THE RADIATION IMPROVEMENT OF POLYETHYLENE PROSTHESES

A PRELIMINARY STUDY

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The radiation crosslinking of high-density polyethylene prostheses was investigated over a wide range of doses in the presence and absence of gaseous crosslinking agents. It was found that in the bulk polymer the crosslinking pattern is completely different from the homogeneous crosslinking that occurs in polymer films. The presence of crosslinking agents causes highly crosslinked polymer to be formed on the surface while the bulk of the polymer is largely unaffected—which is explained in terms of diffusion phenomena. This surface crosslinking has a profound effect on the mechanical properties of the prostheses and restricts cold flow and deformation of the polymer without sacrificing the excellent abrasion-resistance properties of the polyethylene when subjected to high pressures. Based on this research a number of high-density polyethylene knee prostheses have been radiation-crosslinked and the results *in vitro* appear to be very promising.

When high-density polyethylene (HDPE) has been used in total hip replacement for aged and relatively inactive people, the effects of wear and cold flow have proved over the years to be no real problem. Total joint replacement, however, is now being performed in younger patients who are not only more active but also expect a much longer lifespan of the arthroplasty. The same principles and materials are now also being applied to other joints—for example, total knee replacement. Whereas the hip is basically a low-friction joint, the knee imposes greater stresses and higher wear rates on the polyethylene bearing. For these reasons it was considered reasonable to improve the wearing qualities of polyethylene in spite of the high success rate at present offered by the material.

Basically, three elements are of importance in total joint replacement: the metal of the main component, the HDPE bearing, and the polymethylmethacrylate cement which fixes them to the bones. All three of these elements have in the past proved to be fallible. Our present view is that the weakest is the polymethylmethacrylate cement, followed by the metal, which is subjected to corrosion (Semlitsch 1972) and to alternating stresses varying between one and two million cycles per year (Dumbleton and Black 1975a); research on the improvement of these two components is being done, but falls outside the scope of this paper.

Why polyethylene?

There is no doubt that many materials can be considered as bearing material for total joint replacements. Of these, ceramics are probably the most important. They are highly inert (Dumbleton and Black 1975b) and will not be attacked by body fluids. The disadvantages are the very hard and brittle nature of the material, the high friction coefficient and, lastly, serious difficulties in manufacture.

The following are the most important reasons why we have decided to retain polyethylene, but to improve its wearing qualities.

Clinical acceptability. Experience over the past fifteen years has proved that it is clinically a very suitable material (Charnley 1973). In our own research department, polyethylene and polypropylene have been proved to be extremely inert in studies on baboons. The material is well accepted by the tissues, and hardly any foreign-body cell reaction takes place around it. Deterioration *in vivo* may well take place in time, but over fifteen years of experience this has not proved detrimental to clinical results (Charnley 1973). When polyethylene cups that have been in the body for many years have been removed, virtually no wear has been apparent despite a yellowish discoloration.

Chemical structure. A polyethylene chain is built up from carbon and hydrogen atoms only; it is a hydrophobic polymer. It has been reported that hydrophobic polymers can be extremely badly tolerated by the body (Hoffman 1974), but it is possible that other polymers were referred to, for example polytetrafluoroethylene (PTFE): the fluorine present in PTFE makes this polymer very irritative and we have substantial proof that, apart from its mechanical deficiencies,

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physiological side-effects occur when particles of it are freed in the body (Charnley 1978). PTFE granulomata form, which are destructive to the tissue and also cause loosening at the bone–cement interface. We have also observed similar complications with acrylic cement, which, on the other hand, is a hydrophilic polymer. We therefore feel justified in saying that the hydrophobic or hydrophilic nature of polymers is not directly related to their physiological inertness. Irritative elements, such as the halogens, are probably more important causes of undesirable tissue reactions. Hydrophilic polymers absorb 30 to 70 per cent of their weight of water and are mechanically totally incapable of being used as bearing material (Hoffman 1974).

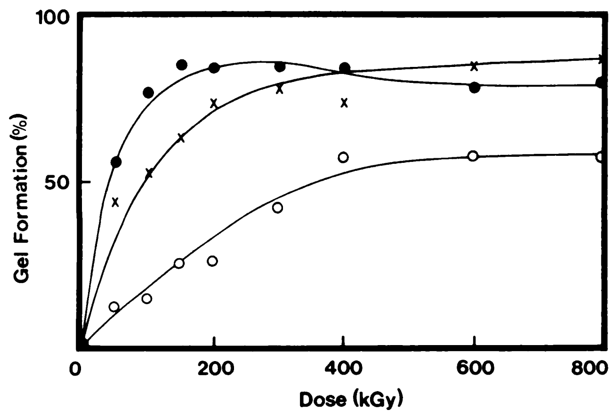

Fig. 1

The percentage gel formation as a function of the irradiation dose for HDPE samples, taken from the surface of the sample, in the presence of crosslinking agents and nitrogen. ○, nitrogen; ×, acetylene; ●, acetylene and CTFE.

Physical properties. The flow characteristics of polyethylene cups have proved to be highly satisfactory when used with femoral heads between 22 and 28 millimetres in diameter (Galante and Rostoker 1973). The type of lubricant is not important in the case of polyethylene: water, oil and synovial fluid are all equally effective when polyethylene is used as the bearing material. This is not the case for many other polymers, for instance PTFE (Dumbleton, Shen and Miller 1974). Polyethylene also responds very well to ionising radiation and can be sterilised by radiation with very little change in its properties (du Plessis 1977).

As radiation crosslinking gives excellent improvements to polyethylene film, its effect on HDPE prostheses was investigated in the search for improved mechanical properties and a longer lifespan of these prostheses. In the absence of crosslinking agents, relatively high radiation doses are required to obtain worthwhile improvements (Dumbleton and Shen 1974): at doses of 200 to 10 000 kilograys (20 to 1000 megarads) the coefficient of friction at low pressures drops noticeably (Dumbleton and Shen 1974; Dumbleton *et al.* 1974). The irradiation dose that is commonly employed for the radiation sterilisation of medical devices is 25 kilograys. Mitsui, Hosoi and Kagiya (1972) and Hagiwara *et al.* (1973) observed that the crosslinking of polyethylene film could be accelerated when irradiated in the presence of acetylene or mixtures of acetylene and chlorotrifluoroethylene (CTFE). We have found that the cold flow of HDPE could be drastically reduced when this polymer was irradiated in the presence of acetylene (du Plessis, Grobbelaar and Marais 1977).

This investigation was carried out in an attempt to improve the cold-flow characteristics of HDPE prostheses through a process of accelerated radiation-crosslinking without sacrificing the excellent frictional properties of this polymer.

MATERIALS AND METHODS

The high-density polyethylene used in this investigation was Hostalen RCH 1000 C* as used in orthopaedic applications with an average molecular weight of between 3.5 and 4 million. The crosslinking gases, acetylene and chlorotrifluoroethylene, as well as the nitrogen which was used as an inert atmosphere, were of an analytical grade.

The irradiations were carried out in a stainless steel container in such a way that an excess of the crosslinking agent was present. A Gammabeam-650 irradiator of the Atomic Energy Board with a nominal activity of 50 kilocuries was used at a constant dose-rate of 10 kilograys (1.0 megarad) per hour and a temperature of 30 degrees Celsius, and the dose range from zero to 800 kilograys was investigated.

A minimum of twelve test samples, both for impact strength and tensile strength tests, were used for every experimental condition. Films of various thicknesses were used to determine the physical changes that result from the crosslinking. The percentage gel formation was determined after a forty-eight hour Soxhlet extraction with decalin as solvent. Standard techniques were used for infrared and thermal analyses.

Tensile strength and impact strength tests were carried out by the National Institute for Defence Research. Monoaxial tensile strength tests were done at 37 degrees Celsius, at speeds that varied from 5 centimetres per minute to 16.7 metres per second. Impact strength tests were done at 37 degrees Celsius according to the Izod method, and surface hardnesses were measured with a Shore-type hardness meter.

The abrasion-resistance tests were carried out by the United States Industrial Chemicals Company using a sand-slurry test in which the samples were rotated for seven hours at a speed of 1750 revolutions per minute, and the percentage loss in weight was determined.

RESULTS

Physical properties. In good agreement with earlier findings (Mitsui *et al.* 1972; Hagiwara *et al.* 1973), our results showed that the presence of acetylene or an equimolar mixture of acetylene and CTFE had a profound effect on the radiation crosslinking of HDPE films when compared with the polymer irradiated in nitrogen as an inert atmosphere (Fig. 1). Below a dose of 400 kilograys the mixture of acetylene and CTFE was the better crosslinking agent, while above this dose acetylene gave the best crosslinking—a phenomenon which can be ascribed to the possible radiation

*Hoechst U.K. Ltd, Hounslow, Middlesex.

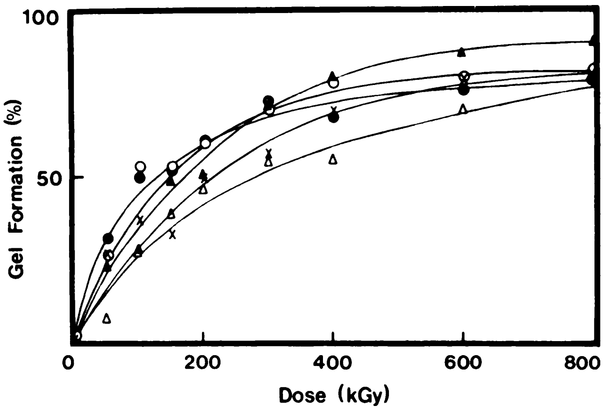

Fig. 2

The percentage gel formation as a function of the irradiation dose for HDPE samples, taken from the inner portion of the sample, in the presence of crosslinking agents, nitrogen, air and oxygen. ○, nitrogen; ×, acetylene; ●, acetylene and CTFE; ▲, air; △, oxygen.

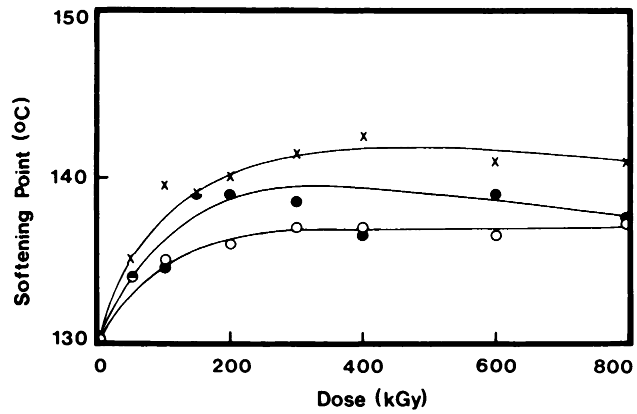

Fig. 3

The softening points of HDPE when radiation crosslinked in the presence of crosslinking agents and nitrogen, as a function of the irradiation dose. ○, nitrogen; ×, acetylene; ●, acetylene and CTFE.

degradation of the halogenated polyethylene above this irradiation dose. For practical considerations it was decided to extend this investigation to polymer samples with physical dimensions similar to that of the knee prostheses which had to be crosslinked, that is 1.0×1.0×5.0 centimetres.

In the case of the bulky HDPE samples it was found that polyethylene taken from within the sample indicated that the presence of a crosslinking agent did not enhance the radiation-induced crosslinking—not even when the irradiation was carried out in an atmosphere of pure oxygen was there any effect on the crosslinking (Fig. 2). Experiments on films of various thicknesses clearly indicated that diffusion of the crosslinking agents into the polymer took place only to a depth of about 300 micrometres. Beyond this depth, as a result of limited diffusion, the radiation crosslinking could not be enhanced by the presence of a gaseous crosslinking agent. It was, furthermore, observed that extending the irradiation time by a series of intermittent irradiation doses, in an attempt to increase the diffusion of the gaseous crosslinking agents into the polymer, had no effect on the depth of the radiation-crosslinking of the polyethylene. This phenomenon was confirmed by infrared analyses of the crosslinked HDPE (du Plessis and Lustig 1977).

Softening point. Both acetylene and a mixture of acetylene and CTFE resulted in a rise in the temperature at which softening of HDPE occurred at irradiation doses up to 200 kilograys. Above this dose no further increase was observed (Fig. 3).

Tensile strength. Tests on tensile strength, carried out on the crosslinked polyethylene at both low and high speed, showed a slight increase in strength with increase in radiation dose. Deformation of the HDPE was severely restricted as a result of the radiation crosslinking, the mixture of acetylene and CTFE being a better crosslinking agent than pure acetylene (Fig. 4). This was in good agreement with the results obtained for the percentage gel formation (Fig. 1). These results indicate that prostheses made from HDPE and treated by radiation crosslinking will have surfaces that will resist mechanical deformation under high pressures.

Surface hardness. Experiments on irradiated polyethylene indicated that the surface hardness of the treated polymer increased markedly with an increase in radiation dose, and the mixture of acetylene and CTFE was again the best crosslinking agent (Fig. 5).

Impact strength. The impact strength of the crosslinked polyethylene decreased drastically with increase in radiation dose, almost independent of the presence of a crosslinking agent (Fig. 6). These results imply that care

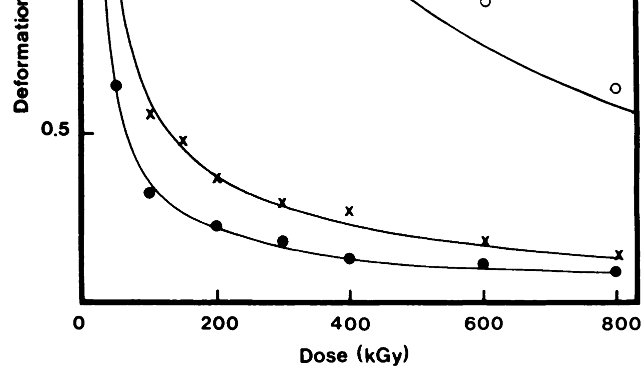

Fig. 4

The mechanical deformation of HDPE when radiation crosslinked in the presence of crosslinking agents and nitrogen, as a function of the irradiation dose. ○, nitrogen; ×, acetylene; ●, acetylene and CTFE.

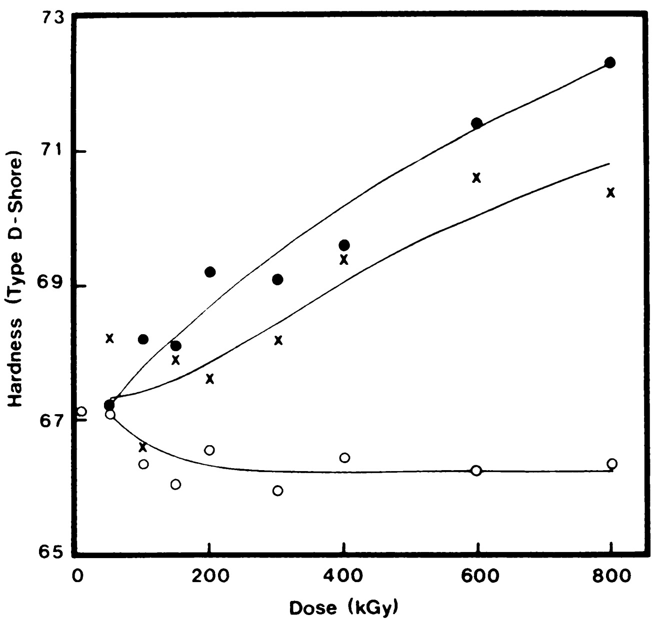

Fig. 5

The surface hardness of HDPE when radiation crosslinked in the presence of crosslinking agents and nitrogen, as a function of the irradiation dose. O, nitrogen, ×, acetylene; ●, acetylene and CTFE.

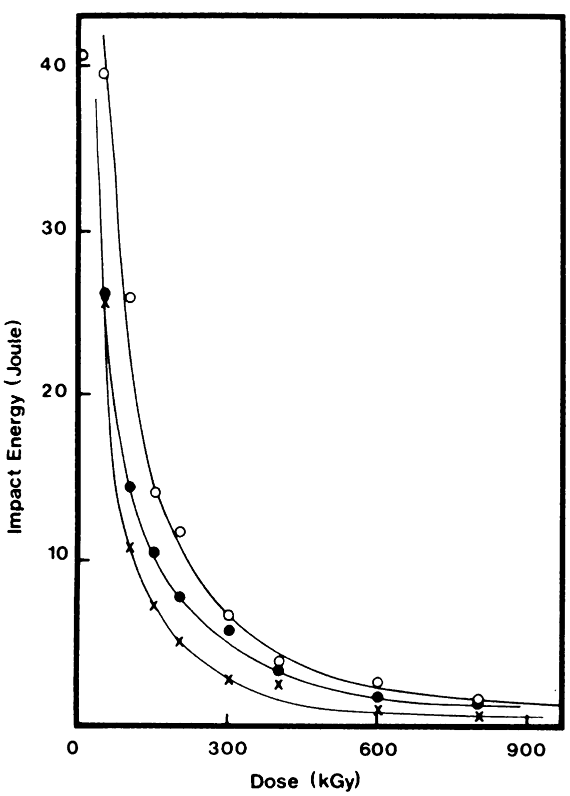

Fig. 6

The impact energy of HDPE when radiation crosslinked in the presence of crosslinking agents and nitrogen, as a function of the irradiation dose. O, nitrogen; ×, acetylene; ●, acetylene and CTFE.

should be exercised not to use irradiation doses in excess of 150 kilograys in order to avoid the serious decrease in impact strength that can result from the crosslinking.

Abrasion resistance. Crosslinked HDPE showed almost 30 per cent improvement in abrasion resistance compared with unirradiated controls (Table I). Although the abrasion resistance was not improved to the same extent as some of the other mechanical properties, there was at least no reduction as was found by Dumbleton and Shen at the high irradiation doses they applied (Dumbleton and Shen 1974; Dumbleton *et al.* 1974). We can therefore expect that the radiation crosslinking of polyethylene prostheses will not impair their wear characteristics.

Table I. Abrasion resistance of HDPE when radiation crosslinked in the presence of acetylene at an irradiation dose of 150 kilograys, compared to that of the unirradiated polymer

Sample	Condition	Percentage weight loss*
1	Unirradiated	0.51
2	Unirradiated	0.42
3	Unirradiated	0.47
4	Irradiated	0.37
5	Irradiated	0.38
6	Irradiated	0.33

*The greater the percentage weight loss, the poorer the abrasion resistance.

DISCUSSION

The crosslinking of bulky HDPE samples is far more pronounced on the surface than in the interior and this leads to interesting mechanical properties of the polymer so treated. A prosthesis is obtained which has a highly crosslinked surface with a marked resistance to cold flow and abrasion, while the bulk of the prosthesis is about eightfold less crosslinked, giving the surface a much better resistance to shock. A material is thus formed with properties similar to those obtained by case hardening in metallurgy. From a mechanical point of view the radiation crosslinking of HDPE presents a unique method of overcoming the present restrictions in the orthopaedic applications of this polymer. Tensile strength, and resistance to abrasion and cold flow can thus be increased without the detrimental effect of brittleness.

When HDPE is irradiated in an atmosphere of inert nitrogen there is improvement in tensile strength, hardness and softening point, but only with an irradiation dose in excess of 400 kilograys. At such high doses the HDPE becomes brittle, impact resistance is reduced drastically and wear increases dramatically. In the presence of oxygen the situation becomes even worse as a result of the radiolytic oxidation of the polymer surface. Through the use of crosslinking agents such as acetylene and CTFE, the irradiation demands are quantitatively reduced so that crosslinking will occur at very low irradiation doses, for example 100 kilograys. Tensile strength, hardness and resistance against cold flow can thus be increased without sacrificing the excellent wear characteristics of this polymer.

The formation of a transfer film in unirradiated polyethylene prostheses has been reported by Dumbleton and Shen (Dumbleton and Shen 1974; Dumbleton *et al.* 1974). They suggest that this film prevents continuous wear, and also that radiation crosslinking will prevent this film from forming; wear will therefore be increased in radiation-crosslinked HDPE prostheses. The present investigation, however, indicates that this is not true for HDPE prostheses that were radiation-crosslinked in the presence of acetylene as a crosslinking agent. Although clinical results are still limited at this stage, evidence from a radiation-crosslinked knee prosthesis, which was recently removed after two years *in vivo*, strongly supports the laboratory results that cold flow in the polyethylene is severely restricted through the process of radiation crosslinking of the HDPE.

High temperatures in the curing of the polymethylmethacrylate cement during the implantation of a polyethylene prosthesis can lead to the deformation of such an implant, thereby impairing its proper functioning. There can be little doubt that the radiation-crosslinked polyethylene prosthesis will have a thermal stability far superior to that of the unirradiated polyethylene prosthesis and very little, if any, deformation of such prostheses will take place as a result of the high temperatures during the curing of the acrylic cement.

Furthermore, although cold flow is apparently not a serious problem in a hip prosthesis with a head diameter between 22 and 28 millimetres, the same may not be said of the total knee replacement where the distribution of forces is rather different. In today's knee prostheses, the pressure exerted by the metal component upon the polyethylene can become extremely high. It is in this area that more research is needed.

At this stage of our research we feel justified in using this radiation-crosslinking technique routinely on the knee prostheses and the total hip prostheses designed and manufactured in Pretoria. It seems likely that we may thus add many years to the lifespan of our present arthroplasties and be closer to our ultimate goal of a prosthesis that will last a lifetime.

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