA. Tan δ as a function of temperature.

supplied by Mimotopes. The lantern was injection-molded from PFA pellets (DuPont, code TE 7132) and had a thickness of 0.486 mm. Parallel plates were used with a static force of 100 mN and a dynamic force of 83 mN at a frequency of 1 Hz.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 7. All runs were performed on 10 ± 0.5 mg samples in a nitrogen atmosphere. Samples were weighed both before and after analysis to check for weight loss due to decomposition during the DSC runs. It was found that in all cases the difference in weight before and after analysis was less than 2% and was ignored for the calculation of the heat of fusion. The apparatus was calibrated using the onset of melting of indium (429.6 K) and zinc (692.47 K) and the heat of fusion of indium (28.45 J g^{-1}). Before each run the baseline was optimized in the range of interest and later subtracted from the corresponding calorimetric curve.

Samples crystallized by uniform cooling were first heated to 613 K and held at this temperature for 10 min. Subsequent cooling and heating scans were performed at 40 K min^{-1}. Isothermal crystallizations were carried out in the DSC instrument in a nitrogen atmosphere by holding the sample at 613 K, then rapidly cooling it using the maximum cooling rate of the instrument (approximately 400 K min^{-1}) to the selected crystallization temperature, and holding it at that temperature for 1 h. The samples were then cooled to 323 K at 20 K min^{-1} and then heated to 613 K at 20 K min^{-1} to measure the melting endotherm. Melting temperatures were taken from the maxima of the peaks.

Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer TGA 7. Samples with weight 10 ± 0.5 mg were heated from 373 to 1246 K at a rate of 10 K min^{-1} in a nitrogen atmosphere.

Preparation of Films for Tensile Measurements. Films were prepared by compression-molding PFA pellets (DuPont code TE 7132). The pellets were first washed with acetone and then pressed in a nitrogen atmosphere between polished Monel 400 plates (Pinch Alloys Australia) heated to 613 K. (Monel is a nickel−copper alloy resistant to hydrofluoric acid.) A minimal pressure was applied for 10 min while the polymer melted, and then the pressure was increased to 2 tons for 2 min to form a film. The thickness of the films was controlled using metal windows (0.5 mm thick) placed between the plates. The heating plates were then cooled using a stream of cool water, and the pressure was released once the plates had cooled to room temperature. Dog bones were cut using a die with gauge length of 15 mm.

Tensile Measurements. Tensile measurements were conducted on an Instron 4505 operated with an Instron 4500 controller and a series IX method editor. Wedge grips (5 kN) were used to hold the dog bones in place. A crosshead speed of 50 mm min^{-1} was used at a temperature of 296 K.

Results and Discussion

Glass Transition Temperature of Unirradiated PFA. The glass transition temperature (T_g) of unirradiated PFA was taken from the maximum in tan δ (Figure 1) measured using DMA. The transition is a broad one ranging from approximately 310 to 460 K with a maximum at 376 K. This value is in good agreement with the literature value of 363 K.[17] As expected, this is lower than the T_g of PTFE of 399 K.[18]

Melting Behavior of Unirradiated PFA. Superheating is an often-cited problem when measuring the melting temperature of fluoropolymers.[5−7,19,20] The most obvious symptom of superheating is that the melting rate of the crystals is lower than the heating rate. This can be detected by a change in the melting temperature with variations in the heating rate. The intrinsic melting temperature can be defined as the equilibrium melting temperature. This is the temperature at which a perfectly formed polymer crystallite melts.

Several methods have been reported in the literature to overcome the shortcomings of superheating of fluoropolymers. Wunderlich and co-workers estimated the equilibrium melting temperature of PTFE by annealing samples for 12 h at a predetermined temperature in the melting range and then quickly cooling the samples to a temperature that was too high to induce crystallization but was significantly below the melting temperature. The annealing temperature at which no melting endotherm was observed on subsequent heating was taken as the equilibrium melting temperature.[5] Hoffman and Weeks determined the equilibrium melting temperature of poly(chlorotrifluoroethylene), PCTFE, using a different method in which the polymer was isothermally crystallized at a temperature T_c. They then plotted the melting temperature (T_m) of the crystals against the crystallization temperature for a range of T_c values. The intercept of the line fitted to the data with the line $T_m = T_c$ was taken as the equilibrium melting temperature.[21] This method is less cumbersome and time-consuming than the method of Wunderlich and co-workers and has also been used by Pucciariello and co-workers to determine the equilibrium melting temperature for FEP and TFE/PMVE polymers.[9,11]

To determine the equilibrium melting temperature of PFA, the isothermal crystallization method of Hoffman and Weeks was used. Unirradiated PFA was cooled from the melt at the maximum rate the instrument would allow and then held at a predetermined temperature between 553 and 565 K for 1 h, cooled to 323 K, and then heated to 613 K at 20 K min^{-1}. If the crystallization temperature (T_c) was above 565 K, an exotherm was observed on subsequent cooling which suggested there was incomplete crystallization at this temperature. For this reason, the highest value of T_c used was 565 K. The DSC traces of the first run of PFA and runs after crystallization are shown Figure 2. The first run was used to determine the initial crystallinity of PFA before any irradiation or heat treatment. The heat of fusion from the area under the melting endotherm was converted to crystallinity based on the value of 82 J g^{-1} reported for the melting of a perfect crystal of PTFE.[5] This gave a crystallinity of the unirradiated pellets of PFA of 34 ± 3%.

The multimodal nature of the endotherms in Figure 2 was due to formation of less perfect crystals (lower melting temperature) among the more perfect ones (higher melting temperature). As T_c was decreased, there is less chance for well-ordered crystals to form, and the melting temperatures were shifted to lower values and the peaks broadened. When a T_c of 565 K was used, there was a broad endotherm at approxi-

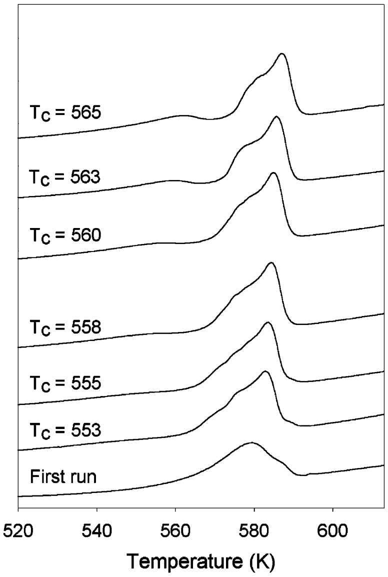

Figure 2. Melting endotherms (positive direction) of as-received PFA and after crystallization at temperatures T_c. The heating rate was 20 K min^{-1}.

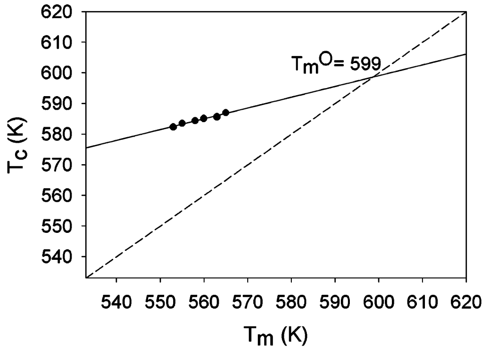

Figure 3. Melting temperature (T_m) plotted as a function of crystallization temperature (T_c). The dashed line satisfies the equation $T_c = T_m$.

mately 561 K and a shoulder at 580 K that can be attributed to melting of less perfect crystals. As T_c was decreased, the broad peak at 561 K shifted to lower temperature and became broader. At T_c less than 555 K this peak became so broad it is almost indistinguishable from the baseline. The shoulder which was at 580 K when T_c was 565 K also shifted to a lower melting temperature as T_c was decreased. Similar observations have been made for isothermal crystallization experiments with TFE/PMVE.[8] It was possible for the less perfect crystals to recrystallize after melting and so form more ordered crystals. However, the areas under the traces for each value of T_c in Figure 2 do not vary by more than 2%, suggesting that this effect, if present, can be ignored for the purpose of this study.

The equilibrium melting temperature was estimated from the plot of T_c vs T_m in Figure 3. Extrapolation of the line of best fit of the data intercepts the line $T_c = T_m$ at 599 K. This value is only marginally below the value found for PTFE of 605 K using the method of Wunderlich[5] and would suggest that the perfluoropropyl ether side chains are excluded from the crystallites. If they were included in the crystallites, the $T_m°$ would be expected to be much lower than for PTFE. This is in agreement with work by Pucciariello and co-workers, who found that small CF_3 side chains in FEP were partially included in the PTFE crystal lattice, while larger perfluoroalkoxy side chains in TFE/PMVE copolymers were excluded.[9−11]

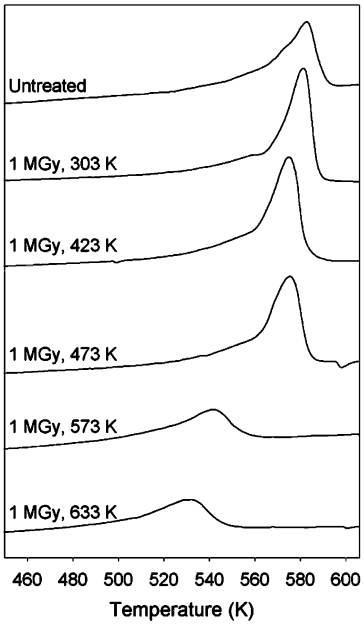

Figure 4. DSC traces of nonirradiated PFA and PFA irradiated to 1 MGy over a range of temperatures. Samples were crystallized from the melt by cooling at 40 K min^{-1} followed by subsequent heating at 40 K min^{-1} to measure the melting endotherms (positive direction).

Thermal Properties of Irradiated PFA. Determination of the equilibrium melting temperature of PFA samples after irradiation was not possible due to the chemical changes within the polymer. ^{19}F NMR spectroscopy studies[12] revealed the formation of CF_3 side chains which may be incorporated or excluded from the crystallites. While the equilibrium melting temperature of FEP has been reported using the method by Hoffman and Weeks,[11] Centore et al. postulated that when FEP is crystallized isothermally, the CF_3 side chain concentration incorporated into the crystallites may change with crystallization temperature; hence, it is not strictly correct to use this method for polymers containing HFP groups.[6] Instead, to compare the effects of radiation and radiation temperature on the melting temperature and melting endotherms for PFA, samples were crystallized from the melt at a constant cooling rate and then heated through the melting transition at the same rate. Since a range of irradiation temperatures were used, it was important to erase the thermal history of the polymers before the melting transition was measured; thus, the first DSC runs after irradiation were ignored.

The effect of irradiation temperature on the melting behavior of PFA is compared in Figure 4 for samples irradiated to 1 MGy and for unirradiated PFA. No transitions were observed below 450 K so this region has been omitted for clarity. The melting temperatures (taken from the maxima in the melting endotherms) and crystallinity (calculated from the area under the endotherms) over the entire dose range examined are plotted in Figure 5 and Figure 6, respectively. The irradiation temperatures used can be split into three regimes: below the T_g maximum (irradiation at 303 K), above the T_g, but below the T_m (irradiation at 423 and 473 K), and at or above the T_m (irradiation at 573 and 633 K). When PFA was irradiated at 303 K, there was little change in the melting temperature while the crystallinity increased significantly. The increase in crystallinity may

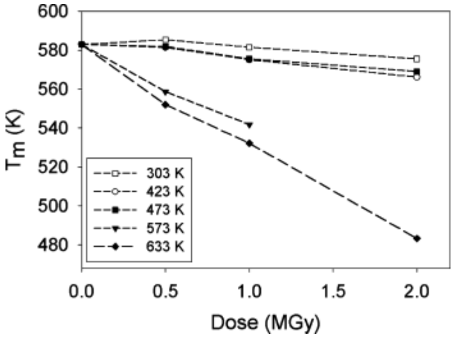

Figure 5. Melting temperature as a function of dose for samples irradiated at 303, 423, 473, 573, and 633 K.

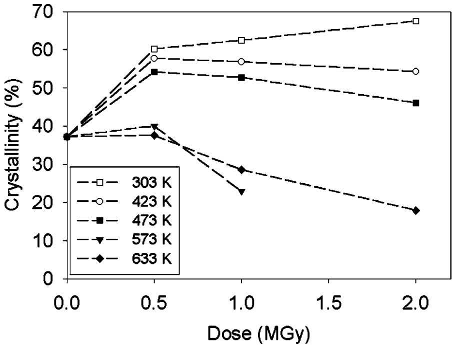

Figure 6. Crystallinity as a function of dose for samples irradiated at 303, 423, 473, 573, and 633 K.

be attributed to loss of alkoxy side chains, cleavage of chains in the amorphous regions interconnecting the crystallites (tie molecules), and an overall lowering of the molecular weight, so allowing better packing of the chains and hence an increase in crystallinity. In support of this argument the melting endotherms of samples irradiated to 1 MGy at 303 K were sharper than the endotherm of the unirradiated sample. The lowering of the molecular weight is supported by the solid-state ^{19}F NMR spectra[12] which showed that the major nonvolatile products resulting from irradiation at 303 K are new saturated chain ends.

Samples irradiated at 423 and 473 K had similar thermal characteristics, namely a slightly lower T_m and a higher crystallinity than unirradiated PFA. The large increase in crystallinity between 0 and 0.5 MGy may again be attributed to cleavage of tie molecules and alkoxy side chains. But above this dose range the crystallinity decreased due to the formation of long and short branches capable of disrupting the chain packing. The short branches (CF_3) may be able to be included in the crystallites, giving rise to less perfect crystal growth that may explain the low-temperature shoulder in the DSC traces (Figure 4) and the lower T_m maximum. An analogous behavior was reported for FEP, for which increasing the comonomer concentration decreased the T_m.[11]

Samples irradiated at or above the T_m of unirradiated PFA (573 and 633 K) had dramatically different DSC traces to the other samples, indicating major structural changes within the polymer. The melting endotherms were broad and shifted to significantly lower temperature when compared with the unirradiated PFA. The crystallinity marginally increased after a dose of 0.5 MGy and may be considered to be a combination of release of strain through cleavage of tie molecules as well as formation of short and long branches. Above 0.5 MGy the crystallinity dropped dramatically—the sample irradiated to 2 MGy at 633 K had a crystallinity of 18% and a melting temperature of 530 K (note that the 2 MGy/573 K sample was lost due to excessive pressure buildup which led to an explosion of the glass tube containing the sample during irradiation). Oshima et al. found that PTFE irradiated in the melt to a dose of 2 MGy became almost completely amorphous.[22]

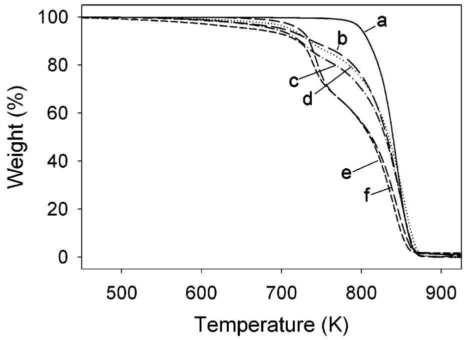

Figure 7. TGA traces of unirradiated PFA and PFA irradiated to a dose of 1 MGy at 303, 423, 473, 573, and 633 K.

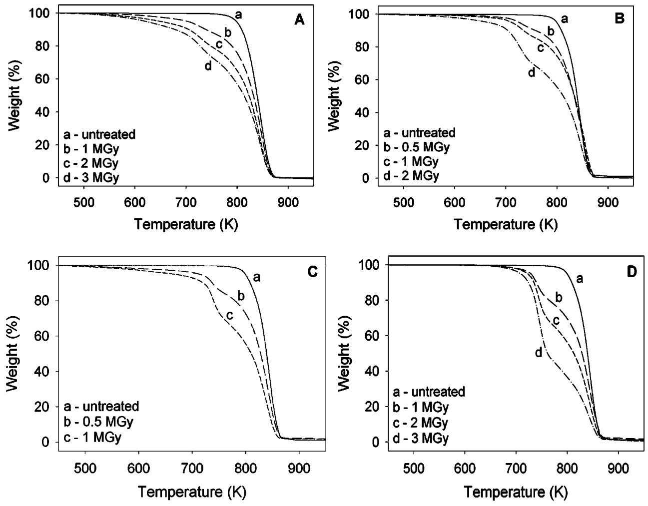

Figure 8. TGA traces: (A) irradiated at 303 K; (B) irradiated at 473 K; (C) irradiated at 573 K (derivative curves are included to highlight the predominately two-step decomposition); (D) irradiated at 633 K.

Thermal Gravimetric Analysis (TGA). The thermal stabilities of PFA with and without radiation treatment were examined by thermal gravimetric analysis (TGA). Figure 7 and Figure 8 show the weight loss as a function of temperature for the various irradiated PFA samples measured by TGA ranging from 373 to 1246 K with a heating rate of 10 K min^{-1}. Below 450 K and above 950 K there was no weight change so these regions have been omitted from the plots for clarity. The decomposition of unirradiated PFA occurred in a one-step process beginning at approximately 725 K, most likely due to depolymerization and the production of predominantly TFE molecules, as is the case for the thermal decomposition of PTFE.[23] The alkoxy side chains may be expected to decompose at a lower temperature than PTFE due to the ether bond, but this is not obvious from the TGA curve.

The onset of decomposition was shifted to a lower temperature by radiation treatment at all temperatures. At all irradiation temperatures, with the exception of 633 K, the initial lower temperature decomposition may be attributed to loss of low molecular weight fragments.

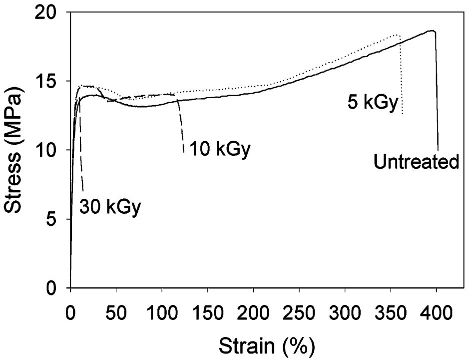

Figure 9. Typical stress−strain plots for unirradiated PFA and PFA irradiated to 5, 10, and 30 kGy, all in a vacuum at 303 K. Measurements were made at 296 K.

The absence of these fragments in the samples irradiated at 633 K was due to the experimental conditions used. At this temperature electron beams were used instead of γ-radiation, and the samples were under continual vacuum pumping; thus, any low molecular weight fragments formed would have been removed by the vacuum during the radiation treatment.

Aside from loss of low molecular weight material below 700 K, all the irradiated samples had essentially a two-step weight-loss profile. The relative proportion of these two steps gives some insight into their possible origins. Examination of Figure 8D (irradiation at 633 K) shows that the low-temperature decomposition step increased with increasing dose while the converse was true for the higher temperature step. ^{19}F NMR spectra showed that in these samples branching and cross-linking increased with dose. Therefore, as a corollary it may be concluded that the first step between approximately 700 and 775 K was due to decomposition of branched or cross-linked PFA while the second step between 775 and 850 K was due to decomposition of non-cross-linked PFA. In support of this argument, Oshima et al. have reported a TGA study of PTFE cross-linked at 610 K in an argon atmosphere and found that the cross-linked material was less thermally stable than unirradiated PTFE.[4] The lower stability of the branched/cross-linked material over the linear material may originate from weak points and defects in the structure. FEP, which contains CF_3 branches introduced by copolymerization of TFE with HFP, decomposes in two steps when heated in a nitrogen atmosphere.[24] The first step is due to the lower stability of the branched structures, while the second step is due to decomposition of TFE units. This supports the observation that branched structures in PFA after irradiation decompose at a lower temperature than nonbranched structures.

Tensile Measurements of Low-Dose PFA. It is known that fluoropolymers degrade when exposed to radiation.[25] When PFA is irradiated in a vacuum, it has a slightly better radiation resistance than FEP and PTFE at low doses (<30 kGy), but at high doses (>100 kGy) all three polymers become embrittled.[26] In fact, a common method of recycling PTFE is to expose it to radiation to break the polymer down into a free-flowing micropowder which can then be used as a lubricant.[27]

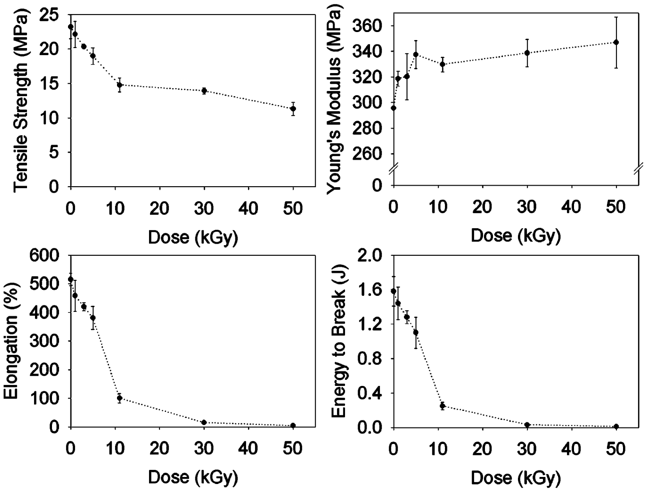

Figure 10. Tensile strength, Young's modulus, elongation, and energy to break of irradiated PFA as a function of irradiation dose.

Figure 9 shows a selection of stress−strain curves for PFA before and after irradiation. The unirradiated material initially displayed Hookean elastic type behavior at low strain where the stress/stain curve is almost linear before reaching a point where there is ductile flow. Upon further strain there was necking and strain-hardening of the polymer before it finally broke. Similar profiles are observed up to a dose of 5 kGy, above which the samples broke without strain hardening. Above 10 kGy, the samples underwent brittle fracture.

In Figure 10 the tensile strength, Young's modulus, elongation, and energy to break are plotted as a function of radiation dose. These figures show that the mechanical properties of PFA were dramatically altered after relatively low radiation doses. The loss in tensile strength, elongation, and energy to break together with the increase in rigidity, as indicated by the increase in the Young's modulus, are consistent with chain scission. Other workers have observed similar trends in the tensile strength and elongation of irradiated PFA.[26,28] This is in agreement with the NMR results for PFA irradiated at 303 K,[12] which showed that chain scission was the main radiation-induced reaction at this irradiation.

The results presented in Figure 10 suggested that when radiation processing PFA, the radiation dose should be kept as low as possible to avoid degradation of the polymer. If the radiation processing involves grafting, then the actual mechanical properties of the grafted copolymer will be different from those of the samples studied here, as the graft may be expected to influence these properties. El-Sawy et al. found that when PFA was grafted with vinyl acetate, there was an improvement in the tensile strength at low graft yields, possibly due to cross-linking of the graft.[29] Another consideration is that grafted supports for solid phase organic chemistry applications would more likely undergo compressive stresses rather than tensile stresses during handling of the support. It is known that fluoropolymers perform better under compression than elongation.[30] On the basis of this information, to maintain matrix stability, the total dose used for grafting monomers onto PFA should preferably be kept below 10 kGy and definitely not exceed 30 kGy.

Conclusions

The thermal properties of PFA before and after irradiation have been examined. The equilibrium melting temperature of unirradiated PFA was estimated to be 599 K, slightly below the corresponding value for PTFE. When PFA was irradiated over a temperature range from below the T_g to above the melting point, the thermal properties of the polymer changed significantly. Low-temperature irradiation resulted in a decrease in thermal stability and an increase in the crystallinity with little change in the melting temperature. This was explained by a lowering of the molecular weight and improved chain packing accompanied by formation of a small amount of short branch structures. When PFA was irradiated at or above the melting temperature the crystallinity, melting temperature, and thermal stability of the resulting polymer decreased, which was attributed to formation of long and short branch and of low molecular weight fragments. At irradiation temperatures above the T_g but below the melting temperature, the properties were intermediate between those observed at the higher and lower irradiation temperatures.

Tensile measurements for PFA irradiated at 303 K showed that the polymer experienced a dramatic loss in the mechanical properties even at low dose. Thus, a recommended upper limit of the total allowable dose to be used for grafting reactions of approximately 30 kGy was suggested in order for the graft copolymer to retain useful mechanical properties.

Acknowledgment. The authors acknowledge the financial support from the Australian Research Council, the Australian Institute of Nuclear Science and Engineering, and Mimotopes Pty Ltd., Clayton, Victoria, Australia.

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MA0302309