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(54) **Title**: SURFACE ADHESIVE FOR DEVICES

Figure 1

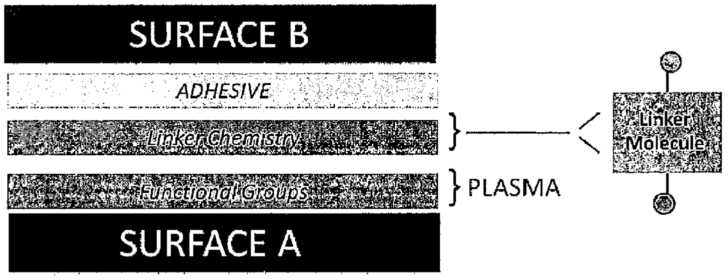

Figure 1. Combinatorial and dual linker molecule approach to increase interfacial adhesion.

(57) **Abstract**: Disclosed in certain embodiments is a composition comprising a first material; an adhesive material attached to the first material; a plurality of linker molecules bonded to the adhesive material; and a second material bonded to the linker molecules.

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SURFACE ADHESIVE FOR DEVICES

FIELD OF INVENTION

[0001] The present disclosure is directed to adhesives and linkers for the connection of two materials (e.g., polymers).

BACKGROUND

[0002] Material interfaces are ubiquitous features on many types of devices. As a result, constant use of different materials must be considered to achieve specific functions within in the device. In order for some of these devices to function, various materials must be attached to one another. One common way of attachment is to use an adhesive.

[0003] The selection of a proper adhesive is dependent on many different factors, including the materials being joined together, curing time, bonding strength, final use of the product, among others. Each of these factors can limit the applicability of adhesives, especially if the adhesive is needed for a specific material or for a sensitive use. Depending on the particular factors, an adhesive may be ideally suited for one situation and may not be functional in another.

[0004] An important consideration in the efficacy and duration of an adhesive bond is the surface of the materials to be used. In some instances, surface preparation allows the adhesive to form bonds with the actual surface of the material and not to other substances or debris located on the material. Often, bonding is dependent on intermolecular interactions between the surface of the material and the adhesive. Given that different materials will have varying characteristics, however, the quality of bonding between an adhesive and two dissimilar materials may be very different.

[0005] A current limitation with many adhesive systems is a lack of control over the reaction rate which can lead to adhesives setting too rapidly or too slowly for optimal performance. When considering bonding of an adhesive to a surface the reaction must proceed at a rate which allows integration of surface functionalities into the bulk reaction of the adhesive. However, if the reaction proceeds too slowly micromotion may interfere with good surface bonding and/or unacceptable time may be needed before an interface can be functionally bonded.

[0006] In addition, adhesives used for medical devices must also consider the possible toxicity of the adhesive to humans and, if implantable, sterility and how the adhesive will react to the conditions within the human body. Medical devices have a wide range of possible applications which require adhesives, including but not limited to, diagnostic products, implants, surgical instruments, dental articles, among others. Recently, certain types of equipment, including items such as surgical instruments and catheters, have become reusable. The reusable nature of these types of products would subject any adhesives used in these devices to the process of cleaning and sterilization over repeated times.

[0007] There exists a need in the art for compositions and methods for bonding two materials in the preparation of a device (e.g., a medical device).

OBJECTS AND SUMMARY OF THE INVENTION

[0008] It is an object of certain embodiments of the present invention to provide a composition where an adhesive material is attached to a first material and where a plurality of linker molecules binds to the adhesive material and also binds to a second material

[0009] It is an object of certain embodiments of the present invention to provide a composition where a material is treated so that linker molecules can form bonds between an adhesive and the treated material.

[0010] It is an object of certain embodiments of the present invention to provide a composition where two dissimilar materials are adhesively bonded together.

[0011] It is an object of certain embodiments of the present invention to provide a composition to increase the strength of an adhesive bond between two materials.

[0012] It is an object of certain embodiments of the present invention to provide a composition to use an adhesive between two materials in a medical device.

[0013] It is an object of certain embodiments of the present invention to provide a preparation for a composition to bond two materials together with an adhesive.

[0014] It is an object of certain embodiments of the present invention to provide a preparation for a composition to bond two materials together with an adhesive using surface modifications which allow for a greater time during which the adhesive can effectively bond the surface.

BREIF DESCRITPTION OF THE DRAWINGS

[0015] FIG. 1 is a schematic of combinatorial and dual linker molecule approach to increase interfacial adhesion.

[0016] FIG. 2 is a list of potential surface chemistry treatments to increase an insulating polyimide film (Kapton®)/acrylated urethane (DYMAX® 204-CTH) adhesion.

[0017] FIG. 3 is a schematic of conceptual peel-test model for film-to-film peel testing.

[0018] FIG. 4 shows a comparison between acrylated urethane (DYMAX® 204-CTH) drop dispensing and acrylated urethane (DYMAX® 204-CTH) line dispensing on a polyethylene terephthalate (PET) film. The difference between the methods is that adhesive line dispensing reduces over spill of adhesive along the length of the insulating polyimide film (Kapton®)-PET and uneven wetting on the top and bottom of the interface.

[0019] FIG. 5 is a graph comparing peel force between silane-treated insulating polyimide film (Kapton®) after 1 hour and 2 days curing.

[0020] FIG. 6 is a graph comparing the effect of different chemistries on insulating polyimide film (Kapton®) adhesion to polyethylene terephthalate (PET).

[0021] FIG. 7 shows photographs comparing visual evidence of the preferential adhesion of acrylated urethane (DYMAX® 204-CTH) towards acroyl chloride treated insulating polyimide film (Kapton®).

DETAILED DESCRIPTION

[0022] The present invention is directed to a composition that in certain embodiments comprises two materials bonded together through an adhesive and linker molecules. In one aspect, the adhesive is bonded to the functional groups of one of the materials and the adhesive is also bound to linker molecules. The linker molecules are then further bonded to functional groups of the second material. The surface of the materials can be modified, such as using oxygen or other gas plasmas, to increase the number of functional groups available to form bonds between the adhesive and/or linker molecules. Gas plasma functions by forming an environment which promotes the formation of hydroxyl, amine, carbonyl and carboxyl groups. The additional functional groups facilitate the binding of the adhesive and/or linker molecules to the treated materials.

[0023] The first and second materials may be selected from, but not limited to, a polymer, a metal, a ceramic, an alloy, a silicon, a glass and/or a fabric and may or may not be different from one another. In certain embodiments, the first and/or second material can be an in-vivo or ex-vivo biological such as a bone, ligament, tendon, etc.

[0024] In certain embodiments, the first and/or second material or the surface of the first and/or second material may be a polymer and may be selected from the group consisting of polyamides, polyimides, polyurethanes, polyureas, polyamines, polyepoxides, polyesters, polysulfonamides and polysulfides. Preferably, the polymer would be polyethylene terephthalate (PET), polyetheretherketones (PEEK), polyetherketoneketones (PEKK) or nylon. Preferably one the material polymer is polyethylene terephthalate and the other material is poly-(4,4'-oxydiphenylene-pyromellitimide).

[0025] In certain embodiments, the first and/or second material or the surface of the first and/or second material may be a metal and may include, but is not limited to, titanium, stainless steel, cobalt chrome, nickel, molybdenum, tantalum, zirconium, magnesium, manganese, niobium or alloys thereof.

[0026] The adhesive may be applied to the first and/or second materials and may be the same or a different material. The adhesives may include, but is not limited to, UV light curable adhesives, epoxy resins, cyanoacrylates, a bone cement such as a polymethylmethacrylate, or activator-cured adhesives. In certain embodiments, the adhesive would be acrylated urethane. In a particular embodiment, the invention is directed to a metal bound with a bone cement such as polymethylmethacrylate and linker molecules.

[0027] In one embodiment, once the adhesive is applied to the surface of the first and/or second materials, linker molecules are added to form covalent bonds between the adhesive and the second material. The linker molecules may be applied to the adhesive on the first and/or second material and may be the same or different linkers. Optionally, the surface of one or both of the materials may be treated to create additional functional groups, such as hydroxyl, amine, carbonyl and carboxyl groups. One such treatment is exposure to oxygen plasma. The additional functional groups may increase the number of single or double covalent bonds created between a linker molecule and the surface of the material. The increase in the number of bonds may enhance the strength of the connection between the first and second materials.

[0028] In another embodiment, the first and second materials may be optionally treated (i.e. with oxygen plasma) to increase the number of functional groups that may bond with the linker molecules. Linker molecules are then added to bond with the first and second materials. The linker molecules added to the first and second materials may be the same or may be different linkers. After the additional of linker molecules to the first and second materials, an adhesive may be added to bond both the linker molecules attached to the first and second materials. The functional groups found on the linkers may then help to cure the adhesive.

[0029] In another embodiment, linker molecules added to the first and/or second materials may be subsequently primed so that the surface is more amenable to participating in the polymerization process of the adhesive. In this embodiment, the surface activation is independent of the activation of the adhesive. The primer can be, e.g., a monomer, an oligomer, a peroxyacid, an activator, a radical initiator or a combination thereof. In certain embodiments, the primer comprises a compound selected from the group consisting of benzoyl peroxide, methylmethacrylate monomer or oligomer, benzophenone and a combination thereof. In certain embodiments, the primer is selected to comport with the polymerization or curing chemistry of the adhesive. Specifically, when using an acrylate based adhesive such as polymethylmethacrylate, coating the surface with a mixture of MMA monomer/benzoyl peroxide prior to contact with the adhesive will increase the working time during which the adhesive can effectively bond to the surface.

[0030] In another embodiment, brush polymerization is used to achieve an increased density of functional moieties capable of bonding to the adhesive per unit surface area. This strategy increases the reactivity of the surface and allows effective bonding with rapidly setting adhesives as well as with improperly formulated adhesives containing suboptimal proportions of monomer.

[0031] The linker molecules may be, but not limited to, a silane moiety, a trimethoxysilane moiety, a radical of a silane acrylate, a trimethoxysilane acrylate, a mercaptosilane moiety, a mercaptoalkylsilane moiety, a radical of mercaptopropyltrimethoxysilane, an acryoyl moiety, a radical of an acryoyl halide, a radical of acryoyl chloride, an alkylene moiety, a phosphonic acid or a radical of propylene.

[0032] The combination of the adhesive with the linker molecule may increase the strength of the connection between the first and second materials, as compared to the adhesive alone. The force between the first and second materials can range, e.g., from about 1N to about 12N. In other embodiments, the force between the first and second materials may be greater than about 1N, greater than about 4N, greater than about 5N, greater than about 6N, greater than about 8N, greater than about 10N or greater than about 12N. In other embodiments, the force between the first and second materials is greater than 100N, greater than 500N, greater than 1000N, greater than 2,500 N or greater than 5,000N. in other embodiments the force between the first and second materials is from about 1N to about 5,000N, from about 5N to about 3,000N or from about 10N to about 2,000N.

[0033] The combination of the adhesive with the linker molecule may increase the strength of the connection between the first and second materials, as compared to the adhesive alone. The adhesion strengths can range, e.g., from about 1Pa to about 1MPa. In other embodiments, the strength between the first and second materials may be greater than about 1MPa, greater than about 4MPa, greater than about 5MPa, greater than about 6MPa, greater than about 8MPa, greater than about 10MPa or greater than about 12 MPa. In other embodiments, the adhesive strength between the first and second materials is greater than 100MPa. In certain embodiments, the adheice strength between the first and second materials is from about 1Pa to about 500MPa., from about 1MPa to about 300 MPa or from about 5 MPa to about 200 MPa.

[0034] The combination of the adhesive with the linker molecule may increase the strength of the connection between the first and second materials, as compared to the adhesive alone. The strength may be increased from about 2x to about 10x. In other embodiments, the strength of the connection between the first and second materials may be greater than about 3x, greater than about about 4x, greater than about about 5x, greater than about 6x, greater than about 8x, greater than about 10x or greater than about 100x. In certain embodiments, the strength of the connection between the first and second materials is from about 2x to about 500x., from about 3x to about 300 MPa or from about 10x to about 100x.

[0035] The invention may be particularly applicable to medical devices. Medical devices are often made of different material types and are required to be rigorous enough to withstand conditions in the human body but must not be harmful to the patient. By virtue of the present invention, the strength of the adhesive bonds between materials and longevity of the medical device may be increased and the risk of harm to a patient may be reduced. Medical devices that may utilize the invention include, but are not limited to, implantable medical devices, vascular devices, artificial hearts and heart assist devices, orthopedic devices, dental devices, drug delivery devices, ophthalmic devices, urological devices, catheters, neurological devices, neurostimulation devices, electrostimulation devices, electrosensing devices and synthetic prostheses, vascular devices, artificial hearts and heart assist devices, orthopedic devices, dental devices, implantable medical device is a dental device or an orthopedic device, vascular device and is selected from the group consisting of grafts, stents, stent grafts, catheters, valves, artificial hearts, pacemakers, fracture repair device and artificial tendon, glaucoma drain shunt, penile devices, sphincter devices, urethral devices, bladder devices, renal devices, breast prostheses, artificial organs, dialysis tubing and membranes, blood oxygenator tubing and membranes, blood bags, sutures, membranes, cell culture devices, chromatographic support materials, biosensors, anastomotic connectors, surgical instruments, angioplasty balloons, wound drains, shunts, tubing, urethral inserts, blood oxygenator pumps, wound tubing, electrical stimulation leads, brain tissue stimulators, central nerve stimulators, peripheral nerve stimulators, spinal cord nerve stimulators and sacral nerve stimulators.

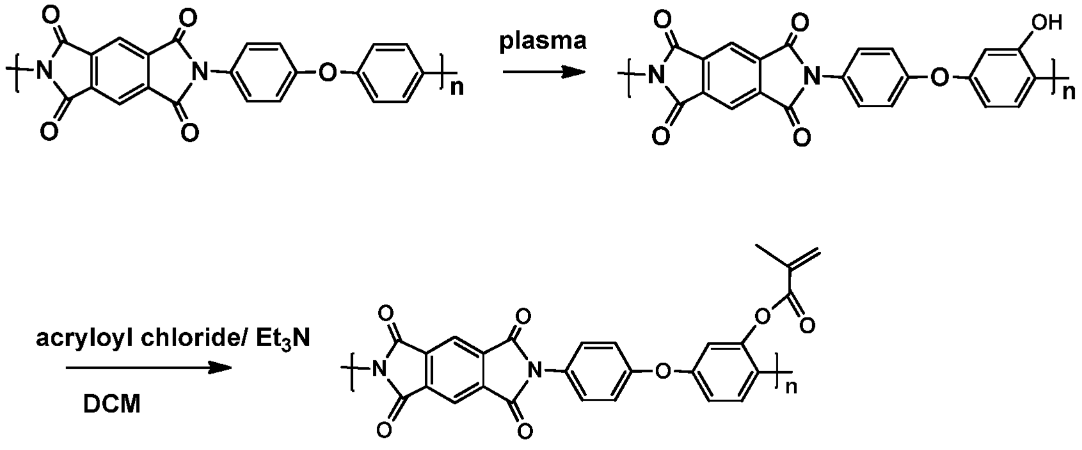
[0036] The invention also teaches a method of preparing a composition of two materials bonded together using an adhesive and linker molecules as disclosed herein.

[0037] The invention teaches a method of treating a patient using a composition of two materials bonded together using an adhesive and linker molecules where the two materials are part of an implanted medical device as disclosed herein.

EXAMPLES

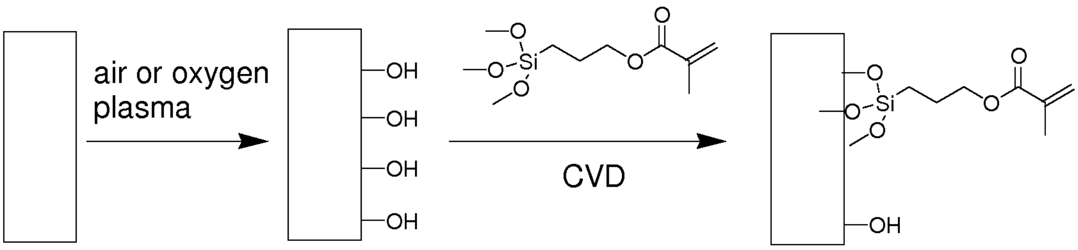
[0038] **Example 1**: Solvent Deposition of Acryoyl Chloride on a Polyimide Surface

[0039] Insulation in the form of a polyimide film (Kapton®) (1-inch by 3-inches) were air plasma treated for 10 minutes at 4 Torr (0.5% Atmosphere) using a Herrick Plasma Cleaning Machine. A surface treatment solution was made using 70-ml of dichloromethane (DCM), triethylamine (Et3N) and acryloyl chloride under static conditions for 10 minutes at -20°C. The solution was stirred for 2 minutes. The polyimide film samples were then transferred into the surface treatment solution and shaken for 18 hours. After 18 hours of surface treatment, the treated polyimide film samples were washed/sonicated with DCM, following with a second wash with reagent alcohol and blow drying process. Below is a schematic of the chemical process involved during acryoyl chloride functionalization of polyimide film samples.



[0040] **Example 2**: Chemical Vapor Deposition of 3-(Trimethoxysilyl)Propyl Methacrylate on Polyimide Film (Kapton®)

[0041] Insulation in the form of polyimide film (Kapton®) (1-inch by 3-inches) were cut and wiped with ethanol, following by sonication in a 1:1 water/ethanol mixture for 15 minutes, then in ethanol for 15 minutes. Samples were blown dry. Cleaned polyimide film samples were placed in a Harrick Plasma Cleaning Machine for 5 minutes at ~1 Torr using "High" energy setting. Plasma treated polyimide film samples were placed in a desiccator with 1-2 ml of 3-(trimethoxysilyl)propyl methacrylate in a vial next to the polyimide film samples. The desiccator was connected to a vacuum pump to start chemical vapor deposition (CVD) for 3 hours After 3 hours, the CVD-treated polyimide film was placed under high vacuum for 1 hour as a post-annealing step. The schematic below is a basic representation of the chemical process involved during silane functionalization of polyimide samples.



Chemical vapor deposition of silane on polyimide film (Kapton®).

[0042] **Example 3:** In-house Peel Test Device and Sample Preparation

[0043] A basic model was developed to test and differentiate the adhesive potential of different chemistry treatments. The equation below describes a mass (m) on an incline frictionless plane with a range of angles theta (θ) attached to the testing polymer film. Under initial conditions and changes of weight and angle, there is a force magnitude (F) dependent on m and angle (θ), pulling at the adhesive interface of two polymer films.

$$F = mg * Sin(\theta) - \mu m$$

[0044] Depending on the final load and angle of testing, the force (F) defines the peeling force. Figure 3 depicts a conceptualized peel-test model for the invention. The system used a weight set which totaled 1,000 grams (set: 500 grams (1), 200 grams (1), 100 grams (2), 50 grams (1), 20 grams (2), 10 grams (1)). A series of carts were built to hold the weights during testing. On one end, the cart had two metal plates with tightening bolts to hold the Kapton® film lip on a Kapton®-DYMAX® 204-CTH adhesive- polyethylene terephthalate (PET) test sample. The bottom of the carts had a 1-inch thick Teflon® sheet; the same material was used to cover the surface of the sliding plane. Both Teflon® surfaces, on the carts and sliding plane, were polished to achieve a reduced friction contact surface to measure the peeling force between the polyimide film (Kapton®) adhered to PET via the acrylated urethane (DYMAX® 204-CTH).

[0045] The PET-DYMAX® 204-CTH-Kapton® samples were optimized for the In-house Peel Test Device (IhPTD). Two important optimization steps were adopted to reduce data variability and false-positive adhesion. Figure 4(top) shows the assembly of the Kapton®-DYMAX® 204-CTH-PET film sandwich onto a PET block. This process requires for the PET film (with dimensions of

1.5-inches width by 2.5 inches in length) to be larger than the Kapton® film (dimensions of 0.5-inch by 2-inches in length), and the PET block (dimensions of 1-inch width by 2-inches in length).

[0046] The following are the steps to prepare a peel test sample, as represented in Figure 4:

- Cut the polyimide film (Kapton®) and PET film for its required sizes 1-inch in width by 3-inches in length and 1.5-inches in width by 2.5 inches in length respectively.
- Clean all polymer films using reagent alcohol and sonication for 5 minutes. Following with pressure air drying for chemistry treatment and control (plasma only).
- Cut control and treated polyimide film (Kapton®) into 0.5-inches in width by 2-inches in length for final testing dimension.
- Fold evenly at the 1-inch end of the polyimide film (Kapton®) film, this is the lip for attachment on the weight cart.
- Using a marker to delineate the polyimide film (Kapton®) adhesion area (0.5-inches width by 2-inches in length) on the larger PET film.
- Carefully and continuously dispense the acrylated urethane (DYMAX® 204-CTH) within the marker-delineated area following the line-method in the shape of an “I”.
- After drawing the “I” on the PET, placing the polyimide film (Kapton®) by the lip and place it carefully on top of the PET film.
- Place the sample inside the UV hardening device, placing the PET facing towards the UV source. Use 2 minutes photo initiation and allow 60 minutes minimum to 2 days curing before adhesion testing.

[0047] Between the two treatments and respective controls (polyimide film (Kapton®), air plasma), means were higher after 1 hour of curing. However, the spread of the data (+/-SEM) in Figure 5 shows no difference in the force to peel the polyimide film (Kapton®) from the PET film in either curing group. It is noted that a few samples from the 1 hour curing group had some of the polymerized acrylated urethane (DYMAX® 204-CTH) on the polyimide film (Kapton®) side after peeling even though the adhesive preferentially adheres to PET vs Kapton. This effect was not seen on any of the tested samples in the 2 day curing group.

[0048] Figure 6 compares the effect of two different chemistries applied to the polyimide film (Kapton®) in the adhesive system (Kapton-Dymax-PET) after curing for two days. In this treatment group, several variables were tested such as plasma exposure and linker chemistry. It was found that the methacrylated silane and oxygen plasma increased adhesion of the polyimide film (Kapton®) towards PET in comparison to plasma alone, with a 3-fold difference. However, this effect does increase for longer plasma treatment (Figure 6, C-D). Besides silane, the effect of acroyl chloride linker chemistry was tested and showed higher fold difference in adhesion when compared to control and silane, with a 4.6-fold and 1.5-fold respectively. Even though the fold different is large, this force to peel the polyimide film (Kapton®) from PET using acroyl chloride as a minimum value, adhesion exceeded the limit of the IhPTH.

[0049] The increased adhesion of a polyimide film (Kapton®) towards PET using acroyl chloride linker chemistry was visually assessed. For the control, plasma-treated and silane-treated cases (treatment of the polyimide), the acrylated urethane adhesive (DYMAX® 204-CTH) after peel testing routinely and reliably remained on the PET half of the glued pair of materials. In the case of acroyl halide-treated polyimide film (Kapton®), peel testing showed a reversal of preference for the surface to which the adhesive would adhere. This was visual confirmation the applied chemistry had had a positive effect on the strength of the polyimide film (Kapton®) adhesive bond.

[0050] Figure 7 is a representative image showing a comparison between control and acroyl chloride treated polyimide film (Kapton®). The left image of Figure 7 shows the control polyimide film (Kapton®) samples did not have polymerized acrylated urethane (DYMAX 204-CTH) on the polyimide film (Kapton®), only on PET film after peeling. However, the right image of Figure 7 shows acroyl treated polyimide film (Kapton®) had polymerized acrylated urethane (DYMAX® 204-CTH) after peeling, with none on the PET. This offers a potential correlation of the linker chemistry increasing adhesion of the (Kapton®) towards the acrylated urethane (DYMAX® 204-CTH) and PET.

We Claim:

1. A composition comprising:
a first material;
an adhesive material attached to the first material;
a plurality of linker molecules bonded to the adhesive material; and
a second material bonded to the linker molecules.

2. The composition of claim 1, wherein the adhesive material is bonded to surface functional groups of the first material.

3. The composition of claim 1, wherein the plurality of linker molecules are bonded to surface functional groups of the second material.

4. The composition of claim 1, wherein the first material is surface modified.

5. The composition of claim 1, wherein the second material is surface modified.

6. The composition of claim 1, wherein the first material is surface modified with plasma.

7. The composition of claim 1, wherein the second material is surface modified with plasma.

8. The composition of claim 1, further comprising a second plurality of linker molecules between the first surface and the adhesive material.

9. The composition of claim 8, further comprising a brush polymerized surface resulting in an increased plurality of linker molecules between the first surface and the adhesive.

10. The composition of claim 8, wherein the first and second plurality of linker molecules are the same.

11. The composition of claim 8, wherein the first and second plurality of linker molecules are different.

12. The composition of claim 8, wherein the linker molecules are coated with a primer which can activate the linker for more rapid reaction with the adhesive.

13. The composition of claim 1, further comprising a second adhesive material between the plurality of linker molecules and the second material.

14. The composition of claim 13, wherein the first and second adhesive materials are the same.

15. The composition of claim 13, wherein the first and second adhesive materials are different.

16. The composition of claim 1, wherein the plurality of linker molecules are covalently bonded to the adhesive.

17. The composition of claim 1, wherein the plurality of linker molecules are covalently bonded to the second material.

18. The composition of claim 1, wherein the plurality of linker molecules are covalently bonded to the adhesive using double bond functionalization.

19. The composition of claim 1, wherein the plurality of linker molecules are covalently bonded to the second material using double bond functionalization.

20. The composition of claim 1, wherein the first material and the second material comprise a component independently selected from the group consisting of a polymer, a metal, a ceramic, an alloy, silicon, glass and fabric.

21. The composition of claim 1, wherein the first material comprises a component selected from the group consisting of a polymer, a metal and a ceramic and the second material comprises a polymer.

22. The composition of claim 1, wherein the first material comprises a polymer and the second material comprises a polymer.

23. The composition of claim 1, wherein a surface of the first material and a surface of the second material comprise a component independently selected from the group consisting of a polymer, a metal and a ceramic.

24. The composition of claim 1, wherein a surface of the first material comprises a component selected from the group consisting of a polymer, a metal and a ceramic and a surface of the second material comprises a polymer.

25. The composition of claim 1, wherein a surface of the first material comprises a polymer and a surface of the second material comprises a polymer.

26. The composition of claim 12 where the primer comprises a compound selected from the group consisting of benzoyl peroxide, methylmethacrylate monomer or oligomer, benzophenone, a peroxyacid, a radical initiator, an activator and a combination thereof.

27. The composition of claim 12 where the primer comprises a combination of methylmethacrylate monomer and benzoyl peroxide.

28. The composition of claim 20 or 24, wherein the polymer is independently selected from the group consisting of polyethylene terephthalate (PET), polyetheretherketones (PEEK), polyetherketoneketones (PEKK) and nylon.

29. The composition of claim 20 or 24, wherein the metal is independently selected from the group consisting of titanium, stainless steel, cobalt chrome, nickel, molybdenum, tantalum, zirconium, magnesium, manganese, niobium and alloys thereof.

30. The composition of claim 20 or 24, wherein the polymer is independently selected from the group consisting of polyamides, polyimides, polyurethanes, polyureas, polyamines, polyepoxides, polyesters, polysulfonamides and polysulfides.

31. The composition of claim 28, wherein the polymer is independently selected from the group consisting of polyethylene terephthalate and poly-(4,4’-oxydiphenylene-pyromellitimide).

32. The composition of claim 1, wherein the first material comprises polyethylene terephthalate and the second material comprises poly-(4,4’-oxydiphenylene-pyromellitimide).

33. The composition of claim 1, wherein a surface of the first material comprises polyethylene terephthalate and a surface of the second material comprises poly-(4,4’-oxydiphenylene-pyromellitimide).

34. The composition of claim 1, wherein the adhesive material comprises a component selected from the group consisting of UV light curable adhesives, epoxy resins, cyanoacrylates, polymethylmethacrylate and activator-cured adhesives.

35. The composition of claim 1, wherein the adhesive material comprises a UV light curable adhesive.

36. The composition of claim 1, wherein the adhesive material comprises acrylated urethane.

37. The composition of claim 1, wherein the plurality of linker molecules comprise a silane moiety or a phosphonic acid.

38. The composition of claim 1, wherein the plurality of linker molecules comprise a trimethoxysilane moiety.

39. The composition of claim 1, wherein the plurality of linker molecules comprise a radical of a silane acrylate.

40. The composition of claim 1, wherein the plurality of linker molecules comprise a radical of a trimethoxysilane acrylate.

41. The composition of claim 1, wherein the plurality of linker molecules comprise a mercaptosilane moiety.

42. The composition of claim 1, wherein the plurality of linker molecules comprise a mercaptoalkylsilane moiety.

43. The composition of claim 1, wherein the plurality of linker molecules comprise a radical of mercaptopropyltrimethoxysilane.

44. The composition of claim 1, wherein the plurality of linker molecules comprise an acryoyl moiety.

45. The composition of claim 1, wherein the plurality of linker molecules comprise a radical of an acryoyl halide.

46. The composition of claim 1, wherein the plurality of linker molecules comprise a radical of acryoyl chloride.

47. The composition of claim 1, wherein the plurality of linker molecules comprise an alkylene moiety.

48. The composition of claim 1, wherein the plurality of linker molecules comprise a radical of propylene.

49. The composition of claim 1, wherein the force to peel the first material from the second material is from about 1N to about 12N.

50. The composition of claim 1, wherein the force to peel the first material from the second material is greater than about 5N.

51. The composition of claim 1, wherein the force to peel the first material from the second material is from about 1Pa to aboyt 1 MPa.

52. The composition of claim 1, wherein the force to peel the first material from the second material is greater than about 8MPa.

53. The composition of claim 1, wherein the force to peel the first material from the second material is increased from about 2x to about 10X as compared to the adhesive alone.

54. The composition of claim 1, wherein the force to peel the first material from the second material is increased greater than about 5 MPa as compared to the adhesive alone.

55. The composition of any of claims 1-54 which is a medical device.

56. The composition of claim 55, which is an implantable medical device.

57. The composition of claim 56, wherein the implantable medical device is selected from the group consisting of vascular devices, artificial hearts and heart assist devices, orthopedic devices, dental devices, drug delivery devices, ophthalmic devices, urological devices, catheters, neurological devices, neurostimulation devices, electrostimulation devices, electrosensing devices and synthetic prostheses.

58. The composition of claim 56, wherein the implantable medical device is selected from the group consisting of vascular devices, artificial hearts and heart assist devices, orthopedic devices and dental devices.

59. The composition of claim 56, wherein the implantable medical device is a dental device or an orthopedic device.

60. The composition of claim 56, wherein the implantable medical device is a vascular device and is selected from the group consisting of grafts, stents, stent grafts, catheters, valves, artificial hearts and pacemakers.

61. The composition of claim 56, wherein the implantable medical device is an orthopedic device and is selected from the group consisting of a fracture repair device, an artificial tendon, a glued orthopedic implant, a hip implant and a knee implant.

62. The composition of claim 56, wherein the implantable medical device is a glaucoma drain shunt.

63. The composition of claim 56, wherein the implantable medical device is a urological device and is selected from the group consisting of penile devices, sphincter devices, urethral devices, bladder devices and renal devices.

64. The composition of claim 56, wherein the implantable medical device is a synthetic prosthesis and is selected from the group consisting of breast prostheses and artificial organs.

65. The composition of claim 52, wherein the implantable medical device is a device is selected from the group consisting of dialysis tubing and membranes, blood oxygenator tubing and membranes, blood bags, sutures, membranes, cell culture devices, chromatographic support materials, biosensors, anastomotic connectors, surgical instruments, angioplasty balloons, wound drains, shunts, tubing, urethral inserts, blood oxygenator pumps and wound tubing.

66. The composition of claim 56, wherein the implantable medical device is a selected from the group consisting of electrical stimulation leads, brain tissue stimulators, central nerve stimulators, peripheral nerve stimulators, spinal cord nerve stimulators and sacral nerve stimulators.

67. A composition comprising:
a first material;
a first plurality of linker molecules bonded to the first material;
an adhesive bonded to the first plurality of linker molecules;
a second plurality of linker molecules bonded to the adhesive; and
a second material bonded to the second plurality of linker molecules.

68. The composition of claim 67, wherein the first and second plurality of linker molecules are the same.

69. The composition of claim 67, wherein the first and second plurality of linker molecules are different.

70. A method of preparing a composition comprising any of claims 1-69.

71. A method of treating a patient comprising implanting a medical device according to any of claims 56-66.

72. The use of a composition of any of claims 1-69 in the preparation of a medical device.

73. The use of claim 73, wherein the medical device is according to any of claims 56-66.

Figure 1

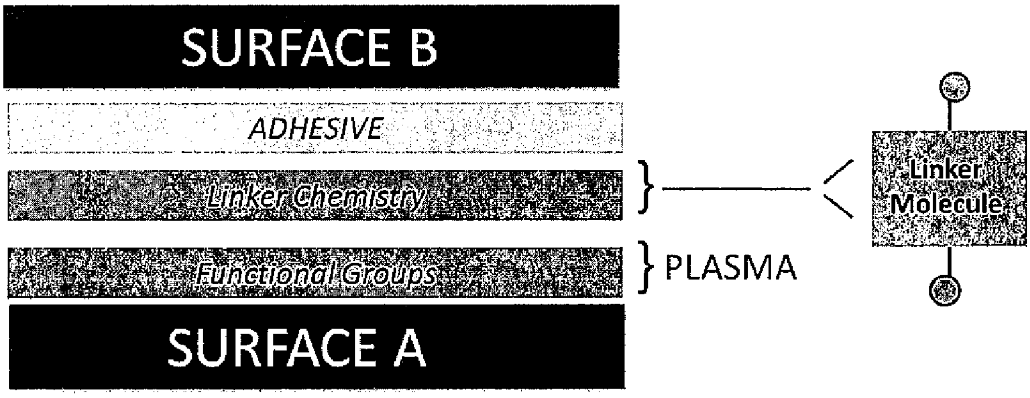


Figure 1. Combinatorial and dual linker molecule approach to increase interfacial adhesion.

Figure 2

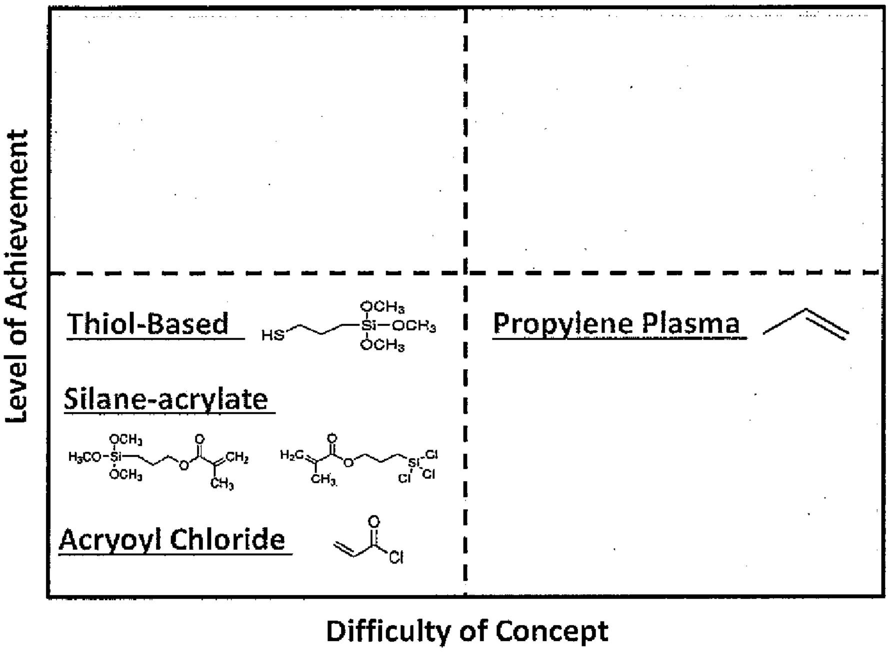
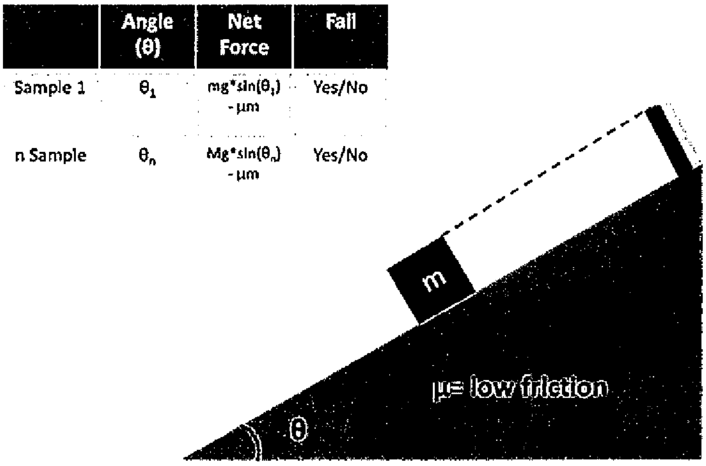


Figure 2. List of potential surface chemistry treatments to increase an insulator polyimide film (Kapton®)/acrylated urethane (DYMAX® 204-CTH) adhesion.

Figure 3



	Angle (θ)	Net Force	Fail
Sample 1	θ_1	$mg*\sin(\theta_1) - \mu m$	Yes/No
n Sample	θ_n	$Mg*\sin(\theta_n) - \mu m$	Yes/No

Figure 3. Conceptual Peel-Test model for film-to-film peel testing.

Figure 4

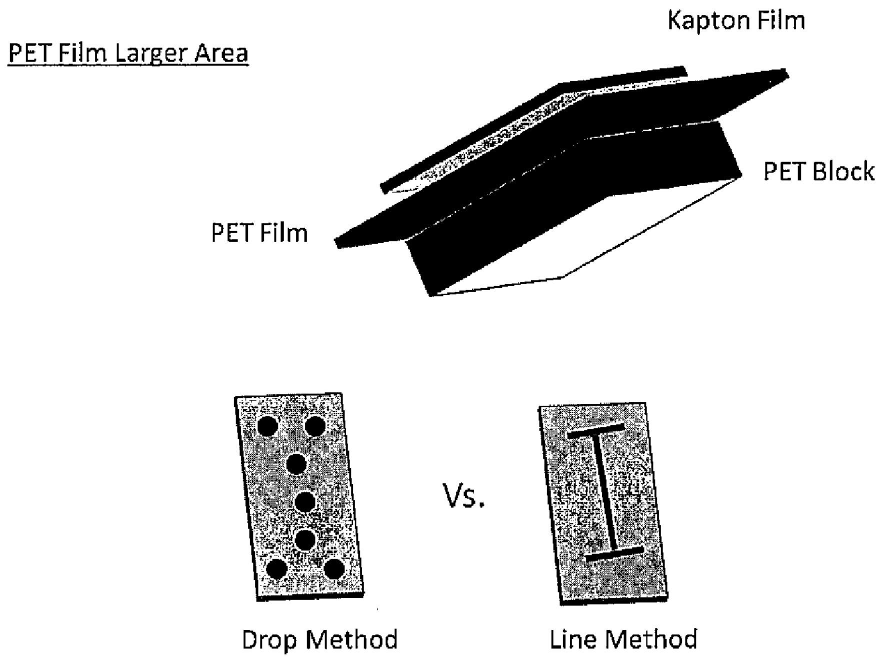


Figure 4. A comparison between acrylated urethane (DYMAX® 204-CTH) drop dispensing and acrylated urethane (DYMAX® 204-CTH) line dispensing on a polyethylene terephthalate (PET) film. The difference between the methods is that adhesive line dispensing reduces over spill of adhesive along the length of the insulation polyimide film (Kapton®)-PET and uneven wetting on the top and bottom of the interface.

Figure 5

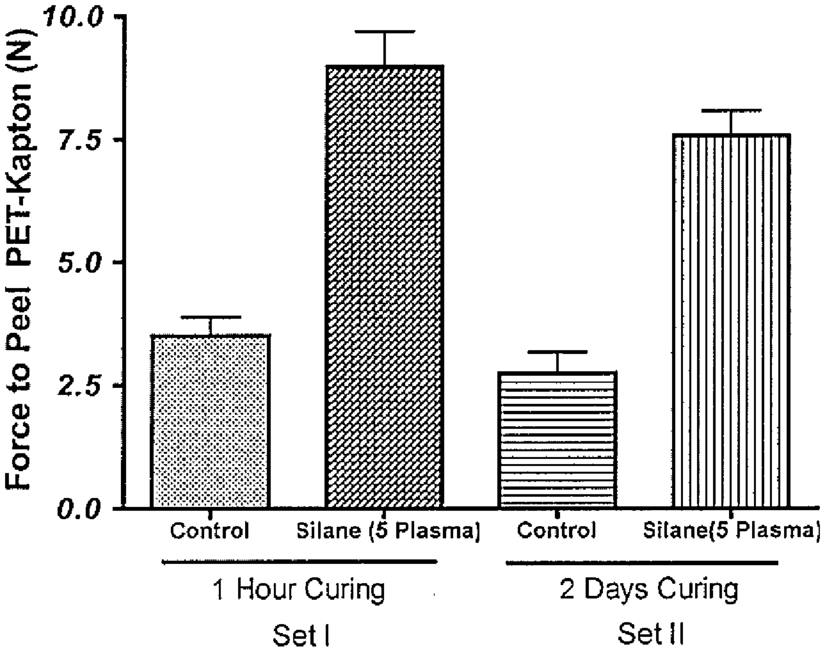


Figure 5. Comparison between silane-treated polyimide film (Kapton®) insulation after 1 hour and 2 days curing.

Figure 6

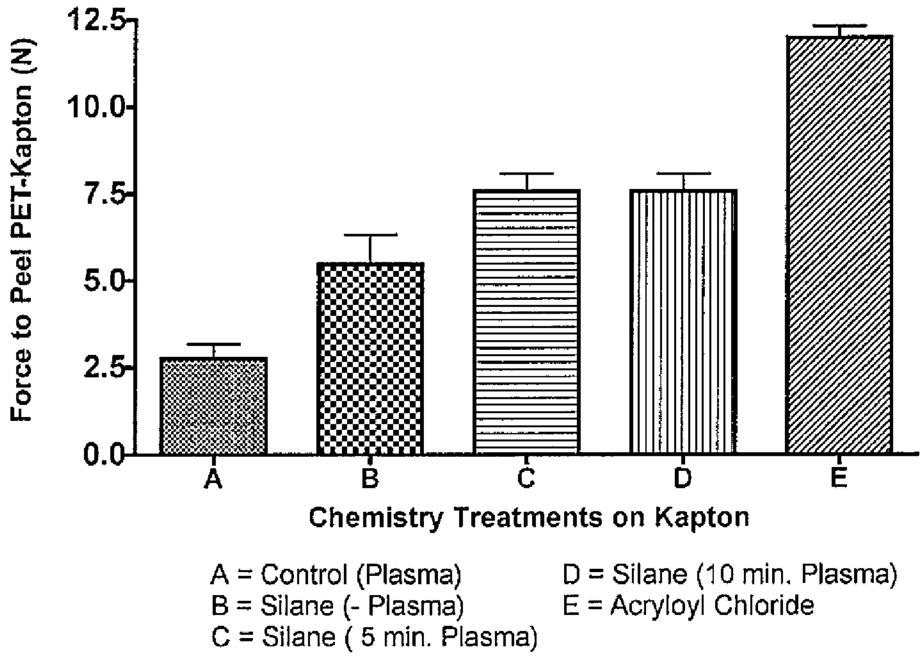


Figure 6. Effect of different chemistries on insulation polyimide film (Kapton®) adhesion to polyethylene terephthalate (PET).

Figure 7

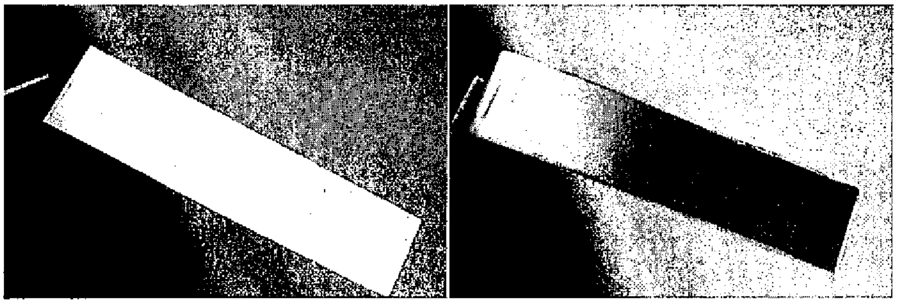


Figure 7. Visual evidence of the preferential adhesion of acrylated urethane (DYMAX® 204-CTH) towards acroyl chloride treated insulation polyimide film (Kapton®).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/10451

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09J 5/02; B32B 7/12, 37/12 (2015.01)
CPC - C09J 5/02; B32B 7/12, 37/12
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8): C09J 5/02, 175/14, 4/02, 133/08, 201/10, 201/04; B32B 7/12, 37/12 (2015.01)
CPC: C09J 5/02, 175/14, 133/08, 201/10, 201/04; B32B 7/12, 37/12

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)
PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); ProQuest; IP.com; Google/Google Scholar; surface, polymer, bond, linker, ligand, attach, adhesive, binder, tie, plasma, polymer brush, primer, covalent, double bond, functionalization, metal, methylmethacrylate, benzoyl peroxide, polyethylene terephthalate (PET), poly-(4,4' -oxydiphenylene-pyromellitimide), Kapton, UV curable

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 8,614,003 B2 (PEKING UNIVERSITY) 24 December 2013; column 8, lines 4-38; column 9, lines 7-24; claims 1, 4-6, 8-10	1, 3, 8-11, 16-25, 67-69 -------------------- 2, 4-7, 12-15, 26-27, 28/20, 28/24, 29/20, 29/24, 30/20, 30/24, 31/28/20, 31/28/24, 32-54
Y	US 4,765,860 A (UENO, S et al.) 23 August 1988; abstract	2
Y	US 6,503,359 B2 (VIRTANEN, J) 07 January 2003; column 4, lines 49-56	4-7
Y	EP 0 251 490 A2 (IMPERIAL CHEMICAL INDUSTRIES PLC) 07 January 1988; abstract; page 2, lines 27-36; page 3, lines 31-45; claim 1	12, 26-27, 29/20, 29/24
Y	US 2012/0231245 A1 (KIM, JS et al.) 13 September 2012; abstract; paragraphs [0030], [0043], [0069]-[0070], [0079], [0081]; claim 9	13-15, 28/20, 28/24, 30/20, 30/24, 31/28/24, 31/28/20, 34-35
Y	US 7,135,979 B2 (SAVAGIAN, MD et al.) 14 November 2006; column 6, lines 7-25; figure 1	32-33
Y	US 2013/0017246 A1 (TUNIUS, M) 17 January 2013; abstract; paragraph [0132]; example 1; table 1	36, 49-51
Y	US 2012/0283375 A1 (KAGEYAMA, Y) 08 November 2012; abstract; paragraphs [0015], [0078], [0091]	37-43

☒ 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
18 March 2015 (18.03.2015)

Date of mailing of the international search report
07 APR 2015

Name and mailing address of the ISA/
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Facsimile No. 571-273-3201

Authorized officer
Shane Thomas
PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/10451

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,787,244 B2 (SEZI, R et al.) 07 September 2004; column 12, lines 40-58; column 21, lines 29-35	44-46
Y	US 5,302,669 A (FURUKAWA, H et al.) 12 April 1994; abstract; column 5, lines 26-48	47-48
Y	EP 0 889 105 A2 (MINNESOTA MINING AND MANUFACTURING COMPANY) 07 January 1999; abstract; example 1; comparative example C1; table 1	52-54
Y	US 5,180,766 A (HAYAMA, K et al.) 19 January 1993; column 3, lines 41-46; claims 1, 5	27
A	WO 2013/139342 A1 (AARHUS UNIVERSITET, et al.) 26 September 2013; entire document	1-27, 28/20, 28/24, 29/20, 29/24, 30/20, 30/24, 31/28/20, 31/28/24, 32-54, 67-69
A	US 2007/0225387 A1 (MAYADUNNE, RTA et al.) 27 September 2007; entire document	1-27, 28/20, 28/24, 29/20, 29/24, 30/20, 30/24, 31/28/20, 31/28/24, 32-54, 67-69
A	US 2009/0026407 A1 (TOMLINSON, MR et al.) 29 January 2009; entire document	1-27, 28/20, 28/24, 29/20, 29/24, 30/20, 30/24, 31/28/20, 31/28/24, 32-54, 67-69

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/10451

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 55-66 and 70-73
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.