

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
15 December 2005 (15.12.2005)

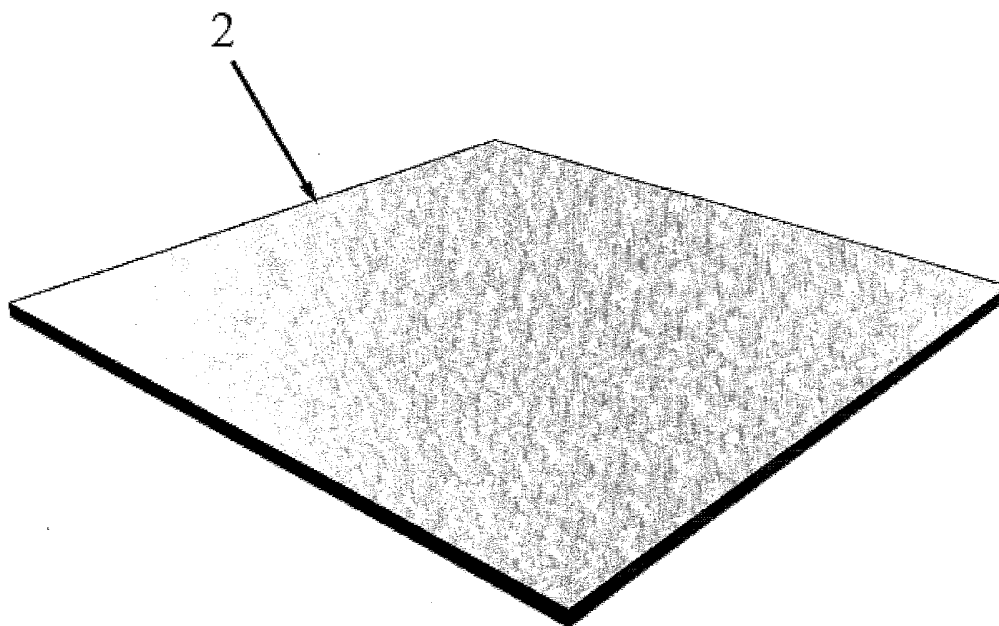
PCT

(10) International Publication Number  
**WO 2005/118248 A2**

- (51) International Patent Classification<sup>7</sup>: **B29C 45/03** **Matthew, C.** [US/US]; 816 Hunters Ridge Road, Fairborn, OH 45324 (US).
- (21) International Application Number: PCT/US2005/019875 (74) Agents: **PEACOCK, Bruce, E.** et al.; Wegman Hessler & Vanderburg, Suite 200, 6055 Rockside Woods Boulevard, Cleveland, OH 44131 (US).
- (22) International Filing Date: 3 June 2005 (03.06.2005)
- (25) Filing Language: English (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (26) Publication Language: English
- (30) Priority Data: 60/577,032 4 June 2004 (04.06.2004) US (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, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO,
- (71) Applicant (for all designated States except US): **CORNERSTONE RESEARCH GROUP, INC.** [US/US]; 2750 Indian Ripple Road, Dayton, OH 45440 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **HOOD, Patrick, J.** [US/US]; 2659 Washington Mill Road, Bellbrook, OH 45305 (US). **STACY, Mark, A.** [US/US]; 3968 Barrymore Lane, Beavercreek, OH 45440 (US). **EVERHART,**

[Continued on next page]

(54) Title: HIGH SPEED MANUFACTURING USING SHAPE MEMORY POLYMER COMPOSITES



(57) Abstract: [0053] Structurally strong composites are formed with shape memory polymer resins to create composites with shape memory properties. A system and method for using these composite structures to quickly manufacture composite products involves: 1) creating a preform composed of a shape memory polymer composite; 2) heating or otherwise activating the shape memory polymer; 3) using a mold to deform the composite material to a desired shape; 4) cooling or otherwise deactivating the shape memory polymer so that the composite structure retains the desired mold shape.

WO 2005/118248 A2



SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

— *without international search report and to be republished upon receipt of that report*

**HIGH SPEED MANUFACTURING USING SHAPE MEMORY**  
**POLYMER COMPOSITES**

**CROSS-REFERENCE TO RELATED APPLICATION**

[0001] Priority benefit of U.S. Provisional Patent Application Serial No. 60/577,032 filed June 4, 2004 is claimed.

**FIELD OF THE INVENTION**

[0002] The present invention relates to a system for using composite materials in a shape memory polymer resin matrix to manufacture composite parts. More specifically, the present invention relates to a system and method for forming a composite fiber-reinforced polymeric structure and the use thereof to quickly and easily manufacture simple or complex parts. The present invention is particularly advantageous for forming quickly and cheaply composite structures such as structural components for automobiles, trucks, recreational vehicles, appliances, and boats.

**BACKGROUND OF THE INVENTION**

[0003] The present invention generally relates to the repair of components made from material such as metals, composites, wood, plastics, glass and other materials. It is to be appreciated that the present invention has general and specific industrial application in the repair of various materials. The term "composite" is commonly used in industry to identify components produced by impregnating a fibrous material with a thermoplastic or thermosetting resin to form laminates or layers.

[0004] Generally, polymers and polymer composites have the advantages of weight saving, high specific mechanical properties, and good corrosion resistance which make them indispensable materials in all areas of manufacturing. Nevertheless, manufacturing costs are sometime detrimental, since they can represent a considerable part of the total costs and are made even more costly by the inability to quickly and easily repair these material without requiring a complete, and expensive, total replacement. Furthermore, the production of complex shaped parts is still a challenge

for the composite industry. The limited potential for complex shape forming offered by advanced composite materials leaves little scope for design freedom in order to improve mechanical performance and/or integrate supplementary functions. This has been one of the primary limitations for a wider use of advanced composites in cost-sensitive large volume applications. Additionally, the nature of composite materials does not lend itself to easy repair, especially on cheap, mass produced items and repair kits for more expensive, specialty items (such as in the aeronautic industry) are bulky, expensive, and require long time to complete the repair.

**[0005]** Shape memory polymers (SMPs) and shape memory alloys (SMAS) were first developed about 20 years ago and have been the subject of commercial development in the last 10 years. SMPs are polymers that derive their name from their inherent ability to return to their original "memorized" shape after undergoing a shape deformation. SMPs that have been preformed can be deformed to any desired shape below or above its glass transition temperature ( $T_g$ ). If it is below the  $T_g$ , this process is called cold deformation. When deformation of the SMP occurs above its  $T_g$ , the process is denoted as warm deformation. In either case the SMP must remain below, or be quenched to below, the  $T_g$  while being maintained in the desired deformed shape to "lock" in the deformation. Once the deformation is locked in, the polymer network cannot return to a relaxed state due to thermal barriers. The SMP will hold its deformed shape indefinitely until it is heated above its  $T_g$ , whereat the SMP stored mechanical strain is released and the SMP returns to its preformed state. While heated and pliable, SMP has the flexibility of a high-quality, dynamic elastomer, tolerating up to 400% or more elongation; however, unlike normal elastomers, an SMP can be reshaped or returned quickly to its memorized shape and subsequently cooled into a rigid plastic.

**[0006]** SMPs are not simply elastomers, nor simply plastics. They exhibit characteristics of both materials, depending on their temperature. While rigid, an SMP demonstrates the strength-to-weight ratio of a rigid polymer; however, normal rigid polymers under thermal stimulus simply flow or melt into a random new shape, and they have no "memorized" shape to which they can return. While heated and pliable, an SMP has the flexibility of a high-quality, dynamic elastomer, tolerating up

to 400% elongation or more; however, unlike normal elastomers, SMPs can be reshaped or returned quickly to their memorized shape and subsequently cooled into a rigid plastic.

[0007] Several known polymer types exhibit shape memory properties. Probably the best known and best researched polymer type exhibiting shape memory polymer properties is polyurethane polymers. Gordon, *Proc of First Intl. Conf. Shape Memory and Superelastic Tech.*, 115-120 (1994) and Tobushi et al., *Proc of First Intl. Conf. Shape Memory and Superelastic Tech.*, 109- 114 (1994) exemplify studies directed to properties and application of shape memory polyurethanes. Another polymeric system based on crosslinking polyethylene homopolymer was reported by S. Ota, *Radiat. Phys. Chem.* 18, 81 (1981). A styrene-butadiene thermoplastic copolymer system was also described by Japan Kokai, JP 63- 179955 to exhibit shape memory properties. Polyisoprene was also claimed to exhibit shape memory properties in Japan Kokai JP 62-192440. Another known polymeric system, disclosed by Kagami et al., *Macromol. Rapid Communication*, 17, 539-543 (1996), is the class of copolymers of stearyl acrylate and acrylic acid or methyl acrylate. Other SMP polymers known in the art includes articles formed of norbornene or dimethanooctahydronaphthalene homopolymers or copolymers, set forth in U.S. Patent 4,831,094. Additionally, styrene copolymer based SMPs are disclosed in U.S. Patent 6,759,481 which is incorporated herein by reference.

[0008] The time and cost of manufacturing have limited use of high-performance composites in many applications. This is particularly the case for mass produced consumer products, such as automobiles, appliances and other consumer products. Typically, a high performance composite is manufactured using a structural thermoset resin infused into an engineering fabric such as carbon fiber, graphite, glass, ceramic, Kevlar or other high-strength, tough woven fiber. In high-performance applications – those where a high-strength-to-weight ratio are needed - thermoset resins are used rather than thermoplastics. Thermoset resins have the desirable property of having a low viscosity prior to curing which allows the resin to infuse into the fabric and possess desired mechanical properties after cure such as high-modulus, toughness and strength. In many applications the high-modulus is

required in order to efficiently distribute the load across all of the fibers in a composite.

**[0009]** One of the major costs of composite manufacturing is the amortized cost of the mold and the labor required to lay up the composite part on the mold.. It is not uncommon for a composite part to take several hours to lay up and can tie up an expensive mold for several hours while it is being cured. This fact has limited the acceptance of composites into mass produced, consumer products.

**[0010]** Composite structures comprising polymeric outer layers and fiber-reinforced foam cores are known in the prior art. For example, U.S. Patent 4,910,067 ("the '067 patent"), discloses a structural composite comprising polymeric outer layers, a layer of fibrous material, and a foam core. It also has been known in the prior art to manufacture this type of composite structure with two polymeric layers, two fibrous layers wherein each fibrous layer is adhesively attached to an inner wall of a respective polymeric layer, and the foam core disposed within the space between the fibrous layers. The polymeric material of the foam core exhibited both a resinous and a foaming character, such that the resinous core material penetrated the fibrous layers, and the foamed core material filled the space between the fibrous layers.

**[0011]** The '067 patent further discloses a method of manufacturing a structural composite comprising the steps of: forming a polymeric layer into a desired shape; treating the surface of the polymeric layer by etching and oxidation; transferring the polymeric layer to a molding surface of a mold; adhesively attaching a layer of fibrous reinforcement to an opposing molding surface of a mold; mating the molding surfaces within the mold to form a cavity therebetween; injecting a foamable polymer into the cavity; permitting the foam to expand and thereby form a fiber-reinforced polymeric composite structure; and curing the structure in the mold. Alternatively, in order to promote the penetration of the fibrous reinforcement by the foam in a resinous state, the '067 patent further discloses that the layer of fiber can be treated with a defoaming agent capable of converting the foamable polymer to a liquid.

**[0012]** One drawback associated with these prior art structural composites, and methods of manufacturing such structural composites, is that the relatively viscous core materials cannot rapidly fill the cavity formed between the outer polymeric layers, and moreover, cannot rapidly and fully penetrate or impregnate the fibrous layers. Accordingly, such prior art structural composites have employed only relatively lightweight, unidirectional fibrous layers, that can be more easily penetrated (or “wetted out”) by the relatively viscous core materials in comparison to heavier, multi-directional fiber reinforcement layers. As a result, such prior art composite structures tend to be relatively weaker than otherwise desired and cannot be used to form primary structural parts or components. In addition, such prior art composite structures and methods have not proven to be cost effective for manufacturing parts in substantial quantities due to the relatively high cycle times required to allow the foam to expand, fill the core, and penetrate the fibrous layers.

**[0013]** Several other methods are known for manufacturing structural composites in various sizes and volumes for use in a number of technical fields and industries, including the automotive, marine, agricultural and recreational machinery, construction and manufactured housing, and industrial enclosure fields and industries. For example, U.S. Patent 5,588,392 to Bailey shows a resin transfer molding process for manufacturing a fiber-reinforced plastic boat hull; U.S. Patent 5,853,649 to Tisack et al. shows a method for manufacturing an interior automotive foam panel using a radio frequency electric field to promote bonding of the foam to the substrate; and U.S. Patent 5,972,260 to Manni shows a process for vacuum forming polyurethane mixed with a pentane blowing agent to manufacture flat insulating panels.

**[0014]** Each process described above and elsewhere in the prior art is uniquely suited for distinctively different segments of various markets based upon the size of the finished part and the volume of demand for the finished part. Some processes are uniquely suited for producing large parts in low volumes, while other processes are uniquely suited for producing small parts in high volumes. As production volumes increase, the complexity of the machinery involved, and the corresponding pressure applied to that machinery, necessarily increases. Accordingly, when employing these prior art processes, the size of a part that can be formed in relatively high volumes

correspondingly decreases because of the processing difficulties associated with molding relatively large parts under relatively higher pressures.

[0015] For example, it is known in the prior art to employ a fiberglass “spray-up” technology to form large parts having surface areas in the range of about 50-200 square feet. However, this technology has not proven to be economically feasible for producing high volumes of parts, such as in excess of 5,000 parts. Instead, resin transfer molding frequently has been used in the prior art to form relatively smaller parts in relatively higher volumes. For example, resin transfer molding typically has been used to manufacture parts having surface areas in the range of about 5-50 square feet, and in volumes of about 5,000-20,000 parts. Similarly, compression molding has been used in the prior art to form relatively smaller parts in relatively higher volumes. For example, compression molding typically has been used to manufacture parts having surface areas less than about 10 square feet, and in volumes of about 25,000-50,000 parts. To form parts in volumes greater than 50,000, the prior art typically has employed injection molding processes. Such processes, however, are generally limited to producing relatively smaller parts in comparison to the above-described processes.

[0016] Accordingly, one drawback associated with these and other prior art processes for manufacturing structural composites is the inability to manufacture relatively large parts, such as parts having surface areas greater than about 25 square feet, in relatively high volumes, in a commercially feasible manner.

[0017] Another drawback associated with these and other prior art methods for manufacturing structural composites, particularly fiber-reinforced polymeric composites with foam cores, is the difficulty in forming relatively large, thin-walled products that retain the composite's strength as well as a high-grade, cosmetic, impact and chemical resistant, weatherable exposed surface.

[0018] A manufacturing goal in the auto industry is to fabricate a composite component within a total cycle time of 60 seconds or less. This goal has been established in order to enable composites to be cost competitive for general acceptance into the auto industry and has been elusive.



**[0019]** Many attempts at achieving a cycle time of 60 seconds have been made. Most of these attempts have revolved around designing new resin systems with fast curing times. Previous attempts at reducing composite part cycle time have focused on developing new resin systems that can be cured rapidly. Such attempts have used different cure initiators and resins. Thermal cures have often been limited by the stability of the resin prior to infusion into the composite (the resin tends to cure at room temperature before it is applied in the mold) and/or the excessive heat generated by the resin cure process which can overheat the cured resin thereby degrading the mechanical properties of the composite. Alternative cure mechanisms have also been attempted such as light and electron beams. However, the ability to expose the composite through a mold and/or the cost of the radiation source has limited these manufacturing processes. In addition, these alternative cure mechanisms also result in heat generation during cure.

**[0020]** However, few, if any of these attempts have produced, repeatable quality parts quickly. Thus, there is a need for an invention that enables product developers and manufacturing engineers to use high performance composites in mass produced, cost sensitive products by reducing the cost of goods through reduced part cycle time while maintaining the strength to weight ratio of a high-performance composite. There is also a need to reduce component cycle time to a fraction of the auto industry goal of 60 seconds per part.

#### SUMMARY OF THE INVENTION

**[0021]** This invention enables product developers and manufacturing engineers to use high performance composites in mass produced, cost sensitive products by reducing the cost of goods through reduced part cycle time while maintaining the strength to weight ratio of a high-performance composite. It is not unreasonable for the composite design combined with the manufacturing process to reduce component cycle time to a fraction of the auto industry goal of 60 seconds per part.

**[0022]** Initially, sheets of preformed shape memory polymer composite are fabricated in a web process in which a shape memory polymer (“SMP”) resin is infused into a 3D or 2D woven fabric and then cured. The preformed composite can

be in any geometric shape, but is typically preformed in a flat square or rectangle shape. This process is well suited to mass production and does not require expensive molds or novel equipment. A similar process is currently used in the manufacture of prepreg composite panels.

[0023] The second step involves using one of the preformed SMP composite panels, cut to the appropriate size, heated above the glass transition temperature of the SMP prior to insertion into a mold. This allows the composite to be easily formed into a new three dimensional shapes which replicate the mold shapes. The heated composite is then moved into a mold and pressed, stamped or otherwise molded into its desired shape. The mold is held at a temperature below the glass transition temperature of the SMP so as to deactivate the composite to lock the composite in the deformed state. Since the SMP is a fully cross-linked and cured system, it does not have to cross-link or cure in the mold like conventional thermoset composites. The time to complete an entire molding cycle of a .375" thick piece of SMP composite which has a  $T_g$  of 185°F, initially heated to a temperature of 203°F, with a mold held at 122°F, and reduce the SMP composite to below 185°F so that it retains the mold shape is approximately 10 seconds or less. From this analysis, it can easily be seen that the auto industry's cycle time goal of 60 seconds is shattered.

[0024] Additional embodiments of the present invention include the use of other means of molding the composite patch and bonding said patch to the damaged part.

[0025] Other objects, features and advantages of the invention will be apparent from the following detailed description taken in connection with the examples and accompanying drawings and are within the scope of the present invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0026] Fig. 1 is a perspective view of preformed shape memory polymer composite sheet that can be used in the present invention;

[0027] Fig. 2 is a perspective view of a press mold with a mold, an upper and lower press, and a piece of shape memory polymer composite ready for deformation;

[0028] Fig. 3 is a perspective view of the press mold while deforming the shape memory polymer composite;

[0029] Fig. 4 is a perspective view of the press mold after molding with the shape memory polymer composite deformed to replicate the shape of the mold; and

[0030] Fig. 5 is an expanded perspective view of shape memory polymer composite deformed to replicate the shape of the mold.

#### DETAILED DESCRIPTION

[0031] Referring to the drawings in greater detail, the method of the invention herein is directed to fabricating and using a composite in a shape memory polymer resin matrix or other shape memory material in the manufacture of castable composite parts.

[0032] Examples 1 and 2 below describe the exemplary methods of creating pre-form shape memory polymer (SMP) composite parts. In general, the preferred SMP is a styrene copolymer based SMP as disclosed in U.S. Patent 6,759,481, however, other types of SMPs such as cyanate ester, polyurethane, polyethylene homopolymer, styrene-butadiene, polyisoprene, copolymers of stearyl acrylate and acrylic acid or methyl acrylate, norbornene or dimethanooctahydronaphthalene homopolymers or copolymers, maleimide and other materials are within the scope of the present invention.

#### Example 1

[0033] A polymeric reaction mixture was formulated by mixing vinyl neodecanoate (10%), divinyl benzene (0.8%), and styrene (85.2%) in random order to yield a clear solution. Benzoyl peroxide paste (4%) which is 50% benzoyl peroxide, was then added to the resulting solution (all composition % are by weight). The resulting solution was kept cold in a refrigerator before use. To prepare the shape memory polymer resin matrix composite sheet, a piece of 3D weave carbon fiber is placed on a glass sheet, ensuring that there are no stray fibers and the carbon fiber piece is smooth. Next, pour some of the polymeric reaction mixture onto the carbon fiber. Use a plastic squeegee or plastic spreader to spread the resin evenly over the

entire surface of the fabric. Thoroughly remove air bubbles and straighten the fabric. Place bleeder and breather fabric on top of the resin soaked carbon fiber. Then place the entire system in a high temperature vacuum bag with a vacuum valve stem and apply vacuum thoroughly, ensuring that there are no leaks. Cure the composite part with the following cycle: 1) A one-hour linear ramp to 75°C in an oven, autoclave, or other form of controlled heating device; 2) A three-hour hold at 75°C; 3) A three-hour linear ramp to 90°C; 4) A two-hour linear ramp to 110°C; 5) A one-hour linear ramp to 20°C. After curing, remove from oven and allow to cool. Remove vacuum bag, bleeder fabric, breather fabric, and glass plates from composite.

#### Example 2

[0034] A polymeric reaction mixture was formulated by mixing vinyl neodecanoate (10%), divinyl benzene (0.8%), and styrene (55.2%) in random order to form a colorless solution. Polystyrene granules (30%) were then added to the resulting solution. The resulting mixture was then allowed to sit at room temperature with occasional stirring until all the polystyrene granules were dissolved to give a clear, viscous solution. Benzoyl peroxide (4%) which is 50% benzoyl peroxide was then added to the resulting solution (all composition % are by weight). The resulting polymeric reaction mixture is continually stirred at or near 25°C, not to exceed 30°C until a clear solution is achieved which can take 2 hours or more. The resulting solution is kept cold in a refrigerator before use. To prepare the shape memory polymer resin matrix composite sheet, a piece of 3D weave carbon fiber is placed on a glass sheet, ensuring that there are no stray fibers and the carbon fiber piece is smooth. Next, pour some of the polymeric reaction mixture onto the carbon fiber. Use a plastic squeegee or plastic spreader to spread the resin evenly over the entire surface of the fabric. Thoroughly remove air bubbles and straighten the fabric. Place bleeder and breather fabric on top of the resin soaked carbon fiber. Then place the entire system in a high temperature vacuum bag with a vacuum valve stem and apply vacuum thoroughly, ensuring that there are no leaks. Cure the composite part with the following cycle: 1) A one-hour linear ramp to 75°C in an oven, autoclave, or other form of controlled heating device; 2) A three-hour hold at 75°C; 3) A three-

hour linear ramp to 90°C; 4) A two-hour linear ramp to 110°C; 5) A one-hour linear ramp to 20°C. After curing, remove from oven and allow to cool. Remove vacuum bag, bleeder fabric, breather fabric, and glass plates from composite.

**[0035]** To achieve more than one fabric layer simply soak two or more layers of fabric in the shape memory polymer and stack on top of each other. The use of other fabrics such as carbon nano-fibers, spandex, chopped fiber, random fiber mat, fabric of any material, continuous fiber, fiberglass, or other type of textile fabric can be used to replace carbon fiber in the above examples. In Example 2 it is essential that while mixing after the addition of benzyl peroxide that the temperature of the resin be maintained below 30°C as the mixture may become hot and explosive. Mixing in a cold water or ice bath ensures the temperature will not exceed 30°C. It can take two hours or more to fully mix. It is to be appreciated that the transition temperature of SMP resin can be tailored to specific requirements by the addition of other agents as disclosed in US Patent 6,759,481.

**[0036]** Additionally, once cured, the shape memory polymer composite can be deformed for easy storage, shipping, or immediate use. If deformed for storage or shipping, simply activating the shape memory polymer resin will restore the composite part to its original, memorized shape.

**[0037]** Referring to the drawings, Fig. 1 shows a flat, square, preformed piece of shape memory polymer ("SMP") composite preformed into its memorized shape, 2. Once heated the SMP composite preform can be inseted into a mold as shown in Fig. 2. In the exemplary process the SMP composite preform will be molded by stamping. Fig. 2. shows the stamp mold with an upper part, 6, and a lower part, 8. Additionally, there is a mold, 4, with raised features, 10, and a back panel, 12, which are to be replicated in the SMP composite preform, 2. The mold, 4, is a simple design for a car hood. In order to ensure adequate molding, the SMP composite preform, 2, is heated above its transition temperature in order to make the SMP composite soft and pliable. It is to be appreciated that different activation methods could be used if appropriate to the type of SMP employed in the composite preform. For example, if the SMP resin used is light activated, instead of the typical heat

activated SMP, the SMP composite preform can be made soft and pliable by exposure to certain light or other electromagnetic radiation.

[0038] Once the SMP composite preform is soft, the mold can be stamped as shown in Fig. 3 where the upper portion, **6**, and lower portion, **8**, of the stamping machine are compressed together. In the exemplary method, the upper and lower portions of the machine are kept at a temperature that is significantly less than the transition, or activation, temperature of the SMP composite such that while the upper and lower portions are compressed together the SMP composite quickly cools to below its transition temperature so that when the upper and lower portions are returned to their original positions, the composite material retains the shape of the mold, **4**. This result is shown in Fig. 4 where the upper portion, **6**, and the lower portion, **8**, have returned to their original positions and the deformed composite, **14**, retains the features and shape of mold, **4**. As can be seen in Fig. 4, the deformed composite has essentially replicated the shape of mold, **4**. The raised parts, **20**, of the deformed composite, **14**, essentially replicate the raised parts, **10**, of mold, **4**. Additionally, the back panel, **22**, essentially replicates the back panel, **12**, of mold **4**. Fig. 5 shows an enlarged view of the final, deformed composite shape. It is to be appreciated that if the SMP used is light activated that the deformed composite part should not be removed from the mold until the SMP has been deactivated by the application of light or other electromagnetic radiation as required to ensure the composite part becomes hard and will retain the desired mold shape. It is also to be appreciated that other molding processes such as draping, hand lay-up, overbraid, coating, painting, dripping, die casting, extrusion, annealing, vacuum forming, and computer aided technology may be used to mold the SMP composite to a desired shape.

[0039] The entire process from initial heating to removal of the final product from the stamping machine can take as little as between 5 and 10 seconds. While the exemplary method uses car hoods as an example of a manufactured part, it is to be appreciated that this process can be used to manufacture any number of simple or complex parts including car bumpers, parts of household appliances, boat hulls, any door, structural deployment devices for remote systems, games and toys, domestic

articles, arts and ornamentation units, medical and paramedical instruments and devices, thermosensitive instruments and security devices, office equipment, garden equipment, educative articles, tricks, jokes and novelty items, building accessories, hygiene accessories, automotive accessories, films and sheets for retractable housings and packaging, coupling material for pipes of different diameters, building games accessories, folding games, scale model accessories, bath toys, boots and shoes inserts, skiing accessories, suction-devices for vacuum cleaners, pastry-making accessories, camping articles, adaptable coat hangers, retractable films and nets, sensitive window blinds, isolation and blocking joints, fuses, alarm devices, sculpture accessories, adaptable hairdressing accessories, plates for braille that can be erased, medical prosthesis, orthopedic devices, furniture, deformable rulers, recoverable printing matrix, formable casts/braces, shoes (soles/in soles), form-fitting spandex, form-fitting clothes, self-ironing clothes, self-fluffing pillow, deployable structures (watertowers), and pipe replacement for underground applications. It is to be appreciated that once removed from the mold the composite material can be further machined or worked with to provide for attachment to other manufacture parts, painted, or cut to remove excess material.

**[0040]** Because of the properties inherent in shape memory polymers, composites utilizing shape memory polymer as the resin matrix can be temporarily softened, reshaped, and rapidly hardened in real-time to function in a variety of structural configurations. They can be fabricated with nearly any type of fabric, and creative reinforcements can result in dramatic shape changes in functional structures and they are machinable.

**[0041]** Therefore, it can readily be seen that the present invention provides a quick and easy way to utilize composite and shape memory polymer technology to create manufactured parts with a preform composite material that has the flexibility of duct tape with the performance of composites and similar metal substances.

**[0042]** It is therefore apparent that in one exemplary embodiment, a process is provided for manufacturing a composite product. The process involves the step of preforming a composite material into a desired shape such as a rectangle, square, triangle, sphere, rolled or other geometric memorized shape. The preformed

composite material is composed of at least one layer of fibrous material that is contained or embedded within a matrix formed of shaped memory polymer. The shape memory polymer resin is activated such that the preformed composite material becomes soft. The shape memory polymer resin is then deformed into the desired deformational state such as that of a mold shape or the like. The composite is then deactivated so that it retains its desired mold shape.

[0043] In one exemplary embodiment of the invention, the deactivation results from reducing the temperature of the shape memory polymer to a temperature that is less than its glass transition temperature and maintaining the shape memory polymer at such temperature for a time sufficient to lock the composite into its desired deformed state.

[0044] A variety of fibrous materials can be used in accordance with the invention including carbon nano-fibers, carbon fiber, spandex, chopped fiber, random fiber mat, fabric of any material, continuous fiber, fiberglass or other type of textile fabrics may be utilized.

[0045] In yet another exemplary embodiment of the invention, the shape memory polymer resin may consist of a styrene shape memory polymer, cyanate ester shape memory polymer, maleamide shape memory polymer, epoxy shape memory polymer, or other shape memory polymer. In some instances, it will be advantageous to utilize a thermoset resin as the shape memory polymer.

[0046] In a further exemplary embodiment, a thermal energy generation means may be embedded into the composite material. Such thermal energy generation means may comprise thermally conductive fibers or electrical conductors or the like.

[0047] In yet another exemplary embodiment of the invention, the activation of the shape memory polymer is achieved by heating the shape memory polymer resin to a temperature above its transition temperature. Such heating may be achieved via inductive heating, hot air, or heat lamps or the like, or the heating could be achieved by applying electrical current to thermal energy generation means that are embedded within the polymer.

[0048] In another exemplary embodiment of the invention, the activation of the shape memory polymer is achieved by application of electromagnetic radiation



thereto. The electromagnetic radiation may, for example, be in the form of visible or ultraviolet light.

**[0049]** The deformation of the preformed composite material may be achieved by a variety of means including mechanical means such as a press roll, or by drawing the material through a rolling die mold.

**[0050]** In yet another exemplary embodiment of the invention, the deactivation of the shape memory polymer resin may be accomplished by reducing the temperature of the shape memory polymer to a temperature below its activation temperature. The reduction of temperature of the shape memory polymer may be accomplished while press molding the composite. Additionally, deactivation of the shape memory polymer resin may be achieved by application of electromagnetic radiation, such as the above mentioned visible light or ultraviolet light electromagnetic radiation.

**[0051]** Although this invention has been described with respect to certain preferred embodiments, it will be appreciated that a wide variety of equivalents may be substituted for those specific elements shown and described herein, all without departing from the spirit and scope of the invention as defined in the appended claims.

**[0052]** What is claimed is:

### CLAIMS

1. A process for manufacturing composite products comprising:
  - a. performing a composite material into a desired shape wherein said preformed composite material is composed of at least one layer of fibrous material contained in a shape memory polymer resin matrix;
  - b. activating said shape memory polymer resin such that said preformed composite material becomes soft;
  - c. deforming said preformed composite material to a desired mold shape; and
  - d. deactivating said composite material so that it retains said desired mold shape.
  
2. A process as recited in claim 1 wherein said step of deactivating comprises reducing the temperature of said shape memory polymer to a temperature that is less than its glass transition temperature.
  
3. The method of claim 1 wherein said fibrous material is carbon nano-fibers, carbon fiber, spandex, chopped fiber, random fiber mat, fabric of any material, continuous fiber, fiberglass, or other type of textile fabric.
  
4. The method of claim 1 wherein said shape memory polymer resin consists of a styrene shape memory polymer, cyanate ester shape memory polymer, maleamide shape memory polymer, epoxy shape memory polymer, or other shape memory polymer.
  
5. The method of claim 4 wherein said shape memory polymer is a thermoset resin.
  
6. The method of claim 1 wherein said composite material comprises an embedded thermal energy generation means.

7. The method of claim 6 wherein said embedded thermal energy generation means comprises thermally conductive fibers.
8. The method of claim 6 wherein said thermal energy generation means comprises an electrical conductor.
9. The method of claim 1 wherein said activation of said shape memory polymer is achieved by heating said shape memory polymer resin to a temperature above its transition temperature.
10. The method of claim 9 wherein said heating is by inductive heating.
11. The method of claim 9 wherein said heating is by hot air.
12. The method of claim 9 wherein said heating is by heat lamps.
13. The method of claim 9 wherein said heating is by applying electrical current to an embedded thermal energy generation means.
14. The method of claim 1 wherein said activation of said shape memory polymer is achieved by application of electromagnetic radiation.
15. The method of claim 14 where said electromagnetic radiation is visible light or ultraviolet light.
16. The method of claim 1 wherein said deforming of said preformed composite material is by mechanical means.
17. The method of claim 16 wherein deforming said preformed composite material by mechanical means is accomplished in a press mold.

18. The method of claim 16 wherein deforming said preformed composite material by mechanical means is accomplished by drawing material through a rolling die mold.

19. The method of claim 1 wherein said deactivation of said shape memory polymer resin is by reducing the temperature of said shape memory polymer below its activation temperature.

20. The method of claim 18 wherein said reducing the temperature of said shape memory polymer is accomplished while press molding said composite.

21. The method of claim 1 wherein said deactivation of said shape memory polymer resin is by application of electromagnetic radiation.

22. The method of claim 21 wherein said aid electromagnetic radiation is visible light or ultraviolet light.

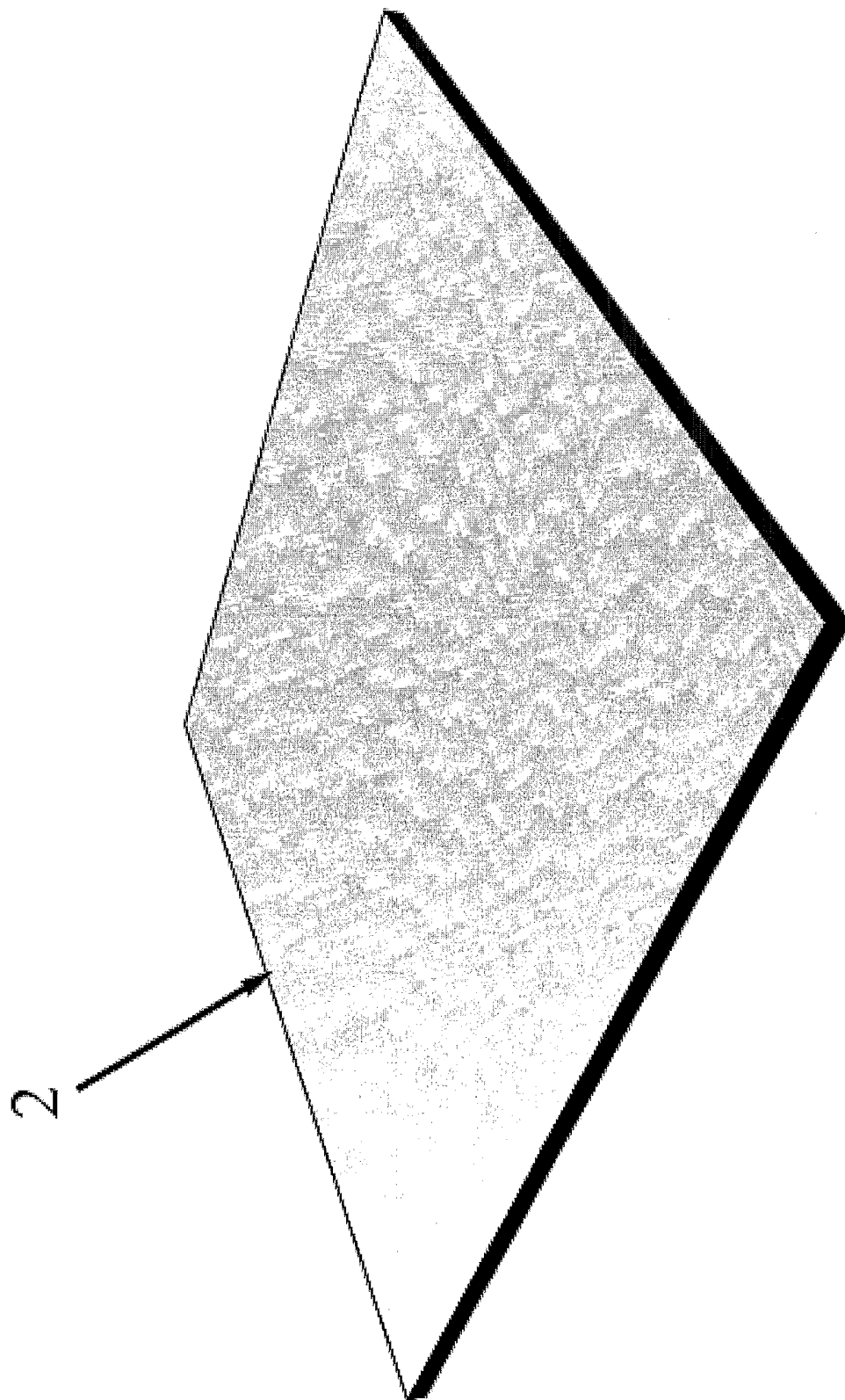


FIG. 1

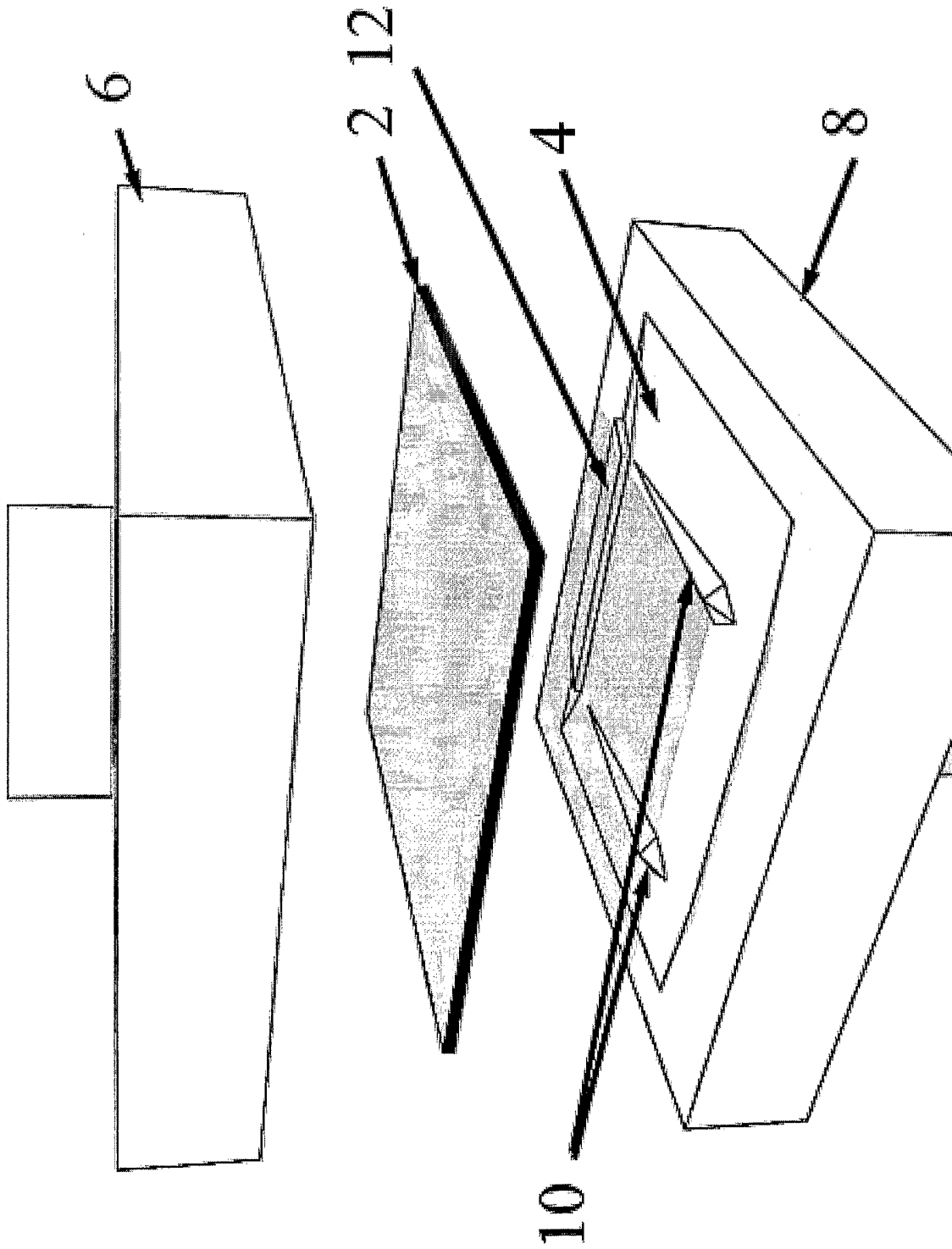


FIG. 2

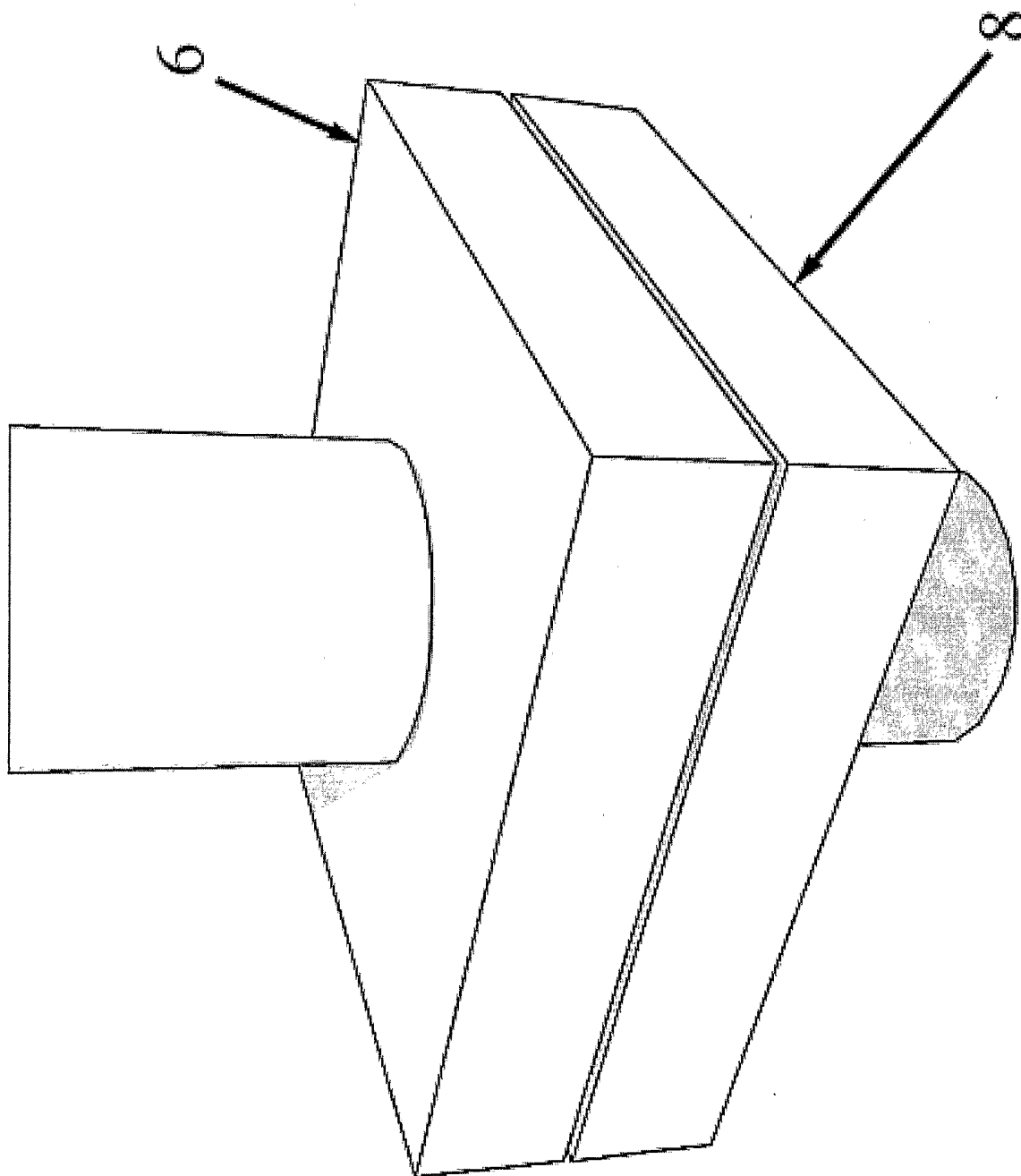


FIG. 3

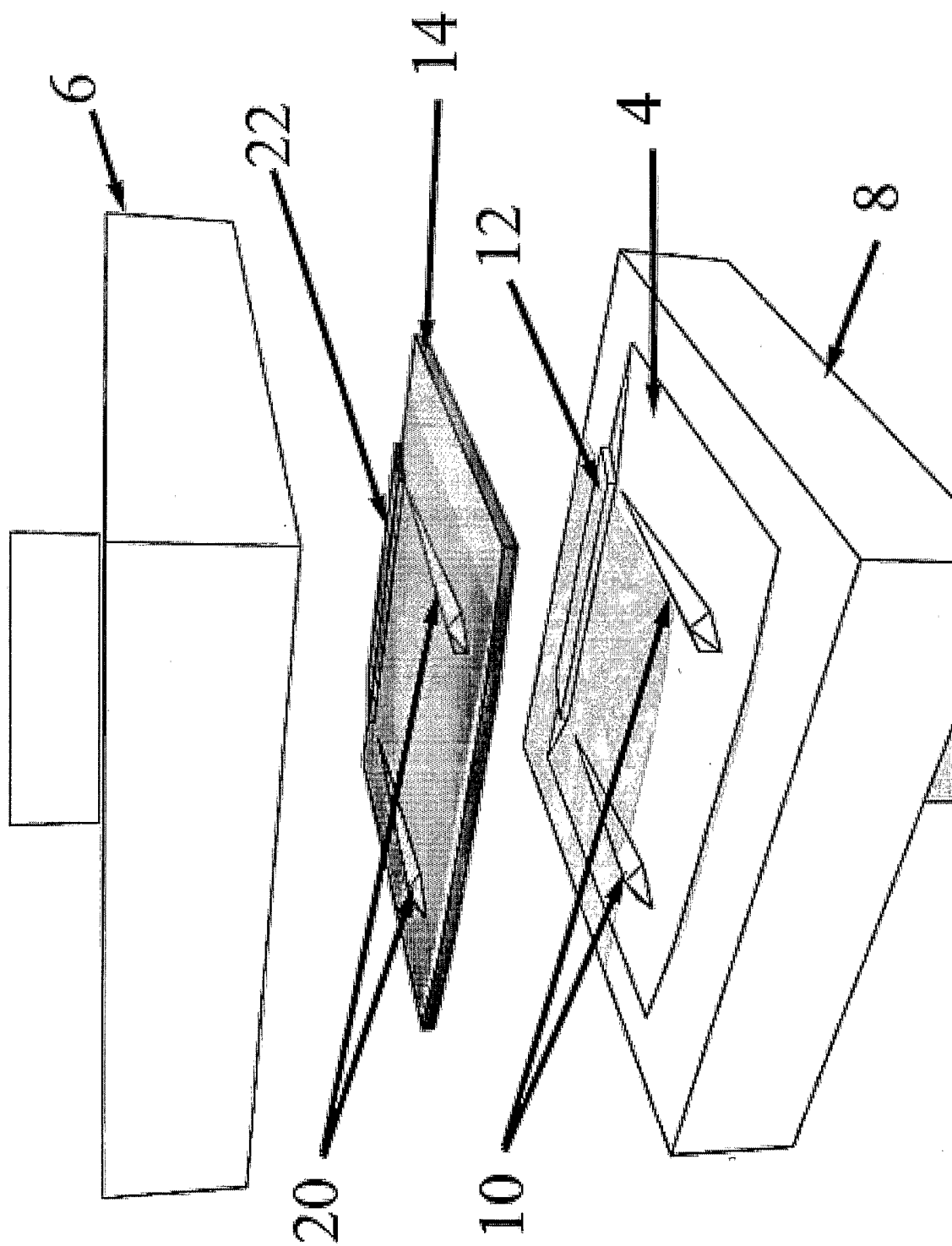


FIG. 4



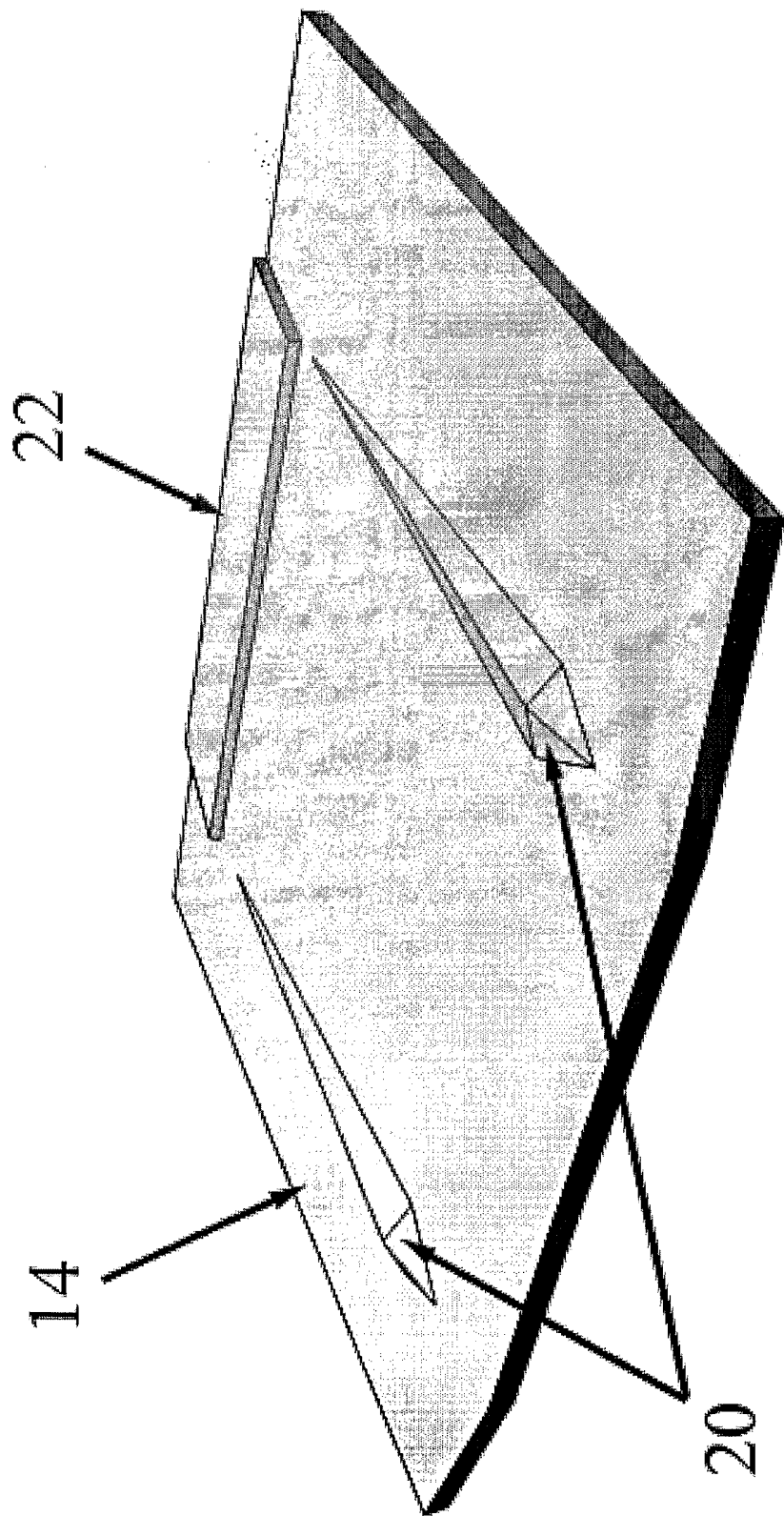


FIG. 5