Polymer 41 (2000) 7635–7639

polymer

Mechanical changes linked to embrittlement at the wear surface of polyethylene implants in hip joints

A. Flores[a], N.D. Jordan[b], F.J. Baltà-Calleja[a], D.C. Bassett[b], R.H. Olley[b,*], N.G. Smith[c]

[a]Instituto de Estructura de la Materia, CSIC, Madrid, Spain
[b]JJ Thomson Physical Laboratory, Polymer Science Centre, University of Reading, Whiteknights, Reading RG6 6AF, UK
[c]Howmedica International, Ash House, Staines, Middlesex, UK

Received 19 October 1999; received in revised form 5 January 2000; accepted 16 February 2000

Abstract

A study of microhardness at the wear surface of polyethylene implants before and after use is reported. The microhardness values support previous electron microscopic observations of an embrittled region extending into used implants by showing that, after use, the hardness of polyethylene implants increases above the initial value the nearer the wear surface is approached. It is shown that these changes accompany a hardening of the surface layer and are related to an increase in the crystallinity of the polymer. The increasing hardness towards the edge of the concave surface of the implant is discussed in terms both of the local variation of crystallinity and changes in the interlamellar regions.

Keywords: Embrittlement; Polyethylene implants; Microhardness

1. Introduction

Replacement surgery is increasingly used for hip joints but suffers from limited lifetimes in the body due, at least in part, to the wear of the implanted polyethylene. In the context of widespread research to understand wear processes aimed at improving materials and so prolonging the effectiveness of the surgery, we have examined a number of polyethylene hip cups (Howmedica ABG design) worn on a cobalt chrome femoral head before and after implantation in the body. In early investigations the use of permanganic etching prior to optical and electron microscopy was shown to be capable of sensitive discrimination between the quality of different moulded materials prepared for possible manufacture of hip cups [1].

More recently, we have had the opportunity to examine used hip cups that have been removed from the body. Of especial interest was that electron microscopy after permanganic etching revealed a layer, at least 10 μm thick extending inwards from the wear surface, of polymer which showed incipient cracking and appeared to have been embrittled by its exposure to the body environment [2]. The present paper reports the results of microhardness tests upon the same worn hip cups in a successful attempt to provide direct supporting evidence for the changed nature of polyethylene adjacent to the wear surface.

Microhardness is an established method for non-destructive testing of the mechanical properties of materials which has been extensively applied to polyethylenes of different molecular weights and crystallization conditions [3,4]. The present study confirms that the mechanical properties of the polyethylene have indeed been altered at the wear surface with the material becoming harder as expected for an embrittled layer.

2. Materials and experimental

Table 1 collects the known insert history of the polyethylene hip cups investigated. A comparable non-implanted acetabular insert was also investigated.

The hemispherical hip cups as received were first cut radially into blocks of ~5 cm size with the concave wear surface on the inside. The lateral surfaces were cut further with a microtome at room temperature to a smooth planar condition (Fig. 1).

2.1. Techniques

Microhardness tests were carried out at a constant temperature of 21°C, using a Vickers diamond and a Leitz microindentation tester. The load applied ranged from 0.049

---

* Corresponding author. Tel.: + 118-931-8572; fax: + 118-975-0203.
E-mail address: r.h.olley@reading.ac.uk (R.H. Olley).

0032-3861/00/$ - see front matter
PII: S0032-3861(00)00132-4

Table 1

Sample	Implant duration (months)	Crystallinity α
Control		0.517
1997-3 (cup 3)	36	0.555
1997-5 (cup 5)	73	0.590

to 0.245 N and was maintained for 6 s except when otherwise stated. Vickers hardness, H, is derived from:

$$H = kP/d^2 \tag{1}$$

where P is the load applied, d the diagonal of the residual impression and k a geometric constant. When P is in N and d in mm a value for k of 1.854 gives hardness values in MPa.

Calorimetric measurements were performed using a Perkin–Elmer DSC4 differential scanning calorimeter (DSC). Samples consisted of a thin layer of the concave surface of the hip cups, weighing some 4–5 mg encased in aluminium pans. Calculation of the degree of crystallinity, α, from the melting enthalpy, ΔH_m used the equation

$$\alpha = \Delta H_m/\Delta H^0 \tag{2}$$

where ΔH^0 is the melting enthalpy of the ideal crystal, taken to be 293 J/g [5].

3. Results

3.1. Microhardness measurements

Preliminary attempts to indent the wear surfaces directly suffered both from intrinsic curvature and non-uniform wear. The former tended to increase the recorded size of the indentation while the latter was a cause of erratic variability. Nevertheless, the increased hardness of the used cups, at their wear surfaces, in comparison to the control was apparent. Attention turned, accordingly, to the lateral surfaces of the blocks (Fig. 1) which approached the smooth planar condition required for optimum hardness measurements. Microindentation experiments on these surfaces yielded the data reported below.

Indentations were made within 1 mm of the concave surface for the control sample and cup 5, and Fig. 2 shows the plot of applied force versus the square of the indentation diagonal. The results are fitted by two straight lines whose slope in Fig. 2 is proportional to the microhardness value according to Eq. (1). The standard error of the estimates is so small that the error bars would be covered completely by the symbols plotted. On the other hand, the intercept on the ordinate is the value of the load below which no plastic deformation takes place and the indentation recovers fully. Inspection of Fig. 2 immediately reveals a higher hardness value for the implanted probe than for the control sample.

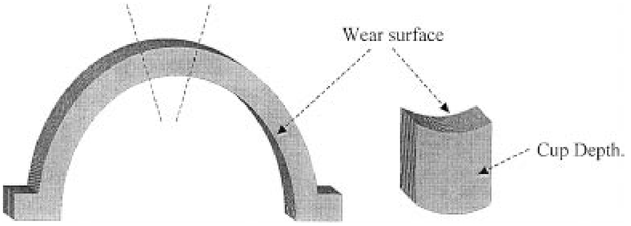

Fig. 1. Schematic representation of the sectioning geometry of the acetabular inserts.

Fig. 3 shows the hardness values measured as a function of the radial distance, h, from the indent to the edge of the concave surface. The hardness value of the control sample ($H \approx 57$ MPa) does not vary with h. On the contrary, H for cups 3 and 5 shows a stepwise increase as the wear surface is approached. An initial H plateau, up to $h \sim 1$–2 mm, has been brought about by in situ conditions at the hip joint. Also notable is the fact that the microhardness in both worn samples at $h > 4$ mm is still higher than that of the non-implanted material.

3.2. Creep behaviour

Fig. 4 shows a double logarithmic plot of the H values of the control sample and cup 5 versus the time for which the load is held. This plot shows that the hardness of the implanted and non-implanted samples follows a power law function with time of the type

$$H = H_0 t^{-\kappa} \tag{3}$$

where κ is the creep constant and H_0 the hardness measured for 1 min holding time. This power law is known to hold for polymers [6,7] with higher values of κ indicating lower viscoelasticity. In contrast to the early data taken from the wear surface themselves which did show a creep constant increasing with wear as would have been anticipated in conjunction with the other changes observed, this was not confirmed by the better measurements on the lateral surfaces. For these the data of Fig. 4 show that the values of the creep constant for the control and cup 5 samples agree within experimental error and lie in the range of other creep constants derived for different polyethylene samples crystallized under various crystallization conditions [8]. In these circumstances the case for a change in viscoelasticity with wear is not proven.

4. Discussion

4.1. Hardening of the amorphous layer

The above results support the previous electron microscope observations [2] showing incipient cracking and embrittlement adjacent to the wear surfaces of polyethylene hip cups after exposure to the body environment by showing suitably altered mechanical properties. A possible mechanism to account for the observed increase of microhardness in the implanted materials (at $h > 4$ mm) is (oxidative) degradation with incorporation of inorganic atoms in the

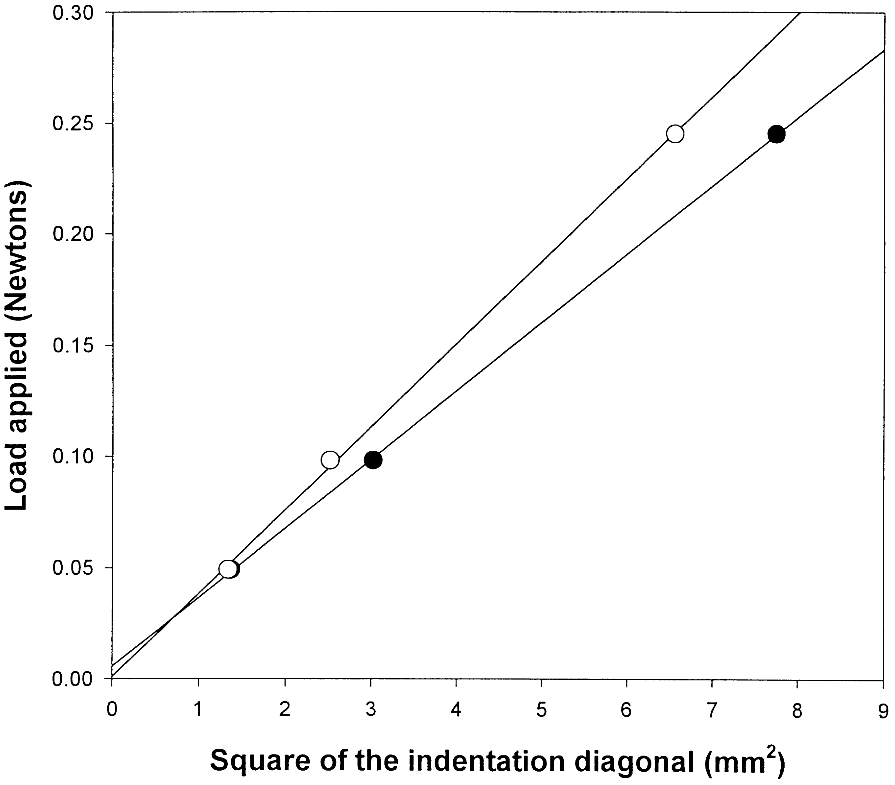

Fig. 2. Load as a function of the square of the indentation diagonal for the control sample (circles) and cup 5 (open circles).

amorphous (interlamellar) component of polyethylene which, according to the crystallinity values of Table 1, comprises about 50% of the material.

It has been shown that chemical treatment of low-density polyethylene with osmium tetroxide produces a drastic increase in hardness which was explained in terms of a reduction in the molecular mobility of the amorphous region [9]. A similar mechanism, leading to a slight hardening of

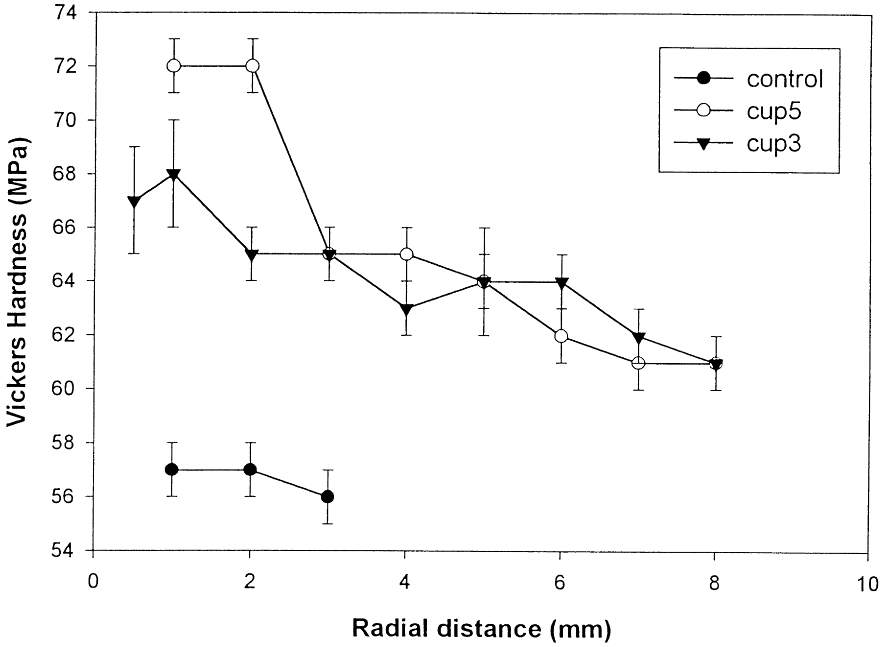

Fig. 3. Variation of hardness as a function of the distance to the concave surface for the control sample (circles), cup 3 (triangles) and cup 5 (open circles).

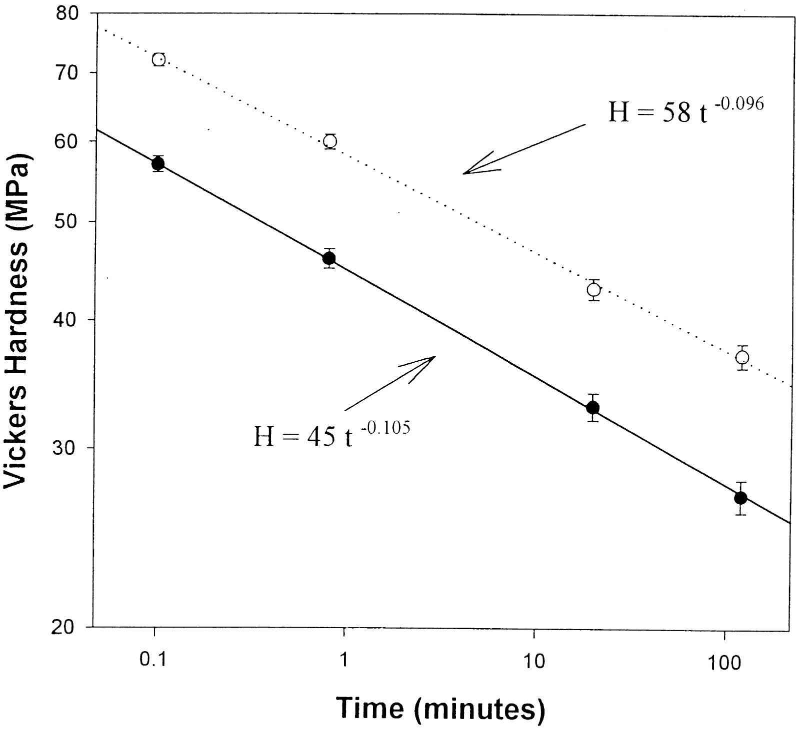

Fig. 4. Time-dependent behaviour of hardness for the control sample (circles) and cup 5 (open circles).

the amorphous phase, could well have taken place in the materials investigated in this paper.

For quantitative evaluation of the hardening effect within the amorphous regions, we make use of the empirical relations describing the hardness of the semicrystalline polymer [10]:

$$H = H_c\alpha + (1 - \alpha)H_a \qquad (4)$$

where H_c and H_a are the intrinsic values of the crystalline and amorphous phases, respectively. For polyethylene at room temperature, $H_a \sim 0$, one can write:

$$H \sim H_c\alpha \qquad (5)$$

Using this equation with $H = 57$ MPa and $\alpha = 0.517$ for the control sample, a value for H_c of 110 MPa is obtained.

In accordance with Fig. 3, H_c and α values are assumed to remain constant after implantation when $h > 4$ mm. Using these values together with Eq. (4) and taking $H \sim 64$ MPa when $h > 4$ mm for the used samples, we derive a value of $H_a = 15$ MPa. Hence, the hardening effect observed on the implanted samples at $h > 4$ mm, can be correlated with the hardness increase of the amorphous regions, from $H_a \sim 0$ in the non-implanted material, up to $H_a \sim 15$ MPa after exposure in the body.

4.2. Hardness changes at the wear surface

The stepwise increase in microhardness of cups 3 and 5 as the wear surface is approached (Fig. 3) is in agreement with their increase in crystallinity observed with respect to the control sample (Table 1 and Eq. (4)). Sample cup 5, with the longest implant-duration, shows the highest degree of crystallinity and, consequently, has the largest hardness value. Its H_c value for $h < 2$ mm can be derived using Eq. (4). Using the α values for the implanted samples, one obtains $H_c = 109$ MPa for cup 3 and $H_c = 112$ MPa for cup 5. These values are comparable to that of $H_c = 110$ MPa derived for the control sample. In view of the known dependence of H_c on the crystalline lamellar thickness [9] it is very likely, as electron microscope images would support, that the crystalline lamellar thickness remains unaltered during implantation. In fact, the constancy of the melting temperature of the three samples, as measured by DSC, confirms that this is so. It also indicates that oxidation has been confined to the non-crystalline regions.

5. Conclusions

The results obtained in this paper complement and support those found in the previous report, in which electron microscopic observations of the wear surface of used acetabular inserts showed incipient cracking and embrittlement [2]. In the present paper, we have demonstrated that the embrittlement of the polyethylene accompanies a hardening of a surface layer and an increase in crystallinity. The two pieces of evidence are complementary and imply a reduction in the crack-blunting ability of the material, i.e. a diminution of the number of interlamellar tie molecules that connect adjacent lamellar stacks. Consequently the elastic properties of the material will diminish and cause the material to harden during wear. The increase of hardness at the wear surface is partly because the amorphous component decreases in quantity and partly because its nature changes as it undergoes simultaneous hardening and loss of elasticity.

References

[1] Olley RH, Hosier IL, Bassett DC, Smith NG. Biomaterials 1999;20:2037.
[2] Jordan N.D., Bassett D.C., Olley R.H., Smith N.G. Submitted for publication.
[3] Bayer RK, Baltà-Calleja FJ, Kilian HG. Colloid Polym Sci 1997;275:432.
[4] Baltà-Calleja FJ, Kilian HG. Colloid Polym Sci 1985;263:697.
[5] Wunderlich B. Macromolecular physics, vol. 3. New York: Academic Press, 1980.
[6] Baltà-Calleja FJ, Bassett DC. J Polym Sci 1977;58C:157.
[7] Baltà-Calleja FJ, Santa Cruz C, Asano T. J Polym Sci Polym Phys 1993;31:557.
[8] Baltà-Calleja FJ, Flores A, Ania F, Bassett DC. J Mater Sci 2000;35:1315.
[9] Baltà-Calleja FJ, Giri L, Michler GH, Naumann I. Polymer 1997;38:5769.
[10] Baltà-Calleja FJ. Trends Polym Sci 1994;2:419.