SECTION 15. POLYMERS AND OTHER ORGANICS

15.1. INTRODUCTION

15.1.1. General

Organic compounds are sensitive to radiation by virtue of the irreversible chemical processes which take place when covalent bonds, in this case C-C and C-H bonds, are excited or ionised by irradiation. Frequently, the bonds are ruptured and the reactive fragments then form new compounds; a process known as radiolysis. One very common effect is the combination of hydrogen atoms from two ruptured C-H bonds to form hydrogen gas. This provides a simple measure of the type and degree of chemical reaction occurring in the organic material. The variety of other possible radiolytic reactions is so large that understanding them is a science in its own right. Naturally, the interpretation of effects in extended structures such as macromolecules (polymers, proteins, etc.) is particularly complex. In this section, we give a brief description of permanent radiation effects in different classes of polymer and discuss also radiation-induced photocurrents in cables, connectors and capacitors.

For electronic systems within spacecraft enclosures, the integrated doses are usually well below the threshold for serious permanent degradation in electrical and mechanical properties (a level of 10^7 rad or more). Also, the dose rates in the enclosures rarely produce photocurrents which affect the operation of equipment. However, some exceptions may be quoted:

- In space, polymers will be directly exposed to bombardment at the surface of the spacecraft and hence receive a high dose;
- Optical properties of some polymers may degrade at doses as low as 10^4 rad, especially in optical fibres.
- Polymeric transducers (e.g. photoconductors) may be extra sensitive to damage;
- Remote manipulators on spacecraft will have to work in especially severe environments, e.g. when changing the isotope charge in a power generator.

In ground installations (accelerators, nuclear-fuel handling, fusion reactors, etc.), radiation-induced effects in polymers will be encountered more frequently.

We will use the term "ionisation effects" to cover the broad range of excitation effects described above. Although damage to properties occurs in organic compounds, the mechanisms are very different from the collisional processes which cause "bulk damage" in electronic crystals. In organic materials, the chemical rearrangements occur after a chain of events which includes

ionisation in the form of low-energy electrons emanating from one high-energy particle or photon. This is why the effects of irradiation with different particles in polymers are qualitatively similar. The degree of damage can be predicted if the energy deposited in rads(C) (or Gy(C)) is calculated, the distribution of dose with depth and the influence of the ambient atmosphere being taken into account.

15.1.2. Bombardment of external coatings

The surfaces of spacecraft are bombarded by photons, electrons, protons and alpha particles. The numbers and energies of these particles are such that, in a skin layer of the order of 0.1 mm, chemical disruption and electrostatic charging effects are produced. The effects will be most pronounced in polymeric insulators and special research is done to ensure that thermal blankets and paints will withstand these effects over the required mission period.

15.2. LONG-LIVED DEGRADATION IN POLYMERS

15.2.1. Relative sensitivity

There are many books and handbooks on the long-lived effects of radiation on the engineering and chemical properties of commercial and pure polymers. Detectable degradation of the mechanical, optical and electrical properties of polymers usually appears at a dose value lower than 100 megarads (10^6 Gy). In some cases, doses less than this can actually improve toughness. Doses in the 3-megarad range are actually used for the routine sterilisation of surgical plastics. An exception to this is the case of fluoropolymers, some of which show catastrophic mechanical degradation if exposed in air at megarad doses. In most polymers, long-lived electrical leakage and increased dielectric loss are likely to appear well before mechanical degradation occurs. Different forms of radiation normally produce the same qualitative effects in polymers, namely the rupture of chemical bonds, the evolution of gaseous molecules, destruction of crystallinity and change of colour. All of these are ionisation effects. Not unexpectedly, the quantitative effect for different forms of radiation can be predicted by calculating the dose.

In polymers, the rupture of chemical bonds results in one of two sequels - cross-linking or scission. Table 15(1) lists the polymer types most likely to undergo cross-linking or scission, as the case may be. As the radiation dose increases, polymers which tend to cross-link show an increase in strength and toughness; however, they ultimately become brittle. Those tending to scission will become steadily weaker and may eventually liquefy. In both groups, hydrogen gas is evolved and colorations are produced due to complex side-reactions.

As may be imagined from the very large variety of plastic compositions, engineering plastics differ greatly from one to the other in radiation tolerance. The threshold dose for radiation damage varies by at least three orders of magnitude. Because the demands made on plastics in different applications are so diverse, it is often difficult to predict degradation effects except by considering individual cases and by radiation testing. Most of the "league tables" compiled are based on the measurement of tensile properties (see e.g. Schönbacher and co-workers, 1979-1982). Kapton, polystyrene, phenylsilicones, polyethylene, Mylar and epoxy are usually near the top of any such tables, while nylon, polyvinylchloride and all elastomers are usually near the bottom.

15.2.2. Polymers in electronics

Polymers are used very widely as sub-elements of electronic piece parts and circuits, e.g.:

- Epoxy resins are used in circuit boards as adhesives and "potting" or encapsulation compounds;
- Mylar, polycarbonate and polystyrene are used in capacitors;
- enamels are used for coil insulation;
- silicones and polyamides have many specialised electronic applications;
- PVC, PTFE and sulphones are used in sockets, connectors and wires.

15.2.3. Effect of additives and fillers

The long-lived effects of radiation on plastics can be strongly affected by the chemical additives used, especially by the quantity of antioxidant and plasticiser present. In both cases, the additives delay the onset of mechanical and other effects caused by oxidation, chain scission and embrittlement. Therefore, to increase radiation tolerance in plastics, we can specify plastics which are rich in these additives. Filler and pigments may sometimes alter the radiation-induced behaviour of the polymeric matrix.

15.2.4. Combined effects of stress (fields, vacuum, temperature) and ageing with irradiation

All plastics age on storage, owing to the evaporation or depletion of antioxidants and plasticisers. Hostile environments may accelerate radiation-induced effects. For example, if plasticisers vaporise in a plastic irradiated in vacuo, then radiation-induced embrittlement can be said to be accelerated by the use of vacuum; however, since oxygen is gradually removed from a plastic in vacuum, oxidative scission may be greatly reduced. Increased temperatures will encourage oxidative attack and outgassing. Exposure to an electrical field or light is also likely to accelerate these effects. PVC

cable material is more severely affected by radiation if irradiated slowly at increased temperature.

15.3. RADIATION TOLERANCE OF PLASTICS ACCORDING TO TECHNOLOGY

15.3.1. General

Engineering plastics are frequently grouped according to the manufacturing processes used and the function required. Broad process classifications are thermoplastics, thermosets and elastomers. Functional classifications include structural, insulating, coating, adhesive and optical. Demands on mechanical, electrical and optical properties vary very widely in these functional groups. Thus, the "bar charts" commonly compiled, which quote the effects of a given dose and use phrases such as "negligible damage" or "severe damage", can be misleading unless the properties measured and the tolerances allowed are specified. For example, bar charts suggest that few plastics show damage in vacuum at doses below 10^6 rad (10^4 Gy). On the contrary, long plastic optical fibres may be rendered useless by a dose of 10^4 rads (10^2 Gy). Therefore, we do not reproduce bar charts here, but give comments derived from them.

15.3.2. Thermoplastics

15.3.2.1. Structural plastics

A very large variety of parts of machines and electronics are made by the injection-moulding of thermoplastics. Radiation tolerance estimates related to the mechanical performance of about 35 different types of polymer are listed by Schönbacher. These indicate that very few thermosetting plastics show damage effects below a dose of 1 megarad(10^4 Gy). Those that may show damage at this dose include polypropylene, polyformaldehyde (Delrin) and PTFE. In the case of PTFE, the results quoted above are for irradiation in air. In vacuum, the tolerance of PTFE is increased tenfold. The most tolerant thermoplastics include polyimides (Kapton), Mylar and polystyrene. In all halogenated polymers (PTFE, PVdF, PVC), the possibility of release of halogen acid vapour must be considered. Rupture strength and elasticity are usually the properties of most interest in this group.

15.3.2.2. Plastic films as dielectrics and coatings

Thin, thermoplastic films (usually extruded or solution-cast) are often used at the limit of their mechanical or electrical strength in capacitors, varnishes or wrappings. Polyester (Mylar) and polyimide (Kapton) films are found to be very stable under irradiation. Little degradation is found at doses of 10^9 rads.

Polyethylene film develops an odour at about 10^7 rads and loses some mechanical strength at 10^8 rads; polypropylene is worse in this respect and becomes brittle. Halogen-containing polymers evolve acid vapours at dose values below 10^8 rads. For example, aluminised PVdF was found to maintain its strength at this dose, but etching of the aluminium occurred as a result of HF evolution. The polyvinylidene series of polymers is said to be less stable than the polyvinyl series.

15.3.3. Thermosetting plastics

Thermosetting plastics are usually formed by the mixture of a fluid prepolymer with an agent which initiates polymerisation (hardener, etc.). This produces highly cross-linked polymer. Composite structural elements, PCBs (printed circuit boards) and adhesives are made from this class of polymer. The manufactured formulas are very varied and, therefore, response to radiation is diverse. However, the radiation tolerance is often good because of the original cross-linking present. Epoxy adhesives lose only about 10% of their tensile shear strength at a dose of 10^9 rads in air. Epoxy glass laminates also show good performance at this dose level.

15.3.4. Elastomers

The need to maintain elasticity is of course the critical property in this group. The most stable elastomers are polyurethanes and phenylsilicones (usable to well above 10^8 rads). Nitriles, butadiene styrenes and natural rubbers also can be used up to 10^8 rads. Butyl rubber liquefies and neoprene evolves HCl at similar dose levels. Most proprietary polyurethane foam rubbers can be used as electrical encapsulant materials at a dose level of 10^9 rads in vacuum at temperatures between -85 and +250°C. Silicone and polysulphide sealants are probably less radiation tolerant.

15.4. RADIATION-INDUCED CONDUCTIVITY IN INSULATORS

The exposure of solids to ionising radiation produces current carriers in the form of electrons and holes. If the original conductivity is small, then the presence of carriers produces an observable increase in the background conductivity of the material σ_B. The increases follow the rules of normal conduction and we can thus calculate a "radiation-induced conductivity" (RIC) value R. Ideally, this will increase instantaneously to a steady level when exposure starts and decay when it stops. If R is large and σ_B is small, we can use the simple formula:

$$R_R = \frac{L}{\sigma_R . A} \qquad \text{.....15(i)}$$

where L is the sample length, A is the sample area and R_R is the resistance of the insulator during irradiation (assumed to be very much greater than the background resistance).

We can say that a new resistor R_R appears in parallel with resistor R_B which represents the small background conductivity.

The expected magnitude of this new resistor R_R can be found from the curve in Fig. 15.1. The ideal radiation-induced response of a polymer is given by the curve:

$$R = 10^{-18} \cdot \sigma_R D \qquad \text{.....15 (ii)}$$

where D is the dose rate in rad min^{-1} and R is the response in $ohm^{-1} .cm^{-1}$.

The measured results for many polymers lie about the curve and the linear formula may be used for approximate predictions of RIC. The photocurrent I_R is of course calculated from R_R by Ohm's Law. For some polymers, the dependence of R_R on D is however not linear, e.g. the points given in Fig. 15.1 for polyethylene show R_R to be proportional to $D^{0.7}$.

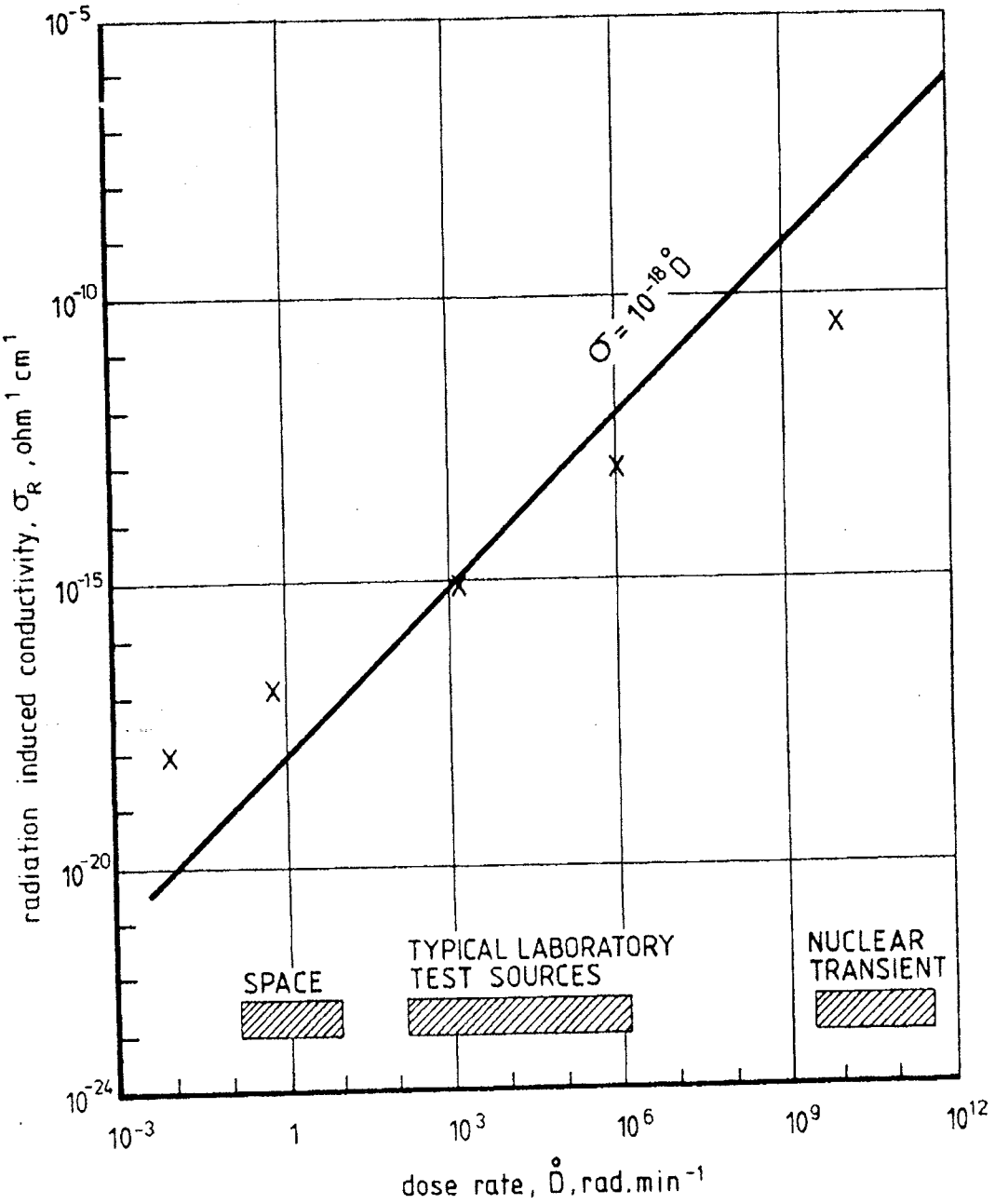
In Fig. 15.1, some representative dose rate values for space vehicles, fusion reactors and gamma pulses from nuclear bursts are marked on the bottom scale. The radiation-induced conductivity values for these three conditions are respectively 10^{-18}, 10^{-13} and $10^{-6}\ \Omega^{-1} . cm^{-1}$. We can see that, for a 1 cm cube of polymer, these represent R_R resistors of values 10^{18}, 10^{13} and $10^6\ \Omega$ respectively. As regards the practical impact, we can see that probably only in the last case would this resistance change produce any noticeable reduction in the performance of a polymer as an insulator. This is because the insulation resistance R_B will be typically of the order of $10^{13}\ \Omega$. Adding a resistor of the same, or higher, value in parallel will not produce a serious disturbance of the insulator's function.

The linear formula shown above (15(ii)) gives us a simple engineering approach to apply to leakage questions for space systems or ground installations. However, Fig. 15.1 shows us that it may not give the "worst case" RIC value for low dose rates.

15.5. SUMMARY

Radiation effects on polymers include permanent degradation and transient conductivity. In spacecraft, internal plastics should not normally be severely affected mechanically or electrically, but optical and other electronic properties may be changed. At the spacecraft surface, heavy particle bombardment may have severe effects on plastic sheeting or coatings.

The commonly published bar charts refer mainly to effects on mechanical properties, not to electrical or optical effects which may be more severe. In engineering terms, designers should recognize that polymeric materials in special high-performance uses may be subject to radiation-induced degradation and, as in the case of electronic piece parts, this should induce them to carefully scrutinise plastic items intended for such use.



(The crosses show an exception, polyethylene)

FIGURE 15.1 - PREDICTION CURVE FOR RADIATION-INDUCED CONDUCTIVITY IN MANY POLYMERS

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