Behaviour of Organic Materials in Radiation Environment

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Extended abstract

Introduction

At the European Organization for Nuclear Research (CERN) several high-energy particle accelerators and storage rings as well as the associated physics detectors have been in operation for more than 40 years. All materials and components in these apparatus are exposed to ionising radiation, and radiation damage is observed. From the very beginning, attention has been given to the effects of ionising radiation on polymeric-based components. For a safe and reliable operation, the radiation behaviour of most of the components is tested prior to their selection. Radiation-resistance tests are performed on a routine basis on magnet-coil insulations, on cable-insulating materials and on structural composites; mechanical tests are carried out in accordance with the IEC 544 standard. Moreover, electrical properties of high-voltage insulations and optical properties of organic scintillators and wave-guides are also studied. For these components, transient effects have also to be taken into account. At dose rates and dose levels encountered around particle accelerators as well as in space, metal alloys and ceramics do not suffer from any radiation damage or particular ageing. Our long-term experience has pointed out many parameters to be taken into account for the estimate of the lifetime of organic components in radiation environments. A large amount of results are published in the form of catalogues for a large variety of commercially available compounds and components.

Primary radiation effects on polymers

As in any material, ionising radiation induce excitation and ionisation of molecules, this leads to a reduction of the resistivity. Electric charges may accumulate in organic insulators irradiated with charged particles. Due to the type of physico-chemical bonds in polymers, several permanent modifications may happen: main-chain scissions, cross-linkings and changes of side groups. From cross-linking a three dimensional network is created in thermoplastics. Cyclisation and changes of side groups lead to the formation of unsaturations and gas evolution. Depolymerization or "unzipping" and phase changes (crystallinity) may also be observed. Some additives become radioactive when irradiated with neutrons or high-energy particles.

Ageing of organic materials

Ageing is the irreversible loss of properties of a material submitted to its environment; it has to be distinguished from the transient change due to a temporary external stress. Ageing always results from a change in the intimate physico-chemical structure. All of the ageing factors depend on the environment. Some may seem to be inherent to the materials which change (evolve) with time because they are not in a stable thermodynamic state. When materials are used as components, they are subject to environmental conditions, and they inevitably age. In polymeric materials, additives such as organic or mineral fillers, and stabilisers such as antioxidant and UV protectors, may also be modified and/or eliminated with time; they usually change the mechanisms and the rate of ageing.

In some cases, a side effect of gas evolution is that the evolved gas can be poisonous and/or corrosive, this may induce further degradation of the component itself as well as of surrounding components. This may be the case, for example, of PVC producing HCl, and of some fluorocarbon used as cooling fluids where

hydrofluoric acid may be produced, this may corrode the tubing.
The surface of a polymer, or the integrity of a thin film may also be altered by the irradiation with heavy ions. This technic is used in a positive way for the fabrication of micro-membranes, but in the case of insulating films, this effect is a damage.

Monitoring of ageing

In order to understand the mechanisms of ageing, physico-chemical analysis have to be carried out. From the user's point of view, ageing has to be followed up by the measurement of one or several macroscopic properties. As materials are used as (part of) components, they have a (or more) specific function(s) requiring specific properties. It seems therefore logical to test the mechanical properties of structural materials, the electrical properties of insulators, the optical properties of optical components, and so forth. But this is not always neither the easiest nor the best way. Experience has shown that it is often possible to assess the ageing of an insulator from the degradation of its mechanical properties. The standard 544 of the International Electrotechnical Commission recommends tomeasure the degradation of insulators from mechanical tests. Flexural tests are carried out on rigid insulators (thermosets, varnish) and tensile tests on flexible insulators (mainly thermoplastics and rubbers used for cable insulation). The standard also recommends that accelerated tests be performed after irradiations at dose rates greater than 1 Gy/s, and that more representative tests be performed after ageing conditions as close as possible to in-life conditions.
For the characterisation of radioinduced effects on cooling fluids, several methods are used: UV-Vis and FT-IR spectrophotometry, gas chromatography, scanning electron microscopy, etc.

Results of radiation-ageing tests – Factors of ageing

In particle accelerators, the most exposed organic components are the insulation of the magnet coils. Aromatic epoxy-resins with specially formulated hardener and accelerator are used; these compounds may today resist up to tens of megagrays. Well-prepared laminates and structural composites may resist doses a factor 10 higher. Due to the tight network, oxygen diffusion is impeded in these materials which present a very limited "dose-rate effect".
At CERN, the use of halogenated compounds is prohibited. Over the years, EPR/EPDM-based rubbers and polyolefin-based compounds used for cable insulation have been tested. The results of radiation tests have shown that polyolefin-based compounds usually present an important dose-rate effect. This is related to the presence of oxygen, it may be combined with a temperature effect. On the other hand, it appears from many results that the degradation of cable insulations does not depend on the radiation type.
Tests of insulating and structural materials after irradiation at cryogenic temperature have shown that there is no significant influence of the irradiation temperature on the radiation degradation of thermosets and composites, while the degradation of plastic films is even less severe as they are protected against oxidation.
Some experiments about the synergy between irradiation and mechanical stress have shown that rubbers and composites under stress are more sensitive to radiation and degrade faster.
Very strong synergistic effects between radiation and other parameters are observed in organic optical materials such as scintillators and optical fibres.
For fluorocarbon cooling fluids, a special care must be paid to alcanes and hydrofluoroalcanes, which are usually present as impurities, and of which the C-H bonds content opens the way to the reactive hydrofluoric acid evolution during the radiolytic process.

Conclusion

At CERN, for almost 40 years, emphasis has been put on the proper selection of organic insulators to be used in the radiation environment around particle accelerators. A particular attention has been brought on the dose-rate effect study. Other ageing parameters have been identified; they have a synergistic effect with radiation. From our experience, it is today possible to have a fair assessment of the lifetime of an organic material in a given radiation environment. Further studies are still ongoing about optical and luminescent materials and about organic cooling fluids.

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