



(51) International Patent Classification:

*A61L 15/58* (2006.01) *B32B 5/26* (2006.01)  
*A61L 24/00* (2006.01) *B32B 37/12* (2006.01)  
*B32B 3/06* (2006.01) *D04H 13/00* (2006.01)

(21) International Application Number:

PCT/US2020/032659

(22) International Filing Date:

13 May 2020 (13.05.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/848,088 15 May 2019 (15.05.2019) US

(71) Applicant: **PRESIDENT AND FELLOWS OF HARVARD COLLEGE** [US/US]; 17 Quincy Street, Cambridge, MA 02138 (US).

(72) Inventors: **WANG, Yecheng**; 295 Harvard Street, Apt. 905, Cambridge, MA 02139 (US). **JIA, Kun**; 60 Empire Street, Allston, MA 02134 (US). **XIANG, Chunping**; 29 Oxford Street Harvard University, Cambridge, MA 02138 (US). **YANG, Jiawei**; 45 Loomis St., Apt. 307, Malden, MA 02148 (US). **YAO, Xi**; Kavli Institute for Bionano Science and Technology, 29 Oxford Street, Cambridge, MA 02138 (US). **SUO, Zhigang**; 88 North Hancock Street, Lexington, MA 02420 (US).

(74) Agent: **HA, Yung-hoon** et al.; Wilmer Cutler Pickering Hale and Dorr LLP, 60 State Street, Boston, MA 02109 (US).

(54) Title: INSTANT AND TOUGH ADHESION

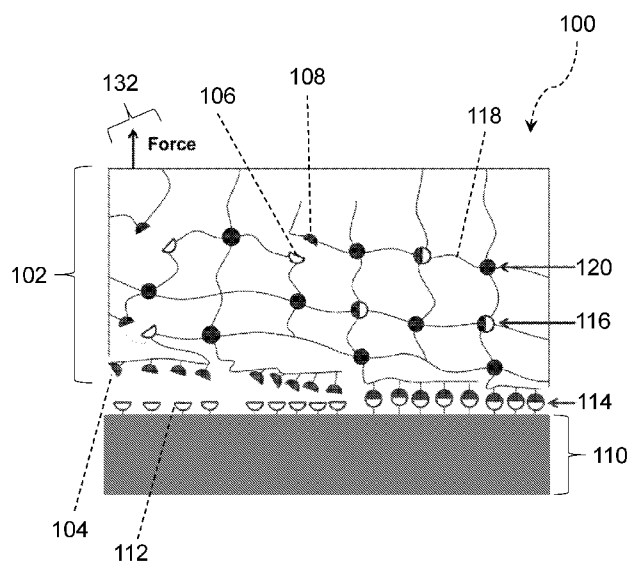


FIG. 1A

(57) **Abstract:** A composite material is disclosed, including: a first material including a plurality of first inter-material bonding units, a plurality of first internal bonding units and a plurality of first complementary internal bonding units; and a second material including a plurality of second inter-material bonding units; where the plurality of first and second inter-material bonding units form a plurality of inter-material non-covalent bonds to adhere the first material and the second material together; where the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and where the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the first intra-material bonds. Methods for adhering a first material and a second material together are also disclosed.



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

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

**Published:**

— with international search report (Art. 21(3))

## **INSTANT AND TOUGH ADHESION**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/848,088, filed May 15, 2019, which is hereby incorporated by reference in its entirety.

### **INCORPORATION BY REFERENCE**

[0002] All patents, patent applications and publications cited herein are hereby incorporated by reference in their entirety in order to more fully describe the state of the art as known to those skilled therein as of the date of the invention described herein.

### **FIELD OF THE INVENTION**

[0003] The present disclosure relates generally to the field of adhesion. More particularly, the present disclosure relates to instant and tough adhesion.

### **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT**

[0004] This invention was made with government support under 1420570 awarded by the National Science Foundation. The government has certain rights in the invention.

### **SUMMARY OF THE INVENTION**

[0005] In one aspect, a composite material is disclosed, including:

- a first material comprising a plurality of first inter-material bonding units, a plurality of first internal bonding units and a plurality of first complementary internal bonding units; and
- a second material comprising a plurality of second inter-material bonding units;

wherein the plurality of first inter-material bonding units and the plurality of second inter-material bonding units form a plurality of inter-material non-covalent bonds to adhere the first material and the second material together;

wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and

wherein the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

[0006] In another aspect, a composite material is disclosed, including:

a first material comprising a plurality of first internal bonding units and a plurality of first complementary internal bonding units; and

a second material;

wherein the first material and the second material are adhered together by topological adhesion or mechanical interlocking;

wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and

wherein the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

**[0007]** In any one of the embodiments disclosed herein, the second material comprises a plurality of second internal bonding units and a plurality of second complementary internal bonding units;

wherein the second internal bonding units form a plurality of second intra-material bonds by bonding with the plurality of second complementary internal bonding units; and

wherein the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the second intra-material bonds.

**[0008]** In any one of the embodiments disclosed herein, the second material comprises a plurality of second internal bonding units and a plurality of second complementary internal bonding units;

wherein the second internal bonding units form a plurality of second intra-material bonds by bonding with the plurality of second complementary internal bonding units; and

wherein the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the second intra-material bonds.

**[0009]** In any one of the embodiments disclosed herein, the first material and the second material are each independently selected from the group consisting of polymers, nonporous inorganics, metal, metal alloy, ceramic, stone, concrete, asphalt, glass, silicon, wood, tissues, organs, arteries, vessels, bone, teeth, fabric, fibers, textiles, foam, plaster, paper, cardboard, fiberglass, semiconductors, biomaterials, composite materials, metamaterials, minerals, elemental materials, plant materials, adhesives, and a combination thereof.

**[0010]** In any one of the embodiments disclosed herein, the first material or the second material is a polymer material.

**[0011]** In any one of the embodiments disclosed herein, the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, or the second complementary internal bonding units comprise a cross-linking agent.

**[0012]** In any one of the embodiments disclosed herein, the cross-linking agent comprises *N,N'*-methylenebisacrylamide (MBAA), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) dimethacrylate (PEGDMA), 3-(trimethoxysilyl) propyl methacrylate (TMSPMA), or a combination thereof.

**[0013]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material are each independently selected from the group consisting of a hydrogel, an elastomer, a rubber, a plastic, and a biological polymer.

**[0014]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material comprises a hydrogel.

**[0015]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material is independently selected from the group consisting of poly(hydroxyethylmethacrylate) (HEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), poly(acrylic acid) (PAA), poly(lactic-co-glycolic acid) (PLGA), poly(ethylene glycol) (PEG), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) methacrylate (PEGMA), poly(ethylene glycol) dimethacrylate (PEGDMA), poly([2-(acryloyloxy)ethyl] trimethylammonium chloride) (PDMAEA), poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), alginate, chitosan, and a combination thereof.

**[0016]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material comprises an elastomer.

**[0017]** In any one of the embodiments disclosed herein, the elastomer is selected from the group consisting of natural rubber, styrene butadiene rubber, polybutadiene rubber, silicone rubber, polyurethane, acrylic foam (Very High Bond™), silicones (Dragon Skin® 20), silicone (Ecoflex™ 00-30), and a combination thereof.

**[0018]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material comprises a biological polymer.

**[0019]** In any one of the embodiments disclosed herein, the biological polymer is selected from the group consisting of polysaccharide, polypeptide, polynucleotides, and a combination thereof.

**[0020]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material comprises a tissue or an organ.

**[0021]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are selected from the group consisting of ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

**[0022]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are ionic bonds.

**[0023]** In any one of the embodiments disclosed herein, the ionic bonds are metal cation-carboxylate bonds or ammonium-carboxylate bonds.

**[0024]** In any one of the embodiments disclosed herein, the first inter-material bonding units and the second inter-material bonding units are selected from the group consisting of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NR}_4^+$ ,  $\text{OH}^-$ ,  $\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ , wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.

**[0025]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are hydrogen bonds.

**[0026]** In any one of the embodiments disclosed herein, the hydrogen bonds are carboxylic acid and hydroxyl hydrogen bonds, amine and hydroxyl hydrogen bonds, amide and carboxylic acid hydrogen bonds, carboxyl and carboxyl hydrogen bonds, hydroxyl and hydroxyl hydrogen bonds, or amine and phenol hydrogen bonds.

**[0027]** In any one of the embodiments disclosed herein, the first inter-material bonding units and the second inter-material bonding units are selected from the group consisting of OH, COOH,  $\text{NH}_2$ , NHR, and a combination thereof, wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.

**[0028]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are hydrophobic interactions or dipole-dipole interactions.

**[0029]** In any one of the embodiments disclosed herein, the first inter-material bonding units and the second inter-material bonding units are selected from the group consisting of alkyl, aryl, heteroaryl, halogen.

**[0030]** In any one of the embodiments disclosed herein, the first material and the second material are adhered together by topological adhesion.

**[0031]** In any one of the embodiments disclosed herein, the first intra-material bonds and the second intra-material bonds are each independently selected from the group consisting of covalent bonds, ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

**[0032]** In any one of the embodiments disclosed herein, the first intra-material bonds or the second intra-material bonds are covalent bonds.

**[0033]** In any one of the embodiments disclosed herein, the covalent bonds comprise  $\sigma$ -bonding,  $\pi$ -bonding, metal-to-metal bonding, agnostic interactions, bent bonds, three-center two-electron bonds, or a combination thereof.

**[0034]** In any one of the embodiments disclosed herein, the first intra-material bonds or the second intra-material bonds are ionic bonds.

**[0035]** In any one of the embodiments disclosed herein, the ionic bonds are metal cation-carboxylate bonds or ammonium-carboxylate bonds.

**[0036]** In any one of the embodiments disclosed herein, the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, and the second complementary internal bonding units are each independently selected from the group consisting of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NR}_4^+$ ,  $\text{OH}^-$ ,  $\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ , wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.

**[0037]** In any one of the embodiments disclosed herein, the first intra-material bonds or the second intra-material bonds are hydrogen bonds.

**[0038]** In any one of the embodiments disclosed herein, the hydrogen bonds are carboxylic acid and hydroxyl hydrogen bonds, amine and hydroxyl hydrogen bonds, amine and carboxyl hydrogen bonds, carboxyl and carboxyl hydrogen bonds, hydroxyl and hydroxyl hydrogen bonds, or amine and phenol hydrogen bonds.

**[0039]** In any one of the embodiments disclosed herein, the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, and the second complementary internal bonding units are each independently selected from the group consisting of OH, COOH,  $\text{NH}_2$ , NHR, and a combination thereof, wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.

**[0040]** In any one of the embodiments disclosed herein, the first intra-material bonds or the second intra-material bonds are hydrophobic interactions or dipole-dipole interactions.

**[0041]** In any one of the embodiments disclosed herein, the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, and the second

complementary internal bonding units are each independently selected from the group consisting of alkyl, aryl, heteroaryl, and halogen.

**[0042]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are hydrogen bonds and the first intra-material bonds and the second intra-material bonds are ionic bonds.

**[0043]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are hydrogen bonds and the first intra-material bonds and the second intra-material bonds are covalent bonds.

**[0044]** In any one of the embodiments disclosed herein, the first polymer material is polyacrylamide (PAAm); the first inter-material bonding units and the second inter-material bonding units comprise amide and carboxylate groups, respectively; and the first internal bonding units comprise  $\text{Ca}^{2+}$  and alginate.

**[0045]** In any one of the embodiments disclosed herein, the second polymer material comprises polyacrylic acid (PAA) and a plurality of second internal bonding units; and the second internal bonding units comprise acrylic acid.

**[0046]** In any one of the embodiments disclosed herein, the first polymer material and the second material are adhered to have an adhesion energy between the first polymer material and the second material is from about  $40 \text{ J/m}^2$  to about  $5000 \text{ J/m}^2$ .

**[0047]** In any one of the embodiments disclosed herein, where the composite material further includes an inter-material layer between the first material and the second material and comprising a tape, a powder, a brush, a solution, or an inter-material complex; wherein the first inter-material bonding units and the second inter-material bonding units are at least partially located in the inter-material layer.

**[0048]** In yet another aspect, a method of adhering a first material and a second material is disclosed, including:

providing a first material comprising a plurality of first inter-material bonding units, a plurality of first internal bonding units, and a plurality of first complementary internal bonding units;

providing a second material comprising a plurality of second inter-material bonding units; and

forming a plurality of inter-material non-covalent bonds between the plurality of first inter-material bonding units and the plurality of second inter-material bonding units to adhere the first material and the second material together;

wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and

wherein the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

**[0049]** In yet another aspect, a method of adhering a first material and a second material is disclosed, including:

providing a first material comprising a plurality of first internal bonding units and a plurality of first complementary internal bonding units;

providing a second material; and

adhering the first material and the second material together by topological adhesion or mechanical interlocking;

wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and

wherein the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

**[0050]** In any one of the embodiments disclosed herein, the second material comprises a plurality of second internal bonding units; the method further comprises forming a plurality of second intra-material bonds among the second internal bonding units; and the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the second intra-material bonds.

**[0051]** In any one of the embodiments disclosed herein, the second material comprises a plurality of second internal bonding units; the method further comprises forming a plurality of second intra-material bonds among the second internal bonding units; and the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the second intra-material bonds.

**[0052]** In any one of the embodiments disclosed herein, the first material and the second material are each independently selected from the group consisting of a polymers, nonporous inorganics, metal, metal alloy, ceramic, stone, concrete, asphalt, glass, silicon, wood, tissues, organs, arteries, vessels, bone, teeth, fabric, fibers, textiles, foam, plaster, paper, cardboard, fiberglass, semiconductors, biomaterials, composite materials, metamaterials, minerals, elemental materials, plant materials, adhesives, and a combination thereof.

**[0053]** In any one of the embodiments disclosed herein, the first material or the second material is a polymer material.

**[0054]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material are each independently selected from the group consisting of a hydrogel, an elastomer, a rubber, a plastic, and a biological polymer.

**[0055]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material comprises a hydrogel.

**[0056]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material are independently selected from the group consisting of poly(hydroxyethylmethacrylate) (HEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), poly(acrylic acid) (PAA), poly(lactic-co-glycolic acid) (PLGA), poly(ethylene glycol) (PEG), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) methacrylate (PEGMA), poly(ethylene glycol) dimethacrylate (PEGDMA), poly([2-(acryloyloxy)ethyl] trimethylammonium chloride) (PDMAEA), alginate, and chitosan, and a combination thereof.

**[0057]** In any one of the embodiments disclosed herein, the first polymer material or the second polymer material comprises a biological polymer.

**[0058]** In any one of the embodiments disclosed herein, the biological polymer is selected from the group consisting of polysaccharide, polypeptide, and polynucleotides, and a combination thereof.

**[0059]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are selected from the groups consisting of ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

**[0060]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are topological adhesion.

**[0061]** In any one of the embodiments disclosed herein, the first intra-material bonds are selected from the group consisting of covalent bonds, ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

**[0062]** In any one of the embodiments disclosed herein, the first intra-material bonds and second intra-material bonds are selected from the group consisting of covalent bonds, ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

**[0063]** In any one of the embodiments disclosed herein, the inter-material non-covalent bonds are hydrogen bonds and the first intra-material bonds or the second intra-material bonds are ionic bonds.

**[0064]** In any one of the embodiments disclosed herein, the adhesion energy between the first polymer material and the second material is from about 40 J/m<sup>2</sup> to about 5000 J/m<sup>2</sup>.

**[0065]** In any one of the embodiments disclosed herein, the first polymer material and the second material are adhered within about 1 second, 30 seconds, 1 minute, 10 minutes, 1 hour, 2 hours, 6 hours, 12 hours, 24 hours, 121 hours, and 1 month after contacting the first and second materials.

**[0066]** In any one of the embodiments disclosed herein, the method further includes providing an inter-material layer between the first material and the second material and comprising a tape, a powder, a brush, a solution, or an inter-material complex; wherein the first inter-material bonding units and the second inter-material bonding units are at least partially located in the inter-material layer.

**[0067]** Any aspect or embodiment disclosed herein may be combined with another aspect or embodiment disclosed herein. The combination of one or more embodiments described herein with other one or more embodiments described herein is expressly contemplated.

**[0068]** As used in one or more embodiments herein, the term “interweave” or “interwoven” can refer to the phenomena where two or more polymer chains or polymeric networks or a polymer chain and a polymeric network weave or become woven together. As used in one or more embodiments herein, the term “topological adhesion” or “topologically adhered” can refer to the phenomena where two or more polymer chains or polymeric networks or a polymer chain and a polymeric network weave or become woven together.

**[0069]** As used in one or more embodiments herein, the term “crosslink,” “crosslinker,” or “crosslinking agent” can refer to the first or second internal bonding units or the first or second complementary internal bonding units. As used in one or more embodiments herein, the term “toughener” may refer to the first or second internal bonding units. As used in one or more embodiments herein, the term “interlink” may refer to the plurality of inter-material non-covalent bonds. As used in one or more embodiments herein, the term “adherend” can refer to the second material. As used in one or more embodiments herein, the term “tough” can refer to the strength of the inter-material non-covalent bonds or the first and second inter-material non-covalent bonds.

**[0070]** Unless otherwise defined, used, or characterized herein, terms that are used herein (including technical and scientific terms) are to be interpreted as having a meaning that is consistent with their accepted meaning in the context of the relevant art and are not to be interpreted in an idealized or overly formal sense unless expressly so defined herein.

**[0071]** Although the terms, first, second, third, etc., may be used herein to describe various elements, these elements are not to be limited by these terms. These terms are simply used to distinguish one element from another. Thus, a first element, discussed below, could be termed a second element without departing from the teachings of the exemplary embodiments. Spatially relative terms, such as “above,” “below,” “left,” “right,” “in front,” “behind,” and the like, may be used herein for ease of description to describe the relationship of one element to another element, as illustrated in the figures. It will be understood that the spatially relative terms, as well as the illustrated configurations, are intended to encompass different orientations of the apparatus in use or operation in addition to the orientations described herein and depicted in the figures. For example, if the apparatus in the figures is turned over, elements described as “below” or “beneath” other elements or features would then be oriented “above” the other elements or features. Thus, the exemplary term, “above,” may encompass both an orientation of above and below. The apparatus may be otherwise oriented (*e.g.*, rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly. Further still, in this disclosure, when an element is referred to as being “linked to,” “on,” “connected to,” “coupled to,” “in contact with,” etc., another element, it may be directly linked to, on, connected to, coupled to, or in contact with the other element or intervening elements may be present unless otherwise specified.

**[0072]** The terminology used herein is for the purpose of describing particular embodiments and is not intended to be limiting of exemplary embodiments. As used herein, singular forms, such as “a” and “an,” are intended to include the plural forms as well, unless the context indicates otherwise. The term “about” as used herein describes a range of a recited value including  $\pm 10\%$ ,  $\pm 5\%$ , or  $\pm 2\%$  of the value. Additionally, the terms “includes,” “including,” “comprises,” and “comprising” specify the presence of the stated elements or steps but do not preclude the presence or addition of one or more other elements or steps.

## DESCRIPTION OF THE DRAWINGS

**[0073]** The invention is described with reference to the following figures, which are presented for the purpose of illustration only and are not intended to be limiting. In the Drawings:

**[0074]** FIG. 1A illustrates the principle of instant and tough adhesion between a first polymer material and a second material, according to one or more embodiments.

**[0075]** FIG. 1B illustrates the principle of instant and tough adhesion between a first polymer material and a second polymer material, according to one or more embodiments.

**[0076]** FIG. 1C shows an inter-material polymer layer in between the first and second polymer materials, according to one or more embodiments.

**[0077]** FIG. 1D shows an inter-material polymer layer in between the first and second polymer materials, according to one or more embodiments.

**[0078]** FIG. 1E shows a hydrogel adhering to another material (“adherend”), according to one or more embodiments.

**[0079]** FIG. 1F illustrates the principle of instant and tough adhesion between a first polymer material and a second polymer material, according to one or more embodiments.

**[0080]** FIG. 2A shows a 90-degree peel test according to one or more embodiments.

**[0081]** FIG. 2B shows force-displacement curves for a 90-degree peel test of a polyacrylic acid (PAA) hydrogel adhered to a liver sample, according to one or more embodiments.

**[0082]** FIG. 2C shows force-displacement curves for a 90-degree peel test of a polyacrylic acid (PAA) hydrogel adhered to a skin sample, according to one or more embodiments.

**[0083]** FIG. 2D shows force-displacement curves for a 90-degree peel test of a polyacrylic acid (PAA) hydrogel adhered to an artery sample, according to one or more embodiments.

**[0084]** FIG. 3A shows the adhesion energy between a polyacrylic acid (PAA) hydrogel and a polyacrylamide (PAAm) hydrogel as a function of contact time, according to one or more embodiments.

**[0085]** FIG. 3B shows the adhesion energy between a polyacrylic acid (PAA) hydrogel and a polyacrylamide (PAAm) hydrogel is insensitive to contact time when the pH of the hydrogels is the same, according to one or more embodiments.

**[0086]** FIG. 3C shows the adhesion energy between a polyacrylic acid (PAA) hydrogel and a polyacrylamide (PAAm) hydrogel decreases as the pH of the former increases, according to one or more embodiments.

[0087] FIG. 3D shows the adhesion energy between a polyacrylic acid (PAA) hydrogel and a polyacrylamide (PAAm) hydrogel is sensitive to temperature, according to one or more embodiments.

[0088] FIG. 3E shows the adhesion energy between a polyacrylic acid (PAA)-co-polyacrylamide (PAAm) hydrogel and a polyacrylamide (PAAm) hydrogel increases with the molar fraction of polyacrylic acid (PAA), according to one or more embodiments.

[0089] FIG. 3F shows the adhesion energy between a polyacrylic acid (PAA) hydrogel and a polyacrylamide (PAAm) hydrogel increases with the monomer-to-crosslinker ratio in the polyacrylic acid (PAA) hydrogel, according to one or more embodiments.

[0090] FIG. 3G shows the bulk toughness of the polyacrylic acid (PAA) hydrogel increases with the monomer-to-crosslinker ratio in the polyacrylic acid (PAA) hydrogel, according to one or more embodiments.

[0091] FIG. 3H shows the adhesion energy between a polyacrylic acid (PAA) hydrogel and a polyacrylamide (PAAm) hydrogel approaches a threshold value at vanishing peel velocity, according to one or more embodiments.

[0092] FIG. 3I shows cyclic adhering and detachment of a polyacrylic acid (PAA) hydrogel to/from a polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

[0093] FIG. 4A shows a loading profile of a stress-relaxation test for a polyacrylic acid (PAA) hydrogel, according to one or more embodiments.

[0094] FIG. 4B shows the nominal stress increases then relaxes to a stable level for a low and high crosslinked polyacrylic acid (PAA) hydrogel, according to one or more embodiments.

[0095] FIG. 5A shows that the adhesion energy between a polyacrylic acid (PAA) hydrogel and several other hydrogels is comparable to the bulk toughness of the hydrogel, according to one or more embodiments.

[0096] FIG. 5B shows adhesion energy between a polyacrylic acid (PAA) hydrogel and different tissues, according to one or more embodiments.

[0097] FIG. 5C shows the adhesion energy between a polyacrylic acid (PAA) hydrogel and different elastomers, according to one or more embodiments.

[0098] FIG. 5D shows the stability of the adhesion energy between a polyacrylic acid (PAA) hydrogel and Very High Bond elastomer, according to one or more embodiments.

[0099] FIG. 6A illustrates instant and tough non-covalent adhesion between a polyacrylic acid (PAA) hydrogel including un-crosslinked PAA chains and an alginate-polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

[0100] FIG. 6B shows the polyacrylic acid (PAA) hydrogel including un-crosslinked PAA chains and alginate-polyacrylamide (PAAm) hydrogel of FIG. 6A adhere within 30s, with an adhesion energy of above  $750 \text{ J/m}^2$ , according to one or more embodiments.

[0101] FIG. 6C shows the adhesion energy between the polyacrylic acid (PAA) hydrogel including un-crosslinked PAA chains and alginate-polyacrylamide (PAAm) hydrogel of FIG. 6A depends on the concentration of calcium in the alginate-polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

[0102] FIG. 6D shows the adhesion energy between the polyacrylic acid (PAA) hydrogel including un-crosslinked PAA chains and alginate-polyacrylamide (PAAm) hydrogel of FIG. 6A can be tuned by varying the amount of uncrosslinked polyacrylic acid (PAA) chains in the polyacrylic acid (PAA) hydrogel, according to one or more embodiments.

[0103] FIG. 7A photographically illustrates different topologies of instant and/or tough non-covalent adhesion, according to one or more embodiments.

[0104] FIG. 7B schematically illustrates different topologies of instant and/or tough non-covalent adhesion, according to one or more embodiments.

[0105] FIG. 7C shows the adhesion energy for each topology of FIGS. 7A and 7B, according to one or more embodiments.

[0106] FIG. 8 shows microgel powders and the fabrication thereof, according to one or more embodiments.

[0107] FIG. 9A shows functionalization of polydimethylsiloxane (PDMS) with covalently grafted polyacrylic acid (PAA) chains, according to one or more embodiments.

[0108] FIG. 9B shows adhesion between polyacrylic acid (PAA)-grafted polydimethylsiloxane (PDMS) and a polyacrylamide (PAAm) hydrogel depends on the concentration of the acrylic acid monomer during grafting, according to one or more embodiments.

[0109] FIG. 10A shows a polyacrylic acid (PAA)-grafted elastomer adhering to an alginate-polyacrylamide (PAAm) hydrogel through hydrogen bonds, according to one or more embodiments.

[0110] FIG. 10B shows the adhesion energy between alginate-polyacrylamide (PAAm) hydrogel of FIG. 10A and different elastomers, according to one or more embodiments.

[0111] FIG. 11A shows a polyacrylic acid (PAA)-grafted rubber adhering a polyacrylamide (PAAm)-grafted rubber through hydrogen bonds, according to one or more embodiments.

[0112] FIG. 11B shows that instant adhesion only occurred between the polyacrylic acid (PAA) brush-grafted rubber and the polyacrylamide (PAAm) hydrogel-grafted rubber of FIG. 11A, according to one or more embodiments.

[0113] FIG. 12 shows the adhesion energy between two polyacrylamide (PAAm) hydrogels through polyacrylic acid (PAA) solution adhesion of FIGS. 7A and 7B as a function of the molecular weight of the polyacrylic acid (PAA) chains, according to one or more embodiments.

[0114] FIG. 13 illustrates the principle of tough adhesion between an adhesive double-network hydrogel and a second double-network polymer material, according to one or more embodiments.

[0115] FIG. 14 illustrates a method for synthesis of a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel, according to one or more embodiments.

[0116] FIG. 15A shows a stress-stretch curve of a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel, according to one or more embodiments.

[0117] FIG. 15B shows a stress-stretch curve of a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

[0118] FIG. 15C shows the shear modulus and water concentration of a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel and a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel, according to one or more embodiments.

[0119] FIG. 15D shows toughness measurements of a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel and a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel, according to one or more embodiments.

[0120] FIG. 16A illustrates a notched hydrogel sample subjected to a monotonic stretch, according to one or more embodiments.

[0121] FIG. 16B illustrates an un-notched hydrogel sample subjected to a monotonic stretch, according to one or more embodiments.

[0122] FIG. 16C shows a stress-stretch curve of a notched poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

**[0123]** FIG. 16D illustrates that the fracture toughness equals the product of the area enclosed by the stress-stretch curve of an un-notched poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel at the stretch limit  $\lambda_c$ , according to one or more embodiments.

**[0124]** FIG. 16E shows a stress-stretch curve of a notched poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel, according to one or more embodiments.

**[0125]** FIG. 16F shows a stress-stretch curve of an un-notched poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel, according to one or more embodiments.

**[0126]** FIG. 17A illustrates an experimental setup of a 90-degree peel test, according to one or more embodiments.

**[0127]** FIG. 17B compares the adhesion energy between a poly(acrylic acid) (PAA) hydrogel and a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel and the adhesion energy between a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel and a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

**[0128]** FIG. 17C shows force-displacement curves of adhesion between a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–poly(acrylic acid) (PAA) hydrogel and a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

**[0129]** FIG. 17D shows force-displacement curves of adhesion between a poly(acrylic acid) (PAA) hydrogel and a poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)–polyacrylamide (PAAm) hydrogel, according to one or more embodiments.

## DETAILED DESCRIPTION

**[0130]** Adhesion of two materials can occur rapidly, for example, through relatively instant formation of noncovalent or covalent bonds. Adhesion of two materials can be tough (i.e., strong), for example, when the bonds between the materials are strong enough to unzip the bonds within the materials (e.g., tougheners) to dissipate energy. When this dissipation effect is absent, the force can lead to destruction of the bonds between the materials and the adhesion is weak. For example, pulling apart two pieces of superglued plastic can result in breakage of each

piece and the adhesion is tough (i.e., strong), while pulling apart two pieces of plastic without superglue donot result in breakage of each piece and the adhesion is weak. There is an unmet need for adhesion that is both instant and tough enough to withstand repeated forces. A non-limiting area that would benefit from such instant and tough adhesion is wound closure, where the wound needs to be closed fast and in a manner that does not lead to damage of the surrounding tissue in response to the forces that can result from normal tissue function or bodily motion.

**[0131]** In some embodiments, as a solution to this unmet need, the inventors surprisingly found that combining an inter-material bonding network (e.g., “interlinks”; between two materials) with an intra-material bonding network (e.g., “tougheners”; within one or both materials) enables instant adhesion when (1) the bonds are capable of forming instantly (e.g., less than about one second) and (2) the plurality of inter-material bonds are stronger than the plurality of intra-material bonds. In some embodiments, when a force acts on the composite material, the intra-material bonds break before the inter-material bonds break as the force propagates to the separation front through the material, thus preserving the integrity of the composite material and the adhesion between each material. In some embodiments, when a force acts on the composite material, the some of the intra-material bonds break but then can optionally reform, thus preserving the integrity of each material.

**[0132]** In one aspect, a composite material is disclosed, including a first material and a second material. In some embodiments, the first material includes a plurality of first inter-material bonding units, a plurality of first internal bonding units, and a plurality of first complementary internal bonding units. In some embodiments, the composite material includes a second material. In some embodiments, the second material includes a plurality of second inter-material bonding units. In some embodiments, the plurality of first inter-material bonding units and the plurality of second inter-material bonding units form a plurality of inter-material non-covalent bonds to adhere the first material and the second material together. In some embodiments, the plurality of first internal bonding units form a plurality of first intra-material covalent or non-covalent bonds with the plurality of first complementary internal bonding units. In some embodiments, the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of first intra-material covalent or non-covalent bonds.

**[0133]** Non-limiting examples of the first material and the second material include polymers (e.g., acrylic, polyethylene terephthalate, biopolymers), nonporous inorganics, metal, metal

alloy, rubber, elastomer, ceramic, stone, concrete, asphalt, glass, silicon, plastics, hydrogels, wood, tissues, organs, arteries, vessels, bone, teeth, fabric, fibers, textiles, foam, plaster, paper, cardboard, fiberglass, semiconductors, biomaterials, composite materials, metamaterials, minerals, elemental materials, plant materials, and adhesives. In some specific embodiments, the first or second material is a polymer material. In some specific embodiments, the first material is a polymer material and the second material is selected from the group consisting of metal, metal alloy, rubber, elastomer, ceramic, stone, concrete, asphalt, glass, silicon, plastics, hydrogels, wood, tissues, organs, arteries, vessels, bone, teeth, fabric, fibers, textiles, foam, plaster, paper, cardboard, fiberglass, semiconductors, biomaterials, composite materials, metamaterials, minerals, elemental materials, and plant materials. In some specific embodiments, both the first and second materials are a polymer material.

**[0134]** As shown in FIG. 1A, in one embodiment, a composite material 100 is disclosed, including a first polymer material 102. In some embodiments, the first polymer material 102 includes a plurality of first inter-material bonding units 104, a plurality of first internal bonding units 106, and a plurality of first complementary internal bonding units 108. In some embodiments, the composite material 100 includes a second material 110, which can be a polymer or non-polymer material. In some embodiments, the second material 110 includes a polymer. In some embodiments, the second material 110 includes a plurality of second inter-material bonding units 112. In some embodiments, the plurality of first inter-material bonding units 104 and the plurality of second inter-material bonding units 112 form a plurality of inter-material non-covalent bonds 114 to adhere the first polymer material 102 and the second polymer material 110 together. In some embodiments, the plurality of first internal bonding units 106 form a plurality of first intra-material bonds 116 with the plurality of first complementary internal bonding units 108. In some embodiments, the plurality of first intra-material bonds 116 include non-covalent bonds. In other embodiments, the plurality of first intra-material bonds 116 include covalent bonds. In some embodiments, the combined bonding strength of the plurality of the inter-material non-covalent bonds 114 is stronger than the combined bonding strength of the plurality of first intra-material bonds 116.

**[0135]** In some embodiments, some portion of the plurality of first polymer chains 118 in the first polymer material 102 can be crosslinked together by a first crosslinking unit 120. In these embodiments, the first crosslinking unit 120 can be a covalent crosslinking unit.

**[0136]** As shown in FIG. 1B, in some embodiments, the second material 110 is a polymer material and includes a plurality of second internal bonding units 122 and a plurality of second

complementary internal bonding units 124. In some embodiments, the plurality of second internal bonding units 122 form a plurality of second intra-material bonds 126 by bonding with the plurality of second complementary internal bonding units 124. In some embodiments, the plurality of second intra-material bonds 126 include non-covalent bonds. In other embodiments, the plurality of second intra-material bonds 126 include covalent bonds. In some embodiments, the combined bonding strength of the plurality of the inter-material non-covalent bonds 114 is stronger than the combined bonding strength of the plurality of the second intra-material bonds 126.

**[0137]** In some embodiments, some portion of the plurality of second polymer chains 128 in the second polymer material 110 can be crosslinked together by a second crosslinking unit 130. In these embodiments, the second crosslinking unit 130 can be a covalent crosslinking unit.

**[0138]** In some embodiments, the plurality of first inter-material bonding units 104 and plurality of second inter-material bonding units 112 are different from the plurality of first internal bonding units 106, the plurality of first complementary internal bonding units 108, the plurality of second internal bonding units 122, and the plurality of second complementary internal bonding units 124. In these embodiments, a stress can be produced when a force 132 (*see, e.g.*, FIGS. 1A and 1B) is applied to the composite material 100 to separate the first and second materials. In these embodiments, such stress can be relieved by separation of at least a portion of the plurality of first intra-material bonds 116 and/or at least a portion of the plurality of second intra-material bonds 126. Applicants have surprisingly found that, in these embodiments, because the combination of the plurality of inter-material non-covalent bonds 114 are stronger than the combination of the plurality of the first and/or the second intra-material bonds, at least a portion of the plurality of the first and/or the second intra-material bonds will de-bond first, thus releasing the stress caused by the separation force and still maintaining the strong adhesion between the first and the second materials. Strong adhesion between the first polymer material 102 and the second material 110 is enabled, at least in part, by these embodiments.

**[0139]** In some embodiments, the inter-material bonds 114 are reversible. Therefore, even after the inter-material are de-bonded by a force (*e.g.*, 132 in FIGS. 1A-1B), the inter-material bonds can reform. In some embodiments, the first intra-material bonds or the second intra-material bonds are reversible. Therefore, even after the first intra-material bonds or the second intra-material bonds are de-bonded by a force (*e.g.*, 132 in FIGS. 1A-1B), the first or the second intra-material bonds can reform so as to maintain the integrity of the first polymer material 102

or the second material 110, respectively. The non-brittle nature of the first polymer material 102 and the second material 110 can be enabled, at least in part, by these embodiments.

**[0140]** As shown in FIGS. 1C and 1D, in some embodiments, the composite material 100' further includes an inter-material polymer layer 134 between the first polymer material 102' and the second polymer material 110'. In FIGS. 1C and 1D, a covalent bond is represented by a filled dot, a non-covalent bond by a half-filled dot, a polymer chain by a line, and a polymer material by an open circle. In some embodiments, the plurality of first inter-material bonding units and the plurality of second inter-material bonding units are at least partially located in the inter-material polymer layer 134. In some embodiments, the plurality of inter-material non-covalent bonds 114' form between the first polymer material 102' and the inter-material polymer layer 134, *e.g.*, by the plurality of first inter-material bonding units and the plurality of second inter-material bonding units. In some embodiments, the plurality of inter-material non-covalent bonds 114' form between the second polymer material 110' and the inter-material polymer layer 134. In some embodiments, the inter-material polymer layer 134 is in the form of a tape, a powder, a brush, a solution, or an interpolymer complex, each of which includes at least a portion of the plurality of first inter-material bonding units and the plurality of second inter-material bonding units.

**[0141]** In another aspect, a method of adhering a first material and a second material is disclosed. In some embodiments, the method includes providing a first material, which includes a plurality of first inter-material bonding units, a plurality of first internal bonding units, and a plurality of first complementary internal bonding units. In some embodiments, the method also includes providing a second material. In some embodiments, the second material includes a plurality of second inter-material bonding units. In some embodiments, the plurality of first inter-material bonding units and the plurality of second inter-material bonding units form a plurality of inter-material non-covalent bonds to adhere the first material and the second material together. In some embodiments, the plurality of first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units. In some embodiments, the plurality of first intra-material bonds include non-covalent bonds. In some embodiments, the plurality of first intra-material bonds include covalent bonds. In some embodiments, the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

**[0142]** In another embodiment, a method of adhering a first polymer material 102 and a second polymer or non-polymer material 110 is disclosed. In some embodiments, the second material 110 includes a polymer. In some embodiments, the method includes providing a first polymer material 102, which includes a plurality of first inter-material bonding units 104, a plurality of first internal bonding units 106, and a plurality of first complementary internal bonding units 108. In some embodiments, the method also includes providing a second material 110. In some embodiments, the second material 110 includes a plurality of second inter-material bonding units 112. In some embodiments, the plurality of first inter-material bonding units 104 and the plurality of second inter-material bonding units 112 form a plurality of inter-material non-covalent bonds 114 to adhere the first polymer material 102 and the second material 110 together. In some embodiments, the plurality of first internal bonding units 106 form a plurality of first intra-material bonds 116 by bonding with the plurality of first complementary internal bonding units 108. In some embodiments, the plurality of first intra-material bonds 116 include non-covalent bonds. In some embodiments, the plurality of first intra-material bonds 116 include covalent bonds. In some embodiments, the combined bonding strength of the plurality of the inter-material non-covalent bonds 114 is stronger than the combined bonding strength of the plurality of the first intra-material bonds 116.

**[0143]** In some embodiments, the plurality of first polymer chains 118 that make up the first polymer material 102 are crosslinked together by a first crosslinking unit 120.

**[0144]** In some embodiments, as shown in FIG. 1B, the second material 110 includes a polymer and a plurality of second internal bonding units 122 and a plurality of second complementary internal bonding units 124. In some embodiments, the plurality of second internal bonding units 122 form a plurality of second intra-material bonds 126 by bonding with the plurality of second complementary internal bonding units 124. In some embodiments, the plurality of second intra-material bonds 126 include non-covalent bonds. In some embodiments, the plurality of second intra-material bonds 126 include covalent bonds. In some embodiments, the combined bonding strength of the plurality of the inter-material non-covalent bonds 114 is stronger than the combined bonding strength of the plurality of the second intra-material bonds 126.

**[0145]** In some embodiments, the first internal bonding units 106, the first complementary internal bonding units 108, the second internal bonding units 122, or the second complementary internal bonding units 124 can include a crosslinking agent. In these embodiments, the crosslinking agent can be a covalent crosslinking agent.

**[0146]** In some embodiments, as shown in FIG. 1F, the composite material 100 may include a first polymer material 102 and second polymer material 110. In some embodiments, the second polymer chains 118' of the first polymer material 102 and the fourth polymer chains 128' of the second polymer material 110 may be the same or different hydrogels. In some embodiments, the first polymer material 102 may include a plurality of the first polymer chains 118 and the second polymer chains 118'. In some embodiments, the first polymer chains 118 are longer than the second polymer chains 118'. In some embodiments, the first polymer chains 118 include a plurality of first inter-material bonding units 104. In some embodiments, some portion of the plurality of the first polymer chains 118 in the first polymer material 102 can be crosslinked together by a first covalent crosslinking unit 116. In these embodiments, the first crosslinking unit 116 can be a covalent crosslinking unit. In some embodiments, the second polymer material 110 may include a plurality of the third polymer chains 128 and the fourth polymer chains 128'. In some embodiments, the third polymer chains 128 are longer than the fourth polymer chains 128'. In some embodiments, the third polymer chains 128 include a plurality of second inter-material bonding units 112. In some embodiments, some portion of the plurality of the third polymer chains 128 in the second polymer material 110 can be crosslinked together by a second covalent crosslinking unit 126. In these embodiments, the first crosslinking unit 116 can be a covalent crosslinking unit. In some embodiments, the crosslinked first polymer chains 118 in the first polymer material 102 and the crosslinked third polymer chains 128 in the second polymer material 110 may be the same or different hydrogels. In some embodiments, the first inter-material bonding units 104 and second inter-material bonding units 112 together form a plurality of inter-material non-covalent bonds 114. In some embodiments, the combined bonding strength of the plurality of the inter-material non-covalent bonds 114 is stronger than the bonding strength of the plurality of the second polymer chains 118' and/or the fourth polymer chains 128'. Without wishing to be bound by any one theory, this preserves the integrity of the composite material 100 when a force 132 acts upon it. That is, one or more of the plurality of the inter-material non-covalent bonds 114 can de-bond in response to the force 132, and then re-bond after the force ceases, leaving the composite material 100 substantially intact. In certain embodiments, one or more of the plurality of the second polymer chains 118' and/or the fourth polymer chains 128' can break in response to the force 132, and then optionally re-bond after the force ceases, leaving each material substantially intact.

#### **Cross-Linking Agents**

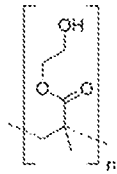
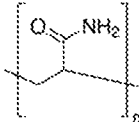
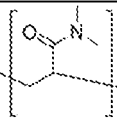
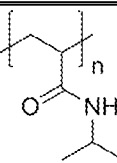
[0147] In some embodiments, the first crosslinking unit 116 and the second crosslinking unit 126 are each independently selected from the group consisting of *N,N'*-methylenebisacrylamide (MBAA), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) dimethacrylate (PEGDMA), and 3-(trimethoxysilyl) propyl methacrylate (TMSPMA).

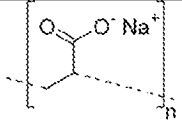
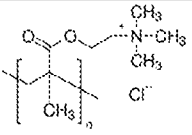
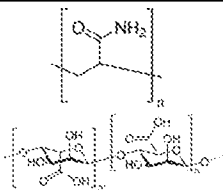
#### First Polymer Material and Second Polymer Material

[0148] In some embodiments, the first polymer material 102 and the second polymer material 110 are each independently selected from the group consisting of a hydrogel, an elastomer, and a biological polymer.

[0149] In some embodiments, the first, second, third, and/or fourth polymer network is a hydrogel. Non-limiting examples of hydrogels include poly(hydroxyethylmethacrylate) (HEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), poly(acrylic acid) (PAA), poly(lactic-co-glycolic acid) (PLGA), poly(ethylene glycol) (PEG), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) methacrylate (PEGMA), poly(ethylene glycol) dimethacrylate (PEGDMA), poly([2-(acryloyloxy)ethyl] trimethylammonium chloride) (PDMAEA), poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), alginate, chitosan, and a combination thereof. Additional non-limiting examples of hydrogels include those listed in Table 1. As used herein, PAAm and PAAM are used interchangeably.

Table 1. Non-Limiting Examples of Hydrogels

| Polymer chain of hydrogel                        | Molecular structure                                                                 | Charges on polymer chains |
|--------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------|
| Poly(hydroxyethylmethacrylate)<br>(HEMA)         |  | Neutral                   |
| Poly(acrylamide)<br>(PAAm)                       |  | Neutral                   |
| Poly(dimethylacrylamide)<br>(PDMA)               |  | Neutral                   |
| Poly( <i>N</i> -isopropylacrylamide)<br>(PNIPAM) |  | Neutral                   |

| Polymer chain of hydrogel                                        | Molecular structure                                                               | Charges on polymer chains  |
|------------------------------------------------------------------|-----------------------------------------------------------------------------------|----------------------------|
| Sodium polyacrylate<br>(NaPAA)                                   |  | Negatively charged         |
| [2-(Acryloyloxyethyl)]<br>trimethylammonium chloride<br>(PDMAEA) |  | Positively charged         |
| Polyacrylamide/alginate                                          |  | Neutral/negatively charged |

**[0150]** In some embodiments, the hydrogel has a toughness of about 100 to about 5000 J/m<sup>2</sup>. In some embodiments, the hydrogel has a toughness of about 500 to about 5000 J/m<sup>2</sup>. In some embodiments, the hydrogel has a toughness of about 1000 to about 5000 J/m<sup>2</sup>. In some embodiments, the hydrogel has a toughness of about 3000 to about 5000 J/m<sup>2</sup>. In some embodiments, the hydrogel has a toughness of about 5000 to about 9000 J/m<sup>2</sup>. In some embodiments, the hydrogel has a toughness of about 100, 200, 500, 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000 or 9000 J/m<sup>2</sup>, or has a toughness in a range bounded by any two toughness values described herein.

**[0151]** In some embodiments, the first polymer material or the second polymer material is an elastomer. Non-limiting examples of elastomers include natural rubber, styrene butadiene rubber, polybutadiene rubber, silicone rubber, polyurethane, Very High Bond™, Dragon Skin® 20, and Ecoflex™ 00-30, and a combination thereof.

**[0152]** In some embodiments, the first polymer material or the second polymer material is a biological polymer. Non-limiting examples of biological polymers include polysaccharide, polypeptide, and polynucleotides, and a combination thereof.

**[0153]** In some embodiments, the first polymer material 102 or the second polymer material 110 is a component of the body of a subject. In some embodiments, the subject is a human or an animal. In some embodiments, the first polymer material 102 is a tissue or an organ. In some embodiments, the second polymer material 110 is a tissue or an organ. Non-limiting examples of tissues or organs include liver, skin, heart, and artery, and a combination thereof.

#### **Inter-Material and Intra-Material Bonds**

**[0154]** In some embodiments, the inter-material non-covalent bonds 114 are each independently selected from the group consisting of ionic bonds, hydrogen bonds, van der Waals

interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, topological adhesions, and a combination thereof. In some embodiments, the inter-material non-covalent bonds 114 are each independently selected from the group consisting of ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

**[0155]** In some embodiments, the first intra-material bonds and the second intra-material bonds are each independently selected from the group consisting of covalent bonds, ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, topological adhesions, and a combination thereof.

**[0156]** In some embodiments, the first intra-material bonds are covalent bonds. In some embodiments, the second intra-material bonds are covalent bonds. Non-limiting examples of covalent bonds include  $\sigma$ -bonding,  $\pi$ -bonding, metal-to-metal bonding, agnostic interactions, bent bonds, and three-center two-electron bonds.

**[0157]** In some embodiments, the inter-material non-covalent bonds are ionic bonds. In some embodiments, the first intra-material bonds are ionic bonds. In some embodiments, the second intra-material bonds are ionic bonds. Non-limiting examples of ionic bonds include metal cation-carboxylate bonds, ammonium carboxylate bonds, and a combination thereof.

**[0158]** In some embodiments, the inter-material non-covalent bonds 114 are hydrogen bonds. In some embodiments, the first intra-material bonds are hydrogen bonds. In some embodiments, the second intra-material bonds are hydrogen bonds. Non-limiting examples of hydrogen bonds include carboxylic acid and hydroxyl hydrogen bonds, amine and hydroxyl hydrogen bonds, amine and carboxyl hydrogen bonds, amide and carboxyl hydrogen bonds, carboxyl and carboxyl hydrogen bonds, hydroxyl and hydroxyl hydrogen bonds, amine and phenol hydrogen bonds, and a combination thereof.

**[0159]** In some embodiments, the first and materials are adhered together by topological adhesions. In some embodiments, the topological adhesions are covalent topological adhesions. In other embodiments, the topological adhesions are non-covalent topological adhesions. In other embodiments, the first and materials are adhered together by mechanical interlocking. In some embodiments, the strength of the topological adhesions is stronger than the combined bonding strength of the plurality of the first intra-material bonds. In some embodiments, the strength of the mechanical interlocking is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

**[0160]** In some embodiments, the inter-material non-covalent bonds 114 are van der Waals interactions. In some embodiments, the first intra-material bonds are van der Waals interactions.

In some embodiments, the second intra-material bonds are van der Waals interactions. Non-limiting examples of van der Waals interactions include dipole-dipole interactions, dipole-induced dipole interactions, hydrophobic interactions, London dispersion forces, and a combination thereof.

**[0161]** In some embodiments, the inter-material non-covalent bonds 114 are  $\pi$ - $\pi$  stackings. In some embodiments, the first intra-material bonds are  $\pi$ - $\pi$  stackings. In some embodiments, the second intra-material bonds are  $\pi$ - $\pi$  stackings. Non-limiting examples of  $\pi$ - $\pi$  stackings include  $\pi$ - $\pi$  interactions, cation- $\pi$  interactions, anion- $\pi$  interactions, polar- $\pi$  interactions, and a combination thereof.

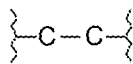
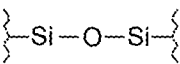
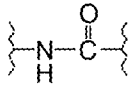
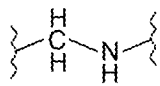
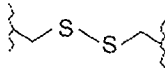
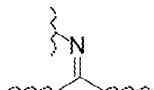
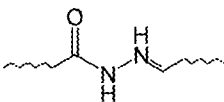
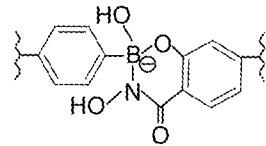
**[0162]** In some embodiments, the inter-material non-covalent bonds 114 are host-guest interactions. In some embodiments, the first intra-material bonds are host-guest interactions. In some embodiments, the second intra-material bonds are host-guest interactions. Non-limiting examples of host-guest interactions include cyclodextrin-adamantane, cucurbit[7]uril-aminomethylferrocene, and a combination thereof.

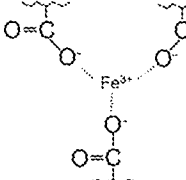
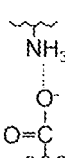
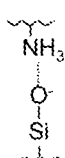
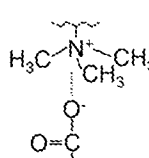
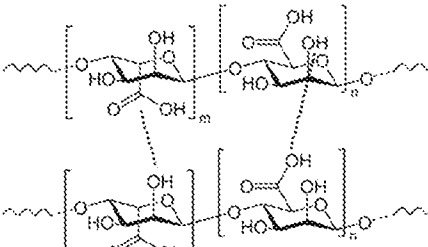
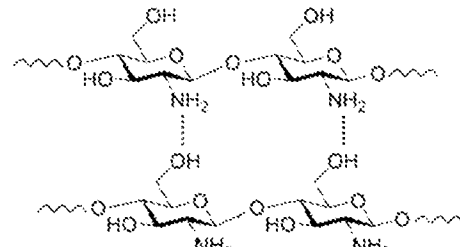
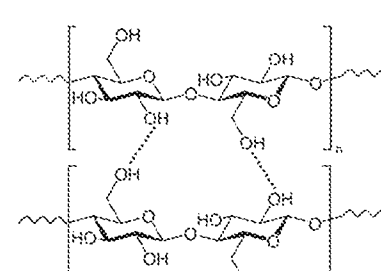
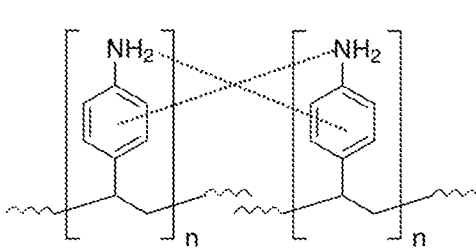
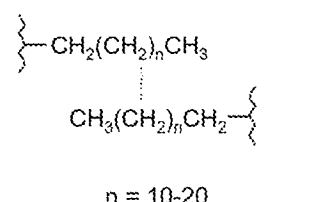
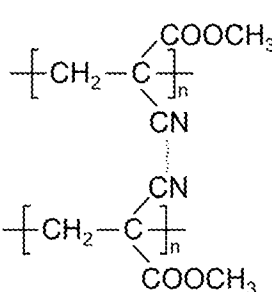
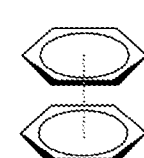
**[0163]** In some embodiments, the inter-material non-covalent bonds are hydrogen bonds and the first intra-material bonds are ionic bonds.

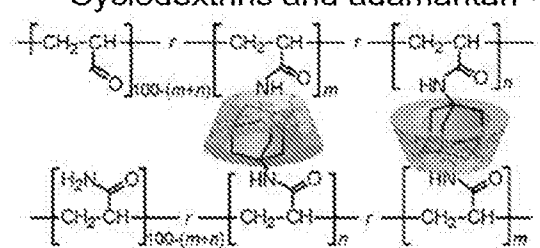
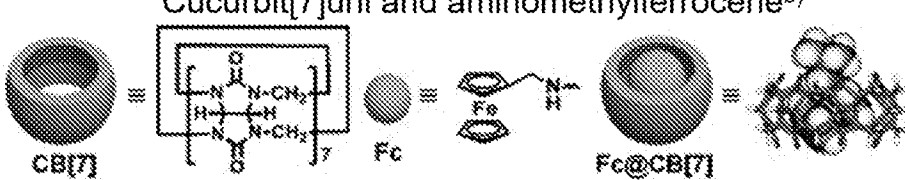
**[0164]** In some embodiments, the inter-material non-covalent bonds are hydrogen bonds and the first or second intra material bonds are ionic bonds.

**[0165]** Additional non-limiting examples of covalent or noncovalent bonds for the inter-material non-covalent bonds, the first intra-material bonds (covalent or noncovalent), and the second intra-material bonds (covalent or noncovalent) are listed in Table 2.

Table 2. Non-Limiting Examples of Bonds According to One or More Embodiments

| Bond types             | Representative bonds                                                                |                                                                                     |                                                                                      |                                                                                       |
|------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Static covalent bonds  | Carbon-carbon bond                                                                  | Siloxane bond                                                                       | Amide bond                                                                           | Carbon-nitrogen bond                                                                  |
|                        |  |  |  |  |
| Dynamic covalent bonds | Disulfide bond                                                                      | Imine bond                                                                          | Acylhydrazone bond                                                                   | Phenylboronate ester complexations                                                    |
|                        |  |  |  |  |

| Bond types                     | Representative bonds                                                                                                                         |                                                                                                        |                                                                                                                                    |                                                                                                                   |
|--------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| Ionic bonds                    | Iron-carboxylate coordination complex<br>                   | Amine-carboxylate<br> | Amine-silanol<br>                               | Tertiary amine-carboxylate<br> |
| Hydrogen bonds                 | Carboxylic acid and hydroxyl<br>                            |                                                                                                        | Amine and hydroxyl<br>                           |                                                                                                                   |
|                                | Hydroxyl and hydroxyl<br>                                  |                                                                                                        | Amine and phenol<br>                            |                                                                                                                   |
| Other noncovalent interactions | Hydrophobic interaction (alkyl chains)<br><br>$n = 10-20$ |                                                                                                        | Dipole-dipole interaction (nitrile groups)<br> |                                                                                                                   |
|                                | $\pi$ - $\pi$ stack (phenyl groups)<br>                 |                                                                                                        |                                                                                                                                    |                                                                                                                   |

| Bond types | Representative bonds                                                                                                                                                                                                                                                                                                                                                                                                       |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|            | <p style="text-align: center;"><b>Host-guest interaction</b></p> <p style="text-align: center;"><b>Cyclodextrins and adamantane<sup>a)</sup></b></p>  <p style="text-align: center;"><b>Cucurbit[7]uril and aminomethylferrocene<sup>b)</sup></b></p>  |

### Inter-Material and Intra-Material Bonding Units

**[0166]** In some embodiments, the first inter-material bonding units 104, the second inter-material bonding units 112, the first internal bonding units 106, the first complementary internal bonding units 108, the second internal bonding units 122, and the second complementary internal bonding units 124 are each independently selected from the group consisting of ions. Non-limiting examples of ions include  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NR}_4^+$ ,  $\text{OH}^-$ ,  $\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ , and a combination thereof, where R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.

**[0167]** In some embodiments, the first inter-material bonding units 104, the second inter-material bonding units 112, the first internal bonding units 106, the first complementary internal bonding units 108, the second internal bonding units 122, and the second complementary internal bonding units 124 are each independently selected from the group consisting of alkyl, aryl, heteroalkyl, heteroaryl, halo, and a combination thereof.

**[0168]** In some embodiments, the first inter-material bonding units 104, the second inter-material bonding units 112, the first internal bonding units 106, the first complementary internal bonding units 108, the second internal bonding units 122, and the second complementary internal bonding units 124 are each independently selected from the group consisting of OH, SH, COOH,  $\text{NH}_2$ , NHR, alkyl, heteroalkyl, haloalkyl, halo, siloxy, silyl, imino, acylhydrazone, phenylboronate ester, aryl, heteroaryl, haloaryl, cyano, phenyl, cyclodextryl, adamantyl, ferrocenyl, aminomethylferrocenyl, cucurbit[7]uril, and a combination thereof, where R is independently H, alkyl, haloalkyl, aryl, or heteroaryl. In some embodiments, the first inter-

material bonding units 104, the second inter-material bonding units 112, the first internal bonding units 106, the first complementary internal bonding units 108, the second internal bonding units 122, and the second complementary internal bonding units 124 are each independently selected from the group consisting of OH, SH, COOH, NH<sub>2</sub>, NHR, and a combination thereof, where R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.

**[0169]** In some embodiments, the first polymer material 102 is polyacrylamide (PAAm); the first inter-material bonding units 104 include amide groups and the second inter-material bonding units 112 include carboxylate groups, respectively, and vice versa; and the first internal bonding units 106 and the first complementary internal bonding units 108 include Ca<sup>2+</sup> and alginate, respectively, and vice versa. In some embodiments, the first polymer material 102 is polyacrylamide (PAAm); the first inter-material bonding units 104 include amide groups and the second inter-material bonding units 112 include carboxylate groups, respectively, and vice versa; the first internal bonding units 106 and the first complementary internal bonding units 108 include Ca<sup>2+</sup> and alginate, respectively, and vice versa; the second polymer material 110 includes polyacrylic acid (PAA) and a plurality of second internal bonding units 122 and a plurality of second complementary internal bonding units 124.

**[0170]** As described herein, in some embodiments, the combined strength of the plurality of inter-material non-covalent bonds 114 is stronger than the combined strength of the plurality of the first and/or second intra-material bonds. In these embodiments, the strength of each inter-material non-covalent bond 114 can be greater than the strength of each of the first and/or second intra-material bond, where number of inter-material non-covalent bonds 114 is about same as or greater than the number of the first and/or second intra-material bonds. In other embodiments, the strength of each inter-material non-covalent bond 114 can be lower than the strength of each of the first and/or second intra-material bonds, but the number of inter-material non-covalent bonds 114 is greater than the number of the first and/or second intra-material bonds.

### **Adhesion Properties**

**[0171]** In some embodiments, the adhesion energy between the first polymer material 102 and the second material 110 is from about 40 J/m<sup>2</sup> to about 1000 J/m<sup>2</sup>. In some embodiments, the adhesion energy between the first polymer material 102 and the second material 110 is from about 40 J/m<sup>2</sup> to about 500 J/m<sup>2</sup>. In some embodiments, the adhesion energy between the first polymer material 102 and the second material 110 is from about 40 J/m<sup>2</sup> to about 200 J/m<sup>2</sup>. In some embodiments, the adhesion energy between the first polymer material 102 and the second

material 110 is from about 40 J/m<sup>2</sup> to about 1000 J/m<sup>2</sup>. In some embodiments, the adhesion energy between the first polymer material 102 and the second material 110 is about 40, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 2000, 3000, 4000, or 5000 J/m<sup>2</sup>, or in a range bounded by any two values disclosed herein.

**[0172]** In some embodiments, the first polymer material 102 and the second material 110 adhere together in less than 1 second to about 120 seconds. In some embodiments, the first polymer material 102 and the second material 110 adhere together in less than about 30 seconds.

**[0173]** In some embodiments, the inter-material non-covalent bonds 114 form in less than 1 second to about 120 seconds. In some embodiments, the inter-material non-covalent bonds 114 form in less than 1 second to about 30 seconds. In some embodiments, the inter-material non-covalent bonds 114 form in less than about 30 seconds. In some embodiments, the inter-material non-covalent bonds 114 form in less than about 1 second.

**[0174]** In some embodiments, the inter-material non-covalent bonds, the first intra-material bonds, or the second intra-material bonds are independently or collectively permanent, transient, or reversible. In some embodiments, the inter-material non-covalent bonds, the first intra-material bonds, or the second intra-material bonds form or de-bond in response to a stimulus. Non-limiting examples of the stimulus include pH, salt, solvents, temperature, light, and a combination thereof. In some embodiments, the inter-material non-covalent bonds, the first intra-material bonds, or the second intra-material bonds form or de-bond in the absence of a stimulus.

**[0175]** In some embodiments, the adhesion energy between the first polymer material 102 and the second material 110 is stable for greater than about 100 cycles of forming and de-bonding the inter-material non-covalent bonds, the first intra-material bonds, or the second intra-material bonds.

## EXAMPLES

**[0176]** In some embodiments, noncovalent adhesion can be advantageous because it can form without catalysts, at room temperature, instantly. In some embodiments, it can also be made nontoxic, reversible, and on-demand detachable. In some embodiments, noncovalent adhesion can be useful for wet materials, such as synthetic hydrogels and living tissues. However, in these embodiments, noncovalent adhesion has low adhesion energy, about 1-10 J/m<sup>2</sup>. In some embodiments, the adhesion energy can be about 10 to about 100 J/m<sup>2</sup>. In some embodiments, a type of noncovalent adhesion, topological adhesion, can be as tough as covalent

adhesion (adhesion energy above 1000 J/m<sup>2</sup>) but forms slowly—on a timescale not useful for time-sensitive applications, such as wound closure.

**[0177]** According to one or more exemplary embodiments described herein, noncovalent adhesion can be both instant and tough (“strong”). In some embodiments, this principle is illustrated for a material (*e.g.*, a hydrogel) adhering to another material (“adherend”) through noncovalent bonds (“interlinks”) (*e.g.*, FIGS. 1A-1C). For example, in some embodiments the hydrogel has a polymer network which is interconnected by covalent bonds (“crosslinks”) and noncovalent bonds (“tougheners”). In some embodiments, brittle noncovalent adhesion can result when similar moieties are used for both the interlinks and the tougheners. In some embodiments when a force separates the adhesion, the covalently crosslinked polymer network transmits the force through the bulk hydrogel to the separation front, which concentrates stress, so that the interlinks de-bond, but the tougheners remain bonded. The instant disclosure remedies this deficiency by, in some embodiments, selecting dissimilar moieties for the interlinks and tougheners. In these embodiments, the adhesion is instant if the interlinks form fast, and is tough if the interlinks are stronger than tougheners. In these embodiments, even though an individual noncovalent bond can be weak, an array of such noncovalent bonds can render the noncovalent interlink as strong as a covalent interlink.

**[0178]** In some exemplary embodiments, achieving high toughness by eliciting inelasticity has been demonstrated for various types of materials (*e.g.*, metals, elastomers, plastics, ceramics, and hydrogels), as well as for adhesion between adhesives and adherends, between metals and ceramics, and between hydrogels and other materials. In some exemplary embodiments, noncovalent adhesion has also been demonstrated for pressure-sensitive adhesives, wound closure, and drug delivery.

### **Principles of Instant Adhesion**

**[0179]** Whereas individual noncovalent bonds can form instantly, adhesion between macroscopic surfaces is a more complex process. In some embodiments, the surfaces of the two adherends are nonconformal at the molecular scale, causing gaps between the adherends at the adhesion site (*e.g.*, interlink) immediately after contact. To accommodate the gaps instantly, the covalent network in the hydrogel was preformed, rather than formed *in situ*. Consequently, the hydrogel could, in these embodiments, not viscously flow, but could elastically deform. It was assumed that capillarity tends to close the gaps—that is,  $S = \gamma_1 + \gamma_2 - \gamma_{12} > 0$ , where  $\gamma_1$  and  $\gamma_2$  were the surface tensions of the two adherends and  $\gamma_{12}$  was their interfacial surface tension. The

capillarity closed the gaps against stiffness when the dimensionless number  $S/E\epsilon^2H$  was large, where  $E$  was the elastic modulus,  $\epsilon$  was the strain, and  $H$  was the amplitude of the gaps.

Taking  $S \sim 10^{-1} \text{ J/m}^2$ ,  $E \sim 10^4 \text{ Pa}$ ,  $\epsilon \sim 10^{-1}$ , and  $H \sim 10^{-5} \text{ m}$ , it was estimated that

$S/E\epsilon^2H \sim 10^2$ , indicating that, in some embodiments, capillarity can overcome stiffness and close the gaps. In some embodiments, an upper bound of the speed for elastic closure is the

elastic wave speed,  $\sqrt{E/\rho}$ , where  $\rho$  is the density. Taking  $E \sim 10^4 \text{ Pa}$  and  $\rho \sim 10^3 \text{ kg/m}^3$ , it

was estimated that  $\sqrt{E/\rho} \sim 1 \text{ m/s}$ . In practice, in some embodiments, the contact needs to push gas or liquid away for adhesion in air or underwater. In these embodiments, the fluid flow can limit adhesion speed, but adhesion can still be fast if the fluid can escape.

**[0180]** In some embodiments, it takes time for the functional groups to form interlinks after the gaps are closed. Because the hydrogel has a preformed covalent network, the time to form interlinks was expected to scale with the polymer chain diffusion over the hydrogel mesh size. According to the Rouse model, in some embodiments, the diffusivity of a polymer chain in water is  $D = kT/(\eta nb)$ , where  $kT$  is the temperature in the unit of energy,  $\eta$  is the viscosity of water,  $b$  is the size of the repeating units of the polymer chain, and  $n$  is the number of units. Taking  $kT = 10^{-21} \text{ J}$ ,  $\eta = 10^{-3} \text{ Pa}\cdot\text{s}$ ,  $b = 10^{-9} \text{ m}$ , and  $n = 1,000$ ,  $D$  was determined to be  $\sim 10^{-12} \text{ m}^2\text{s}^{-1}$ . The time was estimated as  $a^2/D \sim 10^{-4} \text{ s}$ , where  $a \sim 10 \text{ nm}$  was the mesh size.

### Instant Noncovalent Adhesion

**[0181]** In some embodiments, the tougheners and interlinks can include many different types of noncovalent bonds, including, for example, hydrogen bonds, ionic bonds, and host-guest interactions. The fact that carboxyl groups form hydrogen bonds with many functional groups, including, for example, carboxyl, amine, amide, and hydroxyl, was leveraged to demonstrate the principle of instant noncovalent adhesion. In certain embodiments, polyacrylic acid (PAA) hydrogels have abundant carboxyl groups at low pH, and have been used as a mucoadhesive, although the adhesion energy was not high.

**[0182]** In some embodiments, as shown in FIG. 1E, the hydrogel includes a polymer network of covalent crosslinks and noncovalent tougheners, and adheres to the adherend through noncovalent bonds (“interlinks”). In some embodiments, when an external force acts against the adhesion, the polymer network transmits the force, through the bulk of the hydrogel, to the front of the separation. In these embodiments, the crosslinks remain intact, but the interlinks and many tougheners break. In some embodiments, the interlinks need be stronger than the

tougheners. In some embodiments, the other adherend may also have a covalently crosslinked polymer network and noncovalent tougheners.

**[0183]** Instant noncovalent adhesion was demonstrated by adhering polyacrylic acid (PAA) hydrogels to polyacrylamide (PAAm) hydrogels. As shown in FIG. 3A (at inset), the carboxyl groups on polyacrylic acid (PAA) and the amide groups on polyacrylamide (PAAm) formed hydrogen-bonded interlinks. Neither hydrogel contained tougheners, enabling a study of the hydrogen-bonded interlinks themselves. As shown in FIG. 2A, adhesion energy was measured by 90-degree peel test. In FIG. 2A, the dimension of each adherend was  $100 \times 20 \times 3$  mm, the thickness of the inextensible backing layer was 50  $\mu\text{m}$ , and the loading speed was 10 cm/min. As shown in FIG. 3A, adhesion energy exceeded  $160 \text{ J/m}^2$  instantly (*e.g.*, within 30 seconds). The pH was 1.5 for polyacrylic acid (PAA) and 3.5 for polyacrylamide (PAAm). When protons diffused to equilibrate the two hydrogels, the adhesion energy first dropped, and then plateaued. By contrast, as shown in FIG. 3B, when polyacrylic acid (PAA) and polyacrylamide (PAAm) were used with the same pH of 3.5, the adhesion energy was insensitive to contact time.

**[0184]** It was ascertained that the adhesion energy depended on the number of carboxyl groups available for forming hydrogen bonds. Polyacrylic acid (PAA) is a weak acid, with  $\text{p}K_{\text{a}} = 4.5$  at room temperature. As shown in FIG. 3C, when  $\text{pH} > \text{p}K_{\text{a}}$ , less carboxyl groups were available to form hydrogen bonds, and the adhesion energy dropped. As shown in FIG. 3D, as temperature increased, the hydrogen bonds tended to dissociate, and the adhesion energy vanished at  $80^\circ\text{C}$ . As shown in FIG. 3E, when a polyacrylic acid (PAA)-co-polyacrylamide (PAAm) hydrogel adhered to a polyacrylamide (PAAm) hydrogel, the adhesion energy increased as the amount (molar fraction) of polyacrylic acid (PAA) in the polyacrylic acid (PAA)-co-polyacrylamide (PAAm) increased.

**[0185]** As shown in FIGS. 3F and 3G, both the adhesion energy between polyacrylic acid (PAA) and polyacrylamide (PAAm) (FIG. 3F) and the bulk toughness of polyacrylic acid (PAA) (FIG. 3G) increased with the monomer-to-crosslinker molar ratio of the polyacrylic acid (PAA) hydrogel. In some embodiments, it was observed that the polyacrylic acid (PAA) hydrogel often breaks before the interface breaks, indicating that the hydrogen-bonds between the two hydrogels (*i.e.*, the interlink) can be tougher than the covalent crosslinks in the polymer network.

**[0186]** As shown in FIG. 3H, the adhesion energy was measured as a function of the peel velocity. To exclude the effect of migration of water molecules and protons, the two hydrogels were adhered for 24 h before peel. When the peel velocity reduced, the bulk dissipation reduced, and the adhesion energy approached a threshold of  $60 \text{ J/m}^2$ . The magnitude of this

threshold confirmed that the adhesion arose from hydrogen-bonded interlinks, not from physical entanglement of polymer chains. As shown in FIGS. 4A-4B, to further corroborate that the adhesion originated from the interlinks on the interface rather than from the viscoelastic dissipation in the bulk material, a stress-relaxation test for polyacrylic acid (PAA) hydrogels was performed and showed negligible viscoelasticity. In FIG. 4A, the polyacrylic acid (PAA) sample was pulled and kept at 30% strain. As shown in FIG. 4B, the nominal stress increased to a peak, and then relaxed to a stable level within seconds, for both low and high crosslinking density cases. This stress-relaxation test indicated that viscoelasticity of polyacrylic acid (PAA) hydrogels was negligible.

[0187] In some embodiments, the noncovalent adhesion can be reversible. A polyacrylic acid (PAA) hydrogel (pH = 1.5) and a polyacrylamide (PAAm) hydrogel (pH = 7) was adhered and peeled cyclically. As shown in FIG. 3I, the adhesion energy dropped after the first cycle, and maintained a stable level ( $\sim 50 \text{ J/m}^2$ ) for 100 cycles thereafter. The cycle interval was within seconds. As shown in FIGS. 5A-5D, since carboxyl groups form hydrogen bonds with many functional groups, PAA instantly adhered to many materials, including hydrogels, tissues, and elastomers (FIG. 5A-5D). As shown in FIG. 5A, the polyacrylic acid (PAA)-hydrogel adhesion energy was comparable to the bulk toughness of the hydrogel. This finding corroborated that the hydrogen-bonded interlinks are, in some embodiments, strong enough to compete with covalent bonds. As shown in FIG. 5B, to adhere to a tissue, the pH of polyacrylic acid (PAA) was tuned to 4.5-5 in order to avoid tissue damage. As shown in FIG. 5C, to adhere to an elastomer, hydroxyl groups were added to the surface of the elastomer through oxygen plasma. As shown in FIG. 5D, the polyacrylic acid (PAA)-Very High Bond (VHB) adhesion was stable. Similarly, polyacrylic acid (PAA) was expected to adhere inorganic solids that can hydrogen-bond with carboxyl groups.

#### **Instant *and* Tough Noncovalent Adhesion**

[0188] In accordance with some embodiments, it was demonstrated that noncovalent adhesion can be instant *and* tough. As shown in FIG. 6A, tougheners were added to both hydrogels: uncrosslinked polyacrylic acid (PAA) chains in polyacrylic acid (PAA), and calcium-alginate complex in polyacrylamide (PAAm). The precursor of the polyacrylic acid (PAA) hydrogel had a pH of 1.5, the molecular weight of uncrosslinked polyacrylic acid (PAA) chains was 100,000 g/mol, the amount of uncrosslinked polyacrylic acid (PAA) chains was 30.625% the weight of the polyacrylic acid (PAA) hydrogel precursor, the amount of calcium was 13.3% the weight of alginate, and the peel velocity was 10 cm/min. The uncrosslinked polyacrylic acid

(PAA) chains interacted with the polyacrylic acid (PAA) network through carboxyl-carboxyl hydrogen bonds. In these embodiments, the calcium-alginate can de-bond and acts as a toughener. To strengthen the interlinks, the pH of the alginate-polyacrylamide (PAAm) hydrogel was lowered to 4.5 by using alpha-ketoglutaric acid as the photoinitiator. To further toughen polyacrylic acid (PAA) hydrogels, the molar ratios of monomer-to-crosslinker and monomer-to-initiator were increased to 4000 and 3030, respectively. As shown in FIG. 6B, the polyacrylic acid (PAA) hydrogel with uncrosslinked polyacrylic acid (PAA) chains and the alginate-polyacrylamide (PAAm) hydrogel adhered within 30s, with an adhesion energy of above  $750 \text{ J/m}^2$ , and was stable over time.

**[0189]** As shown in FIG. 6C, to demonstrate the significance of the relative strength of the interlinks and the tougheners, the adhesion energy was measured as a function of the amount of tougheners in the alginate-polyacrylamide (PAAm) hydrogel. When calcium concentration was low, the alginate-polyacrylamide (PAAm) hydrogel had few tougheners, and the adhesion energy was comparable to that of polyacrylic acid (PAA)-polyacrylamide (PAAm). When calcium concentration was high, the tougheners were too strong to de-bond, and the adhesion energy also dropped. As shown in FIG. 6D, an alginate-polyacrylamide (PAAm) hydrogel with a fixed calcium concentration, the adhesion energy increased with the amount of mobile chains in the polyacrylic acid (PAA) hydrogel. The amount of calcium in the alginate-polyacrylamide (PAAm) hydrogels was fixed at 13.3% the weight of alginate. The contact time was 10 minutes.

### **Topologies of Instant and/or Tough Non-Covalent Adhesion**

**[0190]** In some embodiments, adhesives of various forms are useful. In some embodiments, tapes are useful for flat surfaces. In some embodiments, glues are useful for unusual configurations. Some embodiments described herein demonstrate one type of topology of noncovalent adhesion: two polymer networks adhered through interlinks. Several other topologies are further identified (*see* FIGS. 1C, 1D, and 7B), including the form of tape, powder, brush, solution, and interpolymer complex. In FIG. 7B, a covalent bond is represented by a filled dot, a noncovalent bond by a half-filled dot, a polymer chain by a line, a polymer network by an open circle, and a microgel by a solid circle.

**[0191]** In some embodiments, a polyacrylic acid (PAA) hydrogel tape instantly adheres two polyacrylamide (PAAm) hydrogels. As demonstrated in some embodiments, the adhesion energy is appreciable for polyacrylic acid (PAA) and polyacrylamide (PAAm) hydrogels, and can be enhanced by adding tougheners. Some embodiments require both tough adhesion and facile detachment. In these embodiments, the polyacrylic acid (PAA) adhesion can detach

without damage by dripping base at the separation front, or by dripping hot water at the separation front. In some embodiments, the polyacrylic acid (PAA) hydrogel is a stretchable, transparent, ionic conductor. A NaCl-containing polyacrylamide (PAAm) hydrogel (2 M), after being cut, was reconnected instantly by a polyacrylic acid (PAA) tape. The adhesion was tough enough for the repaired conductor to be stretchable.

**[0192]** As shown in FIG. 8, a crosslinked polyacrylic acid (PAA) hydrogel was frozen, dried, and ground into powders (scale bar = 300  $\mu\text{m}$ ). A polyacrylic acid (PAA) hydrogel was fully swollen in deionized water for 24 hours, smashed into small pieces, and kept in the refrigerator at -18  $^{\circ}\text{C}$  for 20 hours. Afterwards, the frozen samples were placed in a freeze dryer (Virris Advantage Plus EL-85) for 72 hours to remove the water and make the samples porous. The samples were then ground into powders under liquid nitrogen. The average powder size was 50  $\mu\text{m}$ , estimated using an optical microscope. In some embodiments, the dry powders are easy to store and use. The powders were spread on a polyacrylamide (PAAm) hydrogel surface and another polyacrylamide hydrogel was immediately put on top. Adhesion occurred within seconds, long before the powders swelled to equilibrium. The polyacrylic acid (PAA) powders achieved an adhesion energy above 200  $\text{J/m}^2$ . By comparison, silica nanoparticles achieved about 10  $\text{J/m}^2$ , possibly due to weak noncovalent bonds. The polyacrylic acid (PAA) powders also achieve underwater adhesion. A hydrogel was placed underwater, and lifted out by another hydrogel through powder adhesion.

**[0193]** In some embodiments, polymer brushes act as molecular Velcro. An initiator (benzophenone) created free radicals on the surface of polydimethylsiloxane (PDMS). As shown in FIGS. 9A-9B, polyacrylic acid (PAA) chains were grafted to polydimethylsiloxane (PDMS) through covalent bonds, then the polydimethylsiloxane (PDMS) was contacted with a polyacrylamide (PAAm) hydrogel. The adhesion was through hydrogen bonds and was instant. The adhesion energy depended on the acrylic acid monomer concentration during the graft. With low concentration, the polyacrylic acid (PAA) chains were too short to form hydrogen bonds with polyacrylamide (PAAm). With high concentration, the polyacrylic acid (PAA) chains entangled with themselves and, therefore, did not interact with polyacrylamide (PAAm).

**[0194]** In some embodiments, the molecular Velcro can enable instant and tough noncovalent adhesion between any material. As shown in FIGS. 10A-10B, an adhesion energy between 550-750  $\text{J/m}^2$  was achieved between the alginate-polyacrylamide (PAAm) hydrogel and several elastomers. FIG. 10A shows a polyacrylic acid (PAA) brush grafted to an elastomer through covalent bonds. The polyacrylic acid (PAA)-grafted elastomer adhered an alginate-

polyacrylamide (PAAm) hydrogel through hydrogen bonds. To enable strong hydrogen-bonded interlinks, the pH of the alginate-polyacrylamide (PAAm) hydrogel was lowered to 4.5. FIG. 10B shows instant and tough adhesion between alginate-polyacrylamide (PAAm) hydrogel and diverse elastomers, including Very High Bond (VHB), natural rubber, and polydimethylsiloxane (PDMS).

**[0195]** When two natural rubbers were coated with polyacrylic acid (PAA) and polyacrylamide (PAAm) brushes, adhesion did not occur. However, as shown in FIGS. 11A-11B, when one rubber was coated with polyacrylic acid (PAA) brush, and the other rubber was coated with a crosslinked polyacrylamide (PAAm) hydrogel, tough adhesion occurred instantly. FIG. 11A shows a polyacrylic acid (PAA) brush grafted to one rubber through covalent bonds, in accordance with some embodiments. A polyacrylamide (PAAm) hydrogel and a polyacrylamide (PAAm) brush were grafted to the other rubber through covalent bonds, in that order. The thickness of the polyacrylamide (PAAm) hydrogel was 50  $\mu\text{m}$ . The pH of the polyacrylamide (PAAm) hydrogel was 3.5. The polyacrylic acid (PAA)-grafted rubber adhered the other polyacrylamide (PAAm)-grafted rubber through hydrogen bonds. Figure 11B shows that instant adhesion only occurred in the case of the polyacrylic acid (PAA) brush-grafted rubber-polyacrylamide (PAAm) hydrogel-grafted rubber. No adhesion was achieved in the case of the polyacrylic acid (PAA) brush-polyacrylamide (PAAm) brush. In some embodiments, the rubber was, perhaps, too stiff for the brushes to fully close the gaps between the materials, but a layer of soft hydrogel of sufficient thickness can deform elastically to close the gaps.

**[0196]** Uncrosslinked polyacrylic acid (PAA) chains were also used as an adhesive. The chains were dried powders. When spread in the middle of two polyacrylamide (PAAm) hydrogels, the powders absorbed water and became a solution. The adhesion was instant, but weaker than the crosslinked polyacrylic acid (PAA) tape and powder. As shown in FIG. 12, the adhesion energy depended on the molecular weight of the polyacrylic acid (PAA) chains. When the molecular weight was low, polyacrylic acid (PAA) chains were too short to interact with polyacrylamide (PAAm). Therefore, the adhesion energy was low. When the polyacrylic acid (PAA) layer was thick, each polyacrylic acid (PAA) chain could not adhere to both polyacrylamide (PAAm) hydrogels. Consequently, in some embodiments, the adhesion is due entirely to physical entanglement of polyacrylic acid (PAA) chains, and will not be tough at low peel velocity.

**[0197]** Another topology used interpolymer complexes. Two species of polymer chains formed interpolymer complexes *in situ*, topologically entangled with two preexisting polymer

networks of the adherends. A mixture of uncrosslinked polyacrylic acid (PAA) and polyacrylamide (PAAm) chains (1 : 1 weight ratio) was prepared in deionized water at 2% chain-to-solution weight ratio (pH = 2.5), and spread it in the middle of two polyacrylamide (PAAm) hydrogels (pH = 3.5). At room temperature, polyacrylic acid (PAA) chains interacted with polyacrylamide (PAAm) chains through hydrogen bonds, hindering chain diffusions into the polyacrylamide (PAAm) hydrogels. As shown in FIG. 7A, the solution was not transparent. To break hydrogen bonds, the mixture was kept at 60 °C for 30 minutes. The mixture then became transparent. Then, the mixture was cooled to 4°C and kept for 24 h for hydrogen bonds to reform. The interpolymer complex achieved appreciable adhesion energy, but was not instant.

**[0198]** In FIGS. 3A-3I, FIGS. 5A-5D, FIGS. 6B-6D, and FIG. 7C, the data represent the mean and the standard deviation of n = 3-4 independent measurements.

### **Synthetic Methods, According to One or More Embodiments**

#### *Hydrogel Synthesis, According to one or More Embodiments*

**[0199]** Each hydrogel was made by pouring a precursor into 3-mm thick plastic molds glued on the plastic substrate. A glass sheet was used to seal the molds, where the solutions gelled under UV.

#### *Synthesis of the Precursor of Poly(acrylic acid) (PAA) Hydrogel, According to one or More Embodiments*

**[0200]** The precursor of a polyacrylic acid (PAA) hydrogel was an aqueous solution of acrylic acid (AA) monomer (1.736 mol/L). Also added were *N,N'*-methylenebisacrylamide (MBAA, 0.14% the weight of the acrylic acid (AA) monomer) as the crosslinker, and alpha-ketoglutaric acid (0.2% the weight of the acrylic acid (AA) monomer) as the photoinitiator. The pH of the precursor was tuned by adding NaOH, and was measured by pH test strips.

#### *Synthesis of the Precursor of Poly(acrylic acid) (PAA) Hydrogel with a Covalent Polymer Network and Uncrosslinked Polymer Chains, According to one or More Embodiments*

**[0201]** The precursor of a polyacrylic acid (PAA) hydrogel with tougheners was an aqueous solution of acrylic acid (AA) monomer (1.736 mol/L) and uncrosslinked polyacrylic acid (PAA) chains as tougheners. *N,N'*-methylenebisacrylamide (MBAA, 0.05% the weight of the acrylic acid (AA) monomer) as the crosslinker and alpha-ketoglutaric acid (0.06% the weight of the acrylic acid (AA) monomer) as the photoinitiator were also added. Polyacrylic acid (PAA) chains of an average molecular weight of 100,000 g/mol (Sigma 523925) were used.

#### *Synthesis of the Precursor of Poly(acrylamide) (PAAm) Hydrogel, According to One or More Embodiments*

**[0202]** The precursor of a polyacrylamide (PAAm) hydrogel was an aqueous solution of acrylamide (AAm) monomer (1.916 mol/L). *N,N'*-methylenebisacrylamide (MBAA, 0.058% the weight of the acrylamide (AAm) monomer) as the crosslinker and alpha-ketoglutaric acid (0.2% the weight of the acrylamide (AAm) monomer) as the photoinitiator were also added. The solutions were poured into laser cutting-made 3-mm thick plastic molds glued on the plastic substrate. A second glass sheet was used to seal the molds, where the solutions gelled under UV light. Neutral polyacrylamide (PAAm) was made with the same recipe, using 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (0.033% the weight of the acrylamide (AAm) monomer) as the photoinitiator.

*Synthesis of the Precursor of Poly(acrylic acid-co-acrylamide) Hydrogel, According to One or More Embodiments*

**[0203]** The precursor of a poly acrylic acid (PAA)-co-polyacrylamide (PAAm) hydrogel was a solution of acrylic acid (AA) monomer and acrylamide (AAm) monomer (1.736 mol/L) and HCl solution (pH=1). *N,N'*-methylenebisacrylamide (MBAA, 0.14% the weight of the acrylic acid (AA) monomer and acrylamide (AAm) monomer) as the crosslinker and alpha-ketoglutaric acid (0.2% the weight of the acrylic acid (AA) monomer and acrylamide (AAm) monomer) as the photoinitiator were also added.

*Synthesis of the Precursor of Poly(dimethylacrylamide) (PDMA) Hydrogel, According to One or More Embodiments*

**[0204]** The precursor of a poly(dimethylacrylamide) (PDMA) hydrogel was an aqueous solution of dimethylacrylamide (DMA) monomer (1.66 mol/L). *N,N'*-methylenebisacrylamide (MBAA, 0.078% the weight of the dimethylacrylamide (DMA) monomer) as the crosslinker and alpha-ketoglutaric acid (0.18% the weight of the dimethylacrylamide (DMA) monomer) as the photoinitiator were also added.

*Synthesis of the Precursor of Poly(hydroxyethylmethacrylate) (PHEMA) Hydrogel, According to One or More Embodiments*

**[0205]** The precursor of a poly(hydroxyethylmethacrylate) (PHEMA) hydrogel was an aqueous solution of hydroxyethylmethacrylate (HEMA) monomer (4.6 mol/L). *N,N'*-methylenebisacrylamide (MBAA, 0.06% the weight of the hydroxyethylmethacrylate (HEMA) monomer) as the crosslinker and alpha-ketoglutaric acid (0.1% the weight of the hydroxyethylmethacrylate (HEMA) monomer) as the photoinitiator were also added.

*Synthesis of the Precursor of Poly([2-(acryloyloxy)ethyl] trimethylammonium chloride) (PDMAEA) Hydrogel, According to One or More Embodiments*

**[0206]** The precursor of a poly([2-(acryloyloxy)ethyl] trimethylammonium chloride) (PDMAEA) hydrogel was an aqueous solution of [2-(acryloyloxy)ethyl] trimethylammonium chloride (DMAEA) monomer (2.5 mol/L). *N,N'*-methylenebisacrylamide (MBAA, 0.17% the weight of the [2-(acryloyloxy)ethyl] trimethylammonium chloride (DMAEA) monomer) as the crosslinker and alpha-ketoglutaric acid (0.06% the weight of the [2-(acryloyloxy)ethyl] trimethylammonium chloride (DMAEA) monomer) as the photoinitiator were also added.

*Synthesis of the Precursor of Alginate-Polyacrylamide Hydrogel, According to One or More Embodiments*

**[0207]** The precursor of an alginate-polyacrylamide (PAAm) hydrogel was a solution of 40.54 g acrylamide (AAm) powder, 6.76 g alginate powder, and 300 ml deionized (DI) water. *N,N'*-methylenebisacrylamide (MBAA, 0.06% the weight of the acrylamide (AAm)) as the covalent crosslinker, calcium sulfate slurry (2.2% the weight of the acrylamide (AAm)) as the ionic crosslinker, and alpha-ketoglutaric acid (0.5% the weight of the acrylamide (AAm)) as the photoinitiator.

*Synthesis of Polydimethylsiloxane (PDMS), According to One or More Embodiments*

**[0208]** The base and the curing agent of Sylgard 184 (Dow Corning) at weight ratio 10:1 were mixed to make the polydimethylsiloxane (PDMS) precursor. Then, the precursor was poured into a Petri dish and cured at 65 °C in an oven (Jeio Tech Co., Inc. OF-11E) for 12 hours.

*Synthesis of Ecoflex, According to One or More Embodiments*

**[0209]** The Ecoflex precursor was made by mixing the base and the curing agent of Ecoflex 0030 at weight ratio 1:1. Then, the precursor was cured at ambient condition for 3 hours.

*Method for the 90-Degree Peel Test, According to One or More Embodiments*

**[0210]** Polyacrylic acid (PAA) hydrogels with sample size 100×20×3 mm were prepared. Polyacrylamide (PAAm) hydrogels with the same sample size were prepared. The polyacrylic acid (PAA) hydrogels and polyacrylamide (PAAm) hydrogels were separately stored in sample bags after they were synthesized. After 24 hours, the polyacrylic acid (PAA) hydrogel was glued to a rigid acrylic substrate using cyanoacrylate (Krazy Glue). The polyacrylamide (PAAm) hydrogel was glued to a thin inextensible polyester film (50 μm thickness; McMaster Carr) using cyanoacrylate. The polyester film functioned as a backing layer for the hydrogel, which suppressed the deformation far away from the crack front. For acidic hydrogel, the surface was first neutralized by applying a few drops of 0.1 mol/L NaHCO<sub>3</sub> (Sigma-Aldrich S5761) solution and then dried by blowing air before using cyanoacrylate. After putting the polyacrylic acid (PAA) hydrogel and polyacrylamide (PAAm) hydrogel together, a thin polyester

film was inserted in the middle of the polyacrylic acid (PAA)-polyacrylamide (PAAm) interface at one end to create a pre-crack. The sample with acrylic substrate and polyester backing layer was then loaded by a tensile machine (Instron 5966; 100 N load cell) using the 90-degree peel test. The peel rate was 10 cm/min. The adhesion energy was calculated by the force at the plateau of the force-displacement curve divided by the sample width.

*Plasma Treatment for Elastomers, According to One or More Embodiments*

[0211] Ecoflex 0030, polydimethylsiloxane (PDMS, Sylgard 184) and Very High Bond (VHB, 3M 4905) with inextensible backing layer were inserted in the chamber of plasma cleaner (PDC-002, Harrick Plasma). After evacuation, plasma treatment of the samples was performed in vacuum for 6 minutes. A piece of polyacrylic acid (PAA) hydrogel was immediately placed on the treated surface to achieve strong adhesion via hydrogen bond.

**Synthesis of the Different Topologies, According to One or More Embodiments**

*Synthesis of the Polyacrylic Acid Powder, According to One or More Embodiments*

[0212] First, a preformed polyacrylic acid (PAA) hydrogel was fully swollen in deionized (DI) water for 24 hours. Then, the fully swollen polyacrylic acid (PAA) hydrogel was formed into small blocks by hand, which was kept frozen in the refrigerator for 20 hours. Afterwards, freeze-drying was applied to the frozen samples in a freeze dryer (VirTis Advantage Plus EL-85) to remove the water and make the samples porous. The freeze-drying process took 72 hours. The last step was to grind the dried and porous samples in a mortar to powders with the assistance of liquid nitrogen, which made the samples brittle.

*Synthesis of the Polyacrylic Acid Brush, According to One or More Embodiments*

[0213] Benzophenone solution (0.1 mol/L in ethanol) was poured onto the top surface of polydimethylsiloxane (PDMS) formed in a pre-made acrylic mold. After 2 min, benzophenone was removed and ethanol was used to flush the treated polydimethylsiloxane (PDMS) surface. Afterwards, acrylic acid (AA) monomer solution with various monomer concentrations was poured onto the benzophenone treated surface of polydimethylsiloxane (PDMS). Under ultraviolet (UV) radiation for 1 hour, polyacrylic acid (PAA) polymer chains were grafted to polydimethylsiloxane (PDMS), where benzophenone functioned as the initiator.

*Synthesis of the Polyacrylic Acid Brush, According to One or More Embodiments*

[0214] The polyacrylic acid (PAA)-polyacrylamide (PAAm) complex was a solution of 1 g of polyacrylic acid (PAA) chains with an average molecular weight of 4,000,000 g/mol (Sigma 306231), 1 g of polyacrylamide (PAAm) chains with an average molecular weight of 150,000

g/mol (Sigma 749222), and 8 g of deionized (DI) water. The solution was then subjected to sonication to fully dissolve both chains.

**[0215]** The one or more exemplary embodiments described herein demonstrate that non-covalent adhesion can be both instant and tough by choosing dissimilar noncovalent moieties for interlinks and tougheners. Instant and tough adhesion was demonstrated with tape, powder, and brush. In some embodiments, the abundant diversity of non-covalent bonds provides enormous design space to realize additional functions, such as underwater adhesion, conductive adhesion, reversible adhesion, and easy detach in response to cues.

**[0216]** It will be appreciated that while one or more particular materials or steps have been shown and described for purposes of explanation, the materials or steps may be varied in certain respects, or materials or steps may be combined, while still obtaining the desired outcome. Additionally, modifications to the disclosed embodiment and the invention as claimed are possible and within the scope of this disclosed invention.

#### **Adhesive Double-Network Hydrogel, According to One or More Embodiments**

**[0217]** In some embodiments, tough adhesion between soft and wet materials is important to many applications in medicine and engineering. Examples include, but are not limited to, implants, wound dressing, and soft machines. In some embodiments, tough adhesion can be realized through the synergy of interlink and toughener. An adhesive double-network hydrogel was developed to achieve tough adhesion through noncovalent interlinks and covalent tougheners. The noncovalent interlinks were strong enough to de-bond many covalent tougheners. Adhesion energy above 500 J/m<sup>2</sup> was achieved. Interplay between noncovalent interlinks and covalent tougheners can provide, in some embodiments, a new mechanism for instant and tough adhesion of materials and fundamental knowledge about the mechanics of adhesion.

**[0218]** Hydrogels have been developed for medical applications, including, but not limited to, contact lenses, drug delivery, and tissue regeneration. Hydrogels have been used as stretchable, transparent, ionic conductors to enable devices, such as, but not limited to, soft machines, ionotronics, and noise cancelling devices. For example, when a double-network (DN) hydrogel is stretched, the short-chain network breaks over a substantial volume and the long-chain network remains intact, leading to high toughness (*e.g.*, ~1000 J/m<sup>2</sup>). In such a DN hydrogel, polymer chains of each network can be crosslinked by covalent bonds. In some embodiments, the resulting DN hydrogel is chemically stable and is fully swollen. A DN hydrogel can resolve the stiffness-threshold conflict in single-network hydrogels, *i.e.*, the short-

chain network provides high stiffness while the long-chain network provides high fatigue threshold. In these embodiments, the combined attributes of stability, stiffness, toughness, and fatigue resistance can make DN hydrogels promising for many applications.

**[0219]** Tough adhesion can be achieved between hydrogels and other materials, such as, but not limited to, nonporous inorganics, elastomers, and living tissues. In some embodiments, tough adhesion requires not only a tough hydrogel as dissipative matrix, but also strong interlinks. Examples of interlinks include, but are not limited to, noncovalent bonds and topological entanglement. In some embodiments, noncovalent interlinks can be strong enough to de-bond many noncovalent tougheners to achieve instant and tough adhesion (discussed in the preceding examples). DN hydrogel adhesion is an unmet need of significance in the fields of, for example, antifouling, cartilage regeneration, and bioimplants.

**[0220]** To meet this need, the synergy of interlink and toughener was applied to design an adhesive DN hydrogel which strongly adhered, via noncovalent interlinks, to DN hydrogels having covalent tougheners. As demonstrated herein, noncovalent interlinks can be strong enough for many covalent tougheners to de-bond. To illustrate the principle, chemically crosslinked poly(acrylic acid) (PAA) was used as the long-chain network and poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) was used as the short-chain network. Then, the PAMPS-PAA hydrogel was adhered to another DN hydrogel with the same covalent tougheners (PAMPS), but chemically crosslinked polyacrylamide (PAAm) as the long-chain network (FIG. 13). In some embodiments, hydrogen-bonded interlinks can form between carboxyl groups in PAA networks and amide groups in PAAm networks. Although an individual hydrogen bond is weak, a dense array of hydrogen bonds can be, in some embodiments, as strong as a covalent interlink. As shown in FIG. 13, if an external force acts on the adhesion between the two materials, the covalent polymer networks can transmit the force to the separation front. In these embodiments, the interlinks need to be stronger than the tougheners, so that many tougheners de-bond and dissipate energy, leading to tough adhesion. In some embodiments, a process zone at the separation front can also dissipate energy as the PAMPS network breaks.

**[0221]** FIG. 13 shows, in accordance with one or more embodiments described herein, an adhesive DN hydrogel. The adhesive double-network hydrogel consisted of two interpenetrating covalent networks: a long-chain PAA network and a short-chain PAMPS network. The PAMPS-PAA hydrogel adhered to a PAMPS-PAAm hydrogel through hydrogen bonds formed between carboxyl groups in PAA and amide groups in PAAm. The PAMPS

networks served as tougheners in both hydrogels and enabled the formation of dense array of hydrogen bonds at the interface due to its acidic nature. When an external force acted on the adhesion, the force was transmitted by the covalent networks to the separation front. The crosslinks remained intact but the tougheners and interlinks de-bonded. The interlinks needed to be strong enough to allow many tougheners to de-bond. Along with the advance of separation, a process zone at the separation front dissipated energy.

**[0222]** The adhesion strongly depended on the amount of hydrogen bonds formed at the interface. PAA is a weak acid, with a  $pK_a$  of 4.5 at room temperature. When  $pH < pK_a$ , more carboxyl groups were available to form hydrogen bonds. The precursor of PAMPS has a pH of 0.6, and the precursor of PAAm has a pH of 1.5, which ensured a dense array of hydrogen bonds formed at the interface.

*Material Fabrication, According to Some Embodiments*

**[0223]** A two-step polymerization method was used to fabricate the PAMPS-PAA hydrogel. As shown in FIG. 14, the first network was synthesized from an aqueous solution of 1 M 2-acrylamido-2-methylpropanesulfonic acid (AMPS, Sigma-Aldrich, 818667), containing 4 mol% *N,N'*-methylenebisacrylamide (MBAA, Sigma-Aldrich, M7279) and 0.1 mol% 2-oxoglutaric acid (OA, Sigma-Aldrich, 75890) via ultraviolet photo-polymerization. In the argon gas environment, the prepared AMPS precursor was injected into a mold, which consisted of two parallel glass plates spaced by a 0.5 mm-thick U-shapes silicone rubber. The mold with precursor was exposed to ultraviolet light (15 W, 365 nm wavelength) for 8 hours. Then, the PAMPS hydrogel was soaked in an aqueous solution of 4 M acrylic acid (AA, Sigma-Aldrich, 147230), 0.004 mol% MBAA, and 0.1 mol% OA for 24 hours. After becoming fully swollen, the sample was carefully sandwiched by two glass plates and coated with a transparent polyethylene membrane to avoid dehydration. The PAA network within the PAMPS network was subsequently synthesized by another 8-hour illumination under ultraviolet light. The PAMPS-PAA hydrogel was soaked in deionized (DI) water for 48 hours before use. The DI water was renewed every 8 hours during this period.

**[0224]** FIG. 14 shows, in accordance with one or more embodiments described herein, a two-step polymerization method for the synthesis of a PAMPS-PAA hydrogel. An aqueous solution of 1 M AMPS, containing 4 mol% MBAA, and 0.1 mol% OA was prepared. In an argon environment, the AMPS precursor solution was injected into a glass mold and exposed to ultraviolet (UV) light for 8 hours. The first network was then soaked in an aqueous solution of 4 M AA, 0.004 mol% MBAA, and 0.1 mol% OA for 1 day to reach a fully swollen state. The

sample sandwiched by two glass plates was exposed to UV light for 8 hours. Lastly, the synthesized DN hydrogel was soaked in DI water for 2 days to remove the residual reactants.

**[0225]** The synthesis of the PAMPS-PAAm hydrogel followed the same procedure as described above, with the same recipe: an aqueous solution of acrylamide (AAm, Sigma-Aldrich, A8887), 0.004 mol% MBAA, and 0.1 mol% OA. The thickness of the PAMPS-PAA hydrogel and the PAMPS-PAAm hydrogel were 1.25 mm and 1.65 mm, respectively.

*Mechanical Properties of the PAMPS-PAA Hydrogel, According to Some Embodiments*

**[0226]** The as-prepared PAMPS-PAA hydrogels were cut into dumbbell-shapes for a uniaxial tensile test (by using SHIMADZU AGS-X). Each sample had an effective length of 12 mm and a width of 2 mm. The samples were clamped by a pair of pneumatically-actuated grippers and stretched at a rate of 100 mm/min until rupture. For both the PAMPS-PAA and PAMPS-PAAm hydrogels, 5 samples were tested (FIGS. 15A-B). The nominal stress was defined by the applied force in the deformed state divided by the initial cross-sectional area. Before rupture, the measured stress at each stretch showed good consistence for all the PAMPS-PAA and PAMPS-PAAm samples. The stress-stretch curves of the PAMPS-PAA and PAMPS-PAAm hydrogels showed different behaviors. The PAMPS-PAAm hydrogel was more stretchable and appeared to have noticeable strain stiffening, while the PAMPS-PAA hydrogel yielded at a stretch smaller than 3, and subsequently ruptured. Since the elasticity of DN hydrogels mainly depended on the long-chain network, the difference in stress-stretch curve indicated the difference between PAAm and PAA stretchability. It was also surprising that yielding of one of the PAMPS-PAA samples lasted until the stretch reached 4.5. During this process, the necking phenomenon happened sequentially on two sections of the test sample. One possible explanation for this effect is the more serious inhomogeneity of PAA networks.

**[0227]** FIG. 15C shows the averaged shear modulus of both materials in small-strain status, according to one or more embodiments. The early stage of the stress-stretch curves was used for

fitting to the neo-Hookean model,  $W = \frac{1}{2} \mu (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$ , where  $W$  is the Helmholtz

energy density,  $\lambda_{1,2,3}$  are principal stretches, and  $\mu$  is the shear modulus. In some

embodiments, as  $\lambda_1$  is prolonged in uniaxial stretch and the hydrogel was taken to be

incompressible, we have  $\lambda_2 = \lambda_3 = 1/\sqrt{\lambda_1}$ . In some embodiments, the nominal stress  $s_1$  can

be derived by the derivation of  $W$  to the principle stretch  $\lambda_1$ ,  $s_1 = \mu(\lambda_1 - \lambda_1^{-2})$ . For the linear

section of the stress-stretch curve, in some embodiments,  $\lambda_1$  is around 1, and the above equation

can be simplified to  $s_1 = 3\mu(\lambda_1 - 1)$ . In some embodiments, the initial slope of the stress-stretch curve is three times the shear modulus. In some embodiments, since the PAMPS network contributes to the stiffness, PAMPS-PAA and PAMPS-PAAm have a similar Young's modulus, so as the measured water content (FIG. 15C). In addition, the toughness of the DN hydrogels was measured by a pure shear test (FIG. 15D and FIG. 16). Although the stretchabilities of the synthesized DN hydrogels can vary, the PAMPS-PAA hydrogel and the PAMPS-PAAm hydrogel had a similar toughness of about 4000 J/m<sup>2</sup>.

**[0228]** FIGS. 15A-D show, in accordance with one or more embodiments described herein, mechanical properties of the PAMPS-PAA hydrogel, and comparison to PAMPS-PAAm hydrogel. Unless otherwise specified, the PAMPS-PAA hydrogel and the PAMPS-PAAm were fully swollen and had a thickness of 1.25 mm and 1.65 mm, respectively. FIG. 15A shows a stress-stretch curve of PAMPS-PAA, according to one or more embodiments. FIG. 15B shows the stress-stretch curve of PAMPS-PAAm, according to one or more embodiments. FIG. 15C shows the shear modulus and water concentration of PAMPS-PAAm and PAMPS-PAA, according to one or more embodiments. FIG. 15D shows the toughness of PAMPS-PAAm and PAMPS-PAA, measured by a pure shear test with 50 mm × 10 mm samples, according to one or more embodiments.

**[0229]** A pure shear test was used to measure fracture toughness (FIG. 16), including a notched sample and an un-notched sample. Accordingly, two sets of samples were prepared from the same piece of DN hydrogel with the same geometry (50 mm × 10 mm). For the notched sample, a pre-cut crack with 20 mm length was introduced (FIGS. 16A-B). Both the notched and unnotched samples were subjected to a monotonic stretch until rupture. The loading rate was 30 mm/min. For static fracture, the measurement of one sample took several minutes, leading to the samples being exposed to ambient air. Stress-stretch curves of the notched and un-notched samples were measured for PAMPS-PAAm with 1.65 mm thickness (FIGS. 16C-D) and PAMPS-PAA with 1.25 mm thickness (FIGS. 16E-F). The stretch limit  $\lambda_c$  at which the crack started to propagate was recorded and used to calculate the fracture toughness. According to the definition of fracture toughness, the critical energy release rate for crack propagation was calculated by the integration of stress-stretch below  $\lambda_c$  (FIGS. 16D and 16F). For each measurement, three samples were tested.

**[0230]** FIGS. 16A-F show, in accordance with one or more embodiments described herein, a pure shear test for fracture toughness measurement. FIG. 16A shows a notched sample subjected to a monotonic stretch, according to one or more embodiments. FIG. 16B shows an

un-notched sample subjected to a monotonic stretch, according to one or more embodiments. FIG. 16C shows the stress-stretch curve of the notched PAMPS-PAAm, according to one or more embodiments. The stretch limit  $\lambda_c$  was recorded. FIG. 16D shows that the fracture toughness equals the product of the area enclosed by the stress-stretch curve of the un-notched PAMPS-PAAm at the stretch limit  $\lambda_c$  and the thickness, according to one or more embodiments. FIG. 16E shows the stress-stretch curve of the notched PAMPS-PAA, according to one or more embodiments. FIG. 16F shows the stress-stretch curve of the unnotched PAMPS-PAA, according to one or more embodiments.

#### *Adhesion Energy, According to Some Embodiments*

**[0231]** The adhesion energy between the PAMPS-PAA hydrogel and the PAMPS-PAAm hydrogel was measured using a 90-degree peel test (FIG. 17A). A 1.65 mm-thick PAMPS-PAAm hydrogel and a 1.65 mm-thick PAMPS-PAA hydrogel were prepared and cut into rectangular samples with a length of 100 mm and a width of 2 mm. The PAMPS-PAAm hydrogel was glued to a rigid acrylic substrate using cyanoacrylate (super glue), while the PAMPS-PAA hydrogel was glued to a 50  $\mu$ m-thick thin polyethylene terephthalate (PET) film as inextensible backing layer. The increment in the pull distance equaled the extension of the crack in the steady state. The acrylic substrates and PET film were washed with ethanol and DI water, then dried before use. Since both the PAMPS-PAA and PAMPS-PAAm hydrogels are acidic, the surfaces were treated with a few drops of 0.1 M  $\text{NaHCO}_3$  for 5 minutes and then dried before applying the super glue. A small piece of PET film was inserted into the interface of the hydrogels to introduce a pre-crack. The PAMPS-PAA and PAMPS-PAAm samples were contacted and a weight of 1 kg was applied for 5 minutes before test. The loading rate was 10 cm/min. The adhesion energy was calculated by the average force at the plateau of the force-displacement curve divided by the sample width.

**[0232]** After peel, no hydrogel residues were observed on the surfaces of the DN hydrogels, indicating an adhesion failure mode. As shown in FIG. 17B, the adhesion energy between the PAMPS-PAA and PAMPS-PAAm hydrogels exceeded 500 J/m<sup>2</sup>. By contrast, the adhesion energy between the PAA and PAMPS-PAAm hydrogels was about 180 J/m<sup>2</sup>, which was comparable to the fracture toughness of PAA. This indicated that the interlinks were strong enough and that the adhesion was limited by the brittleness of PAA. The force-displacement curves of adhesion between PAMPS-PAA and PAMPS-PAAm and adhesion between PAA and PAMPS-PAAm were plotted in FIGS. 17C and 17D, respectively.

**[0233]** FIGS. 17A-D show, in accordance with one or more embodiments described herein, the adhesion measurement of DN hydrogels. FIG. 17A shows the experimental setup of the 90-degree peel test, according to one or more embodiments. FIG. 17B shows the adhesion energy between PAA and PAMPS-PAAm hydrogels and that between PAMPS-PAA and PAMPS-PAAm hydrogels, according to one or more embodiments. FIG. 17C shows force-displacement curves of adhesion between PAMPS-PAA and PAMPS-PAAm hydrogels, according to one or more embodiments. FIG. 17D shows force-displacement curves of adhesion between PAA and PAMPS-PAAm hydrogels, according to one or more embodiments. Three samples were used for each test.

**[0234]** In some embodiments, tough adhesion is analogous to tough hydrogel. In addition to the tough hydrogel matrix used either as an adhesive or adherend (or both), it incorporated an additional component, *i.e.*, interlinks on the interface between adhesive and adherend.

Achieving tough adhesion required not only the synergy of an elastic network and tougheners, but also the cooperation of interlinks. When a force separated the adhesion, the stretchable polymer networks in the adhesive or adherend (or both) transmitted the force through the bulk matrix to the separation front, which concentrated the stress. The weaker interlinks de-bonded but the stronger tougheners remained bonded. Therefore, in some embodiments, strong interlinks are important toward affecting the energy dissipation process. In some embodiments, the diversity of available covalent and noncovalent bonds provides enormous design space to realize tough adhesion. The dissociation energy of noncovalent bonds, such as, for example, ionic interactions (42-82 kJ/mol), hydrogen bonds (12-29 kJ/mol), and hydrophobic associations is much lower than that of covalent bonds (> 100 kJ/mol).

**[0235]** In some embodiments, use of non-covalent interlinks is desirable for time-sensitive applications, such as, but not limited to, wound closure, bio-implants, and rapid prototyping. In some embodiments, strength relates to not only the energy of a single bond, but also to the number of such bonds. For example, topological adhesion can incorporate additional “stitch” polymers to form the interlinks and/or interlinks can be formed by the functional groups on the stretchable or sacrificial networks of a tough hydrogel matrix. In some embodiments, hydrogen bonds are strong enough to serve as tougheners. In some embodiments, an adhesive DN hydrogel can achieve tough adhesion through noncovalent interlinks. In these embodiments, the noncovalent interlinks can be strong enough for many covalent tougheners to de-bond by adhering the adhesive DN hydrogel to another DN hydrogel with covalent tougheners. In some

embodiments, adhesion energy above  $500 \text{ J/m}^2$  can be achieved, which may be a useful strategy for energy dissipation for tough adhesion.

## CLAIMS

1. A composite material comprising:
  - a first material comprising a plurality of first inter-material bonding units, a plurality of first internal bonding units and a plurality of first complementary internal bonding units; and
  - a second material comprising a plurality of second inter-material bonding units;
  - wherein the plurality of first inter-material bonding units and the plurality of second inter-material bonding units form a plurality of inter-material non-covalent bonds to adhere the first material and the second material together;
  - wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and
  - wherein the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the first intra-material bonds.
2. A composite material comprising:
  - a first material comprising a plurality of first internal bonding units and a plurality of first complementary internal bonding units; and
  - a second material;
  - wherein the first material and the second material are adhered together by topological adhesion or mechanical interlocking;
  - wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and
  - wherein the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the first intra-material bonds.
3. The composite material of claim 1, wherein the second material comprises a plurality of second internal bonding units and a plurality of second complementary internal bonding units;
  - wherein the second internal bonding units form a plurality of second intra-material bonds by bonding with the plurality of second complementary internal bonding units; and
  - wherein the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the second intra-material bonds.

4. The composite material of claim 2, wherein the second material comprises a plurality of second internal bonding units and a plurality of second complementary internal bonding units;  
wherein the second internal bonding units form a plurality of second intra-material bonds by bonding with the plurality of second complementary internal bonding units; and  
wherein the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the second intra-material bonds.
5. The composite material of any one of claims 1-4, wherein the first material and the second material are each independently selected from the group consisting of polymers, nonporous inorganics, metal, metal alloy, ceramic, stone, concrete, asphalt, glass, silicon, wood, tissues, organs, arteries, vessels, bone, teeth, fabric, fibers, textiles, foam, plaster, paper, cardboard, fiberglass, semiconductors, biomaterials, composite materials, metamaterials, minerals, elemental materials, plant materials, adhesives, and a combination thereof.
6. The composite material of any one of claims 1-4, wherein the first material or the second material is a polymer material.
7. The composite material of claim 6, wherein the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, or the second complementary internal bonding units comprise a cross-linking agent.
8. The composite material of claim 7, wherein the cross-linking agent comprises *N,N'*-methylenebisacrylamide (MBAA), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) dimethacrylate (PEGDMA), 3-(trimethoxysilyl) propyl methacrylate (TMSPMA), or a combination thereof.
9. The composite material of any one of claims 5-8, wherein the first polymer material or the second polymer material are each independently selected from the group consisting of a hydrogel, an elastomer, a rubber, a plastic, and a biological polymer.
10. The composite material of any one of claims 5-9, wherein the first polymer material or the second polymer material comprises a hydrogel.
11. The composite material of claim 10, wherein the first polymer material or the second polymer material is independently selected from the group consisting of poly(hydroxyethylmethacrylate) (HEMA), poly(acrylamide) (PAAm),

poly(dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), poly(acrylic acid) (PAA), poly(lactic-co-glycolic acid) (PLGA), poly(ethylene glycol) (PEG), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) methacrylate (PEGMA), poly(ethylene glycol) dimethacrylate (PEGDMA), poly([2-(acryloyloxy)ethyl] trimethylammonium chloride) (PDMAEA), poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), alginate, chitosan, and a combination thereof.

12. The composite material of any one of claims 5-9, wherein the first polymer material or the second polymer material comprises an elastomer.

13. The composite material of claim 12, wherein the elastomer is selected from the group consisting of natural rubber, styrene butadiene rubber, polybutadiene rubber, silicone rubber, polyurethane, acrylic foam, silicones, and a combination thereof.

14. The composite material of any one of claims 5-9, wherein the first polymer material or the second polymer material comprises a biological polymer.

15. The composite material of claim 14, wherein the biological polymer is selected from the group consisting of polysaccharide, polypeptide, polynucleotides, and a combination thereof.

16. The composite material of any one of claims 5-9, wherein the first polymer material or the second polymer material comprises a tissue or an organ.

17. The composite material of claim 1, wherein the inter-material non-covalent bonds are selected from the group consisting of ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

18. The composite material of claim 17, wherein the inter-material non-covalent bonds are ionic bonds.

19. The composite material of claim 18, wherein the ionic bonds are metal cation-carboxylate bonds or ammonium-carboxylate bonds.

20. The composite material of claim 18, wherein the first inter-material bonding units and the second inter-material bonding units are selected from the group consisting of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NR}_4^+$ ,  $\text{OH}^-$ ,  $\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ , wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.

21. The composite material of claim 17, wherein the inter-material non-covalent bonds are hydrogen bonds.
22. The composite material of claim 21, wherein the hydrogen bonds are carboxylic acid and hydroxyl hydrogen bonds, amine and hydroxyl hydrogen bonds, amide and carboxylic acid hydrogen bonds, carboxyl and carboxyl hydrogen bonds, hydroxyl and hydroxyl hydrogen bonds, or amine and phenol hydrogen bonds.
23. The composite material of claim 21 or 22, wherein the first inter-material bonding units and the second inter-material bonding units are selected from the group consisting of OH, COOH, NH<sub>2</sub>, NHR, and a combination thereof, wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.
24. The composite material of claim 17, wherein the inter-material non-covalent bonds are hydrophobic interactions or dipole-dipole interactions.
25. The composite material of claim 24, wherein the first inter-material bonding units and the second inter-material bonding units are selected from the group consisting of alkyl, aryl, heteroaryl, halogen.
26. The composite material of claim 2, wherein the first material and the second material are adhered together by topological adhesion.
27. The composite material of claims 3 or 4, wherein the first intra-material bonds and the second intra-material bonds are each independently selected from the group consisting of covalent bonds, ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.
28. The composite material of claim 27, wherein the first intra-material bonds or the second intra-material bonds are covalent bonds.
29. The composite material of claim 28, wherein the covalent bonds comprise  $\sigma$ -bonding,  $\pi$ -bonding, metal-to-metal bonding, agnostic interactions, bent bonds, three-center two-electron bonds, or a combination thereof.
30. The composite material of claim 27, wherein the first intra-material bonds or the second intra-material bonds are ionic bonds.

31. The composite material of claim 30, wherein the ionic bonds are metal cation-carboxylate bonds or ammonium-carboxylate bonds.
32. The composite material of claim 30, wherein the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, and the second complementary internal bonding units are each independently selected from the group consisting of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NR}_4^+$ ,  $\text{OH}^-$ ,  $\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ , wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.
33. The composite material of claim 27, wherein the first intra-material bonds or the second intra-material bonds are hydrogen bonds.
34. The composite material of claim 33, wherein the hydrogen bonds are carboxylic acid and hydroxyl hydrogen bonds, amine and hydroxyl hydrogen bonds, amine and carboxyl hydrogen bonds, carboxyl and carboxyl hydrogen bonds, hydroxyl and hydroxyl hydrogen bonds, or amine and phenol hydrogen bonds.
35. The composite material of claim 33 or 34, wherein the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, and the second complementary internal bonding units are each independently selected from the group consisting of OH, COOH,  $\text{NH}_2$ , NHR, and a combination thereof, wherein R is independently H, alkyl, haloalkyl, aryl, or heteroaryl.
36. The composite material of claim 27, wherein the first intra-material bonds or the second intra-material bonds are hydrophobic interactions or dipole-dipole interactions.
37. The composite material of claim 36, wherein the first internal bonding units, the first complementary internal bonding units, the second internal bonding units, and the second complementary internal bonding units are each independently selected from the group consisting of alkyl, aryl, heteroaryl, and halogen.
38. The composite material of claim 3, wherein the inter-material non-covalent bonds are hydrogen bonds and the first intra-material bonds and the second intra-material bonds are ionic bonds.

39. The composite material of claim 3, wherein the inter-material non-covalent bonds are hydrogen bonds and the first intra-material bonds and the second intra-material bonds are covalent bonds.
40. The composite material of claim 3, wherein the first polymer material is polyacrylamide (PAAm); the first inter-material bonding units and the second inter-material bonding units comprise amide and carboxylate groups, respectively; and the first internal bonding units comprise  $\text{Ca}^{2+}$  and alginate.
41. The composite material of claim 40, wherein the second polymer material comprises polyacrylic acid (PAA) and a plurality of second internal bonding units; and the second internal bonding units comprise acrylic acid.
42. The composite material of any one of the preceding claims, wherein the first polymer material and the second material are adhered to have an adhesion energy between the first polymer material and the second material is from about  $40 \text{ J/m}^2$  to about  $5000 \text{ J/m}^2$ .
43. The composite material of claim 1, further comprising an inter-material layer between the first material and the second material and comprising a tape, a powder, a brush, a solution, or an inter-material complex; wherein the first inter-material bonding units and the second inter-material bonding units are at least partially located in the inter-material layer.
44. A method of adhering a first material and a second material comprising:  
providing a first material comprising a plurality of first inter-material bonding units, a plurality of first internal bonding units, and a plurality of first complementary internal bonding units;  
providing a second material comprising a plurality of second inter-material bonding units; and  
forming a plurality of inter-material non-covalent bonds between the plurality of first inter-material bonding units and the plurality of second inter-material bonding units to adhere the first material and the second material together;  
wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and

wherein the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

45. A method of adhering a first material and a second material comprising:  
providing a first material comprising a plurality of first internal bonding units and a plurality of first complementary internal bonding units;  
providing a second material; and  
adhering the first material and the second material together by topological adhesion or mechanical interlocking;

wherein the first internal bonding units form a plurality of first intra-material bonds by bonding with the plurality of first complementary internal bonding units; and

wherein the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the first intra-material bonds.

46. The method of claim 44, wherein the second material comprises a plurality of second internal bonding units; the method further comprises forming a plurality of second intra-material bonds among the second internal bonding units; and the combined bonding strength of the plurality of the inter-material non-covalent bonds is stronger than the combined bonding strength of the plurality of the second intra-material bonds.

47. The method of claim 45, wherein the second material comprises a plurality of second internal bonding units; the method further comprises forming a plurality of second intra-material bonds among the second internal bonding units; and the strength of topological adhesion or mechanical interlocking is stronger than the combined bonding strength of the plurality of the second intra-material bonds.

48. The method of claim 46 or 47, wherein the first material and the second material are each independently selected from the group consisting of a polymers, nonporous inorganics, metal, metal alloy, ceramic, stone, concrete, asphalt, glass, silicon, wood, tissues, organs, arteries, vessels, bone, teeth, fabric, fibers, textiles, foam, plaster, paper, cardboard, fiberglass, semiconductors, biomaterials, composite materials, metamaterials, minerals, elemental materials, plant materials, adhesives, and a combination thereof.

49. The method of claim 48, wherein the first material or the second material is a polymer material.

50. The method of claim 49, wherein the first polymer material or the second polymer material are each independently selected from the group consisting of a hydrogel, an elastomer, a rubber, a plastic, and a biological polymer.
51. The method of claim 49 or 50, wherein the first polymer material or the second polymer material comprises a hydrogel.
52. The method of claim 51, wherein the first polymer material or the second polymer material are independently selected from the group consisting of poly(hydroxyethylmethacrylate) (HEMA), poly(acrylamide) (PAAm), poly(dimethylacrylamide) (PDMA), poly(*N*-isopropylacrylamide) (PNIPAM), sodium polyacrylate (NaPAA), poly(acrylic acid) (PAA), poly(lactic-co-glycolic acid) (PLGA), poly(ethylene glycol) (PEG), poly(ethylene glycol) diacrylate (PEGDA), poly(ethylene glycol) methacrylate (PEGMA), poly(ethylene glycol) dimethacrylate (PEGDMA), poly([2-(acryloyloxy)ethyl] trimethylammonium chloride) (PDMAEA), alginate, and chitosan, and a combination thereof.
53. The method of claim 49 or 50, wherein the first polymer material or the second polymer material comprises a biological polymer.
54. The method of claim 53, wherein the biological polymer is selected from the group consisting of polysaccharide, polypeptide, and polynucleotides, and a combination thereof.
55. The method of any one of claims 44-54, wherein the inter-material non-covalent bonds are selected from the groups consisting of ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.
56. The method of any one of claims 44-55, wherein the inter-material non-covalent bonds are topological adhesion.
57. The method of any one of claims 44-56, wherein the first intra-material bonds are selected from the group consisting of covalent bonds, ionic bonds, hydrogen bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.
58. The method of claim 46 or 47, wherein the first intra-material bonds and second intra-material bonds are selected from the group consisting of covalent bonds, ionic bonds, hydrogen

bonds, van der Waals interactions,  $\pi$ - $\pi$  stackings, host-guest interactions, and a combination thereof.

59. The method of claim 46 or 47, wherein the inter-material non-covalent bonds are hydrogen bonds and the first intra-material bonds or the second intra-material bonds are ionic bonds.

60. The method of any one of claims 44-59, wherein the adhesion energy between the first polymer material and the second material is from about 40 J/m<sup>2</sup> to about 5000 J/m<sup>2</sup>.

61. The method of any one of claims 44-60, wherein the first polymer material and the second material are adhered within about 1 second, 30 seconds, 1 minute, 10 minutes, 1 hour, 2 hours, 6 hours, 12 hours, 24 hours, 121 hours, and 1 month after contacting the first and second materials.

62. The method of any one of claims 44-61, further comprising providing an inter-material layer between the first material and the second material and comprising a tape, a powder, a brush, a solution, or an inter-material complex; wherein the first inter-material bonding units and the second inter-material bonding units are at least partially located in the inter-material layer.

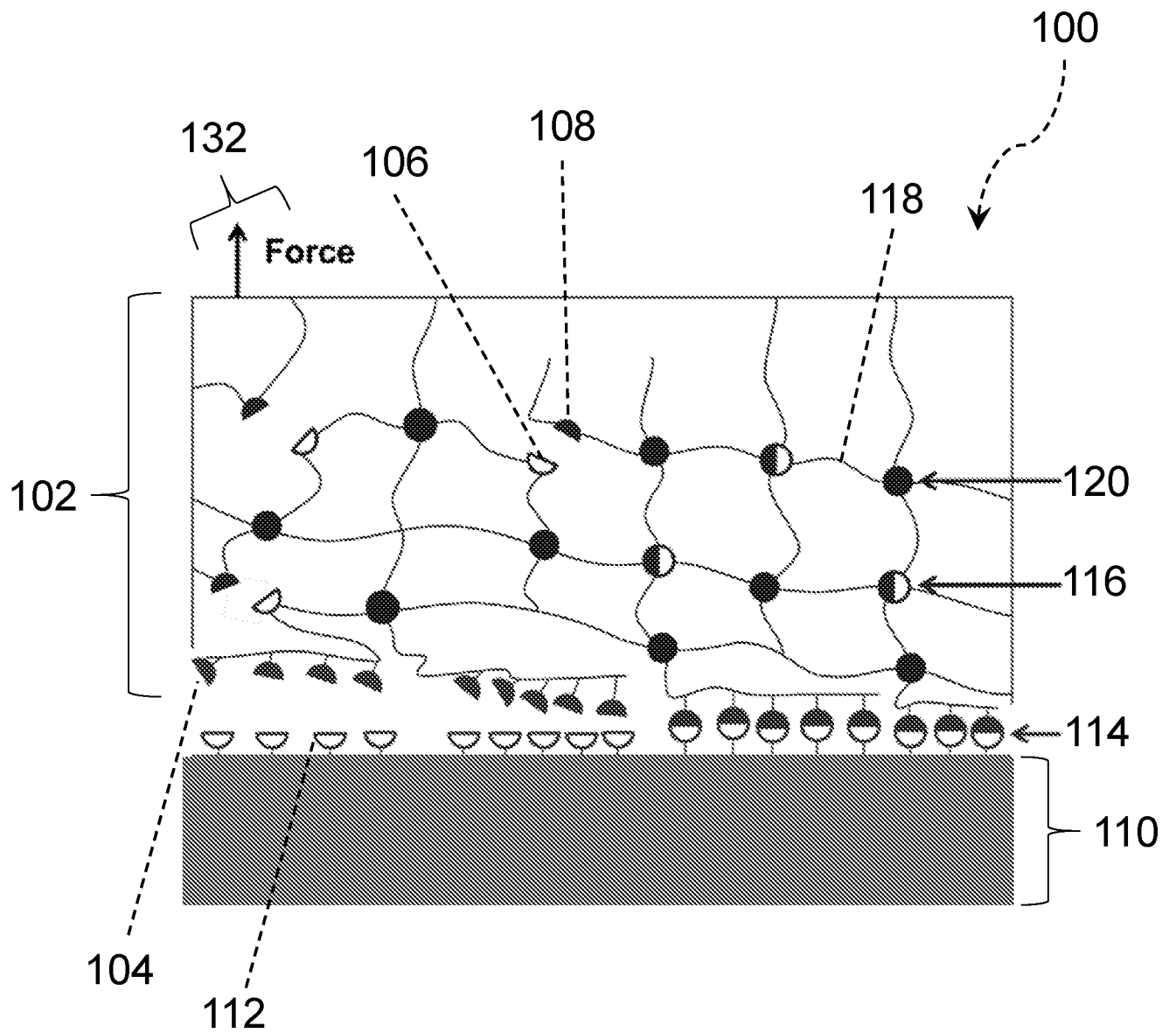


FIG. 1A

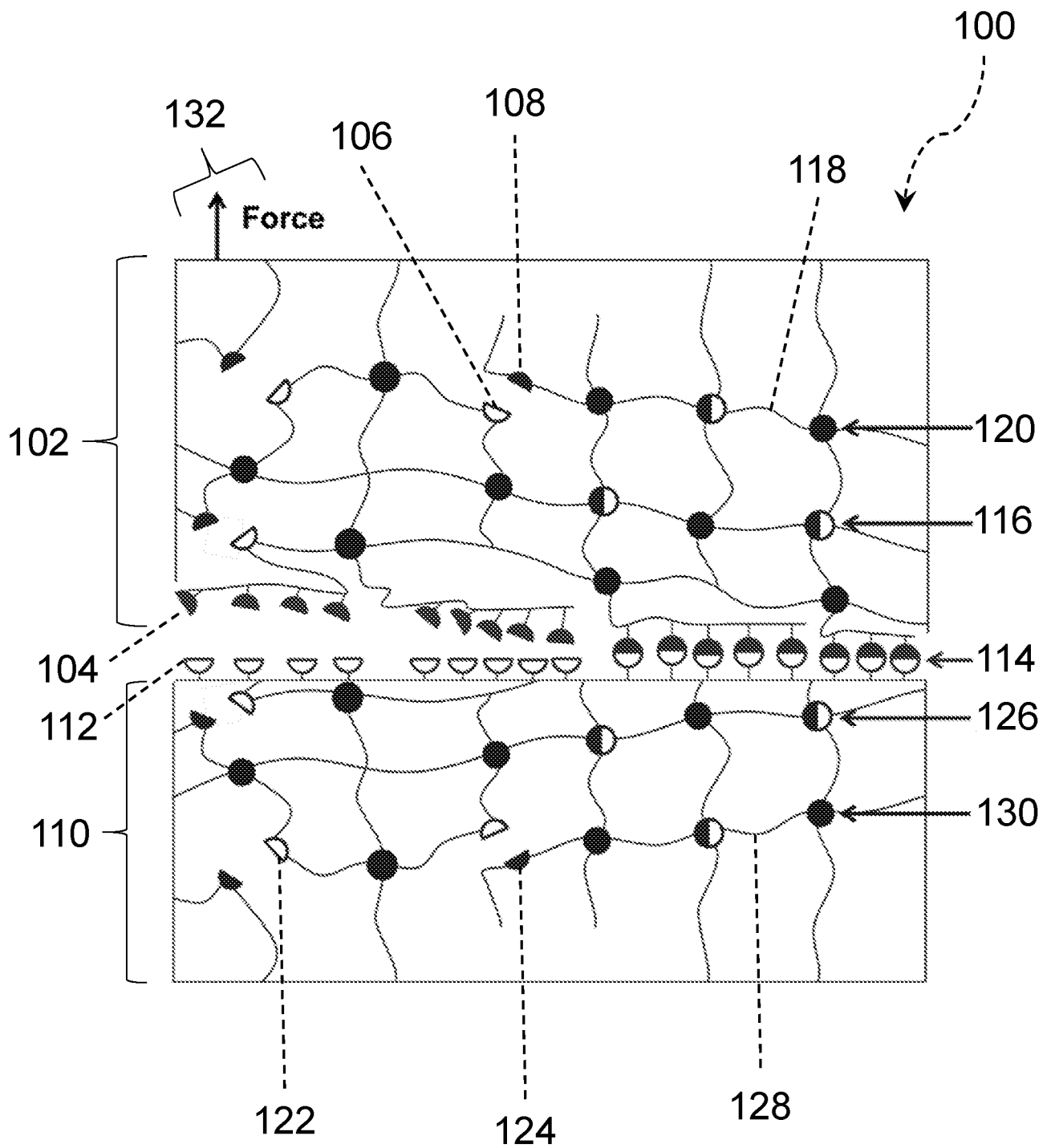


FIG. 1B

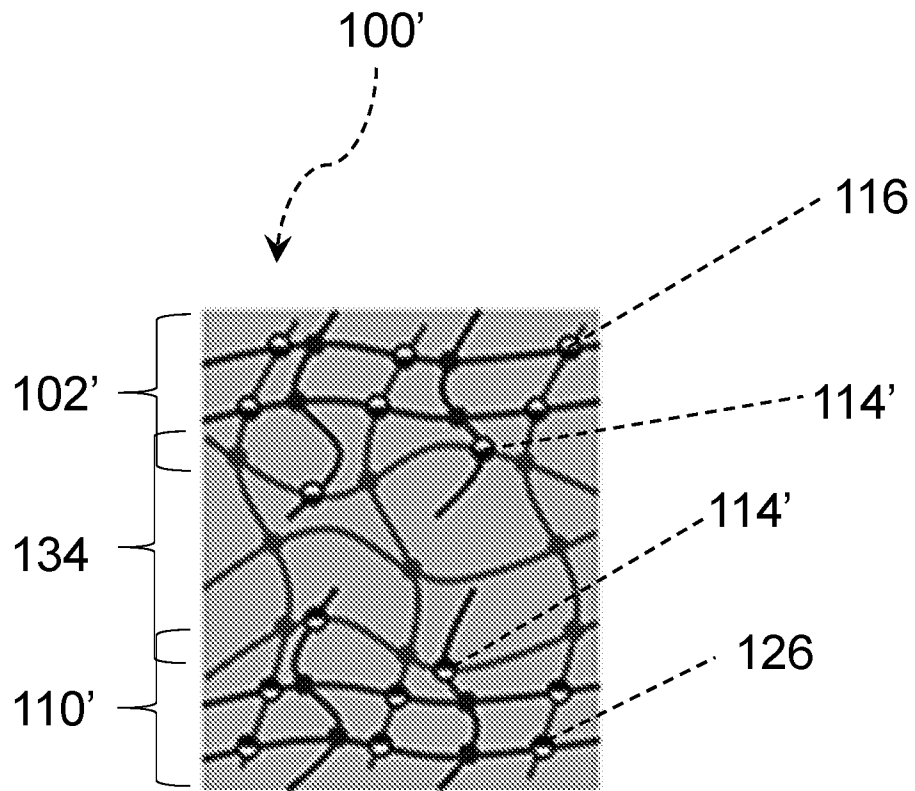


FIG. 1C

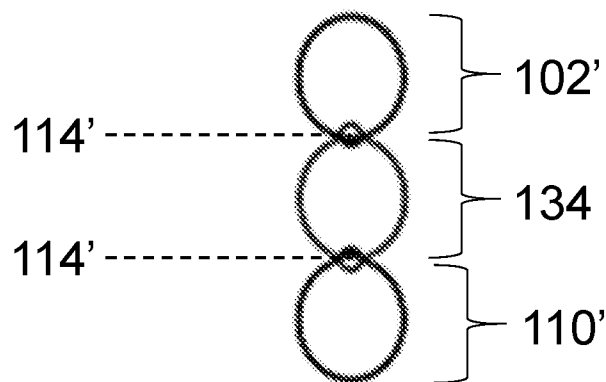


FIG. 1D

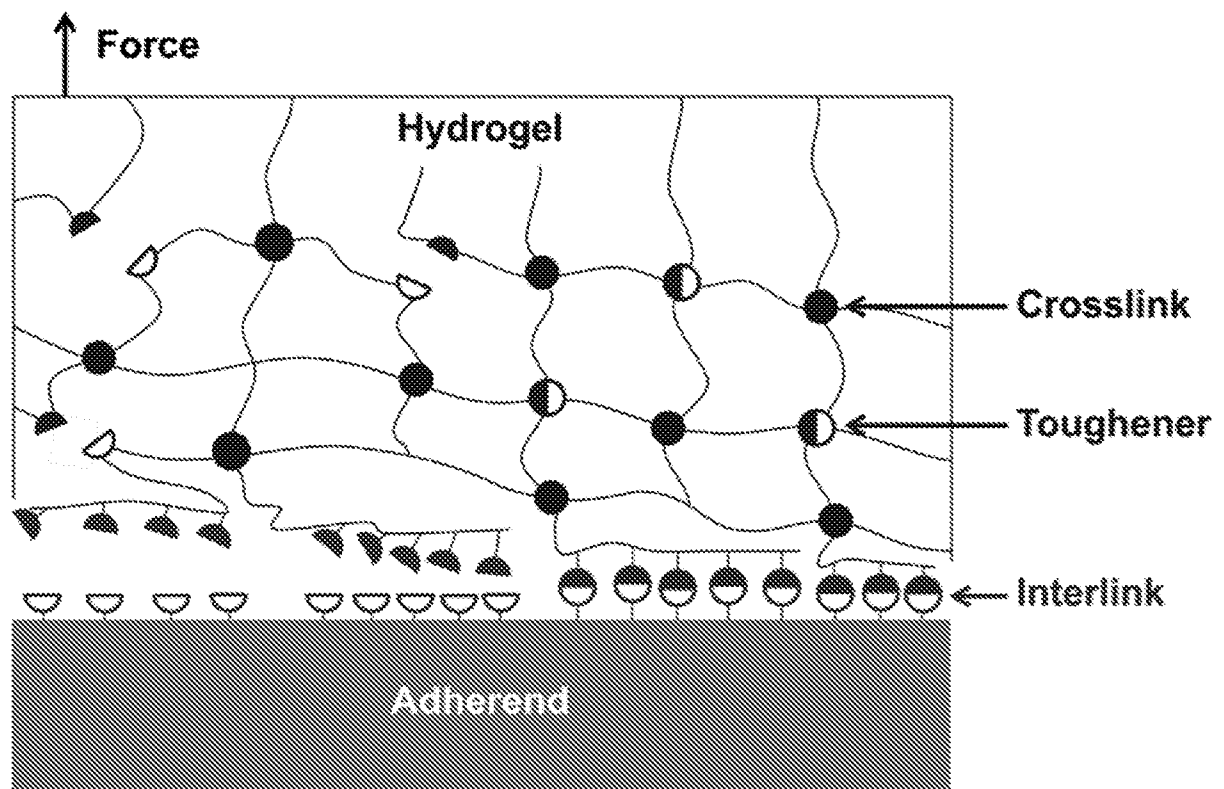


FIG. 1E

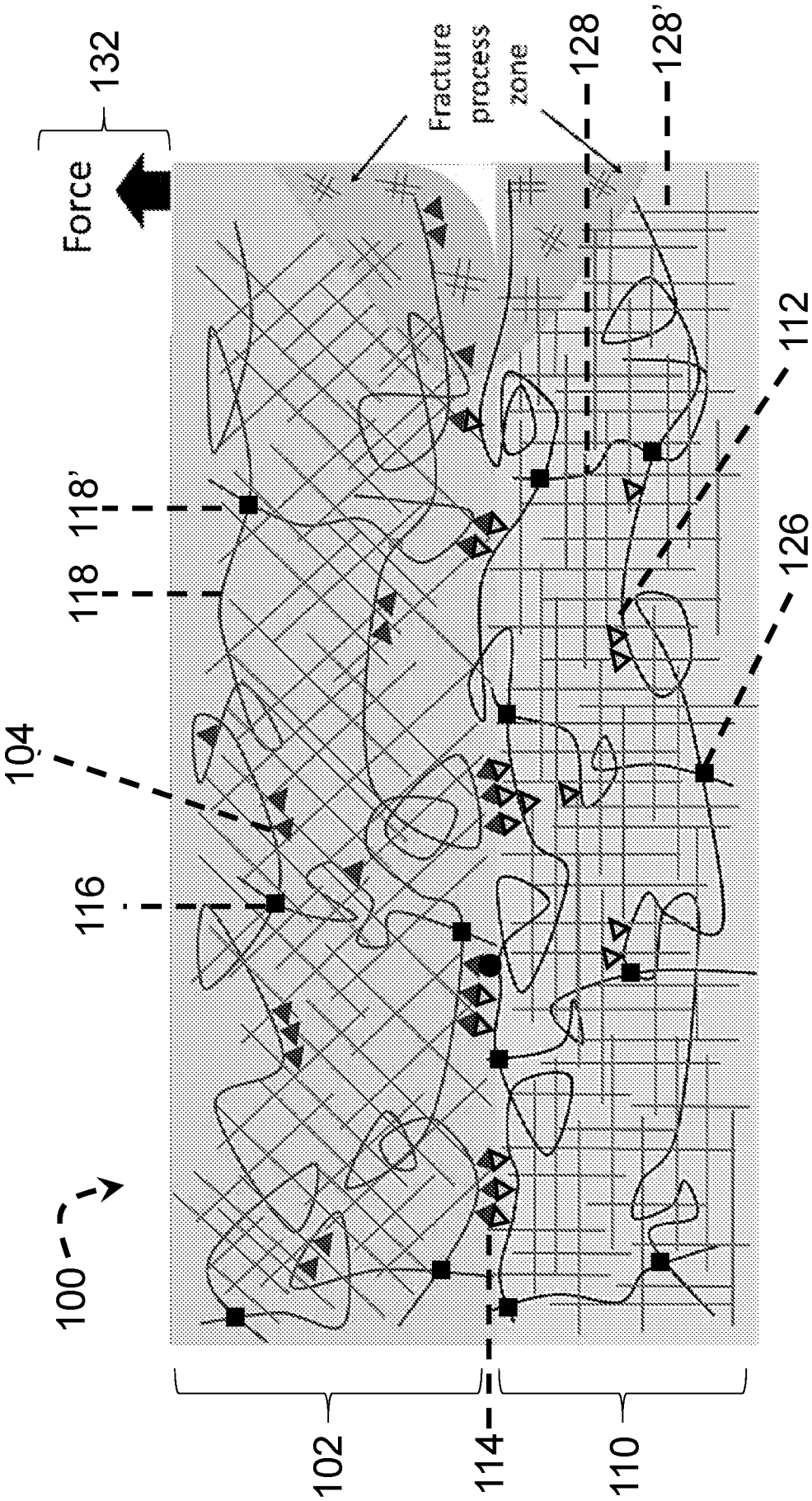


FIG. 1F

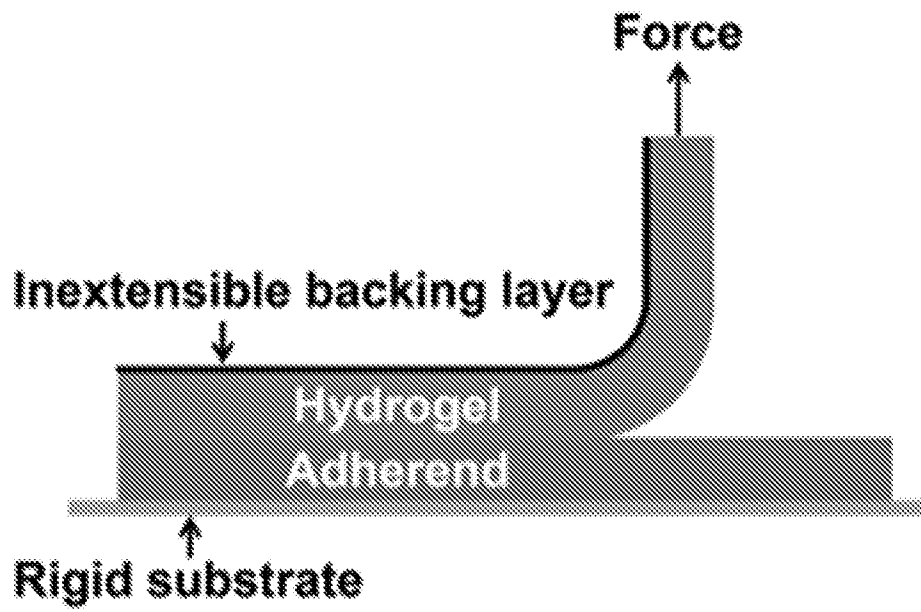


FIG. 2A

FIG. 2B

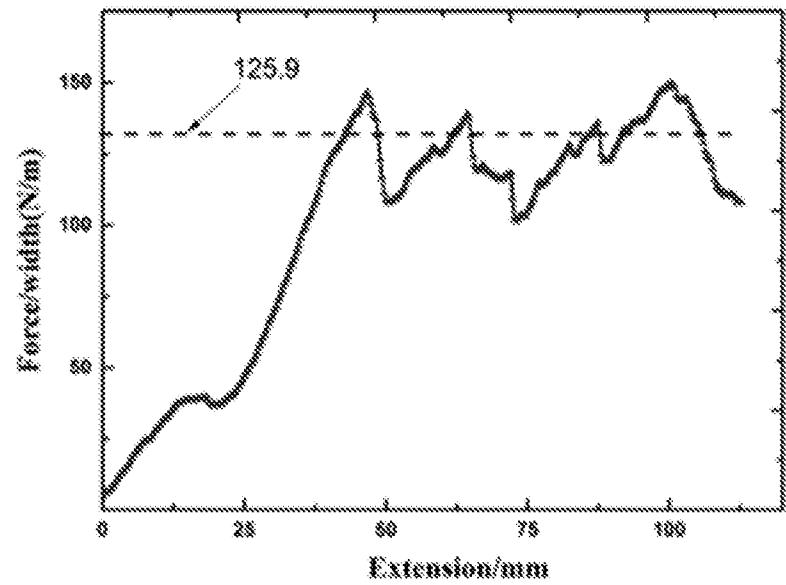


FIG. 2C

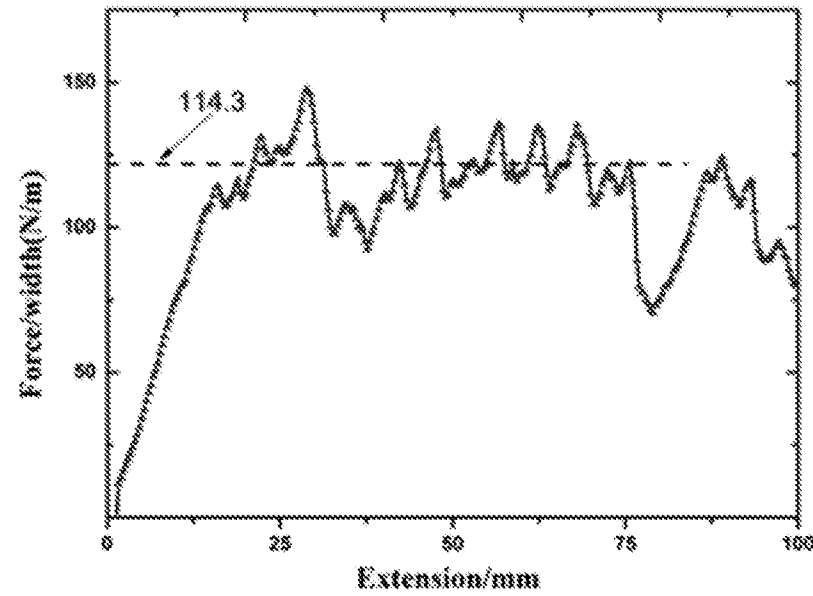


FIG. 2D

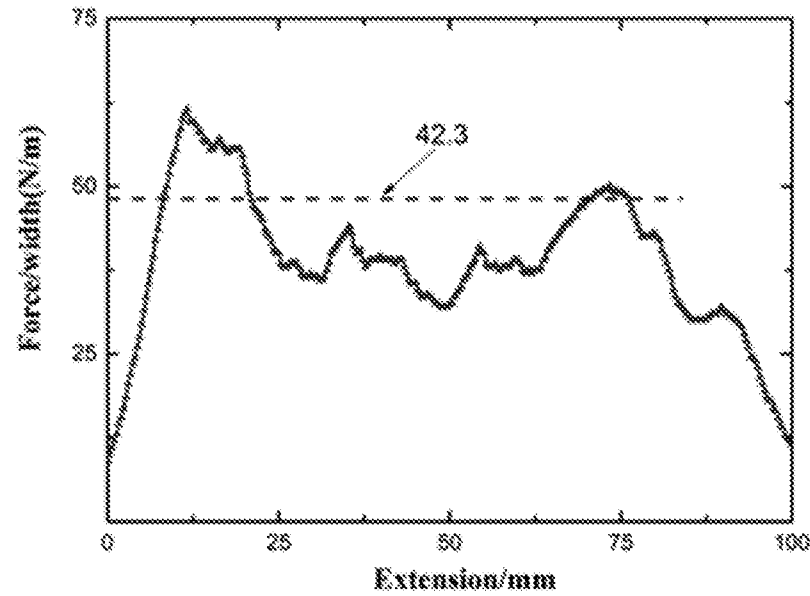


FIG. 3A

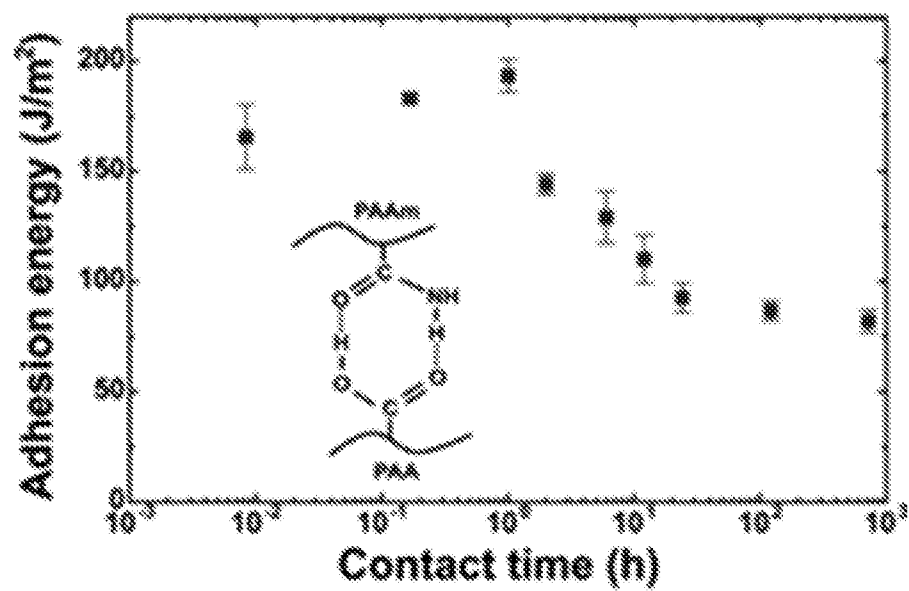


FIG. 3B

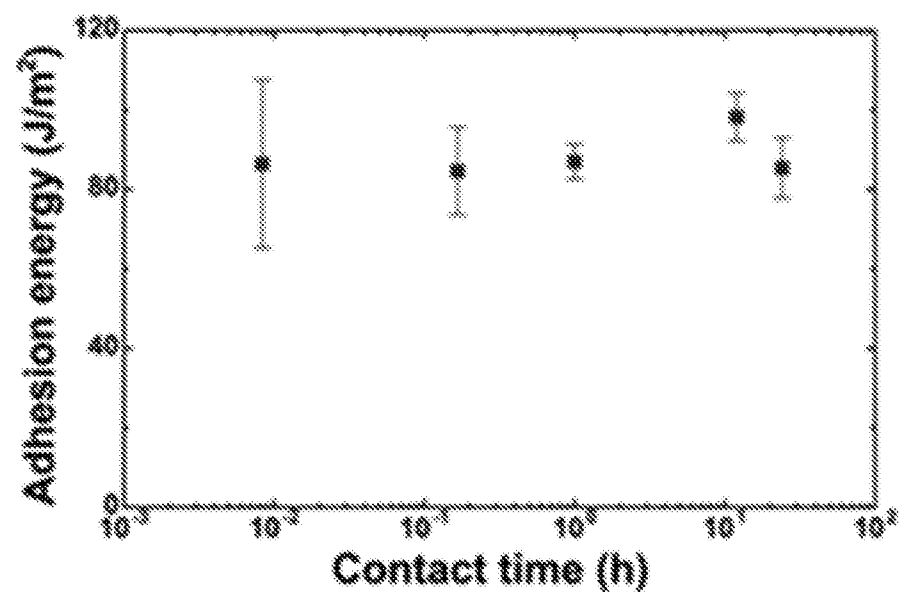


FIG. 3C

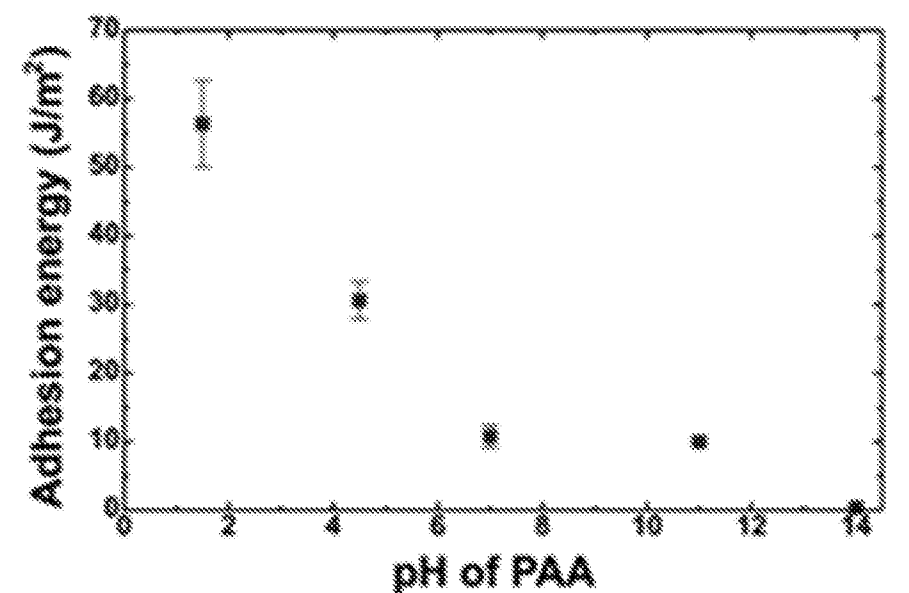


FIG. 3D

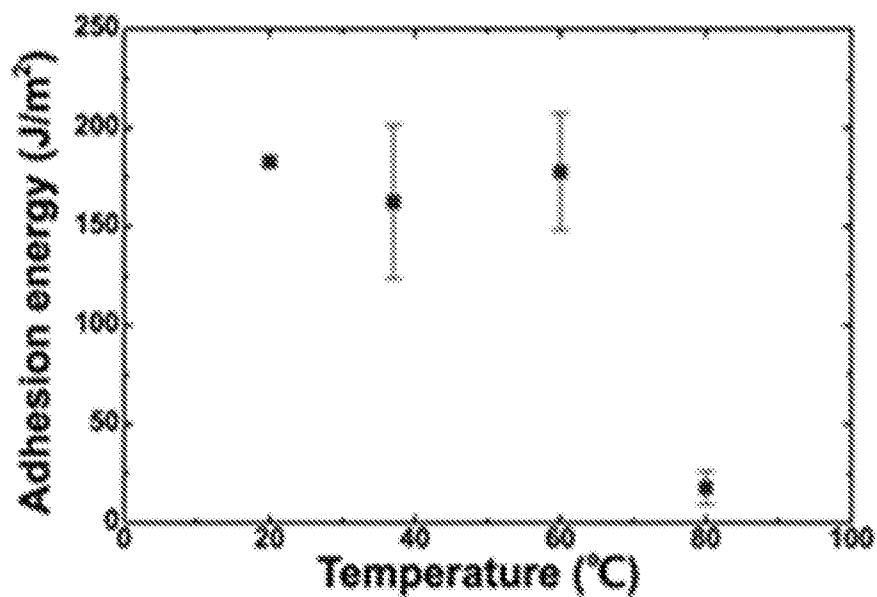


FIG. 3E

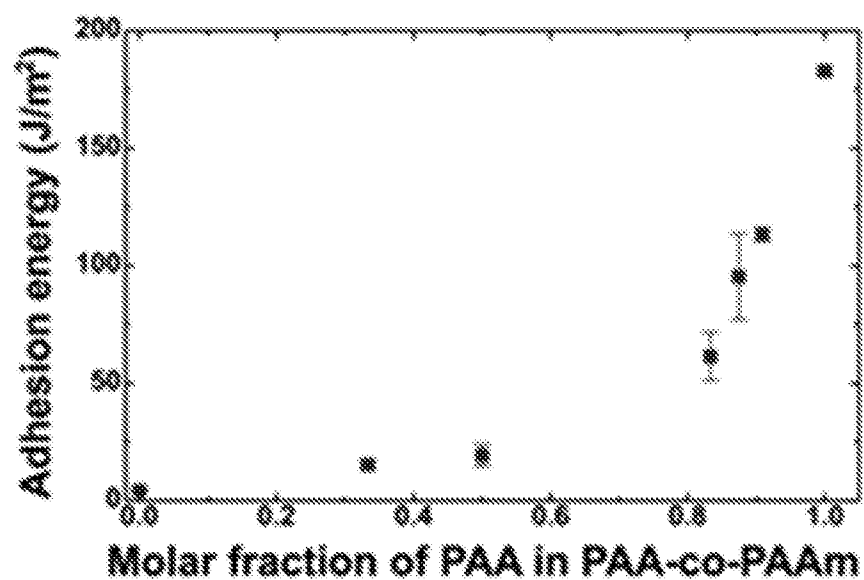


FIG. 3F

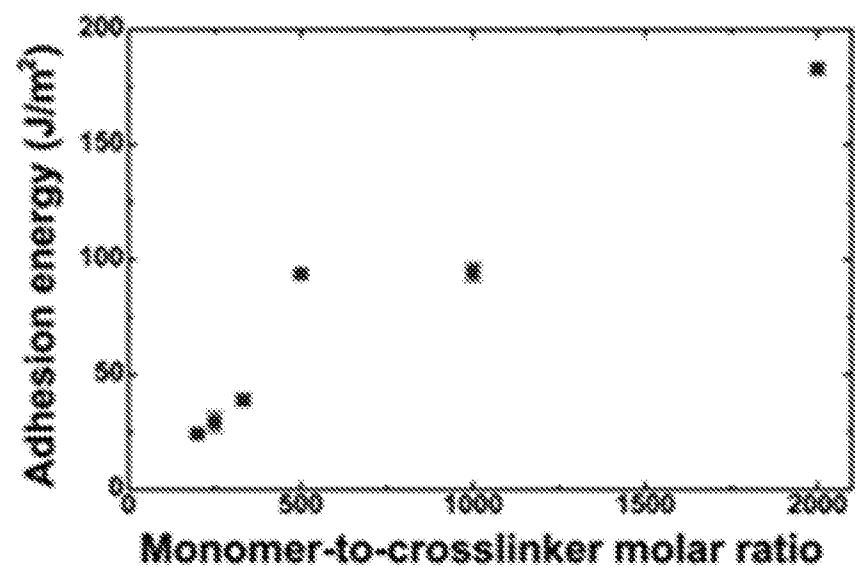


FIG. 3G

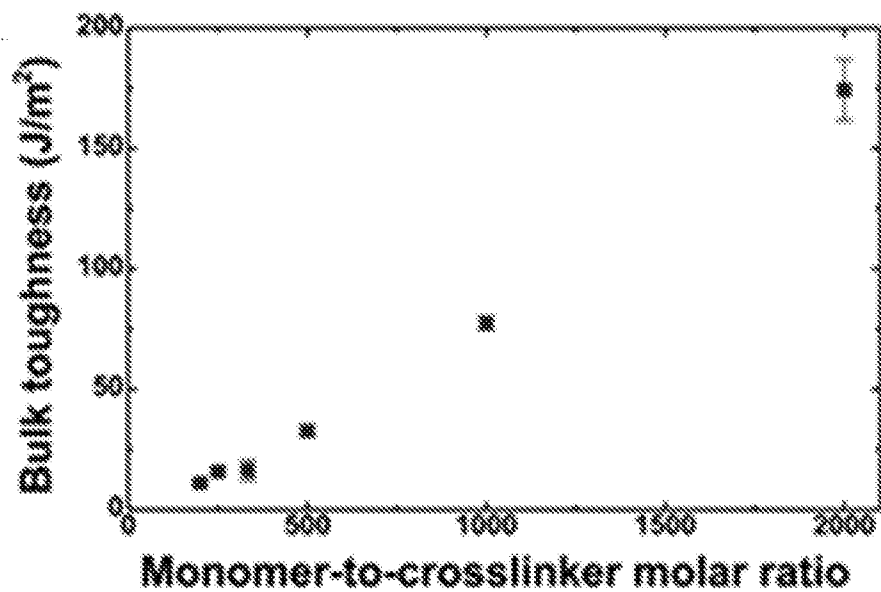


FIG. 3H

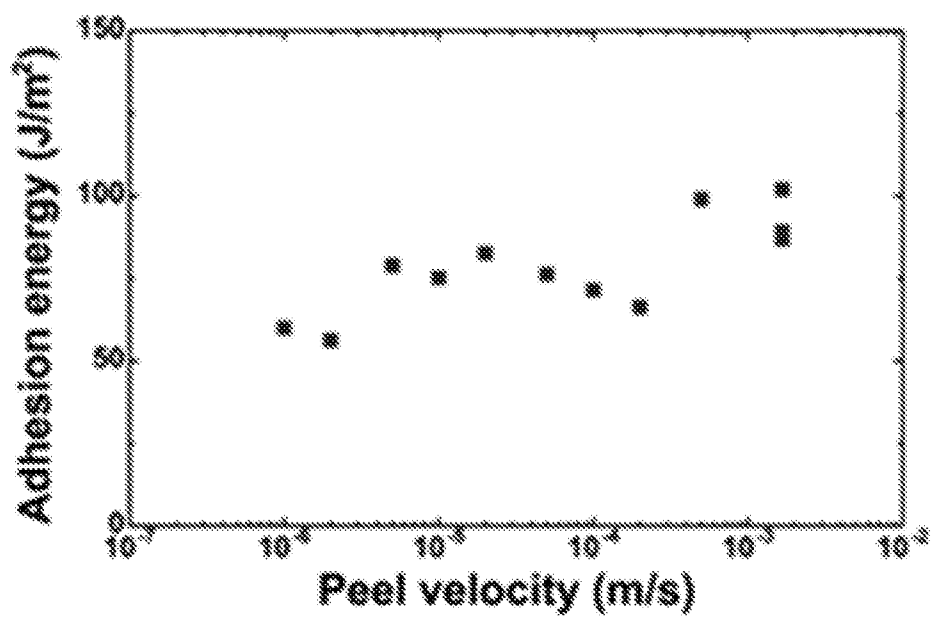
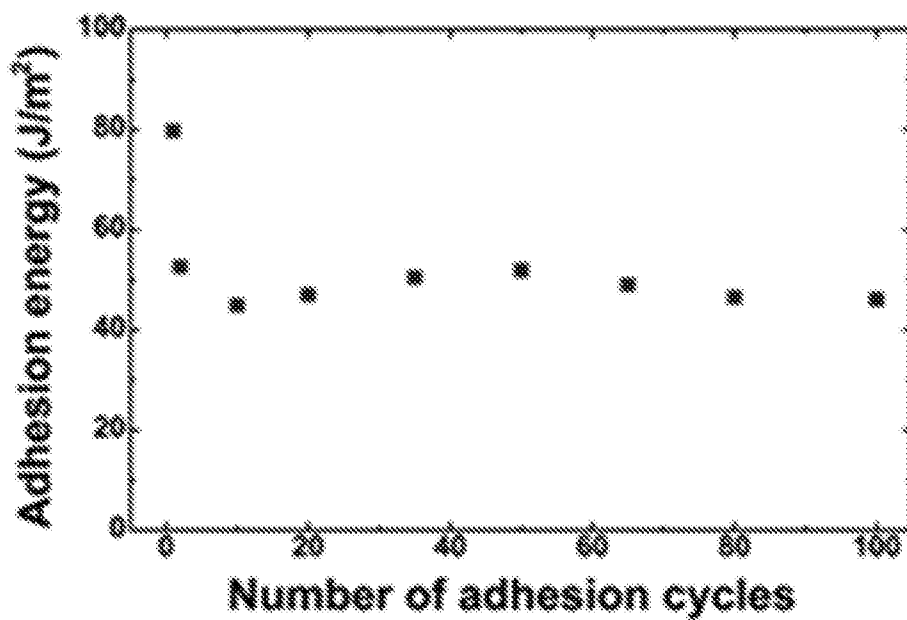


FIG. 3I



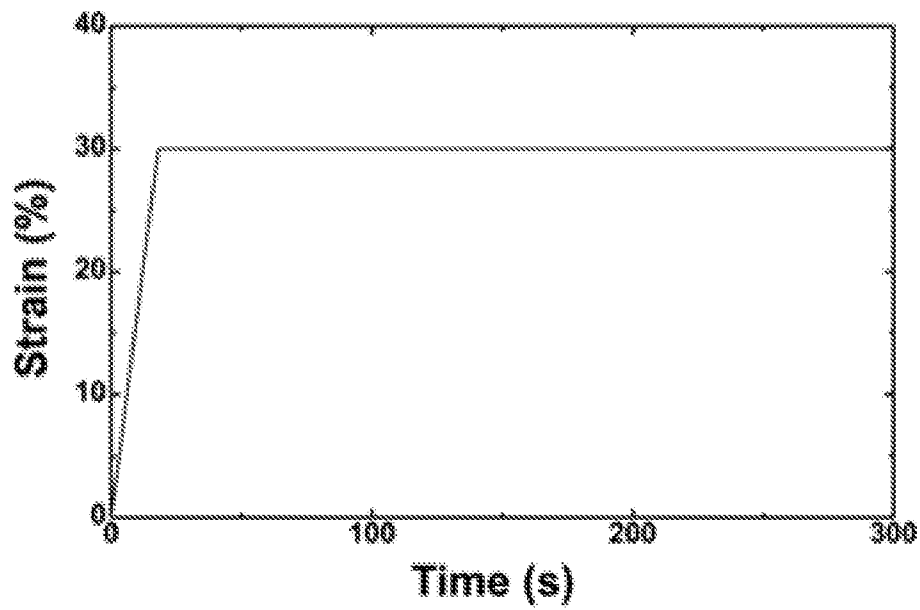


FIG. 4A

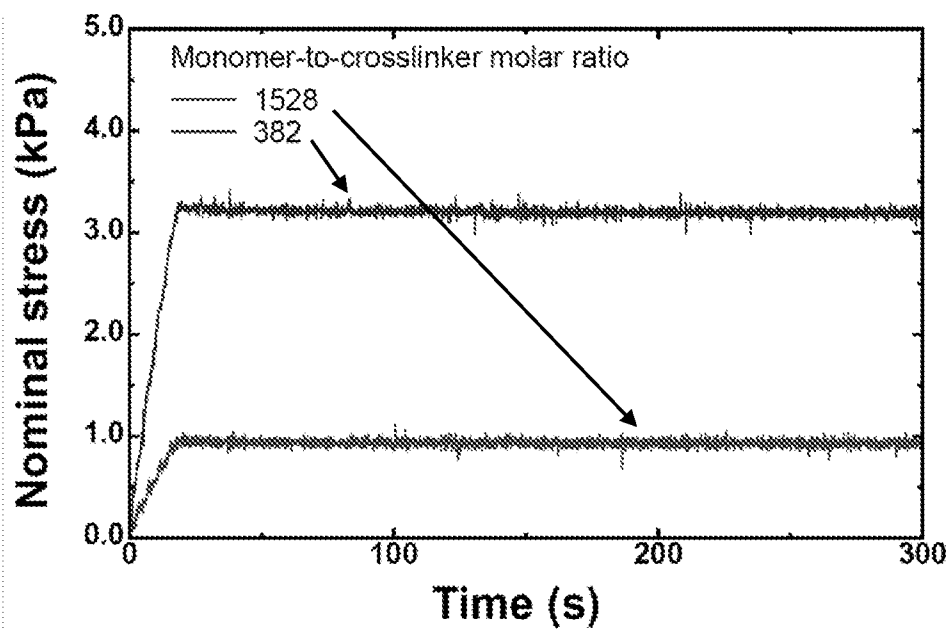


FIG. 4B

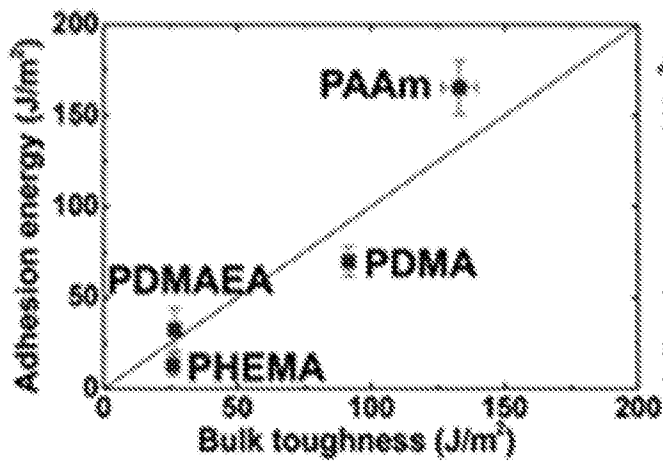


FIG. 5A

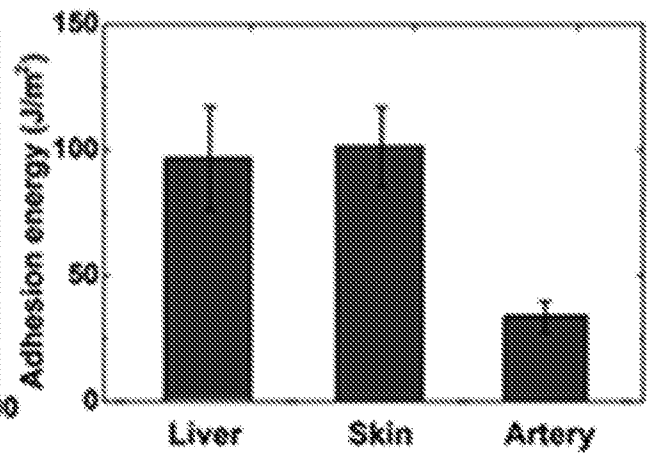


FIG. 5B

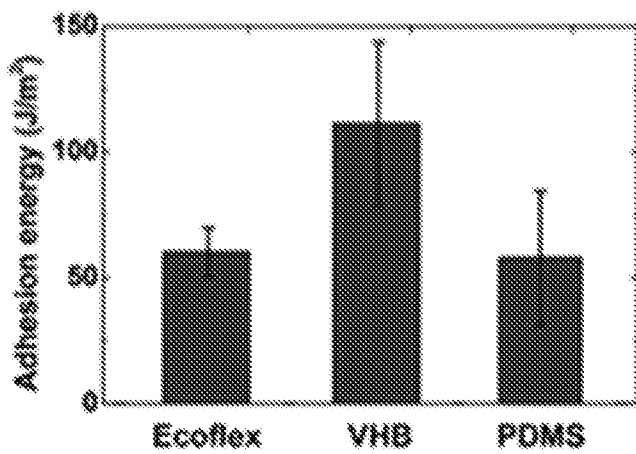


FIG. 5C

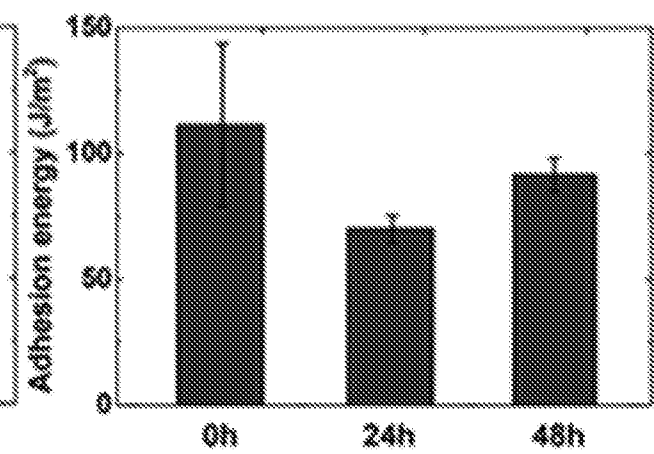


FIG. 5D

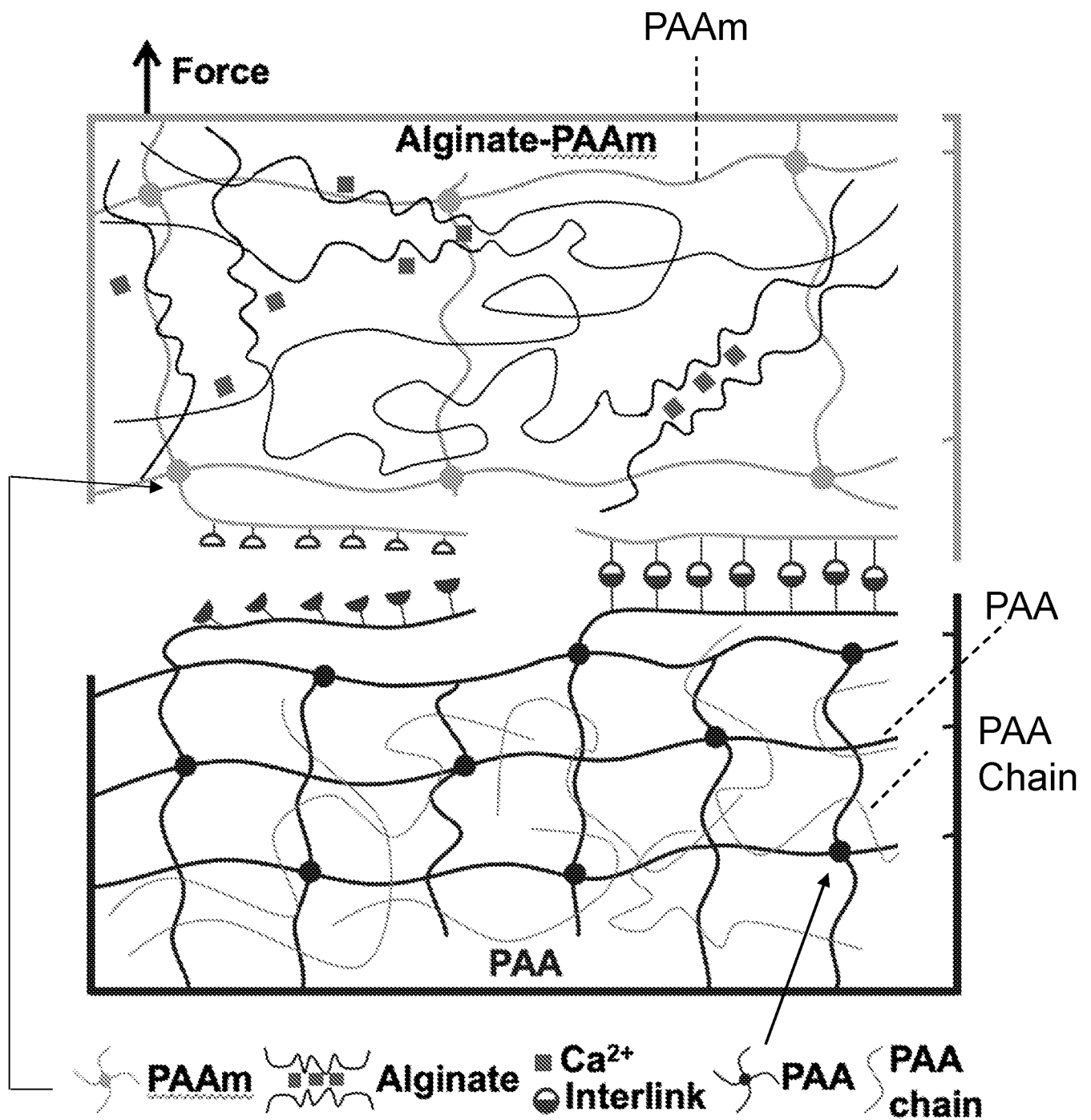


FIG. 6A

FIG. 6B

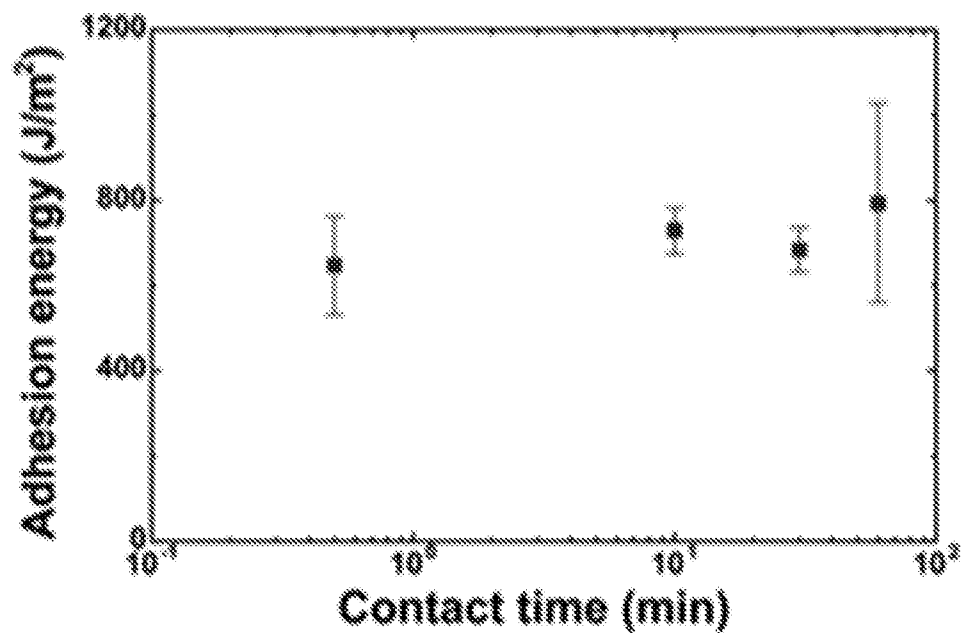


FIG. 6C

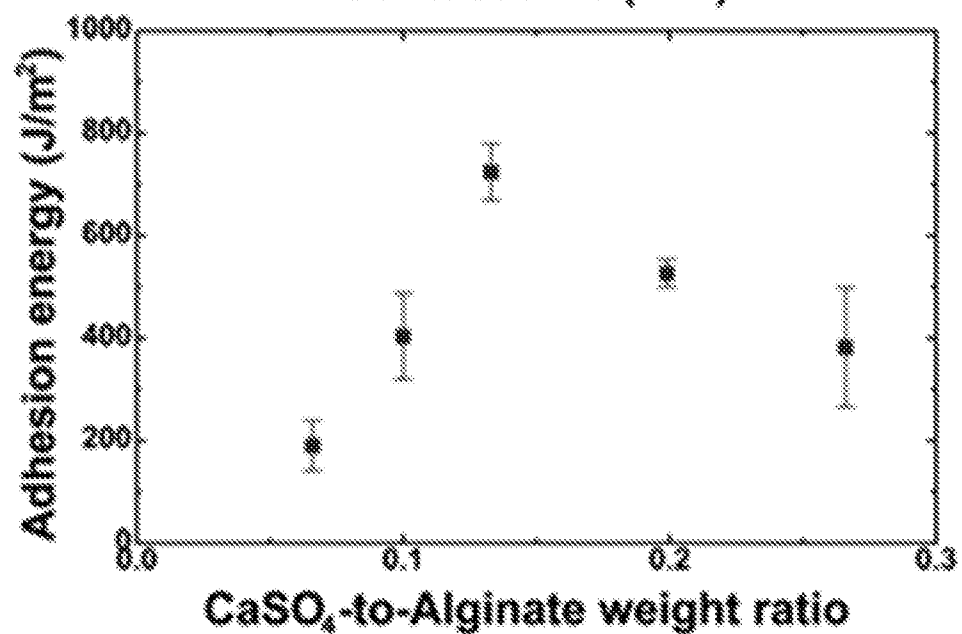
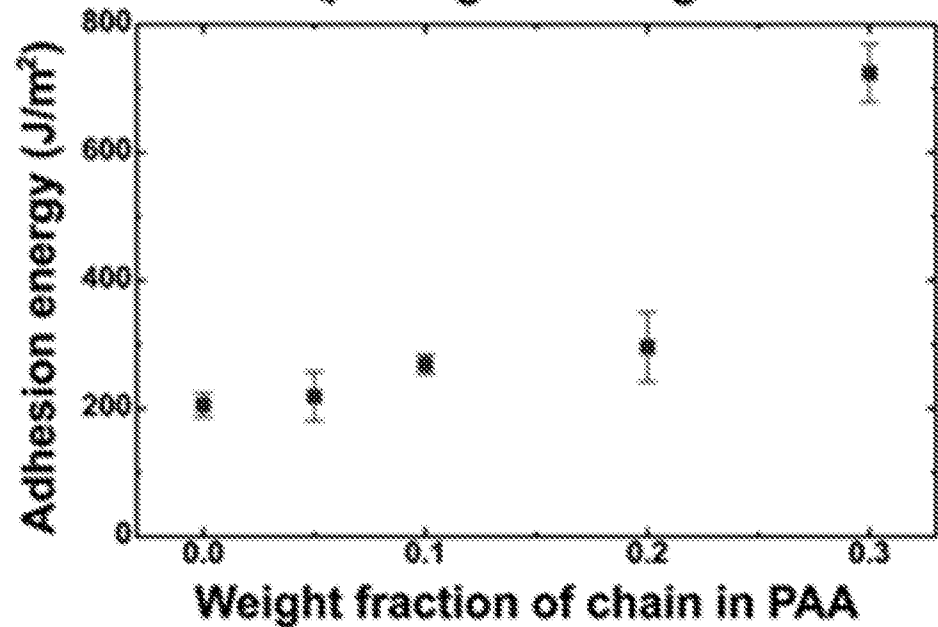


FIG. 6D



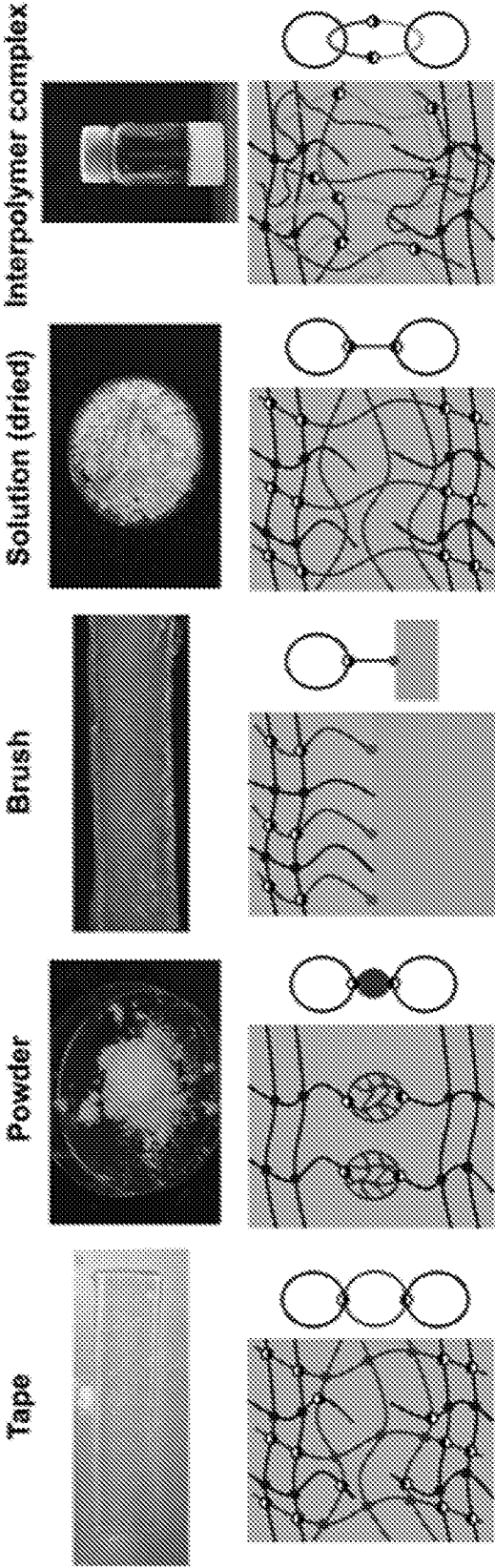
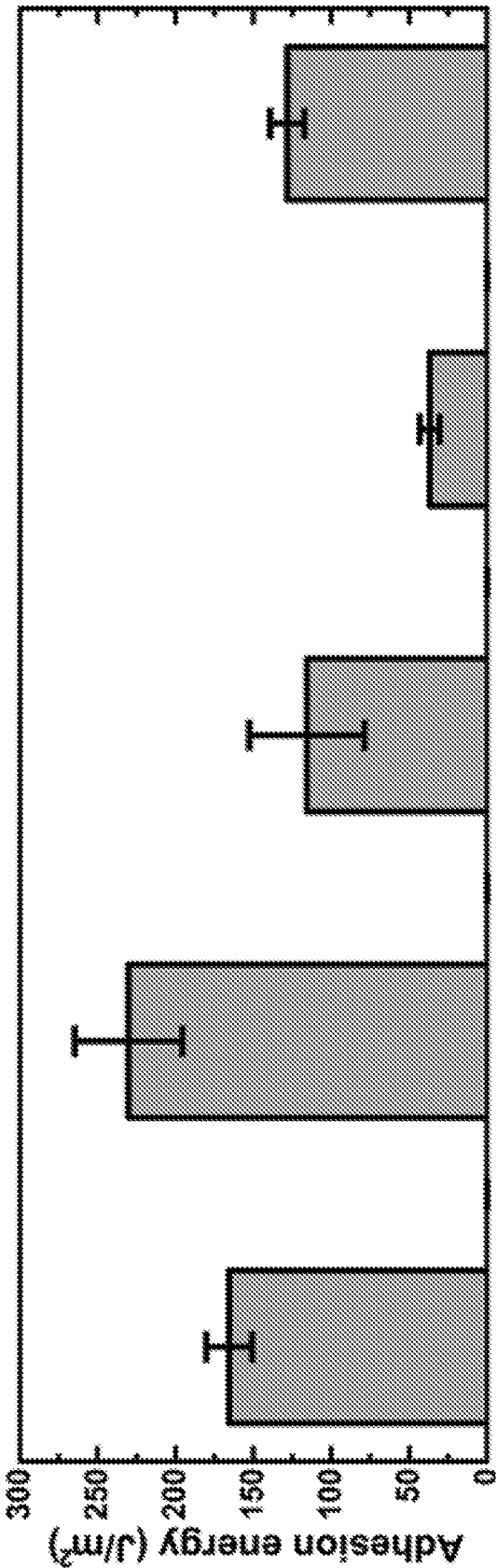


FIG. 7A

FIG. 7B



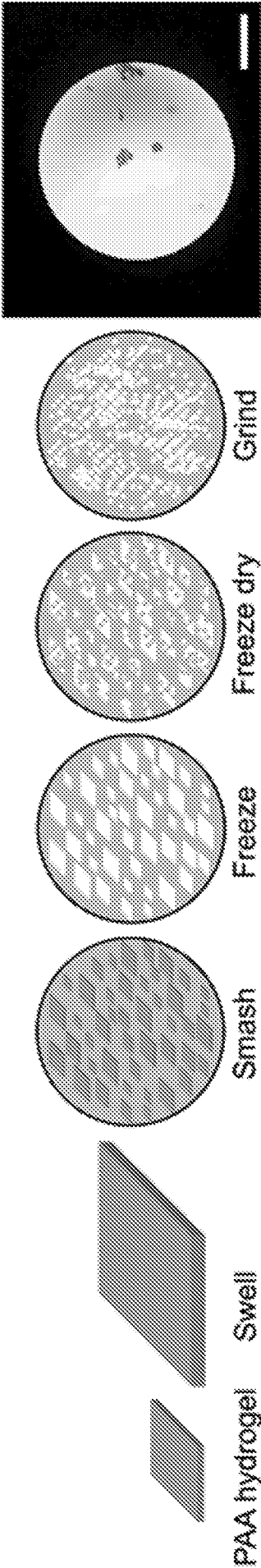


FIG. 8

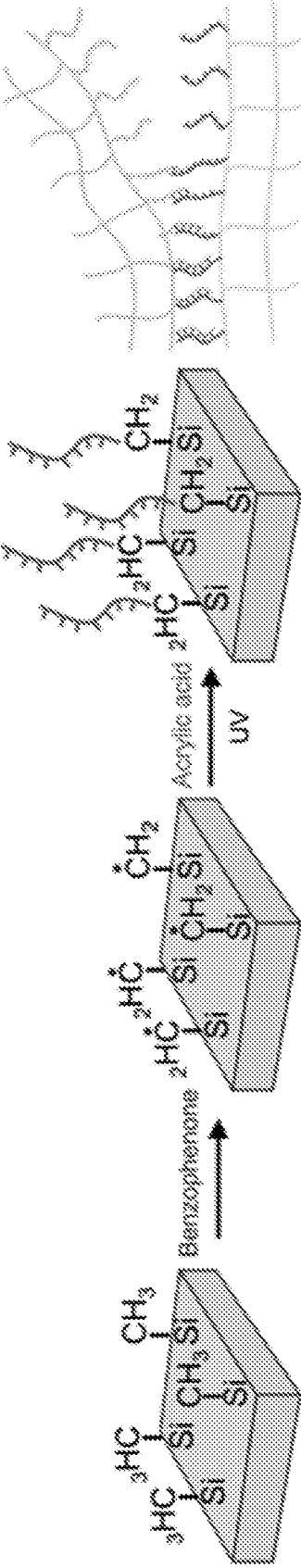


FIG. 9A

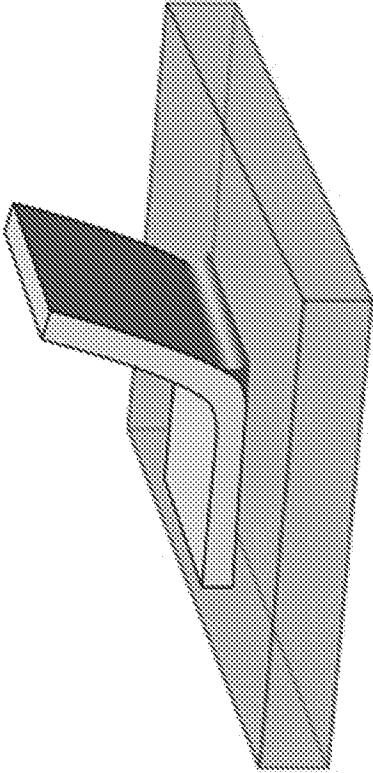
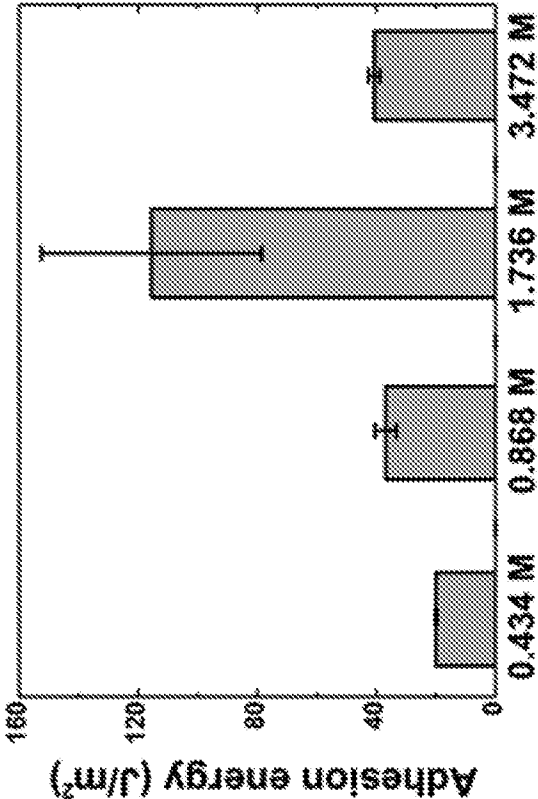


FIG. 9B

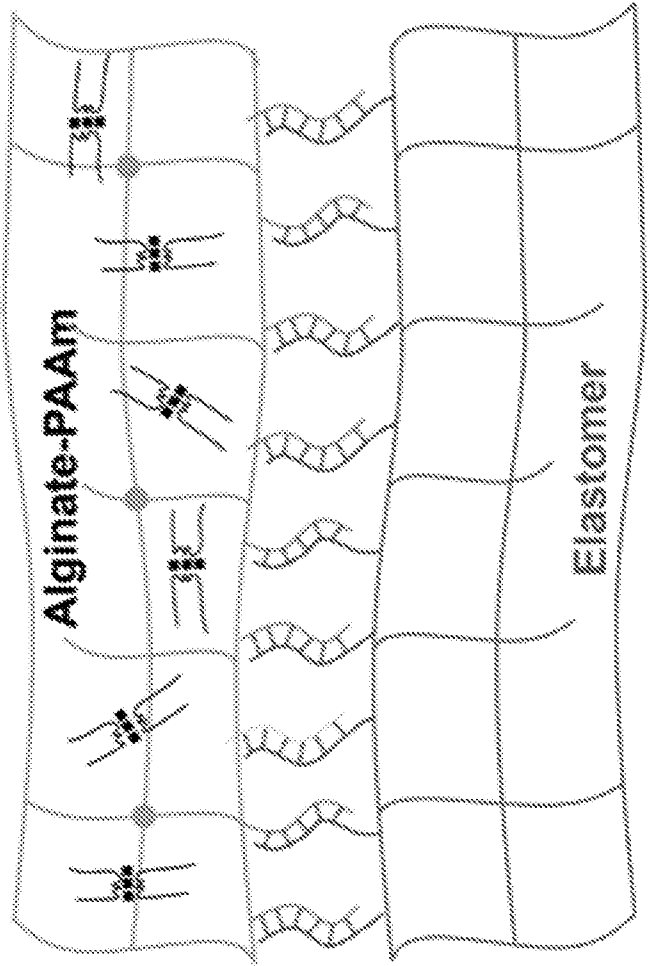


FIG. 10A

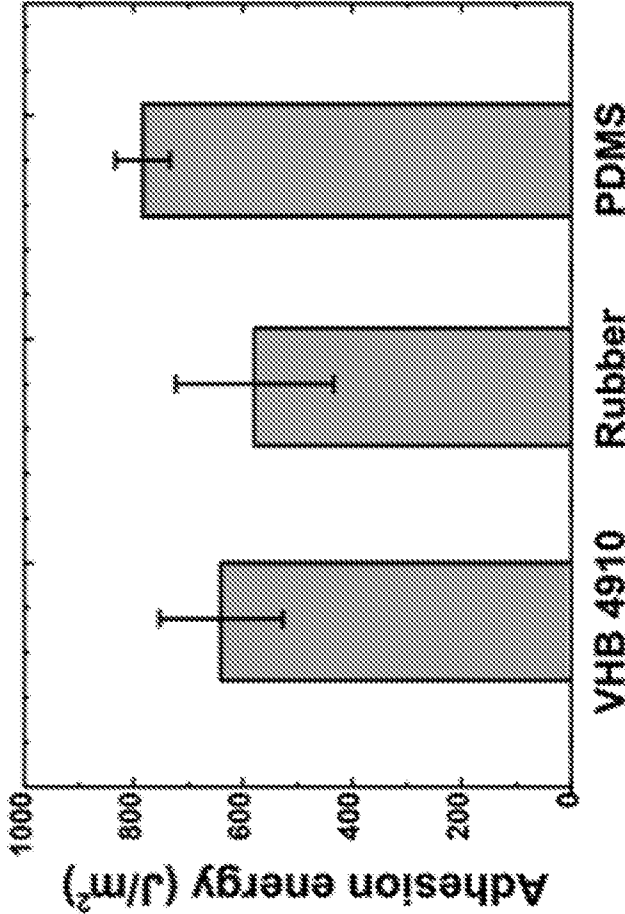


FIG. 10B

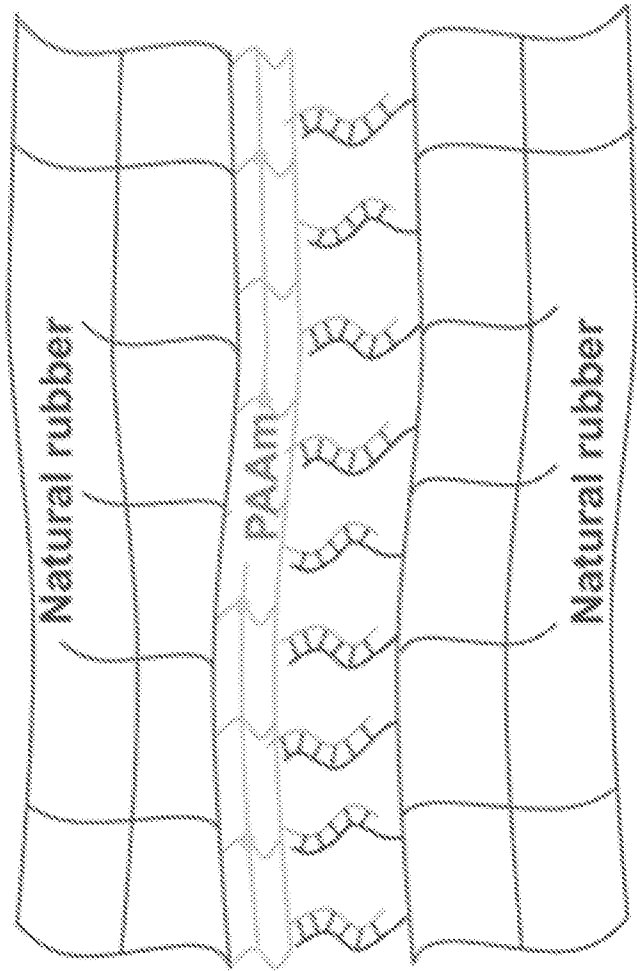


FIG. 11A

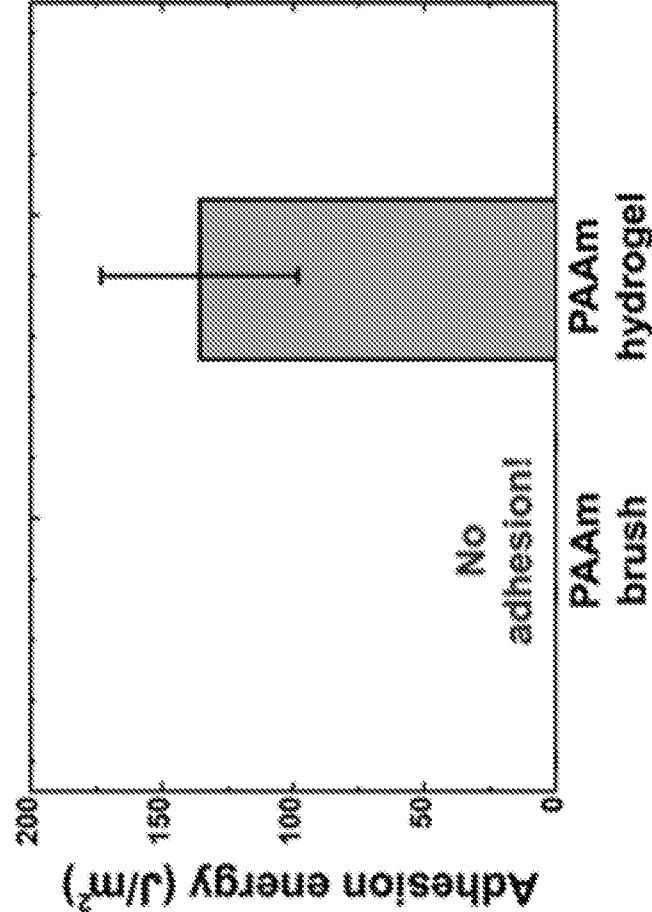


FIG. 11B

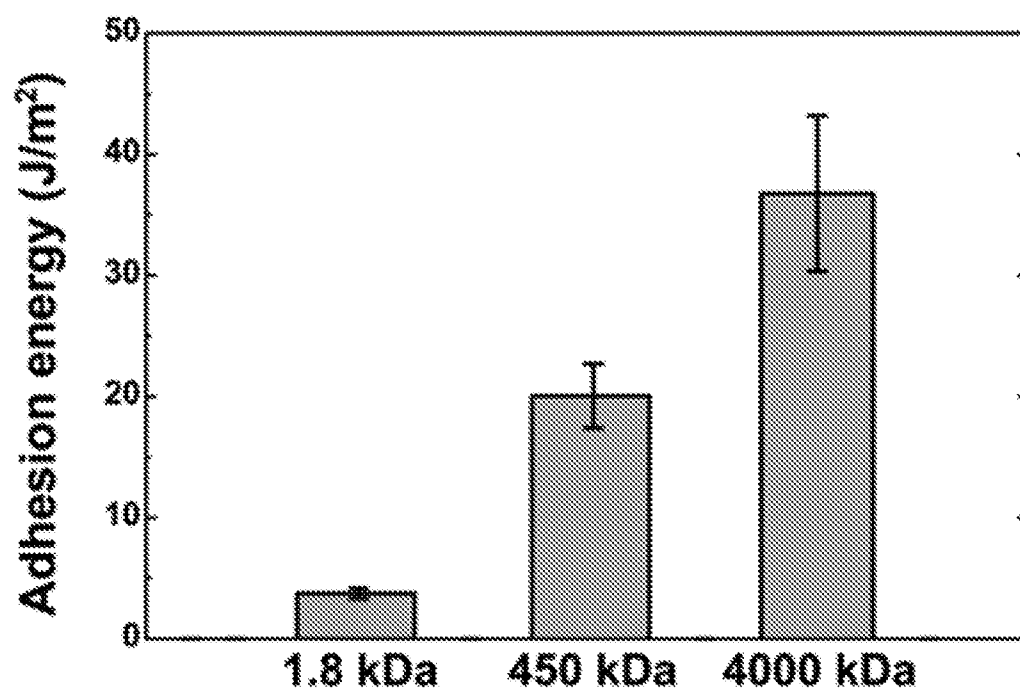


FIG. 12

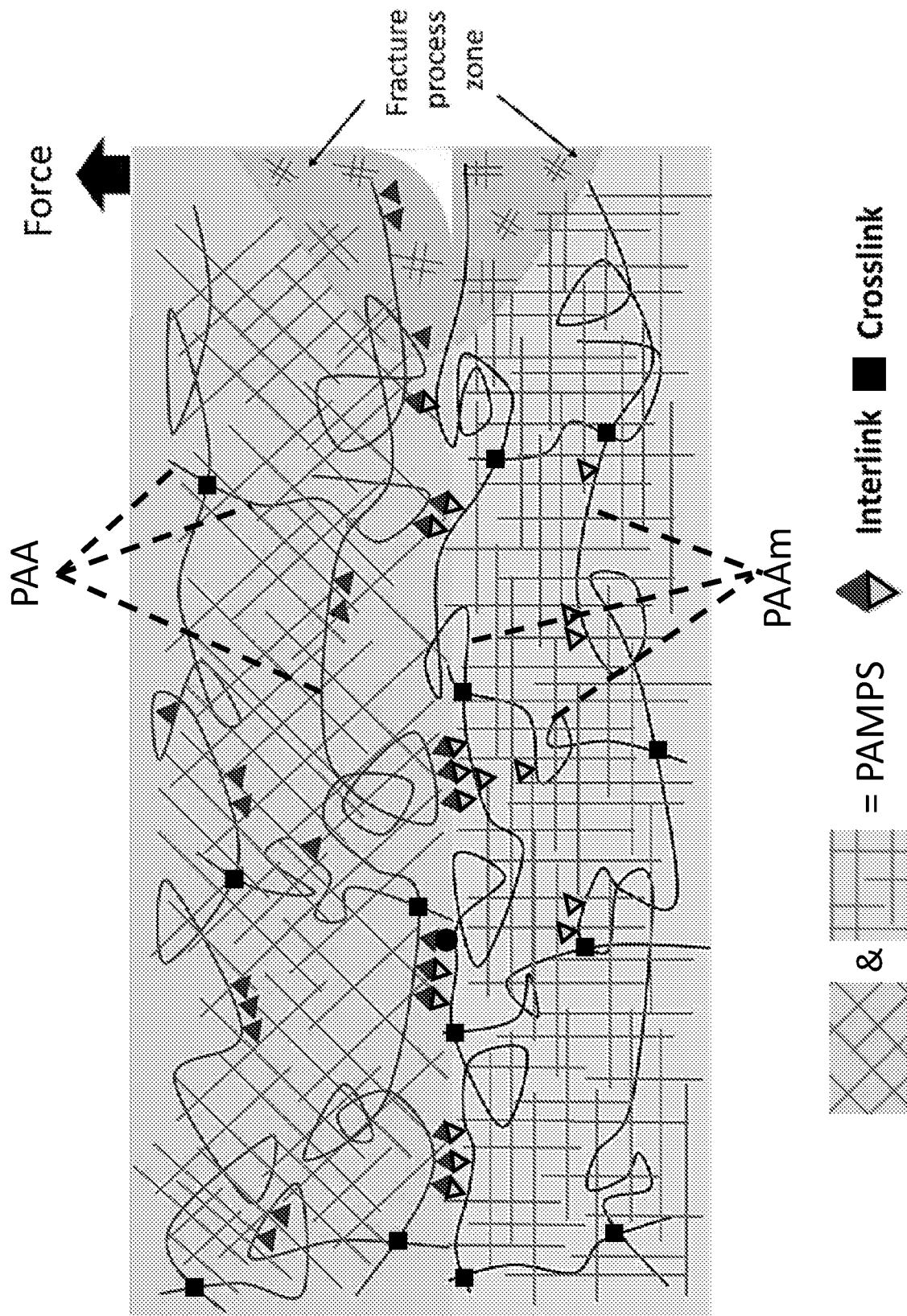


FIG. 13

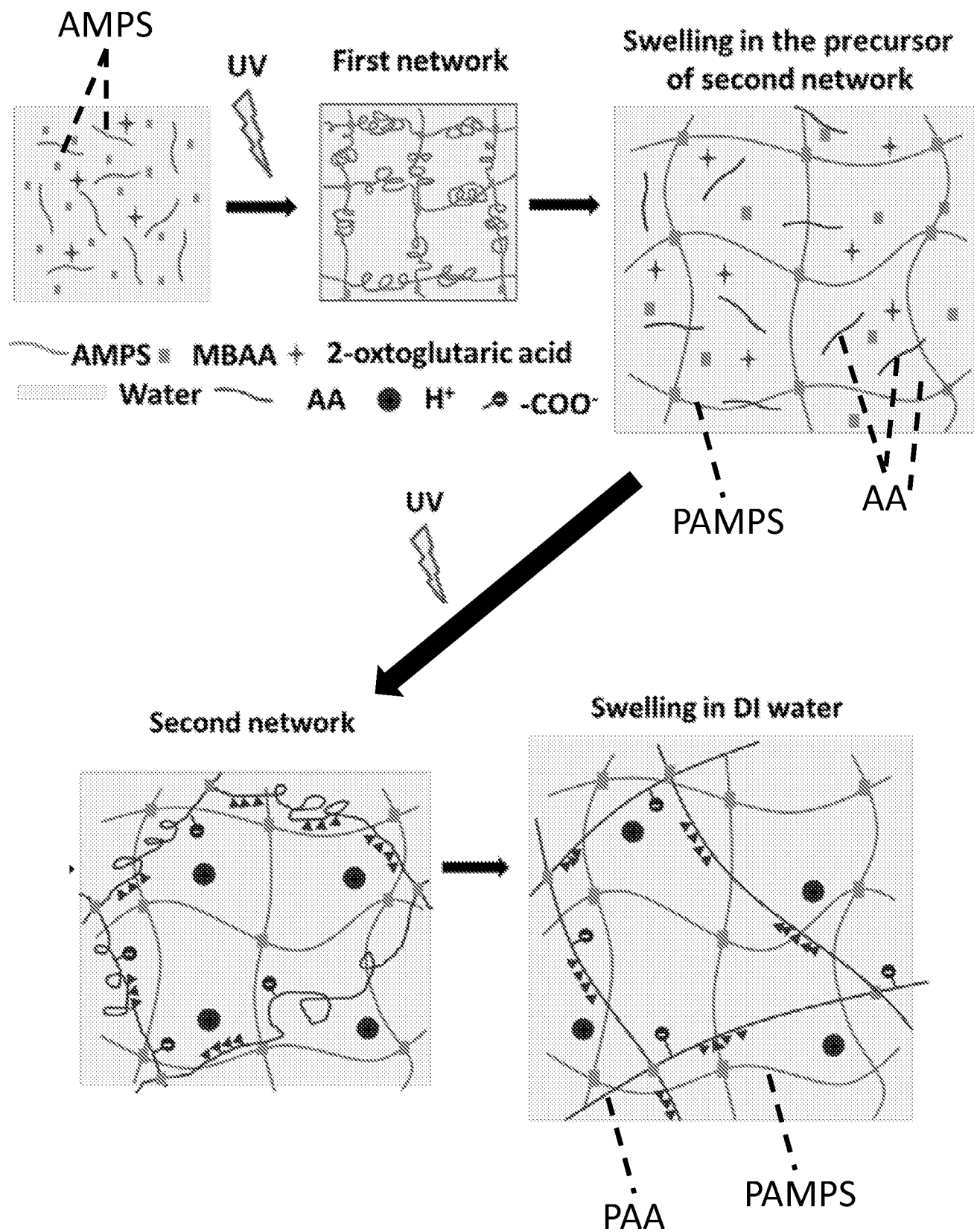


FIG. 14

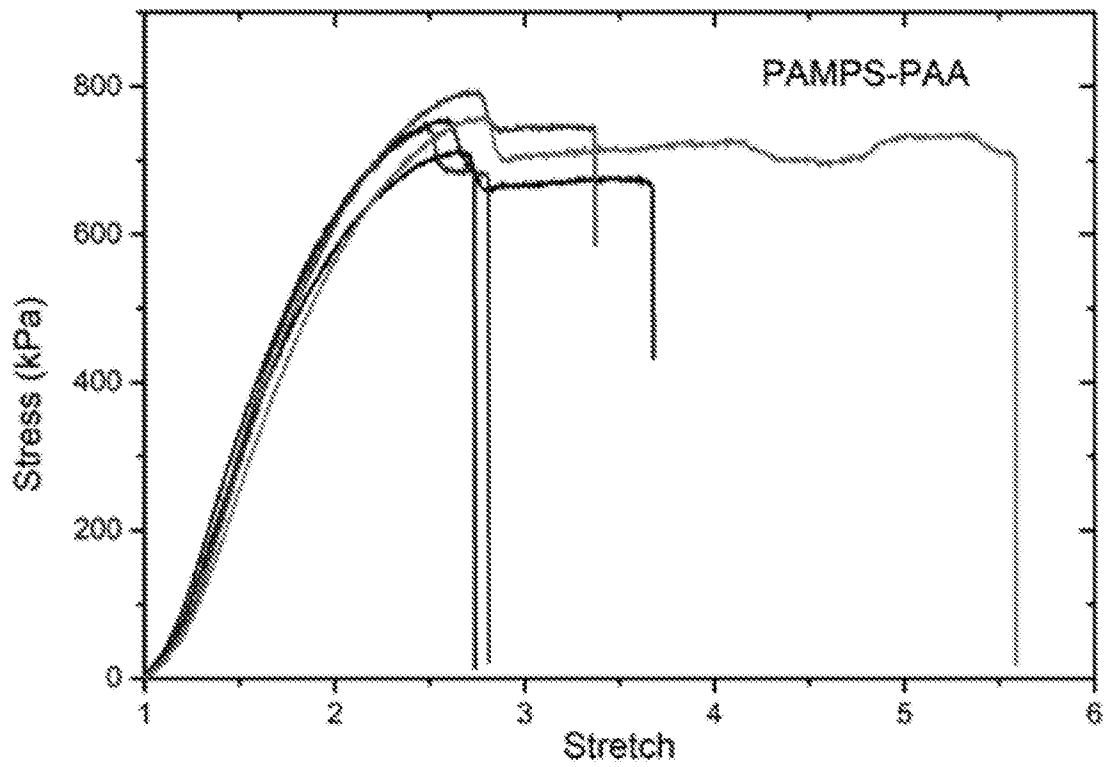


FIG. 15A

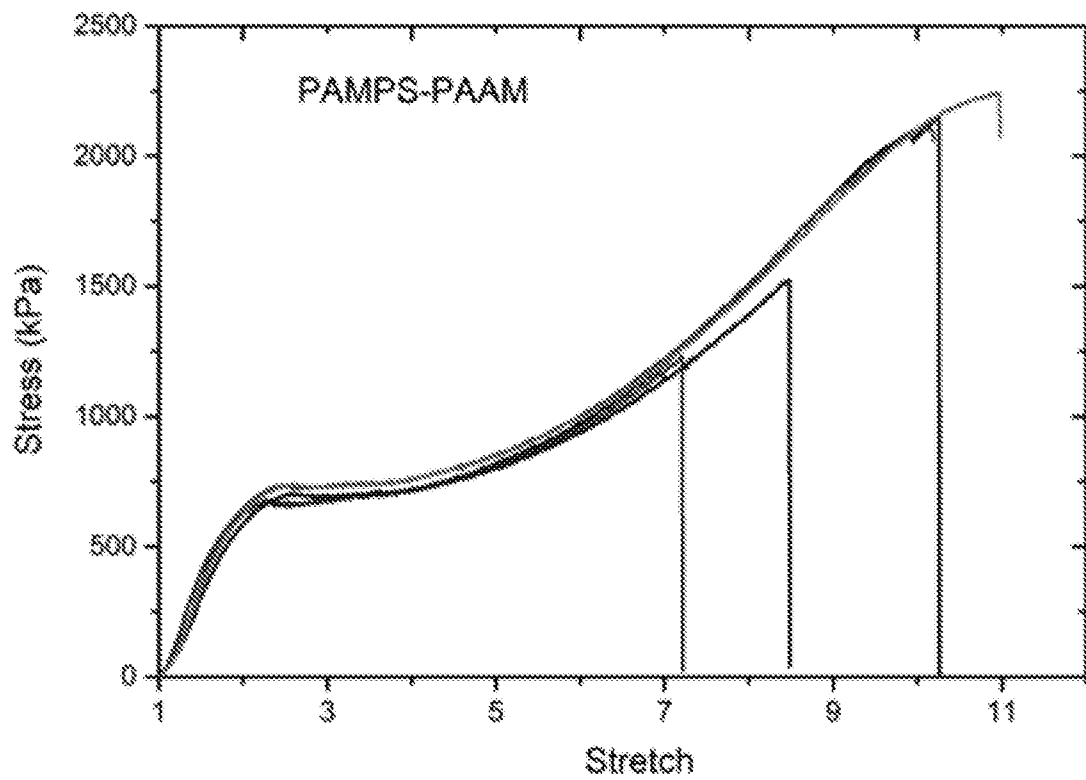


FIG. 15B

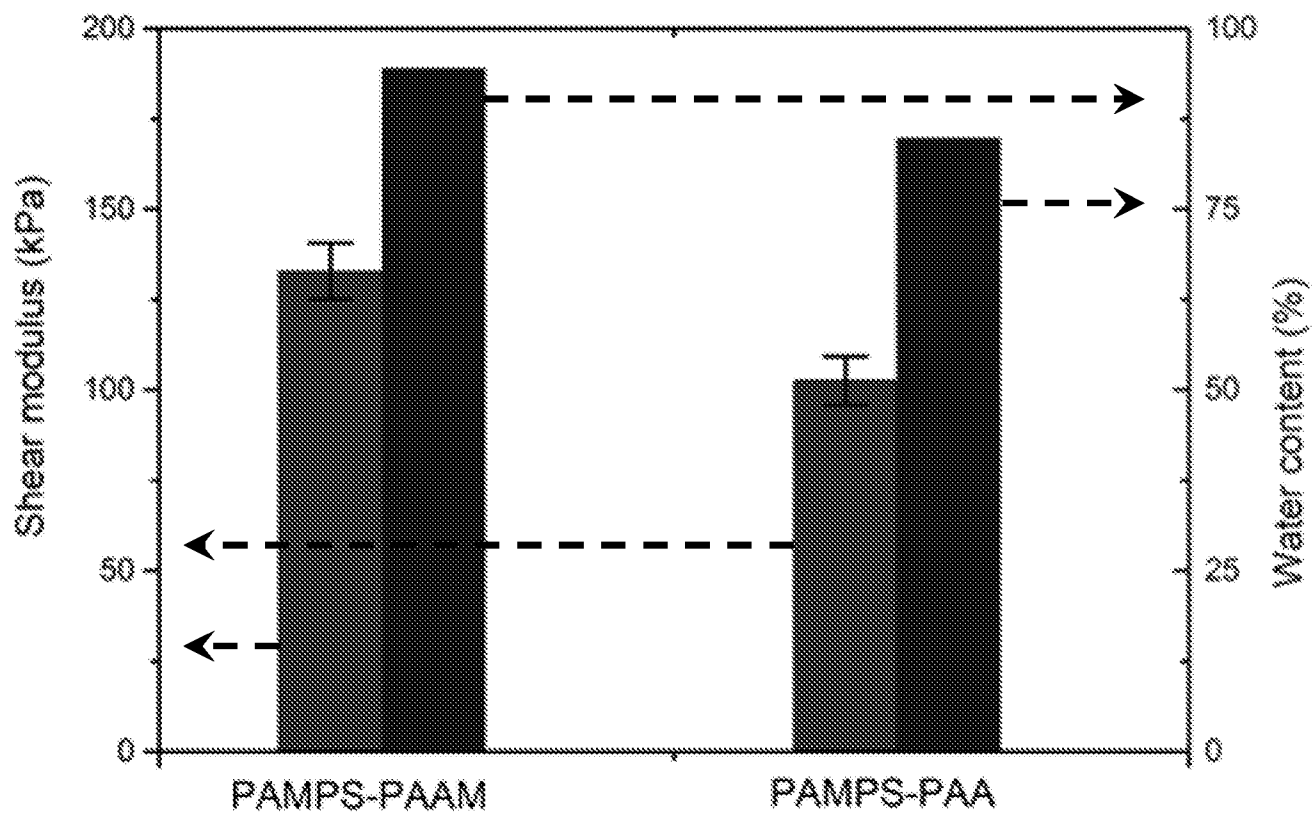


FIG. 15C

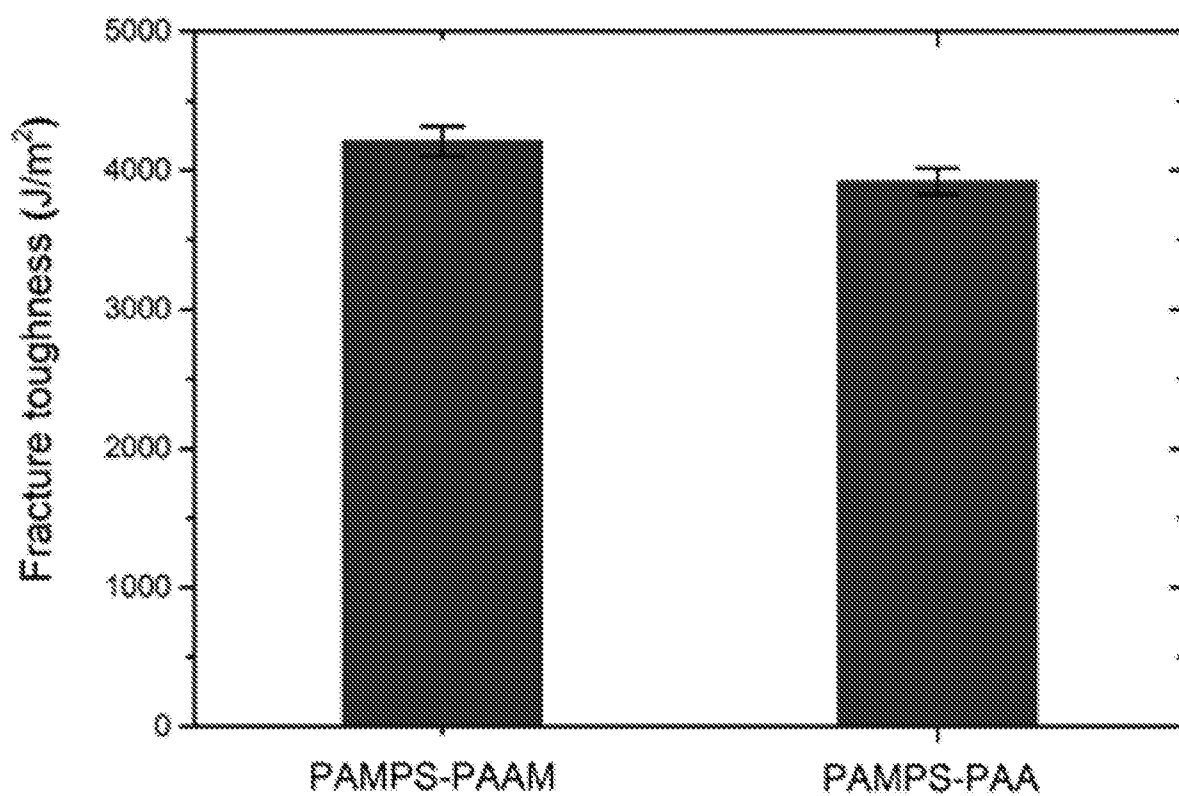


FIG. 15D

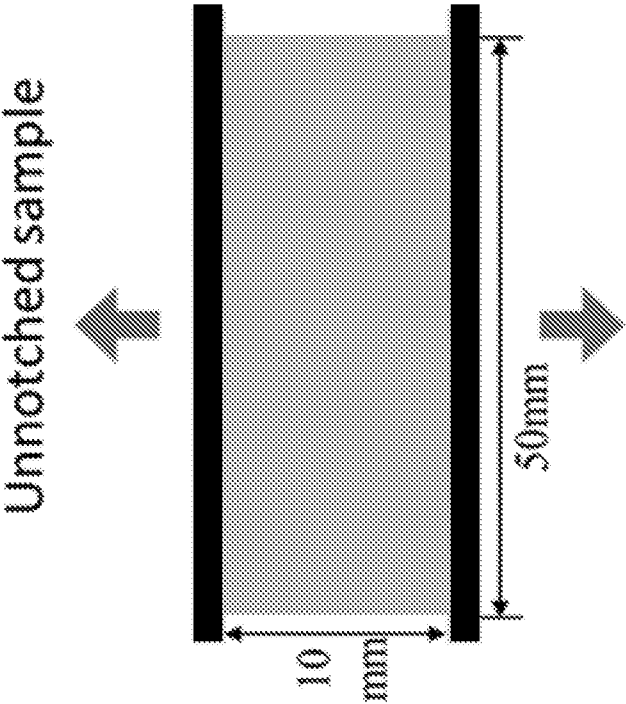


FIG. 16B

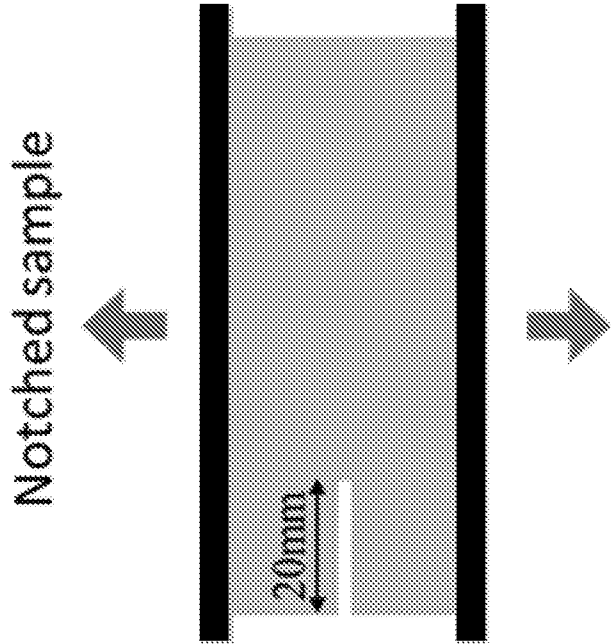


FIG. 16A

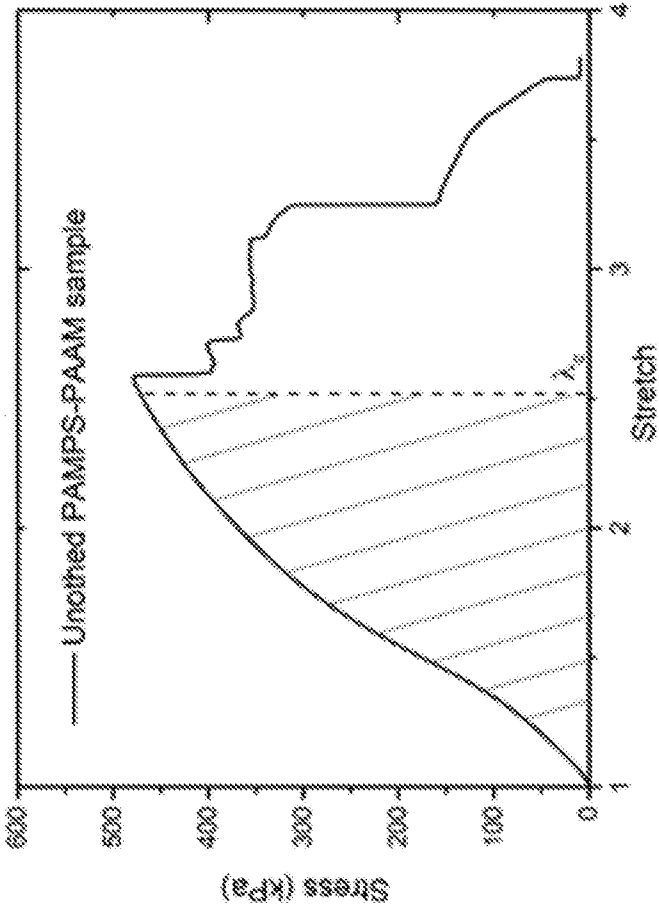


FIG. 16D

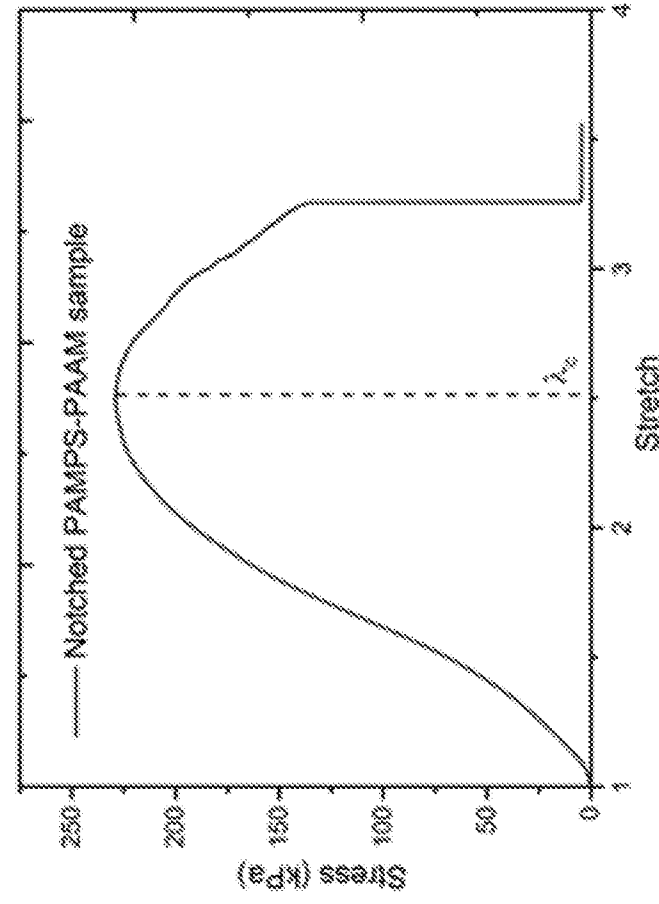


FIG. 16C

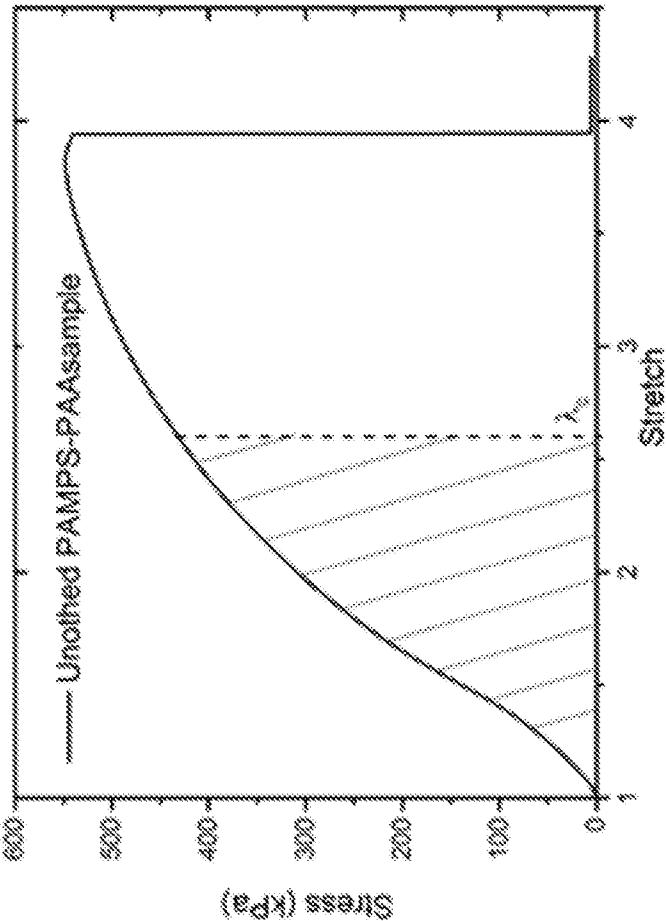


FIG. 16F

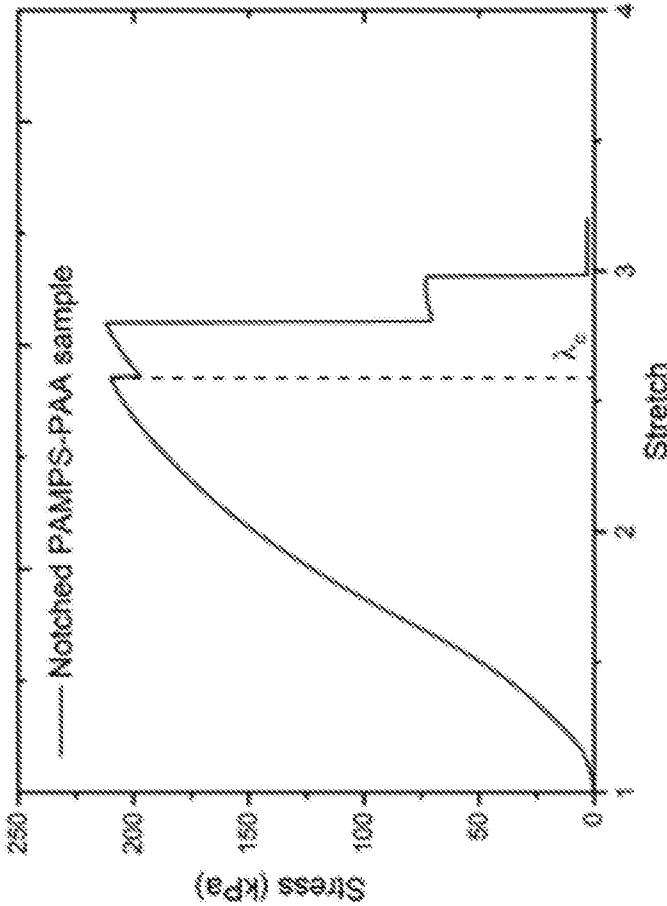


FIG. 16E

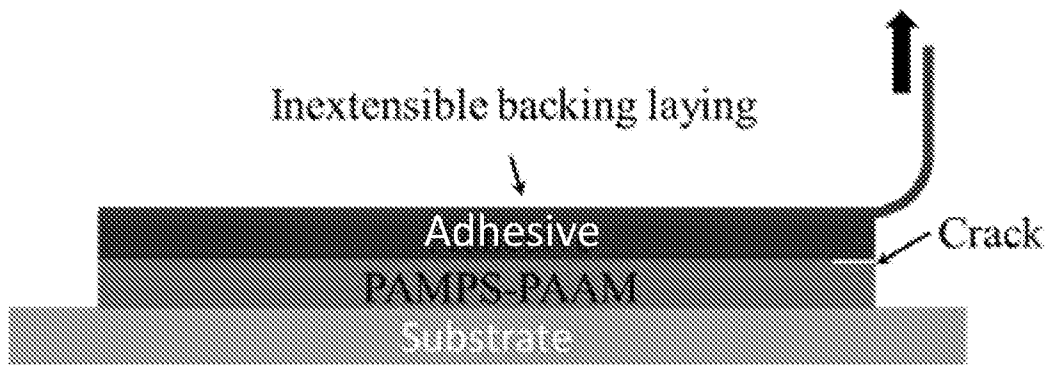


FIG. 17A

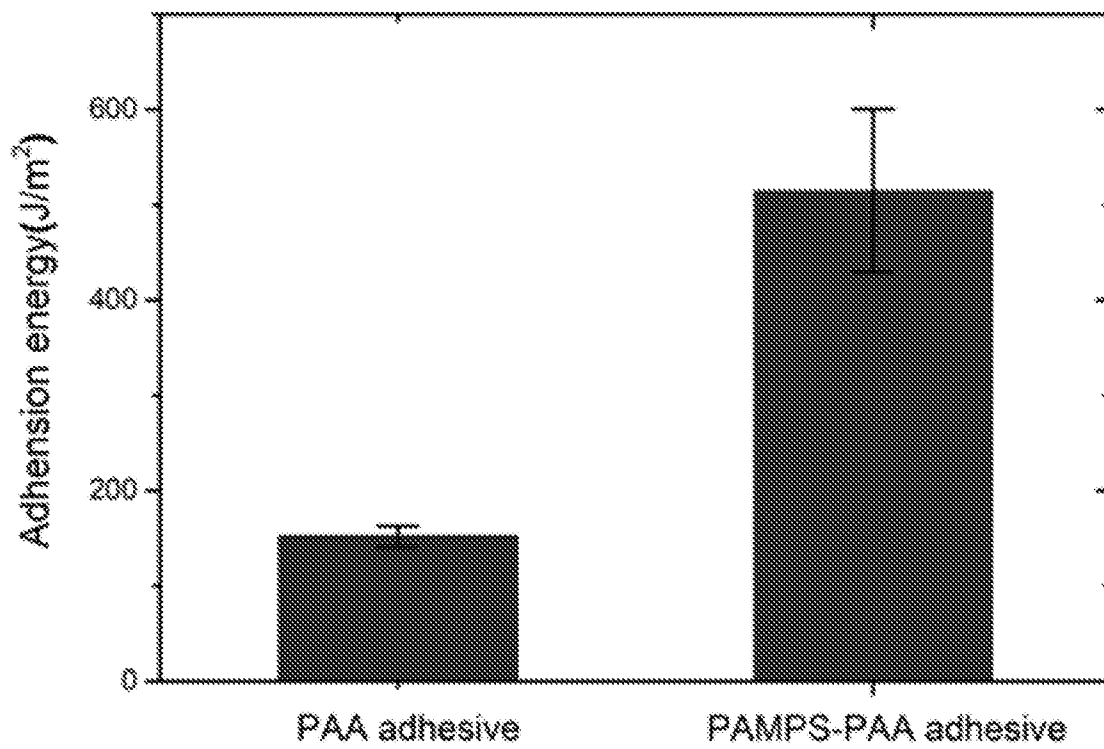


FIG. 17B

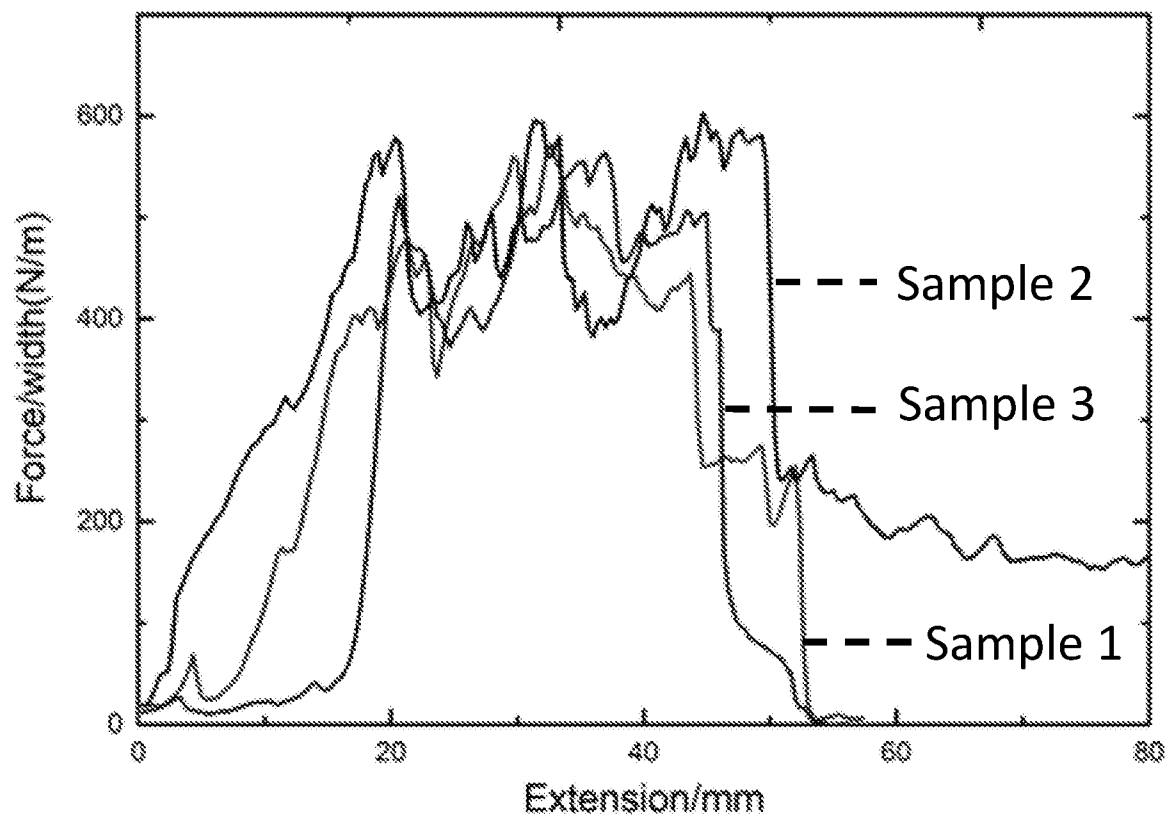


FIG. 17C

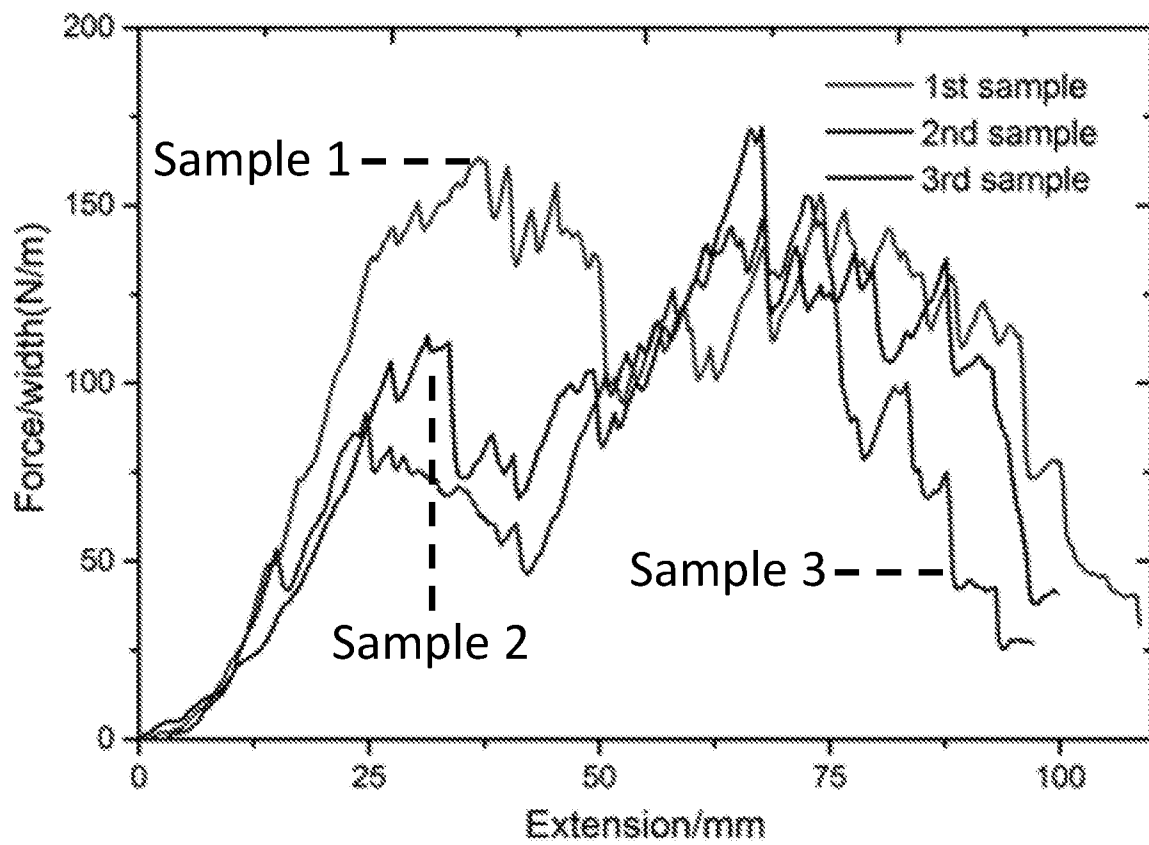


FIG. 17D

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/32659

## A. CLASSIFICATION OF SUBJECT MATTER

IPC - A61L 15/58, A61L 24/00, B32B 3/06, B32B 5/26, B32B 37/12, D04H 13/00 (2020.01)

CPC - A61L 15/58, A61L 15/585, A61L 17/14, A61L 24/0031, A61L 26/0061, A61L 26/008, B29C 37/0082, B29C 45/1657, B29C 65/4855, B32B 3/06, B32B 5/26, B32B 7/05, B32B 37/12, B32B 2038/0076, B32B 2305/72, B32B 2405/00, C08L 101/02, C08L 101/12, C08L 101/14, C08L 2203/02, D04H 1/58, D04H 3/12, D04H 3/14, D04H 5/02, D04H 13/00, D04H 13/003

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)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                              | Relevant to claim No.           |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------|
| Y         | YANG et al. "Topological Adhesion of Wet Materials." Advanced Materials [online], 2018 [Retrieved on 2020-07-21], Volume 30, 1800671, pp. 1-7, Retrieved from the Internet: <URL: <a href="https://doi.org/10.1002/adma.201800671">https://doi.org/10.1002/adma.201800671</a> >, see entire document, especially Figs. 1a-1d; pg 1, col 1, para 1; pg 2, col 1, para 2-3; pg 2, col 2, para 2-4 | 1-8, 17-34, 36-41, 43-52, 58-59 |
| Y         | US 2003/0130427 A1 (CLEARY et al.) 10 July 2003 (10.07.2003), para [0022], [0027], [0052]-[0055], [0063]-[0069], [0072], [0075], [0076], [0081], [0103], [0106]                                                                                                                                                                                                                                 | 1-8, 17-34, 36-41, 43-52, 58-59 |
| A,P       | WO 2019/203974 A1 (PRESIDENT AND FELLOW OF HARVARD COLLEGE) 24 October 2019 (24.10.2019), para [0006]-[0160]                                                                                                                                                                                                                                                                                    | 1-8, 17-34, 36-41, 43-52, 58-59 |
| A         | US 2013/0317131 A1 (JOHNSON & JOHNSON VISION CARE, INC.) 28 November 2013 (28.11.2013), para [0006]-[0302]                                                                                                                                                                                                                                                                                      | 1-8, 17-34, 36-41, 43-52, 58-59 |
| A         | US 2009/0004274A1 (HOORNE-VAN GEMERT et al.) 01 January 2009 (01.01.2009), para [0020]-[0112]                                                                                                                                                                                                                                                                                                   | 1-8, 17-34, 36-41, 43-52, 58-59 |

☐ 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

"D" document cited by the applicant in the international application

"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

21 July 2020

Date of mailing of the international search report

12 AUG 2020

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Lee Young

Telephone No. PCT Helpdesk: 571-272-4300

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/32659

## 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.: 9-16, 35, 42, 53-57, 60-62  
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.