JOURNAL OF APPLIED POLYMER SCIENCE VOL. 9, PP. 483–494 (1965)

Effects of γ-Irradiation on the Loss Properties of Dielectrics in Vacuum*

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Synopsis

Dielectric constant and dissipation factor of six types of dielectrics were measured during irradiation in a Co^{60} source. Tests were made at seven frequencies ranging from 100 cycles/sec. to 100 kcycles/sec. by use of the Schering bridge technique. Polystyrene and polyethylene exhibited no change in loss properties when γ-irradiated to doses as high as 7.7×10^7 and 3.5×10^7 r, respectively. Poly(methyl methacrylate decreased slightly in dielectric constant and was essentially unchanged in dissipation factor after 5.7×10^7. TFE underwent the most drastic changes. At a very low dose (10^6 r) the dissipation factor had increased three orders of magnitude (at 100 cycles/sec.) and one order of magnitude (at 100 kcycles/sec.). After peaking, the loss factor decreased slowly. After removal of the source, the loss factor decreased more; then increased rapidly upon admission of air. Both this and the original increase in dissipation factor are indicative of a dipole with a long relaxation time, in which oxygen plays a role. FEP Teflon increased somewhat less than TFE, and the peak was not reached until a dose of 3×10^7 r. Very little effect was produced by the admission of air after irradiation. Dielectric constant decreased with radiation dose. The dissipation factor and dielectric constant of Rayolin N decreased with dose, until a plateau was reached. Very little effect was seen after irradiation, even upon the admission of air. The changes which took place during the radiation period were, as in the case of the other materials, greater at the lower frequencies than they were at the higher frequencies.

Introduction

Nuclear radiation produces drastic chemical and physical changes in polymeric materials. Many types of basic changes have been observed, such as scission of the main chain, crosslinking, block copolymerization, chain polymerization, and changes in crystallinity. Radiation induces these changes through the production of free radicals and ions, which result from energy deposition in the electron systems.

Since very little data exist on the effects of radiation on the electrical loss properties of polymeric dielectrics in vacuum, a test program was conducted to study these effects on some of the commonly used dielectric materials. Dynamic measurements of the dissipation factor and dielectric constant

* Work performed at Lockheed Missiles & Space Company Research Laboratories under Air Force Contract AF-04(647)-787.

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of these materials in the audio and radio frequency range were made during irradiation by a Co^{60} γ-ray source and while the materials were in a high vacuum.

The question may arise as to why the testing should be done in vacuum. There are two reasons for this. The first is that oxygen can enter into

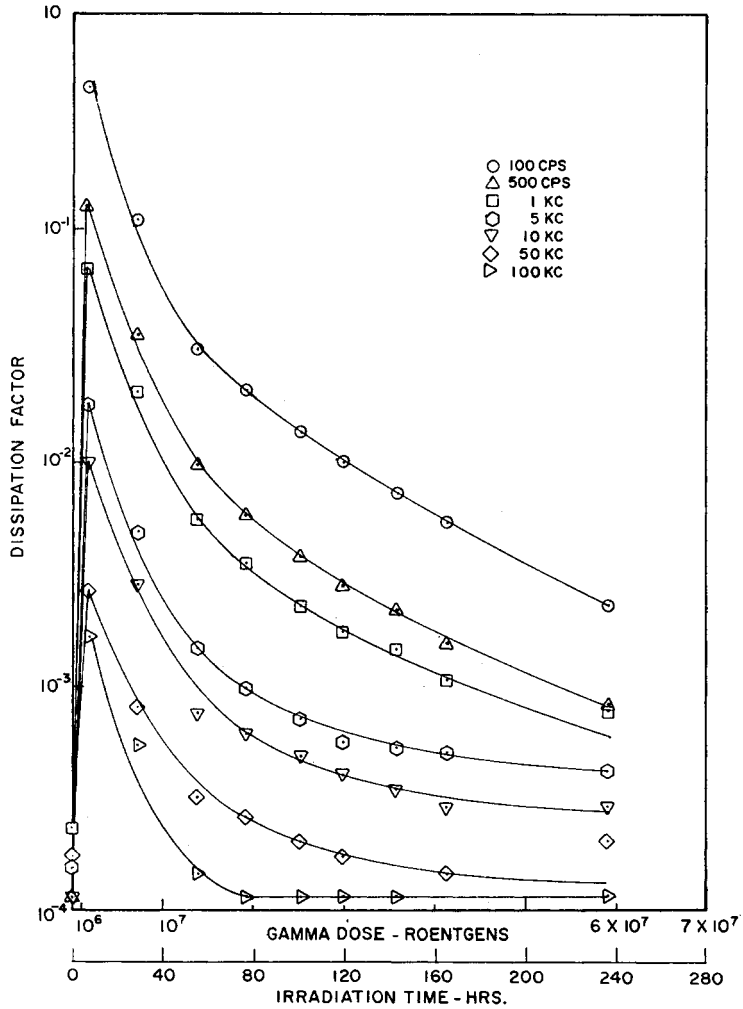

Fig. 1. Dissipation factor of TFE.

radiation degradation reactions very extensively, by forming peroxy free-radical intermediates. The second reason is that vacuum avoids one of the most common and troublesome radiation test problems—that of air ionization in the cables.

Experimental Procedure

Six types of polymers were included in this study: polystyrene, polyethylene, poly(methyl methacrylate), polytetrafluoroethylene (TFE), a copolymer of TFE and hexafluoropropylene (FEP), and Rayolin 77, which is essentially radiation-crosslinked polyethylene containing proprietary

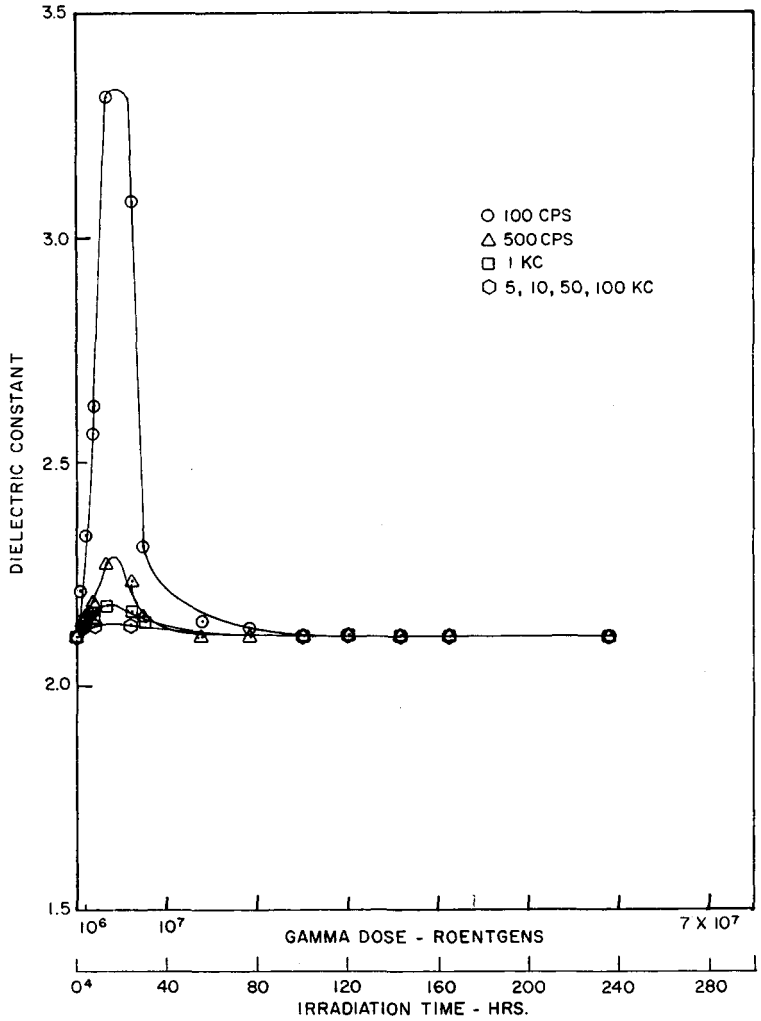

Fig. 2. Dielectric constant of TFE.

additives. These samples were obtained from commercial sources with, in most cases, no knowledge of manufacturer or purity.

The specimens were machined into disks 3.0 in. in diameter with nominal thicknesses of 0.12 ± 0.004 in. Silver paint was used as the electrode material. The nominal diameter of the guarded electrode was 2.5 in.

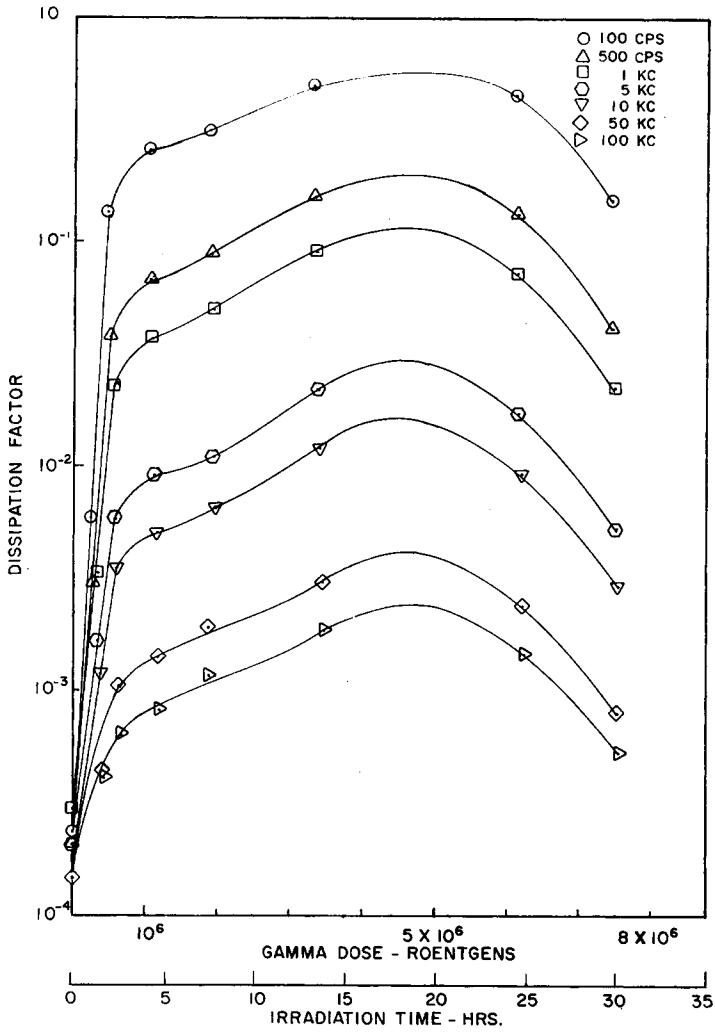

Fig. 3. Dissipation factor of TFE at low doses.

A General Radio Model 716 Schering bridge and associated guard circuit were used to obtain measurements of the dissipation factor and dielectric constant by utilizing the three-electrode technique. The accuracy of this bridge is ± 0.1 pF. for capacitance readings and ± 0.0003 or 2%, whichever is greater, for dissipation factor readings.

The dielectric specimens were enclosed in a guard shield in order to eliminate from the measurement the capacitance to ground of the unguarded electrode. This assembly was shielded from hum pickup by the grounded vacuum chamber.

The vacuum system consisted basically of a roughing pump, a diffusion pump, a liquid nitrogen trap, and the irradiation chamber. Pressure was

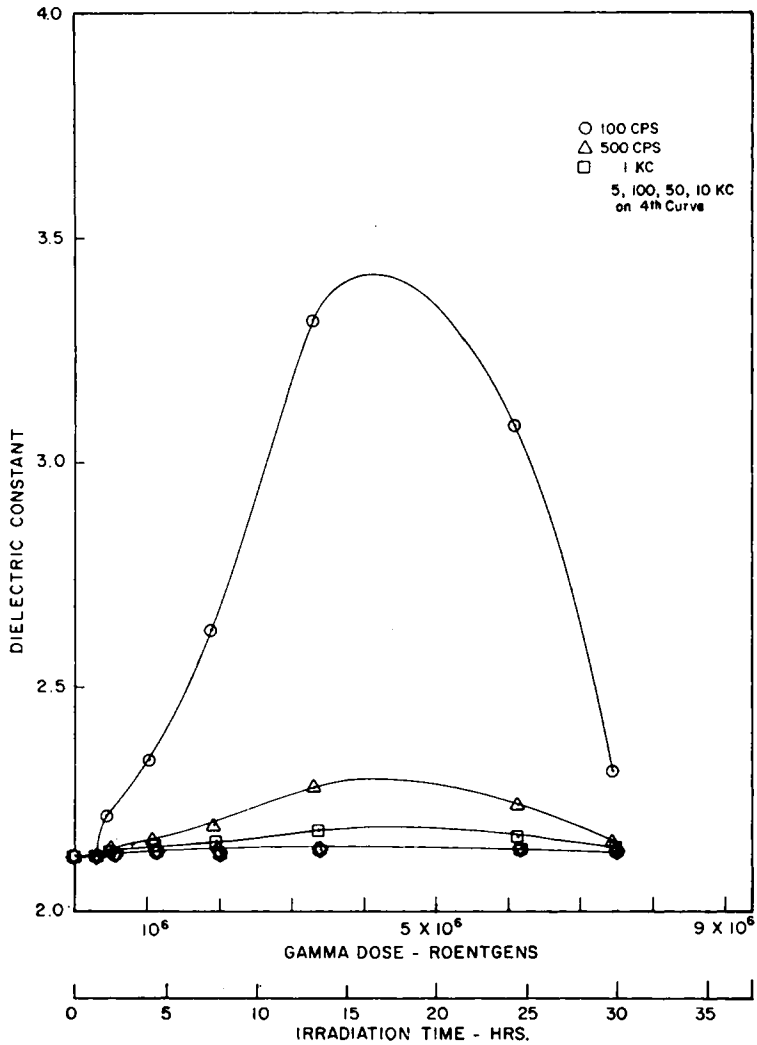

Fig. 4. Dielectric constant of TFE at low doses.

measured by means of an ion gage. The pressure for these irradiations ranged from 5×10^{-7} to 2×10^{-6} torr.

The gamma source at LMSC is a 500-c. Co^{60} source. Primary standardization of this source was performed by using the ferrous sulfate technique. The dose rate at the sample position was measured by means of tetrachloroethylene dosimeters and found to be 2.5×10^{-5} r/hr. $\pm$ 25% over the volume of the sample.

Dielectric specimens were maintained in vacuum for approximately one day before initiation of irradiation. Initial measurements were then taken and the irradiation begun. Dynamic measurements of the capacitance and dissipation factor of each specimen were made at seven frequencies (100

and 500 cycles/sec. and 1, 5, 10, 50, and 100 kcycles/sec.) at various times during the irradiation. Measurements were also made with the source removed in order to check for transient effects; no transient effects were observed. Readings were continued after completion of the irradiation

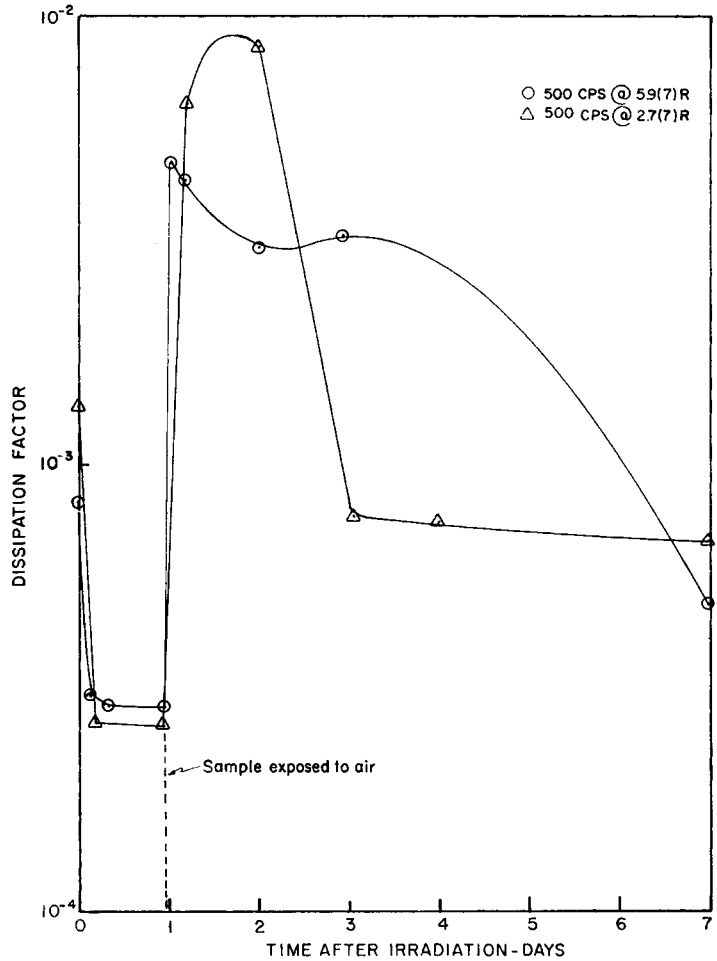

Fig. 5. Behavior of TFE after irradiation.

until the loss properties of the specimen had stabilized in vacuum. The irradiation chamber was then let up to atmospheric pressure, and the effect on the loss properties, if any, was observed.

Results

Specimens of polystyrene and polyethylene irradiated to γ-ray doses of 7.7×10^7 and 3.5×10^7 r, respectively, exhibited no change in loss properties. Poly(methyl methacrylate) irradiated to a dose of 5.7×10^7 r ex-

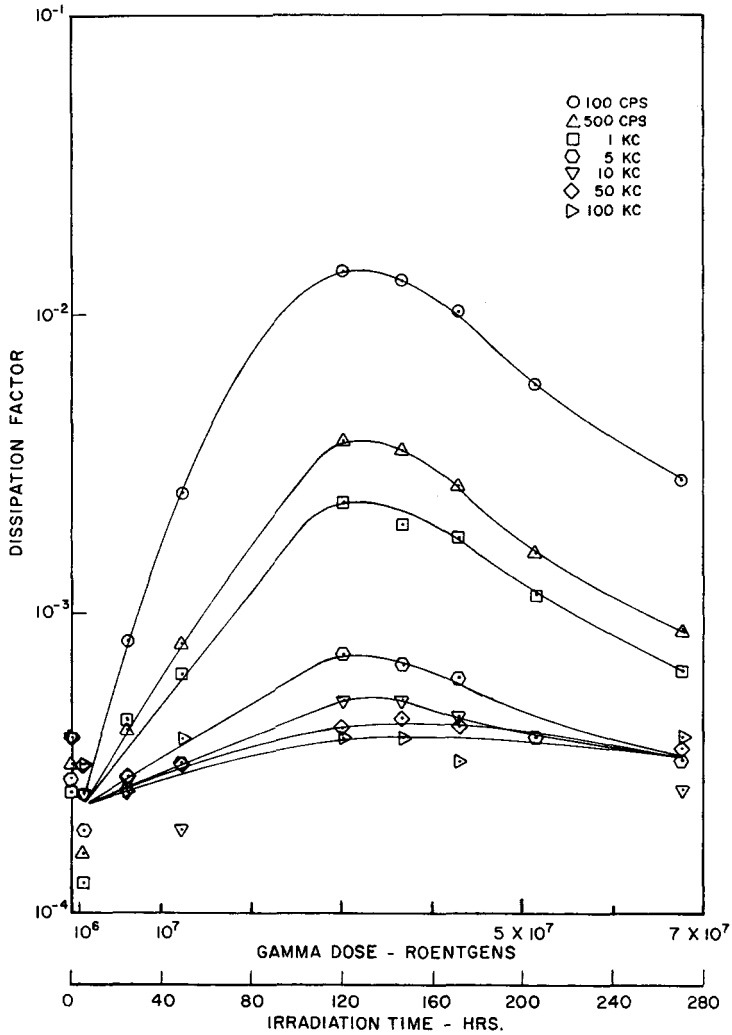

Fig. 6. Dissipation factor of FEP.

hibited only negligible changes—an average decrease in dielectric constant of 3.7% and increase in dissipation factor of 1.5%.

TFE, FEP, and Rayolin N, however, were drastically affected by radiation. The loss properties of these materials as a function of integrated dose are shown in Figures 1–9.

The loss properties of TFE exhibit very dramatic behavior, as shown in Figures 1 and 2, rising to high peaks very rapidly and then decreasing toward initial values. This effect is much more pronounced at the lower frequencies than at the higher. A second sample of TFE was irradiated in order to obtain more data in the low dose region; these data are presented in Figures 3 and 4. The behavior of these samples after irradiation was

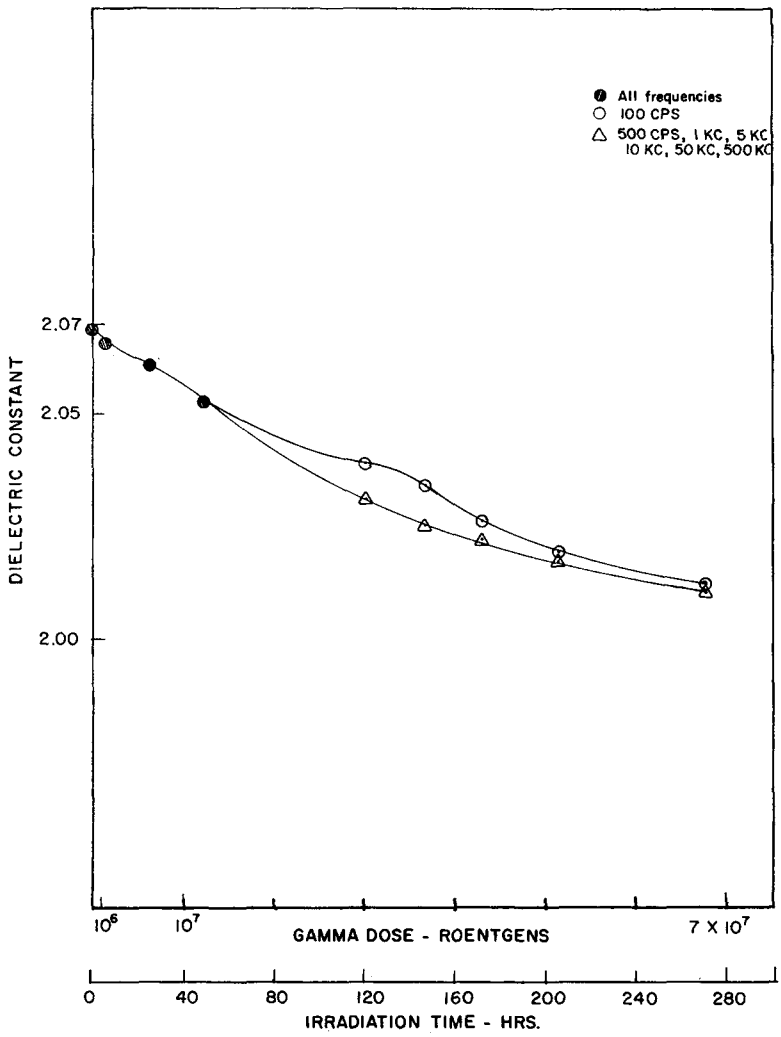

Fig. 7. Dielectric constant of FEP.

equally dramatic, as shown in Figure 5. The dissipation factor decayed very rapidly to the initial value in vacuum and on exposure to air increased rapidly by greater than an order of magnitude and thereafter exhibited complex behavior.

Similar reactions have been observed in TFE irradiated in vacuum by soft x-rays in a study conducted by Frisco.[1] Frisco's data also indicate that the loss properties of TFE irradiated in air are essentially identical to vacuum irradiations at the lower doses, but that upon reaching the maximum loss values the loss properties plateau rather than decaying downward.

The inverse relationship of the dissipation factor and frequency indicates that the dielectric loss is caused by a dipole with a rather long relaxation

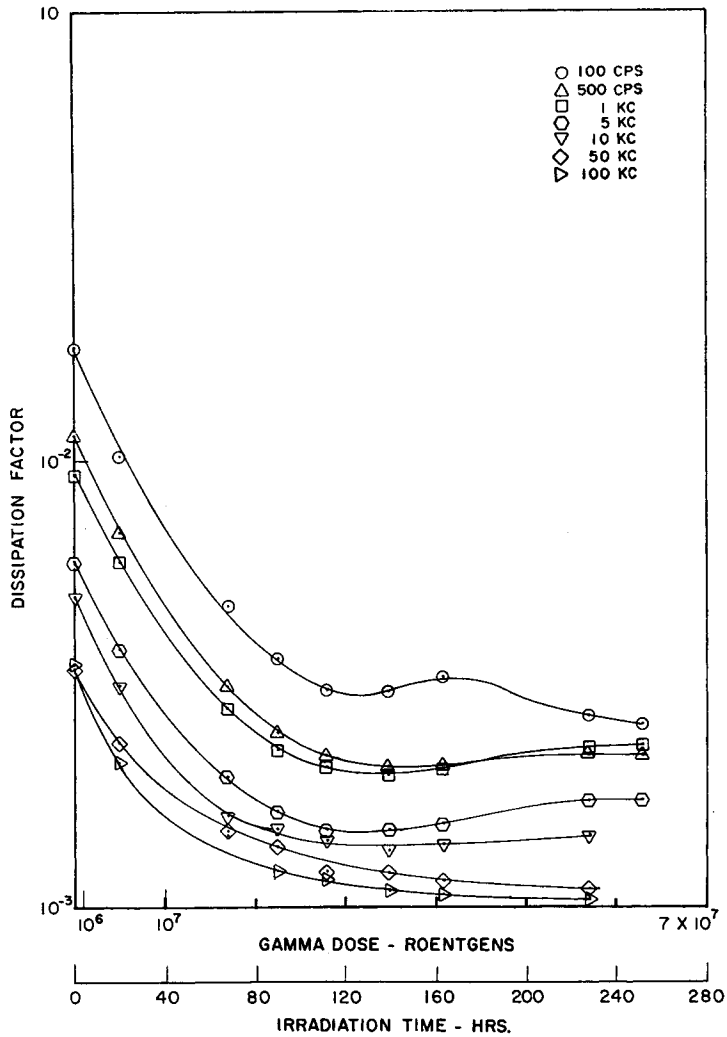

Fig. 8. Dissipation factor of Rayolin N.

time. No more is known at this time of the dipole characteristics. The existence of some short-lived free radicals in irradiated TFE is indicated by the decay in loss properties after irradiation, which suggests radical recombination as a possibility.

The strong similarity between the rapid rise in loss properties upon exposure of an irradiated TFE sample to air and the initial rise of a sample being irradiated in vacuum suggests that oxygen may play a major role in the mechanisms responsible for electrical losses. It is well known that oxygen combines readily with many free radicals to form peroxy free-radical intermediates. It has also been demonstrated by Matsugashita[2] in electron spin resonances studies on TFE irradiated in vacuum that exposure to

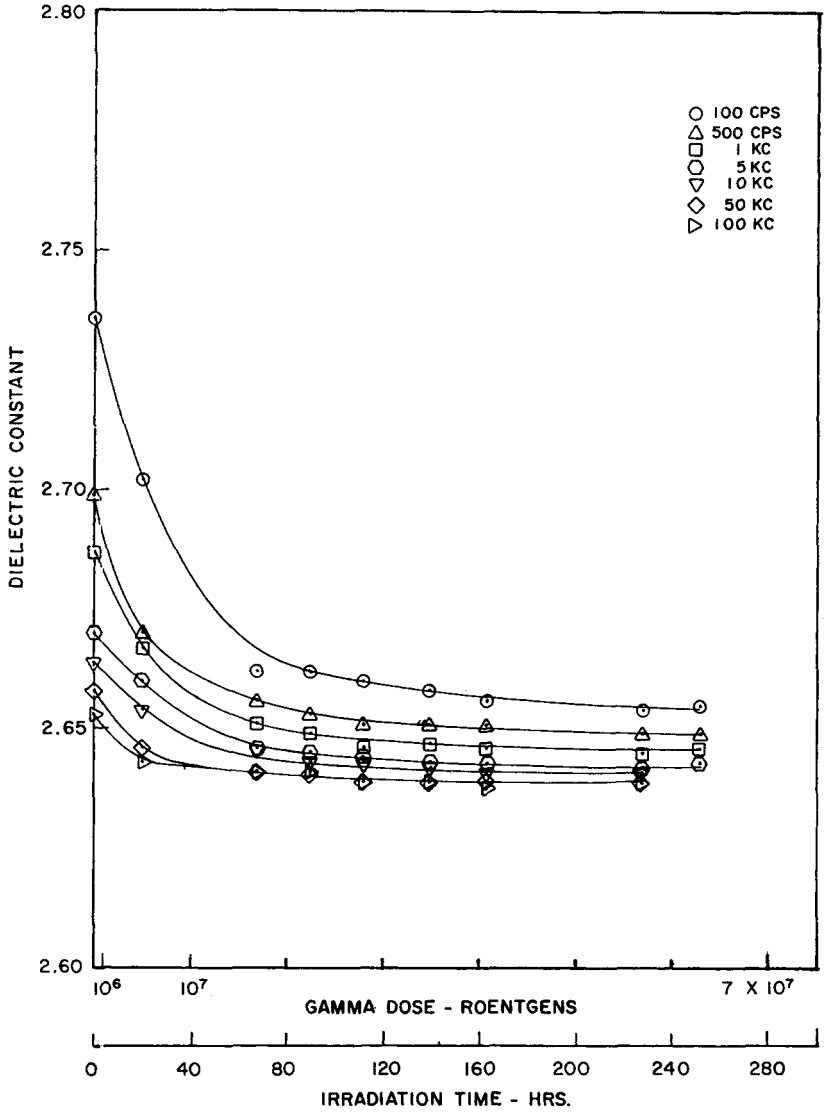

Fig. 9. Dielectric constant of Rayolin N.

air produced a strong resonance signal almost immediately. The oxygenated radicals were stable in air, but re-evacuation of the specimen indicated that the reaction was reversible.

The existence of absorbed atmospheric gases in TFE and FEP has been demonstrated by mass spectrometer studies.[3] This dissolved oxygen may be responsible for the initial rise in loss properties during irradiation.

The dissipation factor of FEP also rises to a peak value and then decays downward, as shown in Figure 6. The peak values are greater than an

order of magnitude lower than those for TFE, however, and occur at dose values which are almost an order of magnitude higher than the corresponding TFE peaks. The dielectric constant of FEP, however, decreases approximately monotonically with dose.

FEP also exhibited decay of loss properties in vacuum after irradiation, but to a much smaller degree than TFE. The introduction of air to the specimen produced very little effect.

The loss properties of Rayolin N decrease at the lower doses and tend to level out at doses greater than approximately 2×10^7 r, as shown in Figures 8 and 9. The specimen exhibited very little decay in vacuum after irradiation and no reaction to the introduction of air.

Acknowledgment is made to Dr. Alan Andrew for helpful suggestions in the course of this study.

References

1. Frisco, L. J., Final Report, March 1959–February 1962, Report No. 3, The John Hopkins University, March 1962.
2. Matsugashita, T., *J. Chem. Phys.*, **30** (1959).
3. E. I. du Pont de Nemours and Co., *J. Teflon*, **4**, No. 6 (July–August 1963).

Résumé

La constante diélectrique et le facteur de dissipation de six types de matériaux diélectriques sont été mesurés sous irradiation avec une source de Co^{60}. Des tests ont été faits à 7 fréquences, allant de 100 C à 100 Kc, par la technique du pont de Schering. Le polystyrène et le polyéthylène ne montraient pas de changement dans leurs propriétés de perte lorsqu'ils sont irradiés avec des doses aussi élevées que 7.7×10^7 et 3.5×10^7 roentgen gamma respectivement. La constante diélectrique du polyméthacrylate de méthyle diminue légèrement et le facteur de dissipation est essentiellement constant après 5.7×10^7. Le TFE subit des changements les plus drastiques. A une dose très basse (de 10^6 r) le facteur de dissipation diminue de trois ordres de grandeur (à 100 C) et d'un ordre de grandeur (à 100 Kc). Après la formation d'un pic, le facteur de perte diminue plus et augmente ensuite rapidement en présence d'air. Cette augmentation et l'augmentation originale du facteur de dissipation indiquent un dipole avec un long temps de relaxation, au cours duquel l'oxygène joue un rôle. Le FEP teflon augmente un peu moins que le TFE, et le pic n'a été atteint que pour une dose de 3×10^7 r. Un très faible effet est obtenu par admission dair après irradiation. La constante diélectrique diminue avec la dose de radiation. Le facteur de dissipation et la constante diélectrique du Rayolin N diminuent avec la dose jusqu'au moment où un plateau est atteint. Un très faible effet se manifeste après irradiation, même après admission d'air. Les changements qui se manifestent durant la période d'irradiation sont comme, dans le cas d'autres matériaux, plus grands à de plus basses fréquences, que pour des fréquences plus élevées.

Zusammenfassung

Die Dielektrizitätskonstante und der Dissipationsfaktor von sechs Dielektrikatypen wurde während der Bestrahlung in der Co^{60}-Quelle gemessen. Die Messung erfolgte bei sieben Frequenzen im Bereich von 100 Hz bis 100 kHz mit einer Schering-Brücke. Polystyrol und Polyäthylen zeigten bei der Bestrahlung mit Dosen bis zu $7{,}7 \times 10^7$ bzw. $3{,}5 \times 10^7$ Röntgen Gammastrahlung keine Änderung der Verlusteigenschaften. Bei Poly(methylmethacrylat) nahm die Dielektrizitätskonstante etwas ab, während der

Dissipationsfaktor nach 5,7 × 10^7 r im wesentlichen ungeändert blieb. TFE erfuhr die eingreifendsten Änderungen. Bei sehr niedriger Dosis (10^6 r) hatte der Dissipationsfaktor um drei Grössenordnungen zugenommen (bei 100 Hz) und um eine Grössenordnung bei 100 kHz. Nach Erreichung eines Maximums nahm der Verlustfaktor langsam ab. Nach Entfernung der Quelle trat eine weitere Abnahme des Verlustfaktors ein; bei Luftzutritt nahm er dann rasch zu. Sowohl diese wie auch die ursprüngliche Zunahme des Dissipationsfaktors spricht für einen Dipol mit langer Relaxationsdauer, bei welchem Sauerstoff eine Rolle spielt. FEP-Teflon nahm etwas weniger zu als TFE, und das Maximum wurde erst mit einer Dosis von 3 × 10^7 r erreicht. Durch Luftzutritt nach der Bestrahlung wurde nur einsehr geringer Effekt erzielt. Die Dielektrizitätskonstante nahm mit der Bestrahlungsdosis ab. Der Dissipationsfaktor und die Dielektrizitätskonstante von Rayolin-N nahm mit der Dosis bis zur Erreichung eines Plateaus ab. Nach der Bestrahlung zeigt sich nur ein sehr kleiner Effekt, sogar bei Zutritt von Luft. Die Veränderungen während der Bestrahlungsperiode waren ebenso wie im Fall der anderen Stoffe bei niedrigen Frequenzen grösser als bei höheren Frequenzen.

Received February 17, 1964