JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **15** (2004) 1339–1347

# The wear and fracture behaviour of ultra high molecular weight polyethylene subjected to $\gamma$-irradiation in an atmosphere of acetylene

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The wear and mechanical properties of GUR 1020 (Perplas IMP 2000-2) Ultra High Molecular Weight Polyethylene (UHMWPE) subjected to $\gamma$-irradiation in an atmosphere of acetylene, were evaluated for a range of processing conditions of irradiation, annealing and ageing. The results were compared with those obtained for the virgin UHMWPE material and material processed using conventional $\gamma$-irradiation in nitrogen. Cross-linking produced by irradiation in acetylene, followed by subsequent annealing was found to be significantly more effective in improving the mechanical and wear properties of UHMWPE compared to when the material was irradiated in nitrogen. Gel fraction analysis on its own, while being able to detect the degree of cross-linking, was found to be insufficient in determining the effectiveness of the cross-links and the resulting mechanical properties of the UHMWPE material. The results suggest that $\gamma$-irradiation in an atmosphere of acetylene may provide significant advantages over conventional UHMWPE processing and irradiation cross-linking techniques.

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## 1. Introduction

Over the past 10 years a multitude of new polyethylene material processing and sterilisation techniques have been introduced for total joint replacement prostheses to minimise the production of wear debris, which is now known to contribute to osteolysis and the eventual loosening of the prostheses. The majority of these new techniques incorporate irradiation sterilisation in a controlled atmosphere where the impregnation gas, the irradiation dose, and the annealing conditions can be varied to control the cross-linking of the material. Irradiation of Ultra High Molecular Weight Polyethylene (UHMWPE) in an inert atmosphere of nitrogen produces a breakdown of the polymer chains, which leaves the material unstable with the presence of free radicals within its structure. These free radicals may recombine and produce no changes, form cross-links to other molecular chains, which will stabilise the material, or remain as highly reactive species, which may cause degradation of the UHMWPE over time [1]. Cross-linking is an attractive method of improving wear resistance, however, it is also a very complex process that changes the mechanical properties of the original material.

The classic work of Charlesby and coworkers [2, 3] showed that when polyethylene is subjected to $\gamma$ or electron beam irradiation active radicals are produced which could lead to either cross-linking or chain scission. It was shown by Ward and coworkers [4] that the cross-linking reactions could be enhanced by irradiation in an atmosphere of acetylene. This result means that satisfactory degrees of cross-linking can be achieved with lower irradiation doses, reducing the amount of chain scission [5, 6]. It was also shown that it is necessary to anneal the irradiated samples, at temperatures close to the melting point of the material, also in acetylene atmosphere, to ensure that all the free radicals produced by the $\gamma$-irradiation are reacted to give a highly cross-linked and very stable polyethylene material.

With regard to mechanical properties, cross-linking has generally been shown to decrease the tensile strength, elongation to break, fracture toughness and fatigue strength of the polyethylene material whilst increasing its hardness and wear resistance [1, 7–10]. The decrease in fatigue strength may be a concern where high cyclic stresses are generated in the prostheses such as in knee tibial inserts where cyclic stresses exceeding

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the yield strength of UHMWPE have been reported and delamination is a concern [9, 11]. Because of this highly cross-linked materials have generally been aimed at the application of hip prostheses where the stresses are relatively low.

With regard to wear performance it has been shown that with virgin UHMWPE under unidirectional motion the molecules at the contact surface experience molecular alignment in the direction of motion. This results in strain hardening parallel to the sliding direction and strain softening in the transverse direction and a general increase in wear resistance [12]. With multidirectional motion strain hardening occurs in the primary direction of motion with strain softening in the transverse direction that results in accelerated wear. Moderate to high amounts of cross-linking within the polyethylene has been shown to resist the molecular orientation effects and result in reduced wear under multidirectional motion compared to virgin UHMWPE [13–17]. For hip prostheses (multidirectional motion) there is, therefore great interest in cross-linked polyethylene to reduce wear volumes generated between the articulating surfaces. However, the benefit of highly cross-linked materials for knee prostheses where more unidirectional motion may exist remains a point of debate when compared to traditional UHMWPE where molecular alignment and strain hardening will reduce wear [18].

It is clear from the literature that processing conditions play an important role in the resulting mechanical and wear properties of UHMWPE. The purpose of this study was to investigate the effects of processing variables and ageing on the mechanical and wear properties of GUR 1020 UHMWPE subjected to $\gamma$-irradiation in an atmosphere of acetylene, followed by an appropriate annealing treatment.

## 2. Experimental

### 2.1. Materials

The samples used in this study were Perplas IMP 2000-2 low calcium implant grade GUR 1020 UHMWPE supplied by Stratec Medical. Pre-forms and pins were supplied for this research. Samples for the fracture and wear tests were machined from the supplied samples following the necessary irradiation and annealing treatments.

### 2.2. Cross-linking by irradiation

The cylinders were packed with UHMWPE test samples and subjected to repeated evacuation ($4 \times 10^{-2}$ Torr) followed by heating at 100 °C. The evacuation time ($t_{Z=0.98}$) was estimated theoretically on the basis of at least 98% removal of gas from the cylinder using the literature data for LLDPE [19, 20]. Gas emission was only assumed to be complete when the cylinders held a vacuum of at least $4 \times 10^{-2}$ Torr for over 24 h. In all cases the time at 100 °C was at least 12 h in excess of the calculated value, to ensure complete evacuation. This removed air from the cylinder and surface moisture on the samples. On a practical level, this was done by placing the cylinder in a fan-assisted oven at 100 °C and checking for out-gassing from the samples by monitoring the pressure. Initially, the pressure obtained was not as low as $4 \times 10^{-2}$ Torr. Therefore, the cylinder was evacuated further (to better than $4 \times 10^{-2}$ Torr) and the cylinder was placed back in the oven. This procedure was repeated until the pressure inside the cylinder, at room temperature, was better than $4 \times 10^{-2}$ Torr.

TABLE I Summary of irradiation and annealing conditions

| Sample | Impregnation gas | Dose | Annealing conditions |
|---|---|---|---|
| *A* | None | Unirradiated | Not annealed |
| *B* | Nitrogen | 2.50 MRad | Not annealed |
| *C* | Nitrogen | 2.50 MRad | Annealed at 100 °C |
| *D* | Acetylene | 2.50 MRad | Annealed at 100 °C |
| *E* | Acetylene | 0.25 MRad | Annealed at 100 °C |

Following evacuation, the cylinders were impregnated with white spot nitrogen or acetylene at atmospheric pressure, again for at least 12 h in excess of the calculated $t_{Z=0.98}$ value. The cylinders were checked for leakage for a further 24 h, before being sent for irradiation. Following irradiation, the cylinders were again checked for leakage. A reduction in pressure was always observed with acetylene irradiations due to extraneous ‘cuprene’ formation. No leak was detected. The cylinders were then quickly evacuated (2 min) and refilled to normal atmospheric pressure with the respective gas, to remove gaseous scission products and in the case of acetylene to replace gas lost due to ‘cuprene’ formation. Finally, the cylinders were annealed at 100 °C for 20 h, cooled down to ambient temperature and the samples were then removed.

The details of the irradiation and annealing conditions performed on the samples are summarised in Table I. A group of samples subjected to irradiation and annealing conditions was aged at 80 °C in air for 21 days. Henceforth, the non-aged samples will be addressed as $A$, $B$, $C$, $D$, and $E$ and the aged samples will be designated as $A1$, $B1$, $C1$, $D1$ and $E1$.

### 2.3. Gel fraction analysis

0.125 to 0.175 g samples were placed in stainless steel gauze containers and subjected to solvent extraction, using Decalin (containing anti-oxidant) as the solvent, for 96 h. Gel Fraction was then obtained by dividing the final sample weight by the initial sample weight as previously described [13].

### 2.4. Slow crack growth test

Samples of dimensions 10 mm thick, 25 mm wide and 50 mm long were machined from the performs. The samples were notched, in the front face and the centre lines on the two long edges in the milling machine, to a depth of 3.5 mm to form a single continuous notch around three sides of the specimen. The machined notch on the front face was then sharpened by tapping a fresh razor blade, mounted on a custom built notching machine [21], at the root of the notch to a depth of 0.2 mm. The geometry of the sample used for the Slow Crack Growth (SCG) measurements is shown in the Fig. 1.

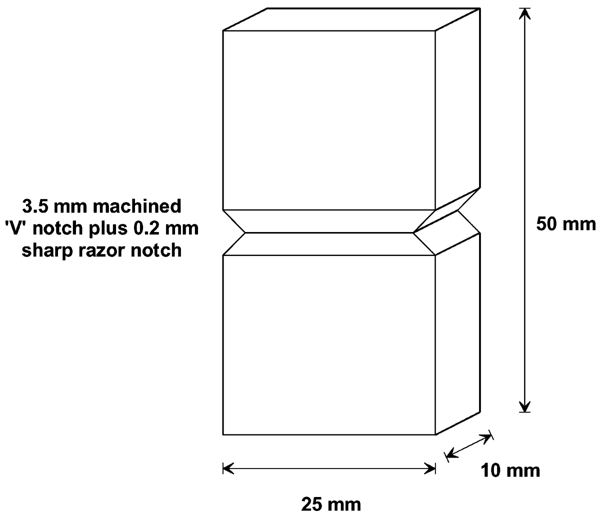


*Figure 1* Geometry of the sample used in the SCG test.

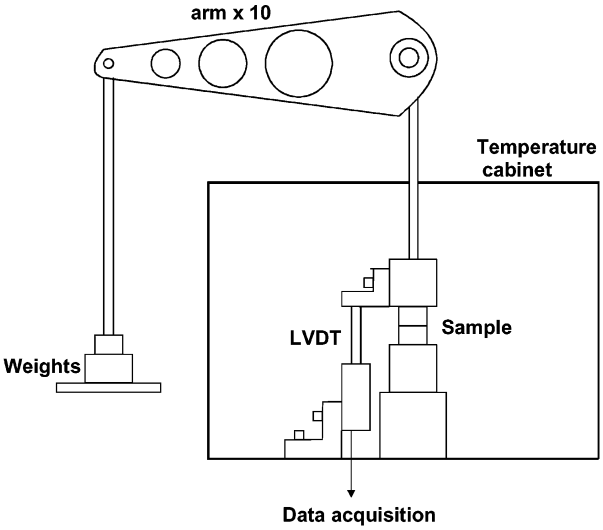


*Figure 2* The slow crack growth rig.

The samples were tested on a custom-built SCG rig. The schematic view of the SCG rig is shown in Fig. 2. The design of the rig was based on the work of Lu *et al.* and consisted of two lever arms mounted side-by-side on a heavy steel frame [22]. The lever arms were pivoted to provide a force-multiplication ratio of 10:1. Thus a force applied to the weight-pan was multiplied 10 times at the sample. The actual set-up has two sets of lever arms but for more detailed picture only one is shown in the Fig. 2.

The samples were held in stainless steel grips, having serrated faces. The gripped samples were housed in the environmental chamber of the testing rig, allowing tests to be carried out at constant temperatures. In these experiments, the samples were placed in the sample housing, without load, at 37 °C (±0.5 °C) for 90 min to establish good thermal equilibrium. After the soaking period, a stress level of 13 MPa was applied on the sample and the Crack Opening Displacement (COD) (Fig. 3) was monitored as a function of time using a displacement transducer connected to the data logging system (Pico Technology ADC-200). A stress level of 13 MPa was found to produce an optimum stress level for these experiments.

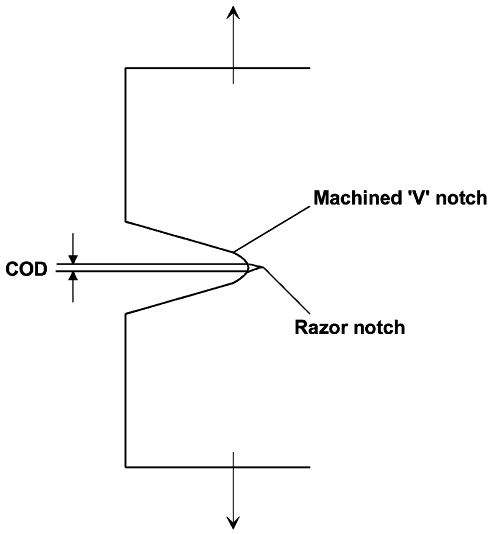


*Figure 3* Side view of the SCG sample illustrating the Crack Opening Displacement (COD).

## 2.5. Wear test

The material showing the best overall slow crack growth behaviour was further selected for wear testing using a consecutive wear study alongside virgin UHMWPE (Sample $A$) and the UHMWPE processed in the conventional manner by gamma irradiation in nitrogen (Sample $B$). Wear tests were conducted using a six station multidirectional pin on plate reciprocator using methods previously published [13]. Polymer pins were machined from processed acetabular insert preforms and then pre-soaked for 3 weeks prior to testing in deionised water. For each processing condition six pins were manufactured, three used for wear testing and three used as moisture controls. Control pins were placed in the same lubricant as the wear pins throughout the study to monitor the moisture uptake in the materials. All tests were conducted using smooth cobalt chromium plates ($R_a \sim 0.01\ \mu$m). A load of 240 N was applied to each test pin (5 mm diameter face) that gave a nominal stress of 12.2 MPa. Tests were conducted at 1 Hz for 2 weeks. During each cycle the plate translated 40 mm while the pin rotated ±45 °.

Wear was determined gravimetrically using a Sartorius microbalance with an accuracy of $\pm 1\ \mu$g. The weight changes of the test pins were adjusted for moisture uptake by adding or subtracting the average weight change of the three control pins. A wear factor was then determined by dividing the volume loss (mm$^3$) by the load (N) and the sliding distance (m). Comparisons of wear results from the different processing conditions were conducted using a one way ANOVA to determine the statistical significance.

# 3. Results and discussion

## 3.1. Gel fraction analysis

Gel fraction analysis provides an indication of the degree of cross-linking in the polymer samples. The average gel fractions of the non-aged and aged samples are shown in Table II along with the standard error (shown in brackets) where available. Published data for the gel fraction of alternative UHMWPE materials was taken

TABLE II Average gel fractions of non-aged and aged irradiated UHMWPE samples

| Non-aged | | Aged | |
|---|---|---|---|
| Sample | Gel fraction | Sample | Gel fraction |
| *A* | 0.4887 (0.062) | *A*1 | 0.1401 (0.019) |
| *B* | 0.8705 (0.012) | *B*1 | 0.8503 (0.032) |
| *C* | 0.9689 | *C*1 | 0.9160 (0.020) |
| *D* | 0.9971 | *D*1 | 0.9865 (0.003) |
| *E* | 0.9485 (0.003) | *E*1 | 0.9260 (0.020) |

TABLE III Gel fractions of non-aged UHMWPE from the literature

| Material | Gel fraction |
|---|---|
| RCH1000-virgin [24] | 0.146 |
| RCH1000-2.5 MRad acetylene, annealed 5 h 100 °C [24] | 0.791 |
| GUR 4150 HP-2.7 MRad $N^2$ [23] | 0.806 |
| GUR 4150 HP-10.7 MRad $N^2$ [23] | 0.884 |
| GUR 1050-Ebeam 10 MRad, Vac, Annealed 100 °C 3d [23] | 0.9 |

from a recent review paper by Lewis and is shown in Table III for comparison to the non-aged samples [8].

The virgin non-aged sample (Sample *A*) had a residual gel fraction of 0.488 after 96 h. This was greater than the value reported by Marrs *et al.* (0.146) for virgin RCH 1000, however, increasing the extraction time was impractical as UHMWPE has inordinately long diffusion times due to its high molecular weight [13]. All of the irradiated samples showed gel fractions greater than 0.87, which increased with irradiation dose confirming that all of the irradiated samples were cross-linked. This supports the general trend found in published literature of increased gel fraction with irradiation dose, as shown in Table III [8]. The acetylene enhanced material (Sample *D*) irradiated with 2.5 MRad and annealed for 12 h at 100 °C produced the greatest gel fraction (0.99), while the equivalent sample (Sample *C*) processed in nitrogen produced a gel fraction of 0.97. In addition, no variation in gel fraction as a function of depth from the polymer surface was observed for the acetylene-enhanced materials.

Radiation induced cross-linking is conducted to improve the polymer integrity over long periods of time. However, irradiation also induces the production of free radicals and the likelihood of post-irradiation oxidation when free radical reactions can cause the samples to deteriorate while in service. It has been shown that the radiation induced cross-linking in the presence of nitrogen, yields products, which react further with time in the presence of air [23, 24]. Further annealing acts to stabilise the polymer by re-combining the free radicals. Accelerated ageing allows the potential degradation of the polymer over time to be assessed.

Ageing at 80 °C for 21 days in air caused a decrease in the gel fraction of all of the samples (Samples *A*1 to *E*1) suggesting that material degradation had occurred. The gel fraction of samples processed in nitrogen (Samples *B*1 and *C*1) decreased by 2 and 5% respectively with the greatest decrease occurring in the annealed sample. The gel fraction of samples processed in acetylene (Samples *D*1 and *E*1) decreased by less than 1% and 2% respectively with the greatest decrease occurring in the sample with the least irradiation dose and, therefore, the least cross-linking. The acetylene enhanced material (Sample *D*1) irradiated with 2.5 MRad and annealed for 12 h at 100 °C produced the greatest resistance to degradation.

Gel fractions, however, only provide information on the degree of cross-linking and not the position of the cross-links within the polycrystalline UHMWPE. For structural implications it is necessary to know where the cross-links are within the morphology and how strong the cross-links are, hence the requirement for mechanical tests such as slow crack growth.

## 3.2. Slow crack growth

Because polymers are visco-elastic materials, their mechanical properties are generally time and temperature dependent. It has been shown, in the case of pipe grade polyethylene, when loaded below a critical stress, the material fractures in a brittle manner and the failure is by slow growth of cracks whereas the fracture mode is ductile otherwise [25]. The "long-term brittle failure" of polymers under low stress (failure under creep conditions) has received considerable interest over the years in load bearing applications such as polyethylene and polyvinyl chloride pressure pipes for gas and water distribution [26–28], variety of polyethylene resins in adhesive joints [29, 30] and polymer composites [31]. The Slow Crack Growth (SCG) test aids in simulating the long time brittle fracture when the test specimen is subjected to a variety of loading conditions, temperatures and stress intensities. The test condition is further severed by introducing a sharp notch in the sample to initiate the fracture process. In SCG tests, the Crack Opening Displacement (COD) is monitored over time and the curves have been related to the sequence of micro-events during the fracture process [32, 33]. The results provide an indication as to how fast cracks propagate through the polymer structure with stronger materials being more resistant to the growth of cracks and ultimate failure. The kinetics of crack growth in this test has been shown to be sensitive to the molecular and morphological changes [27, 34, 35] and thus, this test has been used in the present scenario to compare the fracture behaviour of the materials when subjected to different irradiation conditions and heat treatments.

In this work, the different stages before the ultimate failure of the materials during the fracture process has been compared qualitatively although there are theoretical models [36, 37] available for quantitative assessment. In general the COD vs. time plot for all of the samples can be divided into 4 stages as shown in the representative plot in Fig. 4. The four stages in the SCG test on UHMWPE are:

1. Period when the applied load causes the initiation of crack growth
2. Period of 'unsteady' crack growth after crack initiation

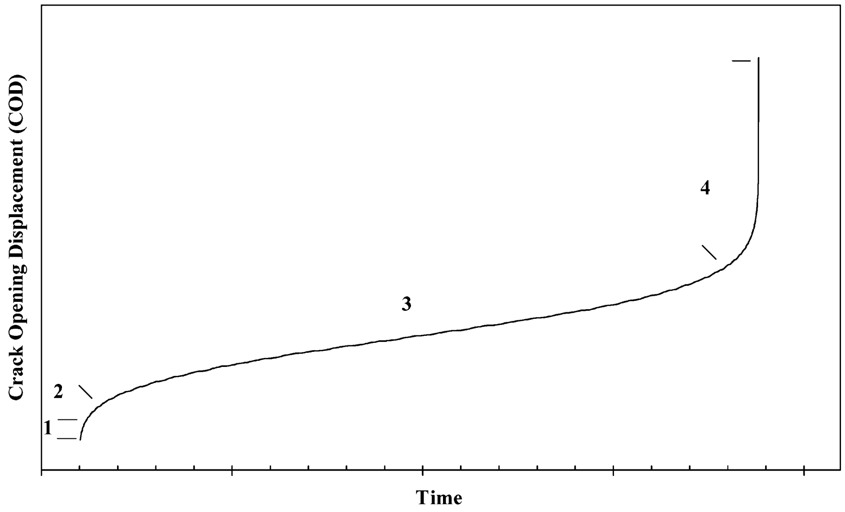


*Figure 4* Typical COD vs. time plot in a SCG test on UHMWPE.

3. Period of 'steady' crack growth
4. Final instability.

### 3.2.1. Slow crack growth in non-aged irradiated UHMWPE

The COD vs. time plots for the non-aged virgin and irradiated samples (Samples *A* to *E*) obtained at a 13 MPa stress level, are shown in Fig. 5. Irradiation in nitrogen (at normal atmospheric pressure) with a dose of $2.5 \times 10^4$ Gy (2.5 MRad) and no annealing (Sample *B*) provided considerable improvement in crack growth resistance (stage 2) when compared with that of the virgin unirradiated sample (Sample *A*). However, when the nitrogen-irradiated sample was annealed at 100 °C (Sample *C*), the crack growth resistance was dramatically reduced to a level similar to the untreated sample, but showing marginal improvement.

Irradiation in acetylene with a dose of 2.5 MRad and further annealing at 100 °C (Sample *D*) produced greater resistance to crack growth than all other samples. Decreasing the irradiation dose (Sample *E*—0.25 MRad in acetylene followed by annealing at 100 °C), however, was found to reduce this effect.

Free radicals can be generated anywhere within the polymer structure including at the core of the crystals, the crystallite boundary, at lamellae of the fold surfaces and at the interfacial zone [8]. The higher the temperature required to anneal radicals, the greater the probability that the radicals are closer to the amorphous-crystalline interfacial regions. As far as creep and polymer integrity under stress are concerned these radicals are the most important. This is to say it is only by cross-linking the crystallite boundaries into the network that we can maximally reduce creep, low stress damage and maintain the polymer integrity. This lack of cross-linking in the inner-interfacial region was demonstrated in that samples *A*, *B* and *C* that underwent creep in the final period before failure (steep gradient). The sample that was irradiated in nitrogen (Sample *B*), would, over a period of time if kept in nitrogen, become annealed at body temperature (37 °C), such that its crack resistance was reduced to nearly that of the annealed samples (Sample *C*). Since in *in-vitro* application, oxygen from the air would be

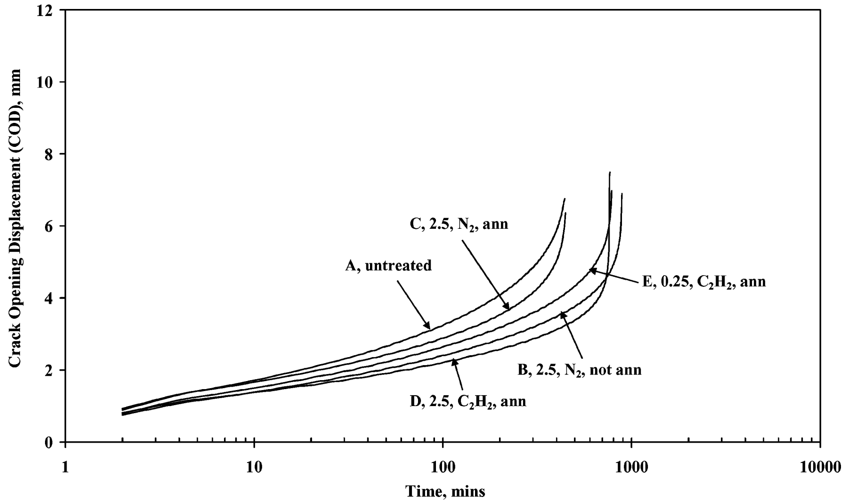


*Figure 5* COD vs. time plot for non-aged irradiated samples.

able to invade the polymer, it can only be assumed that the resistance to crack growth and the time to crack growth onset would be reduced further due to chain scission. Hence, treatment of the polymer with irradiation in nitrogen is not ideal.

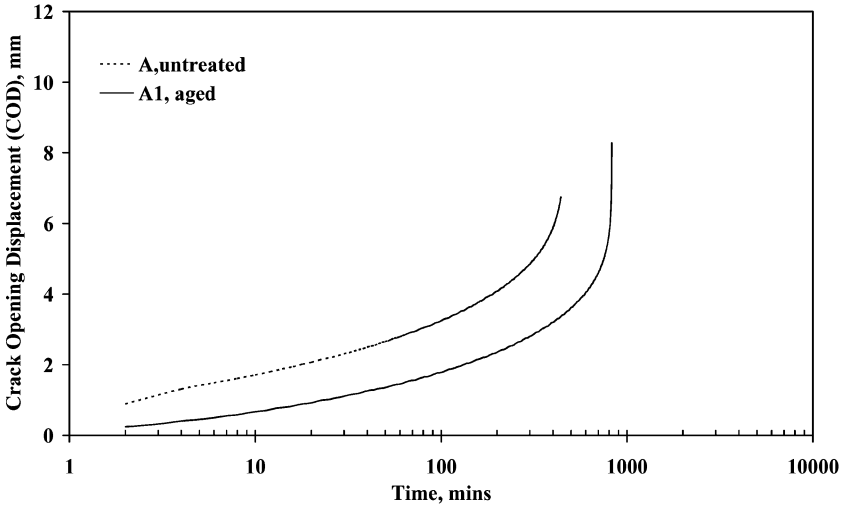
### 3.2.2. Slow crack growth in aged irradiated UHMWPE

The SCG results, obtained at 37 °C and at a stress level of 13 MPa, on the non-aged and aged samples are shown in the linear-log scale time plots (Fig. 6(a) to (e)). For all the cases, ageing at 80 °C for 21 days in air produced an increased resistance to crack propagation (stage 3) when compared with the non-aged irradiated samples but caused embrittlement as observed by the steep gradient in stage 4 for the aged samples.

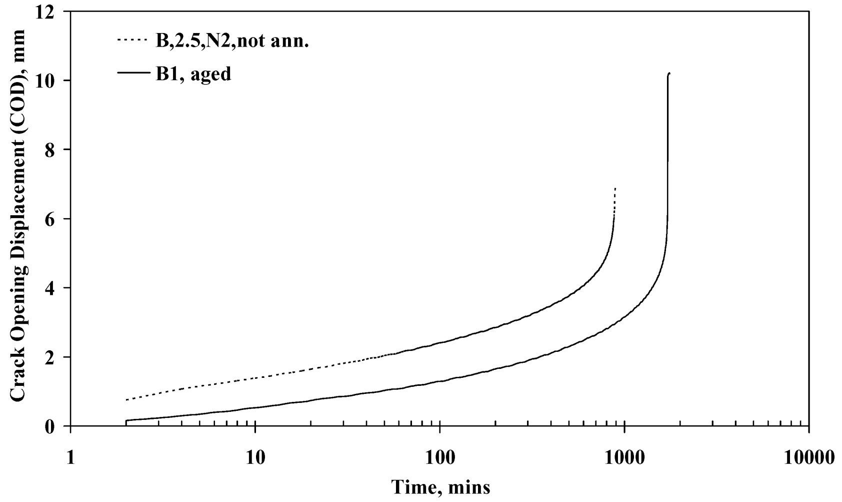
The COD vs. time plot for all the aged samples (Samples *A*1 to *E*1) are compared in Fig. 7. Irradiation in nitrogen at 2.5 MRad and with no annealing (Sample *B*1) provided considerable improvement in crack growth resistance above the aged untreated sample (Sample *A*1) due to the presence of cross-linking. The material irradiated in acetylene with a dose of 2.5 MRad with further annealing at 100 °C (Sample *D*1), provided greater resistance to crack growth in the aged state than all other materials tested.

From the COD vs. time plot for the aged samples (Samples *A*1 to *E*1), it was noticed that there was not a significant change in the crack initiation; 'unsteady' (stage 2); and 'steady' (stage 3) crack growth process, although they were of different magnitude. However, there was a significant difference in the fourth stage, the final instability or rupture stage. Fig. 8 shows the fracture surface of the samples after the slow crack growth test. It is evident from Fig. 8 that the virgin material and the materials irradiated in nitrogen (Samples *A*1, *B*1 and *C*1) exhibited a more ductile mode of failure with a considerable amount of plastic deformation of the ligament area prior to rupture. This confirms that there is ductility in these samples after ageing, which causes chain dis-entanglement leading to cold drawing of the ligament area before final rupture.

The rupture or the final instability of the acetylene enhanced samples (Samples *D*1 and *E*1) were in contrast to what was observed in the virgin material and

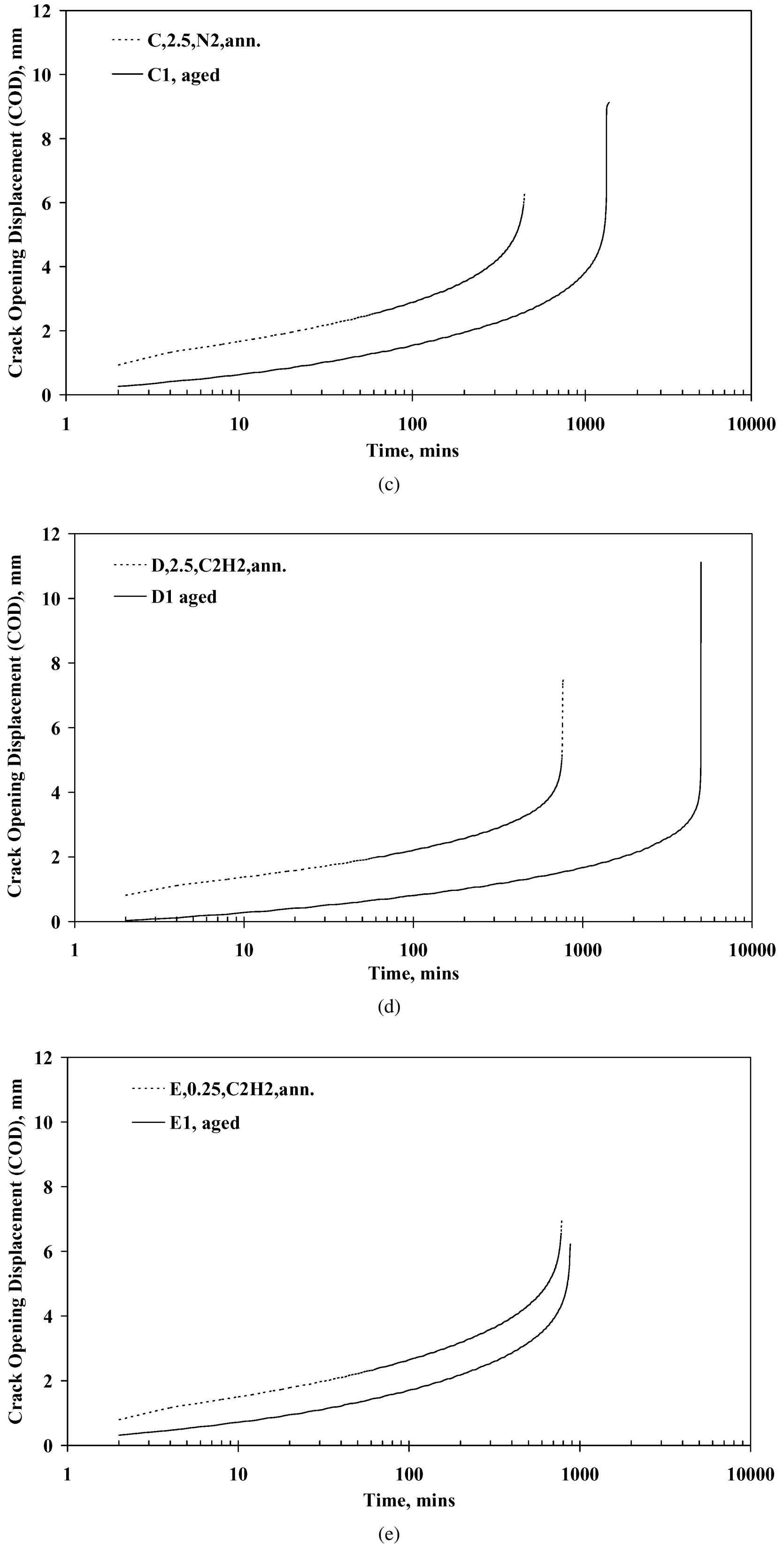


(a)



(b)

*Figure 6* (a) COD vs. time plots for non-aged and aged sample *A*. (b) COD vs. time plots for non-aged and aged irradiated sample *B*. (c) COD vs. time plots for non-aged and aged irradiated sample *C*. (d) COD vs. time plots for non-aged and aged irradiated sample *D*. (e) COD vs. time plots for non-aged and aged irradiated sample *E*. (*Continued on next page.*)



(c)

(d)

(e)

*Figure 6* (*Continued*).

in the nitrogen irradiated samples (Samples *A*1, *B*1 and *C*1). These samples fractured in a brittle manner after the period of stable crack growth. The loss of ductility restricted the disentanglement of molecular chains leading to chain scission of the tie molecules, causing the samples to rupture by the initiation and growth of micro-voids between the fibrils [32, 33].

### 3.3. Wear testing

Sample *D*, UHMWPE irradiated in acetylene gas at a dose of 2.5 MRad and annealed at 100 °C, was selected for wear testing as this material produced the best overall SCG behaviour of the samples irradiated in an acetylene atmosphere. Wear of Sample *D* was compared to that of the virgin UHMWPE

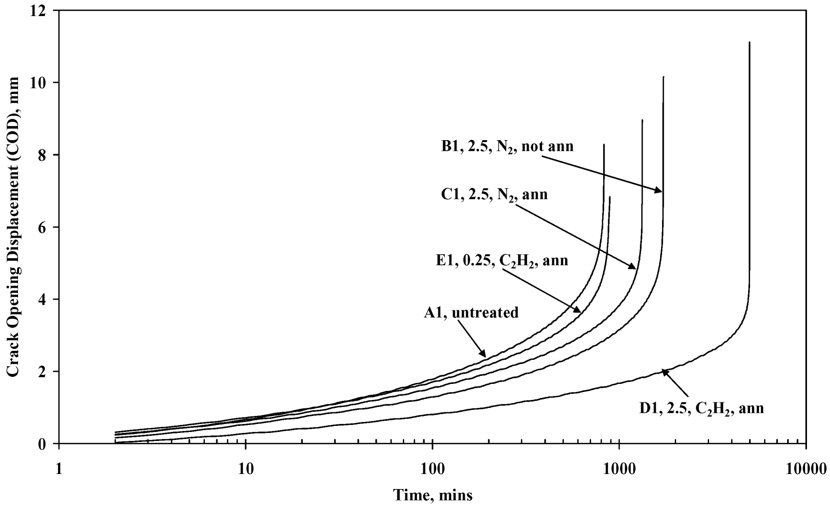


*Figure 7* COD vs. time plot for aged irradiated samples.

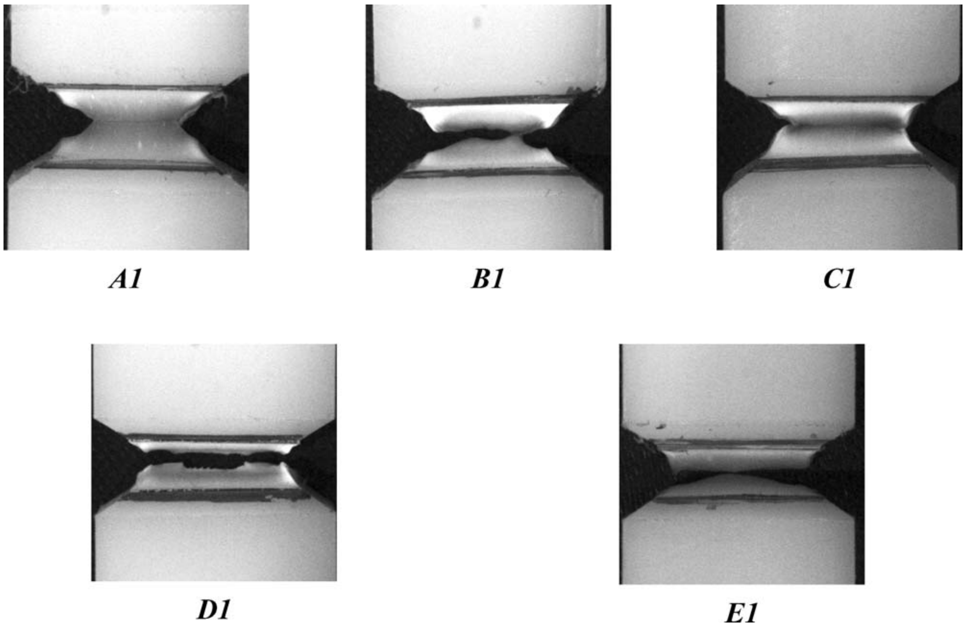


*Figure 8* Fracture surfaces of the aged samples after the SCG test.

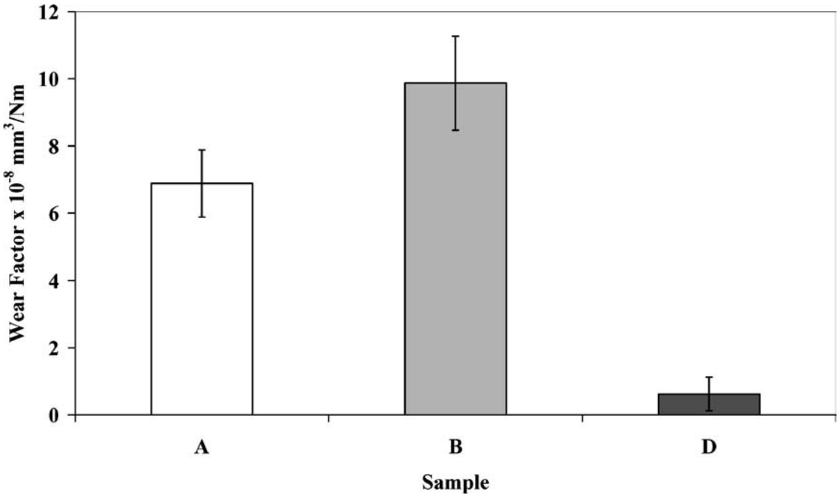


*Figure 9* Wear factors for Sample *A*, *B* and *D* following multidirectional pin-on-plate testing.

(Sample *A*) and the UHMWPE processed in the conventional manner by gamma irradiation in nitrogen (Sample *B*). Wear factors for the three materials are shown in Fig. 9 to allow comparison to previously published data. Wear factors consist of the wear volume results that were normalised according to the applied load and sliding distance. Sample *D* produced a wear factor of $0.62 \times 10^{-8}$ $mm^3$/Nm. This was significantly less than the wear of Sample *A* (virgin) and Sample *B* (2.5 MRad) where wear factors of $6.9 \times 10^{-8}$ mm$^3$/Nm and $9.9 \times 10^{-8}$ mm$^3$/Nm were found respectively.

Wear studies showed that a significant reduction in wear was achieved by $\gamma$-irradiation in an atmosphere of acetylene followed by annealing. GUR 1020 irradiated at 2.5 MRad in acetylene and annealed at 100 °C for 12 h produced significantly lower wear than the virgin material and the material irradiated at 2.5 MRad in nitrogen without annealing ($P < 0.05$). Previous studies by Marrs *et al.* reported wear factors of $0.6 \times 10^{-8}$ mm$^3$/Nm and $5.56 \times 10^{-8}$ mm$^3$/Nm for acetylene enhanced and virgin UHMWPE respectively tested under similar conditions using an RCH 1000 resin UHMWPE [13]. The results in this study are, therefore, comparable.

## 4. Conclusions

It is important to note that GUR 1020 irradiated in nitrogen at 2.5 MRad showed a similar gel fraction to material processed in acetylene although the latter showed much greater resistance to crack propagation in both non-aged and aged conditions. This result shows that gel fraction is not a good guide to the structure of the cross-linked polymer, only a broad indicator that an overall degree of cross-linking which has been achieved. It is clearly important to produce cross-links with as little chain scission as possible, which is the benefit of irradiation in an atmosphere of acetylene.

The multidirectional wear tests show that there is a significant reduction in wear achieved by $\gamma$-irradiation of UHMWPE in an atmosphere of acetylene followed by annealing compared with the traditional $\gamma$-irradiation in nitrogen. The result shows excellent correlation with the results of slow crack growth tests where similar ranking was obtained. GUR 1020 cross-linked by irradiation in acetylene gas at 2.5 MRad, and annealed at 100 °C for 12 h produced the best combination of mechanical properties, degradation resistance, and wear reduction throughout the study and may, therefore, be better suited to orthopaedic applications than the traditional material irradiated in nitrogen.

## Acknowledgments

We wish to thank Dr. A. L. Ward for advice on the construction of the slow crack propagation rig and the associated fracture tests. The fracture studies were funded by Stratec Medical and we wish to thank Dr. A. Montali for his support and interest. We also wish to thank Dr. Christina Doyle who was instrumental in initiating this research.

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*Received 12 March*
*and accepted 29 April 2004*