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Characterization of a polyphenyl ether oil irradiated at high doses in a TRIGA Mark II nuclear reactor

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ABSTRACT

Samples of a commercially available polyphenyl ether (PPE) oil are irradiated in the mixed neutron and gamma radiation field of the Pavia TRIGA Mark II reactor, at irradiation doses ranging from 0.78 MGy to 7.8 MGy. The oil is a nuclear grade product, whose radiation resistance reported in the product specification is based on cobalt-60 gamma irradiation data. The collection of additional data in a nuclear reactor radiation field performed in the present work, is motivated by the need to use this oil in neutron-rich environments such as targets and accelerators.

The post-irradiation characterization of the oil samples here reported includes viscosity measurements, total acid number (TAN), Fourier transform infrared spectroscopy (FT-IR), gas chromatography (GC), gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy.

The presented results evidence a remarkable increase of kinetic viscosity with the absorbed dose. Differences in the radiation-induced viscosity increase are observed comparing the data collected in mixed neutron and gamma radiation with the previous ones collected in cobalt-60 gamma radiation. This result emphasizes the need of further studies on the dependence of the radiation damage on different radiation environments. A negligible increase of TAN is reported. The FT-IR, GC, GPC and NM[illegible] polymerization with increasing dose. The increasing molecular size is in line with the visc[illegible]

1. Introduction

Different types of organic materials are widely used in key functional devices of accelerators and high power targets, thanks to their broad spectrum of properties. However, their functionality is known to degrade in high radiation fields, depending on the absorbed dose [1]. Synthetic lubricants are among the most radiation sensitive non-metallic materials used in such devices. Despite their sensitivity, they are extensively used in the accelerator and target facilities such as the European Spallation Source (ESS) [2], the ISOL facilities [3] and the European Organization for Nuclear Research (CERN) [4] in intense mixed neutron and gamma fields. In particular, lubricants are used in many of the moving components in accelerator and target environments, which include vacuum pumps, neutron choppers, collimators, dumps and drive units of many mobile devices. The understanding of the radiation-induced degradation mechanism of the lubricants is fundamental to secure reliable operation of the accelerators and targets.

The studies on the radiation resistance of lubricants available in the literature were performed in the last decades, for the development of accelerators, aerospace technology, fusion and for nuclear power plants [5–10]. Most of these studies used gamma rays as the radiation source, identifying the total absorbed dose as predictor of radiation damage. It has been commonly believed that similar radiation effects would be induced by same dose levels of other types of radiation [5], though there is a lack of scientific clarification.

Radiation modifies the structure of organic materials inducing chain cleavage and cross-linking or polymerization of the molecular chains [1, 11]. These structural modifications lead to changes in the mechanical, rheological and chemical properties of commercial lubricants, eventually compromising their functionality in operation. Radiation damage studies are needed to select resistant commercial components to be used in high radiation areas, to estimate their lifetime and so reduce the risks and costs of failures and repairs. Radiation effects are the result

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of complex mechanisms, which can be largely influenced by the specific irradiation conditions, such as dose rate, radiation type, amount of available oxygen. As a consequence, the lubricant lifetime specified in terms of gamma dose could be misleading for their use in different radiation fields.

Among lubricating oils, a wide range of radiation sensitivities is reported. Polyphenyl ether (PPE) is considered one of the most radiation resistant chemical formulations to produce lubricating oils and greases [1,6,9,12,13]. The radiation resistance of organic materials is in fact correlated to the amount of aromatic structures in their molecular composition. Other factors, such as the specific manufacturing process and the presence of additives and thickeners in the case of a grease, can contribute in determining the overall radiation resistance of a commercial product.

In a previous study [14], radiation effects in nine commercial greases were investigated after irradiation in reactor mixed neutron and gamma radiation, for their use in the surroundings of high-power targets. Some of the greases experienced dramatic radiation-induced effects at about 0.1 MGy absorbed dose only. Two of them, including MORESCO's 'MORESCO-HIRAD RG-42R-1' grease, remained stable up to about 10 MGy of dose. RG-42R-1 grease is realized with two main components: 'MORESCO-HIRAD RP-42R', the PPE oil here investigated (referred to as RP-42R in the paper), and an inorganic thickener.

In the present work, the radiation effects on RP-42R oil are investigated using mixed neutron and gamma radiation fields available at the research nuclear reactor TRIGA Mark II of the University of Pavia (Italy). The aim is to better understand the radiation damage mechanisms in the pure oil and to verify to which extent the radiation sensitivity of the oil is maintained when the oil interacts with a thickener to comprise the grease. The results are compared with the previous data collected by MORESCO in gamma radiation only. The study represents a first step in the efforts towards the understanding of the dependence of radiation tolerance of lubricants on different radiation sources and irradiation parameters [15,16], and it will find its applications to accelerator and high power target facilities.

The purposes of the present study are summarized as follows:

- to experimentally investigate the effects of mixed neutron and gamma radiation on a commercial lubricating oil at the structural, rheological and chemical level;
- to compare the radiation effects in the base oil RP-42R (irradiated in a pure and homogeneous state) and in the grease RG-42R-1, compounded with the same oil, after irradiation in the same mixed field irradiation conditions;
- to compare the radiation effects in the oil after irradiation in a mixed field with the radiation effects induced by gamma radiation alone from a previous study conducted by the manufacturer.
- to evaluate the radiation tolerance of a commercial PPE-based lubricating oil currently available on the market for use in high radiation areas.

This study has been developed in the framework of a collaboration between the University of Brescia (Italy), the European Spallation Source ESS ERIC (Sweden) and the MORESCO CORPORATION (Japan). Aim of the collaboration is the investigation of the radiation tolerance of commercial lubricants for application in high-radiation areas.

2. Description of the material

RP-42R is a polyphenyl ether (PPE) oil manufactured by MORESCO CORPORATION, a Japanese producer of lubricants. MORESCO specializes in the design and development of high performance products, including radiation tolerant lubricants [12,13].

At the structural level, the oil RP-42R is comprised of the aromatic group which is the main structure, and of the alkyl portion. The molecular structure of RP-42R oil has been designed to combine radiation resistance, provided by the aromatic structure, and the requirements on the temperature dependence of viscosity, provided by the alkyl portion.

Table 1
Elemental composition of RP-42R in weight percent as obtained with CHN analysis [17].

	C %	H %	N %	Others %
RP-42R	85.48	10.16	0.00	4.36

Table 2
Irradiation conditions in the CT facility of the TRIGA Mark II nuclear reactor of the University of Pavia working at the nominal power of 250 kW.

Irradiation facility	Neutron ϕ cm^{-2} s^{-1}	Fast neutron ϕ cm^{-2} s^{-1}	Gamma ϕ cm^{-2} s^{-1}	Temp. °C	Atm
CT	1.72 10^{13}	3.80 10^{12}	1.65 10^{13}	50–70	Air

The oil is declared as radiation resistant up to 15 MGy of dose. The declaration is based on the characterization of the oil irradiated with gamma radiation using a ^{60}Co gamma source. Few lubricating oils available on the market have a declared radiation tolerance higher than 10 MGy.

The carbon, hydrogen and nitrogen composition in RP-42R have been measured by CHN chemical analysis. The results, reported in Table 1 were used to simulate the composition of the materials for dosimetry calculations as reported in Section 4. The measurement errors are contained in the second decimal figure of the quoted results.

3. Irradiation conditions

RP-42R oil samples are irradiated in the main irradiation facility of the TRIGA Mark II nuclear research reactor of the University of Pavia, Italy. The Central Thimble facility (CT) is an in-core irradiation channel reaching the middle of the fuel elements. A mixed neutron and gamma radiation field is present in the CT.

Different reactions occurring in the reactor core and in the reactor materials generate the radiation fields in the CT. Nuclear fission is the main source of neutrons and photons. Photons are mostly produced by fission reactions and by the decay of fission products, referred to as prompt and delayed photons, respectively. An additional minor gamma component is present due to radiative capture reactions occurring in the reactor materials [18].

Neutron and photon fluxes in the CT are calculated using a model of the reactor realized with the Monte Carlo radiation transport code MCNP5 [19,20]. Table 2 reports the most relevant parameters in a reference irradiation position of the CT. In the present work, fast neutrons account for energy higher than 0.5 MeV.

The neutron spectra in the CT, in different possible configurations were measured in previous experimental studies [21–23]. The simulated neutron spectrum shows a satisfactory agreement with the measured one and, for this reason, simulations are used in the present work as reliable representation of the experimental conditions.

The simulated gamma flux takes into account the photons originating from fission and from radiative capture of neutrons on the reactor materials. The delayed photons produced by the decay of the fission products are not simulated. The gamma flux reported in Table 2 does not take into account this component. Data collected on TRIGA Mark II reactors with a similar configuration suggest that this missing gamma component could represent up to 30% of the total gamma flux [24].

In the present work, the reactor was operating steadily at the maximum nominal power of 250 kW.

The neutron energy spectrum in the CT is characterized by two main components. The fast component is comparable to a typical spectrum originating from fission reactions. Another component of slower neutrons in the thermal and epithermal energy range is present as well, originating from the moderation occurring in the reactor materials.

Table 3
Calculated dose rate for RP-42R in the CT at nominal power of 250 kW [17].

Component	Dose rate kGy/h	Fraction %
Neutron	520	67%
Photon	260	33%
Total	780	100%

Table 4
RP-42R oil: irradiation campaign.

Irradiation time (h)	1	2	5	10
Total dose (MGy)	0.78	1.56	3.90	7.80
Neutron fluence (cm^{-2})	6.2 E16	1.24 E17	3.10 E17	6.20 E17
Photon fluence (cm^{-2})	5.9 E16	1.19 E17	2.97 E17	5.94 E17

4. Dosimetry calculations

In the present work, the total absorbed dose and the total particle fluence are used as reference quantities to evaluate radiation induced effects in RP-42R oil. The neutron and photon dose rate components absorbed by the oil samples irradiated in the CT facility are calculated using the Monte Carlo code MCNP5 [19], which simulates interaction processes of neutron and gamma radiation with materials.

The absorbed dose, especially the neutron component, critically depends on the composition of the irradiated material, which needs to be precisely simulated. The simulated composition of the oil in the Monte Carlo model is based on the CHN measurement reported in Table 1. The missing component, referred to as 'others', is assumed to be oxygen. This is compatible with the known chemical composition of the oil. RP-42R does not contain additives. Traces of other elements might be contained in the oil. However, their relevance in the dosimetry assessment is negligible and, as a first approximation, they are neglected.

The systematic error on the calculated quantities introduced by these hypotheses was estimated by varying the assumed composition in several ways. Since the neutron dose mostly depends on the hydrogen content, which is measured, this systematic error is lower than few percent.

Table 3 reports the calculated dose rate for RP-42R in the CT. All the dosimetry units refer to the reactor nominal power of 250 kW. The total dose rate is the sum of the gamma and neutron components. The neutron component dominates, representing about two thirds of the total. The comparison with other lubricants irradiated in the same conditions [14] evidences that the neutron dose rate is roughly proportional to the hydrogen mass content. This suggests that most of the energy is transferred by fast neutrons to hydrogen nuclei via elastic scattering. In fact, this process is very efficient on nuclei having a mass comparable with the one of the incident neutrons, as is the case for hydrogen. Moreover, the amount of transferred energy is proportional to the energy of the incident neutron. For these reasons, fast neutrons are the most effective in delivering dose to RP-42R in the CT.

By contrast, the gamma component is roughly independent on the specific composition.

Measurements on the neutron flux and on its gradient in a specific configuration of the CT have been recently performed [23]. The fluxes simulated with the MC code are in satisfactory agreement with the measured ones. The systematic error associated to the simulated total dose rate is estimated to be not higher than 20%.

5. Experimental methodology

5.1. Preliminary tests

Preliminary tests were performed on small oil samples to assess their general behaviour with dose. Both qualitative and quantitative tests were performed to develop an effective and safe irradiation set-up. Radiation-induced gas evolution was observed in the oil samples. To prevent the development of a critical pressure inside the irradiation set-up, the containers were perforated, to allow for air circulation during irradiation.

The residual radioactivity of the irradiated samples was measured. Radioactive nuclei are in fact usually produced as a result of neutron interaction with organic materials. Residual activation is mostly caused by the activation of metallic traces contained in the material. Given the purity of RP-42R oil, which is realized without additives, the residual activation of the irradiated samples was almost undetectable and its handling was not subjected to limitations according to the radiation protection regulation.

5.2. Irradiation set-up

The irradiation set-up was developed taking into account the very limited available volume in the CT facility. Only about 40–50 cm^3 per irradiated set-up can be used for sample irradiation. The CT is a cylindrical channel having an inner radius of about 2 cm only; cylindrical aluminium containers are filled with the samples and placed at the bottom of the channel to be irradiated.

Disposable commercial plastic syringes (20 mL) were used to irradiate oil samples. Each syringe was filled with a maximum of about 15 mL of oil. The tip of the syringe was sealed to contain the fluid. The syringes filled with oil were then placed inside the cylindrical aluminium containers used for sample irradiation.

5.3. Irradiation campaign

Oil samples were irradiated in the CT at the nominal reactor power of 250 kW for exposure times ranging between 1 h and 10 h. The irradiation times are detailed in Table 4, as well as the corresponding total dose, neutron fluence and photon fluence.

6. Characterization

Oil characterization was performed at the MORESCO Corporation laboratories (Kobe, Japan). The complete oil characterization consists of the six following laboratory tests:

- Kinetic viscosity;
- Total Acid Number (TAN);
- Fourier Transform Infrared Spectroscopy (FT-IR);
- Gas Chromatography (GC);
- Gel Permeation Chromatography (GPC);
- Nuclear Magnetic Resonance (NMR).

All tests are performed on samples unirradiated and irradiated at all the mentioned doses, to assess the evolution of the material as a function of the dose. The experimental techniques are detailed in the following Sections.

6.1. Kinetic viscosity

Kinetic viscosity measurements are realized according to JIS K-2283 standard [25]. Measurements are performed using a Cannon–Frenske viscometer. Oil samples of about 20 mL are required. The viscosity value is determined by the time required for the sample to flow under gravity in a specific capillary container. The system is immersed in a water bath at a controlled temperature of 40 °C.

Fig. 1. Oil samples at different irradiation levels, from unirradiated (left) to 7.80 MGy (right).

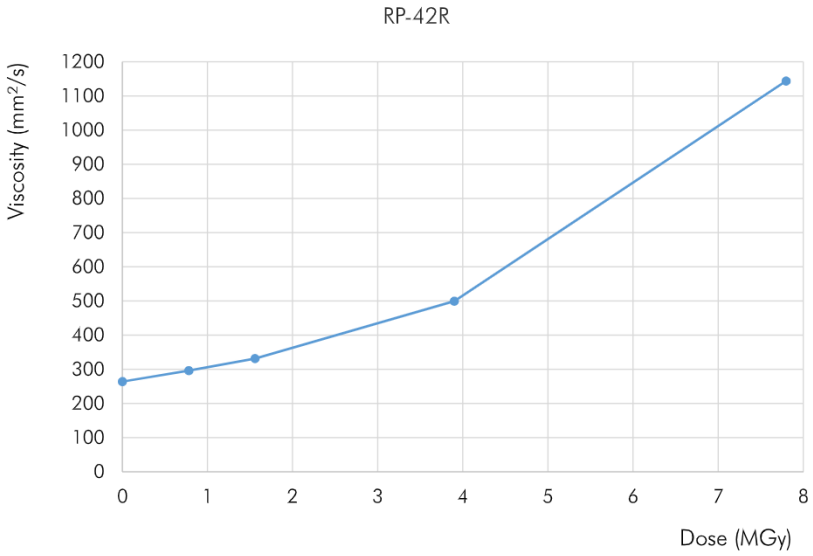

Fig. 2. Kinetic viscosity of the oil with dose. The line connecting the points is a guide for the eye only.

6.2. Total acid number (TAN)

TAN was measured according to JIS K 2501 standard [26]. Oil samples are dissolved in a mixture of 50% toluene and 50% iso-propylene alcohol. The amount of potassium hydroxide (KOH) needed to raise the pH of the solution to a reference value, pH 11.74 in this case, is used to evaluate the sample acidity. An automatic potentiometric titrator is used to measure the KOH mass per tested oil sample, expressed in mgKOH/g.

6.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is used to collect information on the chemical composition and structure of the sample. Spectra were collected using a spectrometer with an attenuated total reflection equipment (diamond crystal). On each sample 32 scans were collected at a resolution of 4 cm^{-1} ranging from 600 cm^{-1} to 4000 cm^{-1}

6.4. Gas Chromatography (GC)

GC is used to separate the chemical components of mixtures. GC spectra were collected using a chromatograph equipped with the Column HP-5, having dimensions ID 0.32 cm x 30 cm and film thickness of 0.25 μm. Helium at the pressure of 59.6 kPa, streaming at the linear velocity of 30.0 cm/s is used as the carrier gas. Oil samples are dissolved in normal-hexane or acetone, with a dilution factor of 10. The duration of a single measurement is 60 minutes, and the split ratio is 20. The column temperature, first held at 50 °C for 1 minute, is then raised at the rate of 10 °C/min to the maximum temperature of 320 °C, which is high enough to allow for a complete sample evaporation. 1.0 μL of solvent-diluted oil sample is injected when the column temperature reaches 320 °C and then it is held for 32 min for detection. The Flame Ionization Detector FID was used, at a temperature of 360 °C.

6.5. Gel Permeation Chromatography (GPC)

GPC allows the separation of the components of an organic sample based on their molecular size and provides information on the molecular weight distribution in the organic material. A chromatographer equipped with a KF-803l Column (Shodex diameter 8 cm x 3 cm x 3 cm connection) and a KF-G Guard column (diameter 4.6 cm x 0.1 cm) was used to collect the spectra. The column temperature is kept at of 40 °C. The oil sample is dissolved in a tetrahydrofuran (THF) with a dilution factor of 100, as the eluent. A volume of 100 μL of the eluent is injected onto the column at a flow volume of 0.7 mL/min at a pressure of 294 N/cm^2.

6.6. Nuclear Magnetic Resonance (NMR)

NMR allows the identification of aromatic rings and hydrocarbon chains in the molecular structure of the samples. A JNM-ECX400 spectrometer was used to collect the spectra. Measurements were performed at a frequency of 400 MHz. The oil samples were diluted in Acetone-d6 solvent with a dilution factor of 10.

7. Results

The oil samples experienced huge modification of their physical properties as a function of the dose. Some of these modifications can be appreciated by manipulation and visual investigation. As shown in Fig. 1 the colour of the samples darkened progressively with dose.

Fig. 3. Oil sample irradiated at 7.80 MGy poured from its irradiation set-up.

7.1. Kinetic viscosity results

Fig. 2 reports the evolution of oil viscosity as a function of the dose. Kinetic viscosity increases from 263.9 mm^2/s (unirradiated sample) to 1140.0 mm^2/s (sample irradiated at 7.80 MGy). Fig. 3 shows an irradiated oil sample being poured from its irradiation container. The flow of the samples irradiated at 3.90 MGy and 7.80 MGy out of their container was appreciably slower than the flow of the unirradiated ones.

7.2. TAN results

Fig. 4 reports the evolution of the TAN as a function of the dose. The TAN of the unirradiated sample is lower than 0.01 mgKOH/g, which is below the instrument's limit of detection. For this reason, this point is not reported in the graph.

The TAN shows a progressive increase with dose. TAN increases from 0.01 mgKOH/g (sample irradiated at 0.78 MGy) to 0.07 mgKOH/g (sample irradiated at 7.8 MGy). Despite the large relative increase with dose, the absolute measured values are very little and the TAN can be considered as almost negligible at all the investigated dose values. The TAN is accordingly considered as stable in the investigated dose range.

7.3. FT-IR results

FT-IR spectra collected on irradiated and unirradiated oil samples are shown in Fig. 5. All the spectra are comparable in terms of the position and of the intensity of the peaks. No significant radiation-induced variations are observed.

7.4. GC results

Fig. 6 shows the GC spectra collected on oil samples. The signal is displaced as a function of the measurement time. The position of the main carbon chains is evidenced in the bottom part of the graph.

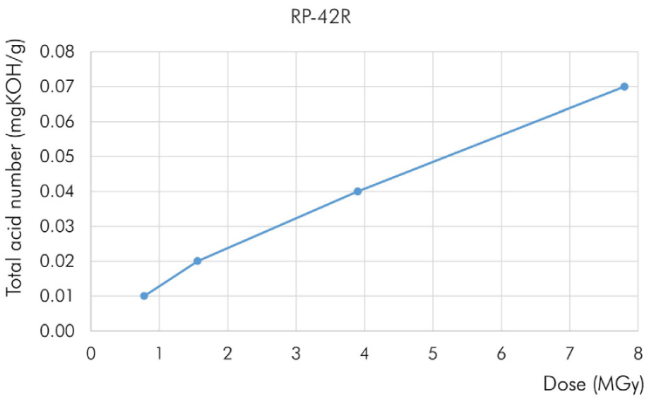

Fig. 4. TAN evolution of the oil with dose. The line connecting the points is a guide for the eye only.

The graph is divided in four sub-areas based on the duration of the test, corresponding to different weight fractions of the molecular chain distribution:

1. area between 5.0 min and 28.0 min;
2. area between 28.0 min and 38.5 min;
3. area between 38.5 min and 40.5 min;
4. area over 40.5 min.

Fig. 7 reports the signal corresponding to each area as a function of the irradiation time, expressed as a percentage of the total graph area.

Area 1 represents the lightest fraction of the oil molecular chains. This contribution is negligible in the unirradiated oil, while it shows an increase with dose up to 5% at the maximum dose. Area 4 represents the heaviest fraction of the oil molecular chains. It shows an increase with dose, from 20% (unirradiated oil) to about 25% at the maximum dose.

Area 2 and area 3, which represent the main fraction of the unirradiated oil composition, show a corresponding decrease.

The unreacted fraction corresponds to the fraction of the oil that did not react during the test. Its contribution is negligible.

7.5. GPC results

Fig. 8 shows the GPC spectra collected on irradiated and unirradiated oil samples. The graph shows the oil molecular weight (MW) distribution, which is calculated based on polystyrene. A remarkable increase in the high MW fraction of the distribution is observed.

To analyse this quantitatively, the graph is divided in the following four areas:

1. area ranging between MW 200 and MW 600;
2. area ranging between MW 600 and MW 1500;
3. area ranging between MW 1500 and MW 2500;
4. area ranging between MW 2500 and MW 30000.

Area 1 and area 2 include two main characteristic oil peaks. Area 3 includes the high MW fraction of the unirradiated oil. Area 4 includes very high molecular weights, which are not present in the unirradiated oil.

Fig. 9 shows the four areas as a function of the dose, as a percentage of the total graph area. Area 1 accounts for more than 70% of the mass distribution of the unirradiated oil. This contribution decreases with dose, dropping below 50% at 7.8 MGy, the maximum dose. Area 2 decreases from about 25% (unirradiated) to about 20% at the maximum dose. Area 3 increases from 5% (unirradiated) to about 15% at the maximum dose. Area 4, which is not present in the unirradiated oil, increases up to 20% at the maximum dose, becoming a relevant

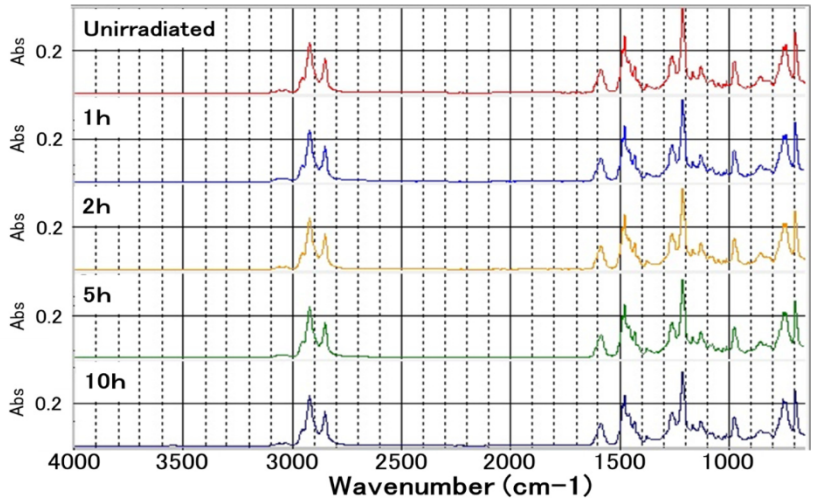

Fig. 5. FT-IR spectra of oil samples. From the top: unirradiated and irradiated at several dose values.

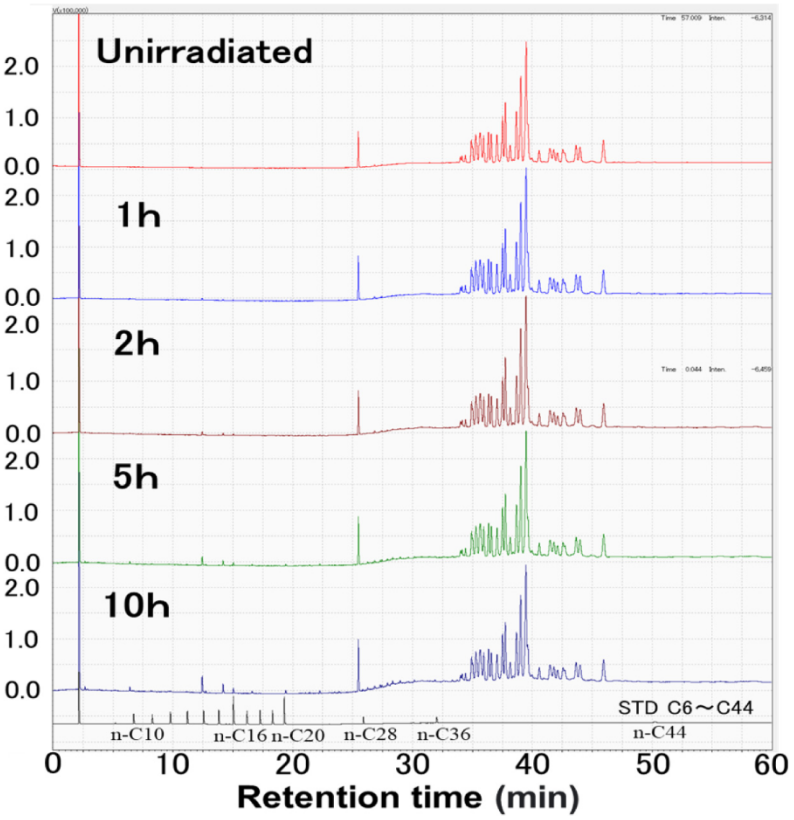

Fig. 6. GC spectra of oil samples. From the top: unirradiated and irradiated at several doses.

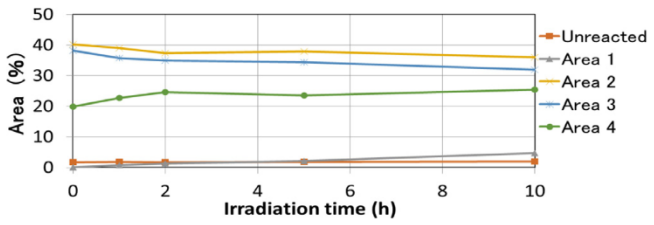

Fig. 7. GC spectra divided in four areas and displayed as a function of the irradiation time.

contribution to the total MW distribution. As discussed in Section 8.2, such an increase of very long molecular chains is crucial in determining the observed viscosity increase.

7.6. NMR results

Fig. 10 shows a sample of NMR spectra collected on the oil samples. It refers to a range between 8.00 ppm and 6.00 ppm. All the collected spectra are stable as a function of the dose. More detailed investigations not reported here evidence very minor radiation-induced differences, associated with the removal of some aromatic rings and of some carbon chains from the main structures.

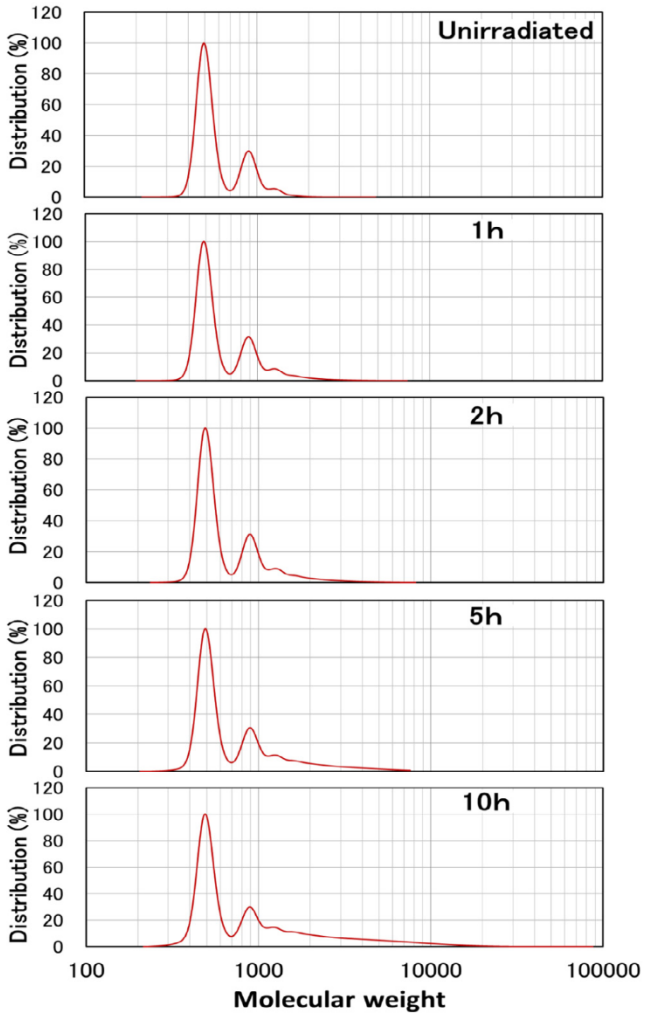

Fig. 8. Molecular weight distribution spectra obtained by GPC analysis. From the top: unirradiated and irradiated at several dose values.

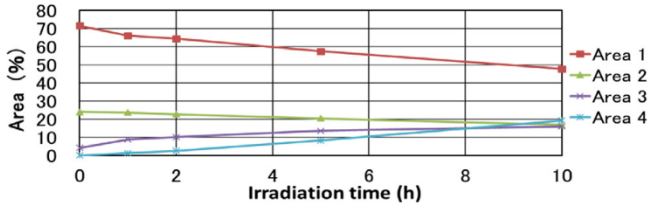

Fig. 9. Molecular weight distribution spectra obtained by GPC analysis divided in four areas and represented as a function of the dose.

8. Discussion

8.1. Structural modifications: polymerization

The results of the performed analyses provide direct and indirect information on the mechanisms of radiation-induced molecule chain cleavage and of polymerization in the oil structure. The GC results evidence a cleavage of the molecular chains of intermediate lengths, leading to the production of chain fragments. Some of these remain as smaller fragments, but the majority of them, as evidenced by GPC results, recombine, leading to an increase of heavier chains. Irradiation promotes the production of long molecular chains over MW 2500. Chains of this length are completely absent in the unirradiated oil, while they represent about 20% of the oil mass for samples irradiated at 7.8 MGy. In the explored irradiation conditions, polymerization is the dominant mechanism.

8.2. Viscosity increase and usability endpoint

The mentioned damage mechanisms impact on the rheological properties of the oil. A considerable radiation-induced viscosity increase is observed in the MGy dose range. The viscosity increase depends on the production of high-weight molecular chains due to the oil polymerization. Viscosity is considered one of the most important properties characterizing a fluid lubricant for mechanical applications. Viscosity variations can compromise the functionality of a lubricated mechanical component in operation and are an indicator of oil degradation.

A viscosity variation of 100% can be used as a general end-of-life condition for oil usability. This endpoint does not take into account the specificity of real life applications but allows for comparisons of degradation mechanisms. Based on this endpoint and using the data shown in Fig. 2, a dose threshold of about 4 MGy can be determined for the oil in mixed field irradiation conditions. It is recalled that the oil has a declared threshold of 15 MGy in gamma radiation, for the same endpoint. The possible reasons for this difference are discussed in the following Section.

8.3. Comparison with similar oils irradiated in different conditions

Polyphenyl ether oils are reported to remain stable up to dose levels ranging between 10 MGy and 100 MGy of gamma radiation [1]. Specifically, several aromatic oils were irradiated using ^{60}Co gamma in other studies on lubricants [6,12,13]. Other MORESCO oils having a composition similar to RP-42R were tested. Samples were irradiated at room temperature at a dose rate of 10 kGy/h in three different conditions: in air, in vacuum and in bubbling oxygen. In all the three investigated conditions, the viscosity increase of synthetic aromatic oils below 10 MGy is not remarkable.

The viscosity endpoint as defined in Section 8.2 for these other products can be interpolated using the data reported in [6]. In all cases it ranges approximately between 8 MGy and 30 MGy, which is a factor 2 to 8 times higher than the value found in this study for RP-42R. In another study conducted on RP-42R oil by MORESCO using gamma irradiation, the endpoint is reached at 15 MGy [27]. Fig. 11 shows the relative viscosity evolution as a function of the dose for samples irradiated in the present study and by MORESCO with gamma radiation. A much higher viscosity increase is reported, at equal dose levels, in neutron and gamma irradiation fields compared to gamma alone.

The reason for such a difference is still under investigation and is probably due to a complex synergy between several ageing factors. Considering that much lower differences are associated to the oxygen effect alone, the difference reported in Fig. 11 is probably caused by other factors as well. Neutrons might be more effective than gamma radiation alone in inducing radiation effects. The present data challenge the generally accepted hypothesis that equal levels of absorbed doses induce equal damage in organic materials regardless of the type of radiation and other irradiation parameters.

The use of the total dose as the unique indicator of radiation damage in materials is not completely legitimate. In fact, radiation damage depends on several parameters as the radiation type and energy spectrum, the dose rate, the diffusion of oxygen in the material, the presence of mechanical and thermal stresses, etc. These ageing factors act in

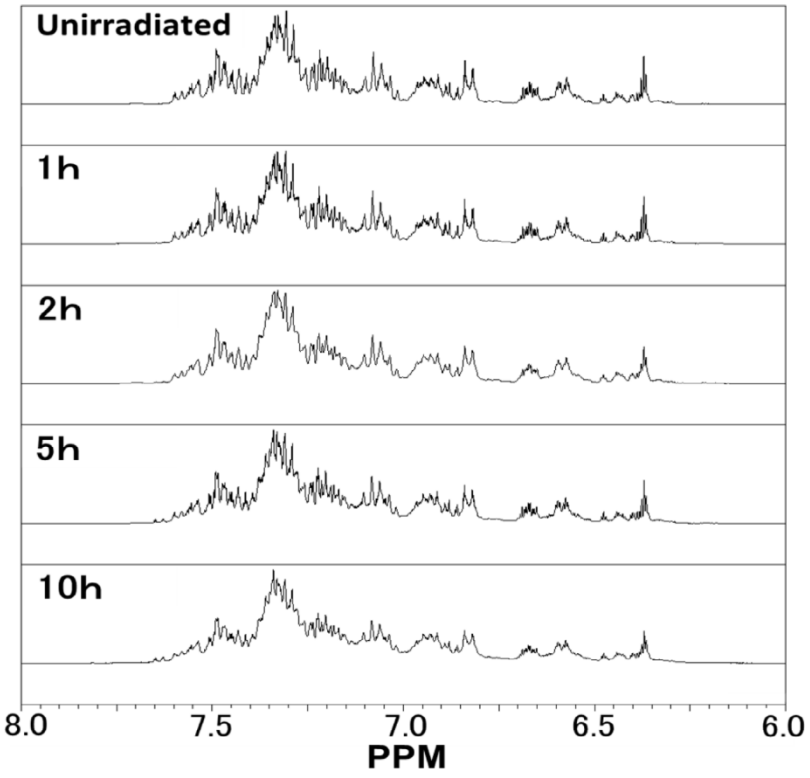

Fig. 10. NMR spectra of irradiated and unirradiated oil samples. From the top: unirradiated and irradiated at several dose values.

synergy to determine the resulting damage. The specific combination of the irradiation conditions is crucial in determining the dominating process and effects.

8.4. Oxygen effect

FT-IR spectra are collected on oil samples in this study, especially to detect and quantify the oxidation deterioration. The peak associated to oxidation was not observed in the present study, meaning that radiation did not induce oxidation. This seems to be confirmed by the TAN results as well. The absence of oxidation could depend on the very high dose rate used for the irradiation. In fact, the role of oxygen as a damage mediator during irradiation is generally less relevant for very high dose rates. When the radiation-induced oxygen consumption in the material is faster than its replacement via oxygen diffusion, the irradiation happens in hypoxic or almost hypoxic conditions, which are generally comparable to vacuum irradiation. The lack of oxidation might be an indicator of hypoxic irradiation conditions.

According to the TAN results, only an almost negligible amount of acid is developed during irradiation. This supports the hypothesis of the hypoxic irradiation conditions due to high dose rate. In fact, for all the irradiated aromatic oils reported in [6], the TAN increased significantly with dose when the oil was irradiated in bubbling oxygen, while it remained almost stable with irradiation in vacuum and with irradiation in poorly oxygenated conditions. For these reasons, due to the very high dose rate, the irradiation conditions used in the present study mimic a hypoxic or almost hypoxic condition, with very limited oxygen effect.

8.5. Chemical stability

The FT-IR and the NMR spectra collected showed no significant evolution with dose. This confirms the overall great stability of the oil structure. Only minor modifications are reported, confirming the outstanding radiation resistance of polyphenyl ether oils.

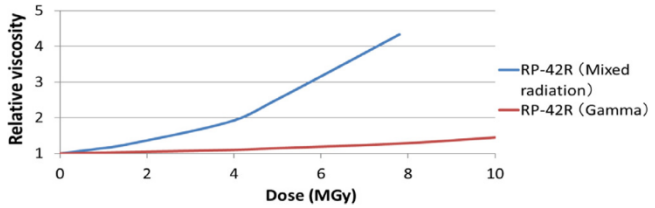

Fig. 11. Viscosity evolution of oil samples irradiated in the mixed field of the reactor (blue) and with a gamma source (red). Viscosity values are normalized to the viscosity of the unirradiated sample.

8.6. Radiation damage to oil and grease: a comparison

Interesting results emerge from the comparison of radiation damage in oil RP-42R and RG-42R-1, which is a grease realized using the oil combined with an inorganic thickener. As reported in [14], the grease consistency remained stable as a function of the dose up to more than 11 MGy in the same reactor irradiation conditions. By contrast, the oil viscosity increases up to about +350% at 7.8 MGy of dose.

These data evidence that the radiation resistance of the grease is only partially determined by the radiation stability of its main element, the oil. The presence of the inorganic thickener, which act as a gelling agent, might influence the type of radiation mechanisms and possibly prevents the polymerization phenomena observed when the oil is irradiated alone. Results suggest that the radiation resistance of the whole grease depends on both the radiation resistance of the oil and of the thickener, and on their interaction.

In the literature, the radiation resistance of the base oil is often reported as the main parameter influencing the radiation resistance of the grease [1]. The collected data support a more complicated scenario,

in which all the components of a mixture and their interaction play a significant role in determining the overall radiation resistance of the final product.

9. Conclusions

In the present study, viscosity, TAN, FT-IR, GC, GPC and NMR analyses are performed on commercial MORESCO-HIRAD RP-42R oil samples, irradiated up to 7.8 MGy in a nuclear reactor by a mixed neutron and gamma radiation field, where the neutron dose accounts for two thirds of the total. The measured properties of irradiated oil samples are compared to those of the unirradiated ones, analysed in parallel. The data show a progressive oil polymerization with increasing dose, which leads to creation of very long molecular chains. The radiation induced formation of long molecular structures affects the oil rheology and functionality. The degree of viscosity increase shows dependence on the irradiation parameters: a larger viscosity increase is reported after neutron irradiation in comparison to the one reported at equivalent gamma doses. This highlights the importance of performing more irradiation studies on organic materials using mixed radiation fields and different sets of irradiation conditions, to better assess the dependence of damage on different parameters.

Despite the large viscosity increase in the MGy dose range, the product remains chemically stable and does not show any sign of oxidation. This qualitatively confirms the radiation resistance of the material, previously assessed by studies performed by MORESCO using gamma radiation only. The collected results prove the importance of testing commercial products in specific irradiation conditions, in view of their use in high radiation areas.

Apart from the significance of the results for the European Spallation Source and for any other facility producing high radiation levels, the results provide a better understanding of the radiation-induced mechanisms of organic materials and specifically of polyphenyl ether based oils. The comprehension of the base mechanisms of radiation damage in lubricants reduce the risk of component failure in operation, of unforeseen repairs and of unnecessary exposure to radiation of human operators, in agreement with the general radiation protection principles.

The present study highlights the need for further and systematic investigations on the radiation effects in lubricating materials and in organic materials in general, for a more complete understanding of the radiation-induced phenomena. The study reports the exceptional resistance of polyphenyl ether oils, that are considered a fundamental component to manufacture radiation resistant greases. For this reason, the experimental investigation of their radiation resistance represent a strategic activity for the development of high-radiation facilities.

CRediT authorship contribution statement

Matteo Ferrari: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Project administration. **Aldo Zenoni:** Conceptualization, Methodology, Validation, Resources, Writing - review & editing, Supervision. **Yongjoong Lee:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision. **Yoshikazu Hayashi:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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