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Friction and wear of hydroxyapatite reinforced high density polyethylene against the stainless steel counterface

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Hydroxyapatite (HA) reinforced high density polyethylene (HDPE) was invented as a biomaterial for skeletal applications. In this investigation, tribological properties (e.g. wear rate and coefficient of friction) of unfilled HDPE and HA/HDPE composites were evaluated against the duplex stainless steel in dry and lubricated conditions, with distilled water or aqueous solutions of proteins (egg albumen or glucose) being lubricants. Wear tests were conducted in a custom-built test rig for HDPE and HA/HDPE containing up to 40 vol % of HA. It was found that HA/HDPE composites had lower coefficients of friction than unfilled HDPE under certain conditions. HA/HDPE also exhibited less severe fatigue failure marks than HDPE. The degradation and fatigue failure of HDPE due to the presence of proteins were severe for low speed wear testing (100 rpm) as compared to high speed wear testing (200 rpm). This was due possibly to the high shear rate at the contact which could remove any degraded film instantaneously at high sliding speed, while with a low sliding speed the build-up of a degraded layer of protein could occur. The degraded protein layer would stay at the contact for a longer time and mechanical activation would induce adverse reactions, weakening the surface layer of HDPE. Both egg albumen and glucose were found to be corrosive to steel and adversely reactive for HDPE and HA/HDPE composites. The wear modes observed were similar to that of ultra-high molecular weight polyethylene. Specimens tested with egg albumen also displayed higher wear rates, which was again attributed to corrosion accelerated wear.

Introduction

Trauma and diseases often cause the destruction of bone and joints in human bodies. It has been a challenge for researchers in the biomaterials field to develop bone replacement materials that should be biocompatible and should not produce chronic foreign body inflammatory response. Moreover, these new materials must not fail within the expected lifetime after implantation. It is also well recognized that the implant material should posses mechanical properties that are identical or close to those of the host tissue [1–3], as mismatch of stiffness between the implant material and bone can result in ''stress shielding'' which leads to bone resorption and hence eventual implant loosening. Since Charnley's efforts in introducing ''low friction arthroplasty'', a variety of materials have been in use for total knee and hip prostheses. The most commonly used materials in orthopaedics include ultra-high molecular weight polyethylene (UHMWPE), Co–Cr alloys, stainless steel, and alumina and zirconia ceramics, owing to their proven biocompatibility, low coefficients of friction and in most cases low wear rates. Among these materials, UHMWPE occupies a prominent position as the material for acetabular cups in hip prostheses. However, difficulties associated with the manufacture of UHMWPE cups and its undesirable wear rates pose problems [4, 5].

A new generation of biomaterials has been developed over the last few decades, taking into account the requirements for biocompatibility and bioactivity. Hydroxyapatite (HA) reinforced high density polyethylene (HDPE) is one such material that is suitable for skeletal applications [6, 7]. Even though extensive research has been conducted on this material [8–18], its tribological properties have never been reported. In this

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investigation, HDPE and HA/HDPE composites were evaluated for their tribological performance against duplex stainless steel under dry and lubricated conditions and in the presence of proteins.

Materials and methods

Injection molded plates and bars of HDPE and HA/HDPE composites were manufactured following a standardized procedure [19]. Specimens for wear tests were cut to the required shape and size (i.e. test pins) using a diamond cutting wheel. They were subsequently polished to the required surface finish and cleaned with ethanol before testing.

A custom-built tri-pin-on-disc testing machine was used for wear tests. Values of temperature close to the sliding surface, frictional force, and wear depth of HDPE or HA/HDPE pins were obtained during the tests. The counterface used in this investigation was a polished duplex stainless steel disc which was rotated by an electric motor at chosen speeds. To run the test, the HDPE or HA/HDPE pins were raised to mate with the counterface. A load cell (Tokyo Sokki Kenkyojo, 200 kgf) placed between the pin holder and a pneumatic cylinder measured the normal force applied to the pins during the test. The initial normal force could be set by adjusting the gas pressure on the pneumatic cylinder. The frictional force was measured using a dynamic accelerometer (Omega, DLC 501) which was suitable for monitoring instantaneous changes. The wear depth was measured using a non-contact laser displacement sensor, and the temperature change close to the sliding surface monitored using a K-type thermocouple. The normal force was recorded every 5 min in a data logger. Values of frictional force, wear depth and temperature were collected at 1-min intervals using a KAYE data acquisition system. During the test, a compressed air jet was aimed at the stainless steel disc surface in order to minimize frictional heating which could cause distortion of the pins. After each test, the surface of pins and the counterface were examined under a scanning electron microscope (JEOL 5600 SEM). The surface roughness of the pins and the counterface was evaluated using stylus profilometry (Taylor-Hobson, Form Talysurf 120L). Wear tests were performed at two rotational speeds (100 and 200 rpm) so as to investigate the effect of sliding speed/distance on the wear behavior. Specimens were tested under dry or lubricated conditions, using distilled water or aqueous solutions of proteins (egg albumen or glucose) as lubricants.

Results

Trial tests showed that testing speeds greater than 200 rpm could cause severe distortion and deformation of HDPE and HA/HDPE pins. Therefore, a maximum speed of 200 rpm was used in the systematic study of these materials in this investigation.

Wear test results indicated that sliding speed had a significant effect on the wear and failure of HDPE and HA/HDPE composites. This can be clearly seen from the average coefficients of friction and wear depths at different testing speeds for HDPE (Figs 1 and 2) as well as HA/HDPE specimens. The coefficients of friction of HDPE obtained from tests conducted in the presence of distilled water and egg albumen at 100 rpm were lower than those from tests conducted in the presence of glucose or under the dry condition. It was also evident that the 100 rpm testing speed normally produced higher coefficients of friction than the 200 rpm testing speed. Figs 3 and 4 are SEM micrographs of the pin surface of HDPE tested in the presence of egg albumen at 100 and 200 rpm, respectively. They provided evidences of fatigue failure and corrosive reactions on the pin surface. The specimen tested at 100 rpm showed damage by fatigue with signs of corrosive reaction, while the specimen tested at 200 rpm exhibited a lower degree of corrosive damage.

Figs 5 and 6 show the average coefficients of friction and wear depths obtained from tests conducted on HA/HDPE composites containing 5–40 vol % of HA. The incorporation of HA into HDPE resulted in decreases in coefficient of friction and wear depth up to 10 vol % of HA. Above 10 vol % of HA, a change in trend in the frictional behavior and wear rate was noticed. Figs 7 and 8 are SEM micrographs of surfaces of composite slid in the presence of egg albumen and glucose, respectively. It can be seen that egg albumen formed a protective layer on the composite surface thus restricting the wear of HA/HDPE. However, adverse reactions weakening the composite surface were also present which was believed to be the cause of rapid wear of HA/HDPE containing high amount of HA. Specimens tested in the presence of low viscosity fluids such as water and glucose solution resulted in rapid wear due to cavitational effect. This was

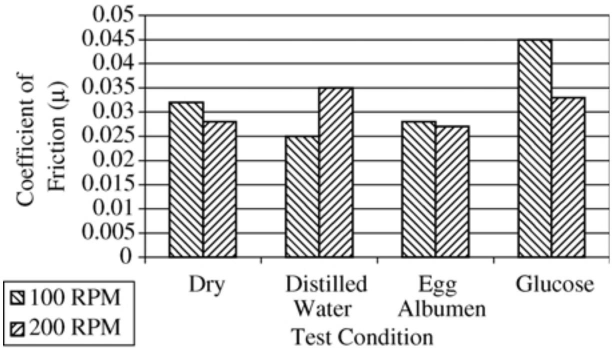

Figure 1 Coefficient of friction of HDPE under various testing conditions.

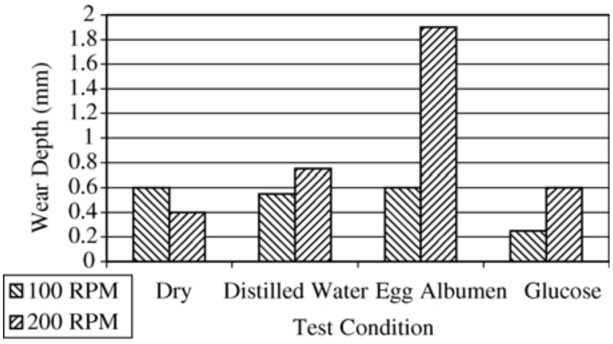

Figure 2 Wear rate of HDPE measured in terms of depth of wear in 8 h under various testing conditions.

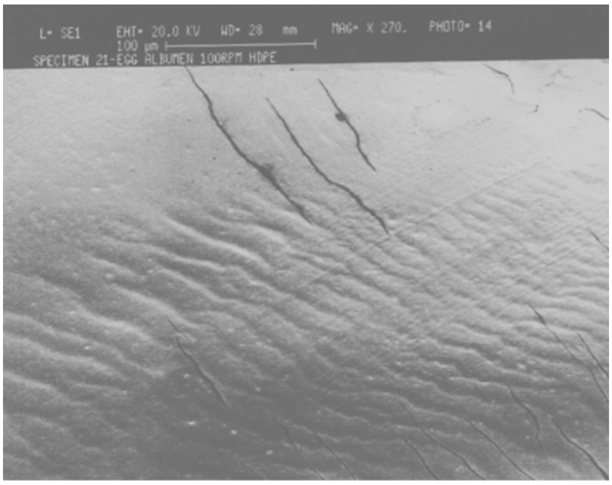

Figure 3 SEM micrograph of the surface of an HDPE pin tested at 100 rpm in the presence of egg albumen.

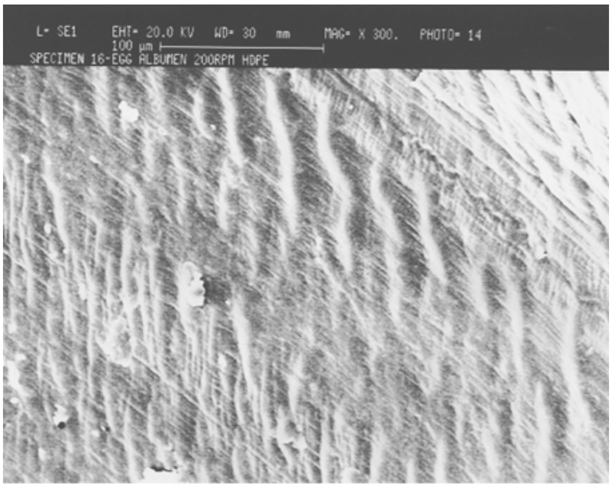

Figure 4 SEM micrograph of the surface of an HDPE pin tested at 200 rpm in the presence of egg albumen.

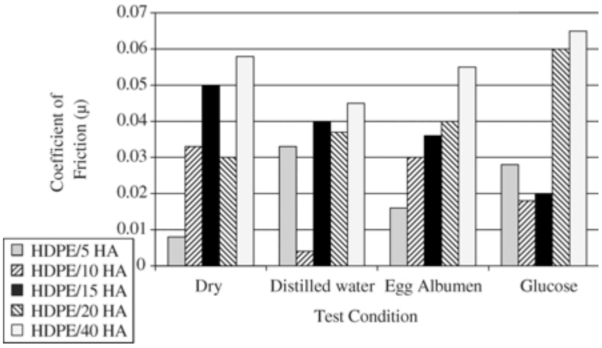

Figure 5 Coefficient of friction of HA/HDPE under various testing conditions (at 200 rpm).

supported by SEM images of specimens tested in the presence of aqueous glucose solution, depicting the release of the HA particles and cracking on the composite surface (Fig. 8).

HDPE and HA/HDPE specimens were also found to undergo a degradation process when tested in the presence of aqueous solutions of proteins. This was confirmed by thermal and chemical analyzes of both tested and untested specimens. DSC results revealed a reduction in heat flow in specimens that had been tested in the presence of proteins.

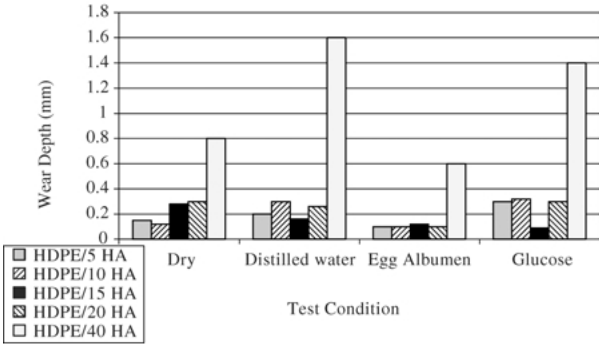

Figure 6 Wear rate of HA/HDPE measured in terms of depth of wear in 8 h under various testing conditions (at 200 rpm).

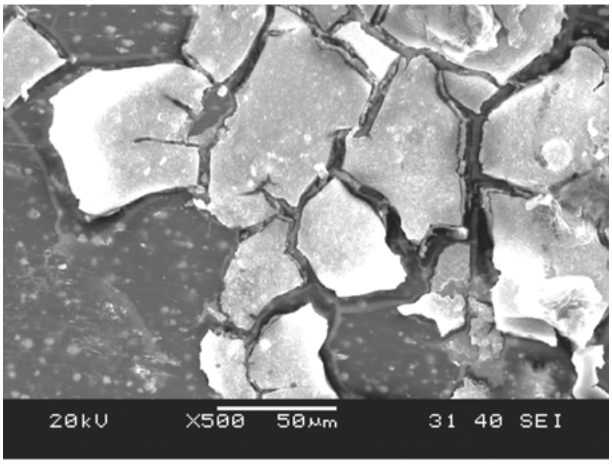

Figure 7 SEM micrograph of the surface of an HA/HDPE (20 vol % HA) pin tested at 200 rpm in the presence of egg albumen.

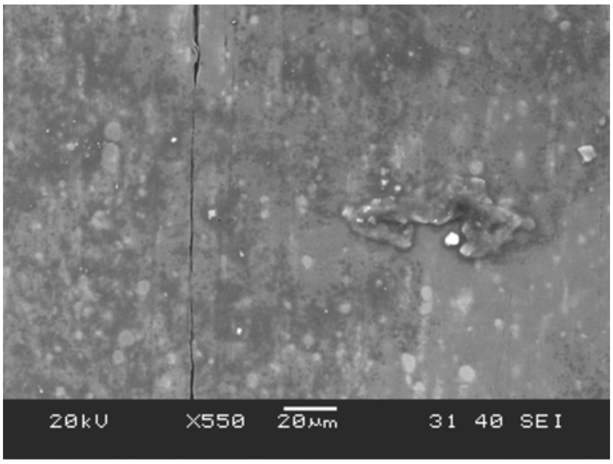

Figure 8 SEM micrograph of the surface of an HA/HDPE (20 vol % HA) pin tested at 200 rpm in the presence of glucose.

The temperature rise close to the sliding surface due to frictional heating was found to be higher for the unfilled polymer than for the filled polymer. (The temperature of the test environment was 23 °C.) This is shown in Figs 9 and 10. As expected, the dry sliding condition exhibited the highest temperature rise for both HDPE and HA/HDPE specimens, followed by sliding in the presence of distilled water, egg albumen and glucose. The rise in

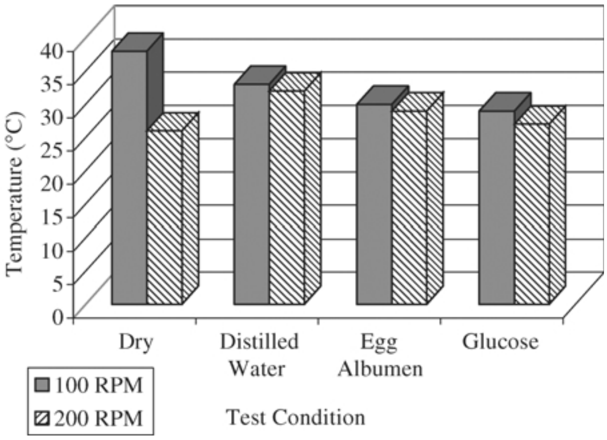

Figure 9 Temperature of wear surface during sliding of HDPE under various testing conditions.

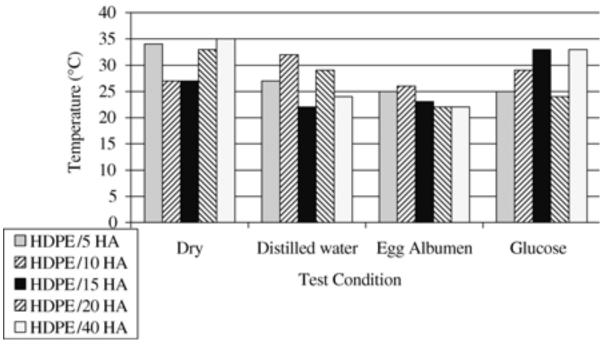

Figure 10 Temperature of wear surface during sliding of HA/HDPE under various testing conditions.

temperature for a given test condition varied for HA/HDPE with different HA contents and there may exist an optimum HA volume percentage (probably 10 vol % in this case) below or above which the temperature rise is higher. The frictional heating was also found to be lower at 200 rpm than at 100 rpm for the HDPE specimens (Fig. 9), which coincided with the lower coefficients of friction obtained at 200 rpm.

Discussion

The low coefficients of friction obtained for HDPE (Fig. 1) are primarily attributed to the lubricity of water due to its low viscosity, and for egg albumen the lubricity is enhanced by the paste-like film formation on the surface of the rotating disc or the stationary pin, acting as an interface with low shear strength. The formation of an adsorbed protein layer on the surfaces of HDPE specimens and the stainless steel disk offered a protection against direct contact between the sliding surfaces. The higher coefficients of friction obtained from tests conducted under the dry condition and in the presence of glucose are possibly due to surface interactions and corrosive reactions that led to the formation of an adsorbed layer at the interface, respectively. Although the adsorbed layer was helpful in restricting surface interactions during sliding, sliding that took place by shearing within the adsorbed layer could result in higher coefficients of friction.

The tests conducted on HDPE specimens indicated testing speed affected failure mode and wear rate. This was supported by SEM images of specimens tested at 100 and 200 rpm (Figs 3 and 4). The excessive damage of the specimen tested at 100 rpm may be due to the shearing of a strong adsorbed layer of protein (egg albumen) on the surface. At 100 rpm, the shear rate is not high enough to remove the adsorbed layer instantaneously, thus allowing a longer time for reaction between the sliding surfaces and the protein. This reaction further increases the strength of the adsorbed layer, requiring higher shear stresses for further sliding to take place. At a higher testing speed, the adsorbed layer formed is instantaneously sheared off to generate new surfaces, thus giving rise to a lower coefficient of friction but a higher wear rate. This is illustrated in the model given in Fig. 11.

The incorporation of HA into HDPE improves tribological properties of the system up to 10 vol % of HA beyond which wear properties deteriorate in the presence of low viscosity fluids. Tests run in the presence of distilled water and glucose did not last for the preset time of 8 h due to rapid wear of specimens. This is due possibly to the release of HA particles during the wear test, leading to three body wear. With an increase in HA volume percentage, more HA particles are present. During the wear test, the abrasive scoring exposes the HA particles in the HDPE to the steel disk. The exposed HA particles act as the bearing surface on the pin where a situation of steel sliding on the HA ceramic embedded in the polymer matrix occurs. This gives rise to a higher coefficient of friction with a very low wear rate. When sliding in the presence of glucose and distilled water, high wear rates in addition to high coefficients of friction were obtained. This behavior is caused by the low viscosity of the fluids used, which seep through the minute gaps between the HA particle and the HDPE matrix. The seeped fluid, i.e., distilled water or glucose, stays in the gap beneath the HA particle and is pressurized by the combined normal and frictional

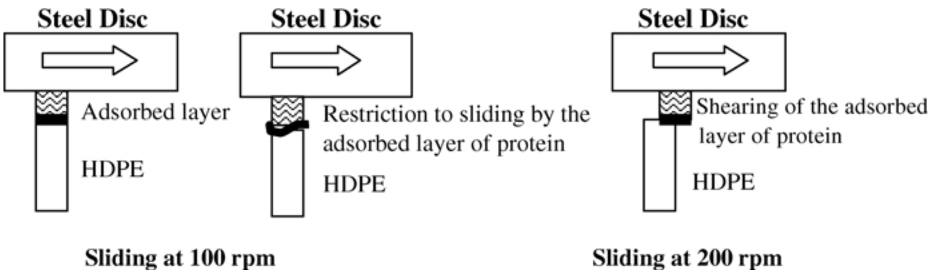

Figure 11 A model showing the difference in sliding behavior at 100 and 200 rpm testing speeds.

(a) **Initial state of sliding** (b) **Lubricant seeping into the HA-HDPE interface**

(c) **Pressurized lubricant at the interface** (d) **HA removed to form an abrasive slurry leading to further particle removal**

Figure 12 A model for the HA particle removal from the HDPE matrix due to lubricant seepage and particle lift-off.

forces when sliding proceeds. The pressurized liquid film can break and thus eject HA particles from the matrix, which leads to a situation of abrasive slurry lubrication instead of the presence of a plain aqueous solution of glucose or distilled water, thus removing the composite surface in flakes and releasing more HA particles into the slurry. This results in rapid wear and hence premature failure of composite specimens. The high wear rates obtained for specimens tested in the presence of aqueous glucose as compared to distilled water is due to the aggravating corrosive reactions of glucose with the sliding surfaces in addition to the effect of the low viscosity of the liquid. Fig. 12 depicts the wear mechanism involved.

The higher than expected surface temperature associated with the testing condition of distilled water is due possibly to the low viscosity of water which does not restrict the surface interaction completely. The rise in surface temperature due to frictional heating in tests conducted with egg albumen serves as evidence for the variation of frictional property which is enhanced by degradation of proteins. The degradation of proteins leads to their decreased lubricating ability, resulting in increases in coefficients of friction which in turn cause temperature rises. A detrimental cycle is therefore set in motion.

Conclusions

Wear tests of HDPE were conducted at 100 and 200 rpm testing speeds, while HA/HDPE specimens were tested at the lower speed of 100 rpm. Lubricants used were distilled water and aqueous solutions of egg albumen and glucose. From the results obtained, following conclusions can be drawn:

1. HDPE undergoes severe deformation and damage at high sliding speeds and hence is not suitable for implants which may be subjected to extreme conditions.
2. For HA/HDPE composites, the lower testing speed induces severe degradative reactions as compared to the higher testing speed in the presence of aqueous proteins.
3. The incorporation of HA up to 10 vol % improves both the friction and wear behavior of HDPE.
4. The addition of HA above 10 vol % deteriorates tribological properties of HA/HDPE composites due to cavitational effect of lubricants and corrosive reactions of proteins.

Acknowledgments

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