

# **Mechanical Changes linked to Embrittlement at the Wear Surface of Polyethylene Implants in Hip Joints.**

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## **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.

## **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 microscopy was shown to be capable of sensitive discrimination between the quality of different moulded materials prepared for possible manufacture of hip cups<sup>1</sup>.

More recently we have had the opportunity to examine used hip cups which have been removed from the body. Of especial interest was that electron microscopy after permanganic etching revealed a layer, at least 10  $\mu\text{m}$  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<sup>2</sup>. 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<sup>3,4</sup>. 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.

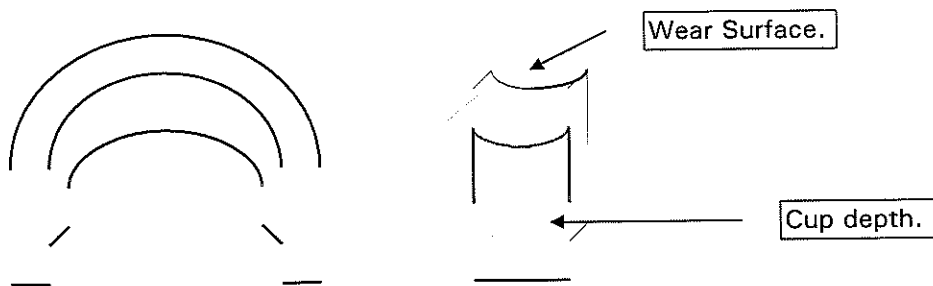
## 2 Materials and Experimental

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

**Table 1**

Acetabular insert	Implant duration months	Design/counterface/size	Patient gender	Patient weight kg
1997-3	36	ABG/CoCr/28mm	Female	
1997-5	73	ABG/CoCr/28mm	Male	65

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.(Figure 1)



**Figure 1**

## 2.1 Techniques

Microhardness test 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 to 0.245 N and was maintained for six seconds except when otherwise stated. Vickers hardness, H, is derived from:

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

where P is the load applied, d is the diagonal of the residual impression and k is a geometric constant. When P is in Newtons 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,  $\alpha$ , from the melting enthalpy,  $\Delta H_m$  used the equation

$$\alpha = \Delta H_m / \Delta H^\circ$$

where  $\Delta H^\circ$  is the melting enthalpy of the ideal crystal, taken to be  $293 \text{ J/g}$ .

### 3 Results

#### 3.1 Microhardness measurements

Preliminary attempts to indent the wear surfaces directly suffered both from the intrinsic curvature and the 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 cups (Figure 1) which did possess the smooth planar condition required for optimum hardness measurements. Microindentation experiments on these surfaces yielded the data reported below.

Figure 2 shows the plot of applied force versus the square of the indentation diagonal for the control sample and cup 5. Indentations were made within 1mm of the concave surface. The slope of the straight lines in Figure 2 is proportional to the microhardness value according to equation 1. 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 Figure 2 immediately reveals a higher hardness value for the implanted probe than for the control sample. In addition, the significantly different intercepts are consistent with the elastic recovery of the polyethylene diminishing after implantation, an effect confirmed by further data which follow.

Figure 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

( $H \approx 57\text{MPa}$ ) 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  $h \sim 1\text{-}2\text{ mm}$ , 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  $h > 4\text{ mm}$  is still higher than that of the non-implanted material.

### 3.2 Creep behaviour.

Figure 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

$$H = H_0 t^\kappa$$

where  $\kappa$  is the creep constant and  $H_0$  the hardness measured for 1 minute holding time. This power law is known to hold for polymers<sup>6,7</sup> with higher values of  $\kappa$  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 Figure 5 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<sup>8</sup>. 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<sup>2</sup> 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 amorphous (interlamellar) component of polyethylene which, according to the crystallinity values of Table 2, comprises about 50% of the material.

**Table 2**

Sample	Crystallinity $\alpha$
Control	0.517
1997-3 (cup 3)	0.555
1997-5 (cup 5)	0.590

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<sup>9</sup>. A similar mechanism, leading to a slight hardening of 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<sup>10</sup>:

$$H = H_c \alpha + (1-\alpha) H_a \tag{4}$$

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

$$H \sim H_c \alpha \tag{5}$$

Using this equation with  $H = 57$  MPa and  $\alpha = 0.517$  (Table 2) for the control sample, a value for  $H_c$  of 110 MPa is obtained.

In accordance with Figure 3,  $H_c$  and  $\alpha$  values are assumed to remain constant after implantation when  $h > 4$  mm. Using these values together with equation (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 (Figure 3) is in agreement with their increases in crystallinity observed with respect to the control sample (Table 2 and equation 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 equation (4). Using the  $\alpha$  values for the implanted samples of Table 2, 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<sup>9</sup> 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. 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 which connect adjacent lamellar stacks. In consequence 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

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## **Legend to Figures**

**Figure 1** Schematic representation of the sectioning geometry of the acetabular inserts.

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

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

**Figure 4** Time dependent behaviour of hardness for the control sample (circles) and cup 5 (triangles).

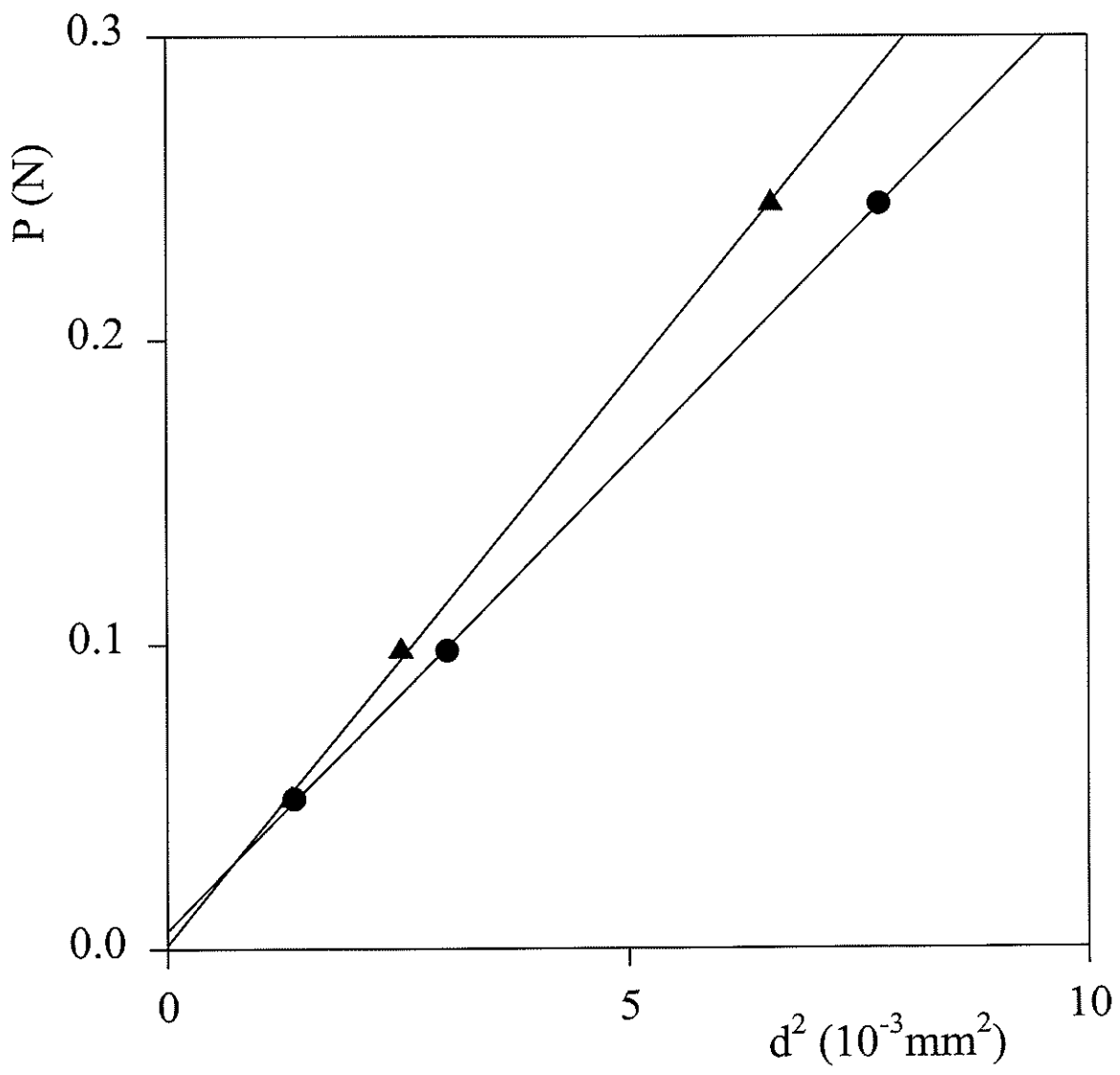


Fig. 2

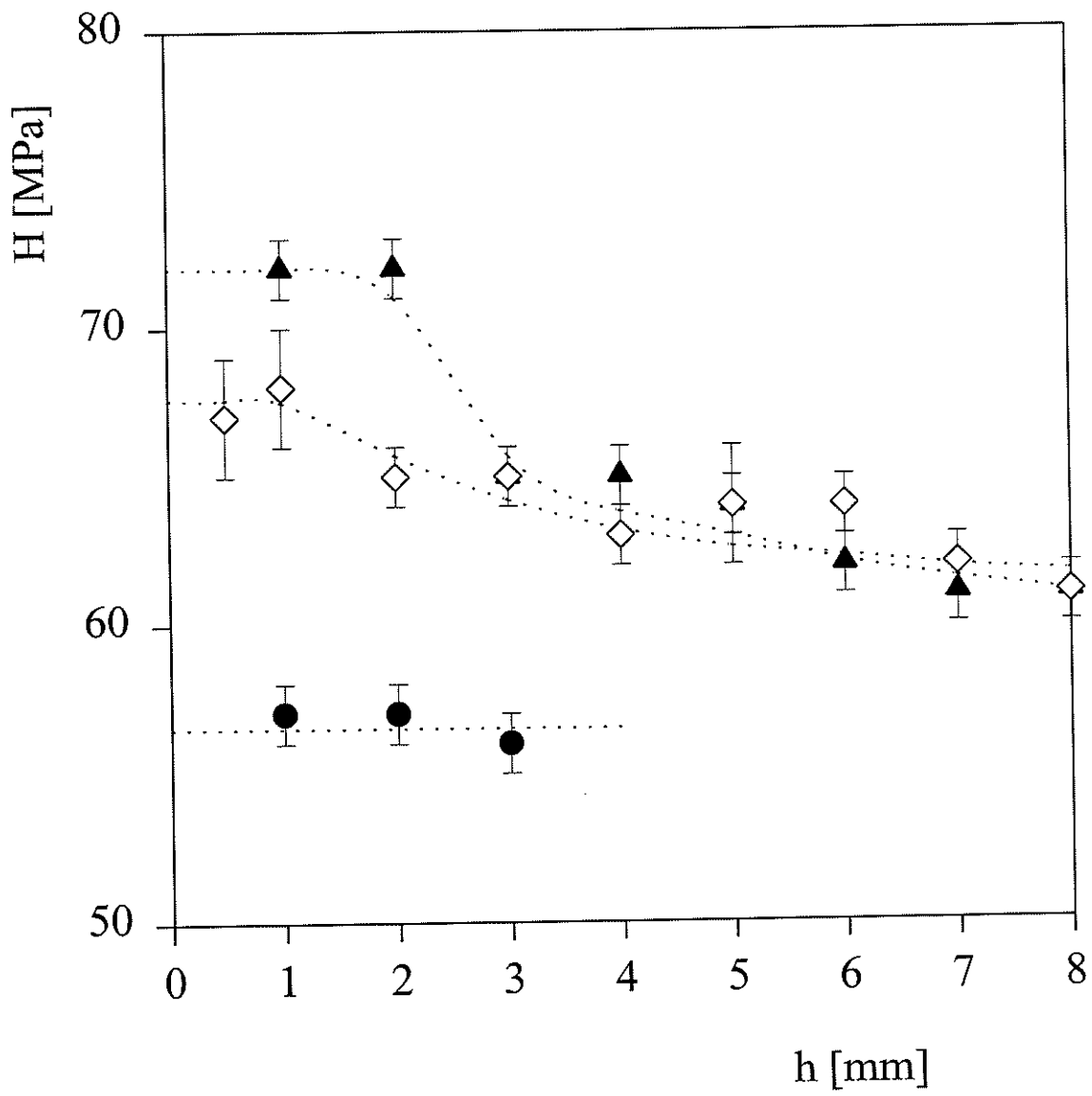


Fig. 3

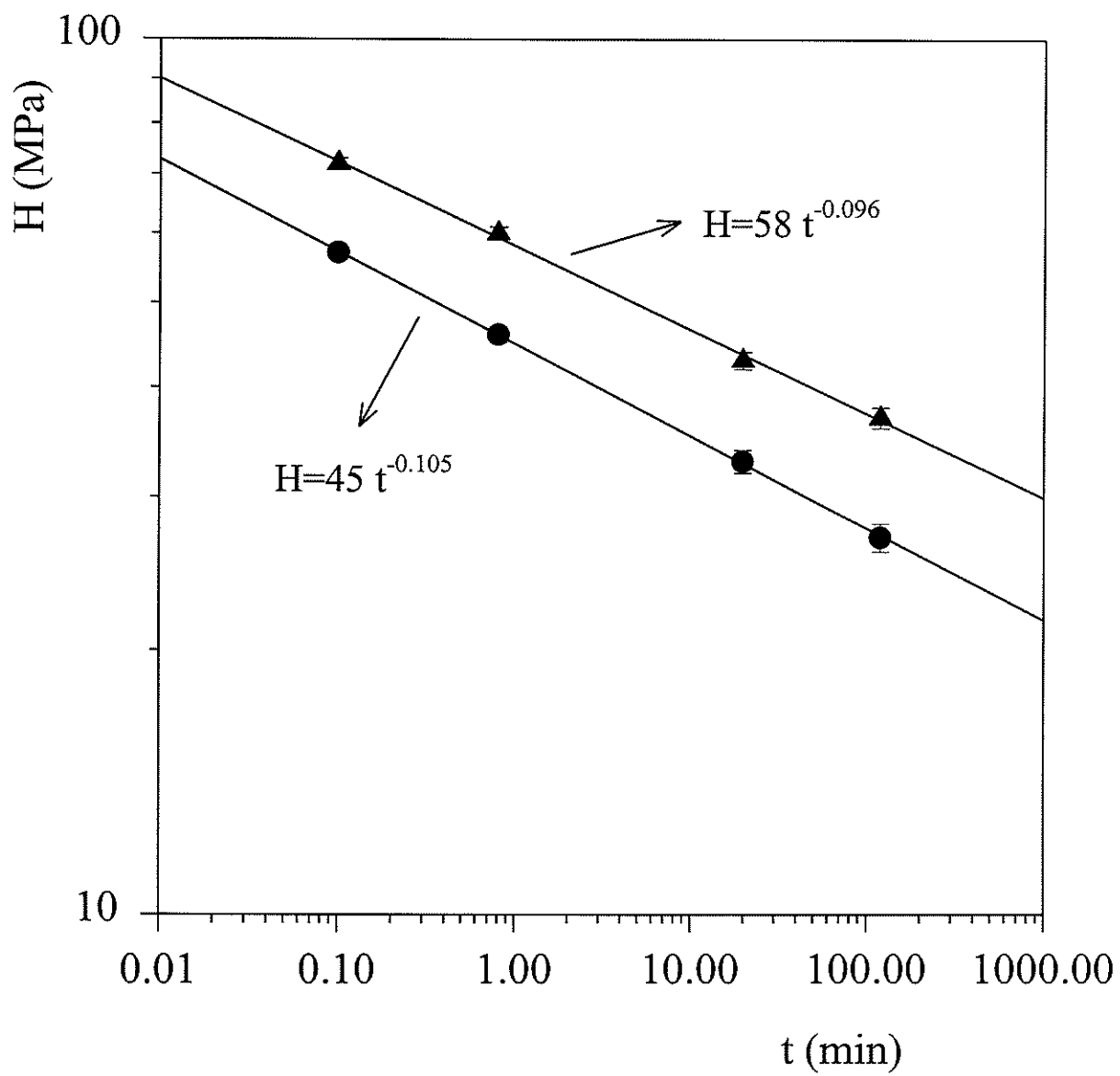


Fig. 4