

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 October 2008 (30.10.2008)

PCT

(10) International Publication Number
WO 2008/129245 A1

(51) International Patent Classification:
B29C 61/06 (2006.01)

(21) International Application Number:
PCT/GB2008/001331

(22) International Filing Date: 16 April 2008 (16.04.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0707467.7 18 April 2007 (18.04.2007) GB
0724216.7 12 December 2007 (12.12.2007) GB

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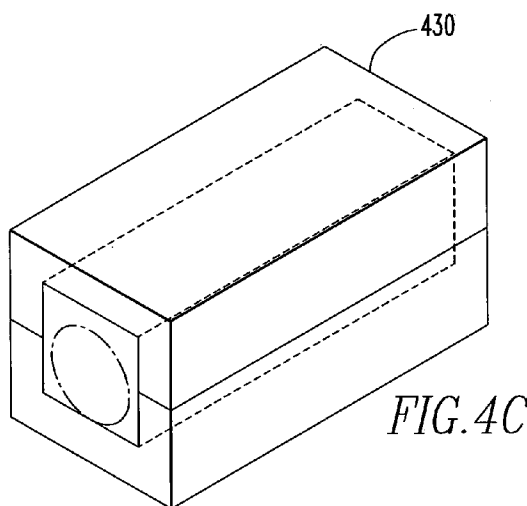
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(54) Title: EXPANSION MOULDING OF SHAPE MEMORY POLYMERS



(57) Abstract: The present invention relates to shape memory materials and to a method for controlling shape change in shape memory materials. In particular, the invention relates to a method and a system for forming complex shapes from shape memory materials and to shape memory materials having complex shapes.

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EXPANSION MOULDING OF SHAPE MEMORY POLYMERS

FIELD OF THE INVENTION

[0001] The present invention relates to shape memory materials and to a method for controlling shape change in shape memory materials. In particular, the invention relates to a method and a system for forming complex shapes from shape memory materials and to shape memory materials having complex shapes.

RELATED ART

[0002] Shape memory polymers (SMPs) are materials that have the ability to "memorize" a "permanent" macroscopic shape, be orientated or manipulated under temperature and/or stress to a temporary or dormant shape, and then be subsequently relaxed to the original or memorized, stress-free condition or shape. Relaxation is usually prompted or encouraged by the application of thermal, electrical, or environmental energy to the manipulated or orientated SMP. This relaxation is associated with elastic deformation energy stored in the SMP during orientation of the SMP. The degree of orientation of the SMP is the driving force that causes relaxation. Thus the greater the degree of orientation, the greater will be the force or energy stored in the SMP and hence the greater will be the force or energy driving relaxation of the SMP when triggered or prompted by an external energy source.

[0003] SMPs like other polymers can be grouped into two main categories; they can be amorphous, thus lacking any regular positional order on the molecular scale, or they can be semicrystalline which contain both molecularly ordered crystalline regions and amorphous regions in the same sample.

[0004] Plastic deformation of amorphous SMPs and SMP composites results in the formation of an orientated amorphous or semi-crystalline polymer network. Orientation of SMPs and SMP composites can be achieved by stretching, drawing or applying a compressive and/or shear force to the SMP. The SMP may be orientated by application of any one or a combination of these forces and can be carried out at ambient temperatures or elevated temperatures. Generally, the temperature of the SMP is raised above ambient temperature to around the glass transition temperature (T_g) of the SMP before application of the orientation force or forces. Raising the temperature of the SMP in this way helps prevent the SMP from rupturing when the orientation force is

being applied thereto. The glass transition temperature is the temperature below which the physical properties of amorphous SMPs behave in a manner similar to a solid, and above which they behave more like a rubber or liquid allowing the SMP to undergo plastic deformation without risk of fracture. After the SMP has been orientated, the temperature is reduced and the SMP is fixed in a temporary or dormant configuration.

[0005] The orientated network is physically stable well below the glass transition temperature (T_g) where molecular mobility is low. However, near or above the polymer's glass transition temperature, molecular motion rapidly increases and causes the orientated network to relax, usually accompanied by physical changes in the dimensions of the SMP. During relaxation, the orientated SMP tends to recover the original dimensions of the unorientated SMP, hence the name shape "memory" material. However, recovery of the original shape depends primarily on the degree of crystallinity, orientation, the micro and nano-structures and the conditions under which the orientated network is relaxed. For copolymers other important factors are their detailed composition and their specific thermal properties, i.e. the glass transition and melting temperatures, of their components.

[0006] It is believed that the relaxation process occurs nearly at constant volume. The degree of recovery during relaxation, for a semi-crystalline orientated SMP, depends on its crystallinity and structure and complete recovery of its original shape is difficult. In contrast, amorphous orientated SMPs, copolymers and their composites can return substantially to their original shape under appropriate relaxation conditions.

[0007] The degree of orientation is the driving force that causes relaxation. The greater the degree of orientation, i.e. the force or forces applied to the SMP, the greater will be the driving force.

[0008] During relaxation, the orientated SMP releases stored internal forces or energy. For example, an SMP of cylindrical shape orientated by applying a stretching force uniaxially along its longitudinal axis will shrink in length and expand in diameter during relaxation under free boundary conditions, i.e. where no physical constraints are imposed. Hence, when the cylindrical shaped SMP relaxes, it will induce a shrinkage force along its longitudinal axis and also an expanding force in the radial direction. These longitudinal and radial forces are proportional to the degree of orientation and mass of orientated polymer. The greater the degree of orientation, i.e. the greater the

forces applied to the SMP during orientation, and the greater the mass of the SMP, the greater these longitudinal and radial relaxation forces will be. For SMPs of other geometries, the relaxation forces will also depend on the degree or magnitude of the orientation force, the direction of the applied orientation force, as well as the mass of the orientated SMP. The rate of relaxation or the rate of shape recovery of the SMP is dependent on sample geometry, processing conditions and more importantly on the mass and thermal diffusivity of the SMP.

[0009] The mechanism of the prior art whereby the shape of an SMP is altered involves applying an orientation force to the SMP. Following orientation of the SMP where the SMP is changed from a first pre-orientated shape to a second orientated shape, the orientated SMP is heated above its glass transition temperature wherein the SMP relaxes back to its original or pre-orientated shape. It is an aim of the present invention to provide a shape memory polymer with tailored relaxation characteristics, capable of relaxing back to a shape which is different to its original shape. It is a further aim of the invention to provide shape memory material with complex geometries and structural assemblies of shape memory polymers with other solid elements such as metals, polymers and ceramics.

SUMMARY OF THE INVENTION

[0010] According to a first aspect of the present invention there is provided a shape memory polymer having a first configuration and a second orientated configuration, the second orientated configuration when at least partially relaxed in a mould by stimulating molecular motion of the SMP, relaxes to a third configuration that is different to the first and second configurations.

[0011] According to a second aspect of the present invention there is further provided a method for manufacturing a pre-relaxed shape memory polymer comprising the steps of:- processing a shape memory polymer having a first configuration to form an orientated shape memory polymer having a second configuration which is different to the first configuration; at least partially relaxing the orientated shape memory polymer by stimulating molecular motion of the shape memory polymer; and controlling the conditions under which the orientated shape memory material is at least partially relaxed to form a pre-relaxed shape memory polymer having a third configuration which is different to the first and second configurations.

[0012] Generally, the term configuration refers to the shape of the SMP but may also refer solely to the dimensions of the SMP. For example, in an embodiment of the invention, the third or final shape of the SMP can be intermediate in dimension between the first shape and second orientated shape. Intermediate in dimension may refer to one or more dimensions of the shape. For example, the SMP may have an initial or first cylindrical shape having radius r and height h and may be orientated, by stretching along its longitudinal axis, to create a cylinder having a second shape with a smaller radius r^- and larger height h^{++} . An example of an intermediate third shape would thus include a cylinder having a radius R and height H , where $r^- < R < r$ and $h < H < h^{++}$.

[0013] Preferably, the third shape is substantially different to the first and second shapes. For example, in an embodiment of the invention, the initial shape of the SMP is cylindrical and the final shape is that of a threaded screw. In another embodiment the initial shape is cylindrical and the final shape is a rod with regular polygonal cross sectional area such as, for example, a triangle, quadrilateral, or pentagon.

[0014] Preferably, the step of processing the shape memory material includes applying a stretching, or drawing or compressive force to the SMP. Typically, these forces may be applied to the SMP by zone drawing, or hydrostatic extrusion, or die drawing, or rolling, or roll drawing, or compression moulding. Alternatively any combination of these forces may be applied to the SMP

[0015] Preferably, the SMP is heated during or prior to application of the one or more of these forces to the SMP. The application of heat to the SMP prevents the SMP from rupturing which may otherwise occur on application of one or more of these forces. Preferably, the SMP is heated to, close to, or above its T_g .

[0016] Preferably, the step of processing the shape memory material includes the addition of particles to the SMP. The particles help to conduct and distribute the heat more quickly to the SMP thus reducing the heating period which would otherwise be required in a less conductive material. The particles also help distribute the heat more evenly over the SMP providing an orientated SMP which has more consistent properties throughout. Preferably, the particles include mineral particles, ceramic particles, or combinations thereof. Preferably the particles are biodegradable inorganic particles. The particles may also be magnetic or photo sensitive particles.

[0017] After processing the SMP in this way, the SMP is now orientated and thus contains trapped energy which is later released during the relaxing step. The energy released during the relaxing step helps drive the shape change of the SMP. The trapped energy of the orientated SMP is released by stimulating molecular motion of the orientated SMP.

[0018] Preferably, stimulation of molecular motion is achieved by the application of energy to the SMP from an external source. Preferably, the energy applied is in the form of heat. Preferably, the SMP is heated above the glass transition temperature (T_g) of the SMP. Alternatively or additionally, the relaxing step and thus the release of trapped energy from the SMP may be prompted or triggered by the application of a different form of energy, for example, a magnetic field, an electric current, ultrasound, electromagnetic radiation such as microwaves, visible and infrared light, or by a combination of any one of these forms of energy.

[0019] Stimulating molecular motion of the SMP may also be achieved by exposing the orientated SMP to a plasticizer. Exposure of the SMP to a plasticizer reduces the T_g of the SMP, thus increasing its molecular mobility. In this way, the molecular mobility of the orientated SMP may be increased sufficiently to cause the orientated network to relax. Where exposure of the orientated SMP to a plasticizer is not sufficient to relax the SMP, energy, in the form of heat for example, may also be applied to the SMP. In this way, the orientated SMP can be relaxed at a temperature less than would be necessary where the SMP is relaxed using heat alone. As such, the SMP can be shaped at lower temperatures, thus allowing the addition of temperature sensitive materials to the SMP. Temperature sensitive materials may include, for example, releasable bioactive agents such as monobutyryl, bone marrow aspirate, angiogenic and osteogenic factors.

[0020] Plasticizers may be in the form of a volatile liquid or a gas. Examples of gaseous plasticizers include but are not limited to, oxygen, nitrogen, carbon dioxide, sulphur dioxide, ammonia, methane, ethane, butane, propane, hexane, decane, ethene, propene, butene, hexene, dodecanene, ethyne, and butyne. Examples of liquid plasticizers include but are not limited too, water, inorganic aqueous solutions such as sodium chloride solution, cyclic alkanes, such as cyclohexane and methylcyclohexane, cyclic alkenes, such as benzene and toluene, cyclic alkynes, halogen substitute alkanes, alkenes, and alkynes, such as carbon tetrachloride and

chloropropane, oxygen substituted hydrocarbons, such as ethylene oxide and ethoxy hexane, aldehydes, such as hexanal, ketones, such as cyclohexanone, alcohols, such as methanol and ethanol, esters, such as butylpropionate, nitrogen substituted hydrocarbons, such as amine- triethylamine, and sulphur substituted hydrocarbons, such as butane thiol and diethyl sulphide.

[0021] The energy stored in the SMP can either be completely released or partially released leading to a completely relaxed or partially relaxed SMP. The resulting SMP is then known as a pre-relaxed SMP. Once the SMP is fully relaxed it can not be further relaxed unless reprocessed or re-orientated.

[0022] Ideally, the step of controlling the conditions under which the orientated SMP is at least partially relaxed includes placing at least part of the orientated SMP in a mould. The shape of the mould determines the third or final shape of the SMP and prevents the SMP from returning to its original or first shape.

[0023] The mould may be of similar dimensions to the second shape and thus restrict the polymer to a third shape very similar to the second shape. Alternatively the mould may be of different dimensions, thus allowing the polymer to relax to a third shape substantially different to the first and second shapes. Complex moulds can be used to form pre-relaxed SMPs with complex shapes.

[0024] Where a plasticizer is used to relax the orientated SMP instead of or in addition to the application of energy, the mould may be porous or perforated, for example, to allow the direct contact of the orientated SMP with the plasticizer.

[0025] The step of controlling the conditions under which the orientated shape memory material is at least partially relaxed may also include control of the energy added to the SMP when relaxing the orientated SMP. Where heat is used as the energy source, variations in the temperature and period of exposure will result in shaped SMP having different properties. For example, where the SMP is exposed to heat for a short period of time, the SMP, although it will have formed its final shape within the mould, will have only given up part of its trapped energy and thus only have partially relaxed. Such a shaped SMP will be capable of further relaxing. This is particularly advantageous where it may be necessary to alter the dimensions, but not necessarily the overall shape, of the final shaped SMP. For example, where the final SMP is in the

shape of a fastening bolt having a screw thread. In this case, the dimensions of the final fastening bolt shape can be altered somewhat to cater for dimension tolerances in a nut having a threaded receiving bore thus providing a bolt which can be more securely fitted in such a threaded bore.

[0026] Varying the orientation and relaxation of different sections of the SMP will also help tailor the final shape of the SMP.

[0027] When a final shape is required having unalterable dimensions, the SMP, whilst in the mould, can be exposed to heat for a longer period of time ensuring that the orientated SMP has released all its trapped energy and is thus fully relaxed. The addition of further energy or the further subsequent heating of such a relaxed SMP will not alter its dimensions. This is particularly useful when a device of exact and fixed shape and dimensions is required regardless of whether it may be subjected to external energy sources, such as heat, when used.

[0028] The particles added to the polymer during the processing step also help control the conditions under which the orientated SMP is at least partially relaxed. The particles help conduct the heat or other applied energy more evenly through the SMP, ensuring that the relaxing is consistent throughout the SMP, thus producing a pre-relaxed SMP having consistent properties throughout. The particles also help reduce the processing and controlling times by conducting the heat or other applied energy more quickly through the SMP than would otherwise occur. The addition of particles also helps improve subsequent machining of the shaped SMP where desired.

[0029] Generally, the larger the size of the particles added to the SMP, the longer it will take the orientated SMP to relax. This longer relaxation time could advantageously be used to tailor the shape of the relaxing SMP as the processing time is increased.

[0030] Suitable particles include but are not limited to inorganic particles such as buffers, radiopaque agents, osteoconductive agents, calcium, sodium, potassium, magnesium, barium, zirconium, bismuth, silver, gold, copper, zinc or any combination thereof. Preferably, the particles are crystalline calcium, sodium, zirconium, bismuth, barium, silicon, tungsten or magnesium salt.

[0031] Optionally, the particles can be calcium carbonate, calcium hydrogen carbonate, calcium phosphate, dicalcium phosphate, tricalcium phosphate, magnesium carbonate, sodium carbonate, hydroxyapatite, bone, phosphate glass, silicate glass, magnesium phosphate, sodium phosphate, barium sulphate, barium carbonate, zirconium sulphate, zirconium carbonate, zirconium dioxide, bismuth trioxide, bismuth oxychloride, bismuth carbonate, tungsten oxide or any combination thereof.

[0032] The particles can have a range of sizes and geometries. For example, the particles may be the shape of a needle, cube, platelet, fibre or sphere. Preferably the particles are shaped to enhance the mechanical properties of the SMP. The particle size is typically between 10nm and 1mm.

[0033] Typically, inorganic particles that act as buffers improve strength retention of degradable systems by reacting with the acidic breakdown products of the amorphous SMP.

[0034] Typical radiopaque agents include barium sulphate, barium carbonate, zirconium sulphate, zirconium carbonate, zirconium dioxide, bismuth trioxide, bismuth oxychloride, bismuth subcarbonate and tungsten oxide.

[0035] Typical osteogenic agents include calcium carbonate, calcium phosphate, dicalcium phosphate, tricalcium phosphate, hydroxyapatite, bone, phosphate glasses, silicate glasses, magnesium phosphate and sodium phosphate.

[0036] The particles may be pre-treated with a coupling agent such as a fatty acid, fatty acid anhydride or siloxane in order to enhance the properties of the SMP.

[0037] The method, useful for producing shape memory materials with complex geometries, is also useful for producing structural assemblies of shape memory polymers with other solid elements such as metals, polymers and ceramics.

[0038] According to another aspect of the present invention, there is provided a system for manufacturing a pre-relaxed shape memory polymer comprising a shape memory polymer as hereinbefore described and a mould.

[0039] Preferably, the mould is a complex mould for forming complex shapes of the shape memory polymer.

[0040] Preferably, the cavity of the mould has a modified surface to determine when the shape memory polymer has at least partially relaxed to form the third configuration. For example, the modified surface of the cavity can be pressure sensitive. In this way, as soon as the SMP has relaxed to form the third configuration or shape, the shaped SMP can be removed from the mould. This ensures that the SMP is relaxed for the minimum period of time resulting in a partially relaxed SMP which can be further relaxed at a later stage if required.

[0041] Generally, the SMP can be modified to produce particular desirable characteristics. The desired characteristics will depend largely on the end use of the pre-relaxed shape memory polymer.

[0042] Therefore, according to yet a further aspect of the present invention, there is provided a device including the pre-relaxed SMP as hereinbefore described.

[0043] The SMP can be of a resorbable, amorphous polymer composition or a non-resorbable, amorphous polymer composition. The SMP can be a homo polymer or a co-polymer, both of which can be linear, branched or cross-linked. The copolymer may comprise a component selected from a group consisting of glycolide, lactide, ethylene glycol or ϵ -caprolactone. For example, the copolymer can include a polylactide-co-glycolide, such as Poly(D,L-lactide-co-glycolide), or poly(methyl methacrylate), or poly(ethyl methacrylate) or other amorphous acrylic based polymers and copolymers. The copolymer can include an amorphous polymer composition and at least one mobile polymer and/or one rigid polymer.

[0044] Alternatively, the copolymer may include a semi-crystalline polymer and at least one mobile polymer and/or one rigid polymer. The mobility of a polymer refers to its ability to soften on application of heat. An SMP may have different areas of mobility relating to the different polymer compositions at different locations along the SMP composite. This allows different parts of the SMP to be orientated and relaxed at different temperatures and rates, thus allowing a finer control or tailoring of the final shape to be exercised. A rigid polymer is a polymer which demonstrates less mobility than a mobile polymer. The mobile polymer can include polyethylene glycol, or ϵ -

caprolactone, or glycolide, or D,L lactide and the rigid polymer can include D-lactide or L-lactide. The co-polymer can be a random arrangement of monomers or a repetitive and sequenced arrangement of monomers.

[0045] Examples of synthetic degradable SMP material include but are not limited to polyhydroxy acids, including polylactide (PLA) based homo and co-polymers such as poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA), poly(D,L-lactic acid) (PDLLA), PLLA-co-PDLLA, PLLA-co-PGA (where PGA is polyglycolide), PDLA-co-PGA, PDLLA-co-PGA, PLLA-co-PCL (where PCL is ϵ -polycaprolactone), PDLLA-co-PCL, PDLA-co-PCL. Co-polymers with poly(ethyleneglycol) (PEG) such as PLLA-co-PEG, PDLA-co-PEG, PDLLA-co-PEG are also suitable examples of synthetic degradable SMP material. Further examples include co-polymers containing three or more of the following blocks: PLA, PEG, PCL or PGA. Polyanhydrides, poly(hydroxybutyric acid), poly(hydroxyvaleric acid), poly(pseudo aminoacids), poly(hydroxyalkanoate) and blends and co-polymers thereof.

[0046] Examples of natural biodegradable SMP material include but are not limited to polysaccharides such as alginate, dextran, cellulose, collagen, and chemical derivatives thereof. Further examples include substitutions and additions of chemical groups such as, for example, alkyl, alkylene, hydroxylations, oxidations, and other modifications routinely made by those skilled in the art. Proteins such as albumin, zein and co-polymers and blends thereof, alone or in combination with synthetic polymers are also suitable examples of natural biodegradable SMP material.

[0047] Examples of synthetic SMP material include but are not limited to polyphosphazenes, poly(vinyl alcohols), polyamides, polyester amides, poly(amino acids), polyanhydrides, polycarbonates, polyalkylenes, polyacrylamides, polyalkylene glycols, polyalkylene oxides, polyalkylene terephthalates, polyortho esters, polyvinyl ethers, poly vinyl esters, poly vinyl halides, polyvinylpyrrolidone, polyesters, polysiloxanes, polyurethanes, polyacrylates such as poly(methyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate), poly(isobutyl methacrylate), poly(phenyl methacrylate), poly(methyl acrylate), poly(isopropyl acrylate), poly(isobutyl acrylate) and poly(octadecyl acrylate), and co-polymers thereof. Further examples include poly(ethylene terephthalate), poly(ethylene), polystyrene, polycarbonate, polysulfones, polyethersulfone, polyetherimide and polypropylene.

[0048] Examples of synthetically modified natural SMP material include but are not limited to cellulose derivatives such as alkyl celluloses, hydroxyalkyl cellulose, cellulose ethers, cellulose esters, nitrocelluloses and chitosan. Examples of cellulose derivatives include methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, hydroxybutyl methyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate butyrate, cellulose acetate phthalate, carboxymethyl cellulose, cellulose triacetate and cellulose sulphate sodium salt.

[0049] The SMP can include a releasable bioactive agent. These agents are included to help promote bone regrowth. Examples include bone morphogenic proteins, antibiotics, anti-inflammatories, angiogenic factors, osteogenic factors, monobutyrim, thrombin, modified proteins, platelet rich plasma/solution, platelet poor plasma/solution, bone marrow aspirate, and any cells sourced from flora or fauna, such as living cells, preserved cells, dormant cells, and dead cells. Other bioactive agents known to one of ordinary skill in the art may also be used. Alternatively or additionally, the SMP can include a porogen, such as sodium chloride. This is particularly useful where the SMP device is required to promote cell growth.

[0050] Further areas of applicability of the present invention will become apparent from the detailed description provided hereinafter. It should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are intended for purposes of illustration only and are not intended to limit the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0051] The accompanying drawings, which are incorporated in and form a part of the specification, illustrate embodiments of the present invention and together with the written description serve to explain the principles, characteristics, and features of the invention. In the drawings:

[0052] Figs 1A to 1D show a schematic illustration of a method, according to the present invention, for manufacturing a pre-relaxed shape memory polymer device in the form of a threaded screw;

[0053] Figs 2A to 2E show a schematic illustration of a method, according to the present invention, for manufacturing a pre-relaxed shape memory polymer device in the form of a cylindrical rod;

[0054] Fig. 3 is a graph showing the effect of different relaxing times on the expansion force along the radial direction of die-drawn shape memory polymer cylindrical shaped rods;

[0055] Figs 4A to 4D show a schematic illustration of a method, according to the present invention, for manufacturing a pre-relaxed shape memory polymer device of square cross section; and

[0056] Figs 5A to 5D show a schematic illustration of a method, according to the present invention, for manufacturing a pre-relaxed shape memory polymer device of triangular cross section.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0057] The following description of preferred embodiments is merely exemplary in nature and is in no way intended to limit the invention, its application, or uses.

[0058] Preparation of Orientated Shape Memory Polymer

[0059] The following description is given by way of example only of an embodiment of processing a SMP according to the present invention to form an orientated SMP and with reference to the examples describing embodiments of how the orientated SMP can be relaxed in a controlled manner to form a pre-relaxed SMP according to the invention.

[0060] In this embodiment the SMP, amorphous poly(D,L lactide-co-glycolide), was mixed with 35% w/w CaCO₃ particles (PLC). The mixture was prepared in a twin screw extruder to form fibres of the mixture. The fibres were palletised and consolidated to form isotropic cylindrical rods 110, 210, 410, and 510 with various diameters ranging from 5mm to 20mm using a ram extrusion technique. Isotropic rods thus formed having diameters of 5mm, 18mm and 20mm were orientated by die drawing using a conical die

at 60°C and a drawing speed of 20mm/min to form orientated rods 120, 220, 420 and 520 having diameters of 3mm, 8mm and 9mm, respectively.

[0061] Example 1

[0062] A prepared orientated SMP as described above in the form of a cylindrical rod 120 having a diameter of 8mm was placed into a mould 130 having a threaded screw shaped cavity such that an end part 125 of the orientated rod 120 protrudes from an end of the mould 130. The mould 130 and orientated rod 120 are immersed in a water bath at 80°C for 60 seconds and then into a water bath at 20°C for another 60 seconds to allow the oriented SMP to relax, resulting in a pre-relaxed screw 140 that has a head portion 150, which expanded freely without the mechanical restraint of the mould 130, having a radius similar to the isotropic rod 110, and a threaded portion 160 having dimensions determined by the dimensions of the mould 130. On removal of the screw 140 from the mould, the addition of further energy to the threaded portion will cause the threaded portion 160 of the screw 140 to further relax and expand radially whilst the head portion 150 will remain substantially of the same radius. Both threaded portion 160 and head portion 150 will remain substantially the same shape. This expansion moulding technique can be applied to other mould geometries.

[0063] Example 2

[0064] A sample of prepared orientated SMP as described above in the form of a cylindrical rod 220 having a diameter of 3mm was placed into a mould 230 having a cylindrical cavity that has substantially the same cavity radius as the radius of the orientated rod 220. The orientated rod 220 was partially relaxed by heating the mould 230 and orientated rod 220 in a fan assisted oven at 80°C for 5 minutes to produce a pre-relaxed cylindrical rod 240 that has substantially the same radius as the orientated cylindrical rod 220. The pre-relaxed cylindrical rod 240 is subsequently immersed in water at 80°C to allow further relaxation without mechanical constraints. The partially relaxed rod 240 was immersed in the water until the diameter of the rod 240 did not appreciably change resulting in a twice-relaxed cylindrical rod 250 having a radius greater than the orientated cylindrical rod 220 but less than isotropic cylindrical rod 210.

[0065] This process was repeated with further sample rods 220 with partial relaxing times from 0 to 120 minutes. It was found that the degree of recovery of the

original diameter of the isotropic cylindrical rod 210 decreased with increased partial relaxing time as can be seen from table 1. It was concluded that by partially relaxing the oriented rods 220 into a suitable mould the degree of recovery of the initial shape, in this case length and diameter, of the isotropic cylindrical rod 210 can be varied from substantially 0% for long partial relaxing times where the orientated rod 220 is substantially fully relaxed to almost 100% for short partial relaxing times where the orientated rod 220 is practically not relaxed at all but still contains substantially all the energy imparted thereto by orientation.

Table 1

Pre-relaxation time (min)	Diameter of pre-relaxed rod (mm)	Diameter of fully relaxed rod (mm)	Degree of recovery (%)
0	3.05	5.20	100
5	3.05	5.20	100
15	3.05	5.20	100
20	3.05	4.35	60
30	3.05	3.65	28
60	3.05	3.17	5
120	3.05	3.09	2

Table 1: Effect of partial relaxation time at 80°C on the degree of recovery of die drawn PLC rods.

[0066] Example 3

[0067] Figure 3 shows a graph plotting the expansion force in Newtons (N) against time for samples of prepared orientated SMP as described above in the form of cylindrical rods having a diameter of 3mm. Some of the samples were partially relaxed in a two piece long metal mould having a cylindrical cavity 3mm in diameter at 80°C with a fan assisted oven for different periods of time and other samples were not relaxed at all. On further relaxing these cylindrical samples at 60°C, the expansion force along the radial direction of the cylindrical samples was measured for specimens having the same volume and partially relaxed for 0, 1 and 3 minutes. The graph shows that the orientated sample rods which had not been partially relaxed have a greater expansion force than

the partially relaxed orientated sample rods. The expansion force of the sample rod was observed to decrease with an increase in time spent partially relaxing the sample rod. For example, 1 minute spent partially relaxing a sample rod in the mould significantly reduced the expansion force of the sample rod when further relaxed, whilst 3 minutes spent partially relaxing a sample rod in the mould reduced the expansion force yet further. It was concluded that the maximum expansion force rapidly decreases due to molecular re-arrangement of the oriented network.

[0068] Example 4

[0069] A prepared orientated SMP as described above in the form of a cylindrical rod 420 having a diameter of 9mm is placed in a cavity mould 430. The cavity of the mould 430 has a 14mm by 14mm square cross-section. The mould 430 and orientated rod 420 are immersed in hot water at 80°C for 2 minutes to allow the orientated rod 420 to relax to produce a pre-relaxed bar 440 shorter in length than the cylindrical rod 420 and with a square cross section having substantially the same dimensions as the square cross-section of the cavity of the mould 430. The pre-relaxed bar 440 is clearly illustrated in Fig. 4D.

[0070] Example 5

[0071] A prepared orientated SMP as described above in the form of a cylindrical rod 520 having a diameter of 9mm is placed in a cavity mould 530. The cavity of the mould 530 has a 16mm equilateral triangle cross-section. The mould 530 and orientated rod 520 are immersed in hot water at 80°C for 2 minutes to allow the orientated rod 520 to relax to produce a pre-relaxed SMP 540 shorter in length than the cylindrical rod 520 and having a triangular cross section with substantially the same dimensions as the triangular cross-section of the cavity of the mould 530. The pre-relaxed SMP 540 is clearly illustrated in Fig. 5D.

[0072] Where plasticisers are used instead of or in addition to energy, the plasticiser must come into direct contact with the SMP. This can be achieved, for example, by employing a porous or perforated type mould. On introduction of the porous mould containing the orientated SMP into an environment containing a plasticiser, the plasticiser will pass through the mould via the pores and directly contact the orientated SMP to stimulate molecular motion and thus relaxation of the orientated

SMP. It will be appreciated that energy in the form of heat for example, may also be used in conjunction with the plasticiser to promote relaxation of the orientated SMP. For example, the plasticiser itself may be used to transfer energy to the SMP by heating the plasticiser.

[0073] As various modifications could be made to the exemplary embodiments, as described above with reference to the corresponding illustrations, without departing from the scope of the invention, it is intended that all matter contained in the foregoing description and shown in the accompanying drawings shall be interpreted as illustrative rather than limiting. Thus, the breadth and scope of the present invention should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims appended hereto and their equivalents.

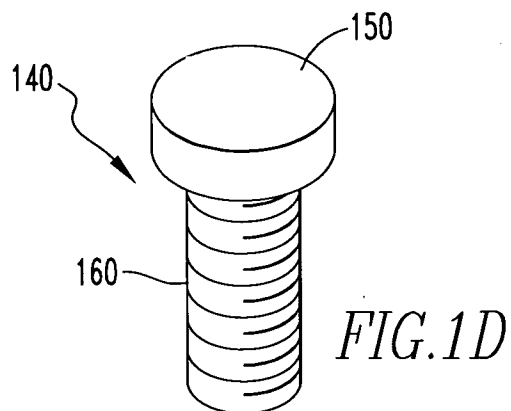
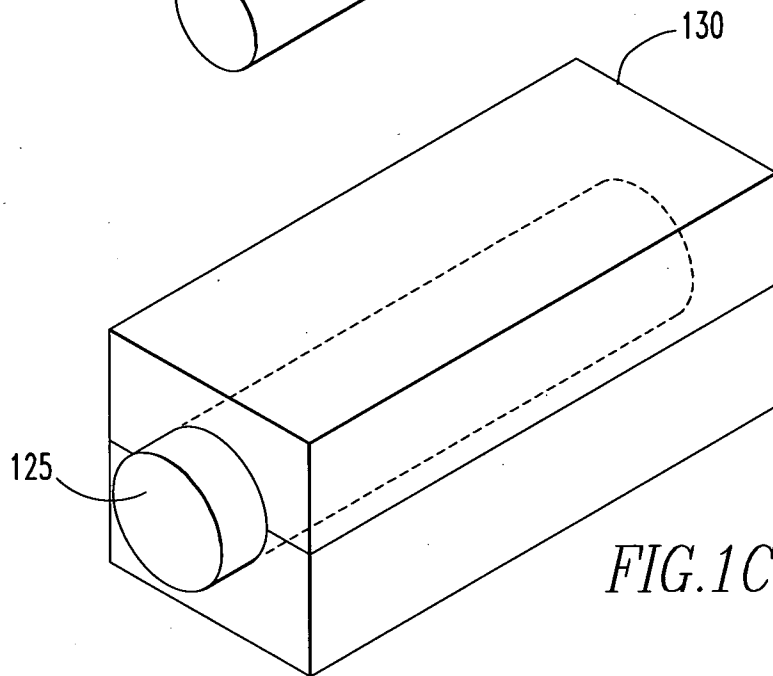
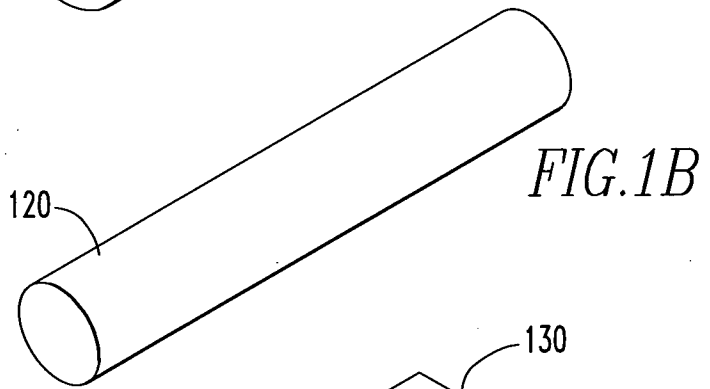
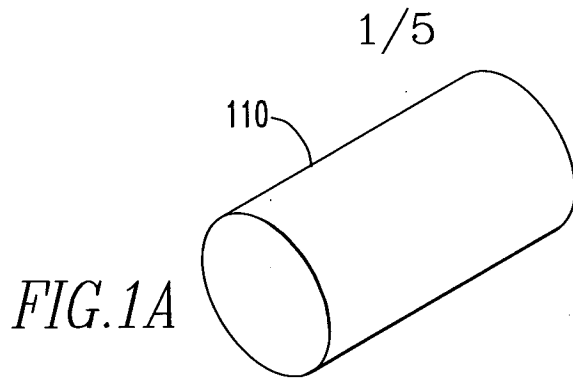
CLAIMS

1. A method for manufacturing a pre-relaxed shape memory polymer comprising the steps of:-
 - processing a shape memory polymer having a first configuration to form an orientated shape memory polymer having a second configuration which is different to the first configuration;
 - at least partially relaxing the orientated shape memory polymer by stimulating molecular motion thereof; and
 - controlling the conditions under which the orientated shape memory material is at least partially relaxed to form a pre-relaxed shape memory polymer having a third configuration which is different to the first and second configurations.
2. A method according to claim 1, wherein the step of processing the shape memory polymer to form an orientated shape memory polymer includes applying a stretching, or drawing or compressive force to the shape memory material or any combination thereof.
3. A method according to claim 1 or claim 2, wherein the step of processing the shape memory polymer includes zone drawing, or hydrostatic extrusion, or die drawing, or rolling, or roll drawing, or compression moulding, or any combination thereof.
4. A method according to any preceding claim, wherein the step of processing the shape memory material includes heating the shape memory material.
5. A method according to any preceding claim, wherein the step of stimulating molecular motion is achieved by the application of energy to the orientated shape memory polymer and/or exposure of the orientated shape memory polymer to a plasticizer.
6. A method according to claim 5, wherein the energy is chosen from a source consisting of a magnetic field, or an electric current, or ultrasound, or electromagnetic radiation, or heat by convection, conduction, or radiation or by any combination thereof.

7. A method according to any preceding claim, wherein the shape memory polymer is heated above the glass transition temperature of the shape memory polymer when at least partially relaxing the orientated shape memory polymer.
8. A method according to any preceding claim, wherein the step of controlling the conditions under which the orientated shape memory material is at least partially relaxed includes placing at least part of the orientated shape memory polymer in a mould.
9. A shape memory polymer having a first configuration and a second orientated configuration, the second configuration when at least partially relaxed in a mould by stimulating molecular motion of the orientated shape memory polymer, relaxes to a third configuration which is different to the first and second configurations.
10. A shape memory polymer as claimed in claim 9, wherein stimulating molecular motion is achieved by the application of energy to the orientated shape memory polymer and/or exposure of the orientated shape memory polymer to a plasticizer.
11. A shape memory polymer formed from any of the method claims 1 to 8.
12. A shape memory polymer as claimed in any of claims 9 to 11, wherein the shape memory polymer is a resorbable amorphous polymer or a non-resorbable amorphous polymer.
13. A shape memory polymer as claimed in any of claims 9 to 11, wherein the shape memory polymer is a copolymer.
14. A shape memory polymer as claimed in claim 13, wherein the copolymer comprises a component selected from a group consisting of glycolide, lactide, ethylene glycol or ϵ -caprolactone.
15. A shape memory polymer as claimed in claim 13 or 14, wherein the copolymer includes an amorphous polymer and at least one mobile and/or rigid polymer.

16. A shape memory polymer as claimed in claim 13 or 14, wherein the copolymer includes a semi-crystalline polymer and at least one mobile polymer and/or one rigid polymer.
17. A shape memory polymer as claimed in claim 15, wherein the amorphous polymer is a resorbable amorphous polymer or a non-resorbable amorphous polymer.
18. A shape memory polymer as claimed in claim 15 or 16, wherein the mobile polymer includes polyethylene glycol, or ϵ -caprolactone, or glycolide, or D,L lactide and the rigid polymer includes D-lactide or L-lactide.
19. A shape memory polymer as claimed in any of claims 9 to 18, wherein the shape memory polymer includes particles, such as mineral particles, or ceramic particles, or magnetic particles, or photosensitive particles, or any combination thereof.
20. A shape memory polymer as claimed in any of claims 9 to 19, wherein the shape memory polymer includes one or more releasable bioactive agents.
21. A shape memory polymer as claimed in claim 20, wherein the releasable bioactive agents include bone morphogenic proteins, antibiotics, anti-inflammatories, angiogenic factors, osteogenic factors, monobutyrin, thrombin, modified proteins, platelet rich plasma/solution, platelet poor plasma/solution, bone marrow aspirate, cells sourced from plants or animals.
22. A shape memory polymer as claimed in any of claims 9 to 21, wherein the shape memory polymer includes a cell growth promoter.
23. A system for manufacturing a pre-relaxed shape memory polymer comprising a shape memory polymer as claimed in any of claims 9 to 22 and a mould.
24. A system as claimed in claim 23, wherein the mould is a complex mould for forming complex configurations of the shape memory polymer.

25. A system as claimed in claim 23 or 24, wherein a cavity of the mould has a modified surface to determine when the shape memory polymer has at least partially relaxed to form the third configuration.
26. A system as claimed in claim 25, wherein the modified surface is a pressure sensitive surface.
27. A system as claimed in any of claims 23 to 26, wherein the mould is a porous or perforated mould.
28. A device including the shape memory polymer as claimed in any of claims 9 to 22.
29. A method as hereinbefore described with reference to the accompanying drawings.
30. A shape memory polymer as hereinbefore described with reference to and as shown in the accompanying drawings.
31. A system for manufacturing a pre-relaxed shape memory polymer as hereinbefore described with reference to and as shown in the accompanying drawings.
32. A device as hereinbefore described with reference to and as shown in the accompanying drawings.



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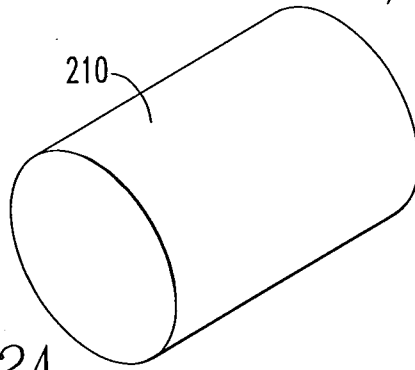


FIG. 2A

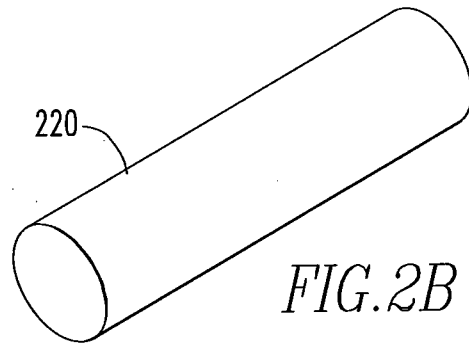


FIG. 2B

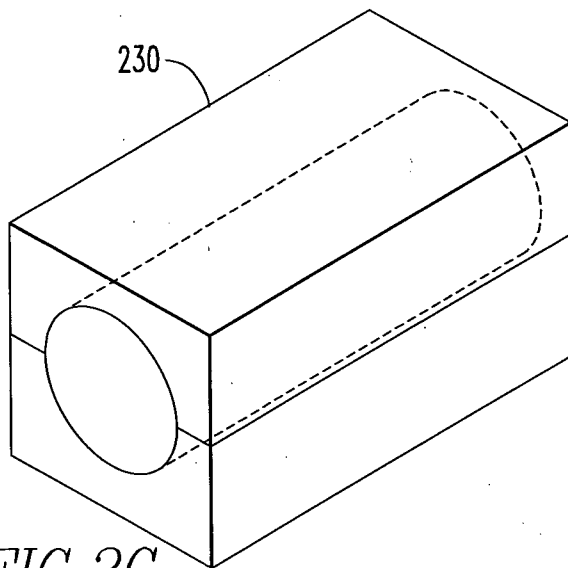


FIG. 2C

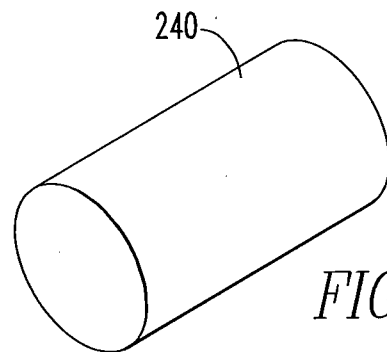


FIG. 2D

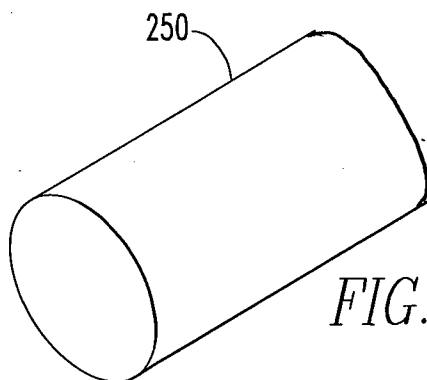


FIG. 2E

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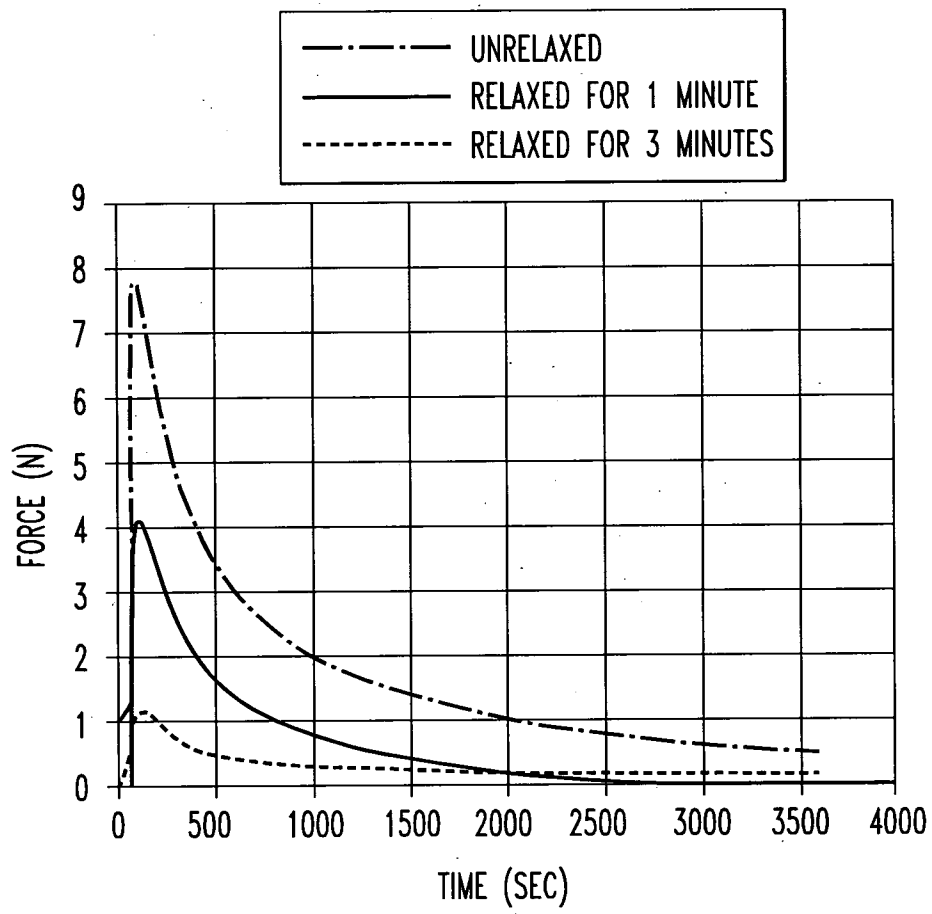


FIG.3

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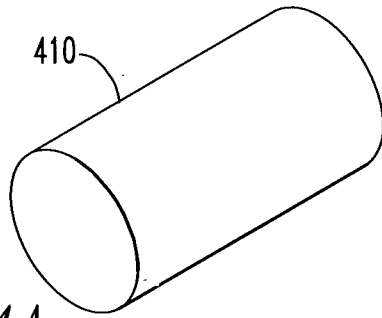


FIG. 4A

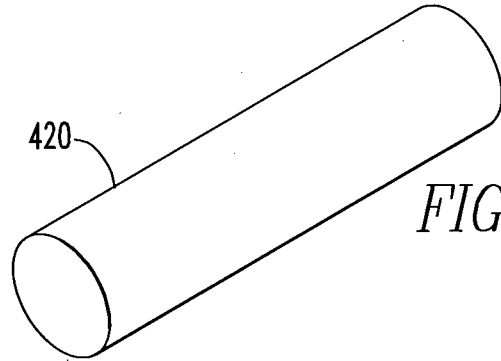


FIG. 4B

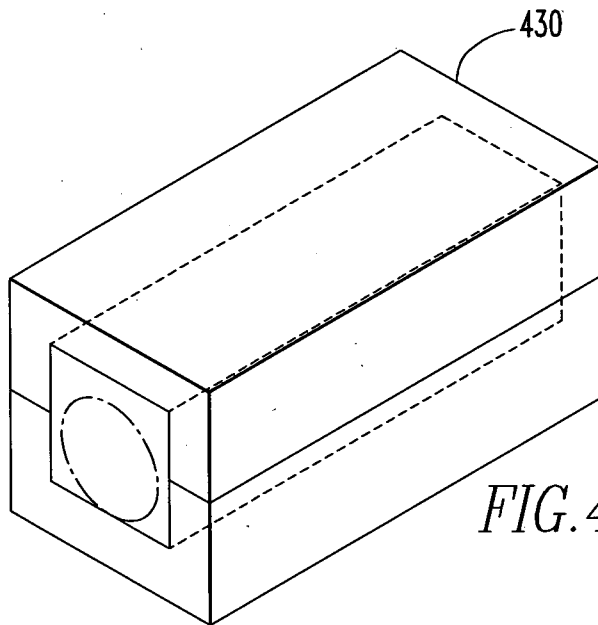


FIG. 4C

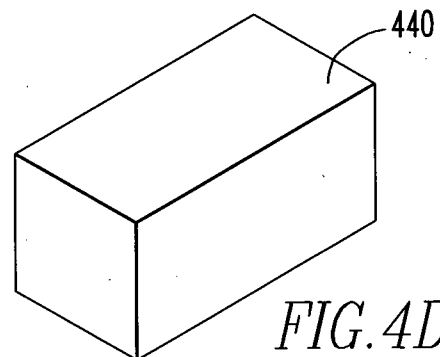


FIG. 4D

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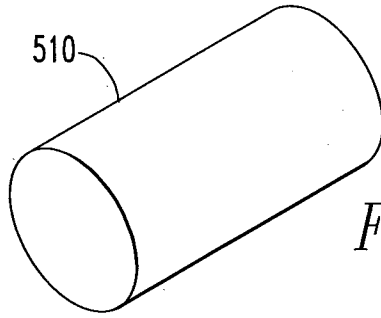


FIG. 5A

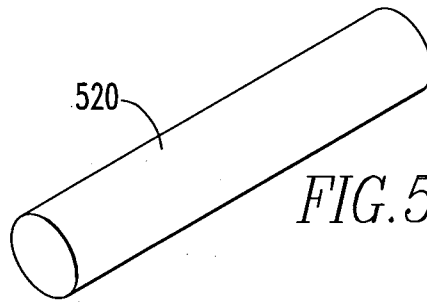


FIG. 5B

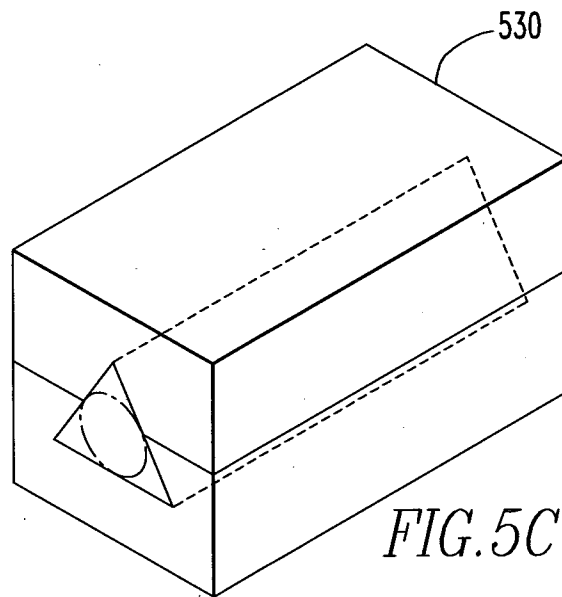


FIG. 5C

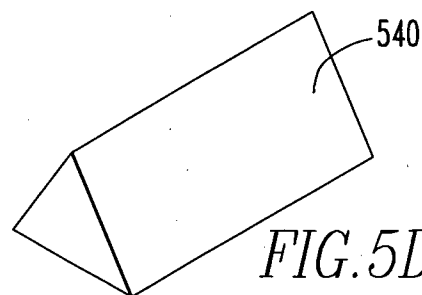


FIG. 5D

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2008/001331

A. CLASSIFICATION OF SUBJECT MATTER INV. B29C61/06		
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) B29C		
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) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A X A	EP 0 404 004 A (NIPPON UNICAR CO LTD [JP]) 27 December 1990 (1990-12-27) page 3, line 24 - line 30 ----- EP 0 326 426 A (NIPPON MEDICAL SUPPLY [JP] JMS CO LTD [JP]) 2 August 1989 (1989-08-02) page 3, line 17 - line 21 page 4, line 28 - line 32; figure 3 page 5, line 3 - line 10 ----- US 5 151 152 A (KAEUFE HELMUT [DE] ET AL) 29 September 1992 (1992-09-29) column 1, line 43 - column 2, line 2 -----	1-7,9-32 8 9,23,28 1
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		
<input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance. *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed		
T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search <p style="text-align: center;">14 August 2008</p>	Date of mailing of the international search report <p style="text-align: center;">25/08/2008</p>	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center;">Attalla, Giancarlo</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2008/001331

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