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**(54) PROCESSES COMPRISING CROSSLINKING POLYETHYLENE OR USING CROSSLINKED POLYETHYLENE**

VERNETZEN VON POLYETHYLEN ODER VERWENDUNG VON VERNETZTEM POLYETHYLEN  
UMFASSENDE VERFAHREN

PROCÉDÉS QUI COMPRENNENT LA RÉTICULATION DE POLYÉTHYLÈNE OU L'UTILISATION  
DU POLYÉTHYLÈNE RÉTICULÉ

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**EP 2 083 981 B1**

**Description**FIELD

5 **[0001]** The present invention relates to processes comprising crosslinking polyethylene or using crosslinked polyethylene, and to products obtained therewith.

BACKGROUND

10 **[0002]** Ultrahigh molecular weight polyethylene (UHMW PE) is well known for, among other properties, its chemical resistance, low friction coefficient, high toughness, and resistance against wear. As a result, it has found numerous applications in demanding environments where some or all of the above properties are required. Equally well known is the intractability of this polymer, which is due to the fact that UHMW PE above its crystalline melting temperature, does not form a fluid phase that is of a viscosity that permits melt-processing techniques used with common thermoplastic polymers.

15 **[0003]** A negative consequence of the fact that above its crystalline melting temperature UHMW PE merely passes into a viscoelastic state, is that the original polymer particles soften but tend to substantially retain their shape. Even after relatively long sintering times at relatively high temperatures, much of the initial powder morphology may still remain. The latter, in fact, is thought to contribute to wear and ultimate failure of, for example, artificial implants made from this polymer. Attempts have been made to design processes that reduce wear. For example, US 2004-0155381 A1, US  
20 4,323,531 A, WO 2005/074619 A2 and WO 2003/064141 A1 describe methods for producing UHMW PE. However, all of these processes have inherent disadvantages, such as those mentioned below, and none of these processes known from the state of the art is suitable for solving the abrasion problem of previously known UHMW PE. These processes are however relatively cumbersome, e.g. are ill defined, require melting the UHMW PE more than once, are time consuming, and/or substantially negatively influence other properties of the UHMW PE such as, e.g., crack resistance.  
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SUMMARY

30 **[0004]** The subject-matter of the present invention is defined in claims 1-38 as attached. In an embodiment, a process is provided comprising:

- compacting a composition comprising virgin ultrahigh molecular weight polyethylene (UHMW PE), said UHMW PE having a weight average molecular weight of at least 1,000,000 g/mol, to provide a compacted composition comprising virgin UHMW PE;
- 35 - sintering said compacted composition; and
- crosslinking said UHMW PE.

**[0005]** In an embodiment, a process is provided comprising:

- 40 - providing a compacted composition, said compacted composition comprising virgin ultrahigh molecular weight polyethylene (UHMWPE), said UHMW PE having a weight average molecular weight of at least 1,000,000 g/mol; and
- crosslinking said UHMWPE.

**[0006]** In another embodiment, a process is provided comprising:

- 45 - providing a compacted composition comprising crosslinked virgin ultrahigh molecular weight polyethylene (UHMW PE); and
- sintering the compacted composition.

50 **[0007]** In addition, in an embodiment there is provided a process comprising

- providing an object consisting essentially of crosslinked compacted virgin polyethylene, and
- sintering the object.

55 **[0008]** Also, provided is a process comprising:

- sintering ultrahigh molecular weight polyethylene (UHMW PE); and
- crosslinking said UHMW PE;

wherein said crosslinking is initiated more than once.

**[0009]** Also provided are objects obtained with the present processes, such as orthopedic implants.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0010]**

Figure 1 is a schematic representation of a compact tension test specimen.

Figure 2 represents results of wear coefficient measurements as a function of sintering time (x-axis).

Figure 3 represents results of charpy impact strength measurements as a function of irradiation dose.

## DETAILED DESCRIPTION

**[0011]** Provided are processes comprising crosslinking polyethylene or processes using crosslinked polyethylene. In an embodiment, the processes further involve compacting polyethylene and/or sintering polyethylene.

## POLYETHYLENES

**[0012]** In an embodiment, the polyethylenes used in the present invention are substantially linear polymers of ethylene.

**[0013]** In an embodiment, the polyethylene has a value of the weight-average molecular weight ( $M_w$ ) of more than 1,000,000 g/mol, for instance more than 1,500,000, more than 2,000,000 g/mol, more than 3,000,000 g/mol, more than 4,000,000 g/mol, more than 5,000,000 g/mol, more than 6,000,000 g/mol, more than 7,000,000 g/mol, and even more than 10,000,000 g/mol. In an embodiment, the weight average molecular weight is below 20,000,000 g/mol, e.g. below 15,000,000 g/mol, below 10,000,000 g/mol, or below 8,000,000 g/mol.

**[0014]** The polydispersity (the ratio between the weight- and number average molecular weight) of the polyethylenes may vary. In an embodiment, the polydispersity is more than 1, for instance more than 2, more than 2.5, or more than 3. In an embodiment, the polydispersity is less than 100, for instance less than 75, less than 50, less than 20, less than 15, or less than 10.

**[0015]** In an embodiment, the polyethylene has a melting temperature of at least 105°C, for instance at least 115°C, at least 125°C, or at least 135°C. In this specification, unless indicated otherwise, "melting temperature" is the peak melting temperature of the polyethylene as determined in differential scanning calorimetry at a heating rate of 10°C/min, after first melting the polyethylene and recrystallizing it at a cooling rate of 10°C/min).

**[0016]** The UHMW PE grades for use in the present invention can be synthesized according to conventional methods for the polymerization of ethylene as described in detail in the literature (for example, Whiteley, K. S., in Industrial Polymers Handbook, Wilkes, E. S. ed., Wiley-VCH, Volume 2, pp. 643-691, 2001) and as practiced in the art. Many UHMW PE grades are products of commerce, and may be used in the present invention.

**[0017]** In an embodiment, the present invention employs compositions comprising at least 35wt% UHMW PE, relative to the total weight of the composition. In an embodiment, the compositions comprise at least 50wt%, at least 65wt%, at least 75wt%, at least 90 wt%, at least 95wt%, or at least 99 wt% UHMW PE. In an embodiment, the compositions consist essentially of UHMW PE.

**[0018]** In an embodiment, the polyethylenes are "virgin" polymers. The term "virgin" is intended to mean that the polymer has not been molten or fully dissolved since its manufacture. Use of virgin polymers may assist in ease of processing when compared with non-virgin polymers. For instance, previously processed, e.g. sintered, UHMW PE would typically have an increased entanglement density when compared with virgin UHMW PE.

**[0019]** In an embodiment, the polyethylene is medical grade UHMWPE, as described by ASTM standards ASTM D4020, F648-00, F2003-00, F2102-01 and F2183-02, and ISO standards ISO 11542.1/2 and 5834.1/2.

## COMPACTING

**[0020]** In an embodiment, the (composition comprising) polyethylene is compacted to form an object (e.g. a block) of compacted polyethylene. Compacting prior to further processing, e.g. sintering, may assist in providing a relatively better wear, impact strength, and/or fatigue crack growth resistance when compared with further processing without compacting. The manner of compacting may vary and depend, e.g., on the size of the object to be formed. In an embodiment, the compacting is effected at elevated temperatures and pressures (the temperature remains below the melting temperature of the polyethylene, however). In an embodiment, the compacting is effected by filling a mold with polyethylene and placing the mold in a press that is at a temperature below the melting temperature of the polyethylene. In an embodiment, the compacting temperature is at least 30°C, for instance at least 60°C, at least 80°C, at least 100°C, at least 110°C, at least 120°C, or at least 125°C. In an embodiment, the temperature is below 135°C, e.g. below 125°C, below 120°C,

below 110°C, or below 100°C. In an embodiment, the temperature is about 120°C. Once placed in the press, pressure is applied to the mold. The pressure may be a single pressure or the pressure may be varied. For instance, an initial pressure of, e.g., at least 5MPa, for instance at least 10MPa, at least 15 MPa, or at least 20 MPa is applied, and held for a certain period of time (e.g. 5-60 minutes, for instance about 10 minutes or about 30 minutes), after which the pressure is raised to, e.g., at least 30 MPa, for instance at least 40 MPa, at least 50 MPa, or at least 60MPa, after which the mold is allowed to cool down to room temperature (preferably under the applied pressure). The pressure may then be removed if still being applied and an object of compacted polyethylene is obtained.

**[0021]** According to the invention, compacting is performed under shear. Compacting under shear generally enhances plastic deformation of the particles and may therewith improve particle contact. In an embodiment, compacting under shear is performed by solid-state extrusion, e.g. sheet extrusion, or rolling.

**[0022]** In an embodiment, compacting is performed in an air atmosphere. In an embodiment, compacting is performed in an inert atmosphere, e.g. an argon or nitrogen atmosphere.

**[0023]** In an embodiment, compacting is performed in a reactive atmosphere, e.g. in an atmosphere comprising (effective amounts of) hydrogen, acetylene (ethyn), ethene, and/or propene.

**[0024]** In an embodiment, additives are added to the polyethylene prior to compacting. In an embodiment, the additives include radical scavengers, for instance vitamin E, vitamin A, vitamin C, phenolic antioxidants (e.g. BHT (E321, 2,6 ditertiarybutyl-4-methylphenol)), irganox 1010, carotenes (such as beta carotene), or mixtures thereof.

## SINTERING

**[0025]** In an embodiment, the (composition comprising) UHMW PE is sintered. In an embodiment, the composition/polyethylene is compacted before sintering. The manner of sintering may vary and may depend, e.g., on the shape and size of the object to be sintered. The temperatures at which the sintering is carried out are above the melting temperature of the polyethylene, but preferably below temperatures at which substantial degradation of the polymer may occur. In an embodiment, the sintering temperature is more than about 2°C above the polyethylene melting temperature, for instance more than about 5°C, more than about 10°C, more than about 20°C, more than about 30°C, more than about 40°C, or more than about 50°C. Absent special precautions, such as the exclusion of oxygen, polyolefins may display signs of degradation at temperatures well above 200°C. Hence, in the absence of special precautions, sintering is preferably carried out at temperatures below 250°C, for instance below 230°C, below 210°C or below 190°C. The time for completion of the sintering process may vary widely, and is dependent on, among other things, the size and shape of the object and the efficiency of heat transfer. In an embodiment, the sintering occurs in an inert atmosphere, e.g. an argon or a nitrogen atmosphere.

**[0026]** In an embodiment, the compacted polyethylene is sintered under pressure. The pressure applied during the sintering process may vary and depend, e.g., on the shape and dimensions of the object. In an embodiment, the pressure is at least 5 MPa, e.g. at least 10 MPa, at least 20 MPa, or at least 40 MPa. In an embodiment, the pressure is less than 500 MPa.

**[0027]** In an embodiment, a process is provided wherein the polyethylene is subjected only once to a temperature above its melting temperature.

**[0028]** In an embodiment, sintering is performed in a reactive atmosphere, e.g. in an atmosphere comprising (effective amounts of) hydrogen, acetylene (ethyn), ethene, and/or propene.

## CROSSLINKING

**[0029]** The present processes comprise crosslinking polyethylene or using crosslinked polyethylene. Crosslinking may assist in further improving the wear resistance of the UHMW PE. In an embodiment, the crosslinking is initiated below the melting temperature of the UHMW PE. In an embodiment, the crosslinking is initiated after compacting but before sintering. In an embodiment, the crosslinking is initiated after compacting and during sintering (i.e. in the melt). In an embodiment, the crosslinking is initiated after compacting and after sintering (i.e. after or during cooling down from the melt). Crosslinking may be initiated, e.g., with reactive additives, with gamma radiation, with electron beam radiation, or combinations thereof. In an embodiment, the crosslinking is initiated with gamma radiation. The dose may vary and depend, e.g., on the size of the object and on whether a certain degree of polymer degradation would be acceptable. In an embodiment, the dose is at least 1 MRad, e.g. at least 4 MRad, at least 7 MRad, at least 10 MRad, at least 12 MRad, or at least 15 MRad. In an embodiment, the dose is at most 50 MRad, e.g. at most 35 MRad, at most 25 MRad, or at most 15 MRad. In an embodiment, the crosslinking is initiated with gamma radiation. In an embodiment, the crosslinking is initiated with electron beam radiation. The dose may vary and depend, e.g., on the size of the object and on whether a certain degree of polymer degradation would be acceptable. In an embodiment, the dose is at least 1 MRad, e.g. at least 4 MRad, at least 7 MRad, at least 10 MRad, at least 12 MRad, or at least 15 MRad. In an embodiment, the dose is at most 50 MRad, e.g. at most 35 MRad, at most 25 MRad, at most 15 MRad, at most 10 MRad, or at most

8 MRad. The energy of the electron beam may vary and be, e.g., at least 100 keV, such as at least 500 keV, at least 1 MeV, at least 4 MeV, or at least 7 MeV. In an embodiment, the energy is below 20 MeV.

**[0030]** In an embodiment, crosslinking is initiated more than once, e.g. 2 times or 3 times. In an embodiment, crosslinking is initiated during compacting and again initiated during sintering. In an embodiment, crosslinking is initiated during sintering and again during cooling. In an embodiment, crosslinking is initiated during compacting, again initiated during sintering, and again initiated during cooling. In an embodiment, the initiation of crosslinking is at increasing dose. For instance, in an embodiment, the first time the dose of radiation is in the range of 1-4 Mrad and the second time the dose is between 4-7 Mrad.

**[0031]** While crosslinking may be beneficial for the wear resistance, it may decrease the crack propagation resistance. One of the possibilities to at least partially offset this potential disadvantage, is to increase the crystallinity of the material. In an embodiment, one or more of the following techniques are employed to keep the crystallinity at, or bring the crystallinity to, a relatively high level.

1. After sintering the polyethylene above the melting temperature of the polyethylene, the polyethylene is cooled down slowly from the melt, e.g. at a rate of less than 10°C/hr, e.g. less than 5°C/hr, less than 3°C/hr, or less than 1°C/hr. In an embodiment, the cooling down is under elevated pressure.

2. After cooling down from the melt after sintering, the object is reheated and cooled down slowly (e.g. at the rates mentioned above under technique 1) under pressure (e.g. above 3 kbar).

3. After sintering, the polyethylene is annealed by cooling down from the melt just above the crystallization temperature (e.g. 1-10°C, for instance 1-5°C or 1-3°C) above the crystallization temperature and holding the object at that temperature for a period of time.

4. The crosslinked object, which may or may not be a sintered object, is placed in a suitable solvent to swell the material and increase the mobility of the molecules in the system to favor the crystallization process. Examples of solvents include e.g. solvents in the liquid phase such as xylene, toluene, decaline but also in the supercritical phase such as supercritical CO<sub>2</sub>, supercritical acetylene, supercritical hydrogen and supercritical ethene. Also radical scavengers may be used to swell the material, such as: vitamine E, vitamin A, vitamin C, phenolic antioxidants like BHT (E321, 2,6 ditertiarybutyl-4-methyl.phenol), irganox 1010, or carotenes such as beta carotene.

5. Nucleating or clarifying agents are added to the polyethylene before compacting. Such agents enhance the nucleation-crystallization process during cooling after sintering. In an embodiment, the nucleating or clarifying agents are added in an amount below 2wt%, relative to the total weight of polyethylene. Nucleating and clarifying agents are known in the art and include for instance inorganic substances, such as talcum, metal oxides (e.g. titanium dioxide or magnesium oxide), phosphates, and carbonates or sulfates of, preferably, alkaline earth metals. Examples of organic nucleating or clarifying agents include for instance compounds based on sorbitol, for instance 1,3-2,4-di(benzylidene)-D-sorbitol (MILLAD 3905, Milliken Chemical Co).

6. The compacted, crosslinked, and sintered object is deformed uniaxially in the solid-state. Upon deformation the crystals may rearrange and orient towards the orientation direction.

7. The compacted, crosslinked, and sintered object is deformed biaxially in the solid-state. Upon deformation the crystals may rearrange and increase the crystallinity.

8. Zone annealing the crosslinked polyethylene (preferably in a relatively small zone).

9. Adding one or more relatively low molecular weight polyethylene to the UHMWPE. In an embodiment, the one or more low molecular weight polyethylenes have a weight average molecular weight of less than 750,000 g/mol, e.g. less than 500,000 g/mol, such as less than 400,000 g/mol, less than 250,000 g/mol, less than 100,000 g/mol, less than 50,000 g/mol, less than 25,000 g/mol, less than 15,000 g/mol or even less than 5,000 g/mol. In an embodiment, the weight average molecular weight is at least 500 g/mol. In an embodiment, the one or more low molecular weight polyethylenes include a polyethylene that phase separates from the UHMWPE. In an embodiment, the one or more low molecular weight polyethylenes comprise, or consist essentially of, one or more polyethylenes with a polydispersity below 20, such as below 10, below 7, or below 4. In an embodiment, the one or more low molecular weight polyethylenes comprise, or consist essentially of, one or more linear polyethylenes. In an embodiment, one or more low molecular weight polyethylenes comprise, or consist essentially of, one or more polyethylenes that can crystallize relatively easily to crystals with nearly 100% crystallinity. In an embodiment, the amount of low molecular weight polyethylene in the polyethylene composition is, relative to the total weight of UHMW PE in the composition, less than 50 wt%, e.g. less than 30 wt%, less than 15 wt%, less than 10 wt%, less than 5 wt%, or less than 3 wt%. In an embodiment, the amount is at least 0.5 wt%, such as at least 1 wt%, at least 3 wt%, at least 5 wt%, or at least 8 wt%.

## APPLICATIONS

**[0032]** The products contemplated according to the present invention are numerous, and cover different fields of applications. Without limiting the scope and use of the present invention, some illustrative products are indicated herein.

**[0033]** In an embodiment, products include biomedical intermediates or products such as artificial implants, for instance orthopedic implants, e.g. parts of an artificial hip, of an artificial knee, of an artificial shoulder, of an artificial toe, of an artificial elbow, or an artificial ankle. Other examples include, e.g., products where the polyethylene forms part or the whole of an automotive part, an outdoor product, a composite material, a mono- or multi-filament fiber, an oriented or un-oriented fiber, a woven or non-woven fabric, a filter, a membrane, a film, a multi-layer- and/or multicomponent film, a barrier film, a container, a bag, a bottle, a rod, a liner, a vessel, a pipe, a valve, an O-ring, a gasket, ski soles, snow board soles, snow mobile runners, sliding parts (e.g. in printing devices, major appliances [dish washers, cloth washers, dryers, etc.], in automotive devices [steering systems, steel cable guides, etc.], in conveyor systems [flights], in elevators and escalators, and the like). Other examples of applications is in the fabrication of industrial parts with abrasion resistance uses such as bearings, sprockets, gaskets, ball valve seats, or conveyor belt parts.

## EXAMPLES

- Materials:

**[0034]** In the below examples, the following materials were used:  
GUR 1020 and GUR 4020 are virgin UHMW PE powders obtained from Ticona, both having a weight average molecular weight of about 3.5 million g/mol (Kurtz, S:M: et al, Biomaterials, 20, 1659, 1999).

- Compacting:

**[0035]** In the below examples, unless explicitly noted otherwise, compacting was performed as follows:  
Samples were preheated to 120°C in a hydraulic Carver press, model M 25T, while no pressure was applied to the samples. After 5 minutes, the pressure was raised to 20 MPa. After 10 minutes at 20 MPa, the samples were removed from the press and placed in a water-cooled Carver press, where they were quenched to ambient temperature under a pressure of 60 MPa.

- Sintering:

**[0036]** In the below examples, unless explicitly noted otherwise, sintering was performed as follows:  
Samples were preheated to 200°C in a hydraulic Carver press, model M 25T, while no pressure was applied to the samples. After 5 minutes, the pressure was raised to 10 MPa. After 10 minutes at 20 MPa, the samples were removed from the press and placed in a water-cooled Carver press, where they were quenched to ambient temperature under a pressure of 60 MPa.

- Charpy impact

**[0037]** Charpy impact strength was determined on rectangular (120x15x10 mm), double notched test specimens prepared according to ISO 11542-2. All Charpy impact tests were performed on a Zwick 5113E pendulum impact tester according to ISO 179-1.

- Fatigue crack growth resistance

**[0038]** For the crack propagation measurements, compact tension (CT) specimens were used according to ASTM E 647. The dimensions of the samples are depicted in Figure 1, with  $W = 32$  mm,  $a_n = 6.4$  mm and sample thickness (B) was  $6 \pm 0.1$  mm. Before testing, each sample was pre-cracked with a sharp razor blade ( $a - a_n = 1$  mm).

**[0039]** Crack propagation measurements were performed on a Walter & Bai 10 kN servo-hydraulic testing machine according to ASTM E 647. Crack propagation was continuously recorded using a macro lens on a Canon EOS 20D single lens reflex camera without unclamping the samples during the measurements. Compact tension samples were subjected to tensile sinusoidal loading with a frequency of 5 Hz to avoid hysteretic heating of the samples. The load ratio  $R = F_{\min}/F_{\max}$  was kept at  $R = 0.1$  and  $F_{\max}$  was incrementally increased to achieve approximately the same crack propagation rate for all samples.

**[0040]** Definition of the load applied for all crack propagation measurements.

**[0041]** According to the theory of elasticity of cracked bodies, the stress intensity factor range  $\Delta K$  is a function of the

applied load and the crack length relative to component size:

$$\Delta K = \Delta F \cdot \frac{F(\alpha)}{B \cdot \sqrt{W}}$$

where  $\Delta F$  is the load amplitude of the fatigue cycle.  $F(\alpha)$  is a geometric factor and  $\alpha$  corresponds to  $a/W$ . The geometric factor for the compact tension geometry is defined as follows:

$$F(\alpha) = \frac{2 + \alpha}{(1 - \alpha)^{1.5}} (0.886 + 4.64\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.6\alpha^4)$$

**[0042]** Crack growth rates during cyclic fatigue tests are related to the stress intensity factor range,  $\Delta K$ , according to:

$$\frac{da}{dN} = C \Delta K^m$$

where  $N$  corresponds to the number of cycles and  $C$  and  $m$  are material constants. This so-called Paris law states that the crack propagation rate ( $da/dN$ ) scales linearly with the stress intensity factor range ( $\Delta K$ ) on a log-log scale. A limiting stress intensity factor range can be defined which represents a service operating limit below which fatigue damage is highly unlikely. According to ASTM E 647, this threshold value,  $\Delta K_{th}$ , is associated with a crack propagation rate of  $10^{-7}$  mm/cycle. Here,  $\Delta K_{th}$  was calculated by determining the best-fit straight line from a linear regression of  $\log da/dN$  versus  $\log \Delta K$  between the lowest detected growth rate and the onset of the  $\log da/dN$ ,  $\log \Delta K$  proportionality (in most cases between growth rates of  $10^{-6}$  and  $10^{-5}$  mm/cycle). Generally, a higher  $\Delta K_{th}$  value can be related to a higher required stress intensity factor (or load amplitude) to initiate crack inception. All experiments were performed at room temperature.

- Wear coefficient

**[0043]** Abrasive wear measurements were carried out using a custom-built device according to specifications and method analogous to those described by Hutchings [Trezona, R. I., Allsopp, D. N., Hutchings, I. M., Wear, 229, 205 (1999)]. In the device, a hard sphere (1" Tungsten Carbide ball with a 400 nm surface roughness, Atlas Ball & Bearing Co. Ltd., UK) clamped between two coaxial driving shafts, rotated at a constant speed of 150 rpm. The sample (circular with a diameter of 20mm; thickness 0.6mm) was placed against the ball with a normal force of 0.27 N, while an abrasive slurry (0.75 g SiC (mean particle size of 4-5 microns) per  $\text{cm}^3$  distilled water) was dripping onto the ball at a feed rate of 5  $\text{cm}^3$  /min. The size of the resulting abrasive wear crater was measured with an optical microscope. In all cases, spherical craters were observed; the corresponding wear volume  $V$  was calculated according to:

$$V = \pi d^4 / (64R)$$

where  $R$  is the ball radius and  $d$  is the surface chordal diameter of the crater [Rutherford, K. L., Hutchings, I. M., J Test. Eval., 25, 250 (1997)]. To correct the measured diameter of the wear craters ( $d_{sup.1}$ ), which typically consist of a central spherical crater surrounded by a roughened or 'scuffed' annular region, the following empirical rule (according to Trezona et al. [Trezona, R. I., Hutchings, I. M., Wear, 235, 209 (1999)]) was applied:

$$\begin{aligned} d &= (d' - 0.1407) / 0.9358 \text{ for } 0.5 \text{ mm} \leq d \leq 2.193 \\ d &= d' \text{ for } d > 2.193 \text{ mm} \end{aligned}$$

**[0044]** For abrasive wear of homogeneous materials the wear volume is expected to be proportional to the product of the sliding distance  $S$  and the normal force  $N$ :

$$V = \kappa \times S \times N$$

which defines the wear coefficient  $\kappa$ .

EXAMPLE 1

**[0045]** GUR 4020 was sintered, and the charpy impact of the sintered GUR 4020 was determined to be 191 kJ/M<sup>2</sup>.

EXAMPLE 2

**[0046]** Example 1 was repeated, except that GUR 4020 was compacted before sintering. The charpy impact of the compacted and sintered GUR 4020 was determined to be 202 kJ/M<sup>2</sup>.

EXAMPLE 3

**[0047]** GUR 1020 was sintered, and the fatigue crack growth resistance of the sintered GUR 1020 was determined to be 1.25 MPa/m<sup>1/2</sup>.

EXAMPLE 4

**[0048]** Example 3 was repeated, except that GUR 1020 was compacted before sintering. The fatigue crack growth resistance of the compacted and sintered GUR 1020 was determined to be 1.32 MPa/m<sup>1/2</sup>.

EXAMPLE 5

**[0049]** Various samples of GUR 4120 were sintered according to the procedure mentioned above in the introductory part of this Example section, except that not all samples remained for 10 minutes under 20 MPa at 200°C. Specifically, samples were prepared that were held, respectively, for 10 minutes (i.e., the regular procedure), 30 minutes, 100 minutes, and 1000 minutes under 20 MPa at 200°C. The wear coefficient of these samples was determined and is shown as triangles in Figure 2.

EXAMPLE 6

**[0050]** Example 5 was repeated, except that all samples were compacted before sintering. The wear coefficient of these samples was determined and is shown as squares in Figure 2.

EXAMPLE 7

**[0051]** Samples of GUR 4020 were compacted. The compacted samples were irradiated at room temperature with gamma rays or with electrons (10 MeV) at room temperature. The dose of gamma radiation that the samples received differed among the samples and ranged from 0 to 15 MRad. Samples that instead received electron (e-beam) radiation all received a dose of 7 MRad. Subsequently, the samples were sintered and their Charpy impact strength was determined. The results are shown in Figure 3, with the gamma irradiated samples indicated as closed triangles (▲) and the e-beam sample as an open triangle (△).

EXAMPLE 8

**[0052]** Samples of GUR 1020 were compacted and subsequently sintered. The thus obtained samples were irradiated with E-beam at 125°C and at a dose of 7MRad, followed by thermal treatment for 9 hours at 150°C (which is above the melting temperature of GUR 1020). After these 9 hours, the samples were allowed to cool down to room temperature. The fatigue crack growth resistance of the thus obtained samples was determined to be 0.92 MPa/m<sup>1/2</sup>.

EXAMPLE 9

**[0053]** Example 8 was repeated, except that the compaction was omitted. The fatigue crack growth resistance of the thus obtained samples was determined to be 0.84 MPa/m<sup>1/2</sup>.

EXAMPLE 10

**[0054]** Samples of GUR 1020 were compacted. The compacted samples were sintered, and during sintering the samples were irradiated with E-beam at a dose of 7MRad. Thus, the crosslinking was initiated after compaction but during sintering (melt irradiation). The fatigue crack growth resistance of the thus obtained samples was determined to



be 0.89 MPa/m<sup>1/2</sup>.

## Claims

1. A process comprising:

- compacting a composition comprising ultrahigh molecular weight polyethylene (UHMWPE), said UHMWPE having a weight average molecular weight of at least 1,000,000 g/mol, to provide a compacted composition comprising UHMWPE;
- sintering said compacted composition; and
- crosslinking said UHMWPE,

wherein said compacting is performed under shear.

2. The process of claim 1, wherein said UHMWPE is virgin UHMWPE.

3. The process according to any one of claims 1-2, wherein said compacting occurs at a temperature in the range of 60-135°C.

4. The process according to any one of claims 1-3, wherein said crosslinking is initiated after said sintering.

5. The process according to any one of claims 1-4, wherein said compacting occurs in an inert atmosphere.

6. The process according to any one of claims 1-4, wherein said compacting occurs in a reactive atmosphere.

7. A process comprising:

- providing a composition compacted under shear, said compacted composition comprising ultrahigh molecular weight polyethylene (UHMWPE), said UHMWPE having a weight average molecular weight of at least 1,000,000 g/mol; and
- crosslinking the UHMWPE.

8. The process of claim 7, wherein said UHMWPE is virgin UHMWPE.

9. The process according to any one of claims 7-8, wherein said UHMWPE has a weight average molecular weight of at least 2,000,000 g/mol.

10. The process according to any one of claims 7-9, further comprising sintering the composition.

11. The process according to claim 10, wherein said sintering occurs in an inert atmosphere.

12. The process according to claim 10, wherein said sintering occurs in a reactive atmosphere.

13. The process according to any one of claims 1-3 or 10-12, wherein said crosslinking is initiated before said sintering.

14. The process according to any one of claims 1-3 or 10-12, wherein said crosslinking is initiated during said sintering.

15. The process according to any one of claims 10-12, further comprising cooling the sintered compacted polyethylene.

16. The process of claim 15, wherein said crosslinking is initiated during said cooling.

17. The process according to any one of claims 15-16, wherein said cooling occurs at a rate of less than 10°C/hr.

18. The process according to any one of claims 15-17, wherein said cooling is temporarily stopped at a temperature about 1-10°C above the crystallization temperature of said UHMWPE.

19. The process according to any one of claims 1-18, wherein said polyethylene is medical grade polyethylene.

20. The process of claim 19, further comprising swelling the crosslinked, sintered UHMWPE in one or more swelling agents.
- 5 21. The process according to any one of claims 1-20, wherein said composition consists essentially of said UHMWPE.
22. The process according to any one of claims 1-21, wherein said composition comprises a linear polyethylene having a weight average molecular weight below 500,000 g/mol.
- 10 23. The process according to any one of claims 1-22, wherein said composition comprises a polyethylene having a weight average molecular weight below 25,000 g/mol.
24. The process according to any one of claims 1-23, wherein said compacted composition has the shape of a block.
- 15 25. The process according to any one of claims 1-24, wherein said process is absent melting the UHMWPE other than during said sintering.
26. The process according to any one of claims 1-25, further comprising machining the crosslinked composition into a part of an orthopedic implant.
- 20 27. The process of claim 26, wherein said orthopedic implant is a hip cup or a part of an artificial knee.
28. An orthopedic implant comprising an article obtained by the process according to any one of claims 1-26.
- 25 29. A process comprising:
  - providing a compacted composition comprising crosslinked ultrahigh molecular weight polyethylene (UHMWPE), said UHMWPE having a weight average molecular weight of more than 1,000,000 g/mol; and
  - sintering the compacted composition.
- 30 30. The process of claim 29, wherein said UHMWPE is virgin UHMWPE.
31. The process according to any one of claims 29-30, wherein said composition comprises, relative to the total weight of said composition, at least 75 wt% of said UHMWPE.
- 35 32. The process according to any one of claims 29-30, wherein said composition consists essentially of said UHMWPE.
33. A process comprising:
  - 40 - sintering ultrahigh molecular weight polyethylene (UHMWPE), said UHMWPE having a weight average molecular weight of more than 1,000,000 g/mol; and
  - crosslinking said UHMWPE;

wherein said crosslinking is initiated more than once.
- 45 34. The process of claim 33, wherein further comprising cooling the sintered UHMWPE.
35. The process of claim 33, wherein said crosslinking is initiated during said sintering and again during said cooling.
- 50 36. The process of claim 35, wherein said crosslinking is effected with radiation, and the dose used during said sintering is smaller than the dose used during said cooling.
37. The process according to any one of claims 32-36, wherein said process is absent compacting virgin UHMWPE before said sintering.
- 55 38. The process according to any one of claims 32-37, wherein said process is absent melting said UHMWPE other than during said sintering.

## Patentansprüche

### 1. Verfahren, umfassend:

Verdichten einer Zusammensetzung, die ultrahochmolekulares Polyethylen (UHMWPE) umfasst, wobei das UHMWPE ein gewichtsmittleres Molekulargewicht von mindestens 1.000.000 g/mol aufweist, um eine verdichtete Zusammensetzung, umfassend UHMWPE, bereitzustellen;  
Sintern der verdichteten Zusammensetzung; und  
Vernetzen des UHMWPE,  
wobei das Verdichten unter Scherung durchgeführt wird.

### 2. Verfahren nach Anspruch 1, wobei das UHMWPE primäres UHMWPE ist.

### 3. Verfahren nach einem der Ansprüche 1-2, wobei das Verdichten bei einer Temperatur im Bereich von 60-135 °C erfolgt.

### 4. Verfahren nach einem der Ansprüche 1-3, wobei das Vernetzen nach dem Sintern eingeleitet wird.

### 5. Verfahren nach einem der Ansprüche 1-4, wobei das Verdichten in einer inerten Atmosphäre erfolgt.

### 6. Verfahren nach einem der Ansprüche 1-4, wobei das Verdichten in einer reaktiven Atmosphäre erfolgt.

### 7. Verfahren, umfassend:

Bereitstellen einer unter Scherung verdichteten Zusammensetzung, wobei die verdichtete Zusammensetzung ultrahochmolekulares Polyethylen (UHMWPE) umfasst, wobei das UHMWPE ein gewichtsmittleres Molekulargewicht von mindestens 1.000.000 g/mol aufweist; und  
Vernetzen des UHMWPE.

### 8. Verfahren nach Anspruch 7, wobei das UHMWPE primäres UHMWPE ist.

### 9. Verfahren nach einem der Ansprüche 7-8, wobei das UHMWPE ein gewichtsmittleres Molekulargewicht von mindestens 2.000.000 g/mol aufweist.

### 10. Verfahren nach einem der Ansprüche 7-9, ferner umfassend das Sintern der Zusammensetzung.

### 11. Verfahren nach Anspruch 10, wobei das Sintern in einer inerten Atmosphäre erfolgt.

### 12. Verfahren nach Anspruch 10, wobei das Sintern in einer reaktiven Atmosphäre erfolgt.

### 13. Verfahren nach einem der Ansprüche 1-3 oder 10-12, wobei das Vernetzen vor dem Sintern eingeleitet wird.

### 14. Verfahren nach einem der Ansprüche 1-3 oder 10-12, wobei das Vernetzen während des Sinterns eingeleitet wird.

### 15. Verfahren nach einem der Ansprüche 10-12, ferner umfassend das Kühlen des gesinterten, verdichteten Polyethylens.

### 16. Verfahren nach Anspruch 15, wobei das Vernetzen während des Kühlens eingeleitet wird.

### 17. Verfahren nach einem der Ansprüche 15-16, wobei das Kühlen mit einer Geschwindigkeit von weniger als 10 °C/Stunde erfolgt.

### 18. Verfahren nach einem der Ansprüche 15-17, wobei das Kühlen bei einer Temperatur von etwa 1-10 °C über der Kristallisationstemperatur des UHMWPE vorübergehend gestoppt wird.

### 19. Verfahren nach einem der Ansprüche 1-18, wobei das Polyethylen ein medizinisches Polyethylen ist.

### 20. Verfahren nach Anspruch 19, ferner umfassend das Quellen des vernetzten, gesinterten UHMWPE in einem oder

mehreren Quellmitteln.

21. Verfahren nach einem der Ansprüche 1-20, wobei die Zusammensetzung im Wesentlichen aus diesem UHMWPE besteht.
22. Verfahren nach einem der Ansprüche 1-21, wobei die Zusammensetzung ein lineares Polyethylen mit einem gewichtsmittleren Molekulargewicht unter 500.000 g/mol umfasst.
23. Verfahren nach einem der Ansprüche 1-22, wobei die Zusammensetzung ein Polyethylen mit einem gewichtsmittleren Molekulargewicht unter 25.000 g/mol umfasst.
24. Verfahren nach einem der Ansprüche 1-23, wobei die verdichtete Zusammensetzung die Form eines Blocks hat.
25. Verfahren nach einem der Ansprüche 1-24, wobei das UHMWPE bei diesem Verfahren nicht geschmolzen wird, außer während des Sinterns.
26. Verfahren nach einem der Ansprüche 1-25, ferner umfassend das Verarbeiten der vernetzten Zusammensetzung zu einem Teil eines orthopädischen Implantats.
27. Verfahren nach Anspruch 26, wobei das orthopädische Implantat eine Hüftpfanne oder ein Teil eines künstlichen Knies ist.
28. Orthopädisches Implantat, umfassend einen Gegenstand, der durch das Verfahren nach einem der Ansprüche 1-26 erhalten wurde.
29. Verfahren, umfassend:  
Bereitstellen einer verdichteten Zusammensetzung, die vernetztes ultrahochmolekulares Polyethylen (UHMWPE) umfasst, wobei das UHMWPE ein gewichtsmittleres Molekulargewicht von mindestens 1.000.000 g/mol aufweist; und Sintern der verdichteten Zusammensetzung.
30. Verfahren nach Anspruch 29, wobei das UHMWPE primäres UHMWPE ist.
31. Verfahren nach einem der Ansprüche 29-30, wobei die Zusammensetzung, bezogen auf das Gesamtgewicht der Zusammensetzung, mindestens 75 % dieses UHMWPE umfasst.
32. Verfahren nach einem der Ansprüche 29-30, wobei die Zusammensetzung im Wesentlichen aus diesem UHMWPE besteht.
33. Verfahren, umfassend:  
  
Sintern von ultrahochmolekularem Polyethylen (UHMWPE), wobei das UHMWPE ein gewichtsmittleres Molekulargewicht von mehr als 1.000.000 g/mol aufweist; und Vernetzen des UHMWPE; wobei das Vernetzen mehr als einmal eingeleitet wird.
34. Verfahren nach Anspruch 33, wobei ferner umfassend das Kühlen des gesinterten UHMWPE.
35. Verfahren nach Anspruch 33, wobei das Vernetzen während des Sinterns und erneut während des Kühlens eingeleitet wird.
36. Verfahren nach Anspruch 35, wobei das Vernetzen mit Strahlung erfolgt und die Dosis, die während des Sinterns verwendet wird, geringer ist als die Dosis, die während des Kühlens verwendet wird.
37. Verfahren nach einem der Ansprüche 32-36, wobei das primäre UHMWPE bei diesem Verfahren vor dem Sintern nicht verdichtet wird.
38. Verfahren nach einem der Ansprüche 32-37, wobei dieses UHMWPE bei diesem Verfahren nicht geschmolzen wird, außer während des Sinterns.

## Revendications

### 1. Procédé comprenant :

5 le compactage d'une composition comprenant du polyéthylène de poids moléculaire ultraélevé (UHMWPE),  
 ledit UHMWPE ayant un poids moléculaire moyen en poids d'au moins 1 000 000 g/mol, pour fournir une  
 composition compactée comprenant l'UHMWPE ;  
 le frittage de ladite composition compactée ; et  
 10 la réticulation dudit UHMWPE,  
 dans lequel ledit compactage est réalisé sous cisaillement.

2. Procédé selon la revendication 1, dans lequel ledit UHMWPE est un UHMWPE vierge.

15 3. Procédé selon l'une quelconque des revendications 1 à 2, dans lequel ledit compactage se produit à une température  
 comprise dans la plage allant de 60 à 135 °C.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ladite réticulation est initiée après ledit frittage.

20 5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit compactage se produit sous une at-  
 mosphère inerte.

6. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit compactage se produit sous une at-  
 mosphère réactive.

### 25 7. Procédé comprenant :

la fourniture d'une composition compactée sous cisaillement, ladite composition compactée comprenant du  
 polyéthylène de poids moléculaire ultraélevé (UHMWPE), ledit UHMWPE ayant un poids moléculaire moyen  
 en poids d'au moins 1 000 000 g/mol ; et  
 30 la réticulation de l'UHMWPE.

8. Procédé selon la revendication 7, dans lequel ledit UHMWPE est un UHMWPE vierge.

35 9. Procédé selon l'une quelconque des revendications 7 à 8, dans lequel ledit UHMWPE a un poids moléculaire moyen  
 en poids d'au moins 2 000 000 g/mol.

10. Procédé selon l'une quelconque des revendications 7 à 9, comprenant en outre le frittage de la composition.

40 11. Procédé selon la revendication 10, dans lequel ledit frittage se produit sous une atmosphère inerte.

12. Procédé selon la revendication 10, dans lequel ledit frittage se produit sous une atmosphère réactive.

45 13. Procédé selon l'une quelconque des revendications 1 à 3 ou 10 à 12, dans lequel ladite réticulation est initiée avant  
 ledit frittage.

14. Procédé selon l'une quelconque des revendications 1 à 3 ou 10 à 12, dans lequel ladite réticulation est initiée  
 pendant ledit frittage.

50 15. Procédé selon l'une quelconque des revendications 10 à 12, comprenant en outre le refroidissement du polyéthylène  
 compacté fritté.

16. Procédé selon la revendication 15, dans lequel ladite réticulation est initiée pendant ledit refroidissement.

55 17. Procédé selon l'une quelconque des revendications 15 à 16, dans lequel ledit refroidissement se produit à une  
 vitesse inférieure à 10 °C/h.

18. Procédé selon l'une quelconque des revendications 15 à 17, dans lequel ledit refroidissement est temporairement  
 arrêté à une température d'environ 1 à 10 °C au-dessus de la température de cristallisation dudit UHMWPE.

19. Procédé selon l'une quelconque des revendications 1 à 18, dans lequel ledit polyéthylène est un polyéthylène de qualité médicale.
- 5 20. Procédé selon la revendication 19, comprenant en outre le gonflement de l'UHMWPE fritté réticulé dans un ou plusieurs agents de gonflement.
21. Procédé selon l'une quelconque des revendications 1 à 20, dans lequel ladite composition se compose essentiellement dudit UHMWPE.
- 10 22. Procédé selon l'une quelconque des revendications 1 à 21, dans lequel ladite composition comprend un polyéthylène linéaire ayant un poids moléculaire moyen en poids inférieur à 500 000 g/mol.
23. Procédé selon l'une quelconque des revendications 1 à 22, dans lequel ladite composition comprend un polyéthylène ayant un poids moléculaire moyen en poids inférieur à 25 000 g/mol.
- 15 24. Procédé selon l'une quelconque des revendications 1 à 23, dans lequel ladite composition compactée a la forme d'un bloc.
- 25 25. Procédé selon l'une quelconque des revendications 1 à 24, dans lequel ledit procédé ne consiste pas à faire fondre le UHMWPE autrement que pendant ledit frittage.
26. Procédé selon l'une quelconque des revendications 1 à 25, comprenant en outre l'usinage de la composition réticulée en une partie d'un implant orthopédique.
- 27 27. Procédé selon la revendication 26, dans lequel ledit implant orthopédique est une cupule de hanche ou une partie d'un genou artificiel.
28. Implant orthopédique comprenant un article obtenu par le procédé selon l'une quelconque des revendications 1 à 26.
- 30 29. Procédé comprenant :  
la fourniture d'une composition compactée comprenant du polyéthylène de poids moléculaire ultraélevé (UHMWPE), ledit UHMWPE ayant un poids moléculaire moyen en poids de plus de 1 000 000 g/mol ; et le frittage de la composition compactée.
- 35 30. Procédé selon la revendication 29, dans lequel ledit UHMWPE est un UHMWPE vierge.
31. Procédé selon l'une quelconque des revendications 29 à 30, dans lequel ladite composition comprend, par rapport au poids total de ladite composition, au moins 75 % en poids dudit UHMWPE.
- 40 32. Procédé selon l'une quelconque des revendications 29 à 30, dans lequel ladite composition se compose essentiellement dudit UHMWPE.
33. Procédé comprenant :  
45 le frittage d'un polyéthylène de poids moléculaire ultraélevé (UHMWPE), ledit UHMWPE ayant un poids moléculaire moyen en poids de plus de 1 000 000 g/mol ; et  
la réticulation dudit UHMWPE ;  
dans lequel ladite réticulation est initiée plus d'une fois.
- 50 34. Procédé selon la revendication 33, comprenant en outre le refroidissement de l'UHMWPE fritté.
35. Procédé selon la revendication 33, dans lequel ladite réticulation est initiée pendant ledit frittage et de nouveau pendant ledit refroidissement.
- 55 36. Procédé selon la revendication 35, dans lequel ladite réticulation est effectuée avec un rayonnement et la dose utilisée pendant ledit frittage est inférieure à la dose utilisée pendant ledit refroidissement.
37. Procédé selon l'une quelconque des revendications 32 à 36, dans lequel ledit procédé ne consiste pas à compacter

le UHMWPE vierge avant ledit frittage.

- 38.** Procédé selon l'une quelconque des revendications 32 à 37, dans lequel ledit procédé ne consiste pas à faire fondre ledit UHMWPE autrement que pendant ledit frittage.

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Figure 1

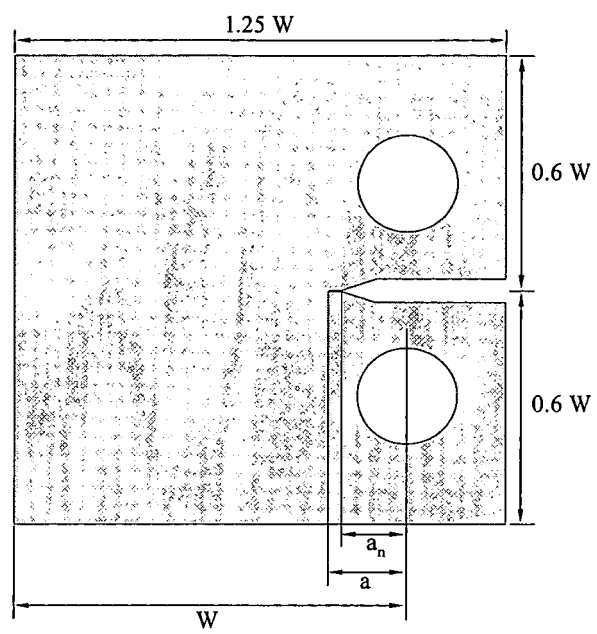




Figure 2

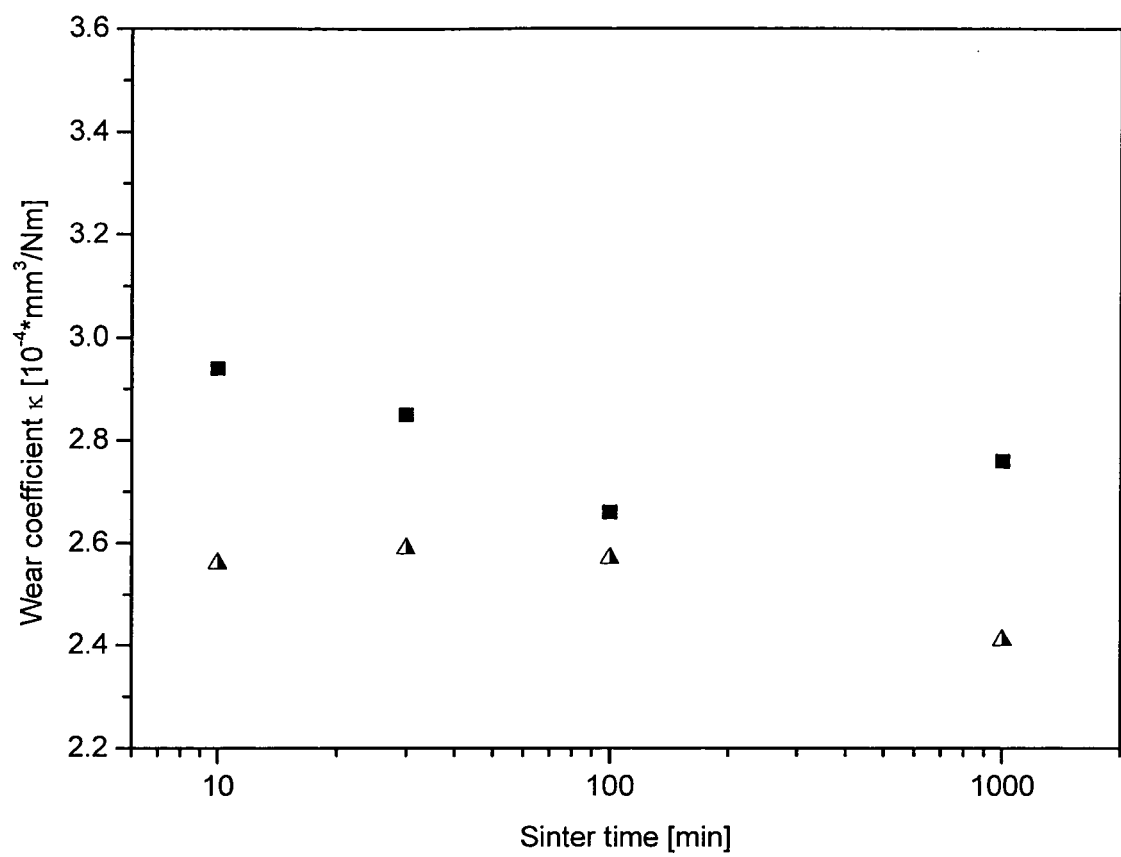
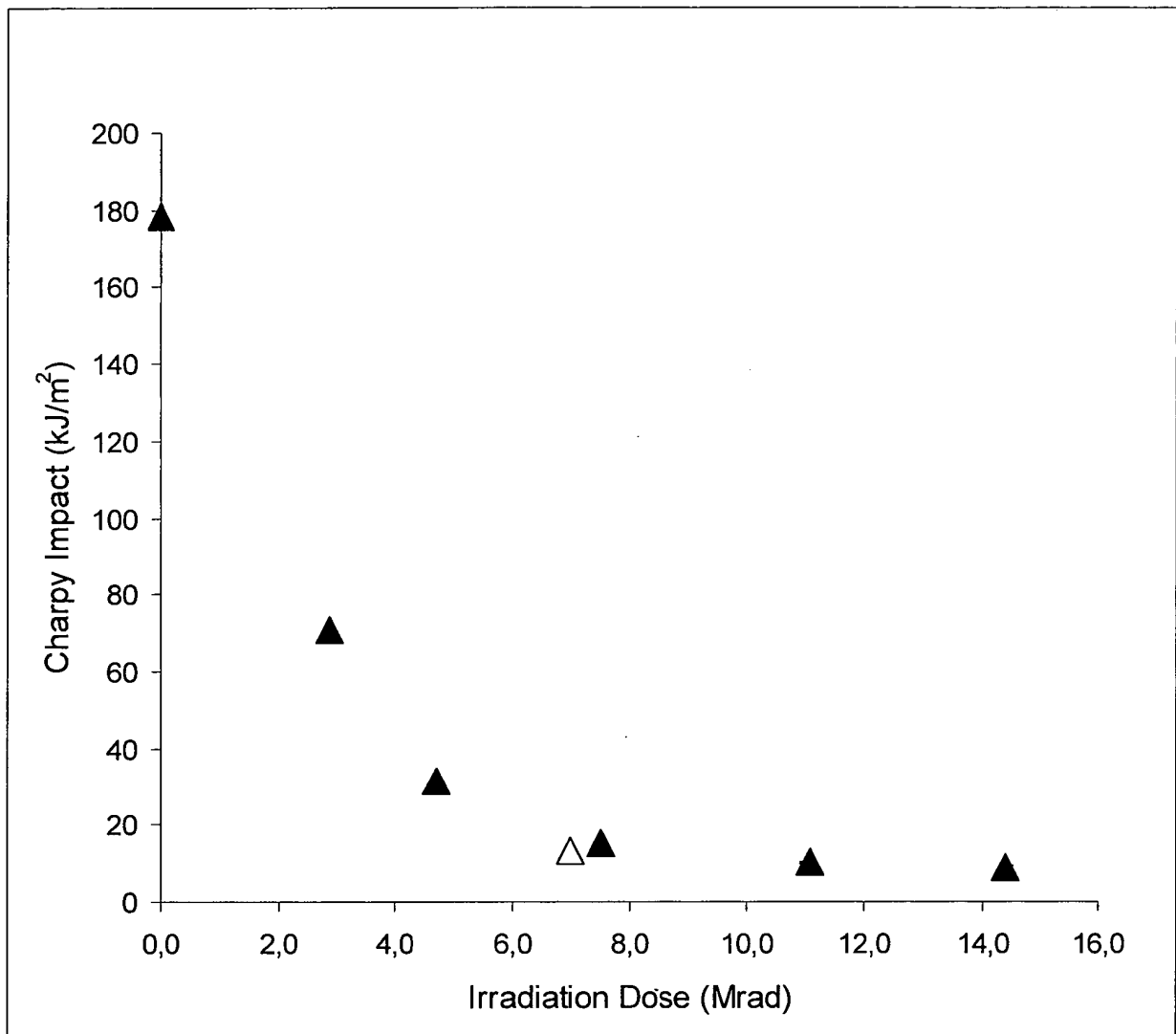


Figure 3



## REFERENCES CITED IN THE DESCRIPTION

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