Radiation Effects in Greases for Use in Facilities producing intense Neutron Fields

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Polymeric components are used in accelerator and target environments where intense neutron and gamma fields are present. Nine commercially available greases were selected to study their radiation-induced functional degradation for use in spallation neutron sources and in facilities producing radioactive ion beams. Grease samples were irradiated in the mixed neutron and gamma field of a nuclear research reactor up to several MGy of total absorbed dose. Methodologies for the irradiation and post-irradiation examination of grease samples are developed. The different degree of radiation tolerance of the tested samples was compared. Some of the greases showed dramatic radiation-induced changes of their physical properties, while others remain stable up to the highest values of delivered absorbed dose.

KEYWORDS: neutron damage, radiation resistance, polymeric materials, spallation materials, lubricant, grease

1. Introduction

Greases are used as lubricating components in target environments of the accelerator facilities for the production of spallation neutrons or radioactive isotope beams. The European Spallation Source (ESS), currently under construction in Lund, Sweden will use a 5 MW primary proton beam to produce neutrons for scientific research \cite{1}. A 2 GeV proton beam will impinge on a rotating tungsten target to induce spallation. A fraction of the spallation fast neutrons could leak from the target area and reach the drive unit, a system devoted to the control of the target rotation. An accurate control on the target rotating drive unit is crucial for a reliable target operation. Stable rotation and precise positioning of the target are provided by a number of components that need lubrication.

The Selective Production of Exotic Species (SPES) facility, currently under construction in Legnaro, Italy will use a 8 kW primary proton beam with 40 MeV energy and 200 \(\mu\)A current. The beam will induce fission in a uranium carbide target at an expected rate of \(10^{13}\) fission reactions per second to produce radioactive beams \cite{2}. The SPES target system has a limited lifetime of 14 days and will need to be regularly replaced. Due to its very high radioactivity, it will be handled by an automatic remote control system including moving components such as bearing, shafts and slides, that require lubrication.

Polymeric materials are in general much more sensitive to radiation than metals \cite{3}. The literature about the radiation resistance of greases is scarce, especially regarding the neutron
Table I. The commercial greases selected for irradiation and testing.

| Product codename | Producer | Base oil | Thick. | Rad. tolerance | Cons. NLGI |
|------------------|----------|----------|--------|----------------|------------|
| G1               | Chemours | PFPE     | PTFE   | 1 MGy          | 2          |
| G2               | Klüber   | Mineral  | Li     | ——             | 2          |
| G3               | Klüber   | Mineral  | Polyurea | ——         | 2          |
| G4               | Lubcon   | Mineral  | Li/Ca  | 1.2 MGy        | 0          |
| G5               | Lubcon   | Polyglycol | Li    | ——             | 2          |
| G6               | Moresco  | PPE      | PC     | 15 MGy         | 1          |
| G7               | M&I Materials | Hydrocarbon | —— | 1 MGy       | ——         |
| G8               | Schaeffler | Mineral | Mixed | ——             | 1-2        |
| G9               | THK      | Mineral  | Li     | ——             | 2          |

damage. Existing data do not provide sufficient information for the selection of commercial products to be used for the construction of the ESS and SPES facilities or for the maintenance and upgrade of other high-power accelerator facilities and neutron sources. Moreover, the scientific and industrial communities do not have a univocal viewpoint on the radiation resistance of polymeric materials. For these reasons, experimental radiation resistance tests of candidate products for use in high-power environment where neutron radiation dominates are necessary. Irradiation and testing methodologies have been developed in the last years, dedicated to the selection of elastomeric O-rings to be used in the SPES project [4, 5]. The objective of this study is to examine nine commercial greases for selection for applying to use in ESS and SPES facilities [6].

2. The irradiation facility

Grease samples were irradiated in the Central Thimble (CT) facility of the TRIGA Mark II research reactor of the University of Pavia, Italy. The CT is a pipe reaching the centre of the reactor core. At the maximum nominal power of 250 kW, the total neutron flux at sample irradiation position is \(1.72 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}\), with a fast neutron component \(4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}\) and a total photon flux \(1.72 \times 10^{14} \text{ ph cm}^{-2} \text{ s}^{-1}\) [7].

Nine lubricating greases of different chemical composition were selected. Samples were provided by major producers including Chemours, Klüber, Lubcon, Moresco, M&I Materials, Schaeffler and THK. Table I reports the most relevant information about the selected grease. These samples were irradiated in the mixed radiation field of the CT [6]. Exposure times for grease samples range from 10 minutes to 10 hours, corresponding to total neutron and photon fluences up to a maximum of about \(6.19 \times 10^{17} \text{ n cm}^{-2}\) and \(5.94 \times 10^{17} \text{ ph cm}^{-2}\), respectively.

3. Radiation Damage in Polymers

Polymeric materials have a complex structure made of long molecular chains of different lengths which can be entangled and cross-linked. Polymers can exist in crystalline state. However, the ordered arrangement involves long molecules while for metals it involves atoms. Due to this structural complexity, only partial and locally ordered structures can be found in polymers. Polymers show different degree of crystallinity, ranging from totally amorphous to almost entirely crystalline [8]. On the contrary, metallic materials generally have an ordered
lattice structure. For this reason, radiation damage in metals is often related to the number of induced displacements per atom (dpa).

Greases are complex multi-phase systems consisting of base oil, thickener and other additives. The interaction among them gives the grease its gel phase [9]. The physical and chemical structure of greases is much less ordered and regular compared to a metallic lattice. For this reason, dpa does not quantitatively describe the degree of radiation damage in greases adequately.

Indeed, fast neutrons interact with greases mainly via elastic scattering, transferring energy to recoiling nuclei. The energy transfer is higher on lighter nuclei and, for this reason, the absorbed dose is highly dependent on the composition of the irradiated grease. The hydrogen content plays a major role in this process. The amount and typology of the interactions produced in the grease by the displaced secondary protons depend on their energy as well.

Underlying mechanisms of radiation interaction in polymers and greases and their dependence of the radiation type are not yet fully understood. In this regard, it is difficult to choose an uncontroversial parameter to be correlated to the degree of radiation-induced damages. The total absorbed gamma dose has been conventionally used to specify the radiation tolerance of polymers, in the scientific and industrial communities. In the present study, we chose to correlate radiation damage in greases to the total absorbed dose delivered by neutron and gammas, and to the total fluence of neutrons and gammas. The total absorbed dose should serve as a good parameter, which can be directly compared to already existing radiation tolerance data on polymers in gamma radiation fields. Considering that the total absorbed dose does not fully explain the underlying radiation damage mechanisms, the damage correlated to particle fluence provides a complementary information for further studies.

4. Dosimetry Calculations

Dosimetry measurements in the CT are complicated by the simultaneous presence of neutron and gamma radiation. A MCNP5 [10] Monte Carlo MC model of the whole TRIGA Mark II nuclear reactor was used to simulate the neutron and photon dose absorbed by each grease sample during irradiation. The radiation fields simulated by the reactor model have been validated by previous measurements of the neutron fluxes in the different irradiation facilities of the plant.

The composition of each grease in terms of carbon, hydrogen and nitrogen was measured by CHN analysis. Based on the CHN results, the accurate compositions of the irradiated greases were used in the MC model, to calculate specific dose rates for each grease. The hydrogen amount varies from 0.00% for a fluorinated grease to 14.13% for a mineral-oil based grease. The total dose rate for greases varies correspondingly from about 300 kGy/h to 900 kGy/h at the nominal reactor power of 250 kW [6].

The photon component of the total dose rate is about 270 kGy/h for all the greases, roughly irrespective of the light element composition. The neutron component varies more than one order of magnitude based on the hydrogen content variation. The grease radiation damage, when expressed in terms of total dose, takes into account the different interaction of neutrons with the different materials compositions.

5. Testing Methodology

Grease samples were irradiated at total absorbed dose levels ranging from 0.1 MGy to 9 MGy. Consistency, acidity, gas evolution and residual activity were measured on irradiated and non-irradiated grease samples.
Consistency is the property most commonly employed by producers and final users to define the overall grease performance [9]. The consistency evolution with increasing dose was measured in the present study as an indicator of radiation-induced functional degradation.

Consistency was measured using a semi-automatic quarter scale penetrometer. The instrument tip penetrates the flat surface of the grease for 5 seconds after a standard manipulation [11]. Results are expressed in tenths of millimetres of tip penetration or in NLGI grades. The NLGI grade is universally accepted to define a grease consistency. NLGI grades range from 000 (soft material and high penetrations) to 6 (hard solid-like material and low penetration).

6. Results and Discussion

Seven out of the nine tested greases showed a high functional degradation as a function of the total absorbed dose, related to a high consistency increase. G1, G4, G5 and G9 grease samples dripped from the testing instrument tip already below 1.0 MGy of total absorbed dose, showing a radiation-induced structural degradation [12]. G2, G7 and G8 grease samples showed the same behaviour at a total dose ranging between 1.0 MGy and 5 MGy. By definition, a grease should remain in place under gravity [9]. Hence, fluidisation is an indicator of a significant and critical modification of the grease structure and physical state. Fluidisation could be related to the radiation-induced cleavage of the thickener structure.

In this study, the radiation-induced functional degradation of grease samples was quantitatively described in terms of the consistency percent variation. The usability criterion for greases was set to a maximum change of 10% in consistency. For the most radiation-sensitive among the tested greases, 60% consistency increase was reported at 1.6 MGy. G3 and G6 grease samples showed a stable behaviour up to the maximum radiation dose of 9 MGy, reporting less than 5% consistency variation [6].

All the tested greases evolved a considerable amount of gas during irradiation. This was qualitatively reported by the increased pressure in the irradiation set-up. As a consequence, the grease sample moved significantly inside the set-up during irradiation, incorporating air bubbles and being displaced from its original distribution. The colour of some of the greases becomes manifestly darker. The grease having a high fluorine content developed acidic gases that corroded the surrounding metallic environment [6, 12]. Similar qualitative radiation-induced effects have been reported by R.O. Bolt and J.C. Carrol on different greases [3]. According to these observed phenomena, chain cleavage seems to be the dominant radiation-induced effect at the molecular level. In fact, it seems like the fragmentation of polymeric chains is responsible for the observed gas production.

The tested greases show a very broad range of sensitivity to radiation. The most sensitive greases showed more than 10% consistency increase already at 0.1 MGy of total absorbed dose, while the most resistant ones show stable consistency values up to about 9 MGy.

Based on the collected data, a meaningful correlation between chemical composition of greases and radiation sensitivity cannot be established. In fact, even greases with similar base composition showed very different radiation resistance. Moreover, the two most radiation resistant greases, codenamed G3 and G6 in Table I, have very different chemical compositions. G3 is based on mineral oil, while G6 is based on polyphenylether oil. For this reason, it is necessary to experimentally evaluate the radiation-induced degradation of specific products individually.
7. Conclusions

The data collected in this study highlight the importance of conducting neutron irradiations and post-irradiation examinations on polymeric materials to be used in neutron radiation environments. In fact, neutron and gamma mixed radiation significantly modified most of the tested products at total absorbed doses comparable to those expected in operation. A similar grease degradation in the ESS and in the SPES facilities could compromise the performance of bearings and of any other lubricated component. The collected results provide a useful input to the selection of products for the construction of new facilities and for the maintenance of the existing ones.

The dependence of the radiation resistance on irradiation parameters such as dose rate, radiation source type and energy spectrum has still to be further investigated. However, the present mixed field results can be compared with the gamma data that are available in research articles, technical reports and catalogues of commercial products. Relying on radiation resistance definitions based on solely gamma data for application in different radiation fields is in general hazardous and groundless. It can lead to an overestimation of the grease performance and operational lifetime.

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