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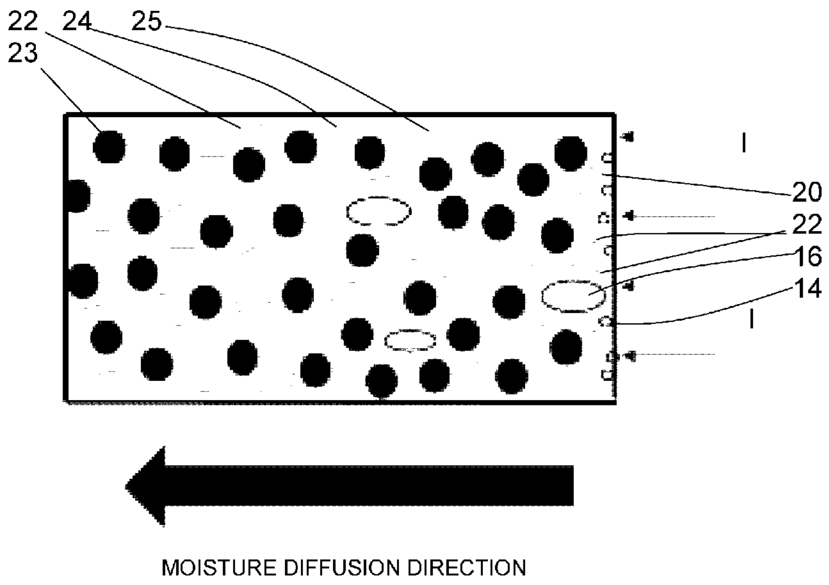

Fig 1b

(57) Abstract: A water-resistant composition 20 includes a graphene material 22 forming a matrix with a resin 23. The matrix can include reinforcing fibres such as glass fibres. The composition can include the graphene material 22, a polyester resin 23 and glass fibre reinforcement. Multiple forms of the composite can be provided in layers, such as a barrier layer containing the graphene material 22 in a resin 23 and a second layer containing reinforcing material. A cosmetic coloured gel coat can be applied to the composition and a clear gel coat applied over the cosmetic coating. The graphene material can include graphene platelets 22 dispersed within the resin. The graphene material can provide up to 5% by weight (%wt) of the composite, preferably up to 2%wt of the composite, more preferably between 1%wt and 2.5%wt of the composite and yet more preferably 2%wt of the composite. The composition can be applied to a boat hull, a pipe, a swimming pool, a spa or a tank, or a surface subject to prolonged contact with or submersion in water.

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RESIN COMPOSITE

FIELD OF THE INVENTION

[0001] The present invention relates to resin based composite, structural or coating systems, such as having a surface exposed to water or other liquids for prolonged periods where penetration of the water or liquid into the structure or coating causes degradation.

[0002] One or more forms of the present invention is particularly applicable to, though not limited to, structures and/or coatings for a swimming pool, a spa, a boat hull, a tank, water and waste water tanks, piping, a storage vessel, cladding or roofing material, or the like, where water penetration, such as by osmosis, into the structure or coating through prolonged exposure to the water causes degradation, such as blistering or cracking.

BACKGROUND TO THE INVENTION

[0003] By way of example, degradation through osmosis is a major problem for products that are immersed in or exposed to contact with water or other liquid for prolonged periods, such as boat hulls, swimming pools and spas, a tank, water and waste water tanks, piping, storage vessels, cladding or roofing, or the like, particularly those created using resin and glass fibre.

[0004] The degradation often presents as blistering or cracking at the surface, thereby reducing structural integrity and aesthetics. This is typically symptomatic of the osmosis leading to moisture build-up in voids. Apart from the cosmetic impact, this could ultimately lead to delamination and loss of mechanical strength.

[0005] It is possible that, particularly under acidic conditions – for example, due to soil pH – calcium carbonate could dissolve into absorbed water pockets, forming carbonic acid. This will encourage osmosis into the system.

[0006] It is known that all resins will absorb moisture. It is therefore important to understand how the absorbed moisture will affect the resin and the resin/fibre bond in a laminate, as this could otherwise lead to a gradual and long-term loss in mechanical properties.

[0007] Hydrolysable ester groups present in polyester and vinylester resins make those resins susceptible to water degradation when the resins are immersed in water for prolonged periods. Over a 1 year period of immersion in water, the interlaminar shear strength (ILSS) retention of the resin may be as low as approximately 65% of its ILSS for a thin polyester laminate and as low as approximately 90% for an epoxy laminate (from Gurit ‘Guide to Composites’).

[0008] The mechanism for water absorption is typically referred to as osmosis.

[0009] All laminates will allow very small amounts of water to pass through in vapour form. As a result, the water will react with hydrolysable components in the laminate, forming tiny cells of concentrated solution. Osmosis then occurs as more water is drawn through the semi-permeable membrane of the laminate to dilute the solution (equalize osmotic pressure).

[0010] This additional water absorbed as a result of osmosis increases the fluid pressure in the cell significantly, eventually distorting, or in extreme cases bursting, the laminate or coating, such as a gel coat.

[0011] A gel coat (or gel coat) is a material used to provide a high-quality protective coating on the visible surface of a fibre-reinforced composite. Thermosetting polymers based on epoxy or unsaturated polyester resins are generally used as gel coats. Gel coats are readily applied to moulds whilst in a liquid state and cure to form cross-linked polymers. The gel coat is typically backed with thermoset polymer matrix composites, such as mixtures of polyester resin and fiberglass, or with epoxy resin which is most commonly used with carbon fibre for higher specific strength.

[0012] Particularly in fibre-reinforced composites, the polymer matrix acts as the membrane. As water diffuses through the polymer, any soluble solid material dissolves, forming a strong/concentrated solution. Water then diffuses (such as by osmosis) into that strong solution until the concentration gradient is reduced to zero.

[0013] The volume of the solution will increase with dilution and exert pressure on the surrounding material. When the stresses exceed a critical level, delamination occurs leading to blistering.

[0014] Resin rich layers are typically applied next to the gel coat to minimise water ingress, by reducing water permeability. Epoxy-based resins are also much better at withstanding water ingress, in addition to improved chemical resistance and mechanical strength.

[0015] A major problem is the potential blistering of boat hulls, pools, spas and like products immersed in or exposed to water for long periods. This is typically symptomatic of osmosis occurring in the system, leading to moisture build-up in voids.

[0016] Apart from the cosmetic impact, this could ultimately lead to delamination and loss of mechanical strength.

[0017] Blisters are cracks that propagate parallel to the surface in the back-up/backing layer, between the gel-coat and the first fibre reinforced layer. As mentioned above, apart from boat hulls, blistering also occurs in other structures based on polyester matrix composites, such as tanks and swimming pools.

[0018] It is possible that, under acidic conditions – for example due to soil pH for in-ground pools and tanks – the calcium carbonate could dissolve into absorbed water pockets, forming carbonic acid. This will encourage osmosis into the system and eventual degradation of the structure.

[0019] Enhanced mechanical strength of a resin composite product is hugely beneficial, particularly where there is an associated reduction in volume of material used in the product's structure and/or a reduction in manufacturing complexity or time.

[0020] It is to be understood that, if any prior art is referred to herein, such reference does not constitute an admission that the prior art forms a part of the common general knowledge in the art, in Australia or any other country.

SUMMARY OF THE INVENTION

[0021] An aspect of the present invention provides a material composition comprising at least a combination of a resin and a graphene material.

[0022] Another aspect of the present invention provides a water-resistant barrier material including a material composition comprising at least a combination of a resin and a graphene material.

[0023] The graphene material is preferably dispersed within the resin e.g. forming a resin-graphene material matrix.

[0024] The composition may preferably include a reinforcing material.

[0025] The composition may be an osmotic barrier, such as for a product configured for prolonged exposure to or immersion in water or other liquid.

[0026] The resin can be or include a polyester resin (PE), vinyl ester, epoxy or other resin base.

[0027] The reinforcing material can include or be glass fibre, carbon fibre, poly-paraphenylene terephthalamide (aka Kevlar®) and/or other synthetic material.

[0028] The reinforcing material may be in the form of fibres, matting or mesh, providing reinforcement, such as used in a laying down/laying on application process. The reinforcing material may be spray, machine or manually applied.

[0029] The graphene material can include at least one of graphene and functionalised graphene, such as graphene oxide (GO).

[0030] The graphene material may include oxygen or at least one oxygen-containing group.

[0031] At least a proportion of the oxygen or the at least one oxygen-containing group may be bonded to or intercalated at the edges of graphene platelets.

[0032] At least a proportion of the at least one oxygen containing group may include at least one of a carboxylate, an ester, an epoxy and a carbonyl group.

[0033] The oxygen or the at least one oxygen containing group is preferably present in the graphene material in quantities of around 0.5% to 10%wt, preferably 1% to 5%wt, more preferably 1% to 3%wt, and yet more preferably 1% to 2%wt.

[0034] The inclusion of oxygen or the at least one oxygen containing group is understood to enhance dispersion of the graphene within the resin.

[0035] The composition can provide a fibre (preferably glass fibre) reinforced system, which can find application in significantly reducing water diffusion into the composition or system. The composition can therefore reduce or prevent damage to the system by hydrolysis and/or by other mechanisms, particularly over time.

[0036] The composition can include graphene as platelets. Providing graphene platelets within the composition beneficially avoids the need for functionalisation or additional modification to incorporate the graphene material with the resin.

[0037] Preferably the graphene includes nano particles, such as at least one of nano-platelets, nano-rods and nano-spheres.

[0038] The oxygen or the at least one oxygen-containing group may be bonded to or intercalated at the edges of the graphene platelets.

[0039] Preferably the graphene material can have a D50 (volumetric) lateral size of at or about 20 microns. Other volumetric lateral sizes are envisaged to fall within the scope of the present invention, such as in the range in the range 100 nanometres to 100 microns, or in the range 500 nanometres to 50 microns, or in the range 1 micron to 50 microns, or in the range 10 microns to 25 microns.

[0040] Fewer component layers of a structural and/or coating arrangement can be required compared to previous structural/coating arrangements, particularly for boat hulls, tanks, pools, spas, storage/reservoir tanks, water and waste water tanks, piping, storage vessels, and the like.

[0041] One or more forms of the present invention can beneficially avoid a need for a ceramic filled polyester (PE) resin layer and the outer calcium carbonate layers in the structure or coating arrangement.

[0042] The graphene material can provide up to 5% by weight (%wt) of the composition. The graphene material can provide up to 3%wt of the composition, preferably up to 2%wt of the composition, more preferably between 1%wt and 2.5%wt of the composition and yet more preferably 2%wt of the composition.

[0043] The composition is preferably for use in a structure for a boat hull, swimming pool, spa, tank or the like, such as where a surface of the structure is immersed/submersed in a liquid, preferably predominantly water, for a prolonged period.

[0044] A further aspect of the present invention provides a product comprising a boat hull, swimming pool, spa, tank, water or waste water tank, piping or storage vessel having a structure including a composition according to one or more of the aforementioned forms of the composition.

[0045] It will be appreciated that the composition can be termed a composite having a composite structure of the graphene material within the resin e.g. forming a matrix.

[0046] A further aspect of the present invention includes a method of producing a product for prolonged immersion or submersion in water, the method including providing an aforementioned form of the composition, coating the composition with a coloured gel coat and subsequently coating the coloured gel coat with a top coat gel coat.

[0047] Another aspect of the present invention provides an osmotic diffusion resistant composite including a matrix of a graphene material, a resin and a reinforcing material.

[0048] The graphene material preferably includes functionalised graphene. The graphene material contains oxygen or at least one oxygen-containing group. The graphene material preferably includes graphene platelets.

[0049] The composite is preferably part of a swimming pool, a spa, a boat hull, a tank, cladding or roofing material.

[0050] Preferably the graphene platelets are dispersed within the resin.

[0051] The composite may include graphene platelets of between 100 nanometres to 100 microns, or in the range 500 nanometres to 50 microns, or in the range 1 micron to 50 microns, or in the range 10 microns to 25 microns, or is at or about 20 microns, such as measured in a lateral dimension of the platelets.

[0052] The graphene material preferably provides up to 5% by weight (%wt) of the composite, preferably up to 2%wt of the composite, more preferably between 1%wt and 2.5%wt of the composite and yet more preferably 2%wt of the composite.

[0053] The composite may be part of a swimming pool, a pipe, a spa, a boat hull, a tank, a water tank or waste water tank, piping, a pipe lining, a storage vessel, cladding or roofing material.

[0054] The composite may be provided as at least one layer. The composite may be provided as a lining or coating over a surface of a substrate, such as an interior and/or exterior surface of the underlying product e.g. a surface of a swimming pool, a spa, a tank, a pipe etc.

[0055] The composite may be provided as at least one layer having an additional reinforcing material and at least one other layer not having the reinforcing material.

[0056] The composite may be provided in multiple layers, at least two said layers having different mechanical properties from each other.

[0057] The different mechanical properties can be due to different sizes of graphene material and/or due to different %wt of the graphene material with respect to the resin of each said layer. At least one of the layers preferably includes at least one of reinforcing fibres, matting or mesh.

[0058] The composite may be one of multiple layers of resin composite in the product (i.e. can be one of two or more differing resin compositions) or may be as two or more layers of the same composite in product (with or without other resin composite layers).

[0059] As a result of having fewer layers, the composition/system of one or more forms of the present invention can overall be thinner than the known composite equivalent. This helps to reduce overall weight, reduces total amount of materials and improves longevity of the finished product.

[0060] Inclusion of the graphene material dispersed in the resin

[0061] It will be appreciated that one or more forms of the present invention may be provided as a first layer of a composition containing a resin and a graphene material, such as a water/water vapour barrier, and a second layer may be provided as a structural layer including resin, graphene material and a reinforcing material.

[0062] The reinforcing material, may be or include glass fibre, carbon fibre poly-paraphenylene terephthalamide (aka Kevlar®) and/or other synthetic material, as mentioned above.

[0063] It will be appreciated that the graphene material enhances at least one mechanical property of the resin, compared to the resin without the graphene material. The at least one mechanical property may include mechanical strength, flexural stiffness, stress and/or strain characteristics.

[0064] A further aspect of the present invention provides a product incorporating at least one resin composite, the at least one resin composite containing a resin and a graphene material dispersed within resin.

[0065] The product may be a swimming pool, a pipe, a spa, a boat hull, a tank, a water tank or waste water tank, piping, a storage vessel, cladding or roofing material.

[0066] A pipe may be lined with the composition. The pipe may be cementitious or of concrete.

[0067] The product may include multiple layers of the at least one composite. At least one of the layers may include a reinforcing material. A first layer may be provided as a water/water vapour barrier layer, and a second may be provided as a structural layer.

[0068] One or more forms of the present invention provides enhanced barrier performance, such as enhanced barrier performance of GRP coatings for pipes, such as concrete pipes. Embodiment of the present invention are particularly beneficial where the reduced permeability can increase the lifetime of the pipe by reducing the amount of water ingress. The water phase could contain salts e.g. sulphates, that could lead to corrosion of the concrete pipe/system, and hence the additional benefit of the composition.

[0069] Preferably the structural layer includes a reinforcing material, such as glass fibre, carbon fibre or other synthetic material.

[0070] A cosmetic layer and/or a protective layer (such as UV protective) may be provided over the first or second layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0071] One or more forms of the present invention will hereinafter be described with reference to the accompanying drawings, in which:

[0072] Figure 1a shows a representation of moisture diffusion into a composite results in degradation.

[0073] Figure 1b shows a representation of resistance to degradation by presence of graphene material within the composite.

[0074] Figure 2 shows a chart of moisture absorption data from comparative trials of at least one embodiment of the present invention relative to a base sample having Reinforced Fibre (RF) Polyester (PE) resin.

[0075] Figure 3 shows a chart of sorption curves from comparative testing of at least one embodiment of the present invention relative to a base sample having Reinforced Fibre (RF) Polyester (PE) resin.

[0076] Figures 4a, 4b and 4c show representations of the cross–section of composite structures showing respective layers. Figure 4a shows the cross-section of a current composite structure for a pool, spa or boat hull or the like, and Figure 4b represents an embodiment of the present invention with a resin incorporating a graphene material. Figure 4c shows an alternative structure with a composite layer as a water barrier and a second layer as a structural layer.

[0077] Figure 5 shows a histogram of flexural stress versus sample grade and concentration of graphene material (platelets in this example) in the composition/composite.

[0078] Figure 6 shows a histogram of flexural modulus versus grade and concentration of graphene material (platelets in this example) in the composition/composite.

DESCRIPTION OF PREFERRED EMBODIMENT(S)

[0079] In the following detailed description, reference is made to accompanying drawings which form a part of the detailed description. The illustrative embodiments described in the detailed description, depicted in the drawings and defined in the claims, are not intended to be limiting. Other embodiments may be utilised and other changes may be made without departing from the spirit or scope of the subject matter presented. It will be readily understood that the aspects of the present disclosure, as generally described herein and illustrated in the drawings can be arranged, substituted, combined, separated and designed in a wide variety of different configurations, all of which are contemplated in this disclosure.

[0080] An osmotic cracking process can occur by the following mechanism:

- Microcavities present in the system are filled by water.
- Small molecules or salts, initially present in the matrix (e.g. catalyst residues) or formed during hydrolysis, are dissolved by water and accumulate into microcavities.

- The material layer separating a microcavity and the water bath is permeable to water, but considerably less permeable to larger molecules.

- This causes it to act as a semi-permeable membrane, leading to osmotic pressure developing in the cavity.

[0081] The following stages of an osmotic cracking process have been identified (see 'Humid Ageing of Organic Matrix Composites' – X. Colin and J. Verdu, as published in 'Durability of Composites in a Marine Environment', P. Davies and Y. D. S. Rajapakse (eds.), Solid Mechanics and Its Applications 208):

- 0 to t_1 - physical water sorption. The system reaches an equilibrium based on water solubility at t_1.

- t_1 to t_2 - system is at a pseudo-equilibrium. Hydrolysis occurs, but the conversion ratio remains low.

- Time > t_2 - propagation of osmotic cracks. The increased rate of mass uptake corresponds to the increase of volume created by cracking. The time to t_2 is representative of the material stability.

- Time = t_3 – crack coalescence. The solutes responsible for osmosis are transferred out of the system, causing a rapid reduction in mass after t_3.

[0082] There are two main matrix categories:

- Polymers which react chemically with water, for instance polyesters. Failure is considered to result from the following causal chain: Polymer + water -> water absorption -> polymer hydrolysis -> degradation of the macromolecular backbone -> embrittlement -> failure:

- Non-reactive polymers, for instance amine cured epoxies. Failure results from the following causal chain: Polymer + water -> water absorption -> polymer swelling -> stress state -> failure.

[0083] For uncoupled fibres, there are various possible causes of a specific attack of water in the interfacial region:

- The presence of interfacial voids allowing a fast penetration of water in deep layers

- Glass fibers have an alkaline character, which may be able to play a catalytic role on ester hydrolysis.

[0084] Hydrolysis is accelerated in the presence of glass, due to basic catalysis, and the coupling agent displays a limited but significant stabilizing effect. Coupling agents are expected to have a positive effect on the composite stability in humid ageing conditions.

[0085] Accelerated immersion testing was conducted using a pressure vessel at temperature to reduce testing time. Accelerated test results are achieved within 10 to 100hrs compared to months using a conventional testing standard of months. The following Table 1 shows samples 1-3 that were tested:

Table 1

Sample	Description	Gradient	D (120°C)	D (25°C)	Relative to base (120°C)
1	5mm Base RF PE sample	0.0016	5.02655E-07	1.71768E-07	100%
2	5mm 1% PG 20 RF PE sample	0.0013	3.31831E-07	1.13394E-07	66%
3	5mm 2% PG 20 RF PE sample	0.0012	2.82743E-07	9.66196E-08	56%

[0086] Figure 1a shows a known composite structure/system 10 wherein water molecules 14 are able to penetrate into the composite 10 at a water-structure interface 'I' due to poor or limited water barrier characteristics of the composite. Water molecules 14 can collect in voids 16 in the resin matrix 12 and can aggregate at fibre reinforcements13 (e.g. glass fibre strands)

[0087] Water penetrating into the composite causes blistering/cracking 18, leading to structural and/or aesthetic degradation of the composite/product.

[0088] Figure 1b shows a composite structure/system 20 according to at least one embodiment of the present invention, wherein graphene material 22, such as in the form of graphene platelets, and a resin 24 form a composite structure matrix 25 that reduces or prevents significant water molecule 14 diffusion into the composite structure/system 20, thereby avoiding or at least reducing degradation and enhancing mechanical strength of the product. Water molecules 14 have reduced penetration into the matrix at the water-matrix interface 'I'. The composite 20 preferably includes reinforcing 23, such as reinforcing fibres e.g. glass fibres.

[0089] The product may be, for example, a swimming pool, a spa, a boat hull, tank (such as a water tank), cladding or roofing, such as formed using reinforcing fibres e.g. glass reinforced composites.

[0090] Figure 2 shows examples (samples 2 and 3) of embodiments of the present invention compared to the base sample of 5mm base reinforce glass fibre (RF) polyester (PE) resin structure (sample 1).

[0091] A composition of at least one embodiment of the present invention includes the graphene material combined with

[0092] The same data of Figure 2 is represented in Figure 3 as sorption curves.

[0093] Curve 1 represents the 5mm base RF PE sample. Curve 2 represents the 5mm 1% graphene material (~20 nanometre particles) in RF PE sample. Curve 3 represents a 5mm 2% graphene material (~20 nanometre particles).

[0094] From the curves in Figure 3, the following conclusions can be drawn:

- There is a two-stage absorption process, consistent with that reported in the literature.
- The gradient of Stage 1 (diffusion control) allows estimation of the diffusion coefficient for the systems. These are shown below.
- For Stage 2, the overlap between the base sample curve (curve 1) and the invention embodiment curves (curves 2 and 3) suggest no difference in the rate of osmosis/change to the system.

[0095] As shown in Figure 4b, one or more embodiments of the present invention can incorporate graphene material in the structure designed for prolonged immersion in water and therefore otherwise at risk of premature delamination, cracking, bubbling etc., due to osmosis of the water into the structure (e.g. of a boat hull, pool, spa tank or the like).

[0096] It will be appreciated that the inventive structure includes use of a composition including a graphene material forming a matrix with a resin and reinforcing fibres.

[0097] According to the embodiment represented in Figure 4b, the composition can include the graphene material, a polyester resin and glass fibre reinforcement.

[0098] As shown in Figure 4c, multiple forms of the composite can be provided in layers, such as a barrier layer containing the graphene material in a resin and a second layer containing reinforcing material.

[0099] Other arrangements and configurations falling within the scope of the present invention are possible.

[00100] A cosmetic coloured gel coat can be applied to the composition and a clear gel coat applied over the cosmetic coating.

[00101] Table 2 shows results for tests as depicted in the chart of Ultimate Flexural Stress vs Sample Grade and Concentration in Figure 5.

Table 2

Sample No.	% graphene platelets to resin	Graphene platelets lateral size (microns)	Ultimate Flexural Stress
1	0	N/A	188
2	0	N/A	172
3	0	N/A	200
4	0	N/A	187
5	0.5	20	228
6	0.75	20	215
7	1.0	20	234
8	0.75	10	250
9	0.5	10	286

[00102] Base samples 1-4 do not contain graphene platelets in the resin of the composite matrix, demonstrating significantly lower ultimate flexural stress compared with samples 5-9 containing graphene platelets according to embodiments of the present invention. The baseline average flexural stress from samples 1-4 is 186.5 MPa. The flexural stress in the samples containing graphene ranges from 215 MPa to 286 MPa.

[00103] Table 3 shows results of tests as depicted in the chart of Flexural Modulus (MPa) vs Grade and Concentration of graphene platelets in Figure 6:

Table 3

Sample No.	% graphene platelets to resin	Graphene platelets lateral size (microns)	Flexural Modulus (MPa)
1	0	N/A	8325
2	0	N/A	7460
3	0	N/A	7797
4	0	N/A	7803
5	0.5	20	8564
6	0.75	20	8750
8	1.0	20	10046
9	0.75	10	11174
10	0.5	10	11245

[00104] Base samples 1-4 do not contain graphene platelets in the resin of the composite matrix, demonstrating significantly lower flexural modulus (MPa) compared with samples 5-9 containing graphene platelets according to embodiments of the present invention.

[00105] Baseline average flexural modulus is 7846 MPa from samples 1-4 and the flexural modulus ranges from 8564 MPa to 11245 MPa for samples 5-9 loaded with graphene according to embodiments of the present invention.

[00106] Structures incorporating one or more embodiments of the present invention can include Interface/Internal surface (immersed/water facing) such as having a clear gel coat 26, a cosmetic layer – coloured gel coat 28, structural – glass fibre/resin layer 30, compressive strength/water resistance – ceramic-filled polyester resin 32, outer layer – calcium carbonate filler with resin 34.

[00107] An alternative structure incorporating one or more embodiments of the present invention can include an Interface/Internal surface (immersed/water facing) – clear gel coat 26, a cosmetic layer – coloured gel coat 28, a multi-functional layer – polyester resin/graphene material/reinforcing material 36 having structural, chemical resistance barrier properties, higher thermal conductivity.

[00108] An alternative structure incorporating one or more embodiments of the present invention can include an Interface/Internal surface (immersed/water facing) – clear gel coat 26, a cosmetic layer – coloured gel coat 28, a composite barrier layer incorporating graphene material 38, a structural composite layer incorporating resin and a reinforcing material 40, (optional graphene material 22).

[00109] In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

CLAIMS:

1. A material composition comprising at least a combination of a resin and a graphene material.

2. The composition of claim 1, further including a reinforcing material.

3. The composition of claim 1 or claim 2, the composition being an osmotic barrier material.

4. The composition of any one of claims 1 to 3, wherein the resin is or includes at least one of a polyester resin (PE), vinyl ester resin, an epoxy resin and any other resin base.

5. The composition of any one of claims 1 to 4, wherein the reinforcing material includes at least one of a glass fibre material, carbon fibre material, poly-paraphenylene terephthalamide and/or other synthetic material.

6. The composition of claim 5, wherein the reinforcing material is in the form of fibres, matting or mesh.

7. The composition of any one of the preceding claims, wherein the graphene material can include at least one of graphene and functionalised graphene, such as graphene oxide.

8. The composition of any one of the preceding claims, wherein the graphene material includes graphene nano particles, such as nano-platelets, nano-rods, nano-spheres, or combinations of two or more thereof.

9. The composition of claim 8, wherein the graphene material has a volumetric lateral size in the range 100 nanometres to 100 microns, or in the range 500 nanometres

to 50 microns, or in the range 1 micron to 50 microns, or in the range 10 microns to 25 microns, or is at or about 20 microns.

10. The composition of any one of the preceding claims, wherein the graphene material provides up to 5% by weight (%wt) of the composition.

11. The composition of claim 10, wherein the graphene material provides up to 5%wt of the composition, preferably up to 2%wt of the composition, more preferably between 1%wt and 2.5%wt of the composition and yet more preferably 2%wt of the composition.

12. The composition of any one of the preceding claims, wherein the graphene material includes oxygen or at least one oxygen-containing group.

13. The composition of claim 12, wherein the oxygen or the at least one oxygen-containing group is bonded to or intercalated at the edges of graphene platelets.

14. The composition of claim 12 or claim 13, wherein the at least one oxygen containing group includes at least one of a carboxylate, an ester, an epoxy and a carbonyl group.

15. The composition of any one of claims 9 to 11, wherein the at least one oxygen containing group is present in the graphene material in quantities of around 0.5% to 10%wt, preferably 1% to 5%wt, more preferably 1% to 3%wt, and yet more preferably 1% to 2%wt.

16. The composition of any one of the preceding claims, the composition for use in a structure for a boat hull, a pipe, a swimming pool, a spa, a tank or the like.

17. The composition of claim 16, wherein a surface of the structure is immersed/submersed in a liquid, preferably predominantly water, for a prolonged period.

18. The composition of claim 16 or claim 17, wherein the composition is provided as a pipe lining.

19. A product comprising a boat hull, a pipe, a swimming pool, a spa or a tank having a structure including a composition according to any one of claims 1 to 17.

20. The product according to claim 19, wherein the product is a pipe having a lining of the composition.

21. The product according to claim 20, wherein the pipe includes a cementitious or concrete pipe.

22. The product according to any one of claims 19 to 21, wherein the composition is in multiple layers.

23. A method of producing a product for prolonged immersion or submersion in water, the method including providing a composition of any one of claims 1 to 17, coating the composition with a coloured gel coat and subsequently coating the coloured gel coat with a protective top coat.

24. The method of claim 23, wherein the composition is provided as at least a first layer and a second layer.

25. The method of claim 24, wherein at least one of the first layer and the second layer is provided as a barrier layer.

26. The method of any one of claims 23 to 25, wherein the composition is applied by at least one of spraying, painting, rollering and pouring.

27. The method of any one of claims 23 to 26, wherein the composition is created by applying the resin with the graphene material dispersed therein to a reinforcing material.

28. A water-resistant composite including a matrix of a graphene material and a resin.

29. The composite of claim 28, further including a reinforcing material.

30. The composite of claim 28 or claim 29, wherein the graphene material includes functionalised graphene.

31. The composite of claim 30, wherein the graphene material contains oxygen or at least one oxygen-containing group.

32. The composite of any one of claims 28 to 31, wherein the graphene material includes graphene platelets

33. The composite of 32, wherein the graphene platelets are dispersed within the resin.

34. The composite of claim 32 or 33, wherein the graphene platelets are between 100 nanometres to 100 microns, or in the range 500 nanometres to 50 microns, or in the range 1 micron to 50 microns, or in the range 10 microns to 25 microns, or is at or about 20 microns, in a lateral dimension of the platelets.

35. The composition of any one of claims 28 to 34, wherein the graphene material provides up to 5% by weight (%wt) of the composite, preferably up to 2%wt of the composite, more preferably between 1%wt and 2.5%wt of the composite and yet more preferably 2%wt of the composite.

36. The composite of any one of claims 28 to 35, wherein the composite is part of a swimming pool, a spa, a boat hull, a tank, a water tank or waste water tank, piping, a storage vessel, cladding or roofing material.

37. The composite of any one of claims 28 to 36, wherein the composite is in at least one layer.

38. The composite of any one of claims 28 to 37, the composite provided in at least one layer having an additional reinforcing material and at least one other layer not having the reinforcing material.

39. The composite of any one of claims 28 to 38, the composite provided in multiple layers, at least two said layers having different mechanical properties from each other.

40. The composite of claim 39, wherein the different mechanical properties are due to different sizes of graphene material and/or due to different %wt of the graphene material with respect to the resin of each said layer.

41. The composite of claim 40, wherein at least one of the layers includes at least one of reinforcing fibres, matting or mesh.

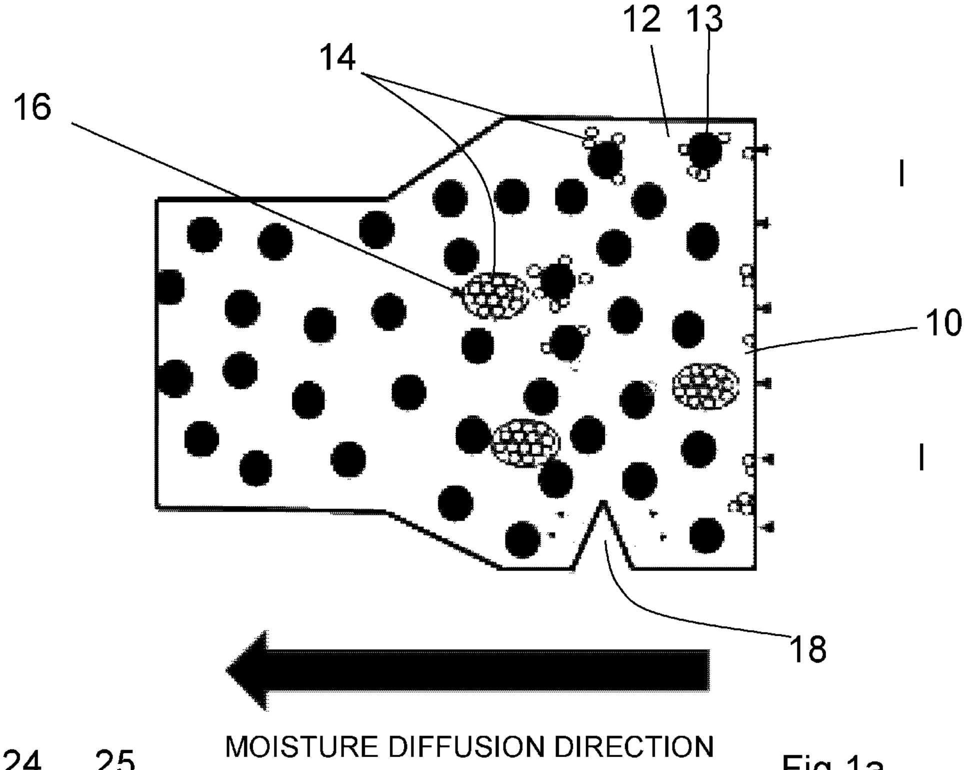
12
13
14
16
I
10
I
18
MOISTURE DIFFUSION DIRECTION

Fig 1a

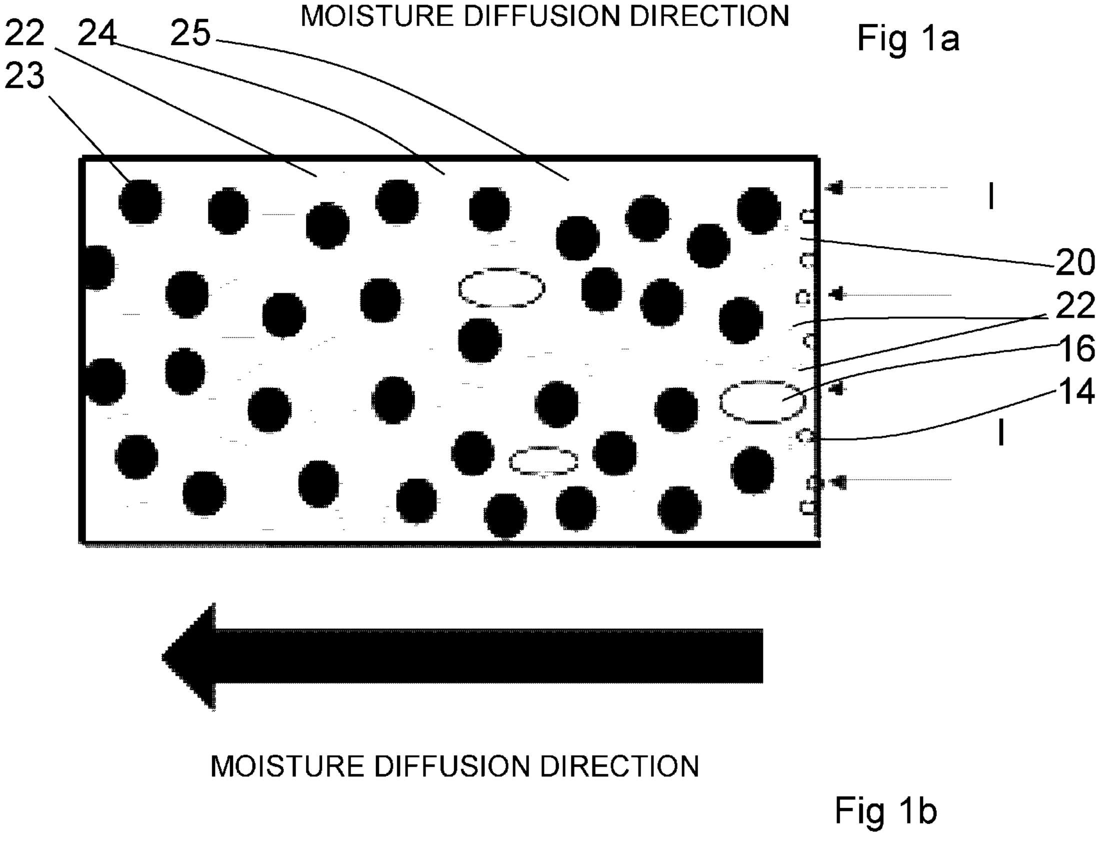
22
24
25
23
I
20
22
16
14
I
MOISTURE DIFFUSION DIRECTION

Fig 1b

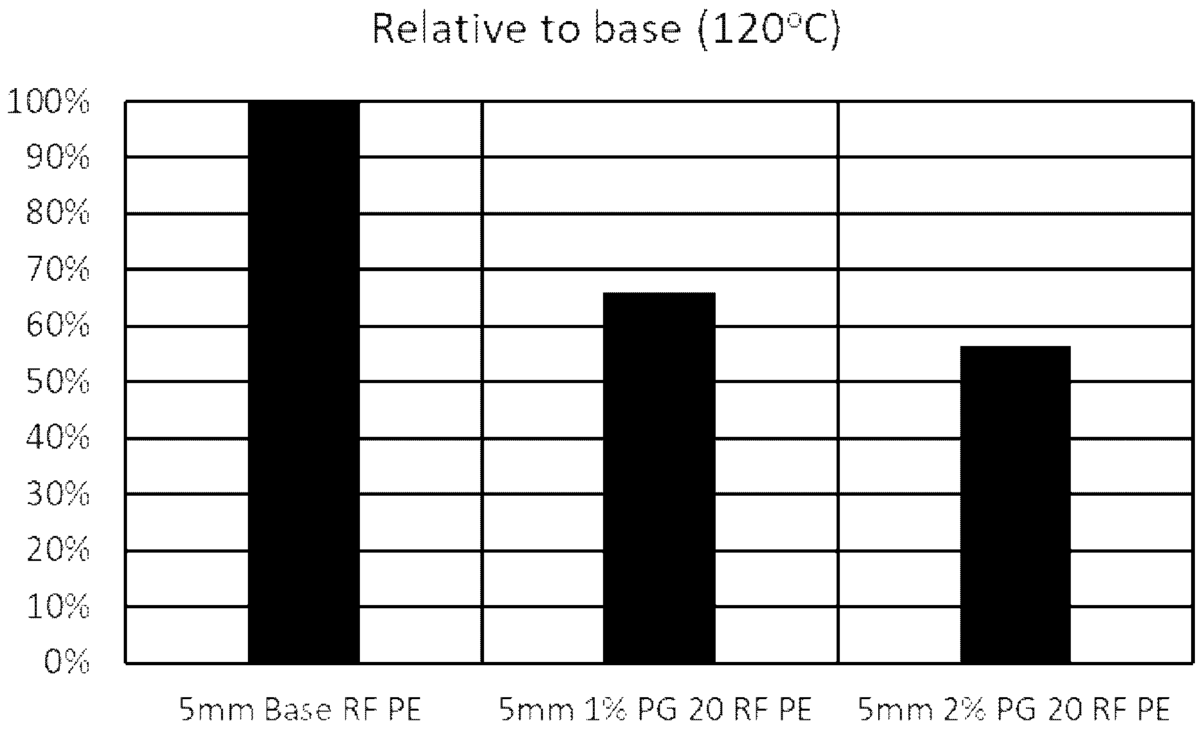

Fig 2

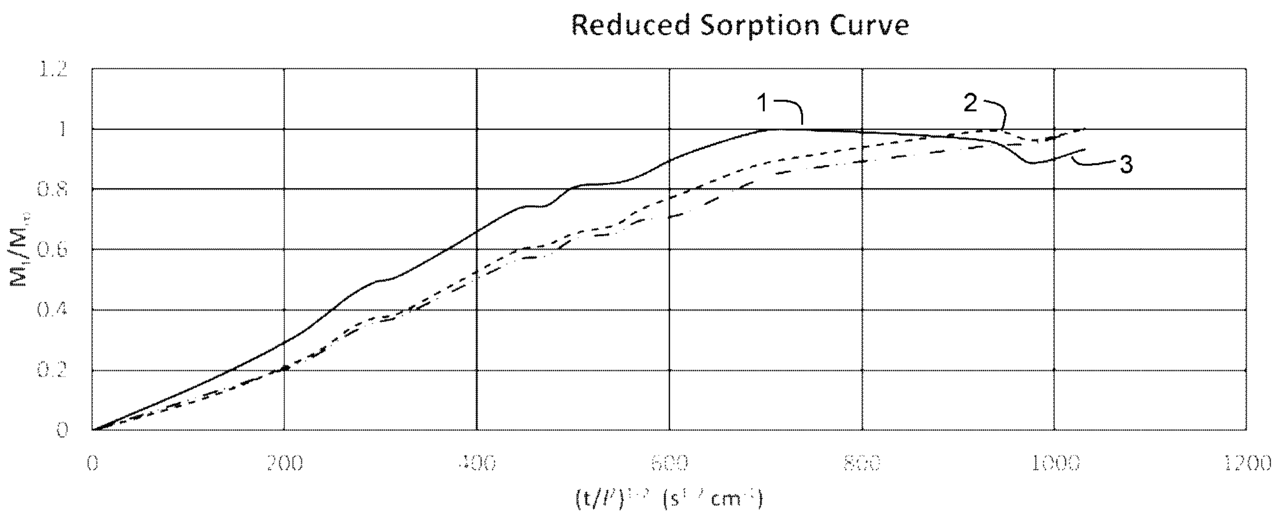

Fig 3

1:5mm Base RF PE sample
2: 5mm 1% PG 20 RF PE Sample
3: 5mm 2% PG 20 RF PE Sample

Water Side

Internal surface (immersed/water facing) – clear gel coat 26
Cosmetic layer – coloured gel coat 28
Structural – glass fibre/resin layer 30
Compressive strength/water resistance – ceramic-filled polyester resin 32
Outer layer – calcium carbonate filler with resin 34

Fig 4a

Water Side

Internal surface (immersed/water facing) – clear gel coat 26
Cosmetic layer – coloured gel coat 28
Multi-functional layer – polyester resin/graphene material/reinforcing material 36 Structural, chemical resistance barrier properties, higher thermal conductivity

Fig 4b

Water Side

Internal surface (immersed/water facing) – clear gel coat 26
Cosmetic layer – coloured gel coat 28
Composite barrier layer incorporating graphene material 38
Structural composite layer incorporating resin and a reinforcing material 40 (optional graphene material 22)

Fig 4c

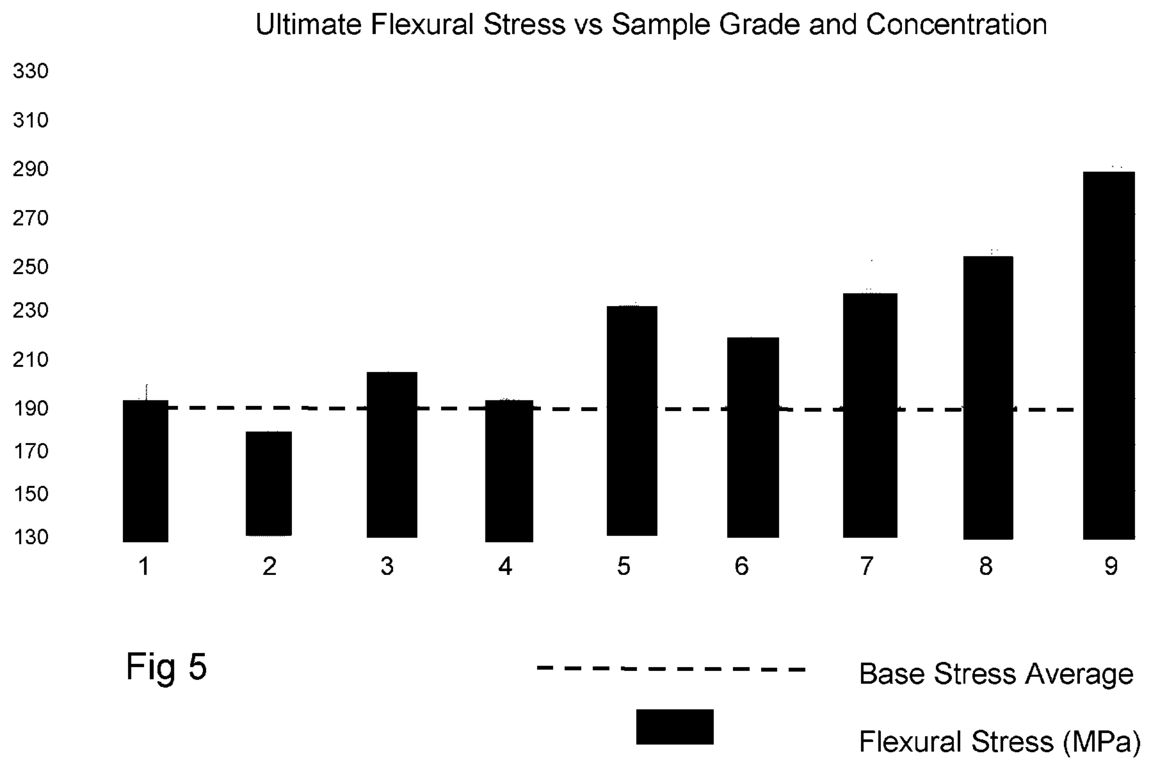
Ultimate Flexural Stress vs Sample Grade and Concentration
330
310
290
270
250
230
210
190
170
150
130
1
2
3
4
5
6
7
8
9
Base Stress Average
Flexural Stress (MPa)

Fig 5

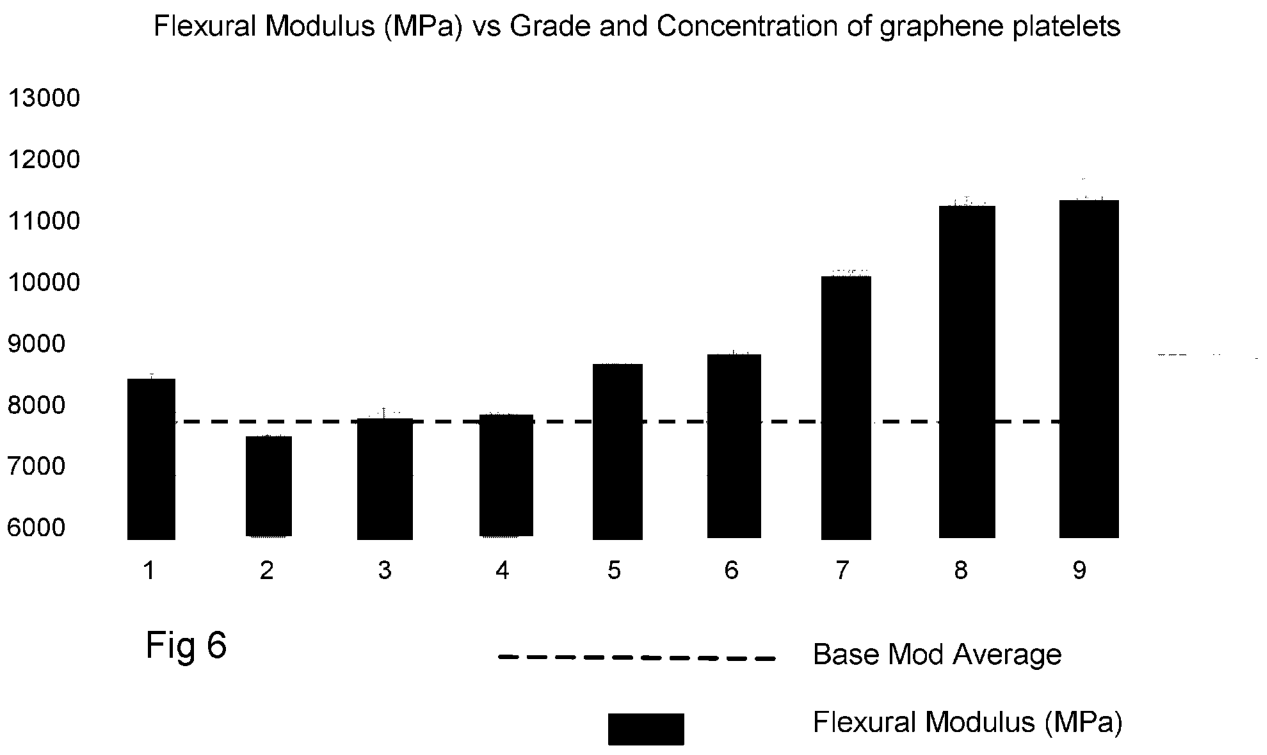
Flexural Modulus (MPa) vs Grade and Concentration of graphene platelets
13000
12000
11000
10000
9000
8000
7000
6000
1
2
3
4
5
6
7
8
9
Base Mod Average
Flexural Modulus (MPa)

Fig 6

INTERNATIONAL SEARCH REPORT	International application No. **PCT/AU2021/050495**

A. CLASSIFICATION OF SUBJECT MATTER

C08K 3/04 (2006.01) C08J 5/04 (2006.01) B32B 5/02 (2006.01)

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)

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)

PATENW, CAPlus, COMPENDEX, EMBASE, Google, Google Scholar, Espacenet; IPC/CPC marks (B29C, B29C63/34, F16L, B63B81, B63, E03, E04H, E04D, B32B27/[36,38], C08J5/04, C08J3/02, C08K3/042, C08L/[63,67], B32B5/02, B323B2255/26, B32B2260/[021,046], B32B2262/[101,106], B32B2264/108, B32B2307/[302,714); Keywords: graphene, resin, ship, pipe, fiberglass and the like terms; IP Australia's internal databases: Applicant/Inventor name search.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C   [X] 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

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"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 29 July 2021	Date of mailing of the international search report 29 July 2021
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	**Authorised officer** Athanasios (Arthur) Zavras, PhD AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832317

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2021/050495**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2019/0322876 A1 (REDJAK , L.L.C) 24 October 2019 [0033], [0035], [0100], [0104], [0111], [0216], [0244], [0282]-[0284], [0287], [0302], [0308], [0367], [0375]-[0379]; Claims 11 and 14.	1-41
X	CN 105504733 A (WUHU EDISON AUTOMATION EQUIPMENT CO LTD) 20 April 2016, Viewed as the English machine translation from Google Patents retrieved from the internet on 27 July 2021 Abstract; Claims 1 and 2	1-41
X	CN 109131748 A (ZHENJIANG BAOHAI SHIP HARDWARE CO LTD) 04 January 2019, Viewed as the English machine translation from Google Patents retrieved from the internet on 27 July 2021 Example 1	1-41

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2021/050495**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 2019/0322876 A1	24 October 2019	US 2019322876 A1	24 Oct 2019
		US 10519327 B2	31 Dec 2019
		US 2019322875 A1	24 Oct 2019
		US 10689527 B2	23 Jun 2020
		US 2020283644 A1	10 Sep 2020
		US 10829649 B2	10 Nov 2020
CN 105504733 A	20 April 2016	CN 105504733 A	20 Apr 2016
CN 109131748 A	04 January 2019	CN 109131748 A	04 Jan 2019

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.