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(54) Title: A METHOD OF ADHERING MATERIALS

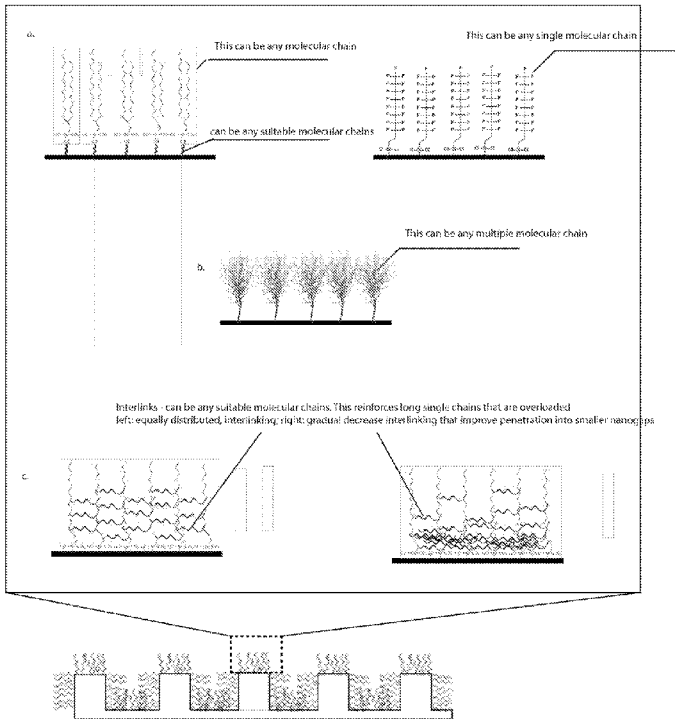

FIG. 2

(57) Abstract: A method of improving adhesion of an adhesive is detailed in the present application. The method includes coupling a layer comprising molecular chains, for example by grafting polymer brushes, to a surface of an adhesive material to form an adhesion promoting layer thereon, wherein the adhesive material with the adhesion promoting layer forms an adhesive product. The method further includes contacting the adhesive product with a surface of a base material, wherein a portion of the molecular chains at distal end penetrates into the surface of the base material, thereby adhering the adhesive material to the base material. The interaction between the molecular chains and the surface of the base material may be selected from the group consisting of physical interlocking, van der Waals force, electrostatic interactions and friction.

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A METHOD OF ADHERING MATERIALS

CROSS-REFERENCE TO RELATED APPLICATION

[001] This application claims the benefit of priority of Singapore Patent Application No. 10201509092U filed November 4, 2015, the contents of which being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[002] The invention relates generally to the field of adhesives, and in particular, to a method of adhering materials.

BACKGROUND

[003] An increasing number of adhesive products make use of van der Waals and affinity forces adhesion technologies. From ordinary duct tapes to microstructured gecko- and beetle-like adhesives, many products utilize this adhesion-inducing phenomenon. More interestingly, some have recognized that incorporation of high stiffness fibers into the adhesive structure provides stiff support which stabilizes the adhesion. The addition of stiffness supports such as nylon fibers, Kevlar fibers, carbon fibers into the adhesive structure means that when shear force that is aimed against the adhesion is applied, the entire structure will need to fail simultaneously before full adhesion failure occurs. This is in contrast to ordinary adhesive tapes that are based on compliant materials. The failure here occurs gradually as the tape gives way at the point of maximum shear and this failure propagates throughout the entire structure assisted by the elasticity of the material.

[004] In applications like pressure sensitive adhesive materials, researchers have started to recognize that micro-structuring or addition of gooey materials to the adhesive interface are not even required. Just by incorporating polydimethylsiloxane (PDMS) with carbon fibers a very powerful adhesive can be formed, as traditional pressure sensitive

materials are using soft or viscoelastic polymers, or any coatings, which depend on the backing materials. Moreover, most sticky polymers are typically not conducive to multiple loading applications due to the irreversible materials processes that are used to produce high levels of tack. Thus, development of structure-based adhesives to overcome this disadvantage has become very important.

SUMMARY

[005] According to one aspect of the invention, there is provided a method of adhering materials. The method includes coupling a layer comprising molecular chains to a surface of an adhesive material to form an adhesion promoting layer thereon, wherein the adhesive material with the adhesion promoting layer forms an adhesive product. The method further includes contacting the adhesive product with a surface of a base material, wherein a portion of the molecular chains at distal end penetrates into the surface of the base material, thereby adhering the adhesion product to the base material.

[006] Advantageously, the present method enables a minimum of 10-fold increase in adhesion strength on a variety of surfaces to be achieved.

BRIEF DESCRIPTION OF THE DRAWINGS

[007] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[008] **FIG. 1** illustrates the mechanism for adhering two materials via molecular chains or a forested layer.

[009] **FIG. 2A-2C** illustrate various embodiments of how an adhesive material may be coupled to the molecular chains.

[0010] FIG. 3 shows an affinity fluid used to further bind the molecular chains to the adhesive material.

[0011] FIG. 4 shows a metallic layer used to bind to the adhesive material.

[0012] FIG. 5 shows air or fluid trapped within the adhesive material.

[0013] FIG. 6 shows SEM images (Left) of ODTS multilayer forest (oxygen plasma linking) and (Right) silk forest (UV linking) when grafted onto polyvinylsiloxane substrates.

[0014] FIG. 7 shows the characterization data of the modified elastomer/s. EDX (Energy-dispersive X-ray spectroscopy) confirms the installation of fluorine atoms onto the elastomeric surface.

[0015] FIG. 8 shows a setup of the adhesion pull-off test.

[0016] FIG. 9 shows Instron results of balloon pull test from submerged artery. Plain surface balloon (upper) and modified balloon (lower).

DESCRIPTION

[0017] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0018] In one aspect of the present invention, a method of adhering materials is disclosed. By "adhering", "adhere", or other like term, is meant generally to bond, attach, stick, cling, hold, cohere, be stuck, be fixed, be pasted, or be glued. In other words, the present method enables two or more materials to be attached to one another.

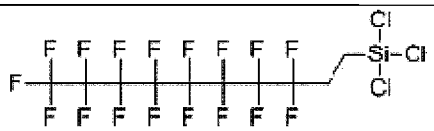
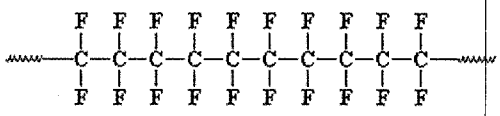
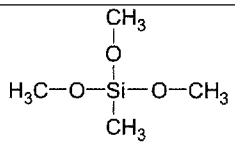
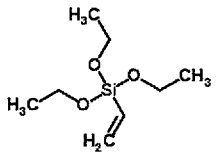
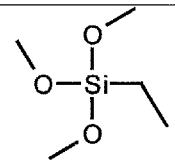
[0019] The method includes coupling a layer comprising molecular chains to a surface of an adhesive material to form an adhesion promoting layer thereon. The adhesive material with the adhesion promoting layer forms an adhesive product, or simply called an adhesive in present context.

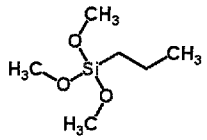
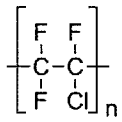
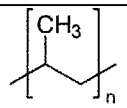
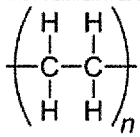
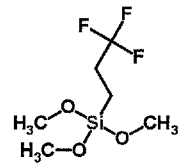
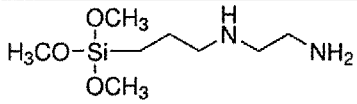
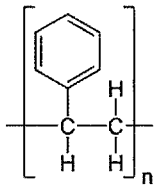
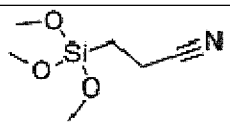
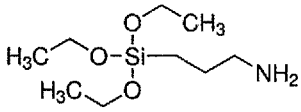
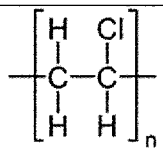
[0020] In various embodiments, coupling the layer comprising molecular chains may include forming an interaction between the molecular chains and the surface of the adhesive material. It is to be appreciated that any form of interaction between the molecular chains and the surface of the adhesive material may exist, so long as the layer and the surface are made to contact (whether spontaneously or not) and remain in contact with each other. In preferred embodiments, the interaction may be covalent bonding, ionic bonding, hydrogen bonding, van der Waals force, physical interlocking, friction, etc. For example, the layer comprising the molecular chains may be covalently bonded (or grafted onto) to the surface of the adhesive material. In another example, the layer comprising the molecular chains may interact with and bind to the surface of the adhesive material via van der Waals force.

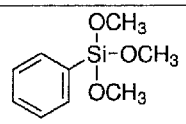
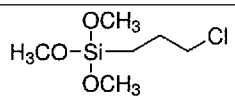
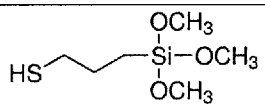
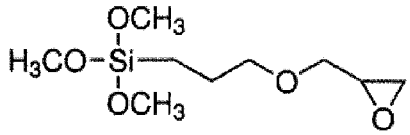
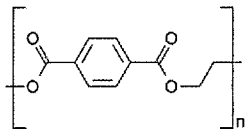
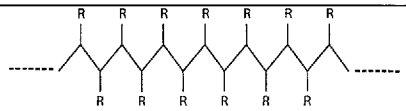
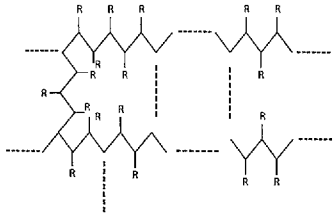
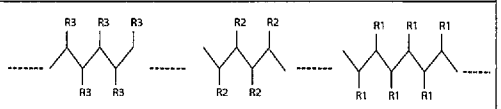
[0021] Molecular chains refer to chains of an organic molecule. In particular, for macromolecules, i.e. polymers, molecular chains conveniently refer to the backbone chains although not necessarily always so. In the present context, preferred molecular chains of the adhesion promoting layer refer to molecular chains of polymers. In more preferred embodiments, the molecular chains of the polymers comprised in the adhesion promoting layer form a dense network of intertwined, interlinked, or otherwise crosslinked chains. In other words, the density of the molecular chains is so high (closely packed, closely intertwined, interlinked, or crosslinked) that a molecular forest may be simply referred to herein.

[0022] In certain embodiments, the adhesion promoting layer may be comprised of polymer brushes. A polymer brush is a brush-like, thin layer of polymer chains with one end (proximal) attached to the surface of the adhesive material and the other end (distal) extended away from the surface of the adhesive material. The densely-packed, surface-tethered polymer chains in close proximity to each other results in a stretched, brush-like configuration.

[0023] Table 1 shows a list of possible molecular chains suitable for use in the present method, such as but not limited to, perfluorocarbons, silanes, polyalkenes, and DNA/RNA single/double strands.

Chemical name	Molecular Formula	Chemical structure
Heptadecafluorodecyl-trichlorosilane	$C_{10}H_4Cl_3F_{17}Si$	
Polytetrafluoroethylene	$(C_2F_4)_n$	
Methyltrimethoxysilane	$C_4H_{12}O_3Si$	
Vinyltriethoxysilane	$C_8H_{18}O_3Si$	
Ethyltrimethoxysilane	$C_5H_{14}O_3Si$	

Propyltrimethoxysilane	$C_6H_{16}O_3Si$	
Polychlorotrifluoroethylene	$(CF_2CClF)_n$	
Polypropylene	$(C_3H_6)_n$	
Polyethylene	$(C_2H_4)_n$	
Trifluoropropyl-trimethoxysilane	$C_6H_{13}F_3O_3Si$	
3-(2-aminoethyl)-aminopropyl-trimethoxysilane	$(CH_3O)_3Si(CH_2)_3NHCH_2CH_2NH_2$	
Polystyrene	$(C_8H_8)_n$	
Cyanoethyl-trimethoxysilane	$C_6H_{13}NO_3Si$	
Aminopropyl-triethoxysilane	$H_2N(CH_2)_3Si(OC_2H_5)_3$	
Polyvinylchloride	$(C_2H_3Cl)_n$	

Phenyltrimethoxysilane	$C_6H_5Si(OCH_3)_3$	
Chloropropyl-trimethoxysilane	$Cl(CH_2)_3Si(OCH_3)_3$	
Mercaptopropyl-trimethoxysilane	$HS(CH_2)_3Si(OCH_3)_3$	
Glycidoxypropyl-trimethoxysilane	$C_9H_{20}O_5Si$	
Polyethyleneterephthalate	$(C_{10}H_8O_4)_n$	
Single chain molecule	-	 (R can mean either the same or different residuals) "----" represents that the motif structure continues as shown (repeats itself to an undetermined extent)
Multiple chain molecule	-	 (R can mean either the same or different residuals) "----" represents that the motif structure continues as shown (repeats itself to an undetermined extent)
		 (R1, R2, R3 can mean either the same or different residuals) "----" represents that the motif structure continues as shown (repeats itself to an undetermined extent)

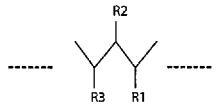
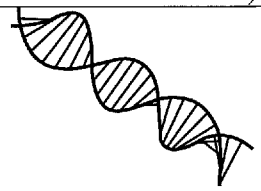
		 (R1, R2, R3 can mean either the same or different residuals) "----" represents that the motif structure continues as shown (repeats itself to an undetermined extent)
DNA / RNA, single or double strands, or branched. This can be used to form "adhesive sensors" that bond differently after exposure to complementary strands. This can be done with other pairs such as antibody-antigen pairs and can provide quantitative data for analyte concentration based on adhesion strength.	-	

TABLE 1

[0024] The adhesive material may comprise of any material suitable for coupling to the layer comprising the molecular chains, thereby acting as a structural support for the adhesion promoting layer. For example, the adhesive material can be an elastomer or gooey material. The adhesive material may be any common adhesive material such as polydimethylsiloxane (PDMS), various silicone, polyvinylsiloxane, VHB (3M's Very High Bond adhesive series), hook-and-loop, mushrooms, and other adhesives and duct tape materials.

[0025] The method further includes contacting the adhesive product with a surface of a base material, wherein a portion of the molecular chains at distal end penetrates into the surface of the base material, thereby adhering the adhesive product to the base material.

[0026] The advantage of forming a layer of molecular chains on an adhesive material and allowing the distal end of the molecular chains to penetrate (or seep) into the surface of a base material can be readily appreciated as follows.

[0027] A molecular forest layer is deliberately coupled to the adhesive material to further increase the bonding interface strength between the surface of the adhesive product and the surface of the base material. This molecular forest is bonded to the interface and is able to penetrate deep into the nanostructure of the base material, dramatically increasing the molecular interactions that generate the adhesiveness. Using this technique, a minimum of 10-fold increase in adhesion strength on a variety of surfaces has been obtained.

[0028] The basic mechanism is illustrated in **FIG. 1**. As can be seen from the figure, distal ends of the molecular chains penetrate into the uneven surface of the base material, thereby increasing contact area with the surface of the base material. By virtue of the increase in the contact area, i.e. increased interaction between the two surfaces, an enhanced adhesion strength can be obtained. The layer comprising the molecular chains or forest therefore acts as an adhesion promoting layer in this context.

[0029] Accordingly, in various embodiments, a portion of the molecular chains penetrates into and further interacts with the surface of the base material. The interaction between the molecular chains and the surface of the base material may be selected from the group consisting of physical interlocking, van der Waals force, electrostatic interactions and friction. Preferably, the molecular chains physically interlock with the surface of the base material. When lateral forces are applied, this is translated to increased friction. van der Waals forces also play a role. The increased contact area allows for more of these momentary forces to develop. The physical interlocking of the molecular chains layer with the base material is very similar to the adhesion technique or fastener

commonly known as Velcro. However, because this invention is at the molecular level, there are also van der Waals and other electrostatic interactions like hydrogen bonds, etc. between the interlocking molecular chains layer and the base material.

[0030] In various embodiments, the surface of the adhesive material includes crevices for the penetration. The crevices may be of nano-size or otherwise. For example, the adhesive material may include a structure selected from the group consisting of a fiber array, pillar array, mushroom-like array, sponge-like array, polygonal epithelial structure, treefrog palm, and a smooth surface.

[0031] In one disclosed embodiment, molecular chains of perfluorocarbons attached to the surfaces of smooth and gecko-like polyvinylsiloxane increased the adhesion by a factor of 14 approximately. Moreover, a molecular forest that utilizes longer molecular chains which contain a mixture of molecules that exhibit higher surface affinity can result in an adhesive that is so strong that the bonding strength would be comparable to the strength of the bulk base material. Yet at the same time, the adhesive can be removed, washed and be reused for multiple times. Furthermore, unlike the conventional non-forested adhesive, present adhesive, if being damaged, can be rejuvenated by simply applying a new forest layer. The same adhesive can be used to adhere to base materials of different surface natures by incorporation of different types of forest layers that exhibit higher affinity to the specific surface. This can be done very quickly and without damage.

[0032] **FIG. 2A-2C** illustrate various embodiments of how an adhesive material may be coupled to the molecular chains.

[0033] **FIG. 2A** shows a surface of an adhesive material coupled to a layer of long molecular chains.

[0034] **FIG. 2B** shows a surface of an adhesive material coupled to a layer of long multiply branched molecular chains.

[0035] **FIG. 2C** shows a surface of an adhesive material coupled to molecular chains which are more intertwined, interlinked, or crosslinked with one another nearer to the proximal end. This arrangement allows very long molecular chains as the interconnection allows for higher survivability of the structure to breakdown and wear. If self-repairing chains are used, the resultant adhesive material would exhibit remarkable survivability.

[0036] In certain embodiments, it may be advantageous to further include adding an affinity fluid to the layer comprising molecular chains, wherein a portion of the affinity fluid adheres to the surface of the adhesive material and another portion of the affinity fluid binds the molecular chains. This embodiment is illustrated in **FIG. 3**. When a high affinity fluid is infused in the surface, the fluid may exhibit in part strong affinity to the molecular forest and in the other part strong affinity to the adhesive material, thus it acts like a glue to stick the molecular forest even more tightly to the adhesive material.

[0037] To further improve the adhesive properties, reinforced fibers can be incorporated to the adhesive material. However, rather than using fibers that are stiff but expensive, it is herein proposed the use of thin metal sheets which are shown to have similar but better adhesive effects. As illustrated in **FIG. 4**, a metallic layer is bound to a second surface of the adhesive material, wherein the second surface is not coupled to the layer comprising molecular chains. The metal is primed to the polymer by using an acid surface treatment followed by silica bonding, for example. Other coupling techniques are also suitable. Besides higher strength and lower costs, the usage of metal reinforcement opens up new applications. If the metal used in the metallic layer is a bimetal, bimorph, or shape memory alloy, applications that exhibit tunable adhesion can be created. The activation of the metal will result in gradual shape change that can either result in the automatic attachment or detachment of the adhesives. If implemented at the micro level, this can be

translated into a "smooth" surface that can attach and detach from a target material with tremendous force.

[0038] Furthermore, smart materials instead of traditional fibers may be used, of which the advantages lie in the activation stimuli that trigger the smart material's shape change which can also turn the adhesives on or off. In one embodiment, nickel titanium shape memory alloys or another type of shape memory, bimorph, or bendable material or actuator as the reinforcement material may be used as the metallic layer. When the shape memory alloy is activated, the whole adhesive structure can be "peeled off" automatically, thus turning off the adhesive. This can make for an autonomous, or robotic actuator that can be used in applications such as robotics, hooks and hangers and even a temperature-sensitive valve or actuator that opens up a lid when a temperature or pressure reaches a certain set-point.

[0039] In a preferred embodiment, it may be advantageous to form funnelling holes in the adhesive material for trapped air or fluid to escape therefrom. This embodiment is shown in **FIG. 5**. A piece of silicone is adhered onto a black base material. The lighter regions represent regions that did not adhere to the base material due to air trapped between the base material and the silicone layer. By forming miniature funneling channels and distributing the channels within the adhesive surface, air, gas or liquid would no longer be trapped but can escape, allowing for a larger surface of the adhesive to come into contact with the base material. In one practical application, this can allow sweat to escape, thus enabling better skin adhesion. The diameter of the pores can range anywhere from picometers to centimeters and various shapes of pores can be used. This can be further developed by using selective pores that allow or induce penetration of some substances but block other substances from passing. These have potential in smart windows, 3D printing, valves, actuators and many other applications.

[0040] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

EXAMPLES

[0041] Example 1

[0042] Polyvinylsiloxane was used as an adhesive material. Several alternative controls were used as follows: bare polyvinylsiloxane, micropillar patterned polyvinylsiloxane, in addition to the two primed onto a steel plate to make four negative controls. These four negative controls were also functionalized by means of oxygen plasma with heptadecafluorodecyltrichlorosilane to form a forest layer. This resulted in significant adhesion increase in both liquid and dry environments of all the forested layers that correlates to an approximate 10-fold increase. The surfaces were tested on target materials such as human skin with and without hair, painted wall, metals, glasses, plastics and wood surfaces and adhesion remained strong even after repeated use. The functionalized polyvinylsiloxane did not lose its adhesion strength when washed with water and detergent. The adhesion increase is attributed to increased surface contact due to the better surface reach of the forested layer which is able to engulf the nano-features of a surface, thus inducing additional physical interaction by which the forest actively is inserted and must be pulled out of a gap to release the surface. Additionally, the forest generates additional van der Waals, chemical affinity bonds, steric bonds, and other chemical and physical bonds with the surface.

[0043] Experimental Procedure

[0044] Firstly, samples were briefly exposed (40s, 60s or 100s) to low pressure (150 to 250 mTorr) radio-frequency (13.56 MHz) oxygen plasma at 100 Watts in order to gently activate the surface to enable reaction with silane. Immediately following plasma

activation, samples were immersed in a liquid heptadecafluorodecyltrichlorosilane solution with different concentrations, 5% v/v, 10% v/v and 15% v/v solutions in anhydrous ethanol were used. The immersion time varies from 15 mins to 2 hours.

[0045] Treated samples were then rinsed with anhydrous ethanol, distilled-deionized water and three times with pure ethanol, then gently blown dry with compressed nitrogen and heated in an oven with desiccant at 60 °C at atmospheric pressure for various time duration (3 hours to 12 hours).

[0046] Example 2

[0047] Succinimidyl-diazirine SDA (NHS-Diazirine) was used to impart NHS functional groups onto the surface of an elastomer. This process is much faster than the silane-induced self-assembled monolayer used previously and it does not require any surface pre-treatment, and is thus more applicable and reliable.

[0048] The NHS is then reacted with the NH_2 group in viscid silks proteins made by orb weaving spiders. Mucilage polymers (polysaccharide + glycoprotein) and Library paste (starch) also works very well.

[0049] Experimental Procedure

[0050] In the first step, 30 µl 1mg/ml fresh prepared NHS-diazirine solution (in DI water) is dropped onto the surface of the elastomer, the sample is exposed to UV light (365 nm) for 5 mins. Afterward, it is washed thoroughly with DI water for 3 times.

[0051] In the second step, 50 µl 5mg/ml solution (containing the molecular chains; in PBS buffer solution, 10 mM, pH 7.4) is dropped on the sample, then kept in a humidity chamber for 1 h at room temperature. After reaction, the sample is washed thoroughly with PBS (10 mM, pH 7.4) for 3 times and DI water for 3 times.

[0052] Alternatively, in the first step, 1.5 µl fresh prepared NHS-diazirine solution (5 mg/ml in DI water) is mixed with 50 µl solution (containing the molecular chains; 5

mg/ml in PBS buffer, pH 7.4). The mixture is kept in dark condition for 1 hour to allow complete reaction.

[0053] In the second step, 30 µl mixed solution is dropped onto the elastomer, the sample is then exposed to UV light (365 nm) for 15 mins. After UV exposure, the sample is washed thoroughly with PBS buffer (10 mM, pH 7.4) for 3 times and DI water for 3 times then dried thoroughly with nitrogen gas.

[0054] Example 3

[0055] Installation of both octadecyltrichlorosilane (ODTS) (or perfluorodecyltrichlorosilane (FDTS)) using oxygen plasma activation and other polymeric substances using carbine precursor photoactive crosslinking onto polyvinylsiloxane resulted in the formation of elastomers that have improved adhesion properties.

[0056] Experimental procedure

[0057] In the first step, treat the elastomer with oxygen plasma for 15 minutes.

[0058] In the second step, immediately after plasma treatment immerse the plasma-treated elastomer in 15% octadecyltrichlorosilane solution in anhydrous ethanol for 60 minutes then wash with anhydrous ethanol and DI water for 3 times each and dry with nitrogen gas.

[0059] In the third step, prepare a mixture solution of carbine photoactive linker with any polymeric substance such as silk polymer chains (molar ratio 10:1). The photoactive linker should have an NHS or another reactive group to react with the polymer first. Immerse the silane-functionalized elastomer topside up a fraction of a millimeter below the solution.

[0060] In the fourth step, shine high power UV light (>200 W) for 1-3 minutes. Then wash the sample with abundant DI water and dry with nitrogen gas.

[0061] Alternative route of the aforementioned third and fourth step: the silane-functionalized elastomer is firstly treated with carbine photoactive linker under UV light (>200 W) for 1-3 minutes to induce a NHS reactive group. Then immerse the treated silane-functionalized elastomer into a polymer solution for 1 hour, followed by washing with DI water and drying with nitrogen gas. The polymer solution may comprise silk polymer chains, for example.

[0062] FIG. 6 shows SEM images (Left) of ODTS multilayer forest (oxygen plasma linking) and (Right) silk forest (UV linking) when grafted onto polyvinylsiloxane substrates.

[0063] FIG. 7 shows the characterization data of the modified elastomer/s. EDX (Energy-dispersive X-ray spectroscopy) confirms the installation of fluorine atoms onto the elastomeric surface. The original polyvinylsiloxane does not have fluorine atoms while FDTS does.

[0064] For the adhesion test, pull-off tests were tested using an Instron machine (Mech Tester Instron 5567) with 10 N head. The sample was held with a custom made holder connected with the upper gripper of the Instron machine. The lower gripper was connected with a tested surface. The adhesion was tested against pig artery under whole human blood.

[0065] FIG. 8 shows a setup of the adhesion pull-off test.

[0066] FIG. 9 shows Instron results of balloon pull test from submerged artery: Plain surface balloon (upper) and modified balloon (lower) whereby the balloon was modified with a FDTS layer.

[0067] In prior experiments, adhesion testing was carried out with Instron force testing machine on several pieces of elastomer. The pieces were pulled at a 45-degree angle from a polystyrene surface. The tests were conducted before and then again after the treatment.

A 1.4 to 11-fold increase in adhesive force was observed when compared to the original adhesive used.

[0068] The prior experiments were initially done in order to reduce adhesion. Surprisingly however, the samples were very difficult to remove from the Petri dishes inside which the reaction took place and this can only be explained by structural changes to the silicone adhesive material. After the reaction, the polyvinylsiloxane was very strongly bonded to the Petri dishes. The silicone adhesive material is an adhesive elastomer as it conforms to the base material it touches, resulting in interlocking and momentary electrostatic interactions. The addition of a monolayer of perfluorodecyltrichlorosilane is supposed to lower the coefficient of friction as the perfluorocarbon chains should be less prone to electrostatic polarization and the closely packed chains should refuse rotation due to the electronegative repulsion between fluorine atoms from adjacent chains. However, due to the nature of tripedal silanes, an amorphous forest, rather than a thin single monolayer was formed. This forest increased the base material penetration of the silicone adhesive material, thus improving adhesion.

[0069] When comparing the adhesion of polyvinylsiloxane elastomer to polyvinylsiloxane modified with a molecular forest layer, a 12-fold increase in adhesive force operated in a wet environment (submerged in human whole blood) was measured.

[0070] In one robotic catheter application, an adhesive made according to present method is applied onto the external sheet surrounding inchworm clampers to improve the adhesion contact between the clamper and the artery, thus allowing application of less pressure on the sensitive endothelium.

[0071] The silk polymer is immunogenic and cannot be used as leech may induce complications to patients. However, non-immunogenic biocompatible glycoproteins and

polysaccharides as well as other polymers can be used as possible molecular forest layers without fear of leech, and are thus hemocompatible.

[0072] Additional applications include, but not limited to, tapes that replace sutures to close a wound; water resistant adhesive for bandages; drug-delivery patches; robots that can climb vertical and chaotic surfaces (military, search and rescue, hobby); the adhesive is self-cleaning; climbing smooth surfaces such as glass; examine the surfaces of aircrafts to replace manual inspection; a tool for manipulating delicate parts such as ultra-miniature circuits, nano-fibres and nanoparticles, microsensors and micro-motors; adhesive in vacuum environment such as space as liquid adhesives will quickly evaporate; increased maneuverability for humans and robots in construction, inspection, and other situations; clean, quick and easy adhesive for household appliances such as pictures, TV for hanging, lights as well as heavy loads; applications in apparels (goalkeeper gloves) and retainers (phone, tablet car holder); fasteners in cleanrooms to replace hook and loop which degrade and contaminate the cleanroom; masking of components and surfaces without contamination (manufacturing); replacement for twisters with zero applied force on the element gripped; CMP polishing and surface finishing pads that can be quickly replaced without need to clean residues; non-slip, improved grip for orthotics, braces, prosthetics, face masks and other medical equipment that come in contact with skin; improved skin contact for leg weights (they tend to slip down which is uncomfortable); replacement for suction board (which are used to hold components, on an electronics printer for example); good for concave surfaces or in situations that need low profile, non-tacky gripping; good for skin adhesion where alternative adhesives become smelly overtime; improve grip on surgical tools without contamination risk; means to grip entertainment, safety and defense masks tightly and securely to the face; firearm grip; hermetic and silent fasteners (for defense vests); protective helmets; apparel friction pads (horse riding, bobsledding,

biking; pants for long boat riding and situation when prolonged rubbing of the apparel to the skin causes irritation; high grip gloves; baby gear (non slip tray to prevent slipping of silverware); fasteners for seat covers; anti slip pads and tapes; art display and transport; packages that can open and close repeatedly without adhesives or cardboard flaps that can rip and break, and many others.

[0073] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0074] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0075] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0076] By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

[0077] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0078] Other embodiments are within the following claims and non- limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

CLAIMS

1. A method of adhering materials, comprising:

coupling a layer comprising molecular chains to a surface of an adhesive material to form an adhesion promoting layer thereon, wherein the adhesive material with the adhesion promoting layer forms an adhesive product; and

contacting the adhesive product with a surface of a base material, wherein a portion of the molecular chains at distal end penetrates into the surface of the base material, thereby adhering the adhesive material to the base material.

2. The method of claim 1, wherein a portion of the molecular chains penetrates into and further interacts with the surface of the base material.

3. The method of claim 2, wherein the interaction between the molecular chains and the surface of the base material is selected from the group consisting of physical interlocking, van der Waals force, electrostatic interactions, and friction.

4. The method of any one of claims 1-3, wherein the surface of the adhesive material comprises crevices.

5. The method of any one of claims 1-4, wherein the coupling comprises grafting the layer of molecular chains to the surface of the adhesive material.

6. The method of any one of claims 1-5, wherein the molecular chains comprise perfluorocarbon ($(C_2F_4)_n$).

7. The method of any one of claims 1-6, wherein the molecular chains comprise a silane.

8. The method of claim 7, wherein the molecular chains comprise heptadecafluorodecyltrichlorosilane ($C_{10}H_4Cl_3F_{17}Si$), methyltrimethoxysilane ($C_4H_{12}O_3Si$), vinyltriethoxysilane ($C_8H_{18}O_3Si$), ethyltrimethoxysilane ($C_5H_{14}O_3Si$), propyltrimethoxysilane ($C_6H_{16}O_3Si$), trifluoropropyltrimethoxysilane ($C_6H_{13}F_3O_3Si$), 3-

(2-aminoethyl)-aminopropyltrimethoxysilane ($(CH_3O)_3Si(CH_2)_3NHCH_2CH_2NH_2$), cyanoethyltrimethoxysilane ($C_6H_{13}NO_3Si$), aminopropyltriethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$), phenyltrimethoxysilane ($C_6H_5Si(OCH_3)_3$), chloropropyltrimethoxysilane ($Cl(CH_2)_3Si(OCH_3)_3$), mercaptopropyltrimethoxysilane ($HS(CH_2)_3Si(OCH_3)_3$), or glycidoxypropyltrimethoxysilane ($C_9H_{20}O_5Si$).

9. The method of any one of claims 1-8, wherein the molecular chains comprise polyalkene.

10. The method of claim 9, wherein the molecular chains comprise polypropylene ($(C_3H_6)_n$), or polyethylene ($(C_2H_4)_n$).

11. The method of any one of claims 1-10, wherein the molecular chains comprise polychlorotrifluoroethylene, ($(CF_2CClF)_n$), polystyrene ($(C_8H_8)_n$), polyvinylchloride ($(C_2H_3Cl)_n$), or polyethyleneterephthalate ($(C_{10}H_8O_4)_n$).

12. The method of any one of claims 1-11, wherein the molecular chains comprise a single or double strand or branched DNA or RNA.

13. The method of any one of claims 1-12, wherein the adhesive material comprises a structure selected from the group consisting of a fiber array, pillar array, mushroom-like array, sponge-like array, polygonal epithelial structure, treefrog palm, and a smooth surface.

14. The method of any one of claims 1-13, further comprising adding an affinity fluid to the layer comprising molecular chains, wherein a portion of the affinity fluid adheres to the surface of the adhesive material and another portion of the affinity fluid binds the molecular chains.

15. The method of any one of claims 1-14, further comprising binding a metallic layer to a second surface of the adhesive material, wherein the second surface is not coupled to the layer comprising molecular chains.

16. The method of claim 15, wherein the metallic layer comprises a bimetal, bimorph or shape memory alloy.

17. The method of any one of claims 1-16, wherein the adhesive material comprises funnelling holes therein for trapped air or fluid to escape therefrom.

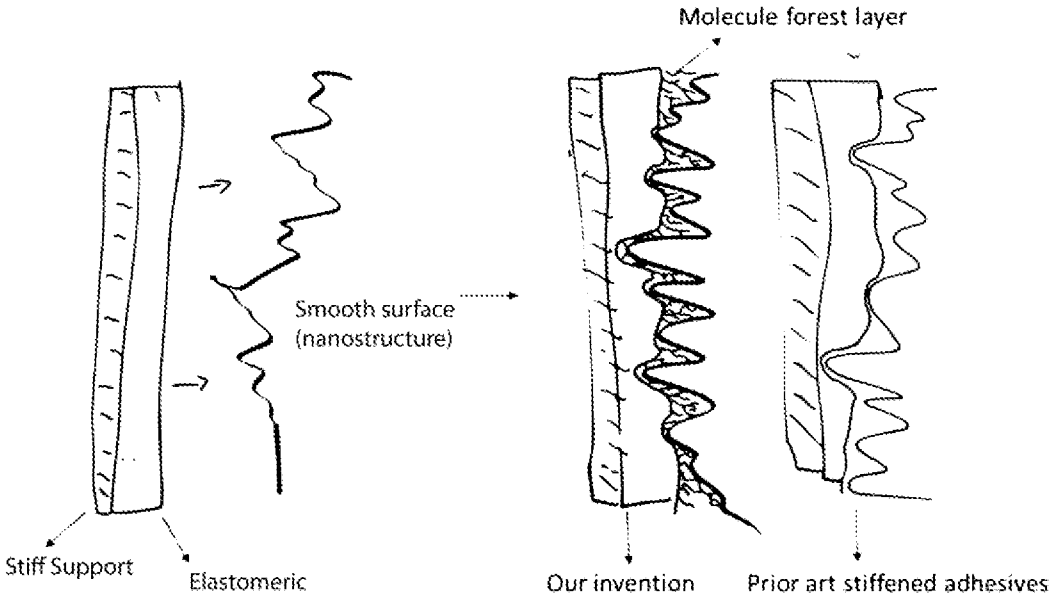

Molecule forest layer
Smooth surface
(nanostructure)
Stiff Support
Elastomeric
Our invention
Prior art stiffened adhesives

FIG. 1

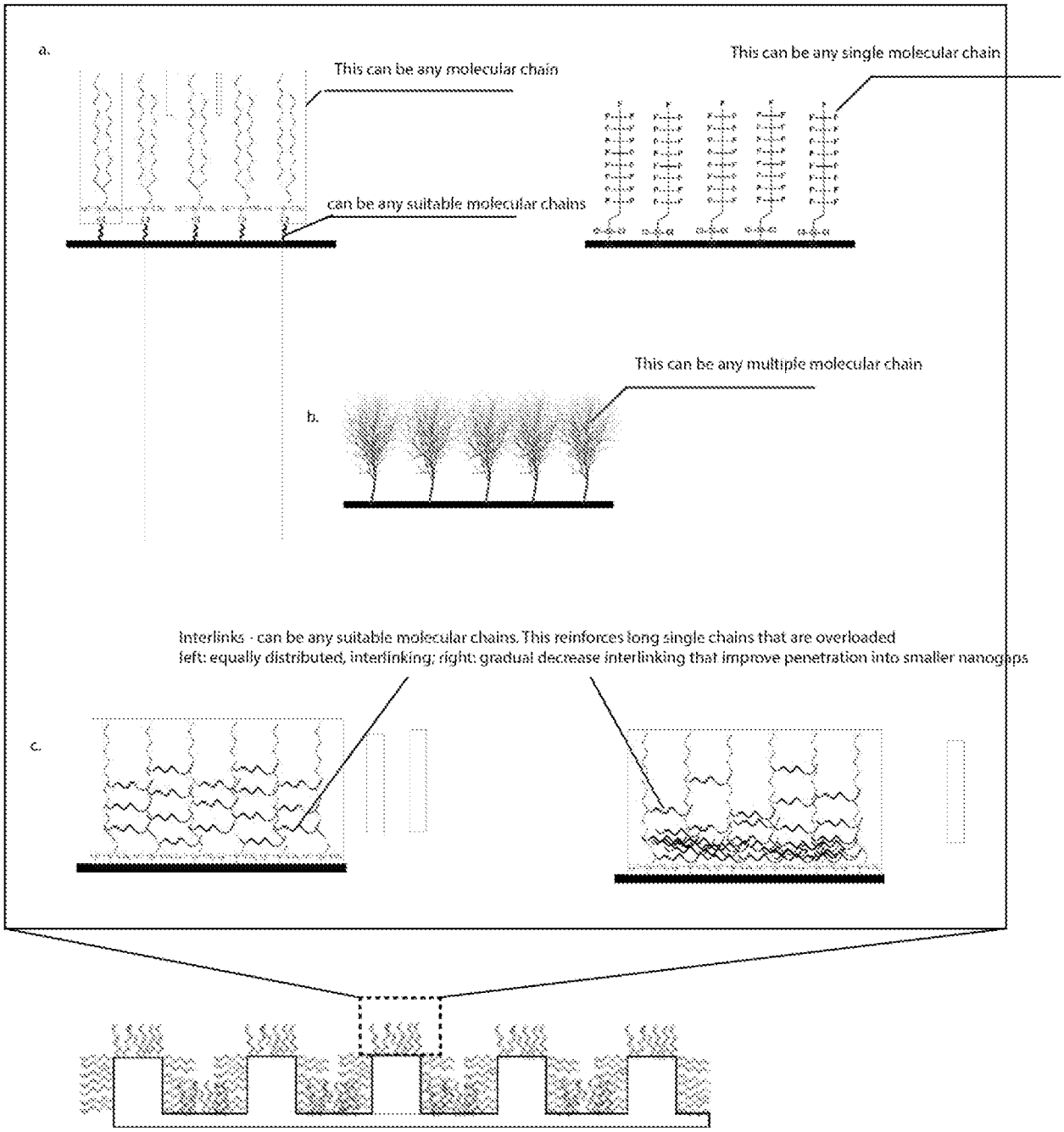

a.
This can be any molecular chain
can be any suitable molecular chains
This can be any single molecular chain
b.
This can be any multiple molecular chain
Interlinks - can be any suitable molecular chains. This reinforces long single chains that are overloaded
left: equally distributed, interlinking; right: gradual decrease interlinking that improve penetration into smaller nanogaps
c.

FIG. 2

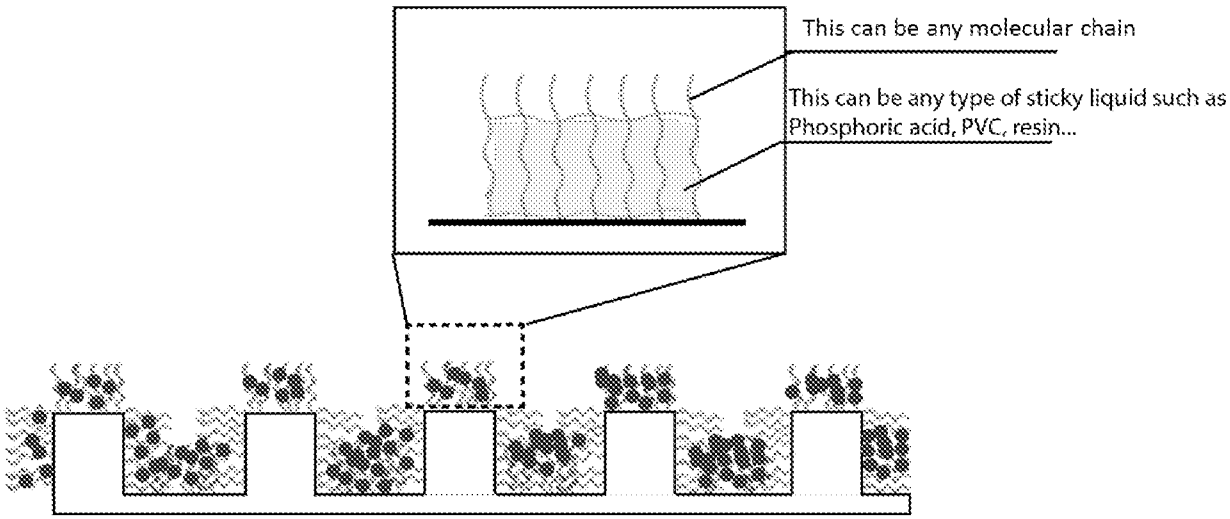

This can be any molecular chain
This can be any type of sticky liquid such as Phosphoric acid, PVC, resin...

FIG. 3

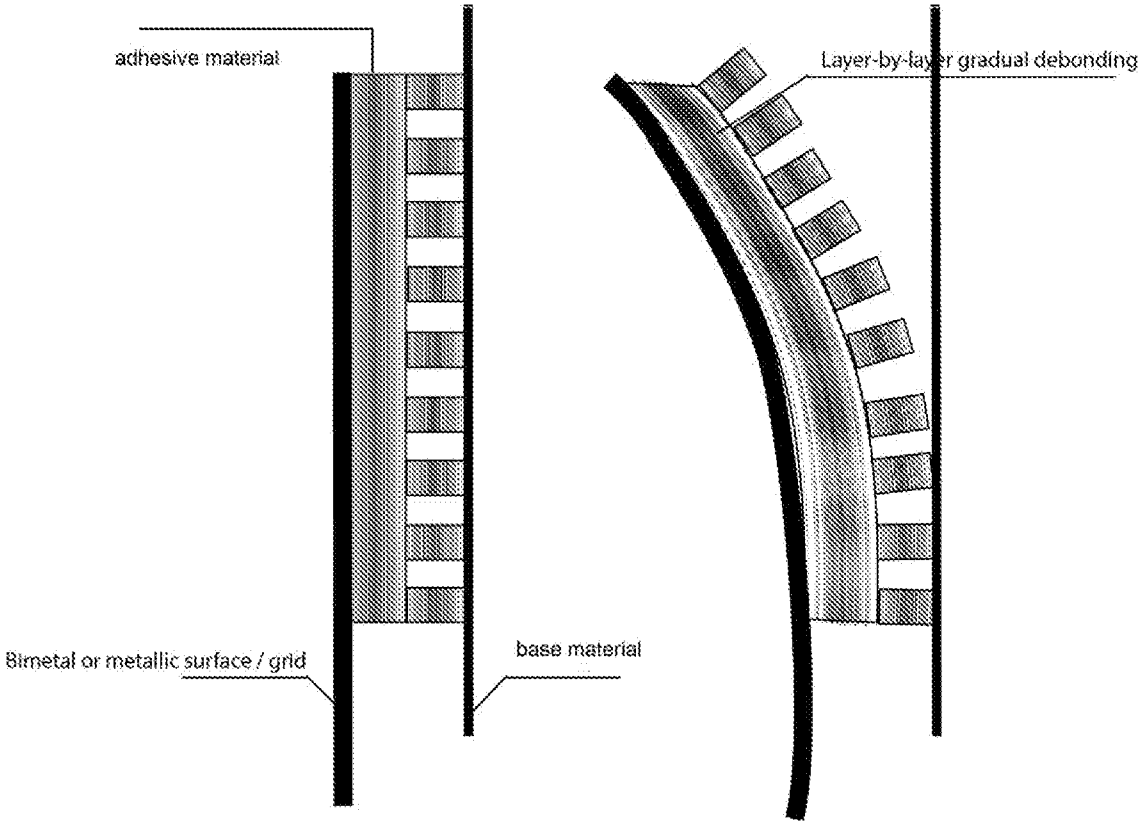

adhesive material
Layer-by-layer gradual debonding
Bimetal or metallic surface / grid
base material

FIG. 4

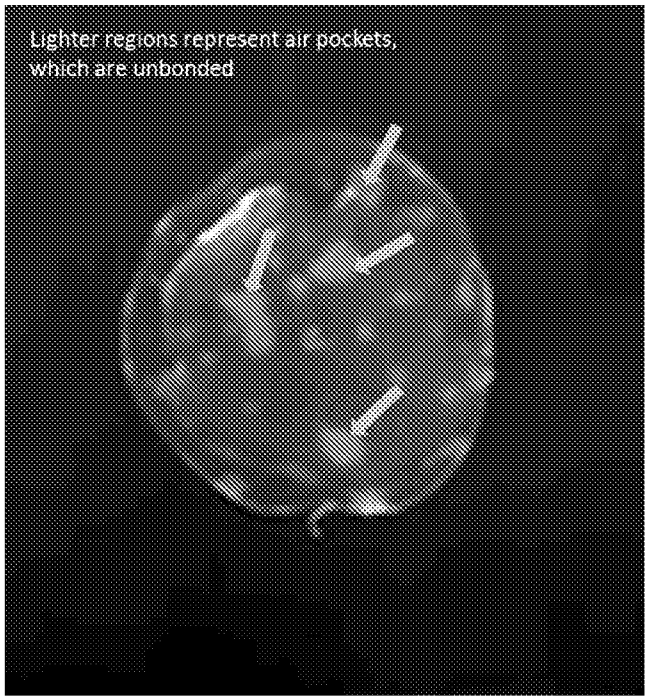


FIG. 5

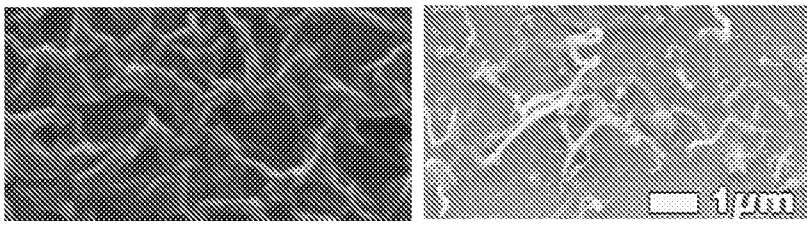


FIG. 6

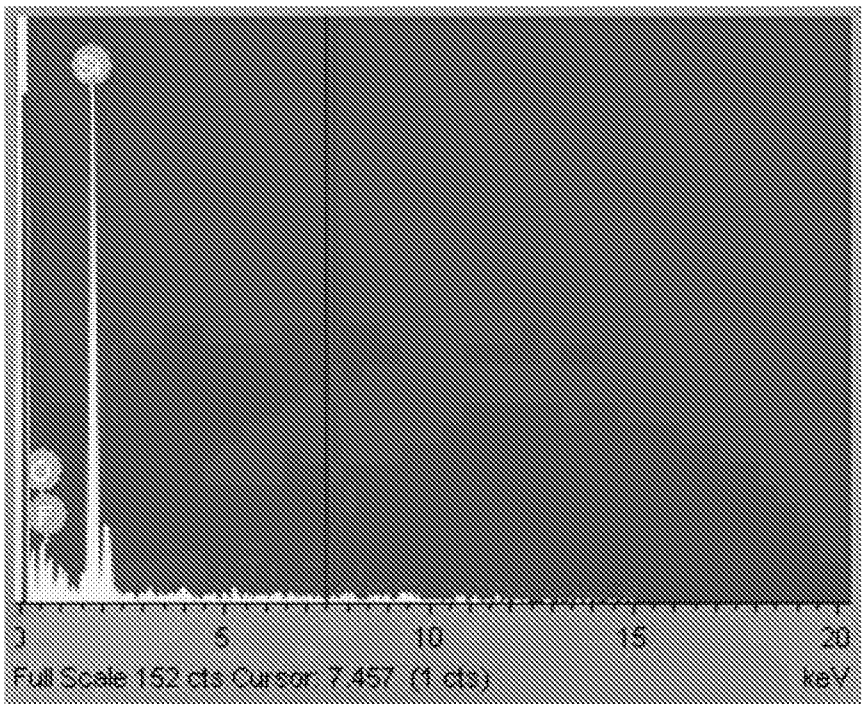


FIG. 7

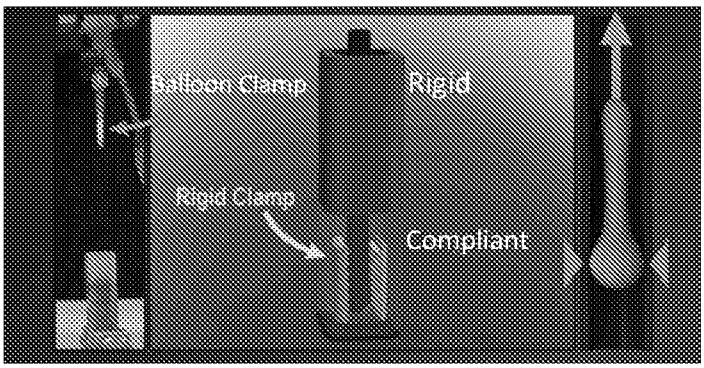


FIG. 8

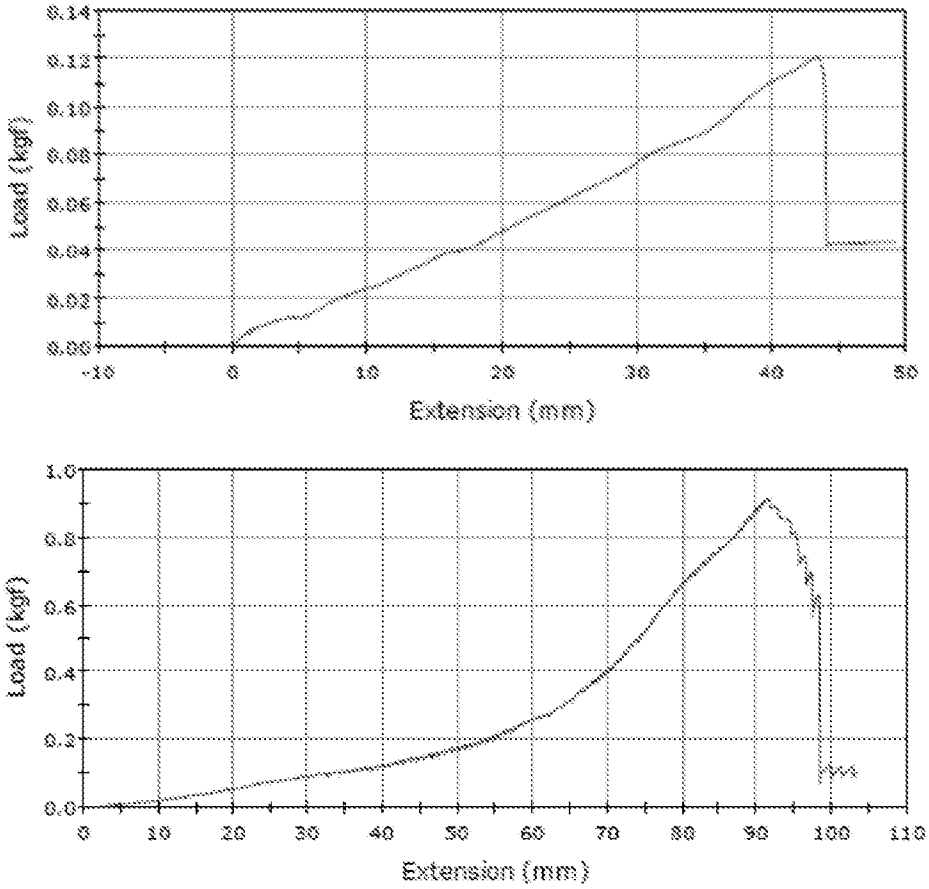

Load (kgf)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-10
0
10
20
30
40
50
Extension (mm)
Load (kgf)
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70
80
90
100
110
Extension (mm)

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050544

A. CLASSIFICATION OF SUBJECT MATTER

C09J 7/02 (2006.01) *C09J 9/00 (2006.01)*

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09J

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 practicable, search terms used)

Databases: REGISTRY, CAPLUS, EPODOC, WPI and SCOPUS

Keywords: adhesive, molecular chains, polymer brushes, adhere, bonding, van der Waals, physical interlocking, electrostatic, friction, silanes, PTFE, DNA, PET, polystyrene and similar terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHAUDHARY, O. J. ET AL., Bioinspired dry adhesive: Poly(dimethylsiloxane) grafted with poly(2-ethylhexyl acrylate) brushes. *European Polymer Journal*, 18 May 2015, Vol. 68, pages 432 – 440 [Retrieved on 2017-01-13] <DOI: 10.1016/J.EURPOLYMJ.2015.05.016> (see Abstract, Section 2.2, Section 2.3, Reaction Scheme A, Figures 1 – 4)	1 – 17
X	GUTOWSKI, W. S. ET AL., The mechanism of adhesion improvement of elastomeric silicone sealants to difficult-to-bond polymeric substrates through reactive or interpenetrating molecular brushes. *Journal of ASTM International*, 31 May 2012, Vol. 9, No. 5, pages JAI104275: 1 - 16 [Retrieved on 2017-01-13] <DOI: 10.1520/JAI104275> (see Introduction (page 1 – 2), Improved Adhesion of Elastomeric Silicone Adhesives through Surface-Grafted Connector Molecule (page 4 – 6), Improved Adhesion of Silicone Adhesives through Surface-Grafted Molecular Brushes (page 6 – 8), Experimental (9 – 11), Adhesion Improvement by Surface-Grafted Connector Molecules Interpenetrating into Silicone Adhesives (page 12 – 14))	1 – 17

☒ Further documents are listed in the continuation of Box C. ☒ 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 application or patent 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	Date of mailing of the international search report
13/01/2017 *(day/month/year)*	20/01/2017 *(day/month/year)*

Name and mailing address of the ISA/SG

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Happy Tan (Dr)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050544

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/0190983 A1 (CAICEDO-CARVAJAL, C. ET AL.) 9 July 2015 (see [0001], [0008] – [0014], [0022] – [0031] and Figures 1 – 2)	1 – 17
X	US 2015/0210896 A1 (RYAN, I. ET AL.) 30 July 2015 (see Abstract, [0004] – [0013], [0015] and [0033] – [0038])	1 – 4, 7 – 8, 13 and 17
X	CHRISSOPOULOU, K. ET AL., Role of molecular parameters on adhesion enhancement due to connecting chains at elastomer-solid interfaces. *Proceedings of the 26th Annual Meeting of the Adhesion Society*, 31 December 2003, pages 25 – 27 [Retrieved on 2017-01-13] <DOI: Not available> (see Abstract)	1 – 17
A	KIM, J. ET AL., Self-Assembly and Properties of Main-Chain Reversible Polymer Brushes. *Advanced Materials*, 19 May 2005, Vol. 17, No. 14, pages 1749 – 1753 [Retrieved on 2017-01-13] <DOI: 10.1002/ADMA.200401355> (see Abstract)	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/SG2016/050544

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015/0190983 A1	09/07/2015	WO 2015/105854 A1	16/07/2015
		EP 3092278 A1	16/11/2016
US 2015/0210896 A1	30/07/2015	NONE	