Annotation

ULTRA HIGH MOLECULAR-WEIGHT POLYETHYLENE (UHMWPE) IN TOTAL KNEE REPLACEMENT: FABRICATION, STERILISATION AND WEAR

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There is a perception that wear of the polyethylene components is a problem in total knee arthroplasty (TKA) with reports of retrieved components which have been grossly damaged.[1,2] There has also been considerable discussion concerning the induction of osteolysis by debris. It has been suggested that the designs of TKA should change, perhaps to meniscal bearings, and that new materials should be introduced such as femoral ceramic or tibial components of highly cross-linked polyethylene.

There have, however, been several reports of the use of cemented condylar TKAs with survival at ten years of 95% or more and with little radiological evidence of osteolysis. A recent paper given at a meeting of ESSKA concluded that at 12 years "………wear was not a problem at all".[3]

We believe that gross wear leading to the destruction of a component and the need for revision is due to delamination, one of the three types of wear to which ultra high molecular-weight polyethylene (UHMWPE) is subject, the other two being abrasion and adhesion. Delamination of loaded UHMWPE is caused by the way in which the material is manufactured and sterilised. It will not occur in normal use over ten years if the UHMWPE has been well compacted and has not been sterilised by gamma irradiation in air (Fig. 1). In the past, some batches of UHMWPE have not been well compacted and the dose of irradiation may have varied from batch to batch and within batches. It has been common practice to seal the components in a package containing air in which they were sterilised and later stored for varying periods of time. These variables are now thought to have accounted for the delamination which has been seen in some components.

The formation of a block

UHMWPE is produced by a chemical process as a powder which must be compacted into a solid before it can be used to manufacture a component. This powder can have different molecular weights. For example, GUR 1020 has an average molecular weight above 2 million and GUR 1050 above 5 million.[4-7] Compaction of the powder, however achieved, produces a solid material by two mechanisms, namely physical compaction in which the polymeric powder melts and the particles then adhere to each other, and chemical compaction in which the polymeric chains become interpenetrated. Both of these processes depend on the local temperature and the time for which pressure is applied[7,8-12] and both may be done well or badly.[11,13,14] In the past voids have been shown to be present in badly compacted materials possibly causing inferior mechanical properties in the resulting mass.[7,8,15-17] Foreign inclusions have also been demonstrated because of impurities in the equipment processing the powder.[5,6] Research has resulted in improvement in the morphology of consolidated UHMWPE.[11-14,18,19]

Compaction can be achieved by one of three processes: ram extrusion, slab compression moulding or direct compression moulding of a component[4-7,12] which, in general, produce equivalent material. The disadvantage of ram extrusion and slab compression moulding is that they may not produce uniform conditions in the compacted mass. In the past these techniques have used calcium stearate as an additive to stabilise the residue of the catalyser, in order to make the material flow more easily and to minimise corrosion of the tools. Calcium stearate, however, may accelerate oxidative degradation of polyethylene after gamma irradiation in air and may also cause poor consolidation of the powder.[19-21] It is therefore not now used. In direct compression moulding, if the surface is overheated there may

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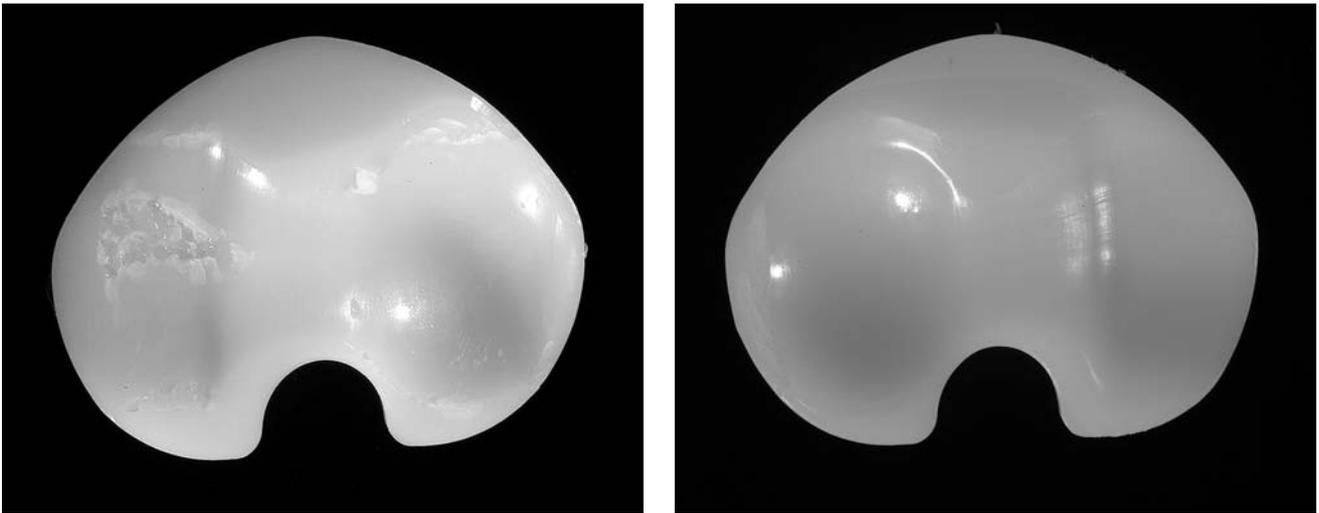
Fig. 1

Two identical prostheses retrieved after use in vivo for about five years. The prosthesis on the left (a) was made from poorly compacted UHMWPE and was gamma-irradiated and stored in air. It has delaminated. That on the right (b) was made from well-compacted UHMWPE and was gamma-irradiated and stored in a vacuum. It has not delaminated.

be more rapid wear. In the case of slab compression and ram extrusion a solid block is produced from which a component is machined. With direct compression moulding a component is formed which requires little or no further machining, but the technique is expensive and hence not suitable for prototypes. The UHMWPE in the manufactured component, regardless of the process of compaction, is composed of two phases, crystalline and amorphous. The proportion of the two depends on the conditions of manufacture. Air may enter a block of polyethylene either by being trapped between the granules as they are compressed or by diffusion from ambient air during storage. Diffusion is much more rapid into the amorphous than into the crystalline phase.[4,22,23]

Gamma irradiation in the absence of air

Sterilisation is usually by gamma irradiation which also has a direct chemical effect on the polyethylene chain, splitting the chemical bonds, so-called 'scission'.[24] This process can occur at carbon-hydrogen bonds or at carbon-carbon bonds. At the latter they split the polymer chain and this process is therefore called 'chain scission'.[4,5,23,25] Scissions produce alkyl radicals ($\sim CH_2$-CH°_2 or $\sim CH_2$-CH°-$CH_2\sim$) and hydrogen atoms (H°) as shown in Figure 2.

In the absence of oxygen, in the amorphous phase of polyethylene, the alkyl radicals produced by irradiation are relatively mobile and have frequent opportunities for conversion into double bonds in the polymer chain or for recombining to produce the original, or occasionally, longer chains, a process called 'cross-linking'. In the crystalline phase the radicals are much less mobile and may persist for many years, gradually leaking into the amorphous phase.[5,23,26-28]

Gamma irradiation in the presence of air (oxygen)

An additional sequence of events may arise after scission by irradiation if the polyethylene contains oxygen, either from the air present before sterilisation or because the component was sterilised and then stored in air, sometimes for years. Since the gamma-sterilised material contains alkyl radicals which also persist in the long term, a reaction between oxygen and alkyl radicals may then occur not only during sterilisation but for many years thereafter (Fig. 3).[4,5,23,28-30] This is known as oxidative chain scission.

Carboxylic acids, a product of chain scission, can be used as a surrogate measure of oxidation by using Fourier-transformed infrared spectroscopy. What were once long polyethylene chains, giving the material a high average molecular weight, have now become short oxidised chains.

The effect of oxidative-chain scission on wear of UHMWPE

As previously noted, abrasion, adhesion and delamination, which has been called subsurface cracking or flaking, are the three modes of wear of UHMWPE. Bond scission followed by oxidation changes UHMWPE into material of lower molecular weight[14,19,23,25,30-32] which is less resistant to wear and, specifically, to delamination.[9,33-35] Once the process of oxidative chain scission has started it is self-perpetuating because further alkyl radicals are generated which in turn react with any oxygen that may be present. Even if the original oxygen derived from the air has been used up, further oxygen,
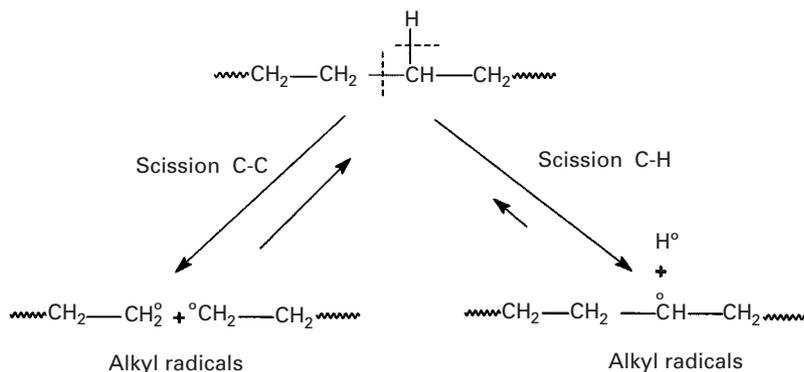
Fig. 2

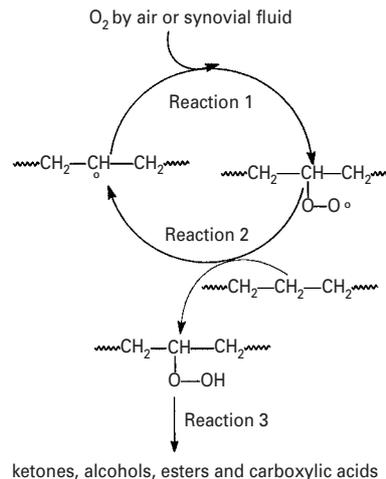The production of alkyl radicals by chain scission.

Fig. 3

The production of carboxylic acid by oxidative chain scission.

although in very small quantities, may continue to be delivered in vivo from synovial fluid. Thus oxidation and progressive weakening of the polyethylene may continue in vivo, although at a very slow rate.[4,20,32]

This sequence of events is well recognised in polymers generally after their irradiation by, for example, ultraviolet light or x-rays and therefore antioxidants are included to stabilise them. Unfortunately, the ASTM document F 648-84 forbids the addition of other materials to medical grade UHMWPE and therefore even non-toxic antioxidants, such as vitamin E, cannot be added.[25,36] Hence, the possibility that irradiated polyethylene, once implanted, may gradually deteriorate mechanically, could be prevented were it not for the existence of an administrative prohibition against the addition of an antioxidant such as vitamin E.

The clinical significance of these observations is that well-compacted UHMWPE will only delaminate under load if it has first undergone oxidative chain scission,[31,32] and that delamination has been by far the most important form of clinical wear in TKA at up to ten years.[1,2] Thus, if poor compaction and oxidative chain scission were avoided, delamination, the major cause of wear in TKA, would disappear. Wear by abrasion and adhesion would remain, but these mechanisms appear to be very slow.[37]

Chain scission followed by oxidation can be prevented in one of only two ways. Either a sterilisation agent other than gamma irradiation, such as ethylene oxide, can be used, or the component can be packaged in a vacuum or in an inert gas such as nitrogen during sterilisation and subsequent storage.[20,38] The attractions of gamma irradiation are that it is widely available and convenient.

Fortunately, the degree of oxidation in a given piece of polyethylene can be measured by Fourier transformed infrared spectroscopy[4,5,7,25,39] so that it is possible to

determine if a batch of components after sterilisation and storage is safe to be used by testing samples. A second method of determining indirectly and approximately the level of oxidation in polyethylene is the demonstration of a subsurface 'white band' in oxidised material. The 'white band' has been used in the surgical literature but since direct measurements can now be made by Fourier transformed infrared spectroscopy it is only of historical interest. It comes about because the polyethylene in this part of the block, all of which contains alkyl radicals after irradiation, is subject to high levels of heat generated by the gamma irradiation which diffuses out from the interior of the block at the same time that high levels of oxygen diffuse into the block from the ambient air. Heat and oxygen meet in the subsurface zone.[4,28,40] When an oxidized piece of polyethylene is sliced, the embrittlement caused by the oxidation results in crazing of the polyethylene which appears white when transilluminated. Unfortunately, the absence of a white band does not mean that there is no oxidation but only that oxidation is below some (unknown) level. The absence of oxidation means that there will be no white band.

A proposal for the future

There are strict quality controls with regard to the metal components of TKAs. We now propose that analogous controls, many of which are already established practice in the manufacturing industry, should be formalised with regard to the UHMWPE component.

1) The original powder must be UHMWPE of good quality and must not contain impurities.

2) The compaction process must be shown to be adequate. This can be done by examining a slice of the compacted

material and demonstrating that it contains neither fusion defects nor impurities.

3) If sterilised by gamma irradiation, it must be shown that the material has not been oxidised by measurement of oxidation using Fourier transformed infrared spectroscopy in sample specimens shortly before despatch to hospitals. We recognise that this would be expensive.

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