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13.4

RADIATION RESISTANCE TESTS*

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Introduction

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As we progress deeper into both the Nuclear and Space Ages, it is inevitable that polymers, both the common place ones of today and the novel ones of tomorrow, will be called upon to perform satisfactorily under various levels of high energy radiations. It is therefore necessary that the engineer, who has the task of choosing materials of construction for various applications, understand some of the problems encountered when radiations of this type interact with the polymers. The situations that can be envisioned range, for instance, from the effects of low intensity, long-term exposure of dielectrics in satellites to the acute effects of high intensity, short duration exposure of gaskets in or near the core of a nuclear reactor.

It is known that the electrical properties of many polymeric dielectrics undergo both transient and permanent changes in a radiation

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field. To what extent these changes may cause or contribute to the malfunction of a component in a space vehicle's control or navigation system is a problem of great importance. Some changes are dependent upon the type, energy, and the intensity of the incident radiation, as well as external parameters of temperature and pressure. The component in question may be subjected in space travel to different combinations of these variables, and hence it is necessary to carry out radiation resistance tests under many combinations of conditions.

At the other end of the spectrum of uses of polymers in a field of radiation, one may be interested in the design of a piece of experimental or ancillary equipment in or near the core of a nuclear reactor. The same problems of type, energy, and intensity of the incident radiations and their effects on properties of interest arise. It may be anticipated at this point that no organic polymers are known which will retain their properties for extended periods of time near the core of reactors usually encountered, where radiation intensities are generally quite high. However, certain materials can be successfully used as long as they are periodically replaced before their properties deteriorate to the point where they will fail in a particular application. It is necessary then to know when to replace the

component, and this requires a knowledge of its resistance to radiation as a function of time under the conditions of exposure that are to be encountered.

The area to be covered in this section is a very broad one, and it will be necessary to present some background material before the main topic can be treated.

It should be recognized at the outset that placing a specimen in a field of high energy radiation is similar to placing it in any other atmosphere from which the specimen can absorb energy. As an example, exposure to high energy radiation can be considered as a type of low temperature ^{y?}pyrolysis. Interaction between the specimen and the field results in the deposition of energy within the specimen, and the chemical and physical changes which occur as a result of this are, to a great extent, governed by known chemical and physical forces. Radiation is merely another environmental factor which may, according to a specific set of conditions, be an experimental parameter whose effect must be studied. In this sense high energy radiation is analogous to temperature or the radiation from ordinary sunlight.

It will not come as any surprise to the reader, then, if no new test methods and procedures are covered in this section. Instead, this section

will be devoted to (1) a brief discussion of the types of radiation and their interactions with materials, (2) a survey of some of the accepted techniques of measuring and/or calculating the amount of energy absorbed in a material from the radiation field, (3) a discussion of present day knowledge of how various parameters and properties of the specimen affect the response of the specimen to the radiation field, as well as the effects of the radiation field on the chemical and physical properties of the specimen, (4) a description of some of the problems which are peculiar to exposing a sample to a radiation field as distinct from other atmospheres, and (5) lastly, a survey of the status of present day standard test methods for irradiated polymers.

13.4.1 Types of Radiation and Their Interactions with Polymers

The types of radiation which will be considered here can be conveniently subdivided into three categories: (1) charged particles, (2) uncharged particles, and (3) electromagnetic radiation. Although the details of the modes of interaction of these various radiations may differ, the effect is to produce ionization and molecular excitation in covalently bonded molecules. These reactive species undergo a complicated set of reactions which are governed by both the energetics and statistics of the

available reaction paths. Although not intended to be an exhaustive treatise on the subject, the brief description of some of the more important modes of interaction of radiation with matter which follows is intended to provide an introduction to and understanding of some of these processes.

To begin with, the energies which are normally encountered in this field are measured in units of million electron volts (Mev) per particle. Expressed on a macroscopic basis this leads to the following approximate relationships:

$$1 \frac{\text{Mev}}{\text{particle}} \equiv 2.3 \times 10^{10} \frac{\text{kilocalories}}{\text{gm mole}} \equiv 4.1 \times 10^{13} \frac{\text{Btu}}{\text{lb mole}}$$

A. Charged Particles

The charged species can be roughly placed in one of two subdivisions: (a) high mass to charge ratio, including protons, alpha particles, deuterons, and fission fragments; and (b) low mass to charge ratio, including artificially accelerated electrons and beta particles. At the energies considered here (below 10 Mev), these particles interact principally with orbital electrons to give rise to electronically excited molecules and, in the extreme case, ionized particles. The major difference is that the heavier particles of any given energy are generally not very penetrating,

whereas the lighter particles are considerably more so. As an example, the entire kinetic energy of a 5-Mev alpha particle is absorbed by a 10-mil sheet of polyethylene, whereas a 1-inch sheet of the same material would be needed to absorb a beta particle of the same energy. Hence the density of energy dissipation is considerably higher for heavy particles than it is for the lighter ones.

In addition to differences in ability to penetrate matter, electrons differ from heavier charged particles in another important way. The electron, being of very low mass, is more readily deflected in its passage through matter. This angular deflection corresponds to a radial acceleration, and an accelerating charged particle emits electromagnetic radiation. The relative ease of deflection of the electron has two important consequences. Firstly, the path of the electron through matter, and hence the molecular events which are caused by interaction of the electron with its surroundings, will not be a straight line. Secondly, the electron will lose some energy through the radiation process, and not solely through direct interactions. The energy thus radiated is generally in the x-ray region of the electromagnetic spectrum, and is graphically called "bremsstrahlung" or "breaking radiation." The relative contribution of this type of energy loss is proportional to both the energy of the electron and the

atomic number of the absorbing medium.

The average atomic number of most organic polymers is low enough so that "bremsstrahlung," as a direct effect within the polymer itself, is not usually a problem with which to be reckoned. However, polymers conveyed on a metal belt under an electron generator, for instance, will be subjected to not only the primary electron irradiation but also the secondary "bremsstrahlung" generated in the conveyor belt.

B. Uncharged Particles

The uncharged particles to be considered are neutrons which may cover the wide spectrum of energy ranging from 0.025 ev (room temperature) to 10-15 Mev. Neutrons react with materials not through the agency of direct electronic excitation, but rather through processes involving interaction with atomic nuclei. The two nuclear interactions that are of significance in this discussion are (1) elastic scattering, and (2) capture. In the former process the energy of the incoming neutron is, after collision, shared with the target nucleus, the amount depending on the geometry of the collision and the mass of the recoiling nucleus. The most favorable type of elastic collision is the head-on collision between a neutron and a hydrogen atom nucleus, in which the recoiling proton carries approximately 100% of the kinetic energy of the incoming neutron. Thus, if

a beam of 2-Mev neutrons were incident on a specimen of polyethylene, or some other hydrocarbon, elastic neutron scattering would result in the internal generation of protons, whose energies would vary from very low energies up to 2 Mev.

The capture of a neutron by a nucleus generally leads to the simultaneous emission of a gamma ray, and, if nothing else occurs during the primary act, the formation of a heavier isotope of the original nucleus which may or may not be stable. Generally the radio-nuclei produced in this process emit beta particles, which then constitute an internal source of beta radiation. As an alternative, upon capturing a neutron the nucleus may instantaneously emit another particle, i.e., proton, alpha particle, etc., and become transmuted to the nucleus of another element, which may or may not be stable itself.

Summarizing, then, neutrons impart energy to matter which they traverse principally through elastic scattering with light nuclei or through the emission of radiation from the new nucleus that results from the absorption of the neutron by a target nucleus.

C. Electromagnetic Radiation

Finally, electromagnetic radiations ranging in energy from a few kilovolts to several Mev (including both hard x-rays and gamma rays)

deposit their energy in materials directly through electronic excitation and ionization. The secondary electrons formed in the process of ionization constitute an internal source of electron irradiation.

Generally speaking, neutrons and gamma rays constitute the most penetrating types of radiation. The former are more efficiently shielded against by either a material with a high bulk concentration of light elements, such as hydrogen, deuterium, and carbon, or by a material whose nuclei strongly absorb neutrons of specified energy ranges. Gamma rays, since they interact principally with orbital electrons, are generally best shielded against by materials of high density, most of which are also of higher atomic number, and hence contain more electrons per unit volume.

Although the above processes are all of importance when these radiations interact with any type of material, the most drastic and permanent effects occur in materials whose molecules are held together by covalent (electron pair) bonds, which is generally the case in most natural and synthetic polymers. In such materials, the energy-rich species that are formed – excited and/or ionized molecules – rapidly react to produce species that were not originally present prior to irradiation, and hence the irradiated sample undergoes permanent chemical and physical changes.

D. Interactions with Organic Molecules

Present day knowledge of the details of these secondary reactions

is very limited, and the best that can be offered, in terms of a reaction mechanism, is a grossly oversimplified mechanistic scheme. This can be summarized as follows:

Reactions (1a) and (1b) depict the initial event in which excitation and ionization occur, respectively. Since Reaction (1b) involves the expenditure of approximately 12-14 electron volts, when Reaction (2) occurs, the molecule which is formed has at least this much energy available as excitation energy, sufficient to cause the rupture of one or

more covalent bonds within the molecule. When rupture occurs, either charged fragments (ions) or uncharged species (free radicals) are formed, all of which are highly reactive and will enter into reaction with each other and their surrounding environment to produce permanent chemical changes.

Regarding the present day controversy over the relative importance of free radicals, excited states and ionic species in radiation processes in organic systems, little will be said here. Most of the changes which have been studied in polymeric systems have been interpreted exclusively in terms of free radical intermediates, although a recent report⁽¹⁾ discusses the cross linking of polyethylene in terms of an ionic mechanism. However, in this section, the active intermediates will generally be referred to as free radicals, with no great loss in generality.

In summary, the interaction of radiation with organic materials leads to the deposition of some fraction of the incident energy in the material. This absorbed energy is used to break bonds that were originally present and to form new ones. The presence of the new bonds is frequently reflected in the changes in physical and chemical properties of the irradiated material. In many instances where changes in polymers irradiated in the bulk state have been measured it has been indicated that

the most important parameter is the total amount of absorbed energy, practically independent of dose rate (except for heating and diffusion effects), or type of particle (except for depth of penetration).

One of the most important steps, then, in carrying out a radiation resistance test is to carefully determine the total energy absorbed by the specimen from the radiation field. This topic is introduced and discussed in the following section.

13.4.2 Measurement of Absorbed Energy

A. The Units of Absorbed Energy

The original, and still basic, unit of radiation dose measurement is the roentgen. As proposed and adopted by the Chicago Conference on Radiology (1937):

“The roentgen shall be the quantity of x- or γ -radiation such that the associated corpuscular emission per 0.001293 gm of air produces, in air, ions carrying 1 esu of quantity of electricity of either sign.”

The term “associated corpuscular emission” refers to the secondary electrons generated by interaction with the incident electromagnetic radiation.

There are certain serious limitations to the application of this unit in measuring the absorbed dose in condensed phases, including organic polymers. The unit contains, in its definition, the specification of the

absorber to which it is applicable - air. If one is interested in how much energy is absorbed in a medium other than air by a given incident flux of photons of a given spectral distribution, it is necessary to relate the absorption characteristics of the medium to that of air. This type of correlation was effected for translating exposure dose, as measured in roentgens, to dose absorbed in soft tissue. The unit of the rep (roentgen equivalent physical) was adopted for this. The rep has since been discarded as a unit of absorbed dose, and it will not be considered here.

A second difficulty in extending the use of the roentgen to studies of radiation effects is that this unit, by definition, is restricted to electromagnetic radiations and excludes all charged particles.

In order to overcome these difficulties, the unit of absorbed dose is now accepted as being the rad. The rad is defined as an energy absorption of 100 ergs per gram of absorber. Thus, the rad is directly applicable to all types of radiation and does not depend on the composition of the absorber. The rad has been recommended by the International Commission on Radiological Units (Copenhagen, 1953); it has been adopted by many standardizing groups, such as the American Standards Association and the American Society for Testing and Materials.

The integral absorbed dose is defined as the integration of the energy absorbed throughout a given region of interest and is expressed in grad-rads. The absorbed dose rate is the time rate of energy absorption and is expressed in rads per second, minute, or hour.

Much of the older literature on radiation effects measurements will be found in which the unit of rep as the absorbed dose is used. On basis of present day data, the rep corresponds to 93-97 ergs per gram (in soft tissue or water). For most practical purposes one can interpret data expressed in rep as being equivalent to having been expressed in rads.

Another unit which occasionally occurs in older literature of polymer studies is electron volts per liter. Assuming a density close to one, this can be converted by the approximate factor: 1.6×10^{-17} rad/ev/liter.

A complete discussion of the measurement of absorbed energy from all types of radiation fields would occupy much more time and space than is intended in this section. Therefore, certain limitations will be set that will reduce the discussion to a practical and manageable size.

B. Heavy Charged Particles

The dosimetry of high mass-to-charge corpuscular radiations will be summarily disposed of, on the grounds that, for the energies most commonly encountered, total absorption of these particles will occur in solid

and liquid specimens that are only a few mils thick. Under the assumption of total absorption, the integral absorbed dose is simply given by the expression

$$\text{Integral dose} = \frac{TI t}{z} \times 10^{11} \text{ gm-rad}$$

where T is the kinetic energy of the particles in Mev, I is the total beam current in amperes, t is the time of exposure in seconds, and z is the nuclear charge of the particle. The beam current, assuming the particles are being delivered by an accelerator, can best be measured by a device known as a Faraday cup, to be more fully discussed later.

C. Electrons and Gamma Rays

Electron and gamma ray dosimetry is complicated by the fact that frequently only a fraction of the incident energy is absorbed by the specimen, and it is generally impractical to directly measure the amount that is absorbed in the specimen. Recourse is frequently had to determining the amount of energy absorbed in a standardized system (dosimeter) placed at the point of interest in the radiation field, and expressing the amount of energy absorbed by the specimen in terms of what was absorbed in the dosimeter both situated at the same place in the field. Since the various processes by which electrons and gamma rays deposit their energy in a

substance depend on the atomic numbers of the nuclei composing the substance, it would appear necessary to have a dosimeter with the same atomic composition as the specimen. This is frequently impractical, and, under proper conditions, not essential.

For corpuscular radiations and electromagnetic radiations of energies greater than 1 Mev, one of the most widely used measuring devices is the cavity ionization chamber. Although a detailed discussion of cavity ionization chamber theory would be out of place here, a brief description of the device will suffice to make the reader acquainted with the principles involved. The theoretical basis of the following argument was given by Bragg and Gray, and has become known as the Bragg-Gray principle (see reference 2).

If a solid medium is traversed by secondary electrons, it can be shown that the introduction of a small gas-filled cavity will not disturb the energy or angular distribution of these electrons at the position of the cavity. Since the ratio of the energy lost by an electron in traversing unit mass per square centimeter of medium to the corresponding quantity in the gas is equal to the ratio of the respective mass stopping powers, then

$$E_m = \frac{S_m}{S_g} E_g$$

where E_m and E_g are the energies imparted by the electrons to unit mass of medium and gas, respectively, and S_m and S_g are the respective mass stopping powers.

In the gas, the energy E_g results in ionization, and, if W is the mean energy expended in the formation of an ion-pair and $\frac{J}{S_g}$ is the number of ion-pairs formed per unit mass of gas, then

$$E_m = \frac{S_m}{S_g} J_g W = J_g \rho_m W$$

where

$$\rho_m = \frac{S_m}{S_g} = \frac{N_m e S_m}{N_g e S_g}$$

where N_m and N_g are the numbers of electrons per gram of medium and gas, respectively, and $e S_m$ and $e S_g$ are the stopping powers per electron for each substance.

Electron stopping powers can be calculated and are found to reach a broad minimum in the electron energy range of 2 to 5 Mev, and are relatively insensitive to the atomic number of the absorber for low atomic number absorbers. Thus,

$$\rho_m = \frac{N_m}{N_g}$$

Moreover, experimental determination of W as a function of radiation energy, for both corpuscular and electromagnetic radiations, and atomic number of the gas gives a fairly constant value of 34 ev per ion pair except at very low energies, below 0.3 kev.

Approximately, then,

$$E_m = 34 J_g \frac{N_m}{N_g}$$

In order to satisfy the Bragg-Gray conditions the cavity must be small enough so that only a very small fraction of the traversing particle's energy will be dissipated within the cavity and direct absorption of electromagnetic radiation within the cavity itself will be negligible. Also, the thickness of medium around the cavity must be sufficient to insure that all particles that cross the cavity have originated in the walls of the cavity.

As an example of the use of such a device, polyethylene chambers filled with ethylene gas have been used with success for gamma ray dosimetry.

A convenient and well standardized means of measuring absorbed doses of gamma rays in the energy interval of 0.1 to 2 Mev is the Fricke dosimeter. This is a chemical dosimeter which consists of an acidified

aqueous solution of ferrous ion. When exposed to ionizing radiation, the ferrous ion is oxidized to ferric. The amount of ferric ion is, under certain limitations, proportional to the energy absorbed in the dosimeter. The relationship is

$$1 \text{ rad} \equiv 15.6 \frac{\text{micromoles of Fe}^{+++} \text{ formed}}{\text{gram of solution}}$$

Now, since the absorbing medium is essentially water, and since as was pointed out above, electron stopping power is essentially constant for all the lighter elements, the energy absorbed in the Fricke dosimeter is almost identical to that absorbed in most unfilled organic plastics, the principal correction being the slightly different numbers of electrons per gram for water and the organic plastic.

For most purposes, if the radiation field is specified in terms of energy absorbed in the Fricke dosimeter, this is sufficient information for comparison of one set of experimental data and another, despite the fact that the true energy absorption in the specimens may not be known.

Fricke dosimetry has been successfully used for softer x-radiations and also accelerated electrons and beta particles. Each of these applications gives rise to complications which are the result of the peculiarities of the incident radiation.

The details of the Fricke dosimeter are given in ASTM D 1671-59 T and elsewhere.⁽³⁾

Accelerated electron dosimetry is frequently accomplished by using a current measuring device known as a Faraday cup. This consists of an evacuated enclosure in which is mounted an insulated block of metal to collect the beam of charged particles transmitted through a thin window. The dose in rads is given by

$$D = q_F \sigma_m \times 10^{11} \text{ rads}$$

where q_F is the charge density collected on the cup in coulombs per square centimeter and σ_m is the mass stopping power of the cup material in Mev per gram per square centimeter.

A schematic diagram of a Faraday cup is shown in Figure 1. Certain errors are inherent in the device and these can be minimized by certain design characteristics. The absorbing block must be long enough to absorb not only the primary beam but also secondaries arising through nuclear interactions. The cross section of the block must overlap the cross sectional area of the incident beam sufficiently that particles are not scattered out of the sides of the block. The residual gas pressure inside the assembly must be kept low enough to minimize the formation of

ions by interaction with the transmitted beam. The window should be thin and spaced not too far from the collecting block.

In practice, the Faraday cup may be used to measure the total beam energy in the presence and absence of absorbing sample. The difference is, to a fairly good approximation, the energy absorbed by the specimen.

D. Neutrons

Neutron dosimetry presents its own peculiar problems. The major proportion of the energy absorbed by an organic substance from a neutron field is by the indirect action of proton recoil, resulting from the elastic scattering of the neutrons by hydrogen atoms. Further contributions are made by elastic scattering from other nuclei. In general,

$$D(E) = E \sum f_i Q_i \sigma_i$$

where E is the neutron energy, Q_i is the number of atoms of the " i^{th} " element in unit mass of sample, σ_i is the elastic scattering cross section for the " i^{th} " element for neutrons of energy E , f_i is the fraction of the energy lost by the neutron in an elastic collision with the " i^{th} " element, and $D(E)$ is the dose in energy units per unit mass of sample.

Since σ_i for any given nucleus varies with the energy of the neutron, either one must resort to some definition of an average value of σ_i ,

averaged over the entire energy spectrum of the neutrons, or one can attempt to specify the distribution function over the energy range of the neutrons. In either event, the problem becomes quite complex.

Nitrogenous materials exhibit an additional mechanism of energy absorption in a flux of thermal neutrons. Nitrogen-14, on absorbing a thermal neutron, will emit a 0.6-Mev proton which, having a very short range, will generally dissipate all its energy within the specimen. Nylon-6, if exposed to a thermal flux of 10^{14} neutrons per square centimeter per second, will absorb energy at the rate of approximately 25×10^6 rads per hour as a result of this process.

Inside a nuclear reactor the specimen will be subjected to gamma radiations in addition to neutrons. The ratio of fluxes of gamma ray photons to neutrons of various energies depends on the type of reactor, including the moderating material and core geometry. There is no simple or general relationship between these two fluxes.

A detailed mathematical analysis of a particular position in a given reactor operating at a specified power level can be made, and a crude approximation of this ratio can be arrived at. On the other hand, it is desirable to be able to empirically determine one or the other components of the field. Although various ingenious schemes have been devised to

accomplish this, one of the more recently developed and promising means is the use of a carbon wall-CO₂ filled thimble ionization chamber.⁽⁴⁾ This device is responsive almost exclusively to the gamma ray component of the mixed radiation; there is a small (approximately 5%) contribution from fast neutron induced recoils from the walls of the chamber.

13.4.3

A. Factors Which Influence the Effects of Radiation

1. Chemical Composition. Radiation changes the properties of a polymer reordering of the chemical bonds within the specimen, with all the ensuing changes in chemical structure, molecular geometry, molecular weight and its distribution, cross link density, crystallinity, plasticization, etc., which may result. The breaking and re-forming of bonds results in a state of affairs which is generally described in terms of two over-all processes, crosslinking and scission. Here we will discuss these two processes in their briefest forms.

The crosslinking process is most readily visualized in terms of vulcanization, in that two polymeric chains are joined together by a chemical bond. Crosslinking can result from two different molecular processes. If the bond is formed between two radicals on adjacent chains, and four polymeric "ends" emanate from the crosslink site, this is truly called

crosslinking. If, on the other hand, the bond is formed by reaction between the end of one chain (usually one that has resulted from main-chain scission, to be covered below) and the interior of another, so that three polymeric "ends" emanate from the crosslink site, this is called "end linking." In either event, changes in molecular weight and its distribution and crosslink density occur. Obviously, in order that the free radicals be formed, certain changes in chemical constitution must also occur; in most cases, the chemical consequences are far outshadowed by the physical consequences of crosslinking, however.

Scission occurs by one of two general types of reaction. If the bond which successfully breaks is in the main chain of the polymer molecule, this is termed main chain scission, and generally results in a drastic decrease in the molecular weight of the polymer. If the bond which is broken involves a pendant atom or group, this is referred to as side-chain scission or elimination. Although this type of scission also decreases the molecular weight of the polymer, the decrease is generally a very small fractional one. The main effect of elimination is the radiolytic release of low molecular weight materials that are frequently volatile at, or slightly above, room temperature. If these gases are very low molecular weight, such as hydrogen, methane, carbon monoxide, etc., they can frequently diffuse through

and escape from the specimen at ordinary temperatures. Higher molecular weight fragments will generally be trapped, and, if formed in sufficient quantity, may act as internally deposited plasticizers.

All of these processes undoubtedly compete with one another when a polymer is irradiated. The competition between crosslinking and main chain scission is perhaps the easiest one to measure, and is also perhaps the most important one in determining the changes in the mechanical properties of bulk polymers. As a general rule, in vinyl polymers, where the repeat unit can be represented as

if either X or Y is a hydrogen atom, crosslinking will predominate over main chain scission, during the irradiation of the bulk polymer. But, if neither X nor Y is a hydrogen atom, as for instance, in the methacrylates, main chain scission will be favored over crosslinking. In addition, phenolics tend to show a net degradation in molecular weight, indicating the preponderance of scission. Cellulose and its derivatives also tend to degrade, although it has recently been reported that under proper conditions of

concentration (in water) and dose rate, this tendency can be reversed.⁽⁵⁾

Another generalization that can be made is that the presence of an aromatic ring in a polymer will confer a degree of radiation stability to the polymer. In fact, this stabilizing effect of resonating structures on organic compounds is a well known and much reported phenomenon.⁽⁶⁾

In concluding these few brief remarks on the effects of chemical structure on the course of the interaction of radiations with polymers, it is interesting to note an apparent anomaly observed in the case of polytetrafluoroethylene. The most abundant reported low molecular weight product formed in the radiolysis of this polymer in the presence of O_2 is carbon tetrafluoride. While polytetrafluoroethylene exhibits greater thermal stability than polyethylene, its radiation stability is orders of magnitude lower than for polyethylene. Recently, it has been reported that oxygen may be responsible for the rapid deterioration in physical properties of polytetrafluoroethylene under irradiation,⁽⁷⁾ and that this polymer may be almost as stable as polyethylene if oxygen is excluded during irradiation.

In addition to the effects of chemical constitution on the interaction of polymers with radiation, other factors also play a role. A few of the more important ones will be discussed below.

2. Crystallinity. Many polymers are partially crystalline or crystallizable. The presence of such crystalline regions affects the chemical and physical properties of the material. For instance, polyethylene is insoluble in all solvents at temperatures below approximately 80°C. It is known that the melting point of the crystallites is in the range of 110°C and above. In the process of dissolution, these crystalline regions are destroyed, and the energy to accomplish this cannot be supplied by solvent-solute interactions alone, but must have a thermal component.

Crystallinity imposes certain constraints on the course of the interaction of polymers with radiation. These constraints do not, in general, apply to the initial ionizing and excitation events, but rather to the subsequent free radical reactions. The former are essentially statistically governed events, but the fate, nature, and stability of the radicals which follow these initial events can be fairly sensitive to the conditions of their surroundings.

Free radicals can be removed from a system only in pairs. Applied to the case of polymeric free radicals in the bulk polymer, this implies that the large polymeric segments to which the free radicals are attached must have sufficient mobility to approach each other and react. Anything

which hinders or obstructs this mobility will have the effect of expanding the time scale over which the radicals remain active. Crystallinity in polymers achieves this in two ways.

Firstly, the presence of crystalline regions restricts the mobility of the chain segments in the non-crystalline regions. In a sense, a crystallite behaves similar to a chemical cross-link. The greater the density of crystallites, the less will be the mobility of chains in the amorphous regions. This will have the effect of inhibiting the radical recombination process.

There is a second effect of crystallinity on radical life-time in irradiated polymers. Radicals which are formed within a crystalline region are virtually trapped, and may have life-times of many months, even years, under certain commonly attainable conditions. For instance, samples of irradiated high density polyethylene powder have been found to have a measurable free radical content 18 months after standing exposed to air at room temperature.⁽⁸⁾ These free radicals, which appear to be trapped in crystalline regions, can be reacted by elevating the temperature to the normal melting point of the crystallites, where sufficient mobility is given to the molecular chains that were formerly held in position by the crystal lattice forces.

Additional evidence for this phenomenon is presented by the experimental finding that the crystallinity of polyethylene is hardly affected by

doses of radiation which are sufficient to cause extensive changes in its physical properties, due to crosslinking. These cross links which are formed during and immediately following irradiation are apparently formed by radicals which are in the amorphous regions.

Consequently, in polymers which exhibit any amount of crystallinity, it is important to specify the amount of crystallinity before irradiation and whether or not any treatment, subsequent to irradiation, was employed which may have caused the trapped radicals to react and thereby affect the value of the property being tested. Among such treatments as may cause these post-irradiation changes are: elevated temperatures, severe mechanical working, infusion and diffusion of reactive materials, e.g., oxygen, vinyl monomers, etc.

A much more subtle effect which crystallinity may have on the over-all interaction of radiation with polymers is to provide a driving force toward favoring certain types of radical formation over others. The driving force derives from the forces which maintain the integrity of the crystal lattice. An example of this would be the case of a crystallite in polyethylene. The abstraction or ejection of a small hydrogen atom from the hydrocarbon chain would be favored over the rupture of a carbon-carbon backbone bond. This is so for two reasons. Firstly, the small hydrogen atom can readily

diffuse through the crystal lattice and remove itself from the zone of interaction with its partner radical. This cannot be done by either of the two radicals resulting from a backbone carbon-carbon bond rupture, with the result that this type of rupture will lead to two very closely spaced free radicals which will probably interact to re-form the original bond. Secondly, the radical resulting from the first type of bond rupture, upon rearrangement of the bond angles around the carbon atom associated with the free radical, can be more easily accommodated within the geometry of the crystal lattice than can the two adjacent radicals resulting from the latter type of bond rupture.

By this close interplay of crystal geometry requirements and crystal potential energy, crystallinity may influence the course of the reaction in this subtle fashion.

The process of radical trapping also occurs under two other frequently encountered circumstances. Just as crystallinity imposes restraints on the mobility of chain segments in adjacent amorphous regions, cross-linking, such as is present in highly vulcanized materials, can achieve the same result. Thus, highly vulcanized rubber, when irradiated, may build up a trapped radical population, which will be affected, either during or subsequent to irradiation, by any factors which will affect the mobility of

chains between crosslinks or provide reactive species to the radicals.

Finally, a glassy structure – an amorphous polymer below its glass transition temperature – is also fertile ground in which to build up a trapped free radical population.

In addition to trapping free radicals, such a glassy polymer also quite frequently traps and stores fairly large quantities of radiolytically formed lower molecular weight compounds, which cannot diffuse through the rigid structure of the polymer at the temperature of the irradiation exposure. A classic example of this process is displayed in poly (methyl methacrylate). If this material is irradiated at or near room temperature, there is at first no apparent change in the macroscopic appearance of the specimen, except for a certain amount of discoloration. If the irradiated sample is heated to its glass transition temperature, large quantities of low molecular weight products begin to diffuse through and out of the specimen. These effects are shown in Figure 2.

As a corollary to the effect of crystallinity, crosslinking, and glassiness on the properties of irradiated polymers, it is apparent that temperature can play an important role in affecting the outcome of the irradiation. To some extent, the effect of temperature is manifested in the usual fashion – through an energy of activation; but, to an even greater extent, its effect may

be manifested by favoring or eliminating the growth of a trapped free radical population. Those free radicals which persist after irradiation, may lead to post-irradiation changes in the physical and chemical properties of the specimen, depending on the conditions that prevail. Such effects were the topic of a Symposium on Post-Irradiation Effects in Polymers, sponsored by the ASTM in San Francisco in 1960. The papers presented were published in ASTM Special Technical Publication No. 276.

3. Atmosphere. The atmosphere surrounding a specimen is generally taken to refer to the external surroundings, while substances internally dispersed are considered additives. However, since in many situations, externally present substances, as for instance oxygen, may diffuse throughout the sample and be present internally in significant concentration, the differentiation between the external atmosphere and internal additives is a rather dubious one. In this section we will consider under the name atmosphere any substance that is in or around the sample under irradiation and will react with the free radicals produced by the radiation to cause measurable differences in the interaction of the sample with the radiation field.

a. Oxygen. The effects of oxygen on plastics has been widely studied. One instance was pointed out above in the case of poly

(tetrafluoroethylene). In many instances the effects have been described in terms of the build-up and decomposition of peroxides and hydroperoxides, with concurrent breaking and forming of network bonds. These reactions generally proceed at a fairly low rate at room temperature because of the activation energy requirements. On the other hand, the presence of ultraviolet radiation from sunlight frequently accelerates the process, as does the presence of considerable quantities of ozone in the surrounding air. The presence of oxygen in and around a polymer during irradiation leads, also, to oxidative attack of the polymer. In kind, this may not be much different than ultraviolet induced oxidation. However, especially with penetrating gamma rays, the reaction may not be confined to the surface of the specimen as happens with the less penetrating ultraviolet radiation.

Moreover, the rate of energy deposition from a high intensity radiation source may be many orders of magnitude greater. In fact, it has been shown in the case of polyethylene that gamma ray dose rates may be readily employed which are so high, compared to the rate of diffusion of oxygen to the interior of the sample, that the effects of oxygen are confined to the surfaces.⁽⁹⁾ This effect becomes more pronounced as the thickness of the sample increases.

Recently the effects of various other gases on the radiation induced

crosslinking of thin polyethylene films have been reported.⁽¹⁰⁾ It was found that NO_2 , O_2 , NH_3 , SO_2 , and Cl_2 depressed the rate of crosslinking; CO and H_2 were found to have no effect; finally, N_2O was found to accelerate the rate of crosslinking.

High energy radiations also have the ability of forming ozone from oxygen. This can lead to phenomena that are typical of ozone, when polymers are irradiated in the presence of oxygen. For instances, rubber samples that are subjected to gamma radiation in the presence of oxygen and while under a bending stress display "cracking" at stressed regions that are typical of that ascribed to ozone attack.⁽¹¹⁾

An incidental but serious sidelight should be pointed out in this regard. The formation of ozone from oxygen can have explosive results, particularly when irradiations are conducted under such conditions that a high concentration of ozone may accumulate, e.g., at very low temperatures. Occasionally, sufficient ozone is formed under these circumstances to cause Dewar flasks to rupture upon reaction with dust, adventitious organic impurities, etc. Although this does not generally constitute a hazardous situation in gamma irradiation facilities, it can lead to nasty situations when such irradiations are conducted within the core of a nuclear reactor. These remarks are inserted here not to discourage irradiations at liquid

nitrogen temperatures, but to point out a situation which may occur and whose potentiality should be recognized.

b. Vinyl monomers. If a vinyl monomer constitutes the atmosphere of an irradiated polymer, the monomer may react with the polymer by at least two processes, both of which are capable of leading to changes in the chemical, physical, and mechanical properties of the polymer. The monomer may add to and propagate from radiation produced radicals within the interior of the polymer and at its surface, or polymerization of the monomer may be initiated by the radiation and the growing chains may transfer their activity to the original polymer. From these indirectly generated radicals in or on the primary polymer component initiation of the monomer may occur. In either event a copolymer is formed. These are generally called graft copolymers.

The details of the radiation induced graft copolymerization process are not of interest here. However, the fact that a polymer subjected to irradiation is susceptible to such a reaction is of some importance in stressing the effect of the surrounding atmosphere on radiation produced changes in such systems. This is especially true since the monomer need not be present during irradiation. The grafting process can occur if the irradiated polymer is contacted with monomer subsequent to irradiation.

The graft copolymerization process has been widely studied, especially as it applies to vinyl monomers. To what extent it, or a similar process, may occur with other singly or multiply unsaturated species is not generally known. If the measurement of a physical property of an irradiated polymer must be done in such a way that the polymer is surrounded by an atmosphere consisting of an organic material, either during or after irradiation, what is measured may be a composite of several processes.

c. Anti-rads. Certain specific compounds, among which are N,N'-cyclohexylphenyl-p-phenylenediamine, quinhydrone, N-p-tolyl-N'-p-toluenesulfonyl-p-phenylenediamine, beta-naphthol, beta-naphthylamine, N,N'-dioctyl-para-phenylenediamine, and pyrogallol have been found to protect natural rubber against the normally expected effects of high energy radiations.⁽¹²⁾ The mechanism by which these substances achieve their results is not known, although much speculation has been offered.

Certain other additives, namely propene and isobutylene, have been reported to reduce the amount of crosslinking in polyethylene per unit of absorbed dose.

Many conventionally employed inorganic fillers appear to accomplish the same thing in various plastics. The extent to which these inorganic

fillers actually operate as protectors is a moot question. They are generally present to a fairly high weight percent in the formulated polymer, and the relative energy deposition in the two phases – organic and inorganic – is not well known. Their effect may be to absorb the incident energy, rather than actually “protect” the organic component. However, in general, it has been reported that unfilled specimens show a much greater radiation effect for a given radiation exposure than similar specimens containing inorganic fillers.

d. Sensitizers. Although in the past more attention seems to have centered on finding materials that would protect polymers from the deleterious action of high energy radiations, some work more recently has been directed towards the equally important and interesting field of developing additives that will sensitize polymers (and other systems) towards radiation. As yet, the work is fragmentary and preliminary, but undoubtedly these materials will be developed and their importance in the radiation testing of polymers will increase.

B. Polymer Properties Affected by Radiation

Due to the extensive changes in chemical composition, cross link density, molecular weight, etc., that occur when a polymer is irradiated, the physical and chemical properties of the specimen will display corresponding

alterations. Most of these changes are readily visualized in terms of one or more of the molecular processes which have already been briefly discussed. The following discussion of some of the changes in properties that have been measured and reported is intended to serve as an introduction to an understanding of some aspects of the radiolysis of polymers.

1. Mechanical Properties. Some of the most dramatic changes that occur when a polymer is irradiated are in its mechanical properties; moreover, from an engineering point of view these are perhaps of most importance. As in the case of various other treatments, the behavior of polymer mechanical properties with increasing dose can exhibit a variety of behavior patterns. The variation of tensile strength with increasing dose is perhaps typical in this respect.

The tensile strength of polytetrafluoroethylene exhibits a rapid and monotonously varying decrease with radiation dose. This is generally interpreted as being due to the overwhelming preponderance of the main chain scission process in this polymer. With polyethylene, on the other hand, the tensile strength at first increases with radiation dose, then reaches a maximum, and finally decreases with dose. The initial increase has been attributed to the predominance of the crosslinking reaction during the initial phases of the process. Later, when sufficient crosslinking has occurred so

as to partially immobilize the chain segments, chain scission may predominate and contribute to the ensuing decrease in tensile strength. Moreover, at sufficiently high doses, the crystallinity of this polymer becomes increasingly destroyed, which probably also contributes to the decrease in tensile strength at very high doses.

In general, an increase in tensile strength, modulus, hardness, density, etc., is interpreted as indicating a predominance of the crosslinking process over either or both of the scission processes. At the same time such properties as elongation at break, viscoelastic flow (creep), etc., are expected to show a decrease in value with increased degree of crosslinking.

The presence of mechanical stress during irradiation may alter the relative amounts of crosslinking and scission, as well as having an effect on the spatial distribution of the crosslinks that are formed. This behavior is quite analogous to the oxidative scission of, for instance, natural rubber, where the relative rates of scission and crosslinking are frequently estimated by comparing measurements of stress decay obtained under continuous and intermittent stress. To the same extent that these conditions affect the molecular processes that occur in oxidative attack they may be expected to affect the over-all response to radiation.

Thus, if one is interested in the behavior of a gasket which, under conditions of actual use will be subjected to a certain stress and with a specific atmosphere, temperature, etc., radiation resistance tests should be performed under conditions that closely approximate, if not exactly duplicate, the desired operating conditions. Unfortunately, insufficient data have been published in the effects of stress on polymers during irradiation, although a great amount of work has appeared on the mechanical, electrical, etc., properties of irradiated polymers after irradiation.

Some of the classical work on the effects of radiation on the physical properties of organic plastics are cited in references 13-16.

2. Optical Properties. The optical properties of many polymers are affected by radiation. The most prevalent change is the development of color, the intensity of which generally increases with absorbed dose. Similar outward manifestations are exhibited by inorganic crystalline substances, where discoloration has been extensively studied. In the latter systems the color is generally ascribed to trapped electrons. This type of color can usually be annealed by heat.

Whether or not a similar process is involved in the discoloration of polymers under irradiation is not entirely clear. Most of the color in irradiated polymethyl methacrylate can be discharged by heating, but only

to that temperature at which the radiolytically trapped volatile products start to distort the sample through expansion and diffusion. At this point, the residual discoloration of the specimen assumes secondary importance in view of the extensive bubble formation which completely destroys the optical clarity of the specimen.

This behavior emphasizes a point made earlier, that frequently post-irradiation treatment may bring about changes that were not immediately observable under the original environmental conditions.

The dependence of color on dose is frequently sufficiently reproducible and linear so that it may be used as a means of measuring absorbed dose. This is true in the case of unplasticized, unfilled polyvinyl chloride. Sheets of this material have been used for dosimetric measurements with enthusiasm and confidence by various workers.⁽¹⁷⁾ Two of the advantages that have been claimed is that the "developed" film provides the experimenter or process engineer with a permanent record, and, secondly, a dose distribution profile can be obtained in a single irradiation.

The formation of color in irradiated polyvinyl chloride has been attributed to the formation of long sequences of conjugated double bonds through elimination of hydrogen chloride. This explanation is not accepted by all. Regardless of the mechanism, however, it appears that one must

adhere to a standardized post-irradiation heat treatment in order to fully "develop" the color, and, according to some, to inhibit subsequent fading of the image with time. The point of immediate interest here is the post-irradiation heat treatment and its effect on the changes in optical properties of the material.

In brief, then, the optical properties of polymers may be altered by radiation in at least two ways, the appearance of discoloration or the development of inhomogeneities such as gas bubbles. The role of post-irradiation treatment is not a minor one in affecting the amount of either of these two processes which will be observed.

3. Electrical Properties. When a polymer is subjected to irradiation, a certain fraction of the absorbed energy is consumed in the process of ionization. Almost immediately a steady state concentration of electrons and ions will be established, and this must undoubtedly alter the electrical properties of the specimen. Indeed, ionizing radiations have been shown to induce direct current conductivity in some polymers. Interestingly enough, in some cases the effect persists even after cessation of irradiation - as long as 80 hours in polystyrene,⁽¹⁸⁾ for instance.

This direct current conductivity observed during irradiation is probably associated with mobile electrons generated by the absorbed radiation.

The persistence of the effect for long times after irradiation is attributed to a certain population of radiation generated electrons which, during the irradiation, became trapped at sites of low potential energy and which slowly escape from these potential wells and return to oppositely charged cations.

If the incident flux of radiation is essentially isotropic, the distribution of trapped electrons will be fairly homogeneous. On the other hand, if the incident flux of radiation is unidirectional, there will be developed in the irradiated sample a degree of electrical polarization. In such polarized dielectrics, depending upon the amount of polarization and its rate of dissipation, a variety of phenomena can occur, ranging from a controlled discharge, of utility in making dosimetric measurements,⁽¹⁹⁾ to a cataclysmic, destructive discharge, capable of shattering the sample or markedly affecting its physical properties.⁽²⁰⁾

To the extent that chemical composition changes during irradiation, such properties as volume resistivity, dielectric strength, arc resistance, dielectric constant, and dielectric loss may also be expected to change. Some data concerning changes in the first three properties with radiation dose are given in references (13,14,16). Very little work has been reported on the last two properties. It might be expected that measurable

changes in both dielectric constant and loss would occur, especially when thin films of polymer are irradiated in the presence of oxygen.

The measurement of those two quantities after a specimen has been irradiated presents no special problems. However, measurement during irradiation may lead to spurious results, especially if one does not account for the large changes in dielectric loss which occur in any air gaps between the measuring electrodes.⁽²¹⁾

4. Chemical Properties. As a result of the various chain scission reactions that can occur when a polymer is irradiated, the chemical composition of the specimen changes. Except in the case of the radiation induced dehydrohalogenation reaction, where it is known that the release of the first molecule sensitizes the adjacent segments to undergo the same reaction, most radiation induced chemical changes in polymers are probably randomly distributed throughout the specimen. Therefore, unless a very great amount of chemical change occurs, the chemical properties of the polymer generally are not observed to change to any marked degree.

A few notable exceptions to this have been reported and studied. As was indicated earlier, irradiation of a polymer in the presence of oxygen can lead to oxidation and peroxidation of the starting material. Taking polyethylene as an example, the carbonyl content of the specimen

increases with increasing absorbed dose. Although this does not affect many of the basic chemical properties of the material to any great extent, it does affect the surface properties sufficiently to render the material more printable by inks and dyes that depend on an oxidized surface for their retention.

In addition to this effect, the peroxides and hydroperoxides in the polyethylene can be utilized to initiate free radical processes, such as graft copolymerization of a vinyl monomer. The process is initiated by the thermal decomposition of the peroxides in the presence of a monomer.

When polyethylene is irradiated in a vacuum, its chemical properties are also altered by the growth of a trapped free radical population. Again, these free radicals can initiate reaction between the irradiated polyethylene and substances which are susceptible to free radical attack, e.g., oxygen, vinyl monomers, etc. Even when oxygen is present during the irradiation, a certain fraction of the free radicals which are formed may be trapped and become available for reaction subsequent to the irradiation.

These processes of oxidation, during and after irradiation, and radical trapping have been studied to a greater extent in polyethylene than in

other polymers. Undoubtedly the same situations arise in other systems and should be recognized if one is interested in making radiation resistance tests that are valid and meaningful.

This has been a brief treatment of the types of changes that occur in polymers under irradiation. Several fairly extensive compilations of experimental data exist in the literature, and these are listed in the bibliography under references (13-16,22,23). In addition to these references, and several other works which have appeared from time to time in the literature, attention is called to the existence of the Radiation Effects Information Center (REIC), operated by the Battelle Memorial Institute under contract with the WADC, Wright-Patterson Air Force Base, Ohio. This group, as its name implies, collects and collates and distributes information on the effects of radiation on various materials, and literally represents a storehouse of such information.

13.4.4 Exposure Methods

A. General Considerations

Having covered some of the basic aspects of the interactions of radiations with organic polymers, some of the methods of measuring the amount of energy absorbed by the specimen from the radiation field, and some of the factors which influence the ultimate results of these interactions, as well as some of the changes in properties that can be expected,

we are in a better position to turn to some of the problems involved with and arising from the actual exposure of the test specimen to the radiation field. Although exposing a sample to a radiation field has already been likened to exposing a material to many other environmental conditions, each type of radiation source entails its own peculiar requirements. In order to simplify the following discussion, let us confine our attention to exposing materials to gamma rays and x-rays, machine-accelerated electrons and neutrons from a nuclear reactor.

Since, as was pointed out in the previous discussion, the rate of change of a property with radiation dose may not be constant over the whole dose range of interest and since the rate of change in a given dose interval may vary markedly from substance to substance, it is recommended that several fixed levels of property change be measured in order that a more accurate picture of the property versus dose behavior be obtained. The fixed levels of property change will vary according to the property being measured, there being no general rule regarding the percent change that will be significant for all properties. This implies a certain amount of preliminary work before detailed accurate determinations are made. In many instances just such a rapid survey may be sufficient in itself, depending on the purposes of the investigations. Frequently, inferences

may be drawn from existing data on similar materials. However, as in most other investigations, such inferences are certainly not to be solely relied upon.

B. Size and Shape of Test Specimens

It is desirable to employ standard test specimens for the particular property that is to be measured; yet it must be recognized that in the case of radiation testing this may not be possible or economical. In the first place, depending upon the geometry of the gamma ray source facility, one may be seriously limited to a small useable volume for irradiated samples. This is especially true if the source is of a cylindrical shape, as many of them are, and only the central volume is utilized for irradiations. This obviously restricts the diameter of the container and hence the width of the sample. In addition, the length of the sample is also restricted since the distribution of the radiation field in the direction of the cylindrical axis will be reasonably uniform along only approximately the central 60 to 70% of the length of the source. This region of uniformity becomes increasingly reduced as the diameter of the source increases.

For the case of accelerated electrons, the beam delivered by any machine will have a certain profile. It is recommended that the specimen

be moved in a plane perpendicular to the beam so that it traverses the beam, and in such a manner that the ratio of exposure time to non-exposure time remains constant. Some machines are equipped with a beam scanning mechanism so that the beam may be swept back and forth across the specimen.

Problems in this area mount as the size of the specimen increases relative to the beam. Care must be taken, either by moving the specimen through the beam or the beam over the specimen, that all regions of the specimen are exposed to the same average total dose at the same average total dose rate.

An additional problem arises frequently with machine irradiations and is associated with the thickness of the sample relative to the penetration of the accelerated electrons. It may even be desirable to irradiate the sample from both sides. In any event, the thickness limitation is generally taken to be such that the variation in dose across the specimen should not be greater than 30%.

Reactor irradiations impose size limitations for a variety of reasons. In the first place, the specimens are generally loaded into a position within the core of the reactor, and hence only a restricted volume is available. Secondly, since reactor irradiations are generally more expensive

and time consuming, it is frequently the experimenter's desire to irradiate many samples simultaneously in the given volume. Also, the flux pattern within a reactor is a sufficiently varying parameter, especially in a research reactor, to make it advisable that sufficient samples be irradiated simultaneously in order that the results of the property tests have statistical significance.

Finally, there is a problem which is almost peculiarly that of reactor irradiations - the question of induced radioactivity. Although this should not present any great problem with pure hydrocarbons, the presence of fillers, plasticizers or even trace impurities can lead to high levels of induced activity. In addition to presenting a problem as to handling the irradiated samples, such a situation frequently demands extended periods of "cooling," which amounts to a post-irradiation storage time that may introduce additional effects in the measured properties of the material.

For all these reasons, then, it sometimes is necessary to use specimen sizes that do not conform to previously adopted specifications. Until miniaturized test specimens and procedures have been developed, the best expediency that can be offered is to use that size of specimen

which best suits the irradiation exposure conditions for both irradiated samples and non-irradiated controls.

C. Induced Radioactivity

To pursue the question of induced radioactivity a bit further, it can be said at the outset that the gamma rays from cobalt-60 and cesium-137 the most widely used sources of isotopic gamma ray energy, are incapable of inducing radioactivity in any material. Electrons from accelerators do not induce radioactivity in targets until the energy of the beam gets into the 10-Mev energy range or higher. Most of the currently available instruments are not as energetic as this. Thus, induced radioactivity in an irradiated sample is almost peculiarly a reactor problem.

Although it is difficult to make any specific comments about trace impurities in polymers, since the identities and masses of the impurities are not known, it can be said that the amount of impurity that can give rise to induced activity may lie at or below the level of detection by ordinary analytical means. It is only at the end of a reactor irradiation that the presence of these substances makes itself known.

With regard to conventional plasticizers, fillers, antioxidants, etc., it is possible to make some simple predictions on the basis of a few assumptions. The data in Table I are based on a total sample weight of

Table I

Induced Activity in Several Polymers and Various Common Additives^(a)

Polymer	Additive	Weight percent target nucleus ^(b)	Active isotope formed	Curies ^(c) of activity	
				Immediately	After 1 day
Polyvinyl chloride	—	13.8	Chlorine-37	5.2×10^{-1}	~0
Polyvinylidenechloride	—	18.0	Chlorine-37	6.7×10^{-1}	~0
Chlorotrifluoroethylene	—	7.4	Chlorine-37	2.8×10^{-1}	~0
Nylon-6	—	12.2	Carbon-14 ^(d)	5.3×10^{-4}	5.3×10^{-4}
—	Sulfur	0.21	Sulfur-35	2.0×10^{-2}	2.0×10^{-2}
—	Tricresylphosphate	0.075	Phosphorous-32	290	277
—	Calcium carbonate	0.016	Calcium-45	7.7×10^{-4}	7.7×10^{-4}
—	Titanium dioxide	0.030	Titanium-51	1.4×10^{-2}	~0

(a) Based on 10-gram polymer sample containing, where applicable, the conventional amount of a given additive, exposed for 10 days to a thermal neutron flux of 10^{14} neutrons per square centimeter per second.

(b) Based on molecular formula of monomer or additive and fractional isotopic abundance of target nucleus.

(c) A curie corresponds to 3.7×10^{10} disintegrations per second.

(d) Derived from nitrogen-14 interaction with fast neutrons, the flux of which is assumed to be equal to the thermal neutron flux used in the other calculations.

10 grams and a total integrated thermal neutron flux of 8.65×10^{19} neutrons per square centimeter, which corresponds to a 10-day exposure to a flux of 10^{14} thermal neutrons per square centimeter per second.

The chlorine-38 activity is composed of both very energetic beta and gamma rays, and, at the level of even 0.5 curies would constitute a radiation hazard. Such a sample would either have to be handled remotely, or it could be "cooled" for approximately six hours and then handled safely. Certainly, after a period of 24 hours sufficient decay would have occurred so as to render the sample completely innocuous.

The carbon-14 activity is made up of fairly weak beta radiation and would not constitute a radiation hazard. However, due to the very long half-life of this isotope an accumulation of samples is equivalent to an accumulation of activity over any period of time and hence adequate storage and disposal procedures would be required.

Sulfur-35 emits weak beta rays and a few hundredths of a curie of activity would not constitute a radiation hazard if the samples were handled with gloved hands or ordinary tongs or forceps. However, since its half-life is 88 days, adequate procedures for storing, handling, and disposing of an accumulation of samples would be required.

Calcium-45 is also a weak beta emitter and has a half-life of almost 200 days. Since the amount of induced activity under the assumed conditions is fairly low, this type of sample should not constitute either a radiation hazard or a storage problem. Safe disposal procedures, however, would have to be taken.

Titanium-51 emits both energetic beta particles and gamma rays, and has a half-life of approximately 6 minutes. Such samples as those considered here would have to be treated similar to those containing chlorine-38, although the former would not require much more than one hour of "cooling" to be considered safe to handle by ordinary means.

Of all the isotopes considered in Table I, phosphorous-32 is the one that constitutes the most serious hazard. It has just that proper combination of rate of formation, energy of beta particles (~ 1.7 Mev), and half-life (14 days) to yield a high specific activity of penetrating rays of long duration.

The shielding problem for phosphorous-32 is not a great one since the betas can be absorbed in as little as one centimeter of Lucite. However, the high level of activity and long half-life means that the samples cannot be handled directly and, after measurement, must be stored for a rather long period of time ($\sim 1/2$ year) before the induced activity has decayed to a negligible level. Over and above these considerations is an

extra precaution that must be taken in this instance. Assuming, as we have, that the phosphorous is in the form of an added plasticizer which may leach or bleed out of the specimen, the problem of contamination of equipment is probably more serious in this case than in the others considered.

It must be emphasized that Table I is not intended to be representative of all possible polymer formulations, but only typical of a few more common cases. Also, it must be restated that the presence of trace impurities can frequently overshadow any of the anticipated problems based on some assumed composition of matter. Therefore, it is recommended that representative small samples of any formulation be tested first, in order to define the actual problems that may arise in the case of the full-scale test samples. In this way, problems may be anticipated and measures may be taken beforehand to control any difficulties, either from radiation hazard during handling and testing, storage difficulties during and after testing, or contamination of equipment, area, etc.

D. Control of Experimental Parameters

The parameters which one generally attempts to control in a well designed experiment include temperature, pressure (or volume), surrounding atmosphere, applied stress, etc. In the more conventional type of

investigation, these, and other, parameters can be maintained constant or controlled in a known fashion by standard procedures. One of the simplest ways is to enclose the specimen in a container which may be heated electrically or heated or cooled by a circulating fluid; both pressure and atmospheric composition may be controlled by suitable inlets and outlets; and, in many instances, mechanical and electrical devices may be installed within the container to control the stress applied to the specimen. Such experimental techniques are well known and will not be dwelled on here any further. Rather, we will look at some of the problems involved in establishing and maintaining an equal degree of control over such experimental parameters in a radiation resistance test.

1. Container Materials. Each type of radiation which we are considering - gamma rays, accelerated electrons, and neutrons - impose their own restrictions on the type of container material which may be used to hold the experimental sample. In general, of course, the material of the container should be essentially transparent to the incident radiations and should be capable of remaining intact and performing its task for at least the duration of the experiment. Moreover, for neutron exposures, it is desirable that the container itself not become overly radioactive.

With respect to the transparency of the container material to the incident radiation, the more serious problems arise in the case of

accelerated electrons, especially if there are abnormal requirements on the mechanical strength of the envelope to withstand high pressures, etc. Thin-walled Pyrex glass ampoules are satisfactory for pressures at or below atmospheric, and will not greatly diminish the incident electron beam intensity. For pressures above atmospheric, thin-wall metal vessels must be resorted to. The disadvantage of enclosing a specimen to be exposed to accelerated electrons in a metal envelope is that the energy spectrum of the transmitted beam may differ significantly from that of the incident (usually monoenergetic) beam and, in addition, x-radiation will be generated in the metal envelope. This latter effect may be minimized by using metals of low atomic number, for instance, aluminum and titanium.

Most metals, excepting those of high absorption cross section, e.g., indium, cadmium, and boron, are fairly transparent to neutrons, as is ordinary Pyrex glass. On the basis of neutron absorption alone one would have a wide choice of container materials for neutron exposure experiments. However, although only a very small fraction of the incident thermal neutron flux will be absorbed in Pyrex glass, sufficient activation of the sodium in the glass will occur so as to render the container highly radioactive. The same can be said of stainless steel and many other substances that would be considered transparent to neutrons.

In the final analysis, samples which must be handled immediately or reasonably soon after removal from a reactor are generally enclosed in fused quartz or reactor grade (e.g., 2S, 21S, etc.) aluminum containers.

Frequently, however, one may use the neutron absorbing qualities of the container material to discriminate between neutron damage and gamma ray damage. For this purpose, the specimen is placed within a cadmium or indium container, or the container may be of quartz or aluminum which is then surrounded by cadmium or indium or some other material of high neutron absorbing characteristics. In this condition, the specimen will "see" primarily the gamma ray flux of the reactor, all neutrons above, below, or within certain energy ranges having been filtered out, depending on the composition of the metal surrounding the container. The effects of this exposure can then be compared to that of another specimen, without neutron filtering, placed in the same position within the reactor. The difference, to a first approximation, can be taken as the effects of the energy absorbed from the neutron field at that position.

Exposure of samples to gamma radiation imposes minimum restrictions as regards transparency of the container material to the radiation. Likewise, container materials do not become activated by the gamma rays conventionally employed. This leaves available practically any material,

with the major consideration being that of mechanical integrity under the experimental conditions employed.

2. Control of Temperature. The control of temperature of a sample being subjected to radiation can be subdivided into two categories. In the first category is the problem of remotely monitoring and controlling the temperature of a specimen at some temperature other than its surroundings. In the second category is the problem of heat dissipation from a specimen which is absorbing energy from the radiation field. To a great extent the latter category is unique to radiation exposures, and this category will be discussed first.

The dose rates presently available from isotopic gamma ray sources have a practical upper limit of approximately 10^7 rads per hour, which corresponds to a specific power absorption in the sample of approximately 24 calories per gram per hour. This is usually insufficient power to sensibly alter the temperature of the sample even in the absence of any provisions for heat removal.

The rate of energy absorption from the usual neutron fields are of approximately the same order of magnitude.

Hence, in the cases of both gamma ray and neutron exposures, the build-up of specimen temperature due to energy absorption of the incident

radiation, per se, is generally of negligible proportions. However, in the event that a chain reaction is initiated by the radiation, the exothermic heat of the chemical process may be sufficient to raise the temperature of the specimen. This generally does not happen in the exposure of polymers to radiation.

The dose rates available from some presently marketed electron accelerators are many orders of magnitude higher than those that have been considered so far. Dose rates of the order of 10^7 rads per second can readily be achieved, and, unless precautions are taken to cool the specimen, temperatures above the softening and melting points of many polymers can be quickly achieved. This problem can be minimized by scanning the electron beam over the area to be irradiated, so that although the instantaneous dose rate may be quite high, it is not maintained long enough in any one pass of the beam to seriously alter the temperature of the specimen.

In view of these remarks it is obvious that one must be much more mindful of possible temperature rises in the specimen being irradiated in the case of accelerated electrons than in the cases of the other types of radiations under consideration. It is therefore recommended that the temperature of electron-irradiated specimens be monitored, at least in a series of blank measurements.

Returning to the question of monitoring, and controlling the temperature of the specimen, in general, we find that many of the previously discussed problems again become involved in this area. Let us assume that we have our sample in a closed container, and then let us discuss the problem of maintaining the temperature of the specimen above or below the ambient temperature of its surroundings.

In the case of a gamma ray exposure, one can resort to either in situ electrical resistance heating of a fluid surrounding the container, or one can heat or cool a fluid external to the radiation source and circulate it into the field around the container that holds the specimen. In the absence of any reaction isotherm within the specimen, either type of temperature control system is adequate. The thermostating fluid, of course, must not too rapidly suffer radiation damage. Furthermore, the small extent that the fluid, its container, and even the container holding the specimen reduce the radiation field intensity can be measured by performing dosimetry at the position of the specimen in a blank run. Once again, the minimum number of problems in this regard arise when one is working with gamma rays.

For reactor irradiations many of the above techniques may be employed, with certain modifications and safeguards. In the first place,

remembering the general problem of induced activity in reactor irradiations, it is obvious that any electrical furnace that surrounds the specimen within the neutron field will become radioactive and, on removal of specimen and furnace from the reactor, a problem of radiation hazard must usually be faced. On the other hand, the circulation of an externally heated or cooled fluid must be treated with care, because the fluid, too, may become activated. Thus in addition to imposing a restriction on the nature of the circulating fluid with respect to its ability to withstand radiation without too much degradation or polymerization, the fluid should not contain elements of high neutron absorption cross section. Even if the temperature control fluid is chosen with great care with respect to neutron activation, it is recommended that the entire circulating system be doubly contained and surrounded by sufficient shielding outside the reactor so as to minimize any activation problems.

The control of temperature of specimens being subjected to accelerated electrons frequently presents a formidable challenge to the ingenuity of the experimenter. In general, in order not to disturb either the intensity or energy distribution of the incident electrons, it is preferable to interpose nothing between the incident beam and the specimen. With this restriction, the techniques mentioned above must be radically

modified. One expedient is to employ a secondary container which surrounds the specimen container on all sides except the one exposed to the electron beam. Through the former container a fluid at the desired temperature can be circulated. Or, if electrical resistance heating is preferred, an aluminum block which surrounds the specimen container as above may be employed. Both of these methods afford a reasonably good degree of heating or cooling.

If it is feasible to dispense with the primary specimen container, it then becomes possible to mount the specimen directly on a heating or cooling block, and, for thin specimens, achieve a more uniform temperature gradient along a direction parallel with the incident beam. However, if a metal block is employed, this may give rise to a problem of dose distribution across the sample due to the absorption of soft radiation back-scattered from the metal block.

3. Control of Pressure. Most reactions which proceed in condensed phases are not particularly sensitive to fairly large variations in pressure. This will also be true of the radiation processes occurring in polymers. A few remarks, however, are probably in order.

In the first place, hydrocarbon polymers, when irradiated, generally

form low molecular weight, volatile products. The rate of diffusion of these gases out of the specimen and hence their relative concentration both inside and outside the specimen will be a function of the total pressure surrounding the specimen. To the extent that these low molecular weight products within the specimen may either alter the physical aspects of the specimen and hence alter its subsequent reaction with radiation or be induced to react with the substrate by radiation, the pressure surrounding the specimen may be of some importance.

The control of pressure on the sample in an irradiation exposure does not cause any particularly unusual problems that have not already been implied in the discussion of container materials.

Whenever high pressure experiments are performed, there is always the possibility of failure of the container. If this should occur in a radiation experiment, certain added hazards may be involved. Discounting the obvious monetary sanctions against performing explosive experiments in a field of radiation in terms of material and equipment damage, the equally serious problem of contamination must be faced.

Spread of contamination will not occur if an explosion occurs in front of the window of an electron accelerator. When the window fractures,

vacuum in the accelerating tube is lost, the beam is attenuated, and serious damage to the accelerator may occur. This will not constitute a radiation hazard or radioactive contamination problem.

An explosion in front of or around a stainless steel encapsulated gamma emitting isotope may, if it is energetic enough, cause rupture of the encapsulation and spread of activity. Likewise, a similar explosion within the core of a reactor may cause serious damage to the reactor and the spread of contamination.

In order to minimize the possibility of these disastrous consequences, if very high pressures are employed, two safeguards should be taken. In addition to testing vessels under static pressures in excess of the highest pressures anticipated, vessels should also be fitted with rupture discs. As an alternative, or even in addition, double containment is desirable.

4. Atmosphere. If a closed vessel is employed to contain the specimen during irradiation, the initial establishment of a desired atmosphere can be readily achieved. Due to the evolution of radiolytically formed gases from the irradiated polymer and also to any reaction that may be induced between the atmosphere and the polymer or the radiolytically formed gases, the composition of the atmosphere may change. If the composition of the atmosphere

is critical in terms of the effect being studied, it will be necessary to continuously flush the interior of the container with fresh gases during the irradiation.

The only time that this procedure may produce some problem is if the circulated material has a high neutron absorption cross section and the irradiation is being performed within a reactor, although the gases that one would normally be circulating might be oxygen, nitrogen, or helium, none of which have high neutron absorption cross sections. In addition, in a reasonably rapid circulating system the average residence time will be quite low. However, in order to eliminate any problem in this regard, it is desirable to monitor the exit gases and to vent the exhaust into a large volume hold-up tank.

C. Data to be Reported

From the above discussion it should be apparent that many factors are interrelated in the net effects which are produced in polymeric materials that are subjected to irradiation. Firstly, there are those factors which are associated with the radiation field itself – type, energy, and intensity of the incident radiation, shape of the source and the resulting radiation field, the energy distribution of the radiation, etc. Secondly, there are factors which are inherent in the specimen itself – crystallinity, presence

of external or internal additives, temperature, stress, thickness and shape, etc. In addition, there are other factors which may or may not be important; the decision on their relevance or non-relevance must await further experimental work. In order that a worthwhile and useable storehouse of data in this area can be amassed, it is important that as much pertinent data as is feasible concerning the irradiation be given.

The "Tentative Recommended Practice for Exposure of Polymeric Materials to High Energy Radiation" (ASTM D1672-61T) specifies the following:

... "13 (a). The report shall include the exposure procedure used, including pertinent details such as temperature, medium, stress on specimen, post-irradiation storage, description of containers,

(b). Irradiation conditions shall be reported as follows:

(1) Type of radiation source and kind of radiation, including energy spectrum, if pertinent.

(2) Irradiation dose rate, rads per hour.

For accelerators list pulse repetition rate, duty cycle, and pulse peak energy; also list traverse cycle of specimen and "in-time" and "out-time."

- (3) Irradiation time.
  - (4) Total dose in rads.
  - (5) For reactors or other neutron sources report
neutron exposure as neutrons per square centimeter for thermal, epithermal, and fast neutrons.
  - (6) Reference to or description of irradiation dose measurement procedure.
- (c). Description of the test specimen size, shape, thickness, etc., shall be reported.
- (d). Description of the material tested, and as much of the following information as is available shall be reported:
- (1) Type and description of polymer. Non-irradiated properties: density, melting point, crystallinity, orientation, solubility, etc.
  - (2) Formulation and compounding data: fillers, plasticizers, stabilizing agent, light absorbers, etc., if available.
  - (3) Manufacturer, manufacturer's designation, trade name.
  - (4) History of material at time of exposure: age, storage conditions, etc. ..."

Items (1) and (5) in paragraph 13 (a) above imply, but do not explicitly state, the necessity of knowing the relative contributions of gamma rays and neutrons to the total absorbed dose in reactor irradiations. The experimental measurement or theoretical calculation of these contributions are not simple tasks, and have been attempted in only a few cases. That this is a problem of some importance can be appreciated from the following estimates. In a water-moderated reactor, approximately 96% of the radiation damage to organic insulating material has been ascribed to the gamma component of the radiation flux, with the remainder being caused by epithermal neutrons.⁽²⁴⁾ In a graphite-moderated reactor, on the other hand, the ratio is more nearly 1:1, with about 57% of the damage in organics being attributable to epithermal neutrons. These figures reflect the differences in epithermal neutron to gamma ray flux ratios caused by differences in the neutron moderation characteristics of water and graphite, and should be interpreted and used only in a gross fashion. The exact ratios will depend on, among other variables, the reactor core fuel geometry and the position within the core which is under consideration.

With these remarks in mind, it would be highly desirable to have included in the report of any radiation damage studies involving reactor irradiations such information as the type of moderator, spacing of the fuel

loading, and exact position within the reactor core in which the radiation studies were performed.

13.4.5 Present Status of Standard Test Methods

At the present writing, only one test method has received any official status, the "Tentative Recommended Practice for Exposure of Polymeric Materials to High Energy Radiation," designated ASTM D1672-61T. Other areas are being worked on by various groups within the American Society for Testing and Materials and other standardizing agencies. Some of these efforts have been directed along more specific lines, such as methods for measuring compression set in rubber due to radiation, tensile strength, etc. Most of these efforts become expanded versions of already accepted procedures for measuring these quantities in any other atmosphere, with added paragraphs that describe the procedures to be followed to achieve the exposure of the specimen or specimen and measuring device to the radiation flux.

Although D1672-61T specifically restricts itself in the opening paragraph to "...define conditions for the exposure of plastics and elastomers to high energy radiation prior to determination of radiation-induced changes..." and excludes its applicability to the problems of measuring these changes

during irradiation, the general principles outlined and followed in this procedure are applicable to either set of conditions. Care, however, must be exercised in taking into account several of the factors which have already been mentioned in this chapter, and some of which will be repeated now for emphasis.

Let us consider a few specific cases, such as the changes in tensile strength, optical clarity, and electrical resistivity during irradiation. The major problems which must be overcome are essentially those imposed by the necessity to make these measurements at some distance from the specimen under irradiation and under such conditions that at least part of the measuring device or instrument is simultaneously interacting with the radiation field. In this day and age, the first problem – that of making measurements remotely – is not a particularly difficult one. Remote tensile measurements can conveniently be made using strain gauges or similar devices, where the mechanical strain or stress can be translated into electrical quantities and the latter can be conducted from the sensor to a suitable indicating device at some great distance. Even optical measurements at a distance can be made by means of photocells, light pipes, etc. Of course, the resistivity measurements offer no problem in this respect.

Unfortunately, although the remote aspects can usually readily be handled by conventional techniques and devices, these same techniques and devices must frequently either be abandoned or drastically modified when they are applied to the testing of specimens during irradiation.

Let us take the first specific case mentioned above, that of making tensile measurements during irradiation, and let us assume that a strain gauge is to be used. In order to assess the effects of radiation on the gauge itself, one would have to run a blank determination with a specimen of known response, which presupposes a previous determination with a device of known response in a radiation field.

To a first approximation, it is probably reasonable to assume that metals do not undergo transient changes in mechanical properties in a radiation field. The measurement of the tensile strength and modulus of a thin metal strip in a radiation field (in the same position as will be used for the polymer sample) using a strain gauge of the same structure and materials as will be used for the polymer sample, but perhaps of higher capacity, should give one a reasonable estimate of any transient radiation effects in the gauge itself.

In addition, one might construct the apparatus so that the gauge itself is well shielded from either the gamma rays of an isotopic source or

the x-rays or accelerated electrons from a machine. This is not a feasible expedient in the usual reactor irradiation experiment.

The response of a photocell or the optical properties of most materials used for piping light will be seriously affected by radiation. For these reasons, the accurate measurement of changes in optical properties during irradiation is not a simple matter. For the usual type of optical measurement - clarity, transparency, color formation, etc. - one can generally obtain useful data by measuring changes in these properties as a function of dose. There is no reason to suspect that there will be significant transients in these properties in the radiation field.

However, if for some reason one is interested in such things as changes in phosphorescence or fluorescence in the field of radiation, such measurements can be made, but only with extremely elaborate instrumentation.

Finally, it is probably easier to make electrical measurements in a radiation field than any of those singled out above as illustrative examples. Once again, however, the effects of the interaction of the radiation not only with the electrical leads and components, but also the effects of radiation on surrounding gases, i.e., air, can be of importance. All of these factors

must be investigated and compensated for, if not instrumentally, at least by calculation.

It is probably partly because of these many and varied problems which arise in conducting tests in a radiation field that no standard test methods in this area have been developed. Most workers are satisfied in making measurements of changes in various properties as a function of dose, either ignoring the presence of transient effects entirely, or, in many specific instances, assuming that any transient effects which may be present will be of secondary importance. Finally, much of the work that has been done has had a specific application in mind and a test has been performed for that specific application only. In many instances, extrapolation of the method to other applications is prevented either through inadequate reporting of the method and data, or total lack of publication of results. Both of these factors, or attitudes, have contributed in the past to confusion and/or duplication of work.

When the limits of an experimental parameter are not definitely stipulated, the blanket statement of a particular order dependence of a given effect on that parameter can be worse than meaningless, even damaging. An example of this can be given in the generally accepted rule that, within

reasonable limits, the change in a physical property of an irradiated polymer is proportional to the total absorbed dose and essentially independent of the dose rate. That this may not be entirely the case has already been alluded to above in the discussion of the competition between dose rate and thickness of sample, where the latter variable controls the rate of diffusion of a substance such as oxygen to the interior of the sample. In this sense, performing a radiation resistance test at dose rates greatly in excess of those to be encountered in the anticipated application is similar to performing an accelerated aging test. In both instances one attempts to obtain useful and meaningful data in a foreshortened period of time. And in both instances one must establish the relevance of the accelerated test to the actual application.

In any new area, such as radiation testing is, the establishment of the relevance of any one parameter, or changes in it, is often a tedious task. Only the careful attention to detail and the complete reporting of results by the pioneers can insure the swift and sure blazing of the trails which lead to acceptable test methods.

In bringing this section to a close, it might prove interesting and instructive to consider briefly some of the applications that have been made

of polymers in and near radiation fields. For all of these applications, tests had to be made and the final choice of the material was based on an over-all evaluation of the behavior of several possible materials. The fact that reasonably satisfactory decisions can be made and working mechanisms can and have been built is both heartening and not particularly surprising.

Up to this point, an extremely conservative and perhaps, in places, a pessimistic view has been adopted. This attitude is not only justifiable but is demanded when one is considering standard test methods which will become the language of negotiation between producer and consumer. On the lighter side, however, a particular individual can, on the basis of roughly designed personalized tests, choose a particular material for a particular application from among the many which are available on the market. It is the latter type of testing procedure which underlies the choices indicated in the following table.

From the above tabulation, and from a more extensive look at the literature, it becomes increasingly apparent that, except for several exceptions, organic plastics are not generally used directly in radiation fields, especially if some other material is available for use. This is so because

Table II

Several Specific Applications of Organic Polymers
In or Near Radiation Fields

<u>Application</u>	<u>Requirements</u>	<u>Material</u>
1. Enclosure and support of capacitor and rectifier units of 480-kev Cockcroft-Walton generator. AC supply of 20 kvp at 800 cps charges each capacitor to 20 kv.	High dielectric strength; high volume resistivity; freedom from arc-tracking; low moisture absorption; good mechanical strength; transparency; low radiation fields.	Polymethyl methacrylate
2. Same as above.	Same as above, but substituting fire-resistance for transparency.	Polyvinyl chloride
3. Same as above.	Same as (1), but incorporating fire-resistance with transparency.	Polyvinyl chloride acetate
4. Window of accelerator tube. Must withstand pressure difference from atmospheric pressure on outside to 10^{-4} to 10^{-5} mm Hg on inner side.	Tensile strength; low mass; reasonable radiation resistance.	Mylar polyester film
5. "Rabbit" for short term reactor irradiations. Generally carried through guide pipe by pneumatic pressure.	Low mass; low coefficient of sliding friction; high purity and freedom from impurities; good radiation resistance.	Polyethylene

Table II (cont.)

Application	Requirements	Material
6. Viewing windows for areas of isolation of radioactivity.	Transparency; machineability; structural strength; very low radiation fields.	Polymethylmethacrylate Polyvinyl chloride acetate
7. Thermal insulation for low temperature facilities.	Light weight; good thermal insulation properties; high radiation resistance.	Polystyrene foam

even the most radiation-resistant substances of this class undergo serious damage to their physical properties at doses of the order of 10^9 rads, with the majority of the materials showing appreciable damage in the vicinity of 10^8 rads or less. Thus, as components of apparatus or devices which will be subjected to long-term or frequent short-term radiation doses, they are not particularly desirable over and above other substitutes, unless cost and convenience are overriding considerations.

On the other hand, there are many applications and uses which do not call for short term high dose rate or high total dose exposures, and in which polymers and polymeric components have other characteristics which dictate their use. In these instances, it becomes of importance to know the long term changes and transient effects which are produced in the polymer by the radiation. For these applications it is particularly important to have standard test methods so that specifications can be stipulated and met. These will be made possible by the careful and meaningful radiation testing by many workers. It is with this end in view, that radiation testing procedures should be designed, performed, and the data reported.

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Figure 1. Gas Formation in Irradiated Poly (methyl methacrylate).

First row: Unirradiated specimen; second row: (left to right), unirradiated specimen, specimen irradiated to 5×10^6 rads and specimen irradiated to 15×10^6 rads; third row: left to right, same as second row, except specimens heated to 150°C for one half hour. Note bubble formation in irradiated specimens, and its increase with increased dose.

Figure 2. Schematic Diagram of Faraday Cup.