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<p>(21) International Application Number: PCT/GB95/00211</p> <p>(22) International Filing Date: 2 February 1995 (02.02.95)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>9402102.9</td> <td>3 February 1994 (03.02.94)</td> <td>GB</td> </tr> <tr> <td>9402103.7</td> <td>3 February 1994 (03.02.94)</td> <td>GB</td> </tr> </table> <p>(71) Applicant (for all designated States except US): SMITH & NEPHEW PLC [GB/GB]; 2 Temple Place, Victoria Embankment, London WC2R 3BP (GB).</p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (for US only): FARRAR, David, Franklin [GB/GB]; 6 Edgware Road, Fulford, York YO1 4OG (GB).</p> <p>(74) Agent: CORPORATE PATENTS & TRADE MARKS DEPARTMENT; Smith & Nephew Group Research Centre, York Science Park, Heslington, York YO1 5DF (GB).</p>	9402102.9	3 February 1994 (03.02.94)	GB	9402103.7	3 February 1994 (03.02.94)	GB	<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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<p>(54) Title: SURFACE TREATMENT</p> <p>(57) Abstract</p> <p>A method for improving the wear resistance of a wear surface of a medical prosthetic device wherein the wear surface comprises plastics material, the method comprising subjecting a surface region of the wear surface to plasma treatment. The plastics material may be UHMWPE and the surface region is cross-linked to a depth of at least 0.3 μm as detectable by the presence of IR absorption bands at 2890 cm^{-1}.</p>							

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SURFACE TREATMENT

The present invention relates to medical devices which have improved properties due to surface treatment. In particular the
5 present invention relates to jointed prosthetic devices and to implant devices and to a method for improving the wear surface of a prosthetic device.

Many medical devices have surfaces which are prone to wear
10 (referred to herein as "wear surfaces"). Such surfaces are found, for example, at articulating surfaces of jointed prostheses which bear against one another when a joint is articulated. These surfaces can be surfaces of various hard materials. Typically, different materials are used for two co-operating bearing surfaces e.g. one bearing
15 surface may be a surface of a hard polished metal material such as a cobalt steel alloy and an opposing bearing surface may be a plastics material which has low frictional resistance properties.

Ultra high molecular weight polyethylene (UHMWPE) which
20 has a molecular weight of about 4.5×10^6 or higher is conventionally used in these applications. It has been found that in this situation the plastics material is prone to wear. This is a particular problem for implanted prostheses since debris formed by wearing of UHMWPE may stimulate adverse cellular reactions leading to resorption of
25 bone around the implant. This, and also the reduced thickness of the plastics material which can occur due to wear, may result in loosening of the fit of the prosthesis so that adjustment or replacement is necessary by revision surgery.

30 Irrespective of any possible problems caused by wear it may be the case than an exposed plastics material used in an implant device is not completely biocompatible.

In this situation the plastics material may be provided with a
35 biocompatible coating. However this can be expensive and may result in reduced performance of the device e.g. due to increased weight.

The present invention aims to overcome or at least to alleviate some of the above-mentioned disadvantages by providing a jointed prosthetic device in which at least one of the articulating surfaces of the joint comprises a surface modified UHMWPE having improved wear properties.

According to the present invention there is provided a method for improving the wear resistance of a wear surface of a medical prosthetic device wherein the wear surface comprises plastics material, the method comprising subjecting a surface region of the wear surface to plasma treatment.

The present invention also provides a medical prosthetic device comprising a plastics material wherein at least a surface region of the plastics material has been plasma treated.

Plasma treated UHMWPE exhibits increased hardness compared to untreated UHMWPE.

Without wishing to be bound by theory, it is believed that plasma treatment can result in an increase in cross-linking at a surface region of the plastics material and that this cross-linking can result in increased hardness, and/or wear-resistance. Plasma treatment may also result in increased wettability and this can provide increased biocompatibility.

Preferably the surface region comprises a wear surface. This surface may bear against another co-operating surface so that the surfaces are in sliding, pivoting or rotating relationships to one another.

The surface region can aptly be present at a joint of a prosthetic device. The device may be an implantable prosthetic device e.g. an artificial knee or hip joint.

Increased biocompatibility is advantageous since this can reduce the likelihood that the device will need to be replaced and also reduces the risk of adverse effects on the patient.

5 Corresponding cost reductions can therefore be achieved.

It is not essential however that the implantable device be a jointed device or indeed that it have a wear surface since the increased biocompatibility and hardness achievable with the present
10 invention can be advantageous for a large variety of implantable devices.

The plastics material can be any plastics material which is cross-linkable by plasma-treatment. Suitable plastics materials
15 include:-

UHMWPE	Polystyrene
Polypropylene	Polyethylene
Polyolefins	Polymethylmethacrylate
20	and Polyacetals

The materials may be of low, medium or high density.

The UHMWPE may be present on a medical device in the
25 form of a coating or may extend across the whole of the device or of a component thereof.

A preferred plastics material for use in the present invention is an ultra high molecular weight plastics material e.g. an ultra high
30 molecular weight material polyalkylene which is preferably an ultra high molecular weight polyethylene:- referred to herein as UHMWPE. The ultra high molecular weight plastics materials may comprise one or more substituent groups and may include one or
more copolymers.

35

The term ultra high molecular weight is used herein to refer to a molecular weight of at least 10^6 and preferably of from 3×10^6 to 8×10^6 .

Desirably the surface region is cross-linked to a depth of at least $0.3\mu\text{m}$ by the plasma treatment. The surface region may be cross-linked to a depth of between $0.3\mu\text{m}$ and $500\mu\text{m}$. One way of determining the depth of cross-linking is provided in the example which is given later under the title "Estimation of Plasma Penetration Depth" wherein the presence of absorption bands at 2890 cm^{-1} is taken to indicate cross-linking occurring (due to the formation of tertiary -CH groups). Preferably the surface region has a Vickers Hardness of at least 6.0. The surface region may have a Vickers Hardness of from 6 to 25 (figures used herein for hardness are Vickers Hardness numbers). Hardness can be determined using the method described in the example under the heading "Micro-Hardness Testing".

The term "surface region" is used herein to include both the surface of a plastics material which has been cross-linked by plasma treatment and such material which underlies this surface.

Thus in accordance with the present invention there is provided a device having a surface region at least $0.3\mu\text{m}$ deep comprised of ultra high molecular weight cross-linked polyethylene having a Vickers Hardness number of at least 6.0 and whose infra-red spectrum exhibits absorption bands at 2890 cm^{-1} .

The device of the present invention demonstrates a high degree of hardness, which correlates with a high wear resistance. It is thus useful in applications where surfaces bear against one another, e.g. in sliding, pivoting or rotating relationship to one another.

Desirably, the surface region is part of a larger mass of ultra high molecular weight polyethylene. The surface region may provide one of a pair of mutually co-operating bearing surfaces. The other

co-operating bearing surface may comprise a metal or a ceramic material.

5 Aply the device is a medical prosthetic device or part of such a device and the surface region provides a wear surface for the device e.g. at a joint.

10 Since a device of the present invention can be provided which is highly biocompatible, the present invention is particularly advantageous for use in prosthetic devices which are implanted in a patient's body. Increased biocompatibility results in a reduced likelihood that the implant will need to be replaced and also reduces the risk of adverse effects on the patient. Corresponding cost reductions can therefore be achieved.

15 Plasma treatment can increase the wettability of a polymer surface and thus can increase biocompatibility by lowering surface tension. This is in addition to any improved hardness which can result from cross-linking.

20 The particular plasma-treatment used to achieve cross-linking can vary with the type of plastics material to be cross-linked but can be determined by the skilled man using no more than trial and error.

25 The present invention also provides a process for providing a cross-linked, UHMWPE surface region of a medical device which comprises cross-linking that region by subjecting it to plasma treatment. Initially, UHMWPE material to be cross-linked may be plasma treated and then this may be formed into a device/part of a device after cross-linking. Alternatively, cross-linking may be performed in situ on a pre-formed device/a preformed part of a device.

35 Plasma treatment is a process whereby a material is exposed to a gas composed of excited charged particles such as ions and electrons. These particles collide with the material surface causing modification due to gas particles chemically bonding to the surface or

due to removal of material from the surface. As excited species fall to lower energy states photons are emitted and ultra violet (UV) cross-linking can occur.

- 5 Plasma may be generated by applying micro/radio waves to a gas at low pressure.

Suitable methods for performing plasma treatment are disclosed in the article by M.S. Sheu et al in J.Adh. Sci. Tech. 6,
10 995,1992.

Plasma treatment can be used to provide a device according to the present invention by plasma treating a region of high molecular weight polyethylene so that the region becomes cross-linked to a
15 depth of at least 0.3 μ m and a Vickers Hardness of at least 6.0 is achieved. The cross-linking is detected by the presence of infra-red absorption bands at 2890cm⁻¹.

The depth of cross-linking and the hardness of the cross-
20 linked region can be assayed using the method described later in this specification in the example.

The plasma treatment improves wettability of a polymer surface, which can increase biocompatibility by lowering interfacial
25 tension. Desirably, plasma treatment is carried out for up to 60 mins (e.g. from 1 to 30 mins) and at a power level of from 10-300 watts (e.g. from 60 to 200 watts). At high power levels it is generally the case that treatment can be performed for shorter periods of time than
30 for lower power levels in order to achieve the same degree of cross-linking. Desirably the temperature of the UHMWPE should not exceed 100°C during plasma treatment in order to avoid problems of thermal degradation. The temperature of the UHMWPE can be monitored during treatment and if it gets close to 100°C the treatment can be stopped or the power level can be reduced accordingly.
35 Desirably during plasma treatment a chamber in which the treatment is carried out is maintained at a pressure within the range of 0.1 to 1m.bar preferably within the range of 0.1 to 0.3 m.bar.

The present invention will now be described without limitation thereof, by way of example.

5 EXAMPLE

a) Plasma Treatment

10 UHMWPE plaques measuring approx. 2.5 x 3.5 x 0.1 cm were cut from polyethylene sheets supplied by Goodfellows, Cambridge, UK. These plaques were then polished with silicon carbide paper using a Buchler Metasem Polisher, the final finish being achieved with 1200 grade paper.

15 Two adjacent corners of the plaques were trimmed to mark a handling area and they were washed in IMS (which is an abbreviation for Industrial Methylated Spirit) and dried overnight. Forceps were used to handle the samples. For each treatment, five plaques were mounted on a microscope slide using "BLUE TACK"
20 (Trade Mark).

The slide was placed inside the plasma barrel of a plasma barrel etcher sold under the Trade Mark of "PT7300 VG Microtech" (obtainable from Fisons Instruments of Bishopmeadow Road,
25 Loughborough), after which the chamber was evacuated twice and flushed with argon before the plasma was initiated. The pressure inside the chamber and the plasma power were held constant. After treatment the plaques were kept in an argon atmosphere for a few minutes before exposure to air. Samples were treated as indicated
30 in Table 1. Plasma treatment was carried out with the chamber pressure at 0.2 m. bar.

Some of the plaques were then sterilised using gamma ray irradiation treatments.

35

The samples were gamma sterilised by Isotron, Swindon, UK and were given a dose of 2.5 MRad.

Table 1

Plasma Treatment				
Sample No	Power(Watts)	Time (min)	Max ^m temp.	Gamma Sterilisation
A61	60 (+/-2)	1	25°C	√
B610	60 (+/-2)	10	35°C	√
C630	60 (+/-2)	30	45°C	√
D121	120 (+/-5)	1	45°C	√
E1210	120 (+/-5)	10	65°C	√
F1230	120 (+/-5)	30	45°C	√
G201	200 (+/-5)	1	45°C	√
H2010	200 (+/-5)	10	65°C	√
I2030	200 (+/-5)	30	90°C	√
J1210X	120 (+/-5)	10	65°C	X
K00X	0	0	0	X
L00	0	0	0	√

- 5 For each plasma-treated sample the time of plasma treatment is indicated for given wattages. Control samples include plasma treatment without gamma sterilisation (J1210X), gamma sterilisation without plasma treatment (L00) and no plasma treatment or gamma sterilisation.

10 b) Micro-hardness Testing

The treated samples were then tested for micro-hardness using the method described below.

- 15 The specimens were tested in a Shimadzu microhardness tester with a pyramidal shaped indenter. The diagonals were measured at 400 x magnifications and the Vickers Hardness number calculated. At least 10 indents were measured for each sample.
- 20 The results (Vickers Hardness numbers) are indicated in Table 2 for the various samples and control samples.

Table 2

Sample	Vickers Hardness Numbers
A61	8.3 +/- 2.1
B610	17.5 +/- 5.1
C630	23.8 +/- 3.8
D121	11.1 +/- 3.1
E1210	14.7 +/- 4.8
F1230	8.3 +/- 2.3
G201	11.9 +/- 3.6
H2010	10.6 +/- 2.7
I2030	14.6 +/- 7.8
J1210X	12.0 +/- 3.6
K00X	6.36 +/- 1.12
L00	5.95 +/- 0.92

c) Surface Analysis

5

This was performed upon samples **I2030** (plasma treated @ 200W for 30 min, gamma sterilised) and **L00** (no plasma treatment, gamma sterilised), and **K00X** (control no plasma treatment, no gamma sterilisation). Infra red spectroscopy was performed on the above samples using a Perkin Elmer 1750 FTIR spectroscope and a 45° angle of incidence of IR light using a fixed ATR device (ATR is an abbreviation for Attenuated Total Reflectance). This device is obtainable from Graseby Specac.

10

15

The samples were analysed for the presence of absorption bands at 2890cm⁻¹. Such bands are characteristic of tertiary CH groups which would be formed by cross-linking of the UHMWPE.

The results obtained were as follows:-

Table 3

5

IR Number	Sample Details	Tertiary CH Present/Absent
7941	L 00 No plasma treatment, gamma sterilised	Absent
7961	K 00X not plasma treated or sterilised (side 1)	Absent
7962	K00X not plasma treated or sterilised (side 2)	Absent
7963	I230 plasma treated @ 200W for 30 min and gamma sterilised (side 1)	Present
7964	I2030 (side 2)	Present

The references to "side 1" and "side 2" refer to the two major sides of the polyethylene plaques, which were each tested.

10 These results indicate that cross-linking of the UHMWPE is induced by plasma action. Gamma irradiation does not appear to affect cross-linking.

Estimation of Plasma Penetration Depth

15

Penetration depth of the plasma was investigated using a variable angle ATR device obtainable from Graseby Specac. The refractive index of the sample permitted the use of angles between 42 deg. and 60 deg. Both sides of sample I2030 were examined at
20 each angle. Spectra were recorded as follows:-

IR Number	Angle of incidence	Infrared penetration depth of 2890 cm ⁻¹	2890 cm ⁻¹ present/absent
7965 (side 1)	42 deg	0.58 micrometres	Absent
7966 (side 2)	42 deg	0.58 micrometres	Absent
7963 (side 1)	45 deg	0.48 micrometres	Present
7964 (side 2)	45 deg	0.48 micrometres	Present
7967 (side 1)	60 deg	0.31 micrometres	Present
7968 (side 2)	60 deg	0.31 micrometres	Present

These results imply that the effective penetration depth of the plasma is of the order of 0.5 microns.

5

d) Water Contact Angle Results

10 Samples prepared as described in a) above were analysed using a Cahn DCA-322 Dynamic Contact Angle Analyser obtainable from Scientific & Medical Product Limited of Mancheser, UK.

The results are shown below for θ_A (advancing contact angle) and θ_R (receding contact angle).

15 The advancing angle is the angle measured as the sample is being immersed into the liquid. The receding angle is that measured as the sample is withdrawn from the liquid.

The results are indicated below. \bar{X} = mean average

Table 4

Sample No.	A61	D121	G201
θA	75.4 79.6 $\bar{x} = 81.2$ 88.7	85.1 72.0 $\bar{x} = 75.2^\circ$ 68.4	77.3 77.8 $\bar{x} = 77.7$ 78.0
θB	0 11.9 $\bar{x} = 8.3^\circ$ 12	0 0 0	0 0 $\bar{x} = 1.6^\circ$ 4.7
Sample No.	B610	E1210	H2010
θA	2.0 9.1 $\bar{x} = 54.3^\circ$ 1.7	59.1 58.4 $\bar{x} = 56.6^\circ$ 52.2	58.8 58.2 $\bar{x} = 57.$ 54.1
θB	0 $\bar{x} = 0^\circ$ 0 0	0 0 $\bar{x} = 0^\circ$ 0	0 0 $\bar{x} = 0^\circ$ 0
Sample No.	C630	F1230	12030
θA	51.4 68.2 $\bar{x} = 64.9^\circ$ 75.1	56.6 65.5 $\bar{x} = 57.6^\circ$ 50.7	72.7 64.5 $\bar{x} = 62.1$ 59.0
θB	0 0 $\bar{x} = 2.4^\circ$ 7.3	14.4 0 $\bar{x} = 4.8^\circ$ 0	0 0 0 $\bar{x} = 0^\circ$

5

The results indicate that plasma treatment improves wettability of the polymer surface. It may therefore improve biocompatibility of jointed devices implanted in a patient by reducing inter-facial tension.

10

CLAIMS

1. A method for improving the wear resistance of a wear surface of a medical prosthetic device wherein the wear surface comprises plastics material, the method comprising subjecting a surface region of the wear surface to plasma treatment.
2. A method as claimed in claim 1 wherein the surface region is subjected to plasma treatment such that a Vickers Hardness of at least 6.0 is achieved.
3. A method as claimed in claim 1 or 2 wherein the surface region is subjected to plasma treatment and the surface region is cross-linked to a depth of at least $0.3\mu\text{m}$ and wherein cross-linking is detectable by the presence of infra-red absorption bands at 2890cm^{-1} .
4. A medical prosthetic device comprising a wear surface of plastics material wherein the surface region of the wear surface has been subjected to plasma treatment.
5. A medical prosthetic device comprising a wear surface of plastics material wherein the surface is cross-linked to a depth of at least $0.3\mu\text{m}$ and wherein the cross-linking is detectable by the presence of infra-red absorption bands at 2890cm^{-1} .
6. A medical prosthetic device as claimed in claim 5 wherein the surface has a Vickers Hardness of at least 6.0.
7. A medical prosthetic device as claimed in any of claims 4 to 6 wherein the plastics materials are chosen from ultra high molecular weight polyethylene (UHMWPE), polystyrene, polypropylene, polyolefins, polyethylene, polymethylmethacrylate and polyacetals.
8. A medical prosthetic device as claimed in any of claims 4 to 7 wherein the surface region is present at a joint of a prosthetic device.

INTERNATIONAL SEARCH REPORT

Inter. Appl. Application No
PCT/GB 95/00211

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J/12 A61F2/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J A61F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 348 252 (NITRUVID) 27 December 1989 see claims see page 2, column 1, line 40 - column 2, line 21	1,4,7,8
X	US,A,5 236 563 (LOH INH-HOUNG) 17 August 1993 see claim 1	1,4
X	US,A,5 223 309 (FARIVAR R.S. ET AL) 29 June 1993 see claims 1,2,4,5,7 see figure 3	1,4

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search 13 June 1995	Date of mailing of the international search report 26.06.95
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0348252	27-12-89	FR-A- 2631832 DE-T- 68907806 ES-T- 2045487	01-12-89 10-03-94 16-01-94
US-A-5236563	17-08-93	NONE	
US-A-5223309	29-06-93	NONE	