

Effects of Gamma Radiation on Some Physical Properties of Polytetrafluoroethylene Resin

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INTRODUCTION

Polytetrafluoroethylene, which is a well known fluorocarbon polymer with excellent heat-resistant and chemically noncorrosive properties, had been found to be degraded when irradiated with high energy radiation,¹ but no full report has as yet been made on the effects of irradiation on the physical properties of this polymer.

In reference to mechanical properties, we have recently reported the viscosity and elasticity of this polymer above the melting point (327°C.).² The extremely high melt viscosity (of the order of 10^{11} poises) found at such high temperatures means that the chain length is very great, and the fact that the elastic modulus increases with temperature above the melting point suggests that there is entanglement of molecular chains accompanied by the rubbery elasticity.

It is already known that on gamma irradiation of this polymer, fluorine or monomer gases are evolved³ and molecular chains are broken.⁴ This degradation produces a decrease in the melt viscosity and in mechanical strength. On the other hand, the highly irradiated samples have shown some cracks and have been very brittle. These changes in the polymer would suggest that there is an increase in crystallinity.

To confirm these effects, we have studied the changes of melt viscosity, elastic modulus, Zero Strength Time (ZST), density, and x-ray diffraction caused by Co^{60} gamma irradiation, and recently some of these effects have been reported briefly in our previous letters.^{5,6} In this paper we shall discuss fully the degradation effected in this polymer by gamma radiation.

EXPERIMENTAL

The specimens were cut from a molded disk of Teflon No. 5, about 10 cm. in diameter and 1-2 mm.

in thickness, and exposed in air to gamma irradiation from a Co^{60} source to a dose of 10^2 - 10^7 roentgens.

For the measurement of melt viscosity and elastic modulus the fiber elongation method^{7,8} was used. The schematic arrangement of the apparatus is shown in Figure 1. The specimen is suspended from the lower end of a fixed quartz tube in the furnace, and a load is hung at the lower hook of the specimen by a quartz rod. The temperature was measured near the upper hook of the specimen by a Pt-Pt Rh thermocouple inserted into the bottom of the upper quartz pipe. The temperature difference between the two ends of the specimen was kept within $\pm 0.2^\circ\text{C}$. and the fluctuation of the furnace temperature was kept within $\pm 0.5^\circ\text{C}$. The creep of the specimen at constant temperature was observed with a traveling microscope within an accuracy of 1/1000 mm., and retardation elasticity and flow behavior were observed by adding or removing a definite load. Melt viscosity was estimated from the linear part of creep curve over a time interval of 10 minutes, and retardation elasticity was measured by extrapolation of the linear part of creep curve obtained by the usual procedure of viscoelasticity measurement. In the ordinary creep curve there is, at first, an instantaneous elastic region, which is followed by a retarded viscoelastic region. The former, usually considered to be due to crystallinelike rigidity, appears at lower temperatures, such as glassy state of polymers, and the modulus of this region is usually observed to be the order of 10^{10} dynes/cm.² in many polymers. Although we have reported in previous letters that an instantaneous elastic modulus was observed, the order of magnitude was 10^7 dynes/cm.², which is the same order of magnitude usually observed in rubber elasticity. Because the contribution from a crystallinelike instantaneous elastic modulus would

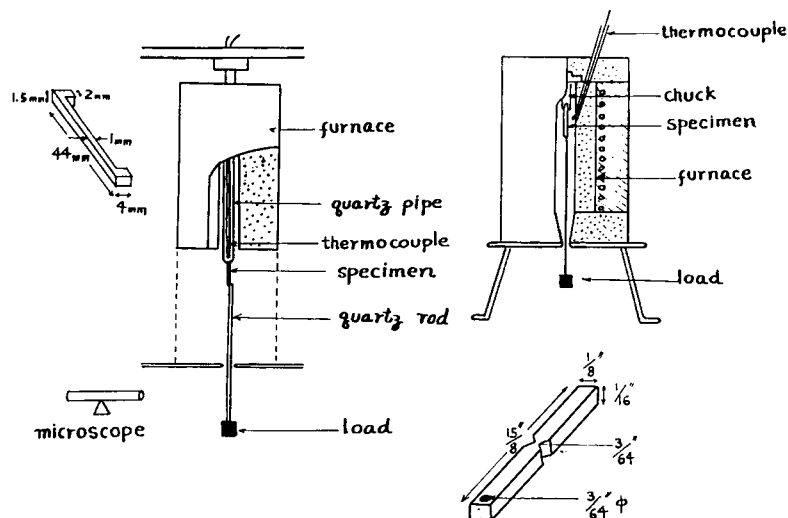


Fig. 1. Experimental apparatus and the shape of the specimens: (left) fiber elongation method; (right) zero strength time test.

be negligible at these high temperatures and masked by the larger contribution from rubberlike elasticity, it should not be correct to ascribe the observed instantaneous elongation to so-called instantaneous elastic modulus; it would be more reasonable to ascribe this large instantaneous elongation to the contribution from retarded elasticity. By the usual procedure of analysis of the creep curve in the four-element Voigt model, the retarded elastic modulus could be obtained from extrapolating the time-dependent linear portion of the creep curve. As the retarded viscoelastic region covered in a very short time, it is almost impossible to obtain the viscoelastic frequency spectrum with sufficient accuracy. Therefore, in this case we have estimated only the retarded elastic modulus.

Zero Strength Time (ZST) is a creep fracture test performed above the melting point of a crystalline polymer which was developed by Kaufman,⁹ who showed a linear relationship between \log ZST and solution viscosity in the case of polymonochlorotrifluoroethylene. We have tried to extend this method to polytetrafluoroethylene resin and have suggested it to be a convenient method for determining the apparent molecular weight of this polymer.¹⁰ We have measured the time required to break a notched strip weighted with a 200-g. load at $360 \pm 2^\circ\text{C}$. The apparatus is shown in Figure 1.

Density was measured by the weighing method, ethyl alcohol at 21°C . being used as the standard liquid. The specimens were hung by a nylon fiber from one arm of a chemical balance.

X-ray diffraction was measured at room tempera-

ture by the Geiger counter method on a $20 \times 20 \times 2$ mm. disk. A sharp peak was observed at $2\theta = 18^\circ$ in the diffraction pattern, and the height of this peak was compared in all samples at the same experimental conditions.

RESULTS AND DISCUSSION

The changes of melt viscosity, retardation elasticity, and ZST are shown in Figures 2, 3, and 4 for materials reviewing various radiation doses. The

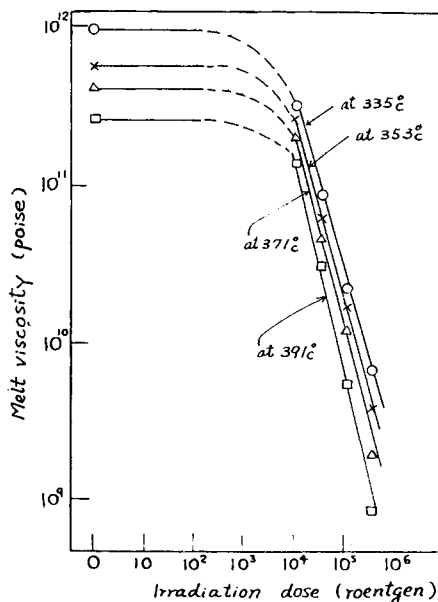


Fig. 2. The relation between melt viscosity of polytetrafluoroethylene and irradiation dose at various temperatures.

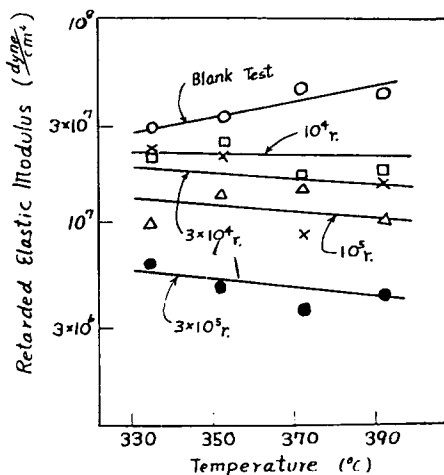


Fig. 3. The relation between retarded elastic modulus of polytetrafluoroethylene and temperature.

decrease of melt viscosity and ZST with increasing radiation dose would be reasonably explained by a decrease of molecular weight as a result of chain scission caused by gamma radiation. Also, the decrease of the slope of the retardation elastic modulus versus temperature would suggest that the rubbery elasticity accompanied by the entanglement of molecular chains decreases with chain scission, which causes a decrease in the entanglement of main chains.

At a given temperature, the elastic modulus decreases with increasing radiation dose. This fact could be explained as the effect of decreasing molecular weight, accompanied by irradiation, and may be consistent with the tendency of elastic modulus to decrease with molecular weight which is usually observed in the viscoelastic region of rubbery to flow transition in linear chain

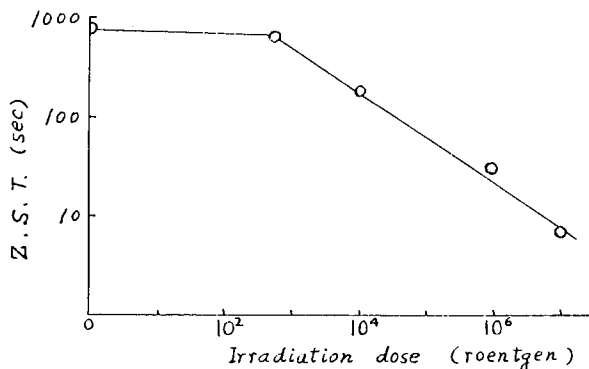


Fig. 4. The relation between Z.S.T. of the specimens and irradiation dose.

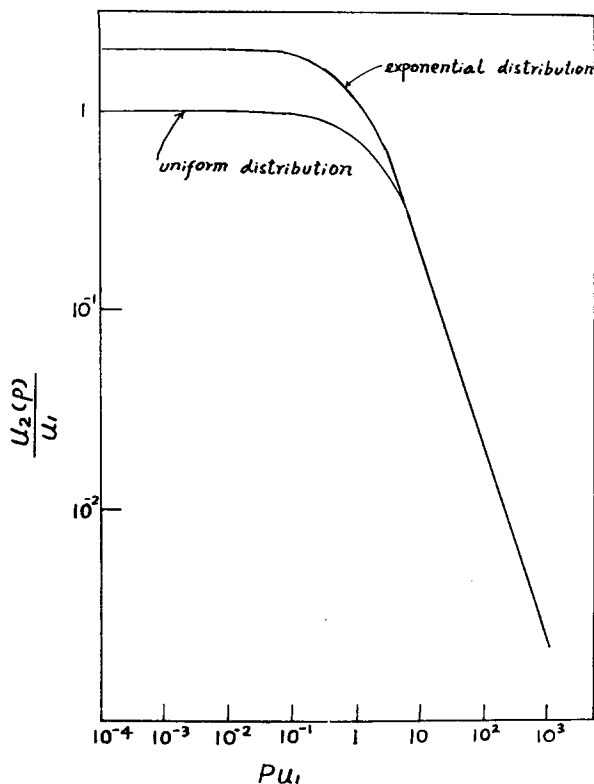


Fig. 5. Plot of $\log u_2(p)/u_1$ vs. $\log pu_1$.

polymers such as polyisobutylene¹¹ and polymethyl methacrylate.¹²

In our previous letter⁶ we have suggested an experimental formula to explain the relationship between the melt viscosity and the radiation dose, but after more detailed consideration we have found that our results would be satisfactorily explained by the degradation theory of Charlesby.¹³

The characteristic feature of our results in melt viscosity and ZST is in a tendency for these quantities to decrease only slightly below about 10^4 r., but to decrease markedly above this dose; in the latter region, a log-log plot of these quantities is linear with radiation dose. Now we shall compare this experimental relation with the degradation theory of Charlesby.¹³

In his theory the changes of average molecular weight with irradiation are described in the following equation

$$u_2(p) = u_2 - \frac{1}{3} pu_3u_2 + \frac{1}{12} p^2u_4u_3u_2 - \dots$$

where p is defined as the probability of any given bond between two successive monomer units in the main chain being fractured and is proportional to radiation dose in the case of degradation by high-energy radiation, and wu_2, wu_3, wu_4 are the weight-

average (\bar{M}_w), z -average (\bar{M}_z), and $z + 1$ -average (\bar{M}_{z+1}) molecular weights of the initial distribution. If we plot $\log u_2(p)/u_1$ vs. $\log pu_1$ in place of $\log(1 + pu_1)$ in Charlesby's paper, using the initial number-average molecular weight u_1 in two extreme cases of uniform and random (Poisson) distributions, we obtain the distribution shown in Figure 5. As seen from this figure, the decrease of molecular weight below $pu_1 = 1$ is very slight, but above $pu_1 = 1$, the decrease becomes very sharp, and both quantities are in linear relation in the log-log plot as well as the experimental relation (Figs. 2 and 4). On the other hand, the melt viscosity of long chain polymer has been found to be in definitely related to weight-average molecular weight, such as¹⁴ $\eta \propto \bar{M}_w^{3.4}$; thus, the logarithm of melt viscosity will be proportional to the logarithm of the weight-average molecular weight. Therefore the experimental relation between melt viscosity and radiation dose is found to be qualitatively in good agreement with the theoretical relation derived from Charlesby's paper. If we take account of the molecular weight distribution, we would be able to discuss qualitatively in more detail the comparison with Charlesby's theory. Another interesting point is the inflection in the curve at $pu_1 = 1$, which means that one degradation occurs in one polymer molecule; in other words, an observable decrease in melt viscosity occurs at about 10^4 r., and theoretically the decrease of molecular weight becomes sharp at about that point at which one degradation occurs in every molecule. It is reasonable that melt viscosity begins to decrease when each molecule suffers more than one fracture; thus, we consider that the change in slope marks the point at which $pu_1 = 1$. Then, as suggested by Charlesby,¹⁵ the number of fractures per molecule may be roughly estimated by

$$n = GMD \times 10^{-6}$$

where G , M , and D are defined as the G value, the molecular weight, and the radiation dose, respectively. The molecular weight is not known exactly for this polymer, but by the use of radioactive catalyst it is estimated to be of the order of 10^6 in number-average value.¹⁶ Therefore, if we put $D = 0.01$, corresponding to the condition $pu_1 = 1$, n is of the order of $0.01G$. From the above condition, $n = 1$, and the G value is estimated to be of the order of 10. Though the G value of this polymer is not known, the value obtained on the basis of gas evolution data appears to be below

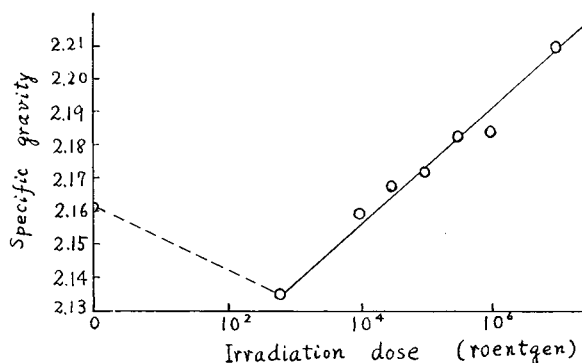


Fig. 6. Specific gravity vs. irradiation dose.

the true value, as the diffusion rate depends on the gas evolution. The above value of G is slightly higher than the value estimated from gas evolution, but recent calculations by Watababe¹⁷ suggest a value of G of about the same order on the basis of his theory.¹⁸ A factor other than chain fracture, e.g., double bond formation, may be involved to some extent, but as this would probably be not so important, and the rigorous estimation of G becomes very difficult.

Next, as mentioned in the introduction, the highly irradiated specimen appears to be very brittle. This is logically attributed to the effect of mechanical degradation by chain fracture, but in addition to this effect, a decrease in molecular weight may be considered to promote the crystallization effect. To clarify this, density and x-ray diffraction were measured. As shown in Figure 6, the density at room temperature initially decreases with increasing radiation dose, but at doses above 10^3 roentgen it began to increase. Furthermore, as seen from Figure 7, the x-ray crystalline-sensitive peak heights change in the same way as does the density, and especially at high radiation dose it is confirmed that both density and the x-ray peak height increase with the logarithm of radiation dose. These effects may suggest that there is an increase in crystallinity with high irradiation, which is considered to be reasonable because low molecular weight chains could attain a higher degree of crystallinity than can higher molecular weight chains in ordinary crystalline polymers.

The third point to be noticed is the appearance of minima in plots of the activation energy of melt viscosity (Fig. 8) density, and x-ray crystallinity versus radiation dose. These parallel trends would suggest that some mechanisms are operative in the processes induced by gamma radiation.

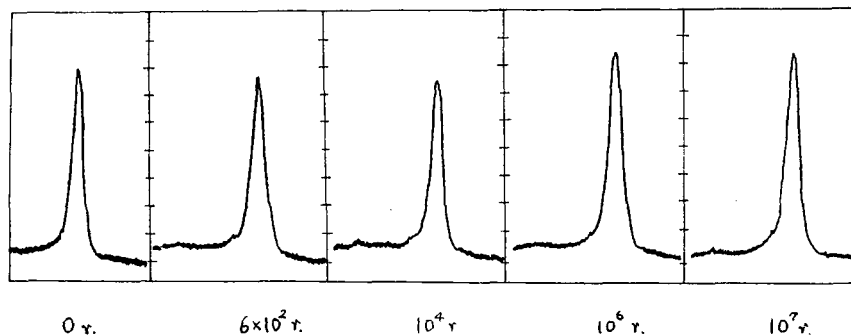


Fig. 7. X-ray diffraction patterns at $2\theta = 18^\circ$ for various irradiation doses.

At low radiation doses, gamma radiation produces some excess voids in the polymer as a result of gas evolution, but these gases could probably not diffuse out easily because of the low degree of chain fracture. These spaces would contribute to the decrease in the activation energy of melt viscosity and density, but the accompanying effect of chain fracture in the region of higher crystalline content as well as in the amorphous region may lower, to some extent of crystallinity. On the other hand, at higher radiation dose, since the chain degradation effect would be promoted and large quantities of gas are evolved, internal cracks, which would be formed would permit gas evolved to escape easily from the interior of the polymer. The combination of this effect and that of the decrease in molecular weight would increase the unit of flow segment effective in melt viscosity, which would in turn increase the activation energy. The evolution of gases and increased crystallinity both contribute an increase in density.

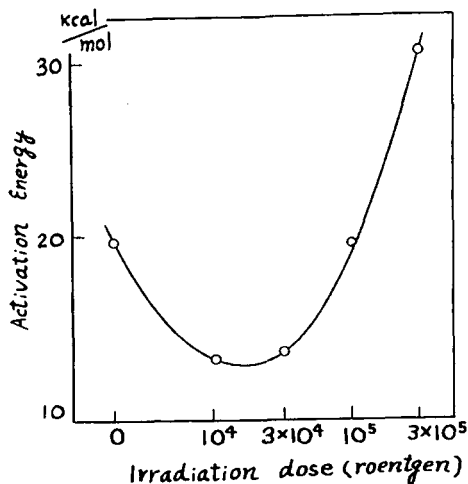


Fig. 8. Activation energy of viscosity vs. radiation dose.

CONCLUSIONS

The results obtained through the study of melt viscosity and elasticity above the melting point, zero strength time test, density, and x-ray crystallinity are conclusively summarized as follows.

Polytetrafluoroethylene belongs to the group of polymers degraded by high energy radiation. Chain scission produces a decrease in the melt viscosity, rubbery elasticity, and creep fracture time and results in increases in the density and crystallinity. The increase in crystallinity is conclusively evidence for the occurrence of chain fracture, and the crosslinking effect would therefore appear to be negligible in this polymer during gamma radiation.

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Synopsis

Effects of gamma radiation on the properties, such as melt viscosity, elastic modulus above the melting point, creep fracture time above the melting point, density, and the degree of crystallinity by x-ray diffraction, of polytetrafluoroethylene resin were studied. When exposed to the radiation from a Co^{60} gamma source, the melt viscosity falls rapidly with increasing radiation dose above 10^4 roentgens, and the rubber elasticity above the melting point decreases with increasing irradiation. Also, Zero Strength Time (a creep fracture time test) above the melting point decreases rapidly with irradiation above 10^3 roentgens; this behavior is attributable to the chain scission and the accompanying decrease in average molecular weight. Density was found to increase with radiation dose at doses higher than 10^4 roentgens; also, at $2\theta = 18^\circ$ peak in the X-ray diffraction pattern, which is indicative of crystallinity, increases slightly in sharpness with irradiation.

These facts suggest that gamma irradiation of this polymer produces chain scission and decreases the average molecular weight, and also causes partial crystallization followed by an increase in the density in the amorphous region. Therefore, crosslinking would probably be negligible in this polymer.

Résumé

Nous avons étudié les effets d'irradiation aux rayons-x sur les propriétés caractéristique du polytétrafluoroéthylène, telles que la viscosité à l'état fondu, l'élasticité au dessus du point de fusion et la rupture au choc. De même la densité du matériel irradié a été mesurée et sa cristallinité étudiée par diffraction aux rayons-x. Sous l'influence des rayons-x provenant d'une source de Co^{60} , la viscosité à l'état fondu ne change guère jusqu'à une dose de 10^4 röntgens; au delà de

celle-ci, elle décroît rapidement avec la radiation. Par suite de l'irradiation, le matériel perd l'élasticité gommeuse qu'il a au dessus de son point de fusion. Quant au "Zero Strength time," de même que la viscosité à l'état fondu il décroît rapidement au delà de doses de 10^3 röntgens. Ces effets indiquent qu'il y a rupture des chaînes moléculaires et diminution du poids moléculaire. La densité croît avec l'irradiation au delà de 10^4 röntgens. L'irradiation fait croître le pic du réseau de diffraction des rayons-x qui se situe à $2\theta = 18^\circ$. Ces résultats montrent que l'irradiation aux rayons-x rompt les chaînes moléculaires, diminue le poids moléculaire moyen, et provoque la recristallisation des parties amorphes précédemment rompues. Les auteurs admettent que la réticulation en croix au sein de cette résine est négligeable.

Zusammenfassung

Der Einfluss von Gammastrahlen auf folgende Eigenschaften von Polytetrafluoräthylenharze wurde untersucht: Schmelzviskosität, Elastizitätsmodul, Kriechgrenze oberhalb des Schmelzpunktes, Dichte und Kristallinitätsgrad. Bei Einwirkung der Strahlung einer Co-60 -Gammaquelle, hat diese bis zu 10^4 Röntgen keinen Einfluss auf die Schmelzviskosität. Oberhalb dieser Grenze nimmt die Schmelzviskosität mit steigender Strahlungs-dosis rasch ab und die Kautschukelastizität oberhalb des Schmelzpunktes wird bei der Bestrahlung schwächer. Ebenso nimmt die "Zero Strength Time," ein Kriechgrenzetest oberhalb des Schmelzpunktes, rasch bei der Bestrahlung oberhalb 10^3 Röntgen ab. Diese Erscheinung kann auf den Kettenabbau und die damit verknüpfte Abnahme des mittleren Molekulargewichts zurückgeführt werden. Es wurde gefunden, dass die Dichte bei stärkerer Bestrahlung oberhalb 10^4 Röntgen zunimmt; ebenso nimmt das scharfe Maximum bei $2\theta = 18^\circ$ im Röntgendiagramm, das ein Mass für die Kristallinität bildet, bei Bestrahlung ein wenig zu. Die angeführten Ergebnisse sprechen dafür, dass die Gammastrahlung dieses Polymeren Kettenabbau und Abnahme des mittleren Molekulargewichts hervorruft; ebenso wird eine teilweise Rekristallisation des abgebauten amorphen Bereichs bewirkt, die von einer Dichtezunahme gefolgt ist. Vernetzungseffekte können daher bei diesem Polymeren wahrscheinlich vernachlässigt werden.

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