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Effect of Gamma Radiation on Sealing Capacity Characteristics of Three Commercially Available Nitrile Rubber Samples Compared Against an Industrial Seal Used in AGR Power Plants

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ABSTRACT

The maintenance of the Fuelling Machine operating in an AGR reactor consumes a large number of working hours and operational budget. As part of an optimisation programme research work is currently being carried out to investigate the degradation mechanism on the dynamic seal on one of these machines. The aim of this work is to understand seal behaviour under reactor working conditions in a bid to develop a mechanistic understanding of its long-term degradation and optimise the component's maintenance schedule.

The deleterious operational conditions have been identified as; activation of the sealing face through compression, exposure to a low radiation dose and cycle exposure to pressurised carbon dioxide. This part of the work investigates the effect of radiation damage on the CO_2 uptake and swelling behaviour, mechanical properties and physical and chemical structure of three commercially available nitrile rubber samples which are then compared against the characteristics for the chosen seal.

Exposure to radiation resulted in increased mechanical strength and resilience of the rubber as well as decreased CO_2 loading capacity and swelling, further supporting the theory of cross-link formation. The seal was more resistant to the effects of radiation than the three nitrile rubber samples, however scanning electron microscopy identified the initiation and propagation of cracks without any external stress applied on the irradiated samples, the result of in-built stresses created during the manufacturing process. The next stage of this work will investigate the effect of the local environment on the radiation-induced changes in the sample's ultimate sealing capacity.

INTRODUCTION

Nitrile Rubber (NBR) is a base material used in the manufacture of seals – a co-polymer blend of acrylonitrile and butadiene, the polarity of which provides the material with its characteristically good oil and grease resistivity making it an ideal choice for dynamic seals. However, in a Nuclear Power Plant the material is also subject to cyclic pressurised carbon dioxide (CO_2), mechanical activation and gamma irradiation.

These individual degradation pathways have been extensively researched in the literature (Briscoe and Zakaria, 1990, Briscoe and Zakaria, 1991, Neogi and Zahedi, 2014, Robeson, 2013, Cardona et al., 1999, Ahmed et al., 2012, Davenas et al., 2002, Makhlis et al., 1971, Persson, 2001), however it has been noted in other papers (Celina et al., 2005, Ezrin and Lavigne, 2007) that synergistic effects of independent mechanisms can result in unexpected failures. Some effort has been placed in prediction and modelling of failure of elastomeric components (Celina et al., 2005, Gillen et al., 2003, Hansen, 2002, Maxwell et al., 2005) but extensive work is required to improve the accuracy and validation of these systems.

Research work is currently underway investigating the degradation mechanisms on one elastomeric seal in one Nuclear Power Plant that have an effect on the capacity of the seal to perform its function. Typically, compression set is found to inform as to the sealing capacity of the material, however this test method does not provide a detailed picture of the changes in structure. This paper analyses a pre-service seal against three different commercially available samples of NBR in the properties that are deemed relevant for an elastomer to have a sufficient sealing capacity:

- Mechanical Compression – a measure of the energy dissipated (ED) through visco-elastic deformation can be attributed to the energy spent in breaking bonds to allow chain movement. This therefore means that a higher ED value will correlate to a reduced internal chain mobility.
- Absorption Behaviour – due to the increased physical wear resulting from the swelling behaviour of elastomeric components under certain conditions, an assessment of the ultimate loading capacity and absorption behaviour of such gases will not only provide information on the physical structure within the seal but also the effect on the expected physical wear
- Swelling Capacity – the degree to which a nitrile rubber elastomer will expand when placed in a solvent is indicative of its cross-link density
- Glass Transition Temperature – the glass transition temperature (T_g) will provide information on the amorphous content within the rubber which will increase its tendency to compress

METHODS

The Samples

Commercially available nitrile rubber at grades BA40, BA50 and BA60 have been purchased from Whitby & Chandler Ltd., the BA grade refers to their overall hardness. No further information is available on the chemical makeup of the seals as this is considered to be proprietary information. EDF Energy has donated a seal, manufactured by James Walker, used in the field. The seals are made from a nitrile elastomer reinforced with carbon black and incorporating a sulphur based curing system. A plain weave glass cloth is interwoven into the elastomer and brass wire is incorporated in both the war and weft yarns with a composition of 77% glass to 23% brass wire. Where the samples are dissected a sharp fresh blade on a Stanley knife has been used to minimise contamination and provide an as sharp as possible cut.

Mechanical Analysis

A rotary drill was used to segment the sample sheets into separate cylindrical sample pieces. These were then placed in a Lloyds Texture Analyser 500 with two flat plates. A compression programme designed to stop after 1, 2, 3, 4 and 5 mm deflection for each sample piece was utilised and the load and deflection after preload were recorded.

The area of the hysteresis loop of a polymer under compression testing gives the ED within the rubber. The trapezoidal method was used to calculate the area under the curves and the ratio of the area of the hysteresis loop to the area of the compression curve was averaged at each deflection to give a consistent value for the sample.

CO_2 Loading Behaviour

Samples segments between 50 and 80 mg in weight were dissected into as small as reasonably practicable monoliths. These were placed in a small mesh basket that was then loaded into an Intelligent Gravimetric Analyser (IGA) 002 from Hiden Isochema. The IGA relies on the use of an ultra-sensitive microbalance to record any microscopic changes in mass while measuring the ambient pressure and temperature of the sample as the environment undergoes incremental pressure increases, whilst allowing for any buoyancy discrepancies (Hiden Isochema Ltd.). The sample is initially taken down to a vacuum of 1 mbar to remove any previously absorbed gases before beginning the programme.

The IGA raises the pressure in the environment to a set value using CO_2 whilst recording the change in mass of the sample. It then undergoes a sufficient delay that either allows the system to reach equilibrium or allows the gathering of enough data to be able to plot the equilibrium point. This was carried out at 0.5 bar CO_2 and subsequently 1 through 10 at 1 bar intervals. Due to the slow uptake of CO_2 into nitrile rubber the system never reached equilibrium and thus the data gathered at each pressure increment were placed into Origin Pro and fitted to an exponential curve to find the ultimate loading

capacity. Further work is required on identifying the absorption kinetics of CO_2 into nitrile rubber, looking at all three samples and the seals so as to improve the accuracy of the ultimate loading capacity.

Swelling Capacity

Samples were dissected into approximately 7 mm diameter stubs and weighed on a TP214 Denver Balance with a repeatability of 0.1 mg and measured using a Carbon Fiber Composites Digital Caliper with an accuracy of ± 0.2 mm. Analytical grade toluene sourced from VWR International was added to a boiling tube to ensure satisfactory covering of the sample and was replenished every 24 hours. After 72 hours the samples were removed, quickly dipped in Acetone and dried on filter paper before using the same apparatus to find the new weight and dimensions of the sample. This method is adapted from ASTM Standards D6814, 2002 (2013).

The Percentage Mass Increase (PMI) was calculated with the following equation:

$$\Delta_M = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

Where Δ denotes percentage change, M denotes recorded mass and the subscripts 0 and t denote before and after the experiments respectively.

Differential Scanning Calorimetry (DSC)

Approximately 4 – 5 mg of the elastomer sample was weighed on a TP214 Denver Balance and placed in an aluminium pan. An aluminium lid was then crimped onto the pan and the sample container was placed in a PerkinElmer Diamond Differential Scanning Calorimeter with an attached Intracooler and ran through a programme with an initial temperature of -60°C, final temperature of 20°C and a ramp rate of 10°C per minute.

A line of best fit is applied to the heat flow vs temperature curve both before and after the resultant step change in base line. A tangent line is then placed at the point of highest gradient of the step change and its intersection with the two previously drawn lines of best fit are the start and stop positions of the glass transition. The T_g is then taken at 63% along this baseline transition step (College, 2007).

Scanning Electron Microscopy (SEM)

Approximately 7 mm^2 samples were trimmed away and coated by a thin layer of gold. The prepared samples were then placed in an Hitachi TM3030, which is a low vacuum SEM to allow the imaging of insulating material. Images were taken in backscattered mode allowing the different contrasts to represent different chemical compositions within the material. An EDX map was also ran to obtain elemental information.

RESULTS

Mechanical Analysis

Parabola fits have been plotted on the graphs (dashed lines) to aid the eye in identifying any trends. It can be seen from Figure 1 that of the commercial samples BA40 shows the lowest ED and BA60 the highest. This is to be expected as the BA grades refer to the overall hardness of the elastomer which will increase as the internal chain mobility decreases. The industrial seal shows a significantly higher ED rating suggesting its chains in the amorphous regions have a lower freedom of movement which is to be expected as it is well known that crosslinking elastomers improves their performance.

From Figure 1 it could be inferred that ED reduces with radiation dose. However, it is important to note that increasing radiation dose increases the strength of the elastomers and thus increases the area under the loading curve on a stress-strain plot. For the results carried out in this study, the area under the loading curve increased at a far greater rate than the ED decreased. This would suggest that crosslinking

does reduce the internal chain mobility as suggested in the literature, however, for the samples examined the crosslinks had a greater effect on the overall rigidity of the material.

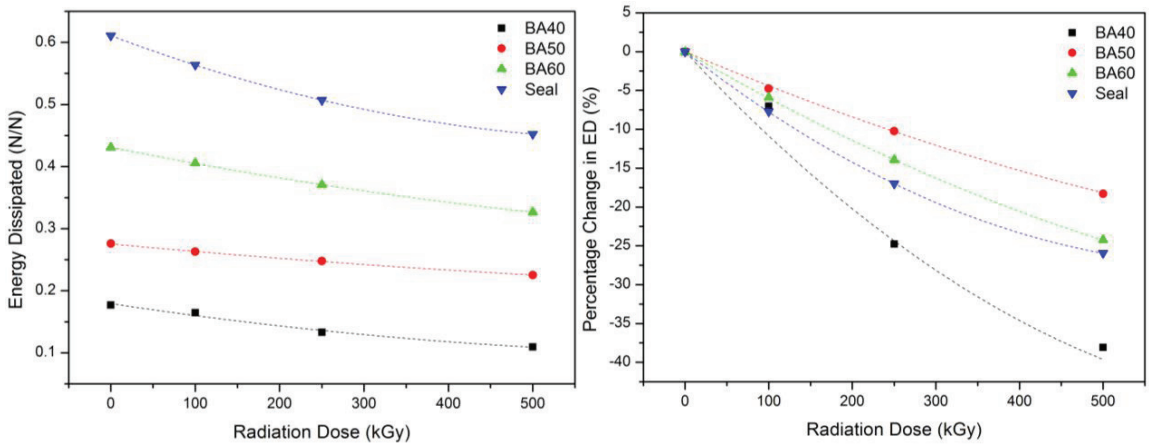

Figure 1. The Energy Dissipated and Percentage Change in Energy Dissipation Against Radiation Dose for All Four Samples

In service, the ED can be related to the closing force applied by the seals upon entering their housing. A portion of the force placed on them from the restricted dimensions of the housing is spent in overcoming internal bonds to allow the movement of chains within the amorphous regions; the remaining portion is converted to heat and also applied as a closing force creating the pressure boundary. As the seals are exposed to radiation, an increased amount of force is required to allow compression and relaxation, thus reducing the amount that can be applied a closing force and decreasing the materials effectiveness as a seal.

CO_2 Loading Behaviour

Despite the incomplete set of data seen in Figure 2, a decreasing trend is observed in the CO_2 loading capacity with increasing radiation dose. The softer BA40 sample has the highest absorption with the BA50 sample in the middle and the BA60 sample the lowest. The BA40 sample also appears to be affected the least by the radiation damage with regards to CO_2 loading behaviour.

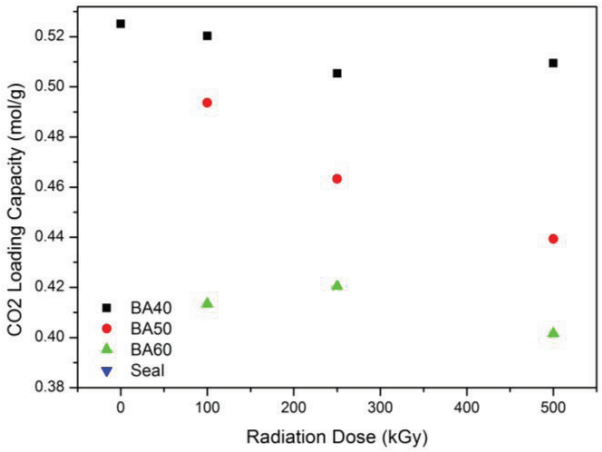

Figure 2. The CO_2 Loading Capacity Against Radiation Dose for All Four Samples

The absorption of CO_2 into the elastomer will not only cause it to swell, which is looked at more in depth in the next section, but will also permit the phenomenon known as Environmental Stress Cracking (ESC) whereby the presence of an ESC active agent in the elastomer increases the rate of deformation of chains within the internal structure. This results in early failure of the seals and increased damage from physical wear.

Swelling Capacity

As with ED, one would expect the PMI of the three commercial samples to follow a trend with respect to their BA ratings. However, Figure 3 shows the BA50 sample having a larger PMI than the other two. The industrial seal has a much lower PMI compared with the commercial elastomers.

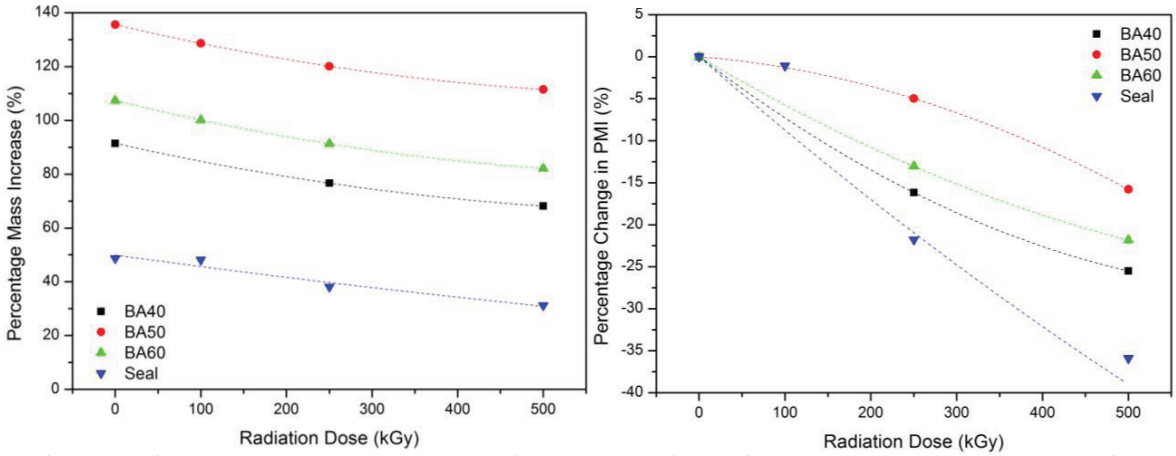

Figure 3. The Percentage Mass Increase and Percentage Change in Percentage Mass Increase Against Radiation Dose for All Four Samples

The BA50 sample again shows a high resistance to radiation damage displaying the least percentage change with radiation dose. The parabola fit suggests an increasing trend with the percentage change, however one would expect this to be due to experimental error as opposed to an actual trend. The seal shows the largest percentage change, decreasing the PMI by almost 40% following exposure to 500 kGy of gamma radiation.

A decrease in PMI would indicate the formation of crosslinks hindering the amorphous regions of the elastomer from expanding as the solute absorbs into the bulk of the elastomer. During service the seal is compressed into a dimensionally restrictive housing, providing the closing force against the outer wall that creates the pressure boundary. However, as the elastomer swells the closing force will increase. The dynamic nature of the service of the seal means that physical wear is a contributing factor to its degradation. If the elastomer is swollen, its closing force is increased and the damage due to physical wear will also increase. The low swelling capacity of the seal indicates it will be least affected by these dynamic motions. Whilst it also exhibits the largest degradation due to radiation damage, its overall PMI is still comparably small and the large percentage changes may be due to the low absolute values. Figure 1 shows that, for the seal, the chains in the amorphous regions have a high degree of mobility, however, the swelling capacity suggests the presence of an unknown that hinders the expansion of these chains. This could be due to the inclusion of brass wires that will provide physical barriers preventing further expansion at certain points within the structure.

Differential Scanning Calorimetry

It has previously been shown (Ambler 1973) that increasing T_g is indicative of lower acrylonitrile content in NBR and an increase in acrylonitrile is often utilised to increase the hardness of the elastomer. It stands to reason, therefore, that BA40 would exhibit the highest T_g and BA60 the lowest, as is evident in Figure 4. The seal has a relatively high T_g which would suggest a low acrylonitrile content.

Figures 1 and 3 suggest that the BA50 sample is more resistant to radiation damage. However, Figure 4 contradicts this as the BA60 sample shows the lowest percentage change in T_g. The BA40 and BA50 samples follow a similar trend while the industrial seal's percentage increase in T_g appears to begin to tail off at 500 kGy.

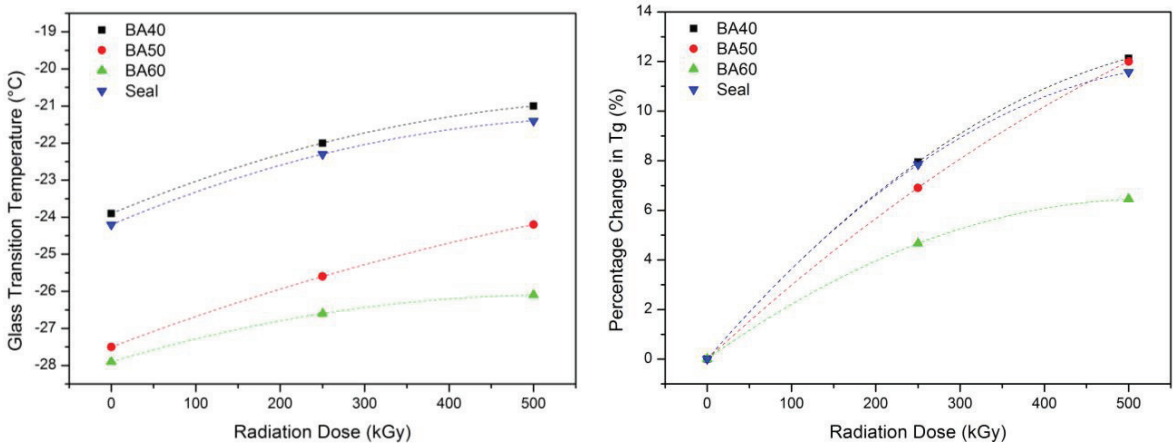

Figure 4. The Glass Transition Temperature and Percentage Change in Glass Transition Temperature Against Radiation Dose for All Four Samples

The T_g is inversely proportional to the polymer chain's freedom of movement. Thus as the T_g increases, the elastomer chains become more restricted in their movement. Figures 1 and 3 imply the BA50 sample has the greatest resistance to gamma-induced crosslinking. However, Figure 4 suggests that the restriction of movement in the chains in the BA60 samples increases the least and thus this is the sample that has the least amount of gamma-induced crosslinks. One explanation for this could be the formation of crosslink clusters within the BA50 sample that limit the freedom of movement of the chains when looked at as a whole but still permit the expansion and compression of the elastomer in localised regions. The high T_g of the industrial seal indicates a low freedom of movement which agrees with the data seen in Figure 1 and the reduced swelling capacity seen in Figure 3.

Scanning Electron Microscopy

Figure 5a is an SEM image of the un-irradiated seal depicting breakages in the surface of the elastomer from the protrusion of fibres. As the fibres travel further into the bulk of the elastomer, the cracks terminate.

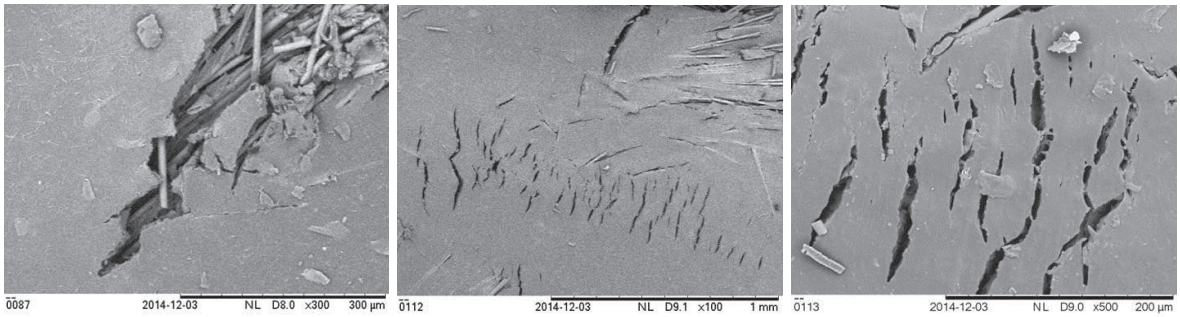

Figure 5. Scanning Electron Microscopy Images of the Industrial Seal Following Gamma Radiation Doses of a) 0 kGy at x300 magnification, b) 500 kGy at x100 magnification and c) 500 kGy at x500 magnification

It can be seen in figures 5b and 5c that following exposure to 500 kGy of gamma radiation and no external stresses the seal begins to crack. The cracks seen are all parallel and follow the curvature of the seal's design. These cracks are the result of in-built stresses produced during the manufacturing process that exposure to gamma irradiation cause to initiate and propagate through the elastomer structure.

These cracks are detrimental to the life of the elastomer as they will not only allow the increased absorption of gases into the bulk of the elastomer but will pose significant weak points at which further propagation may occur following dynamic movements and will lead to eventual tearing.

CONCLUSIONS

This report has investigated the effect of gamma radiation up to a dose of 500 kGy on three types of commercial nitrile rubber and one industrial NBR seal with respect to the following properties:

- Energy dissipated through visco-elastic deformation
- CO_2 loading behaviour
- Percentage mass increase following exposure to a solvent
- Glass transition temperature

Scanning electron microscopy has also been utilised to inspect the surface of the industrial seal both before and after exposure to the pinnacle radiation dose.

It has been found that the BA50 sample of commercial NBR appears to be most resistant to gamma induced crosslinking when inspecting the ED and PMI properties. However, following the investigation into the T_g it can be concluded that the BA50 samples produce crosslink clusters that limit the effect on the ED and PMI properties as the crosslinks hinder a smaller proportion of the amorphous chains due to their close proximity and the probable overlap of crosslinks on the same chain segments.

The industrial seal exhibited a far lower swelling capacity than would otherwise be inferred when inspecting figures 1 and 4. This has been attributed to the presence of an external factor that is not a constituent of the elastomer but hinders the elastomers swelling when exposed to a solvent. This could be the inclusion of brass wire during the manufacturing process that provides a physical barrier against the further expansion of the chain segments.

NOMENCLATURE

Δ_M – Percentage change in mass
DSC – Differential Scanning Calorimetry
ED – Energy dissipated through visco-elastic deformation
EDX – Energy Dispersive X-Ray Spectroscopy
ESC – Environmental Stress Cracking
IGA – Intelligent Gravimetric Analyser

M_t – Recorded mass after experiments
M_0 – Recorded mass before experiments
NBR – Nitrile rubber
PMI – Percentage mass increase following exposure to a sufficient solvent
SEM – Scanning Electron Microscopy
T_g – Glass transition temperature

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