JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 341–355 (1967)

Density–Dose Behavior of Irradiated Polytetrafluoroethylene

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Synopsis

The nature of the room temperature density–dose relationships in polytetrafluoroethylene (PTFE) have been studied over the dose range of 10^4 to 10^9 rads. Under various conditions, samples of PTFE were irradiated in combinations of neutron and gamma (reactor and ^{60}Co) radiation fields resulting in density increases up to approximately 5%. For the dose range 10^5 to 10^8 rads, the increase in density measured at 0°C. is approximately proportional to the logarithm of the radiation dose. For doses less than about 10^6 rads, the increase in density appears to be directly proportional to the dose, while above 10^8 rads the density reaches a maximum and then begins to decrease. By examining the changes in slope and displacement of the curves which occur under various conditions, several effects are discernible. Compared to the effects of γ-rays alone, the density increase per dose in the 10^5 to 10^8 rad region is lower for cases where both neutrons and γ-rays are present in the radiation field. This may suggest that competing processes are involved in producing density changes. The discernible difference between effects of γ-radiation and reactor radiation appears to be unique in polymers. The ambient temperature during irradiation and the post-irradiation heat treatment of the specimens affect the changes in density. For dose rates over the range 0.1×10^6 to 13×10^6 rads/hr., no dose rate effects have thus far been observed. The feasibility of using PTFE for some types of radiation dosimetry has been demonstrated, and its possible usefulness is being investigated.

I. INTRODUCTION

One of the interesting effects which has been noted in irradiated polytetrafluoroethylene (PTFE) is a rather pronounced change in density.[1–4] It has been shown that the increase in density is accompanied by an increase in per cent crystallinity,[1–4] which is not considered usual for irradiated polymers. It has also been observed in our laboratory that density and crystallinity changes in PTFE can be employed for dosimetry measurements. In this connection, it was demonstrated that a simple hydrometer dosimeter can feasibly be made to operate.

Kline and Sauer[1] reported that a sample of PTFE irradiated in a reactor to 10^8 rad underwent a room temperature density increase from 2.17 to 2.24 g./cc. for a 3.23% increase. Concurrently it was shown that the per cent crystallinity, as indicated by infrared measurements, increased from 56 to 83%.[1] The dynamic modulus also increased significantly, consistent with an increase in crystallinity.

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Licht and Kline[2,3] later observed that the increase in density reached a maximum in the range of 1×10^8 to 3×10^8 rad (^{60}Co irradiation), and thereafter decreased with increasing dose. It has been noted[5] that the increase in crystallinity is proportional to the logarithm of the dose in the 10^6–10^7 rad range for PTFE subjected to ^{60}Co radiation.

The present study was undertaken to investigate the density–dose behavior of PTFE over a wide range of radiation doses (approximately 10^4–10^9 rad) and to obtain data which would reflect on the further possible use of PTFE in radiation dosimetry. The investigation included the effects of dose rate and temperature.

The study was also undertaken to analyze possible differences in the effects of neutron radiation as compared to γ-radiation in PTFE. To date, no differences in the effects have been reported for most polymers and organic and inorganic solutions if the radiation dose, in units of energy absorbed, is the same. It now appears that differences in radiation effects for PTFE are detectable in comparing results for reactor irradiations (neutron and γ) to results for ^{60}Co irradiation (γ only).

II. EXPERIMENTAL PROCEDURES

Sample Preparation and Analysis

A polytetrafluoroethylene, TFE resin #7 (commercial product of the E. I. du Pont de Nemours and Co., Inc.), was used for all experiments carried out in relation to this work. The molecular weight of this resin has been given as 1.6×10^7.[6] TFE resin #7 was also used in previous studies on PTFE carried out at The Pennsylvania State University,[1–3,7] permitting some referencing of results with those of previous experimenters. Material used had an initial density near 2.15 g./cc. at room temperature and an initial per cent crystallinity value of about 55%. The as-received material, in the form of $^1/_2$-in. diameter rods, was machined to make samples about 1 in. in length. A $^1/_8$-in. diameter hole was bored along the axis of the cylindrical sample.

Densities were analyzed before and after irradiation by the displacement method (a procedure similar to ASTM Designation D792-64T). A standard reference temperature, 0°C., was selected because it is below the first-order crystalline transitions in PTFE, even for samples irradiated in 10^8 rads.[2]

The flask in which the samples were immersed contained distilled water with a very slight amount of soap added to impede the formation of bubbles on the surface of the sample. The density of the soap and water solution was determined from the weight lost by a standardizing solid, the volume of which was carefully determined. In order to minimize error it was desirable to select a standardizing material with a low coefficient of thermal expansion and one that would not absorb the solution to any detectable degree. On this basis a glass-ceramic, Pyroceram 9608, was selected.

TABLE I
Summary of Experimental Conditions for PTFE Irradiations

Experiment designation	Source	Position and/or conditions	Figure number	Dose rate, Mrad/hr.	Neutron composition, % (rads)	Irradiation temperature, °C.	Least-squares fit $10^5 < D < 10^8$, D in rads
A	NBS Co-60 facility	Central position, 50 kcurie source	2	8.0	0	~41	$D = 10^6 \times 0.025e^{100\Delta\rho}$
B	PSU nuclear reactor (200 kw.) operation	10 cm. from core, loading 37	2	6.6	9	25–26	$D = 10^6 \times 0.024e^{108\Delta\rho}$
C	PSU nuclear reactor (200 kw.) operation	2 cm. from core, loading 37	2	13.8	17	37–38	$D = 10^6 \times 0.0031e^{153\Delta\rho}$
D	PSU ^{60}Co facility	Configuration #1, room temperature	3	1.06	0	25–27	$D = 10^6 \times 0.058e^{98\Delta\rho}$
E	PSU ^{60}Co facility	Configuration #2, room temperature	3	0.16	0	25–27	$D = 10^6 \times 0.051e^{99\Delta\rho}$
F	PSU ^{60}Co facility	Configuration #1, elevated temperature (75°C.)	3	1.06	0	73–77	$D = 10^6 \times 0.028e^{90\Delta\rho}$
D′	PSU ^{60}Co facility	Configuration #1, room temperature[a]	3	1.06	0	25–27	$D = 10^6 \times 0.051e^{95\Delta\rho}$

[a] Before testing, each of the samples in this series was heat-treated at 75°C. for a time equal to its respective irradiation time.

In order to remove the slight variations involved in the density values of the as-received specimens, the results are given in terms of the change in density, $\Delta\rho$, i.e., $\Delta\rho = \rho_I - \rho_0$ where ρ_I is the density of the irradiated sample measured at 0°C. and ρ_0 is density of the unirradiated sample measured at 0°C. While all irradiated PTFE specimens were analyzed at 0°C., sufficient expansion data for unirradiated PTFE were available from previous[2,3] and current studies to permit unirradiated samples to be analyzed at room temperature where desirable. In the latter case, the values were then adjusted to the reference temperature (0°C.).

Irradiation of Samples

To determine the effects of neutron and γ-irradiation it would be desirable to irradiate the samples in a pure neutron field, a mixed neutron and γ field and a pure γ field. Since no pure neutron source was available where samples could be conveniently irradiated to high doses, samples were irradiated only in mixed neutron and γ fields (reactor radiation) and in pure γ fields (^{60}Co radiation).

Because of the difference between the neutron and γ relaxation lengths in water, it was possible to vary both the dose rate and the percentage neutron and γ-ray composition of the dose received in reactor irradiations by varying the distance from the reactor core. For reactor irradiations, samples were placed in positions 2 cm. and 10 cm. from the core face of the PSU nuclear reactor, the PSU core loading #37 being used.

The γ-irradiations were carried out in ^{60}Co sources (Table I) at The National Bureau of Standards (NBS), The Brookhaven National Laboratories (BNL), and The Pennsylvania State University (PSU). Dose rates of ^{60}Co sources were estimated and cross-referenced from cobalt glass dosimetry and/or ferrous-ferric sulfate dosimetry measurements. Reactor dose rates were estimated from the work of Jacobs and Kline.[7] For γ-irradiations the conversion factor, rads in PTFE/roentgen (air) = 0.843, was used.

For ^{60}Co-irradiations it is estimated that variations in the dose rate over the dimensions of the sample and the limits of accuracy for the various dose rate determinations together result in a maximum error of $\pm 10\%$ for the dose rate values given in Table I. In a given radiation field, the relative values (from sample to sample) can be more closely compared, however, since these depend only on careful positioning and timing. In reactor irradiations, it is estimated that the possible limits of error are $\pm 20\%$, and again the relative values are somewhat more accurate. As will be noted in the discussion, most of the conclusions do not depend on absolute dose measurements.

III. EXPERIMENTAL RESULTS

If the change in density ($\Delta\rho$) is plotted as a function of absorbed dose D, the results tend to follow an exponential (or logarithmic) relationship in

the dose range 10^5–10^8 rad, i.e., $\ln D \propto \Delta\rho$ (Fig. 1). On a semilogarithmic plot, the data in this range may then be approximated by a straight line, and, from a least-squares fit of this line to the data, one can obtain the coefficients (α and β) of the exponential relationship $D = \alpha \exp\{\beta\Delta\rho\}$. Relationships for the irradiations are given in the last column of Table I. Below 10^5 rad the change in density appears to rapidly increase in a linear fashion from zero to the value noted at the beginning of the region of exponential behavior. Above 10^8 rad the change in density reaches a maximum and thereafter decreases, as has been previously shown.[2,3]

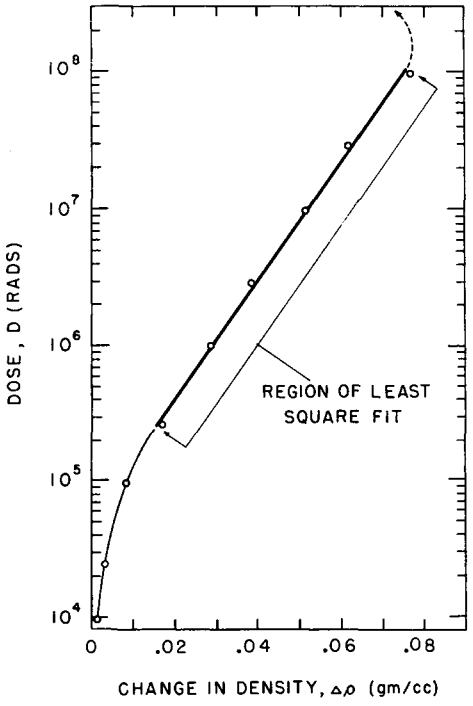

Fig. 1. Change in density vs. dose for ^{60}Co-irradiated polytetrafluoroethylene (experiment D, PSU).

The composite graph for the results obtained in irradiations at the NBS ^{60}Co facility (A) and the PSU reactor (B and C) are presented in Figure 2. Results indicate that the slope which is 100 cc./g. for a pure γ field (A), increased to 108 cc./g. when 9% of the dose in rads was a result of neutron interactions (B), and further increased to 153 cc./g. when the total dose included a 17% neutron contribution. For a sample irradiated at the PSU reactor (2 cm. position), a maximum change in density with dose occurred between 10^8 rad and 2×10^8 rad. The density at 2×10^8 rad was noted to decrease by 0.0135 g./cc. over the value noted at 1×10^8 rad with a probable maximum density change near 0.065 g./cc. Licht and Kline[2,3] noted the maximum change in density for γ-irradiated samples to be slightly more than 0.08 g./cc. and to occur between 10^8 and 3×10^8 rad.

The composite graph of PSU ^{60}Co results is given in Figure 3. There is no apparent difference between the results for sample D (dose rate 1.06 $\times$ 10^6 rad/hr.) compared to the results for E (0.16 $\times$ 10^6 rad/hr). Additional experiments carried at the BNL ^{60}Co facility (γ dose rates of $\sim 10^6$–8 $\times$ 10^6 rad/hr.) further confirm this. Experiments were also carried out with the PSU reactor where the dose rate was varied by changing the reactor power level. No discernible difference in results, which could be attributed to dose rate variation alone, were observed for dose rates between 10^5 and 10^7 rad/hr. (data not presented).

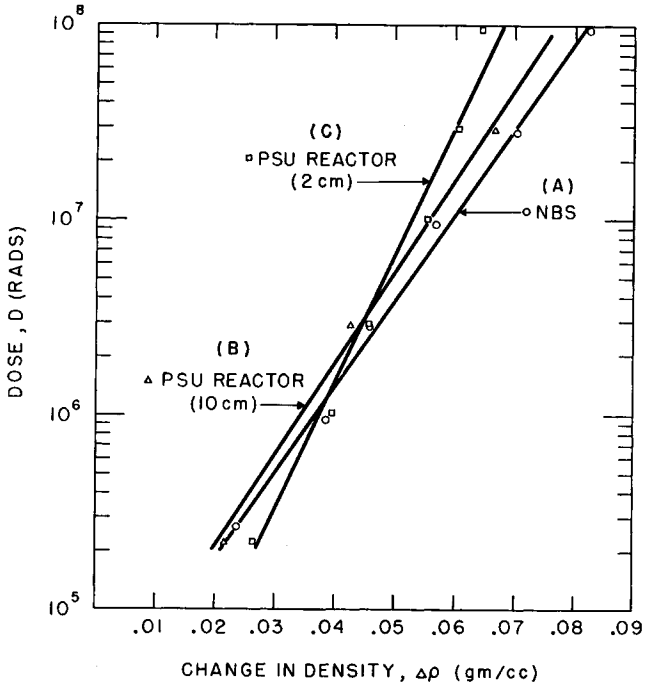

Fig. 2. Comparison of the change in density vs. dose behavior for polytetrafluoroethylene subjected to reactor radiation or ^{60}Co radiation.

From Figure 3 and Table I, it is also observed that data for samples irradiated at 75°C. (designation F) correspond to a slope $\beta = 90$. The curve for F, Figure 3, as compared to D and E, is also shifted to higher values of $\Delta\rho$ (i.e., to the right about 0.01 g./cc. at room temperature). Since the slope of the lines is not the same, this shift is not a constant amount at each dose. When the series of room-temperature irradiated samples (D) were later heat-treated at a temperature of 75°C. (designation D′) for a time equal to their irradiation time, a slight shift of the line to higher $\Delta\rho$ values was observed, and the slope of the curve decreased from 98 to 95, but it is notable that neither the shift nor the change in slope due to

post-irradiation heat treatments is as large as the corresponding shift of the line and the change in slope which occurred in elevated temperature irradiations.

An approximate 0.01 g./cc. shift was noted between the NBS ^{60}Co results (A) and the PSU ^{60}Co results (D). From further tests, on samples irradiated at the same location in the PSU reactor this shift was attributed to differences in samples which were taken from two different rods of the PTFE starting material, although both rods of PTFE were received from the supplier at the same time. Samples for designations A, B, and C were

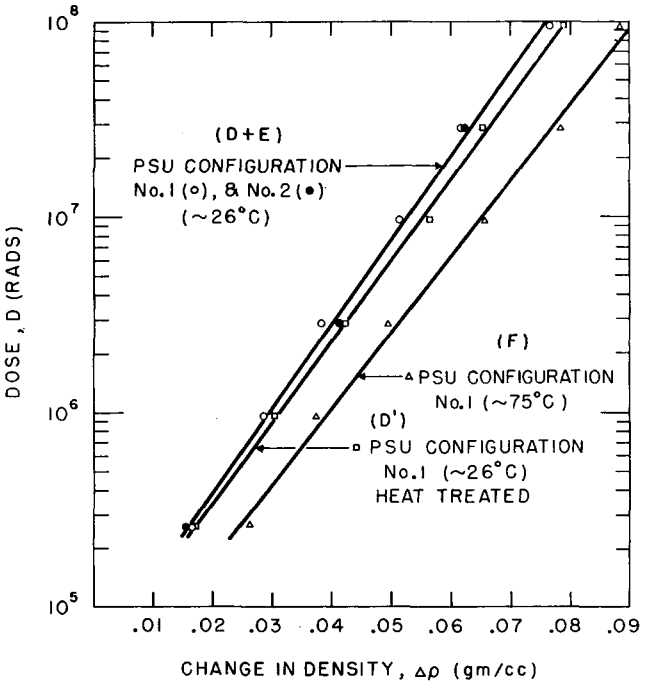

Fig. 3. Effect of ambient temperature and post-irradiation heat treatment on the change in density vs. dose behavior of polytetrafluoroethylene.

machined from one rod, while samples for designations D, E, and F and for BNL were machined from the second rod. For this reason absolute values of Figures 2 and 3 cannot be directly compared.

Sample color changes from white to a light brown (manila), which were reported by Licht,[2] were in evidence, to some degree, in all the samples irradiated to greater than 10^7 rad. The intensity of the color change increased with an increased dose. Densities of samples were determined within a few days after irradiation. Later the samples were remeasured as a function of time over a period of several months, and, in some cases, a few years. For samples stored in normal atmosphere at room temperature, no changes in density were observed as a function of time.

IV. DISCUSSION

γ-Irradiation at Room Temperature

Many polymers decrease in density upon irradiation.[8] This is considered to be a result of defects produced in the crystallites and/or a decrease of per cent crystallinity at doses of about 10^8–10^9 rad and beyond. Heat treatment at temperatures beyond the melting point causes further decreases in density in some cases. It is considered probable that the radiation-induced defects, in the form of branches, scission points, crosslinks, etc., retard recrystallization upon cooling of the material, and thus the density is irreversibly changed. Polytetrafluoroethylene appears to be somewhat more sensitive to irradiation as compared to other polymers,[8] and, although at doses comparable to the above (10^8–10^9 rad) it also decreases in density with increasing dose,[2,3] at lower doses ($<10^8$ rad) the reverse is true, i.e., the density has been noted[1–4] to increase significantly with irradiation dose.

It is notable that, during irradiation at relatively low ambient temperatures (25–50°C.), increased crystallization occurs which, in unirradiated PTFE, would require heat treatment in the neighborhood of the melting point temperature (327°C.). The crystallization process may be assisted to some extent by effectively higher local temperatures produced by the interaction of radiation particles with the structure. Post-irradiation heat treatments at 150°C. have also indicated[3] that further crystallization can occur at relatively low ambient temperatures in the absence of a radiation field.

Previous work[1–4] has shown that the increase in density of PTFE upon irradiation is closely related to an increase in crystallinity for doses up to about 10^8 rad. At low doses ($\sim 10^5$ rad) it seems probable that the rather rapid rate of increase in density with increasing dose may be primarily a result of crystallization of previously amorphous regions brought about by radiation interactions and accompanied by few other effects. It has been pointed out[9] that scission, crosslinking, branching, etc., are considered probable in PTFE under irradiation, and it appears that permanent scission is a predominant reaction, at least in the presence of air. At low doses it would seem probable that relatively few scission events in the amorphous regions may be rather important in inducing further crystallization by reducing chain entanglements, hindrances, etc. while a defect density of the same magnitude might be rather unimportant in affecting the crystallite density.

At higher doses (up to $\sim 10^8$ rad), the crystallinity, as determined by infrared measurements,[1,3] has been shown to increase with increasing dose, but at a slower rate.[3] This is also supported here by the density data of Figure 1. Since the density reached a maximum near 10^8 rad and gradually decreased,[2,3] it has been suggested that the rather slow increase in crystallinity at these higher doses was overshadowed by a proportionately rapid increase in apparent void content leading to an overall decrease in

density with dose. The PTFE material also appeared to approach the character of a fluorocarbon wax, and the material flowed at temperatures somewhat below the melting point[3] (~275°C. or less versus 327°C.).

If, in the present case, the data at low doses (~10^4 to 2×10^5 rad) are plotted on linear paper rather than on semilog paper as in Figure 1, the increase in density is approximately proportional to the dose received as indicated above. One explanation for this is based on the assumption that the rate of decrease of the amorphous fraction due to crystallization is proportional to the magnitude of the amorphous fraction. Let the density ρ be expressed as $\rho = X\rho_X + A\rho_A$, where ρ_X is the crystalline density, ρ_A is the amorphous density, X is the fractional crystalline content, and A is the fractional amorphous content.* For a dose D, the above assumption is that:

$$dA/dD = -k_1A = -dX/dD$$

where k_1 is a constant. Thus

$$d\rho/dD = \rho_X(dX/dD) + \rho_A(dA/dD)$$
$$= (\rho_X - \rho_A)k_1A$$

At low doses where the overall change in A is not large, the integration yields

$$\rho = (\rho_X - \rho_A)k_1AD + \rho_0$$

where ρ_0 is the density at $D = 0$. The change in density $\Delta\rho$ is then,

$$\Delta\rho = \rho - \rho_0 = (\rho_X - \rho_A)k_1AD$$

If the data of Figure 1 are plotted on linear paper, $\Delta\rho/\Delta D$ at low doses is about 0.95×10^{-7}. Therefore k_1 can be estimated to be $\sim 7 \times 10^{-7}$/rad. It is assumed that k_1 could be a function of ambient temperature. It is also notable that k_1 could actually be composed of a sum of terms such as $k_1 = k_{1a} + k_{1b} + \ldots$, where the terms k_{1a}, k_{1b}, etc. could be separate processes, without changing the above analysis. A negative value for one of these terms would indicate possible disordering of the crystallites with radiation (directly proportional to the crystalline fraction), and a tendency to decrease the density.

If one continues the previous analysis to higher doses, where the variation of A must be included in the integration of the equation $d\rho/dD = (\rho_X - \rho_A)k_1A$, a substitution can be made for A using $A = (\rho_X - \rho)/(\rho_X - \rho_A)$. This yields

$$d\rho/dD = (\rho_X - \rho)k_1$$

or

$$d\rho/(\rho_X - \rho) = k_1dD$$

* One might reasonably be inclined to begin with an expression for the specific volume rather than the density. The development is essentially the same if the overall changes in the density are small.

Upon integration this leads to

$$\rho_X - \rho = (\rho_X - \rho_0)e^{-k_1 D}$$

or,

$$\Delta\rho = \rho - \rho_0 = [\rho_X - \rho_0] - [\rho_X - \rho]$$
$$= [\rho_X - \rho_0]\,[1 - e^{-k_1 D}]$$

The foregoing analysis predicts a linear rate of increase at low doses followed by a continuing decrease in $d\rho/dD$ at higher doses and finally saturation of the effect. The behavior is similar to the curves of Figures 1–3, allowing for variations in k_1. In the dose range $\sim 10^5$–10^8 rad, the least-square values obtained from fitting a straight line to the data of Figures 1–3 suggest a relationship $d\rho/dD = 1/\beta D$ rather than $d\rho/dD \propto \rho$, as deduced in the above analysis. However, the straight-line relationship ($D = \alpha e^{\beta\Delta\rho}$) cannot be used at low doses because it does not predict that $\rho \rightarrow \rho_0$ as $D \rightarrow 0$.

Examination of Figures 2 and 3 and the data of Table I in the dose region 10^5 to 10^8 rad suggests that the slope β changes very little with dose rate for γ-irradiated samples. Experiment A (8×10^6 rad/hr.) has a β value of 100 while experiments D (1.06×10^6 rad/hr.) and E (0.16×10^6 rad/hr.) have β values of 98 and 99, respectively. Near room temperature (25–41°C.), the ambient temperature also appears to have little effect on the results. This lack of dose rate effects is generally consistent with other typical results in the literature[8] for polymers.

As in the case of the k_1 values, it would appear that the β (or $1/\beta$) value could also be a composite value representing the activity of more than one process. Thus, in the region of 10^5–10^8 rad, where $d(\Delta\rho)/dD \approx 1/\beta D$, the factor β could be logically composed of parameters such that $1/\beta = 1/\gamma + 1/\delta + 1/\epsilon \ldots$, where γ, δ, ϵ, could, in principle, be positive or negative as long as $1/\beta$ remained positive. Although the initial low-dose increases in the crystallinity and density may possibly be viewed in a rather simplified manner, further increases might be more complex as the radiation-induced defect population in the structure reaches higher levels. Defects in the amorphous region may eventually retard further crystallization, and the already-formed crystallites would tend to be disordered by irradiation-induced events. The value of β presumably is an overall measure of these effects.

At doses above 10^8 rad, the density reaches a maximum and begins to decrease as the dose is increased. It has been shown,[3] however, that the percentage crystallinity as measured by infrared continues to increase slowly, at least to about 8.9×10^8 rad. It was further noted[3] that, following post-irradiation heat treatment at temperatures of 150–275°C., the PTFE irradiated to 8.9×10^8 rad cracked, lost low molecular weight products, and increased in density, although the density did not reach the maximum density achieved as a result of irradiation to about 10^8 rad. It thus

appears probable that, although the percentage crystallinity (according to infrared measurements) continues to increase as amorphous regions are irradiated to higher doses, defect formation, expansion due to trapped gases, and loss of volatile products may more than compensate for the contraction associated with the increased crystallization, leading to an overall decrease in density with dose at high doses.

Comparison of Effects of Reactor Radiation and ^{60}Co Radiation

It has been consistently reported that the overall radiation effects in polymers appeared to be only a function of the dose received, in terms of energy absorbed per unit mass of material, rather than the type of radiation or the dose rate. This is in contrast, for example, to irradiations of metals where neutron and γ doses of the same magnitude have widely different effects. From the data presented herein, it appears that the effect of reactor radiation ($n + \gamma$) is different from the effect of the same dose of ^{60}Co (γ) radiation on PTFE (Fig. 2 and Table I). The PSU reactor (2 cm.) experiment, termed C, contained about a 17% neutron dose contribution to the total while PSU (10 cm.) experiment, B, contained about a 9% neutron dose contribution. As the percentage neutron contribution increases, it is noted that the value of β increases from about 100 (pure γ) to 108 for 9% neutron contribution and 153 for 17% neutron contribution. It should be observed that this difference cannot be attributed to errors in dose measurement since these would not effect the value of β on a log D versus linear ρ plot, but only the vertical displacement of the data (i.e., α). The PSU reactor (2 cm.) curve also indicates that, at very low doses, the reactor radiation is more effective in increasing the density, i.e., at 2×10^5 rads $\Delta\rho$ for the PSU reactor (2 cm.) is about 30% more than $\Delta\rho$ for the NBS (pure γ) experiment (A) while the dose rates were of the same order.

The latter observation regarding low dose levels would seem to imply that neutrons are initially more effective than γ-rays in scissioning, etc. of the molecular chains in the amorphous regions, possibly because effectively higher local temperatures (spikes) may be reached during reactor irradiation. (In some cases, higher temperatures appear to hasten the radiation-induced changes, as will be pointed out later in the analysis.) At the same time, radiation-induced defects in the crystallites at low doses (including neutron-induced defects) are probably largely ineffective in expanding and disordering the crystallites because the defect density is relatively low compared to the number required for significant overall density changes.

In the dose region of $\sim 10^5$–10^8 rad, the higher β values (lower $d\rho/dD$) for the rector radiation experiments as compared to ^{60}Co experiments seem to suggest that neutrons in the radiation flux retard the overall rate of increase of density with dose. Since the curves indicate that $d\rho/dD = 1/\beta D$, the rate of increase of density with dose varies as $1/\beta$. One explanation for the higher value of β associated with reactor radiation might be that neutron and γ-radiation doses produce somewhat equivalent results in the

amorphous regions for these doses, but that neutrons are more effective in reducing the density in the crystalline regions. This relative neutron effectiveness could be a result of forming more defects or larger defects in the crystallites, as compared to γ-radiation, since neutron interactions result in a larger fraction of displaced atoms per unit dose. Calculations indicate that neutron radiation averaged at 1 M.e.v. causes approximately 10^4 more atomic displacements per rad than ^{60}Co radiation. From this consideration, it would also appear that a process such as the recombination of scissioned ends in crystallites would be somewhat less probable following displacement of atoms as opposed to leaving adjacent free radicals in the lattice. Thus, following neutron interactions it would appear that proportionally more permanent defects remain in the lattice.

Using data of experiments C and A, one can make an estimate of the relative effectiveness of neutron irradiation compared to γ-irradiation. Earlier it was shown that the least-squares relationship implied that:

$$\frac{d\rho}{dD} = \frac{d(\Delta\rho)}{dD} = \frac{1}{\beta D}$$

For ^{60}Co irradiation, $\beta = 100$, while for experiment C the value of β was found to be 153. If β_n (17%) is a value of β associated with a 17% neutron contribution,

$$\frac{d\rho}{dD} = \frac{1}{D}\left[\frac{1}{100} + \frac{1}{\beta_n(17\%)}\right] = \frac{1}{D}\left[\frac{1}{153}\right]$$

or

$$\beta_n(17\%) \simeq -290$$

The negative sign indicates that replacing 17% of the γ dose by an equivalent neutron dose (in terms of energy absorbed) results in a reverse effect from that of the γ-rays alone. The magnitude of β_n (17%) is such that the overall effect of a 100% neutron dose would predict a negative value for β, i.e., the density would decrease with dose if the results were simply extrapolated. No practical pure neutron source was available for experiments in the dose range required, but the prediction should be viewed with caution. A simple extrapolation in to lower percentages of neutron dose (neutron dose contribution about 9%) predicts a result for β which is different than the β value observed for experiment B.

Data taken in the present experiments indicate that the reactor-irradiated PTFE reached a maximum in density near the same dose where γ-irradiated PTFE reached the maximum density;[3] however, the maximum value for the reactor-irradiated material was less. This difference in maximum value appears to be consistent with the hypothesis that the inclusion of neutrons in the radiation field results in effects which are different, or at least proportionally different, from effects of γ-rays on PTFE.

According to the data presented herein, the same increase in ρ could be attained for a given dose of reactor radiation or ^{60}C radiation, provided this

dose occurred near the region where the curves crossed. Regarding this, it is notable that a study of the dynamic mechanical properties of reactor-irradiated and γ-irradiated samples at one given dose[10] appeared to reveal no major differences in the dynamic mechanical spectrum.

Temperature Effects

It has previously been noted that the density of PTFE increases upon irradiation when the temperature is in the region of 25–41°C. Center temperature of the samples can differ from the surface temperature by several degrees. For instance, at 10^7 rad/hr., the equilibrium temperature difference for $^1/_2$-in. diameter solid samples is about 10C.° if a thermal conductivity of 6 cal./cm.-sec.-°C. is postulated.[11] Because of the sample geometry in the present investigation, it is probable that this differential would be somewhat less. It has also been noted[3] that post-irradiation heat treatment of PTFE specimens further increases the density. No significant density changes occur in unirradiated specimens heat-treated at 150°C. and somewhat higher temperatures. Although increased crystallization during irradiation at room temperature might be attributed to high local temperatures resulting from nuclear particle interactions, it would appear that increased crystallization during post-irradiation heat treatment at moderate temperatures would require further explanation. Some disappearance of radicals has been observed in post-irradiation heating at 150°C.[12]

In an attempt to investigate temperature effects in PTFE tests were conducted on several groups of PTFE specimens (see data of Figure 3 and Table I). At two different dose rates (1.06 and 0.16 $\times$ 10^6 rad/hr.), sample series D and E were irradiated over a wide dose range. The values of β obtained from a least-squares plot of the data for these series was 98 and 99, respectively, which compares closely to the β value of 100 for the NBS irradiation series (A) at the higher dose rate of 8 $\times$ 10^6 rad/hr. Another series of samples (F) was then irradiated at 75°C. and a dose rate of 1.06 $\times$ 10^6 rad/hr. Two distinct effects were noted when compared to series D. For a given dose, series F data shifted to a somewhat higher $\Delta\rho$ value suggesting that, at higher temperatures, irradiation is initially more effective in increasing crystallization of PTFE as compared to room temperature. Secondly, the β value of series F was reduced to 90, compared to 98 for series D. This suggests that the relative effectiveness of higher temperatures in increasing the rate of crystallization continues as the dose is increased.

Series D was subsequently heat-treated at the irradiation temperature used in series F for times approximately equal to the time of irradiation. The data for this new series (D′) indicate that a post-irradiation heat treatment of the same temperature and duration is only slightly effective compared to a higher temperature during irradiation. For a given dose, the data of series D′ undergo a shift (compared to series D) to higher ρ values which is only about 20% of the shift noted in series F. The β values de-

creased from 98 for D to 95 for D', whereas the β value of series F was 90. It would thus appear that from very low γ doses, possibly somewhat below 10^5 rad, and continuing to about 10^8 rad, a higher ambient temperature of irradiation (75°C.) is much more effective in increasing the rate of density increase of PTFE than a comparable post-irradiation heat treatment. Based on previous work,[3] it appears that the higher rate of density increase is a result of a higher rate of crystallization under these conditions.

The authors are indebted to Drs. Florin and Wall of The National Bureau of Standards for comments and discussions concerning this research. Cooperation of The National Bureau of Standards (Polymer Chemistry Section), The Brookhaven National Laboratory, and the Pennsylvania State University Nuclear Reactor Facility in performing irradiations is gratefully acknowledged. This work was supported, in part, by the National Aeronautics and Space Administration.

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Résumé

La nature des rapports densité à température de chambre-dose d'irradiation pour le polytétrafluoroéthylène (PTFE) a été étudiée dans un domaine de 10^4 à 10^9 rads. Sous diverses conditions les échantillons de PTFE ont été irradiés en combinaison de radiation neutron et gamma (réacteur et Co^{60}) résultant en un accroissement de densité jusque 5%. Pour des doses de 10^5 à 10^8 rads, l'augmentation de densité mesurée à 0°C est environ proportionnelle au logarithme de la dose de radiation. Pour des doses inférieures à 10^5 rads, l'augmentation de densité apparaît directement proportionnelle à la dose tandis que au-dessus de 10^8 rads, la densité atteint un maximum et ensuite commence à diminuer. En examinant les variations de tangentes et les variations de courbes, qui se passent au cours de diverses conditions, différents effets sont discernables. Comparés aux effets des rayons gamma seuls, l'augmentation de densité par dose de 10^5 à 10^8 rads est plus petite dans les cas où à la fois les neutrons et les rayons gamma sont présents dans le champ de radiation. Ceci peut suggérer que des processus compétitifs sont en question pour produire les changements de densité. La différence discernable entre les effets de la radiation gamma et la radiation des réacteurs, semble être unique dans les polymères. La température ambiante au cours de l'irradiation et le traitement thermique à post-irradiation des échantillons affecte les changements de densité. Pour les vitesses de dose au-dessus du domaine 0.1×10^6 à 13×10^6 rads par heure, aucun effet de vitesse de dose n'a été observé jusqu'ici. L'utilisation du PTFE pour certains types de dosimétrie sous radiation a été démontrée, et son utilité possible a été envisagée.

Zusammenfassung

Die Natur der Dichte-Dosisbeziehungen bei Raumtemperatur bei Polytetrafluoräthylen (PTFE) wurde im Dosisbereich von 10^4 bis 10^9 rad untersucht. Unter verschiedenen Bedingungen wurden PTFE-Proben in kombinierten Neutronen- und γ-Strahlungsfeldern (Reaktor und Co^{60}) bestrahlt, wobei Dichtezunahmen bis zu etwa 5% auftraten. Im Dosisbereich von 10^5 bis 10^8 rad ist die bei 0°C gemessene Dichtezunahme angenähert dem Logarithmus der Strahlungsdosis proportional. Bei Dosen unterhalb etwa 10^5 rad scheint die Dichtezunahme der Dosis direkt proportional zu sein, während die Dichte oberhalb lo^8 rad ein Maximum erreicht und dann abzufallen beginnt. Aus den Neigungsänderungen und Verschiebungen der Kurven, die unter verschiedenen Bedingungen auftreten, kann auf mehrere Einflüsse geschlossen werden. Im Vergleich zu den Effekten der γ-Strahlen allein, ist die Dichtezunahme pro Dosis im 10^5–10^8 rad-Bereich bei gleichzeitiger Anwesenheit von Neutronen und γ-Strahlen im Strahlungsfeld niedriger. Das könnte so zu verstehen sein, dass für die Dichteänderungen kompetitive Prozesse verantwortlich sind. Der erkennbare Unterschied zwischen den Effekten der γ-Strahlung und der Reaktorstrahlung scheint bei Polymeren einmalig zu sein. Die Raumtemperatur während der Bestrahlung und di Strahlungs-Wärmenachbehandlung der Proben beeinflusst die Dichteänderungen. Bei einer Dosisleistung im Bereich von $0{,}1 \times 10^6$ bis 13×10^6 rad pro Stunde wurden bis jetzt keine Dosisleistungseffekte beobachtet. Die Eignung von PTFE für einige Strahlungsdosimetriezwecke wurde gezeigt und seine mögliche Verwendbarkeit wird untersucht.

Received July 30, 1966
Prod. No. 1472