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The effect of chromic acid treatment on the mechanical and tribological properties of aramid fibre reinforced ultra-high molecular weight polyethylene composite

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Surface oxidation of ultra-high molecular weight polyethylene (UHMWPE) powder has an influence on the mixing procedure of chopped fibres and UHMWPE powder. Due to this oxidation hydrogen bonds can be formed between the fibres and powder particles, leading to a more homogeneous fibre–powder mixture. This treatment improves the fibre–matrix interface and thus the physical properties of the composite. Chromic acid treatment also has an influence on the mechanical and tribological properties of the aramid–UHMWPE composite. Although only a relatively small improvement is observed in the modulus, yield stress and stress at break, of 33, 17 and 9%, respectively, a substantial enhancement in wear resistance of 117% is observed.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is frequently used in artificial joints because of its high wear resistance. The wear of UHMWPE has generated new concern regarding the long-term clinical performance of total joint replacements [1–6]. According to Cooper *et al.* the major concern is adverse tissue reactions caused by the generation of UHMWPE debris [3]. The debris is transported to the tissues surrounding the joint and causes a chronic inflammatory reaction and bone resorption. It has been suggested that due to the presence of debris, macrophages release various cytokines and growth factors that induce a loss of bone [7, 8]. One way to improve the wear resistance of UHMWPE is to incorporate aramid fibres. In a previous study it has been shown that the wear resistance of UHMWPE increases by a factor of 2.5 if the UHMWPE is blended with 5 vol% aramid fibres [9].

A problem of this composite is the poor fibre–matrix adhesion. For a good reinforcement fibre–matrix interaction is crucial. At the interface loads are transferred from the matrix to the fibre [10–12]. This load transfer depends, among other things, on the degree of fibre–matrix adhesion. To improve chemical interaction between the aramid fibre and the UHMWPE matrix it is necessary to modify one of the two surfaces. The aramid fibres are based on poly(p-phenylene terephtalamide) chains that are oriented along the longitudinal direction of the fibre and are hydrogen bonded to each other [13–17]. The adhesion between aramid fibres and most matrices is poor, due to the chemical inertness and smooth surfaces of the fibres which prevent chemical as well as mechanical bonding. A number of methods have been developed to introduce reactive sites on the fibres, such as plasma treatment [18–22] and chemical modification [23–31]. For example, Penn and coworkers [26, 28] and Tidrick and Koenig [29] have chemically modified aramid fibres with isocyanates, like hexanediisocyanate, *n*-butylisocyanate, tolylene 2,4-diisocyanate, and chloropropylisocyanate to enhance the adhesion between the aramid fibres and an epoxy matrix. Takayanagi *et al.* [30, 31] modified aramid fibres via the metalation reaction to provide fibres with several functional groups such as *n*-octadecyl, carboxymethyl and acrylonitrile in order to improve adhesion between the fibres and matrices like epoxy, polyethylene and ionomer.

In the polyolefine world plasma [32–34], corona discharge [4, 35], flame treatment [35–37] and chemical etching [32, 38–43] are used to treat surfaces. In this way it is, for instance, possible to enhance the adhesion between an epoxy matrix and UHMWPE fibres [32, 40]. Chemical etching is an effective method of surface modification that changes both surface chemistry and surface roughness. The modification mechanism consists of the abstraction of hydrogen atoms from the polymer back-bone and their replacement with polar groups (hydroxyl, carbonyl,

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carboxylic acid and sulphonic acid groups) from the oxidizing agents [38–43].

In this study UHMWPE powder has been modified by chemical oxidization of the surface with chromatic acid and the influence of this modification on the mechanical and tribological properties has been studied.

2. Experimental procedure

2.1. Sample preparation

The sizing of the Aramid, Twaron® (Akzo Nobel), fibres 6 mm in length was removed by Soxhlet extraction with dichloromethane. The fibres were vacuum-dried prior to all experiments. UHMWPE (Hifax 1900 from Hercules), with molecular weight $M_w = 4 \times 10^6\,\mathrm{kg\,kmol^{-1}}$ and molecular number $M_n = 2 \times 10^5\,\mathrm{kg\,kmol^{-1}}$, was used as received.

In order to obtain a fairly homogeneous composite, mixing was accomplished by swirling UHMWPE powder and chopped fibres with compressed dry nitrogen. Composites were obtained by compression moulding the UHMWPE powder–aramid fibre mixtures at a temperature, $T = 225\,^{\circ}\mathrm{C}$ for 3 h at a pressure of 37 MPa. The composites were slowly cooled to room temperature. The same procedure was used to prepare the UHMWPE samples. The samples used to determine the wear behaviour of the composites were obtained by compression moulding powder–fibre mixtures at a temperature of 300 °C for 3 h at a pressure of 300 MPa.

The composites were studied by scanning electron microscopy (SEM) on cryofractured specimens, using a Jeol 6320 F field emission SEM.

2.2. Chemical etching of UHMWPE

UHMWPE powder was immersed in $K_2Cr_2O_7$–H_2O–H_2SO_4 (7 : 12 : 150 by weight) at room temperature for different exposure times. After this treatment the powder was rinsed with concentrated HCl, water and acetone, after which it was dried in a vacuum oven at $T = 30\,^{\circ}\mathrm{C}$. The powder was stored in an air medium.

2.3. Tensile test

Tensile tests were performed on dumb-bell shaped specimens (dumb-bell shape: ASTM D1708-93, thickness 1 mm) at room temperature using an Instron (4301) tensile tester, equipped with a 5 kN load-cell, at a crosshead speed of $20\,\mathrm{mm\,min^{-1}}$. The gauge length was 25 mm. The reported tensile data are the mean values of at least eight tests. Although the ASTM D1708-93 samples are not meant for the determination of moduli, we have used the values obtained primarily for the sake of comparison. The moduli presented are therefore only relative values.

2.4. Sliding wear test

Pins for the wear tests with a length of 20 mm and surfaces of $16\,\mathrm{mm}^2$ (4 × 4 mm) were machined out of the moulded samples. Owing to the mixing procedure and compression moulding, the composites have a two-dimensional discontinuous fibre orientation in the *xy*-plane. The pins were machined in such a way that the *z*-plane was the contact surface, so that part of the fibres were normal to the contact surface.

Dry sliding experiments were carried out using a steel roll 25 cm in diameter [9]. The counterface used was stainless steel with a surface roughness, R_a, of 0.1 μm and a hardness of 180 HRB. Wear tests were carried out at a normal load of 96, producing a nominal contact stress of 6 MPa at a sliding velocity of $0.24\,\mathrm{m\,s^{-1}}$. All experiments were carried out in triplicate. The influence of a rise in the interfacial temperature, caused by friction, on the wear behaviour was ruled out by cooling the steel roll with compressed air. The pins were removed, cleaned and weighed, at daily intervals. The mass loss was determined by weighing the test specimens on an analytical balance before and after every test run. The specific wear rate, W_p, was calculated from the expression [44]

$$\dot{W}_p = \frac{\Delta m}{\rho L A_p} = \frac{\dot{W}_v}{p} \qquad (1)$$

where Δm is the mass loss, ρ the density of the material, L the sliding distance, A the contact area, p the contact pressure, and W_v the dimensionless wear rate. W_p has the dimension of millimetre cubed per Newton per metre. The reciprocal of the specific wear rate is considered to be the wear resistance of the material.

3. Results and discussion

3.1. Mechanical properties

The major demand of a surface modification is that it is effective and that the modification is restricted to the outermost surface in order to maintain the original mechanical properties. The oxidation of polyethylene may cause chain scission of the macromolecules and thus a decrease in molecular weight that can have an influence on the mechanical behaviour of UHMWPE. Fig. 1 shows the stress–strain curve of oxidized (10 min) and unoxidized UHMWPE without aramid fibres. From this figure it can be seen that the mechan-

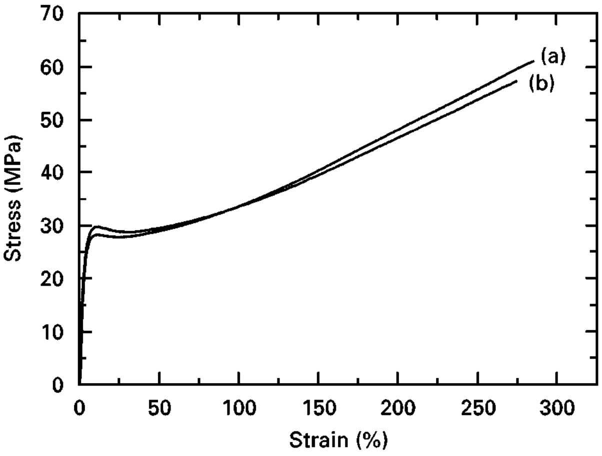

Figure 1 Stress–strain curve of (a) unoxidized and (b) oxidized UHMWPE without aramid fibres.

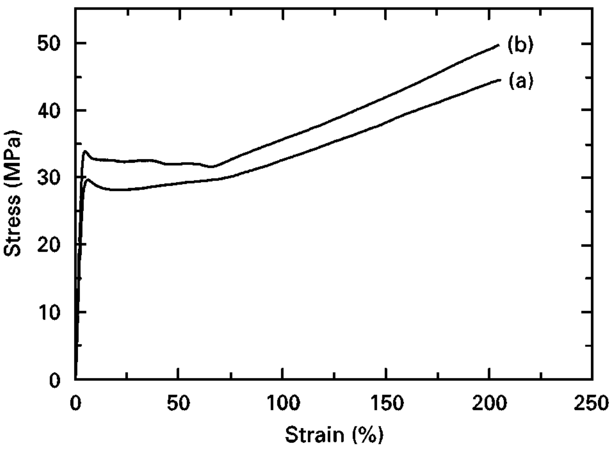

Figure 2 Stress–strain curve of (a) unoxidized and (b) oxidized UHMWPE with 5 vol % aramid fibres.

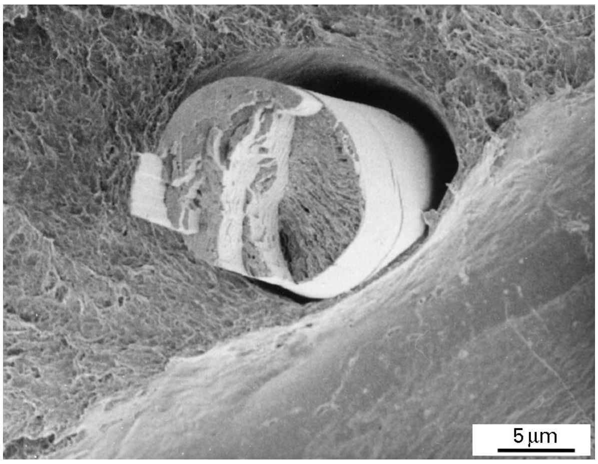

Figure 3 SEM micrograph of a cryofractured surface of an oxidized UHMWPE aramid fibre composite compressed at a pressure of 300 MPa and a temperature of 300 °C.

ical behaviour is hardly affected by the chemical etching technique.

Fig. 2 shows the stress–strain curves of oxidized and unoxidized (exposure time 1 min) UHMWPE reinforced with 5 vol % aramid fibres. From this graph it becomes clear that the mechanical properties are indeed modified by oxidation. The yield stress, stress at break and modulus of the oxidized composite are improved compared with those of the unoxidized composite. The unoxidized composite shows a yield point at 29 MPa, and plastic deformation after which it breaks at 43 MPa at an elongation of 200%, while the oxidized composite shows a yield point of 34 MPa, stress at break of 47 MPa, and strain at break of 180%. This means an improvement of 17 and 9% for the yield stress and stress at break, respectively. The modulus increases from 900 to 1200 MPa, an enhancement of 33%.

In the literature several models are used to describe the mechanical properties of composites, such as those by Termonia [45–47]. With this model it is possible to calculate the reinforcement efficiency for the modulus, G_E, using the following equation

$$G_E = \frac{(E_c/E_f \times V_f) - (E_c/E_f \times V_f)_0}{1 - (E_c/E_f \times V_f)_0} \qquad (2)$$

where E_c and E_f are the modulus of the composite and the fibre respectively. The subscript 0 denotes a limiting value for $l/l_c \rightarrow 0$ and it is assumed that $(E_c/E_f \times V_f) \rightarrow 1$ as $l/l_c \rightarrow \infty$. It seems that the larger the ratio E_f/E_m, the slower the increase of G_E with fibre length. The G_E for the unoxidized composite is 0.0312, while the oxidized composite has a G_E value of 0.125. Termonia has determined the dependence of G_E on aspect ratio. The G_E factors found in the model of Termonia for composites with randomly oriented fibres all level off at virtually the same $G_E = 0.125$, irrespective of the E_f/E_m factor.

It is thought that this improvement of the properties is caused by a stronger fibre–matrix interaction. Chemical etching introduces polar groups, like hydroxyl, carbonyl, carboxylic acid and sulphonic acid groups, on the surface of the polyethylene. The polar groups should increase surface tension, wettability, and are possible sites for chemical or physical interactions with the substrate. Fig. 3 shows an SEM photograph of a cryofractured surface of an oxidized UHMWPE–aramid composite compressed at a pressure of 300 MPa. It can be seen that the difference in thermal expansion coefficient still forms a problem. One side of the fibre is connected to the UHMWPE matrix. It may be possible that this is caused by oxidation of the UHMWPE, resulting in better fibre–matrix adhesion. The fibres are not totally embedded in the matrix because the matrix shows an enormous volume change on cooling from the processing temperature to ambient temperature, which is much stronger than the adhesion.

Another very important phenomenon, which probably also has an influence on the properties of the composite, is the distribution of the fibre. Proper dispersion of the fibres is necessary to achieve optimal composite properties [48]. On a macroscopic scale the distribution of fibres of oxidized composite appears to be much better than for the unoxidized composite [49].

Fig. 4 shows the effect of exposure time on the mechanical properties. From these graphs it appears that an exposure time of 1 min already gives an interesting improvement, but no further enhancement is observed after longer exposure times. On the contrary, Mercx [32] has shown that the oxygen concentration and adhesion of polyethylene to epoxy increases with exposure time. He studied the adhesion of chromic acid etching of polyethylene to epoxy resin. It is possible that in our experiments the oxygen concentrations at the surface also increase but have no effect on the adhesion between the aramid fibres and UHMWPE matrix so that no influence on the mechanical properties with exposure time is observed.

3.2. Tribological properties

From previous studies it is known that the addition of aramid fibres to UHMWPE improves not only its mechanical properties, but also its tribological properties [9]. The wear improvement caused by the blending with fibres may be explained by the

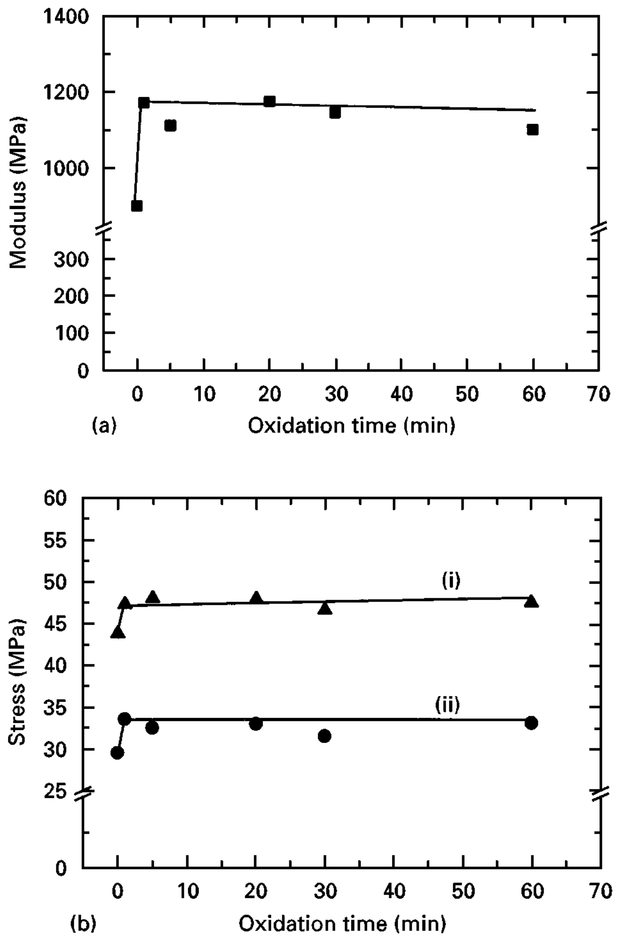

Figure 4 The influence of oxidation time on (a) modulus and (b) ultimate stress, (▲) and yield stress (●) of an aramid fibre reinforced UHMWPE composite processed at a pressure of 37 MPa and a temperature of 225 °C.

load-supporting action of fibres proposed by Lancaster [50–52]. The contact load is transferred from the matrix to the fibre. This preferential load support of the normal load by the fibres shields the matrix, causing the contact pressure of the matrix to be less than the nominal pressure.

It is known that the wear behaviour of a material depends critically on its ultimate tensile strength, σ_u, and breaking elongation, ε_u. The experimental Ratner–Lancaster correlation, $\Delta V \propto (\sigma_u \varepsilon_u)^{-1}$, describes this relationship [53–56].

Because fibre–matrix interaction is probably increased by chemical etching, more stress can be transferred from the UHMWPE matrix to the aramid fibres, leading to an improvement of the modulus, yield stress and stress at break. Elongation of the composite decreases. In the preferential load-supporting action, contact load is transferred from the matrix to the fibre. This load transfer is dependent, among other things, on fibre–matrix adhesion, which may improve through the chemical etching technique. On account of these two effects it can be expected that the modification also has an influence on the tribological properties.

Fig. 5 shows volume loss as a function of sliding distance for unoxidized and oxidized UHMWPE reinforced with 5 vol % aramid fibres, at a nominal contact stress of 6 MPa and a sliding velocity of $0.24\,\mathrm{m\,s^{-1}}$. A substantial wear improvement is observed. The unoxidized UHMWPE–aramid composite shows a much higher volume loss than the oxidized UHMWPE–aramid composite. Both composites show a running-in period after which a steady-state period is observed. From this steady-state period the specific wear rates can be calculated from Equation 1. The specific wear rates, W_p, are 2.4×10^{-9} and $1.1 \times 10^{-9}\,\mathrm{mm^3\,N^{-1}\,m^{-1}}$ for the unoxidized and oxidized UHMWPE–aramid composite, respectively. The wear resistances, W_p^{-1}, of these two materials are 4.2×10^8 and 9.1×10^8, respectively. Although a relatively small enhancement in the mechanical properties is observed after chemical etching UHMWPE (the modulus, yield stress and stress at break show an improvement of 33, 17 and 9%, respectively) a relatively large wear improvement is achieved; the wear resistance increases by 117%. Thus, chemical etching of UHMWPE indeed has a large positive effect on the wear behaviour of short aramid fibre reinforced UHMWPE composites.

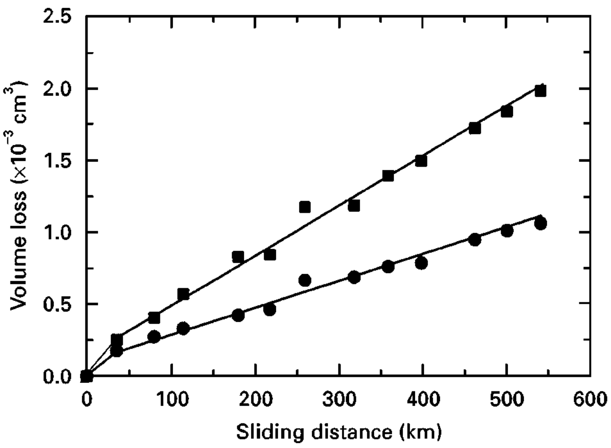

Figure 5 Volume loss as a function of sliding distance for the unoxidized (■) and oxidized (●) UHMWPE reinforced with 5 vol % aramid fibres, processed at a pressure of 300 MPa and a temperature of 300 °C.

3.3. Ageing of the chromic acid etched surface

The problem with oxidized surfaces is that they are not stable in time [33, 57–62]. Due to ageing, the oxidatively functionalized polyethylene surface may become hydrophobic again. Macromolecules at the surface of a polymeric solid have a degree of mobility leading to a rearrangement of the functional groups at the surface. These reorientation processes are a function of the storage conditions, like the nature of the contacting phase (vapour or liquid). It seems that the instability of the surface is caused by the high surface energy of the system. The system will try to reach a low interfacial free energy, which is possible when the functional groups on the surface migrate into the bulk. This can occur with, for instance, hydrophilic modified surfaces exposed to air or vacuum, or hydrophobic modified surfaces exposed to water.

In this study it was found that the modulus decreases from about 1200 MPa for the composite made of freshly oxidized UHMWPE to 1000 MPa for the composite made of oxidized UHMWPE after a storage time of 35 days. The unoxidized composite has a modulus of 900 MPa. The yield stress decreases from 33.5 to 29.5 MPa, while the stress at break decreases from 47.5 to 44 MPa. The yield stress and stress at break of the unoxidized composite are 29.5 and 43 MPa, respectively. Probably, the polar groups at the surface migrated into the bulk, because the system will try to reach a low interfacial free energy. Because less functional groups exist at the UHMWPE surface, a lower fibre–matrix adhesion is the result and the mechanical properties of the composite will decrease.

4. Conclusions

This study describes the influence of chromic acid etching on the mechanical and tribological properties of aramid fibre reinforced UHMWPE. Both properties are enhanced due to this surface modification. The unoxidized composite shows a modulus of 900 MPa, a yield point at 29 MPa, and an ultimate tensile strength of 43 MPa. The oxidized composite shows a modulus of 1200 MPa, a yield point at 34 MPa, and an ultimate tensile strength of 47 MPa. This means an improvement of 33, 17 and 9% in the modulus, yield stress and stress at break, respectively. The elongation decreases from 200 to 180%. It is thought that the improvement in mechanical properties is caused by better fibre–matrix adhesion and better fibre distribution. A wear improvement is also observed. Although a respectively small improvement in the mechanical properties is found, the wear resistance increases by 117%, i.e. from 4.2×10^8 to 9.1×10^8. Owing to better fibre–matrix adhesion more stress can be transferred from the matrix to the fibres, which has a tremendous impact on the wear behaviour of the composite.

For the properties of aramid fibre reinforced UHMWPE composites the storage time of the oxidized UHMWPE is crucial. It seems that the properties decrease with time. A problem of oxidized surfaces is that they are not stable in time. During storage the polar groups at the surface will migrate into the bulk and the surface will become hydrophobic again. This process is influenced by the environment and is driven by the tendency of the system to minimize its surface energy.

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