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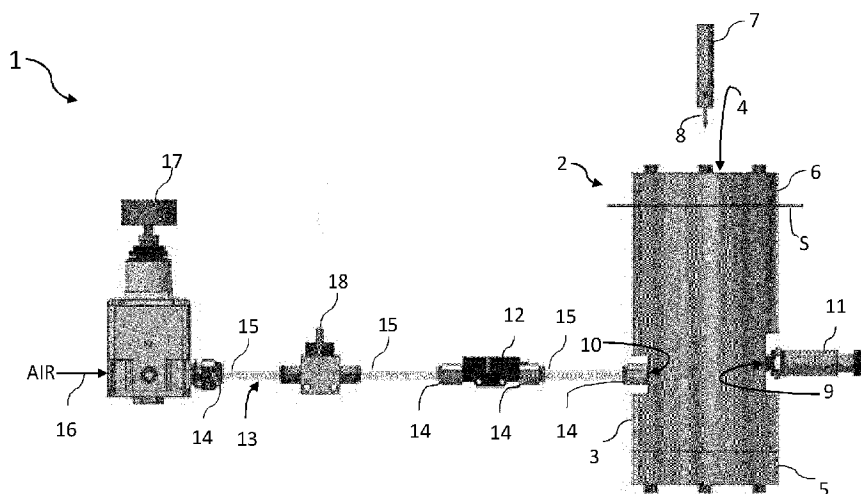


FIG. 1

(57) Abstract: The invention relates to a multi-layered garment comprising at least an inner layer, an outer layer and an intermediate layer located between said inner layer and said outer layer, wherein said intermediate layer is made from a composition comprising: a first polymer comprising a backbone chain consisting of a plurality of non-ionisable recurring units and further comprising a plurality of ionisable acid groups or ionisable amino groups, and either a second polymer comprising a backbone chain consisting of a plurality of non-ionisable recurring units and further comprising either a plurality of ionisable amino groups if the first polymer comprises ionisable acid groups or a plurality of ionisable acid groups if the first polymer comprises ionisable amino groups, or a molecule comprising a UV- reactive functional group reactive to UV light and either an ionisable amino group if the first polymer comprises ionisable acid groups or an ionisable acid group if the first polymer comprises ionisable amino groups.



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Description

Self-healing garment

This application claims priority to European application EP19212425.3 filed on 29/11/2019, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0001] The present invention relates to a self-healing garment, for example to a self-healing inflatable garment. More in particular, the present invention relates to a self-healing space suit for extravehicular activity.

Background Art

[0002] Garments and, more in general, textiles lack the ability to respond to damage and to self-heal or regenerate. In cases where the cost of repairing a garment is higher than the cost of replacing it, the latter option is generally preferred. However, it may have very negative long-term environmental impact.

[0003] The capability of garments to heal automatically upon physical tearing or rupture would certainly lead to long lasting products without much maintenance and, therefore, to a huge cost saving for consumers. Furthermore, the capability of garments to seal tears and, therefore, increase their durability would help reducing the amount of wastage and resources required to produce garments with a positive environmental impact.

[0004] Inflatable protective garments are garments that can be inflated with a gas, such as life jackets. Inflatable pressure garments provided with self-healing capabilities would avoid depressurization upon rupture of the inflated garments, thus carrying on providing the required protection to the wearer even in case of damage.

[0005] Inflatable protective garments also include space suits, for example extravehicular activity (EVA) space suits (also referred to below as EVA suits), which are used outside spacecrafts for either planetary exploration or spacewalks. They must protect the wearer against all conditions of space, in particular they must provide the pressurized environment

necessary for life sustaining functions in the space and protection against micrometeoroid/orbital debris (MMOD) impacts. To achieve these requirements, EVA space suits are constructed from many fabric layers.

[0006] Main risks to the EVA space suits include exposure to sharp objects and penetrations from MMOD impacts, which could puncture the suit and depressurize it, thus compromising the safe environment the suit must provide.

[0007] Many attempts have been made so far to resist cut and puncture threats and to avoid or withstand penetration of the EVA space suit from MMOD impacts, thereby preventing the loss of pressurization from the EVA space suit. Self-healing materials have been developed to this end, notably self-healing materials including viscoelastic materials such as elastomers, which are made from long and flexible elastomeric chains. By incorporating a small number of chemical bonds (i.e. crosslinks) between the elastomeric chains, permanent structures with optimal crosslinking density are formed. Silicone and urethane polymers were found to be promising self-healing materials capable of puncture healing upon impact.

[0008] Nevertheless, need is still felt to provide self-healing materials intended for use in space suits, which are able to self-repair cuts, punctures and internal structural breaches caused by micrometeoroid impacts, thus allowing the retention of pressure to the greatest extent possible.

[0009] More in general, need is felt for garments which are responsive to tearing and disruption so as to meet all the aforementioned requirements.

Summary of invention

[0010] The present invention relates to a multi-layered garment comprising at least an inner layer, an outer layer and an intermediate layer located between said inner layer and said outer layer, wherein said intermediate layer is made from a composition [composition (C)] comprising:

- at least one first polymer [polymer (P1)] comprising a backbone chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units

(U)], said polymer (P1) further comprising a plurality of ionisable acid groups or a plurality of ionisable amino groups, and either

- at least one second polymer [polymer (P2)] comprising a backbone chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal to or different from that of polymer (P1), and further comprising either a plurality of ionisable amino groups if the polymer (P1) comprises ionisable acid groups or a plurality of ionisable acid groups if the polymer (P1) comprises ionisable amino groups, or
- at least one molecule [molecule (M)] comprising a functional group reactive to UV light and either an ionisable amino group if the polymer (P1) comprises ionisable acid groups or an ionisable acid group if the polymer (P1) comprises ionisable amino groups,

preferably the chain (R) of said polymers (P1) and (P2) being independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester chain and a polybutadiene chain.

[0011] The Applicant has surprisingly found that the garment according to the present invention is able to autonomously repair itself after being damaged mechanically.

Brief description of the drawing

[0012] Figure 1 is a schematic representation of a device used to test the healing properties of a garment according to the invention, in particular of a space suit according to the invention.

Detailed description of the invention

[0013] Described herein is a multi-layered garment comprising at least an inner layer, an outer layer and an intermediate layer located between said inner layer and said outer layer, wherein said intermediate layer is made from a composition [composition (C)] comprising at least one first polymer

[polymer (P1)] comprising a backbone chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said polymer (P1) further comprising a plurality of ionisable acid groups or a plurality of ionisable amino groups, and either at least one second polymer [polymer (P2)] or at least one molecule [molecule (M)] which are able to react with the polymer (P1) providing supramolecular assemblies joined together through ionic interactions.

[0014] In a first embodiment, the composition (C) comprises at least one polymer (P1) and at least one polymer (P2) comprising a backbone chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal to or different from that of polymer (P1), and further comprising either a plurality of ionisable amino groups if the polymer (P1) comprises ionisable acid groups or a plurality of ionisable acid groups if the polymer (P1) comprises ionisable amino groups.

[0015] In a second embodiment, the composition (C) comprises at least one polymer (P1) and at least one molecule (M) comprising a functional group reactive to UV light and either an ionisable amino group if the polymer (P1) comprises ionisable acid groups or an ionisable acid group if the polymer (P1) comprises ionisable amino groups.

[0016] The chain (R) of polymers (P1) and (P2) are independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester chain and a polybutadiene chain.

[0017] It was surprisingly found that the above identified supramolecular assemblies have excellent self-healing properties and, therefore, are able to provide an autonomous repair response to tearing or damage of the garment.

[0018] In the present description, unless otherwise indicated, the following terms are to be meant as follows.

[0019] The expression "supramolecular polymer" is intended to denote a structure consisting of polymeric units held together by ionic interactions.

- [0020] The expressions “ionisable amino groups” and “ionisable acid groups” identify amino or acid groups able to form ionic groups, namely cationic and anionic groups respectively. In greater detail, an ionisable amino group identifies a primary, secondary or tertiary amino group, while an ionisable acid group identifies an acid group comprising at least one hydroxyl function in its protonated form, i.e. a protic acid group.
- [0021] A “hydrocarbon group” is a radical derived from a hydrocarbon by removal of one or more atoms of hydrogen from carbon atoms; a hydrocarbon group thus comprises one or more ends able to form a linkage with another chemical group.
- [0022] An “alicyclic group” is an aliphatic cyclic group consisting of one or more all-carbon rings which may be either saturated or unsaturated.
- [0023] The adjective “aromatic” denotes any mono- or polynuclear cyclic group (or moiety) having a number of π electrons equal to $4n+2$, wherein n is 0 or any positive integer; an aromatic group (or moiety) can be an aryl or an arylene group (or moiety).
- [0024] An “aromatic group” consists of one core composed of one benzenic ring or of a plurality of benzenic rings fused together by sharing two or more neighboring ring carbon atoms. Non limitative examples are benzene, naphthalene, anthracene, phenanthrene, tetracene, triphenylene, pyrene, perylene.
- [0025] Alicyclic and aromatic groups can be substituted with one or more straight or branched alkyl or alkoxy groups and/or halogen atoms and/or can comprise one or more heteroatoms, like nitrogen, oxygen and sulfur, in the ring.
- [0026] The “backbone chain” is the longest series of covalently bonded atoms that together create a continuous chain of molecules. A “side chain” is a chain that is attached to the backbone chain. A “linear polymer” is a polymer with a linear backbone chain, while a “branched polymer” is a polymer further comprising side chains.

[0027] The expression “terminal position” as used herein encompasses the terminal position of the backbone chain and the terminal position of a side chain in case of branched polymers.

[0028] M_n refers to the number average molecular weight.

[0029] The use of parentheses “(…)” before and after the names of compounds, symbols or numbers identifying formulae or parts of formulae like, for example “polymer (P1)”, has the mere purpose of better distinguishing those names, symbols or numbers from the remaining text; thus, said parentheses could also be omitted.

[0030] When ranges are indicated, range ends are included.

FIRST EMBODIMENT

[0031] Preferably the polymer (P1) has two chain ends (E1, E1’), each end comprising at least one ionisable acid group, and the polymer (P2) has two chain ends (E2, E2’), each end comprising at least one ionisable amino group.

[0032] Preferably, polymer (P1) and polymer (P2) are amorphous and have a T_g lower than $-35\text{ }^\circ\text{C}$, preferably from $-35\text{ }^\circ\text{C}$ to $-120\text{ }^\circ\text{C}$.

[0033] Preferably, the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) ranges from 1.4 to 0.6, preferably from 1.2 to 0.8, more preferably from 1.1 to 0.9.

[0034] POLYMER (P1)

[0035] Polymer (P1) can be represented with the following formula:



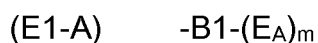
wherein R is a polymer chain, as defined above, and E1 and E1’, equal to or different from one another, are end groups each comprising at least one ionisable acid group.

[0036] Chain ends E1 and E1’

[0037] Chain ends E1 and E1’ of polymer (P1) preferably comprise at least one ionisable acid group selected among carboxylic acid groups, phosphonic acid groups and sulfonic acid groups. Each of said ionisable acid groups is able to form an anionic group via acid/base reaction with the at least one ionisable amino group at one end of polymer (P2).

[0038] Preferably, groups E1 and E1' are equal to one another.

[0039] Preferably, groups E1 and E1' comply with formula (E1-A) here below:



wherein:

E_A represents a $-COOH$, a $-P(O)(OR_{EA})_2$ or a $-S(O)_2OH$ group, wherein one of R_{EA} is hydrogen and the other one is hydrogen or straight or branched alkyl, preferably C_1-C_4 alkyl;

m is a positive number equal to or higher than 1, m being preferably 2;

$B1$ is a hydrocarbon group preferably comprising from 1 to 20 carbon atoms and possibly comprising one or more than one heteroatom, said heteroatom(s) being preferably selected among N, S and O.

[0040] Preferably, $B1$ comprises at least one cyclic hydrocarbon group, which may be selected from: alicyclic groups, aromatic groups, heterocyclic groups comprising one or more than one heteroatom, and heteroaromatic groups comprising one or more than one heteroatom, said one or more than one heteroatom being preferably selected from N, S and O. Said at least one cyclic hydrocarbon group may comprise one or more substituents. In case $B1$ comprises more than one cyclic group, i.e. at least two cyclic groups, said cyclic groups may be condensed or may be connected through a bond or through any (hydro)carbon divalent group optionally comprising one or more than one heteroatom, said heteroatom(s) being preferably selected from N, S and O.

[0041] Preferably, $B1$ comprises one or more of the groups selected from: $-O-$, $-S-$, $-OC(O)O-$, $-OC(O)NH-$, $-NH-C(O)-$, $OC(O)S-$, $-SC(O)S-$, $-NHC(O)NH-$, $-NH-C(=S)$ and $-NHC(S)NH-$.

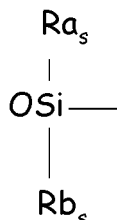
[0042] Chain (R)

[0043] As said, chain (R) is independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester chain and a polybutdiene chain. Preferably, said chain (R) is selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain and a polyoxyalkylene chain.

[0044] Polyalkylsiloxane chain (R_S)

[0045] According to an embodiment, said chain (R) is a polyalkylsiloxane chain [chain (R_S)] comprising, preferably consisting of, recurring units [units (U_S)], equal to or different from each other, of formula:

(U_S)



wherein Ra_s and Rb_s, equal to or different from one another, are independently selected from hydrogen, straight or branched (halo)alkyl and aryl, with the proviso that at least one of Ra_s and Rb_s is not hydrogen, Ra_s and Rb_s being preferably straight or branched alkyl groups comprising from 1 to 4 carbon atoms, Ra_s and Rb_s being preferably methyl groups.

[0046] In a preferred embodiment, said chain (R_S) has formula (R_S-I) here below:



with n_s being a positive number selected in such a way that the M_n of the [Si(CH₃)₂O]_{n_s} chain preferably ranges from 500 to 50'000, more preferably from 500 to 30'000.

[0047] Minor amounts (e.g. <1%(wt), based on the weight of chain (R_S-I)) of spurious units, defects or recurring unit impurities may be comprised in chain (R_S-I) without this affecting chemical properties of the chain.

[0048] According to a preferred embodiment, polymer (P1) complies with the following formula (P_S1-A) here below:



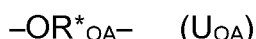
wherein R_S has formula (R_S-I) above, n_s^{*} is 0 or a positive number equal to or higher than 1, preferably ranging from 1 to 10, more preferably ranging from 2 to 5, and R_{B1} is a C₁-C₁₀ straight or branched aliphatic group, a C₄-C₆ alicyclic group or heterocyclic group, a C₅-C₆ aromatic group or heteroaromatic group.

[0049] Preferably, R_{B1} is an aromatic group. More preferably, R_{B1} is a C₆ aromatic group. According to various embodiments, each -COOH group may be in

ortho, meta, para positions with respect to $-\text{NHC(O)}-$. According to various embodiments, each $-\text{COOH}$ group may be in ortho, meta, para positions with respect to each other.

[0050] Polyoxyalkylene chain (R_{OA})

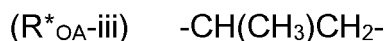
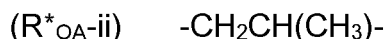
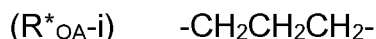
[0051] According to an embodiment, said chain (R) is a polyoxyalkylene chain [chain (R_{OA})] comprising, preferably consisting of, recurring units [units (U_{OA})], equal to or different from each other, of formula:



wherein R^*_{OA} is a straight or branched alkylene divalent group.

[0052] Said chain (R_{OA}) has a M_n preferably ranging from 500 to 10,000, more preferably from 500 to 5,000.

[0053] Preferably, said chain (R_{OA}) comprises, preferably essentially consists of, oxypropylene or oxytetramethylene recurring units or a mixture thereof. Accordingly, in formula (U_{OA}), each R^*_{OA} , equal to or different from each other, is independently selected among propylene groups of formulae ($R^*_{\text{OA-i}}$) – ($R^*_{\text{OA-ii}}$) and a tetramethylene group of formula ($R^*_{\text{OA-iv}}$):

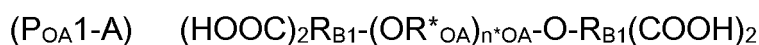


[0054] Minor amounts (i.e. $< 1\%$ in moles) of groups R^*_{OA} other than those specified may be present as impurities, defects or spurious components without this affecting chemical properties of the chain (R_{OA}).

[0055] In a preferred embodiment, said chain (R_{OA}) is a polyoxypropylene chain and each R^*_{OA} is independently selected among propylene groups of formulae ($R^*_{\text{OA-i}}$) - ($R^*_{\text{OA-iii}}$) above.

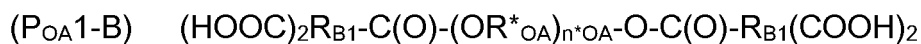
[0056] In another preferred embodiment, said chain (R_{OA}) is a polytetramethylene glycol chain and each R^*_{OA} is a tetramethylene group of formula ($R^*_{\text{OA-iv}}$) above.

[0057] According to a preferred embodiment, polymer (P_1) complies with the following formula ($P_{\text{OA1-A}}$):



wherein R_{B1} and R^*_{OA} are as defined above, and n^*_{OA} is a positive number selected in such a way that the M_n of the chain (R_{OA}) preferably ranges from 500 to 10'000, more preferably from 500 to 5'000; R^*_{OA} is as defined above.

[0058] According to another preferred embodiment, polymer (P1) complies with the following formula (P_{OA1-B}):



wherein R_{B1} , n^*_{OA} and R^*_{OA} are as defined above with respect to polymer (P_{OA1-A}).

[0059] In the above formulae (P_{OA1-A}) and (P_{OA1-B}), R_{B1} is preferably an aromatic group. More preferably, R_{B1} is a C_6 aromatic group. According to various embodiments, each $-COOH$ group may be in ortho, meta, para positions with respect to $-C(O)-$. According to various embodiments, each $-COOH$ group may be in ortho, meta, para positions with respect to each other.

[0060] Fully or partially fluorinated polyoxyalkylene chain (R_F)

[0061] According to an embodiment, said chain (R) is a fully or partially fluorinated polyoxyalkylene chain [chain (R_F)] comprising, preferably consisting of, recurring units [units (U_F)], equal to or different from each other, having at least one catenary ether bond and at least one fluorocarbon moiety.

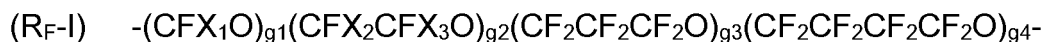
[0062] Preferably, said chain (R_F) comprises units (U_F) selected among:

- (U_F -i) $-CFXO-$, wherein X is F or CF_3 ;
- (U_F -ii) $-CFXCFXO-$, wherein X, equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X is $-F$;
- (U_F -iii) $-CF_2CF_2CW_2O-$, wherein each of W, equal or different from each other, is F, Cl, H,
- (U_F -iv) $-CF_2CF_2CF_2CF_2O-$;
- (U_F -v) $-(CF_2)_j-CFZ-O-$ wherein j is an integer from 0 to 3 and Z is a group of general formula $-OR_f^*T$, wherein R_f^* is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : $-CFX^*O-$, $-CF_2CFX^*O-$, -

CF₂CF₂CF₂O-, -CF₂CF₂CF₂CF₂O-, with each of each of X* being independently F or CF₃ and T being a C₁-C₃ perfluoroalkyl group.

[0063] When units (U_F) are different from one another, they are randomly distributed along the chain.

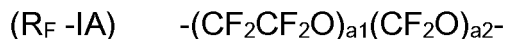
[0064] Preferably, said chain (R_F) has formula (R_{F-I}):



wherein:

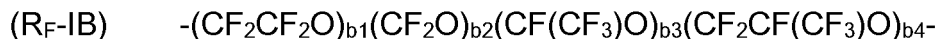
- X₁ is independently selected from -F and -CF₃;
- X₂, X₃, equal or different from each other and at each occurrence, are independently -F, -CF₃, with the proviso that at least one of X is -F;
- g₁, g₂, g₃, and g₄, equal or different from each other, are independently integers ≥ 0, selected in such a way that the M_n ranges from 400 to 10'000; should at least two of g₁, g₂, g₃ and g₄ be different from zero, the different recurring units are generally statistically distributed along the chain.

[0065] More preferably, said chain (R_F) is selected from chains of formulae (R_{F-IA}) - (R_{F-IE}) here below:



wherein:

- a₁ and a₂ are independently integers ≥ 0 such that the M_n ranges from 400 to 10'000, preferably from 400 to 5'000, more preferably from 400 to 4'000; both a₁ and a₂ are preferably different from zero, with the ratio a₁/a₂ preferably ranging from 0.1 to 10, preferably ranging from 0.2 to 5;



wherein:

- b₁, b₂, b₃, b₄, are independently integers ≥ 0 such that the M_n ranges from 400 to 10'000, preferably from 400 to 5'000; preferably b₁ is 0, b₂, b₃, b₄ are > 0, with the ratio b₄/(b₂+b₃) being ≥ 1;



wherein:

- cw = 1 or 2;

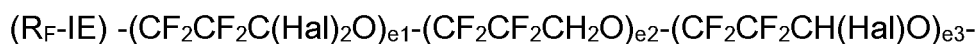
c₁, c₂, and c₃ are independently integers ≥ 0 such that the M_n ranges

from 400 to 10'000, preferably from 400 to 5'000; preferably c1, c2 and c3 are all > 0, with the ratio c3/(c1+c2) being generally lower than 0.2;



wherein:

- d is an integer >0 such that the M_n ranges from 400 to 10'000, preferably from 400 to 5'000;

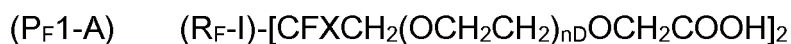


wherein:

- Hal, equal or different at each occurrence, is a halogen selected from fluorine and chlorine atoms, preferably a fluorine atom;

- e1, e2, and e3, equal to or different from each other, are independently integers ≥ 0 selected in such a way that the such that the $(e1+e2+e3) M_n$ ranges from 400 to 10'000.

[0066] According to preferred embodiments, polymer (P1) is selected from a polymer complying with any of the following formulae (P_F1-A) to (P_F1-C):



wherein:

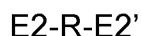
nD is 0 or an integer ≥ 1 ,

R_{B1} is a C₁-C₁₀ straight or branched aliphatic group, a C₄-C₆ alicyclic group or heterocyclic group, a C₅-C₆ aromatic group or heteroaromatic group, optionally comprising one or more -COOH groups, and

X is as defined above.

[0067] POLYMER (P2)

[0068] Polymer (P2) can be represented with the following formula:



wherein R is a polymer chain, as defined above, and E2 and E2', equal to or different from one another, are end groups each comprising at least one ionisable amino group.

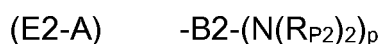
[0069] Chain ends E2 and E2'

[0070] Chain ends E2 and E2' preferably comprise at least one ionisable amino group selected among primary, secondary or tertiary amino groups.

“Ionisable primary, secondary or tertiary amino group” means that the amino group is in its free form, so that it is capable to form a cationic group via acid/base reaction with the at least one acid group at one end of the polymer (P1).

[0071] Preferably, groups E2 and E2' are equal to one another.

[0072] Preferably, groups E2 and E2' comply with formula (E2-A) here below:



wherein:

each of R_{P2} , equal to or different from each other at each occurrence, is hydrogen or straight or branched alkyl, preferably C_1 - C_4 alkyl;

p is a positive number equal to or higher than 1, p being preferably 1 or 2;

B2 is a hydrocarbon group preferably comprising from 1 to 20 carbon atoms and optionally comprising one or more than one heteroatom, said heteroatom(s) being preferably selected among N, S and O.

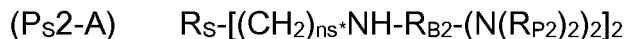
[0073] B2 optionally comprises one or more than one cyclic hydrocarbon group, which may be alicyclic group(s), aromatic group(s), heterocyclic group(s) comprising one or more than one heteroatom, and heteroaromatic group(s) comprising one or more than one heteroatom, the heteroatom(s) being preferably selected from N, S and O. Each of said cyclic hydrocarbon groups may comprise one or more substituents. In case B2 comprises more than one cyclic group, i.e. at least two cyclic groups, said cyclic groups may be condensed or may be connected through a bond or through any (hydro)carbon divalent group possibly comprising one or more than one heteroatom, said heteroatom(s) being preferably selected from N, S and O.

[0074] B2 optionally comprises one or more than one group selected from the following: -O-, -S-, -OC(O)O-, -OC(O)NH-, -NH-C(O)-, OC(O)S-, -SC(O)S-, -NHC(O)NH-, -NHC(S)NH-, -N(R_{P2})- wherein R_{P2} represents hydrogen or straight or branched alkyl, preferably C_1 - C_4 alkyl, more preferably methyl.

[0075] Chain (R)

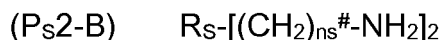
[0076] Chain (R) is as defined above for polymer (P1).

[0077] According to an embodiment, polymer (P2) complies with the following formula (P_S2-A) here below:



wherein R_S has formula (R_S-I) above; ns* is 0 or a positive number equal to or higher than 1, preferably ranging from 1 to 10, more preferably ranging from 2 to 5; R_{P2} is as defined above, preferably being hydrogen, and R_{B2} is a C₁-C₁₀ straight or branched aliphatic group, a C₄-C₆ alicyclic group or heterocyclic group, a C₅-C₆ aromatic group or heteroaromatic group. Preferably, R_{B2} is a heteroaromatic group. More preferably, R_{B2} is a C₆ heteroaromatic group. Even more preferably, R_{B2} is a triazine. Still more preferably, R_{B2} is a 1,3,5-triazine.

[0078] According to another embodiment, polymer (P2) complies with the following formula (P_S2-B) here below:



wherein ns# is a positive number from 1 to 20, preferably from 1 to 10, and R_S is a chain of formula (R_S-I) above.

[0079] Yet, according to an embodiment, polymer (P2) complies with the following formula (P_{OA}2-A):



wherein R_{B2} is a C₁-C₁₀ straight or branched aliphatic group, a C₄-C₆ alicyclic group or heterocyclic group, a C₅-C₆ aromatic group or heteroaromatic group; n*_{OA} is a positive number selected in such a way that the M_n of the chain R_{OA} preferably ranges from 500 to 10'000, more preferably from 500 to 5'000; R*_{OA} and R_{P2} are as defined above.

[0080] According to a further embodiment, polymer (P2) complies with the following formula (P_{OA}2-B):

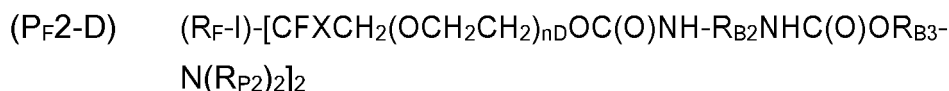
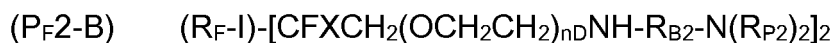


wherein R_{B2}, n*_{OA}, R*_{OA}, R_{P2} are as defined above with respect to polymer (P_{OA}2-A).

[0081] In the above formulae (P_{OA}2-A) and (P_{OA}2-B), R_{B2} is preferably a heteroaromatic group. More preferably, R_{B2} is a C₆ heteroaromatic group.

Even more preferably, R_{B2} is a triazine. Still more preferably, R_{B2} is a 1,3,5-triazine.

[0082] Yet, according to further embodiments, polymer (P2) is selected from a polymer complying with any of the following formulae (P_{F2}-A) to (P_{F2}-D):



wherein:

nD is 0 or an integer ≥ 1 ,

R_{B2} is a C_1 - C_{10} straight or branched aliphatic group, a C_4 - C_6 alicyclic group or heterocyclic group, a C_5 - C_6 aromatic group or heteroaromatic group,

R_{B3} is a C_2 - C_{10} straight or branched aliphatic group, optionally interrupted by one or more $\text{-N}(\text{R}_{P2^*})\text{-}$ groups wherein R_{P2^*} represents hydrogen or straight or branched alkyl,

R_{P2} is hydrogen or straight or branched alkyl, and

X is as defined above.

[0083] COMPOSITION (C)

[0084] Composition (C) can be prepared by mixing polymer (P1) and polymer (P2) according to conventional mixing techniques at an equivalent ratio between polymer (P1) and polymer (P2) ranging from 1.4 to 0.6, preferably from 1.2 to 0.8, more preferably from 1.1 to 0.9. Mixing can be carried out with or without solvents, using appropriate mixing equipment. For the avoidance of doubt, the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) is referred to the acid/base reaction between the ionisable amino group(s) in each end group of polymer (P1) and the ionisable acid group(s) in each end of polymer (P2).

[0085] One or more polymers (P1) can be used in the manufacture of composition (C). "More polymers" means that polymers (P1) can be used which differ from one another in the kind of recurring units (U) of the chain

(R), in the kind of end groups (E1) and (E1') or in both of them, or in the number average molecular weight.

[0086] One or more polymers (P2) can also be used in the manufacture of composition (C). "More polymers" means that polymers (P2) can be used which differ from one another in the kind of recurring units (U) of the chain (R), in the kind of end groups (E2) and (E2') or in both of them, or in the number average molecular weight.

[0087] According to a preferred embodiment, one polymer (P1) and one polymer (P2) are used in the manufacture of the composition (C); the chain (R) of polymer (P1) can be equal to or different from the chain (R) of polymer (P2). In a preferred embodiment, said polymer (P1) has four ionisable acid groups and said polymer (P2) has four ionisable amino groups. Preferably, said polymer (P1) has two ionisable acid groups on each chain end (E1, E1'), and said polymer (P2) has two ionisable amino groups on each chain end (E2, E2').

[0088] It is further understood that polymer(s) (P1) and polymer(s) (P2) may have polymer chains consisting of same recurring units (U) or may have polymer chains differing for nature of units (U) and/or molecular weight and/or any other structural feature.

[0089] Without being bound to theory, it is believed that, when a polymer (P1) and a polymer (P2) are mixed in the above equivalent ratio, the ionisable acid group(s) at each end of polymer (P1) undergo(es) acid/base reaction with the ionisable amino group(s) at each end of polymer (P2), thus forming a supramolecular polymer. It will thus be understood by a person skilled in the art that any optional ingredient in the composition (C) will have to be selected in such a way and amount that it does satisfy the ionisable acid and amino groups of polymers (P1) and (P2).

[0090] It is interestingly found that the so obtained supramolecular polymer has viscoelastic properties, which can be easily tuned from elastic material to elastic gel by an appropriate selection of the molecular weight and the stoichiometry of polymers (P1) and (P2) without changing the chemical structure of the chain (R). Accordingly, a large set of self-healing materials

ranging from gels to elastomers can be easily obtained by varying the molecular weight and the stoichiometry of polymers (P1) and (P2).

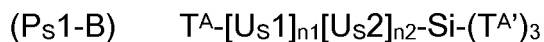
SECOND EMBODIMENT

[0091] The polymer (P1) comprises a backbone chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)] and, optionally, one or more side chains [chain(s) (R_{side})] also consisting of units (U). Therefore, the polymer (P1) may be linear or branched.

[0092] As said, the polymer (P1) comprises either a plurality of ionisable acid groups or a plurality of ionisable amino groups. According to various embodiments, the ionisable amino groups and the ionisable acid groups are pendant groups from at least one of said chain (R) and chain(s) (R_{side}) and/or are positioned at a terminal position of one or more of said chain (R) and chain(s) (R_{side}) or at a position adjacent to said terminal position.

[0093] In a particular embodiment of the invention, the chain (R) of polymer (P1) is a polyalkylsiloxane chain and the ionisable groups (either amino or acid) are pendant groups from said polyalkylsiloxane chain.

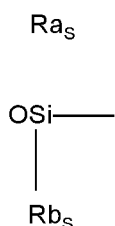
[0094] In an even more particular embodiment, the chain (R) of polymer (P1) has the following formula:



wherein:

repeating units U_{S1} , equal to or different from each other at each occurrence, have formula:

U_{S1}



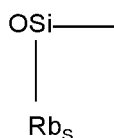
wherein:

R_{a_s} and R_{b_s} , equal to or different from one another, are independently selected from hydrogen, straight or branched (halo)alkyl and aryl, with the proviso that at least one of R_{a_s} and R_{b_s} is not hydrogen, R_{a_s} and R_{b_s}

being preferably straight or branched alkyl groups comprising from 1 to 4 carbon atoms, R_{a_s} and R_{b_s} being preferably methyl groups; repeating units U_{s2} , equal to or different from each other at each occurrence, have formula:

U_{s2}

$R_{c_s}-X$



wherein:

R_{c_s} is a divalent hydrocarbon radical selected from straight or branched (halo)alkylene and arylene groups, R_{c_s} being preferably a straight or branched alkylene group comprising from 1 to 4 carbon atoms, R_{c_s} being preferably a straight alkylene group comprising 3 carbon atoms;

X is an ionisable amino group or an ionisable acid group;

R_{b_s} is as defined above,

n_1 and n_2 are positive numbers selected in such a way that the Mn of the chain (R) ranges from 500 to 50'000, preferably from 500 to 30'000,

T^A and $T^{A'}$, equal to or different from each other, are independently selected from straight or branched (halo)alkyl and aryl groups, T^A and $T^{A'}$ being preferably straight or branched alkyl groups comprising from 1 to 4 carbon atoms, T^A and $T^{A'}$ being preferably methyl groups.

[0095] Preferably X is an ionisable amino group, more preferably a $-N(R_{P2})_2$ group, wherein each of R_{P2} , equal to or different from each other at each occurrence, is hydrogen or straight or branched alkyl, preferably C_1 - C_4 alkyl, R_{P2} being preferably hydrogen.

[0096] According to various embodiments, recurring units U_{s1} and U_{s2} are arranged in blocks, in alternation or randomly.

[0097] As said, the molecule (M) comprises a functional group reactive to UV light. Preferably, said functional group reactive to UV light is a double bond.

[0098] Preferably the polymer (P1) comprises a plurality of ionisable amino groups, preferably said amino groups being pendant groups from the chain (R), and the molecule (M) is acrylic acid or methacrylic acid.

[0099] Preferably, the ratio between the equivalents of molecule (M) and the equivalent of polymer (P1) ranges from 0.3 to 1.0, preferably from 0.3 to 0.9, more preferably from 0.5 to 0.8.

[00100] COMPOSITION (C)

[00101] Composition (C) can be prepared by mixing polymer (P1) and molecule (M) according to conventional mixing techniques at the above identified equivalent ratio between polymer (P1) and molecule (M). Mixing can be carried out with or without solvents, using appropriate mixing equipment. For the avoidance of doubt, the ratio between the equivalents of molecule (M) and the equivalents of polymer (P1) is referred to the acid/base reaction between the ionisable group of molecule (M) and the ionisable groups of polymer (P1).

[00102] One or more polymers (P1) can be used in the manufacture of composition (C). "More polymers" means that polymers (P1) can be used which differ from one another in the kind of recurring units (U) of the chain (R), or in the number average molecular weight, or in both.

[00103] One or more molecules (M) can also be used in the manufacture of composition (C). In case the composition (C) comprises more molecules (M), all these molecules comprise an ionisable group of the same nature, that is either an ionisable amino group or an ionisable acid group.

[00104] According to a preferred embodiment, one polymer (P1) and one molecule (M) are used in the manufacture of the composition (C).

[00105] Preferably, the composition (C) comprises a UV initiator.

[00106] Without being bound to theory, it is believed that, when a polymer (P1) and a molecule (M) are mixed in the above equivalent ratio and are exposed to UV radiation, the ionisable groups of polymer (P1) undergo acid/base reaction with the ionisable groups of molecule (M) and the UV-reactive functional groups react thus forming a supramolecular polymer. It will thus be understood by a person skilled in the art that any optional ingredient in

composition (C) will have to be selected in such a way and amount that it does satisfy the ionisable acid and amino groups of the polymer (P1) and the molecule (M).

[00107] In a particular embodiment, the intermediate layer of the garment according to the invention is made by exposing the composition (C) to a UV radiation. Put in other words, the intermediate layer of the garment according to the invention is made by reacting the polymer (P1) and the molecule (M) in the presence of UV light.

[00108] According to both the first embodiment and the second embodiment of the invention, the composition (C) may further comprise one or more organic polar protic or aprotic solvents. Non limiting examples of solvents are alcohols, ketones, acetates, dimethylacetamide (DMA), hydrofluoroethers, toluene, bis-trifluorodimethylbenzene, ethers. Preferred organic solvents are ketones, like methylethylketone (MEK), acetates, like ethylacetate and butyl acetate, and ethers, like ter-Buthylmethylether. When present, said one or more than one organic solvent is comprised in compositions (C) in an amount ranging from 1% to 99.9%(wt) with respect to the overall weight of the composition.

[00109] Composition (C) may further comprise suitable additional ingredients. Said additional ingredients are preferably selected among organic and inorganic fillers. Said inorganic fillers include notably silicate compounds (e.g. metal silicate, such as aluminium silicate), titanium dioxide, alumina, silica, zeolites, mica, talc, kaolin, chalk, carbon fibers, carbon nano-tubes, glass fibers, calcium carbonate, potassium titanate, metal sulfates (e.g. barium sulfate, calcium sulfate, strontium sulfate). Said organic fillers notably include cellulose and other polymers, e.g. aromatic polycondensates, such as polyamides and polysulfones.

GARMENT

[00110] The garment of the invention is a type of clothing selected from the group comprising shirts, coats, skirts, dresses, suits, shorts, pants, jackets, vests, swimsuit, and the like.

- [00111] According to an embodiment, the garment of the invention is selected among inflatable garments, notably inflatable safety garments such as life jackets, for example designed to protect motorcycle riders from crashes or falls in general and to assist wearers to keep afloat in water.
- [00112] According to a preferred embodiment, the inflatable garment is a space suit, notably an extravehicular activity (EVA) space suit. According to this embodiment, the intermediate layer made from the above defined composition (C) is preferably located between an inner layer made from an airtight sealing polymer film (e.g. Nylon® film) and an outer layer made of a polymeric fabric (e.g. Kevlar® fabric). Preferably, the EVA space suit comprises a plurality of intermediate layers located between an innermost layer in contact with the skin and an outermost layer in contact with the space environment. Preferably, at least one of said intermediate layers comprises the composition (C) as defined above.
- [00113] The invention is described in greater detail in the following experimental section by means of non-limiting examples.

Experimental section

[00114] Materials

[00115] Trimellitic anhydride, 2-chloro-4,6-diamino-1,3,5 triazine, potassium hydrogen carbonate, 1,4-dioxane, 2-propanol (IPA), t-butylmethyl ether (TBME) and dichloromethane were purchased from Aldrich® and used as received.

[00116] Polymer of formula:

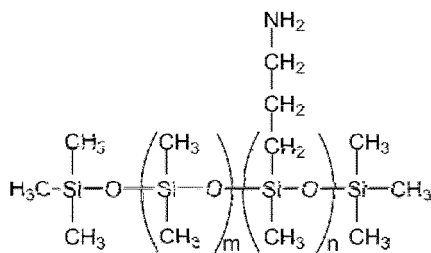


with Rs being a poly(dimethylsiloxane) chain, ns = 3 and Mn = 27000

[herein after polymer (P2B)] was obtained from Gelest®.

[00117] Methacrylic acid was purchased from Aldrich®.

[00118] (20-25% Aminopropylmethylsiloxane)-dimethylsiloxane copolymer of formula:



with $M_n = 20'000$ [herein after polymer (P2C)] was obtained from Gelest®.

[00119] 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone was purchased from Aldrich® and used as UV-initiator.

[00120] Methods

[00121] *Test 1*

[00122] *Preparation of samples*

[00123] The samples were prepared by positioning each of the compositions C1 to C4 as described below between a 0.63 mm thick layer made from Kevlar® 29 and a 0.05 mm thick vacuum bag layer. The layer made from Kevlar® 29 reproduces the outermost layer of a space suit, while the vacuum bag layer mainly serves to keep the composition in place. Compositions C2 to C4 were exposed to UV radiation before preparation of the corresponding samples, and a UV-light source LQ-400® (Dr. Gröbel UV-Elektronik GmbH) was used for the irradiation.

[00124] *Puncture of the samples and determination of the healing properties*

[00125] The samples were punctured with a dedicated device represented in Figure 1 with the reference number 1. The device 1 comprises a pressure vessel 2 consisting of a hollow cylinder 3 which defines an internal cavity 4. The cylinder 3 is provided with a bottom cap 5 and a top sealing ring 6. The top sealing ring 6 is arranged to block the sample S, allowing overpressurization of the internal cavity 4 with respect to the external ambient. O-rings (not shown) are provided in the cap 5 and the sealing ring 6 to avoid air leakage.

[00126] A puncture probe 7 with a 2 mm diameter hole keeps the puncheon 8 in place and pierces the sample S during tests, generating a hole in the sample S and creating an outward air flow from this hole. The puncture

probe 7 is held by grips (not shown) and set in motion by a MTS 858 Mini Bionix II® machine (not shown).

- [00127] Two threaded holes 9, 10 are present on the hollow cylinder 3 as a connection with a pressure transducer 11 and a flow meter 12, which measure respectively the relative pressure and the flow rate. The pressure transducer 11 is a Pressure Sensor Limited® PSC217-B-4-5-A 11 and the flow meter 12 is a SMC® PFMV530-1.
- [00128] The pressure transducer 11 is directly screwed to the cylinder 3 and monitors the relative pressure inside the pressure vessel 2. The flow meter 12 is set between the cylinder 3 and a pneumatic supply line 13, and is connected to them through fittings 14 and flexible tubes 15 of 6 mm external diameter. The flow meter 12 measures the air getting from the feed line 16 to the cylinder 3 and passing through its body.
- [00129] The device 1 also comprises a precision pressure regulator 17 (SMC® IR2000-F02) and a finger valve 18 (SMC® VHK2-06F-06F).
- [00130] Except for the pressure vessel 2, all parts of the device 1 are attached to a plexiglass slab (not shown). The terminal box (not shown) that connects the instruments to a computer used for acquisition is also fixed to this support.
- [00131] At the beginning of the experiments the pressure vessel 2 was pressurized to 0.3 bar relative pressure and placed on the test machine support, above which the puncture probe 7 is fixed. Continuous air supply was granted to the system. The puncture probe 7 was then set in motion, thus generating a hole in the sample S under study.
- [00132] The flow rate of the air passing through the generated hole in the sample S was measured as a function of time. In particular, the maximum (or peak) flow rate and the minimum flow rate after puncture were measured. In addition, the lost volume of the sample S after puncture was calculated through integration of the volumetric flow rate in time, specifically in a period of 180 seconds starting from the peak value after puncture. As commented in detail below, these parameters give an indication of the healing properties of the sample S.

[00133] Test 2

[00134] Preparation of samples

[00135] A sample was prepared by enclosing the composition C4 between two 0.05 mm thick vacuum bag layers. The upper vacuum bag layer was covered by a 0.015 mm thick aluminum foil. The aluminum foil was used to prevent reticulation of the composition C4 due to exposure to light, thus simulating the UV shielding of a space suit.

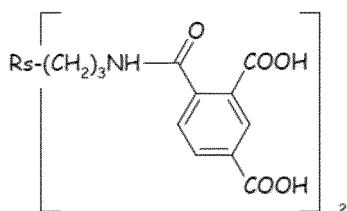
[00136] Puncture of the samples and determination of the healing properties

[00137] The sample was punctured with the device represented in Figure 1. As soon as the puncture probe 7 generated a hole in the sample and the composition C4 flowed out of the generated hole, the latter was exposed to a UV radiation. A UV-light source LQ-400® (Dr. Gröbel UV-Elektronik GmbH) was used to irradiate the composition C4. The flow rate of the air passing through the generated hole was measured and the lost volume of the sample was calculated, as per "Test 1".

[00138] ¹H NMR

[00139] NMR analyses were performed on a Bruker Avance™ 400 MHz spectrometer with a 5 mm probe and the obtained spectra were processed using Bruker's TopSpin™ software (3.2 ver.).

[00140] The number average molecular weight (Mn) of the polymers (P1A) and (P2A) were estimated by polymer end group analysis (using ¹H NMR spectra).

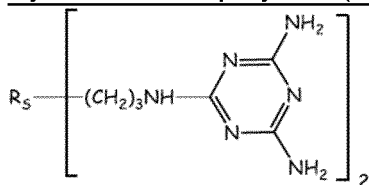
[00141] **Synthesis examples**[00142] Synthesis of a polymer (P1A) of formula:

wherein Rs is a poly(dimethylsiloxane) chain, Mn 27300 [herein after (P1)].

[00143] A glass reactor was charged with polymer P2B (100 g, 3.7 mmol, Mn 27000) and dried under vacuum for two hours under mechanical stirring at

70 °C. 1,4-dioxane (100 ml) and trimellitic anhydride (1.9 g, 10 mmol) were added to the reactor and stirred at 100 °C for 24 hours. The reaction completion was monitored by ¹H-NMR. The NMR analyses confirmed the obtainment of title product, with purity higher than 99%.

[00144] Synthesis of a polymer (P2A) of formula:



wherein Rs is a poly(dimethylsiloxane) chain, Mn 27400 [herein after (P2C)].

[00145] A glass reactor was charged with 2-chloro-4,6-diamino-1,3,5-triazine (2 g, 13.7 mmol), KHCO₃ (1.4 g, 13.7 mmol), 2-propanol (40 mL) and water (5 mL). P2B (123 g, 4.6 mmol, Mn 27000) was added to the reaction mixture and stirred at 90 °C. The completion of the reaction was monitored by ¹H-NMR. The solvent was evaporated under reduced pressure and the polymer was purified by selective impurity precipitation in ethyl acetate solvent. All analyses confirmed the obtainment of the title product, with purity higher than 99%.

[00146] Preparation of composition C1

[00147] Polymers (P1A) and (P2A) were individually dissolved in a suitable solvent (1-99 wt% for instance in tert-Butyl methyl ether or ethyl acetate or dichloromethane) and then mixed together at an equivalent ratio of 1 [i.e. nr acidic groups of polymer (P1A) = nr basic groups of polymer (P2A)] inside a reactor equipped with a mechanical stirrer at room temperature (30 °C). The mixture was kept at room temperature (25 °C) for 12 hours, after that the solvent was removed at 70 °C under reduced pressure (0.001 torr).

[00148] Preparation of composition C2

[00149] A solution of methacrylic acid containing 2%(wt) of 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone was prepared. The polymer (P2C) (17.57 g) and the methacrylic acid solution (2.04 g) were introduced in a beaker. The so obtained blend was subsequently mixed

and a vacuum treatment was carried out to minimize the formation of the air bubbles.

[00150] Preparation of composition C3

[00151] A solution of methacrylic acid containing 2%(wt) of 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone was prepared. The polymer (P2C) (27.33 g) and the methacrylic acid solution (4 g) were introduced in a beaker. The so obtained blend was subsequently mixed for one hour and a vacuum treatment was carried out to minimize the formation of the air bubbles.

[00152] Preparation of composition C4

[00153] A solution of methacrylic acid containing 2%(wt) of 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone was prepared. The polymer (P2C) (35 g) and the methacrylic acid solution (6.4 g) were introduced in a beaker. The so obtained blend was subsequently mixed for one hour and a vacuum treatment was carried out to minimize the formation of the air bubbles.

[00154] **Results**

[00155] Table 1 reports the results obtained from "Test 1". In particular, Table 1 reports the maximum flow rate of the air through the generated hole, the minimum flow rate after puncture, the lost volume in 180 seconds after the peak flow rate and the time from maximum to minimum flow rate for the samples prepared using compositions C1 to C4 (which are according to the present invention) and for samples prepared with materials known in the art, namely Sylgard® Q3-6636 (which is a silicone polymer), TyrLyner® urethane, Conathane® EN-11 and Rucothane® CO-AX-5294 (which are polyurethane polymers).

[00156] As said, the above parameters were determined for the samples according to the present invention using the device represented in Figure 1.

[00157] The values of the above parameters for the samples prepared with known materials are taken from the "NASA Research Announcement Final Report

for Space Suit Survivability Enhancement”, September 25, 1998, submitted by J. S. Ware, J. K. Lin, T. H. Fredrickson and C. M. Pastore.

[00158] These parameters provide indications about the self-healing properties of the samples according to the invention with respect to known materials.

Table 1

	Sylgard® Q3-6636	TyrLyner® urethane	Conathane® EN-11	Rucothane® CO-AX-5294	C1	C2	C3	C4
Max. flow rate [l/min]	0.208	4.523	1.727	3.866	1.982	3.455	0.183	1.422
Min. flow rate after puncture [l/min]	0.054	0.085	0.249	1.497	0	0	0	0
Lost volume [cm ³]	227.250	524.200	995.950	5773.000	8.795	272.877	0.421	2.173
Time from max to min flow rate [s]	110.000	153.750	222.250	349.700	31.380	83.800	22.550	48.960

[00159] As evident from Table 1 above, the samples prepared with compositions C1 to C4 (which are according to the invention) provide for a flow rate after puncture which is null, meaning that they provide for a complete healing of the hole. On the other hand, the materials already known in the art provide for a flow rate after puncture which is different from zero, therefore they do not provide for complete healing of the hole.

[00160] Furthermore, the lost volume in the samples prepared with compositions C1, C3 and C4 is much lower than the lost volume in the materials known in the art. This means that space suits comprising at least one intermediate layer made from compositions C1, C3 and C4 undergoes much lower depressurization when punctured than the space suits comprising at least one intermediate layer made from known materials.

[00161] The samples prepared with compositions C1 to C4 also guarantee the shortest time from the maximum flow rate to the minimum flow rate,

meaning that the holes generated in the samples according to the invention close much quicker than the holes generated in the samples of the prior art.

[00162] Accordingly, the holes generated by puncturing the samples prepared with compositions C1 to C4 close completely and, therefore, repair themselves in a short time and with a small lost volume with respect to the holes generated by puncturing the samples prepared with known materials. Therefore, the samples prepared with compositions C1 to C4 exhibit better self-healing performances.

[00163] Table 2 reports the results obtained from "Test 2". In particular, Table 2 reports the maximum flow rate of the air through the generated hole, the minimum flow rate after puncture, the lost volume in 180 seconds after the peak flow rate and the time from maximum to minimum flow rate for the sample prepared using composition C4 obtained by exposing the composition C4 to UV radiation upon generation of the hole and for the sample prepared using composition C4 obtained without exposing the composition C4 to UV radiation upon generation of the hole.

Table 2

	C4 (with UV radiation)	C4 (without UV radiation)
Max. flow rate [l/min]	0.075	> 3 (sensor saturates)
Min. flow rate after puncture [l/min]	0	1.278
Lost volume [cm ³]	0.692	8961.197
Time from max to min flow rate [s]	0.820	0.500

[00164] It is evident from Table 2 that the sample prepared with composition C4 performs very well when the composition C4 reticulates *in situ* upon exposure to UV radiation after flowing out of the generated hole, while it does not when the composition C4 is not exposed to UV radiation.

Claims

Claim 1. A multi-layered garment comprising at least an inner layer, an outer layer and an intermediate layer located between said inner layer and said outer layer, wherein said intermediate layer is made from a composition comprising:

- at least one first polymer [polymer (P1)] comprising a backbone chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said polymer (P1) further comprising a plurality of ionisable acid groups or a plurality of ionisable amino groups, and either
- at least one second polymer [polymer (P2)] comprising a backbone chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal to or different from that of polymer (P1), and further comprising either a plurality of ionisable amino groups if the polymer (P1) comprises ionisable acid groups or a plurality of ionisable acid groups if the polymer (P1) comprises ionisable amino groups, or
- at least one molecule [molecule (M)] comprising a functional group reactive to UV light and either an ionisable amino group if the polymer (P1) comprises ionisable acid groups or an ionisable acid group if the polymer (P1) comprises ionisable amino groups,

preferably the chain (R) of said polymers (P1) and (P2) being independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester chain and a polybutadiene chain.

Claim 2. The garment according to claim 1, wherein said composition comprises the polymer (P1) and the polymer (P2), said polymer (P1) having two chain ends (E1, E1'), each end comprising at least one ionisable acid group, and said polymer (P2) having two chain ends (E2, E2'), each end comprising at least one ionisable amino group.

Claim 3. The garment according to claim 2, wherein polymer (P1) and polymer (P2) are amorphous and have a T_g lower than $-35\text{ }^\circ\text{C}$, preferably from $-35\text{ }^\circ\text{C}$ to $-120\text{ }^\circ\text{C}$, and wherein the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) preferably ranges from 1.4 to 0.6, more preferably from 1.2 to 0.8, even more preferably from 1.1 to 0.9.

Claim 4. The garment according to claim 2 or 3, wherein the chain ends (E1, E1') of polymer (P1), equal to or different from each other, comply with the following formula (E1-A):



wherein:

E_A represents a $-\text{COOH}$, a $-\text{P}(\text{O})(\text{OR}_{E_A})_2$ or a $-\text{S}(\text{O})_2\text{OH}$ group, wherein one of R_{E_A} is hydrogen and the other one is hydrogen or straight or branched alkyl, preferably $\text{C}_1\text{-C}_4$ alkyl;

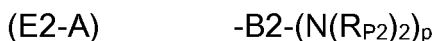
m is a positive number equal to or higher than 1, m being preferably 2;

$B1$ is a hydrocarbon group preferably comprising from 1 to 20 carbon atoms and possibly comprising one or more than one heteroatom, said heteroatom(s) being preferably selected among N, S and O;

$B1$ preferably comprises at least one cyclic hydrocarbon group, said cyclic hydrocarbon group being preferably selected from: alicyclic groups, aromatic groups, heterocyclic groups and heteroaromatic groups;

$B1$ preferably comprises one or more of the groups selected from: $-\text{O}-$, $-\text{S}-$, $-\text{C}(\text{O})-$, $-\text{OC}(\text{O})\text{O}-$, $-\text{OC}(\text{O})\text{NH}-$, $-\text{NH}-\text{C}(\text{O})-$, $\text{OC}(\text{O})\text{S}-$, $-\text{SC}(\text{O})\text{S}-$, $-\text{NHC}(\text{O})\text{NH}-$, $-\text{NH}-\text{C}(=\text{S})$ and $-\text{NHC}(\text{S})\text{NH}-$.

Claim 5. The garment according to any one of claims 2 to 4, wherein the chain ends (E2, E2') of polymer (P2), equal to or different from each other, comply with the following formula (E2-A):



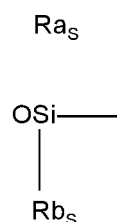
wherein:

each of R_{P2} , equal to or different from each other at each occurrence, is hydrogen or straight or branched alkyl, preferably $\text{C}_1\text{-C}_4$ alkyl;

p is a positive number equal to or higher than 1, p being preferably 1 or 2;
 B2 is a hydrocarbon group preferably comprising from 1 to 20 carbon atoms and optionally comprising one or more than one heteroatom, said heteroatom(s) being preferably selected among N, S and O;
 B2 optionally comprises at least one cyclic hydrocarbon group, said cyclic hydrocarbon group being preferably selected from: alicyclic groups, aromatic groups, heterocyclic groups and heteroaromatic groups;
 B2 optionally comprises one or more of the groups selected from: -O-, -S-, -OC(O)O-, -OC(O)NH-, -NH-C(O)-, OC(O)S-, -SC(O)S-, -NHC(O)NH-, -NHC(S)NH-, -N(R_{P2*})- wherein R_{P2*} represents hydrogen or straight or branched alkyl, preferably C₁-C₄ alkyl, more preferably methyl.

Claim 6. The garment according to any one of claims 2 to 5, wherein the chain (R) of polymer (P1) and/or polymer (P2) is a polyalkylsiloxane chain [chain (R_S)] comprising recurring units [units (U_S)], equal to or different from each other, of formula:

(U_S)



wherein Ra_s and Rb_s, equal to or different from one another, are independently selected from hydrogen, straight or branched (halo)alkyl and aryl, with the proviso that at least one of Ra_s and Rb_s is not hydrogen,

Ra_s and Rb_s being preferably straight or branched alkyl groups comprising from 1 to 4 carbon atoms,

Ra_s and Rb_s being preferably methyl groups,

said chain (R_S) preferably having formula (R_S-I):



with n_s being a positive number selected in such a way that the number average molecular weight (M_n) of the [Si(CH₃)₂O]_{n_s} chain preferably ranges from 500 to 50'000, more preferably from 500 to 30'000.

Claim 7. The garment according to claim 6, wherein polymer (P1) complies with formula (P_S1-A):

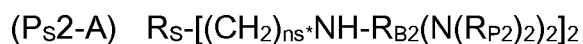


wherein:

ns* is 0 or a positive number equal to or higher than 1, preferably ranging from 1 to 10, more preferably ranging from 2 to 5, and

R_{B1} is a C₁-C₁₀ straight or branched aliphatic group, a C₄-C₆ alicyclic group or heterocyclic group, a C₅-C₆ aromatic group or heteroaromatic group, R_{B1} being preferably an aromatic group, more preferably a C₆ aromatic group,

and/or polymer (P2) complies with formula (P_S2-A):



wherein:

ns* is as defined above;

R_{B2} is a C₁-C₁₀ straight or branched aliphatic group, a C₄-C₆ alicyclic group or heterocyclic group, a C₅-C₆ aromatic group or heteroaromatic group, R_{B2} being preferably a triazine, more preferably a 1,3,5-triazine, and

R_{P2} is preferably hydrogen.

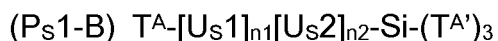
Claim 8. The garment according to claim 1, wherein said composition comprises the polymer (P1) and the molecule (M), said plurality of ionisable amino groups or ionisable acid groups are pendant groups from said chain (R) and/or are positioned at a terminal position of said chain (R) or at a position adjacent to said terminal position.

Claim 9. The garment according to claim 8, wherein the ratio between the equivalents of molecule (M) and the equivalent of polymer (P1) ranges from 0.3 to 1.0, preferably from 0.3 to 0.9, more preferably from 0.5 to 0.8.

Claim 10. The garment according to claim 8 or 9, wherein said functional group reactive to UV light is a double bond.

Claim 11. The garment according to any one of claims 8 to 10, wherein the chain (R) of polymer (P1) is a polyalkylsiloxane chain and the ionisable amino groups or ionisable acid groups are pendant groups from said polyalkylsiloxane chain.

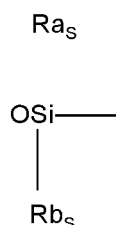
Claim 12. The garment according to claim 11, wherein the chain (R) of polymer (P1) has formula:



wherein:

repeating units U_{S1} , equal to or different from each other at each occurrence, have formula:

U_{S1}

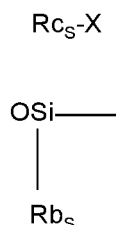


wherein:

R_{a_s} and R_{b_s} , equal to or different from one another, are independently selected from hydrogen, straight or branched (halo)alkyl and aryl, with the proviso that at least one of R_{a_s} and R_{b_s} is not hydrogen, R_{a_s} and R_{b_s} being preferably straight or branched alkyl groups comprising from 1 to 4 carbon atoms, R_{a_s} and R_{b_s} being preferably methyl groups;

repeating units U_{S2} , equal to or different from each other at each occurrence, have formula:

U_{S2}



wherein:

R_{c_s} is a divalent hydrocarbon radical selected from straight or branched (halo)alkylene and arylene groups, R_{c_s} being preferably a straight or branched

alkylene group comprising from 1 to 4 carbon atoms, R_{CS} being preferably a straight alkylene group comprising 3 carbon atoms;

X is an ionisable amino group or an ionisable acid group;

R_{BS} is as defined above,

n_1 and n_2 are positive numbers selected in such a way that the Mn of the chain (R) ranges from 500 to 50'000, preferably from 500 to 30'000,

T^A and $T^{A'}$, equal to or different from each other, are independently selected from straight or branched (halo)alkyl and aryl groups, T^A and $T^{A'}$ being preferably straight or branched alkyl groups comprising from 1 to 4 carbon atoms, T^A and $T^{A'}$ being preferably methyl groups.

Claim 13. The garment according to claim 12, wherein X is an ionisable amino group, preferably a $-N(R_{P2})_2$ group, wherein each of R_{P2} , equal to or different from each other at each occurrence, is hydrogen or straight or branched alkyl, preferably C_1 - C_4 alkyl, R_{P2} being preferably hydrogen.

Claim 14. The garment according to claim 13, wherein said molecule (M) is methacrylic acid.

Claim 15. The garment according to any one of claims 8 to 14, wherein said intermediate layer is made by reacting in the presence of UV light said polymer (P1) and said molecule (M).

Claim 16. The garment according to any one of the previous claims, said garment being an inflatable garment, preferably a space suit, more preferably an extravehicular activity (EVA) space suit.

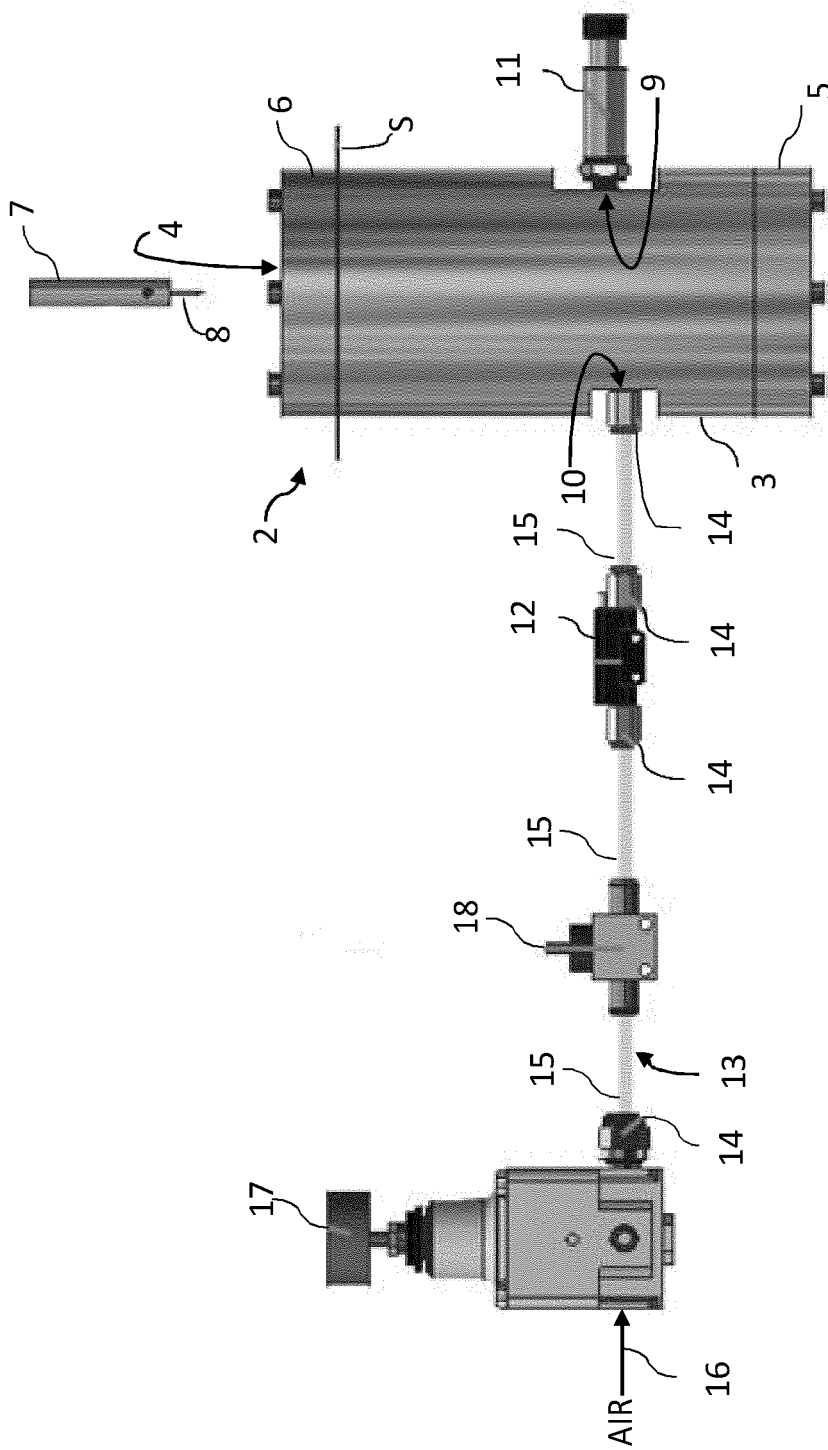


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/083417

A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B27/00 B64G6/00 C08G18/48 C08G77/04
ADD.
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)
B32B B64G C08G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2016/167811 A1 (GORDON KEITH L [US] ET AL) 16 June 2016 (2016-06-16)	1,16
A	paragraphs [0030], [0031]; claims	2-15
Y	WO 2014/090646 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 19 June 2014 (2014-06-19)	1,16
A	examples	2-15
A	WO 2018/078001 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 3 May 2018 (2018-05-03)	1-16
A	claims; examples	
A	WO 2010/028226 A2 (ARROWSTAR LLC [US]; COLLIER ROBERT B [US]; FORD GEARY [US]) 11 March 2010 (2010-03-11)	1-16
	claims; examples	
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search 15 February 2021	Date of mailing of the international search report 23/02/2021
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ibarrola Torres, O
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/083417

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/060101 A1 (CADOGAN DAVID P [US]) 13 March 2008 (2008-03-13) claims	1,16
A	<p style="text-align: center;">-----</p> DAVID CADOGAN ET AL: "Intelligent Flexible Materials for Deployable Space Structures (InFlex)", 47TH AIAA/ASME/ASCE/AHS/ASC STRUCTURES, STRUCTURAL DYNAMICS, AND MATERIALS CONFERENCE 14TH AIAA/ASME/AHS ADAPTIVE STRUCTURES CONFERENCE 7TH, 1 May 2006 (2006-05-01), XP055692613, Reston, Virigina DOI: 10.2514/6.2006-1897 ISBN: 978-1-62410-040-6 page 1; figures 2,3 <p style="text-align: center;">-----</p>	1,16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2020/083417

Patent document cited in search report	Publication date	Publication date	Patent family member(s)
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			EP 2931776 A1 21-10-2015
			JP 6326063 B2 16-05-2018
			JP 2016507600 A 10-03-2016
			US 2015322313 A1 12-11-2015
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			WO 2010028226 A2 11-03-2010

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