LETTER TO THE EDITORS

*Polytetrafluoroethylene—A Radiation-Resistant Polymer**

The reputed sensitivity[1] to ionizing radiation of poly(tetrafluoroethylene) is not readily accepted by one familiar with its unusually high thermal stability.[2] Very little had been known about the radiation chemistry of fluorocarbons until recently when studies on the radiation of various fluorocarbon liquids and polymers demonstrated that bond rupture and radical formation are not disproportionately large for these substances.[3,4]

The rapid loss in strength reported for polytetrafluoroethylene upon irradiation may be partly caused by the fact that for optimum strength molecular weights greater than 10^6 are required.[5,6] Thus a few chain scissions are disastrous.

On the other hand, the results of measurements of electron spin resonance (ESR) on the nature and lifetime of radicals in irradiated polytetrafluoroethylene are not consistent with those from a degrading type polymer. In the first place, the structure of the radicals observed by ESR appears to be of the secondary type, $\sim\sim CF_2-\dot{C}F-CF_2\sim\sim$.[7,8] Secondly, upon heating the irradiated polymer at 300°C. *in vacuo*, polytetrafluoroethylene produces none of its monomer, tetrafluoroethylene, unlike poly(methyl methacrylate),[9,10] suggesting that the fluorocarbon radicals are very stable. Estimated values of the heat of polymerization also support this view.[11] It has also been reported as the result of ESR studies that the radicals in irradiated polytetrafluoroethylene react with oxygen to form peroxy-type radicals.[4] In view of these facts and the previous observation that the thermal decomposition of polytetrafluoroethylene is accelerated by the presence of oxygen,[12] tensile strength comparisons were made on films of the polymer irradiated to various doses in air and *in vacuo*.

A few of the results are presented in Table I.

TABLE I. Effect of Gamma Radiation on the Tensile Breaking Strength of Polytetrafluoroethylene

Conditions of irradiation	Radiation dose, e.v./g. $\times 10^{-20}$	Relative breaking strength, % of original
In air	2.4	2
	4.1	0
In vacuo	0.7	73
	4.1	51
	32.0	43

Thus it is evident that the combination of oxygen and gamma rays leads to a very rapid deterioration of the polymer, while the material is relatively resistant to the radiation alone. Since previous work on tensile strength had been carried out in air but with thicker samples, the effect of air was probably less pronounced. Also, the initial decrease in strength from irradiation *in vacuo* was probably caused by traces of oxygen in the sample and from the walls of the tube. It is known that radiation causes gases to be released from container walls. Impurities in the polymer from the production processes may also have been involved. However, from this more recent preliminary work it is evident that polytetrafluoroethylene is quite stable to radiation in the absence of oxygen.

Since in the absence of oxygen it was concluded that quite stable secondary radicals are produced by radiation in polytetrafluoroethylene, then crosslinking should be occurring albeit very slowly. Qualitatively there appears to be an increase in stiffness in the vacuum-irradiated material, which is believed to indicate some crosslinking. Also changes in the zero-strength-time data for samples of irradiated Teflon 100-X have been suggestive of crosslinking.[13] Further work along these lines is in progress.

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