

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization

International Bureau

(43) International Publication Date
25 May 2023 (25.05.2023)



(10) International Publication Number
WO 2023/089326 A1

(51) International Patent Classification:

C08K 3/04 (2006.01) C08K 3/38 (2006.01)
C08K 3/28 (2006.01)

DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI,
SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/GB2022/052926

(22) International Filing Date:

17 November 2022 (17.11.2022)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2116666.5 18 November 2021 (18.11.2021) GB

(71) Applicant: **SENERGY INNOVATIONS LIMITED**
[GB/GB]; 6 Baronscourt Lane, Carryduff, Belfast, Antrim
BT8 8RR (GB).

(72) Inventors: **BOYLE, Christine**; Senergy Innovations Limited, 6 Baronscourt Lane, Carryduff, Belfast, Antrim BT8 8RR (GB). **STRAIN, Findhan**; Senergy Innovations Limited, 6 Baronscourt Lane, Carryduff, Belfast, Antrim BT8 8RR (GB). **MCGONIGLE, Niall**; Senergy Innovations Limited, 6 Baronscourt Lane, Carryduff, Belfast, Antrim BT8 8RR (GB). **MCNALLY, Tony**; Warwick Manufacturing Group, University of Warwick, Coventry, West Midlands CV4 7AL (GB). **KUMAR, Sandeep**; Warwick Manufacturing Group, University of Warwick, Coventry, West Midlands CV4 7AL (GB).

(74) Agent: **HGF LIMITED**; Document Handling - HGF
Leeds, 1 City Walk, Leeds, West Yorkshire LS11 9DX
(GB).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,

(54) Title: CONDUCTIVE POLYMER COMPOSITE

(57) Abstract: The present invention relates to a composite comprising a polymer matrix, graphene and at least one thermally conductive inorganic filler, wherein the graphene and the at least one thermally conductive inorganic filler are dispersed within the polymer matrix. The composites have high thermal conductivities and are particularly useful in solar thermal collectors and other heat exchangers.



Conductive Polymer Composite

[0001] The present invention relates to a composite comprising a polymer matrix, graphene and at least one thermally conductive inorganic filler, wherein the graphene and the at least one thermally conductive inorganic filler are dispersed within the polymer matrix. The composites have high thermal conductivities and are particularly useful in solar thermal collectors and other heat exchangers.

Background

[0002] Polymer composites comprising thermally conductive filler materials offer new possibilities for replacing metal parts in applications such as thermal collectors. Polymer composites are light weight and therefore easier to install and handle than their metal counterparts. The filler material dispersed within the polymer matrix may be carefully selected to ensure efficient and effective infra-red absorption and/or thermal conduction.

[0003] Polyphthalamides (PPA) are a class of polyamide polymer that have improved chemical resistance and UV-stability compared to other polymers, including other polyamides.

[0004] Graphitic forms of carbon, such as graphite and graphene, possess high thermal conductivities.

Summary of the Invention

[0005] In a first aspect of the invention, there is provided a composite comprising a polymer matrix, graphene and at least one thermally conductive inorganic filler, wherein the graphene and the at least one thermally conductive inorganic filler are dispersed within the polymer matrix.

Graphene

[0006] A single molecular layer of graphene is one atom thick and can therefore be described as a single atomic layer ("layer"). Typically, the graphene will have an average thickness of <10 layers.

[0007] The average particle size of the graphene may be $>1\ \mu\text{m}$, e.g. $>10\ \mu\text{m}$. The average particle size (e.g. the D_{V50}) of the graphene may be $<200\ \mu\text{m}$, e.g. $<75\ \mu\text{m}$. It may be that the average particle size (e.g. the D_{V50}) of the graphene is between $10\ \mu\text{m}$ and $60\ \mu\text{m}$. The average particle size of the graphene (e.g. the D_{V50}) may be between $40\ \mu\text{m}$ and $60\ \mu\text{m}$, e.g. between $45\ \mu\text{m}$ and $55\ \mu\text{m}$.

[0008] It may be that greater than 50% by weight (e.g., greater than 75%, greater than 90% or greater than 98% by weight) of the graphene has a particle size of $>1\ \mu\text{m}$, e.g. $>10\ \mu\text{m}$. It

may be that greater than 50% by weight (e.g., greater than 75%, greater than 90% or greater than 98% by weight) of the graphene has a particle size of <200 μm , e.g. <75 μm . It may be that greater than 50% by weight (e.g., greater than 75%, greater than 90% or greater than 98% by weight) of the graphene has a particle size of between 10 μm and 60 μm .

5 [0009] It may be that the oxygen content in the graphene is >2 wt%, e.g., >5 wt%. It may be that the oxygen content in the graphene is <50 wt% e.g., <35 wt%.

[0010] The graphene may be pristine graphene, e.g. that which has been directly exfoliated from graphite. The graphene may be reduced graphene oxide. It may be that the graphene is functionalised graphene. It may be that the graphene is graphene nanoplatelets.

10 [0011] It may be that the wt% of the graphene in the polymer matrix is >25 wt%, e.g. >30 wt%. It may be that the wt% of the graphene in the polymer matrix is <80 wt%. It may be that the wt% of the graphene in the polymer matrix is <60 wt%. It may be that the wt% of the graphene in the polymer matrix is in the range from 25 wt% to 70 wt%, e.g., from 30 wt% to 65 wt%. It may be that the wt% of the graphene in the polymer matrix is in the range from 35 wt%
15 to 65 wt%. It may be that the wt% of the graphene in the polymer matrix is in the range from 40 wt% to 60 wt%.

Thermally Conductive Inorganic Filler

[0012] It may be that the at least one thermally conductive inorganic filler comprises a group 13 nitride. It may be that the group 13 nitride is boron nitride or aluminium nitride. It may be
20 that the group 13 nitride is boron nitride. Preferably, the group 13 nitride is aluminium nitride. It may be that the at least one thermally conductive inorganic filler comprises more than one group 13 nitride. It may be that the at least one thermally conductive inorganic filler comprises a combination of group 13 nitrides selected from boron nitride, aluminium nitride, gallium nitride and indium nitride. It may be that the at least one thermally conductive inorganic filler
25 comprises aluminium nitride and an additional group 13 nitride selected from boron nitride, gallium nitride and indium nitride. It may be that the at least one thermally conductive inorganic filler comprises boron nitride and aluminium nitride

[0013] The inventors have found that the dispersion of both graphene and a group 13 nitride, e.g. aluminium nitride, within a polymer matrix provides a composite with favourable thermal
30 conductivity. Without wishing to be bound by theory, it is thought that the group 13 nitride particles associate with the graphene flakes, forming a scaffold in which the particles of group 13 nitride are situated between flakes of graphene.

[0014] It may be that the at least one thermally conductive inorganic filler comprises a metal oxide or a carbide, e.g. SiC. It may be that the at least one thermally conductive inorganic filler

comprises an aluminium oxide, e.g. AlO, Al₂O or Al₂O₃, or magnesium oxide. It may be that the at least one thermally conductive inorganic filler does not contain carbon.

[0015] It may be that the wt% of the at least one thermally conductive inorganic filler in the polymer matrix is in the range from 0.1 wt% to 50 wt%. The wt% of the at least one thermally
5 conductive inorganic filler in the matrix may be in the range from 5 wt% to 40 wt%. The wt% of the at least one thermally conductive inorganic filler in the matrix may be in the range from 10 wt% to 30 wt%, e.g., from 15 wt% to 25 wt%.

[0016] In embodiments where the at least one thermally conductive inorganic filler comprises aluminium nitride, the average particle size of the AlN may be <10 µm, e.g. <5 µm. The
10 average particle size of the AlN may be from 0.1 µm to 5 µm, e.g. 0.1 µm to 3 µm. It may be that greater than 50% by weight (e.g., greater than 75%, greater than 90% or greater than 98% by weight) of the AlN has a particle size of <10 µm, e.g. <5 µm. It may be that greater than 50% by weight (e.g., greater than 75%, greater than 90% or greater than 98% by weight) of the AlN has a particle size of from >0.1 µm to 5 µm, e.g. >0.1 µm to 3 µm.

[0017] The ratio of graphene particle size:AlN particle size may in the range from 1:1 to
15 100:1. The ratio of graphene particle size:AlN particle size may in the range from 5:1 to 60:1. The ratio of graphene particle size:AlN particle size may be in the range from 10:1 to 30:1.

[0018] In embodiments where the at least one thermally conductive inorganic filler comprises boron nitride (BN), the BN may be hexagonal boron nitride (h-BN). It may be that the BN is
20 boron nitride nanosheet. The BN may have an average particle size of <2 µm, e.g. <1 µm.

Total Loading

[0019] It may be that the total wt% of the graphene and the at least one thermally conductive inorganic filler (i.e. the total wt% of filler) in the polymer matrix is >40 wt%. It may be that the
25 total wt% of filler in the polymer matrix is >50 wt%, e.g. >60 wt%. It may be that the total wt% of filler in the polymer matrix is <90 wt%, e.g. <80wt%. It may be that the total wt% of filler in the polymer matrix is in the range from 40 wt% to 90 wt%, e.g., from 50 wt% to 80 wt%. It may be that the total wt% of filler in the polymer matrix is in the range from 60 wt% to 80 wt%.

[0020] It may be that the weight ratio of graphene:at least one thermally conductive inorganic filler in the polymer matrix is from 1:1-10:1. It may be that the weight ratio of graphene:at least
30 one thermally conductive inorganic filler in the polymer matrix is from 3:2 to 7:1. It may be that the weight ratio of graphene:at least one thermally conductive inorganic filler in the polymer matrix is from 2:1 to 4:1, e.g. from 2:1 to 3:1.

[0021] It may be that the wt% of the graphene in the polymer matrix is greater than the wt% of the at least one thermally conductive inorganic filler in the matrix.

Polymer

[0022] The polymer matrix material may include any one of the following polymer matrices:

5 acrylonitrile butadienestyrene (ABS) (chemical formula $(C_8H_8 \cdot C_4H_6 \cdot C_3H_3N)_n$);
polycarbonate/acrylonitrile butadiene styrene alloys (PCABS); polybutylene terephthalate
(PBT); polyphenylene oxide; polyphthalamide (PPA); polyphenylene sulfide (PPS);
polyphenylene ether; modified polyphenylene ether containing polystyrene; liquid crystal
polymers; polystyrene; styrene-acrylonitrile copolymer; rubber-reinforced polystyrene; poly
10 ether ketone (PEEK); acrylic resins such as polymers and copolymers of alkyl esters of acrylic
and methacrylic acid styrene-methyl methacrylate copolymer, styrene-methyl methacrylate-
butadiene copolymer, polymethyl methacrylate and methyl methacrylate-styrene copolymer;
polyvinyl acetate; polysulfone; polyether sulfone; polyether imide; polyarylate; polyamideimide;
polyvinyl chloride; vinyl chloride-ethylene copolymer; vinyl chloride-vinyl acetate copolymer;
15 polyimides, polyamides; polyolefins such as polyethylene; ultra-high molecular weight
polyethylene; high density polyethylene; linear low density polyethylene; polyethylene
naphthalate; polyethylene terephthalate; polypropylene; chlorinated polyethylene; ethylene
acrylic acid copolymers; polyamides; polyanilines; polypyrroles; polyurethanes; polyepoxides;
epoxy resins; phenylene oxide resins; phenylene sulfide resins; polyoxymethylenes;
20 polyesters; polyvinyl chloride; vinylidene chloride/vinyl chloride resins; vinyl aromatic resins
such as polystyrene; poly(vinylnaphthalene); poly(vinyltoluene); polyimides;
polyaryletheretherketone; polyetheretherketones; and polyaryletherketone, or a mixture of
copolymer thereof.

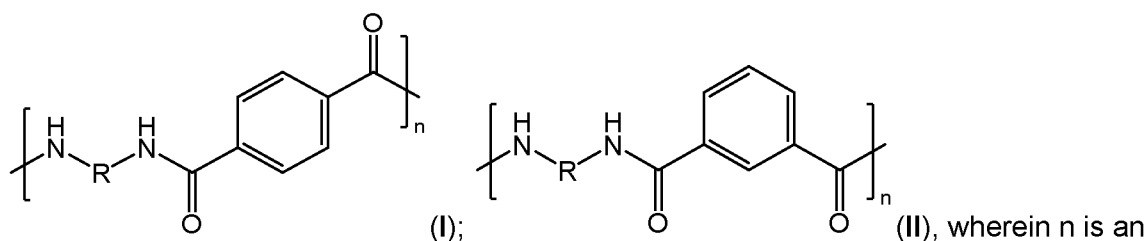
[0023] The matrix may comprise an aromatic polymer. The inventors have surprisingly found
25 that composites comprising an aromatic polymer, e.g. PPA, matrix provide good thermal
conductivity.

[0024] The matrix may comprise polyphenylene sulfide (PPS).

[0025] The matrix may comprise a phenyl ether polymer. The phenyl ether polymer may
comprise polyphenyl ether (PPE) or poly(*p*-phenylene oxide) (PPO). The matrix may comprise
30 polystyrene. The matrix may comprise a blend, e.g. an amorphous blend of a phenyl ether
polymer and polystyrene. The matrix may comprise a blend, e.g. an amorphous blend, of a
polyphenyl ether (PPE) and polystyrene. The matrix may comprise a blend, e.g. an
amorphous blend of a polyphenyl ether (PPE) and polyphenylene sulfide (PPS). The matrix

may comprise a blend, e.g. an amorphous blend of a polyphenyl ether (PPE) and polyphthalamide (PPA).

[0026] The matrix may comprise a polyamide (nylon). The polymer matrix may comprise an aliphatic polyamide or an aromatic polyamide, e.g. a polyphthalamide. The polymer matrix
5 may comprise an aromatic polyamide (i.e. an aramid). The polymer matrix may comprise an aliphatic polyamide or a polyphthalamide. The polymer matrix may comprise an aliphatic polyamide. For example, it may be that the matrix comprises nylon 6, nylon 66, or a mixture thereof. The polymer matrix may comprise nylon 11 (PA 11). The polymer matrix may
10 comprise a polyphthalamide. Polyphthalamide (PPA) may be selected from a polymer having general formula (I), a polymer having general formula (II), a polymer composed of a combination of units of formulae (I) and (II) in the same polymer chain and a mixture thereof:



integer and R is an alkylene, e.g. C₂-C₈-alkylene. For the absence of doubt, when the polyphthalamide is composed of a combination of repeating units of formulae (I) and (II) in the
15 same polymer chain, the terminal amino group of one repeating unit is bonded to the terminal carbonyl group of another repeating unit.

[0027] It may be that the polymer matrix comprises a compound of formula (I), wherein R is C₂-C₆-alkylene. It may be that the polymer matrix comprises a compound of formula (II),
20 wherein R is C₂-C₆-alkylene. It may be that the polymer matrix comprises a polymer composed of a combination of repeating units of formulae (I) and (II) in the same polymer chain, wherein R is C₂-C₆-alkylene.

[0028] The polymer matrix may comprise a crystalline polymer. The polymer matrix may
25 comprise a semi-crystalline polymer. The polymer matrix may comprise a thermoplastic polymer, a thermosetting polymer or an elastomer. The polymer matrix may comprise a thermoplastic polymer. The polymer matrix may comprise a homopolymer or a copolymer.

[0029] It may be that the polymer matrix in which the graphene and the at least one thermally
conductive inorganic filler is dispersed consists of >75 wt%, e.g. >80%, of a single polymer. It
may be that the polymer matrix consists of >90 wt%, e.g., >98 wt% of a single polymer. The
single polymer may be any polymer referred to above.

[0030] It may be that the composite further comprises an additional filler dispersed within the polymer matrix. It may be that the additional filler is carbonaceous filler, e.g., carbon nanotubes or carbon fibers.

Solar Thermal Collector

5 [0031] In a second aspect of the invention is provided a solar thermal collector comprising a composite according to the first aspect.

[0032] It may be that the solar thermal collector comprises a hollow body having a lower wall, an upper wall and lateral side walls and an internal cavity within said hollow body for receiving a heat exchange medium, wherein at least a portion of the upper wall is formed from a
10 composite according to the first aspect.

Optically Transmissive Panel

[0033] The solar thermal collector may further comprise an optically transmissive panel located above the upper wall of the body. The optically transmissive panel may comprise glass, polycarbonate or PMMA glazing. The upper wall of the body and the optically
15 transmissive panel may form an air gap therebetween. The upper wall of the body and the optically transmissive panel may form a vacuum therebetween. The solar thermal collector will still be effective irregardless of whether the upper wall of the body and the optically transmissive panel form an air gap or a vacuum therebetween. The upper wall may comprise a series of integrally formed vertically extending ribs or projections that support the optically
20 transmissive panel. At least a portion of the upper surface of the optically transmissive panel may be abraded to reduce reflectivity thereof.

Heat Exchange Medium

[0034] The heat exchange medium will typically be a liquid. The heat exchange medium may be selected from water, glycol, oils, or a combination thereof. It may be that the heat
25 exchange medium is water. It may be that the heat exchange medium is a mixture of water and glycol.

Cavity

[0035] A plurality of flow diverter baffles or vanes may be located within the internal cavity of the solar thermal collector for directing the flow of the heat exchange medium. The plurality of
30 flow diverter baffles or vanes may direct the flow of the heat exchange medium in a direction substantially perpendicular to two of the lateral side walls of the body. It may be that the flow diverter baffles or vanes are formed from a corrugated sheet inserted within the cavity of the body, said corrugated sheet having corrugations arranged perpendicular to the two of lateral

side walls of the body. The peaks of at least some of the corrugations of the corrugated sheet may be adhered to the upper wall of the body.

End Caps

5 [0036] The solar thermal collector may further comprise one or more end caps for closing the open ends of the hollow body. One or both of the end caps may include at least one port for delivering a heat transfer liquid into or out of the cavity with the body of the collector. At least one of the end caps may be provided with one or more drain holes for preventing the accumulation of external liquid within the air gap formed between the upper wall of the body and the optically transmissive panel.

10 Thermally Insulating Material

[0037] It may be that a layer of thermally insulating material is applied to at least the lower wall of the hollow body. The layer of thermally insulating material may extend around to at least a lower portion of the lateral sides of the hollow body. The thermally insulating material may comprise polyurethane foam, mineral wool, fiberglass or another insulating material.

15 [0038] The invention may be as described in one of the following numbered paragraphs:

1. A composite comprising a polymer matrix, graphene and at least one thermally conductive inorganic filler, wherein the graphene and the at least one thermally conductive inorganic filler are dispersed within the polymer matrix.
2. A composite according to paragraph 1, wherein the wt% of graphene in the matrix is in
20 the range from 30 wt% to 70 wt%.
3. A composite according to paragraph 1 or paragraph 2, wherein the average particle size of the graphene is between 10 μm to 70 μm .
4. A composite according to any preceding paragraph, wherein the wt% of the at least one thermally conductive inorganic filler in the matrix is in the range from 10 wt% to 30 wt%.
- 25 5. A composite according to any preceding paragraph, wherein the at least one thermally conductive inorganic filler comprises a group 13 nitride.
6. A composite according to paragraph 5, wherein the group 13 nitride comprises aluminium nitride (AlN).
7. A composite according to paragraph 6, wherein the average particle size of the AlN is
30 from 0.1 μm to 5 μm .
8. A composite according to any preceding paragraph, wherein the polymer matrix comprises a polyamide.

9. A composite according to paragraph 8, wherein the polymer matrix comprises a polyphthalamide.

10. A solar thermal collector comprising the composite of any preceding paragraph.

11. A solar thermal collector according to paragraph 10 comprising a hollow body having a lower wall, an upper wall and lateral side walls and an internal cavity within said hollow body for receiving a heat exchange medium, wherein at least a portion of the upper wall is formed from the composite.

Brief Description of the Drawings

[0039] Embodiments of the invention are further described hereinafter with reference to the accompanying drawings, in which:

Figure 1 is an exemplary solar thermal collector with a hollow body having a lower wall (1), an upper wall (2) and lateral side walls (3) and an internal cavity (4) within said hollow body for receiving a heat exchange medium. The solar thermal collector also has flow diverters (baffles) (7). At least a portion of the upper wall is formed from a composite of the present invention.

Figure 2 is an exemplary solar thermal collector containing all the features described in Figure 1 and further containing an optically transmissive panel (5) located above the upper wall (2) of the hollow body, the upper wall of the body and the optically transmissive panel forming an air gap (6) therebetween. The solar thermal collector also has a layer of thermally insulating material (10) applied to the lower wall of the hollow body.

Figure 3 is an exemplary solar thermal collector containing all the features described in Figure 1 and further containing end caps (8) for closing the open ends of the hollow body. The end caps include a port (9) for delivering a heat transfer liquid into or out of the cavity with the body of the collector.

Detailed Description

[0040] Graphene is the name given to a flat sheet, e.g. a flat monolayer, of sp²-hybridised carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. Typically, graphene consists of 10 layers or less stacked on top of each other.

[0041] The “average particle size” may be the median particle size (or median particle diameter), i.e. the particle size of which approximately 50% of the particles are smaller in size than and approximately 50% of the particles are larger in size than, commonly referred to as the D₅₀. For example, graphene having a D₅₀ of 50 μm means that approximately 50% of the graphene particles are smaller in size than 50 μm (and approximately 50% of the graphene

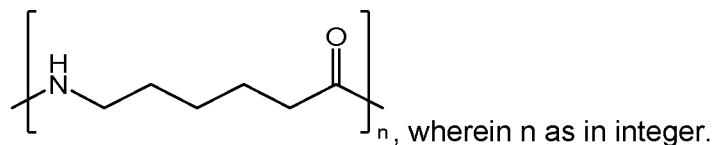
particles are larger in size than 50 μm). The term “average particle size” used herein may therefore be the D_{50} .

[0042] D_{50} may be measured by methods well known in the art. A common method is particle size screening by laser diffraction (this technique is an international standard recognised by the ISO; ISO 13320:2020). Laser diffraction provides a particle size of which approximately 50% by volume of the particles are smaller in size than (since this technique assumes a spherical particle shape in its optical mode). This may be referred to as the D_{V50} .

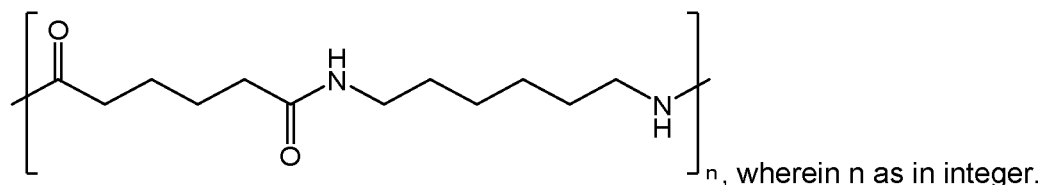
[0043] The term “aromatic polymer” is intended to cover any polymer comprising a repeating unit that comprises an aromatic ring system (i.e. a ring system containing $2(2n + 1)\pi$ electrons). Typically, aromatic polymers comprise a repeating unit that comprises a phenyl ring. Examples of aromatic polymers include polyphthalamide (PPA), polyphenylene sulfide (PPS), polyphenyl ether (PPE) and poly(*p*-phenylene oxide) (PPO).

[0044] For the absence of doubt, the term “polyamide” and “nylon” are interchangeable in this specification.

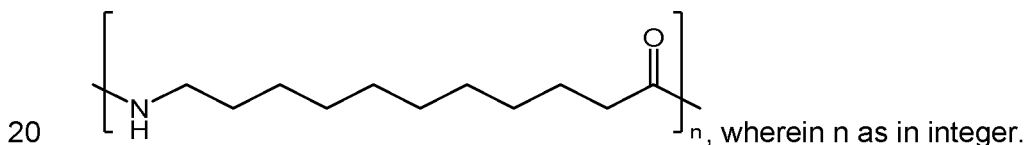
[0045] For the absence of doubt, “nylon 6” has the following structure:



[0046] For the absence of doubt, “nylon 66” has the following structure:



[0047] For the absence of doubt, “nylon 11” has the following structure:



[0048]

[0049] The term “alkylene” refers to a bivalent linear or branched saturated hydrocarbon chain. For example, “ $\text{C}_2\text{-C}_6$ -alkylene” may refer to methylene, ethylene, *n*-propylene, *iso*-propylene, *n*-butylene, *sec*-butylene, *tert*-butylene, *n*-pentylene or *n*-hexylene.

[0050] The term “inorganic filler” is intended to refer to any chemical compound comprising two or more elements that lacks carbon-carbon bonds or carbon–hydrogen bonds. It excludes metals, e.g. pure metals and metal alloys. It may be that the inorganic filler does not comprise carbon.

5 **[0051]** Boron nitride nanosheet is a two-dimensional crystalline form of hexagonal boron nitride, which has a thickness of one to few atomic layers.

[0052] The term “heat exchange medium” is intended to cover any substance that can store heat in a reversible form and that can be circulated around a heating system.

10 **[0053]** The term “upper wall” used to define the solar thermal collector of the second aspect equates to the upwards facing wall of the collector when the solar collector is in normal use, i.e. the wall that would face in the direction of the sun when the the solar collector is in normal use. The “lower wall” equates to the wall opposite the upper wall, i.e. the wall that would face in the opposite direction to the sun when the solar collector is in normal use. The same logic applies to the “upper surface” of the optically transmissive panel, i.e., the surface that would
15 face in the direction of the sun when the the solar collector is in normal use.

[0054] The upper wall may comprise a series of integrally formed vertically extending ribs or projections that support the optically transmissive panel. The term “vertically” used in this context is intended to mean substantially perpendicular to the upper surface of the upper wall, the upper surface of the upper wall being the surface of the upper wall that would face in the
20 direction of the sun when the the solar collector is in normal use.

[0055] For the absence of doubt, unless stated otherwise, wt% is the weight % of the specified component relative to the total weight of the composite.

25 **[0056]** The composites of the present invention may be used in a heat exchanger. Heat exchangers are used to transfer heat from one medium to another. The media may be a gas, liquid, or a combination of both. Heat exchangers can improve the energy efficiency of certain systems by redistributing (transferring) heat from an area where it is not needed to an area of the system where it can be usefully used.

30 **[0057]** Heat exchangers have a number of applications, such as in battery packaging and powertrains, under the hood electronics, automotive lighting, home heat recovery in heating, ventilation, and air conditioning (HVAC), industrial heat recovery, applications using sea water or greywater, general electrical and electronics, e.g. thermal management of motherboards and chips, in healthcare and in aerospace. The heat exchanger may be a heat sink.

[0058] Throughout the description and claims of this specification, the words “comprise” and “contain” and variations of them mean “including but not limited to”, and they are not intended to (and do not) exclude other moieties, additives, components, integers or steps. Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

[0059] Features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

[0060] The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

Examples

The composites of the present invention can be manufactured according to the following procedure.

Preparation of Composites: Compounding

- Prior to manufacture, the polymer, graphene, the thermally conductive inorganic filler and any additives are dried in a desiccant or oven dryer at 100 °C for upwards of 8 hours, e.g. for 24 hours.
- The polymer is then ground to a powder on a micron level via a freezer mill using liquid nitrogen for ~20 minutes.
- The polymer and fillers (graphene, thermally conductive inorganic filler and any additives) are then dried again for 24 hours.

- The polymer and fillers are dry mixed at ~2000rpm for 5 minutes.
 - Within less than a day after drying, the dry mixture is directly fed into a co-rotating twin screw extruder for compounding the material, with temperatures in the range of 300 – 340 °C.
- 5
- The extrude is cooled by passing it through a water bath as per typical industrial methods known in the art associated with the base polymer.
 - The extrude is then pelletised as per typical procedures known in the art, collected and stored.
 - Prior to any further use, samples are dried again.
- 10
- Composites can then be moulded by compression moulding, extrusion moulding or injection moulding. A method of compression moulding is described below.

It is critical that during compounding moisture levels within the polymer are kept to a minimum (ideally <0.1%). This may be done, e.g. by drying in a desiccant oven and drying samples again before moulding.

15 Preparation of Composites: Compression Moulding

- The compression moulding machine is pre-heated to within 300-340 °C.
 - The composite pellets are placed into a 50mm diameter disc shaped compression mould, enabling a finished sample thickness of just under 2.5mm. Pre-heating takes several minutes.
- 20
- The plattens are closed to approximately 1 Bar pressure maintained for approximately 10 minutes to facilitate polymer melting.
 - Following this, 100 bar pressure is applied for approximately 25 minutes to enable full consolidation.
 - Cooling of the plattens takes place at 20 °C per minute to 50 °C prior to sample
- 25
- removal.
 - Sample conditioning then takes place based on the subsequent relevant test procedure.

It will be evident to those skilled in the art that certain parameters, e.g. the temperature of the twin screw extruder, will be determined by the specific polymer used.

30 Measuring Thermal Conductivity

The thermal conductivity of the composites obtained by the procedures outlined above can be measured according to the to the ASTM E1530 method; a standard test method for evaluating the resistance to thermal transmission by the guarded heat flow meter technique. This method is commonly used in the art to measure thermal conductivity.

5 Thermal Conductivity Data

Certain composites according to the present invention were manufactured according to the above-mentioned method. The thermal conductivity of these composites was then measured according to the above-mentioned method. The results can be seen in the table below.

Composite	Polymer	Weight % of filler material relative to the total weight of the composite					Total	Thermal conductivity (W/m.K)
		GNP P20	AIN	BNNS	CF	SGL EG		
1	PPA	25	25				50	1.41
2	PPA	25		25			50	1.90
3	PPA	25	15	10			50	1.50
4	PPA	25	15		10		50	1.00
5	PPA	25		15	10		50	1.39
6	PPA	50	20				70	18.80
7	PPA		10			30	40	4.32

- 10 In all tested composites, the polyphthalamide polymer used was the base resin DuPont™ Zytel® HTN FE8200.

Details of the filler materials used in each composite can be seen in the table below.

Abbreviation	Filler	Manufacturer	Particle size	Diameter	Length
GNP P20	Graphene nano platelet	First Graphene	20 µm	-	-
AIN	Aluminium nitride powder	Goodfellow	1.4 µm	-	-
BNNS	Boron nitride nanosheet		<1 µm	-	-
CF	Carbon fibre		-	13 µm	700 µm
SGL EG	Expanded graphite	SGL Carbon	200 µm	-	-

Claims

1. A composite comprising a polymer matrix, graphene and at least one thermally conductive inorganic filler, wherein the graphene and the at least one thermally conductive inorganic filler are dispersed within the polymer matrix.
- 5 2. A composite according to claim 1, wherein the wt% of graphene in the matrix is in the range from 30 wt% to 70 wt%.
3. A composite according to claim 1 or claim 2, wherein the average particle size of the graphene is between 10 μm to 70 μm .
4. A composite according to any preceding claim, wherein the wt% of the at least one
10 thermally conductive inorganic filler in the matrix is in the range from 10 wt% to 30 wt%.
5. A composite according to any preceding claim, wherein the wt% of the graphene in the polymer matrix is greater than the wt% of the at least one thermally conductive inorganic filler in the matrix.
6. A composite according to any preceding claim, wherein the at least one thermally
15 conductive inorganic filler comprises a group 13 nitride.
7. A composite according to claim 6, wherein the group 13 nitride comprises aluminium nitride (AlN).
8. A composite according to claim 7, wherein the average particle size of the AlN is from 0.1 μm to 5 μm .
- 20 9. A composite according to any preceding claim, wherein the polymer matrix comprises a polyamide.
10. A composite according to claim 9, wherein the polymer matrix comprises a polyphthalamide (PPA).
11. The composite according to any one of claims 1 to 8, wherein the polymer matrix
25 comprises an aromatic polymer.
12. The composite according to any one of claims 1 to 8, wherein the polymer matrix comprises either polyphenylene sulfide (PPS) or an amorphous blend of a polyphenyl ether (PPE) and polystyrene.
13. A solar thermal collector comprising the composite of any preceding claim.
- 30 14. A solar thermal collector according to claim 13 comprising a hollow body having a lower wall, an upper wall and lateral side walls and an internal cavity within said hollow body for

receiving a heat exchange medium, wherein at least a portion of the upper wall is formed from the composite.

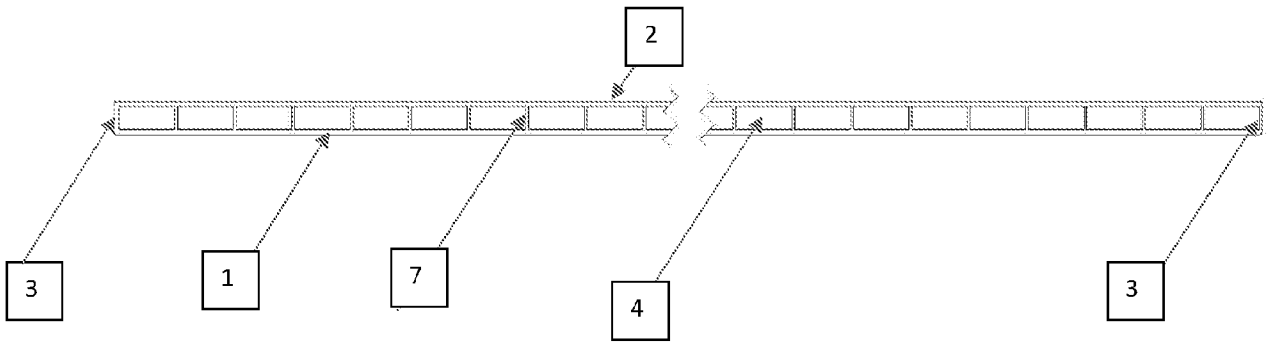


Figure 1

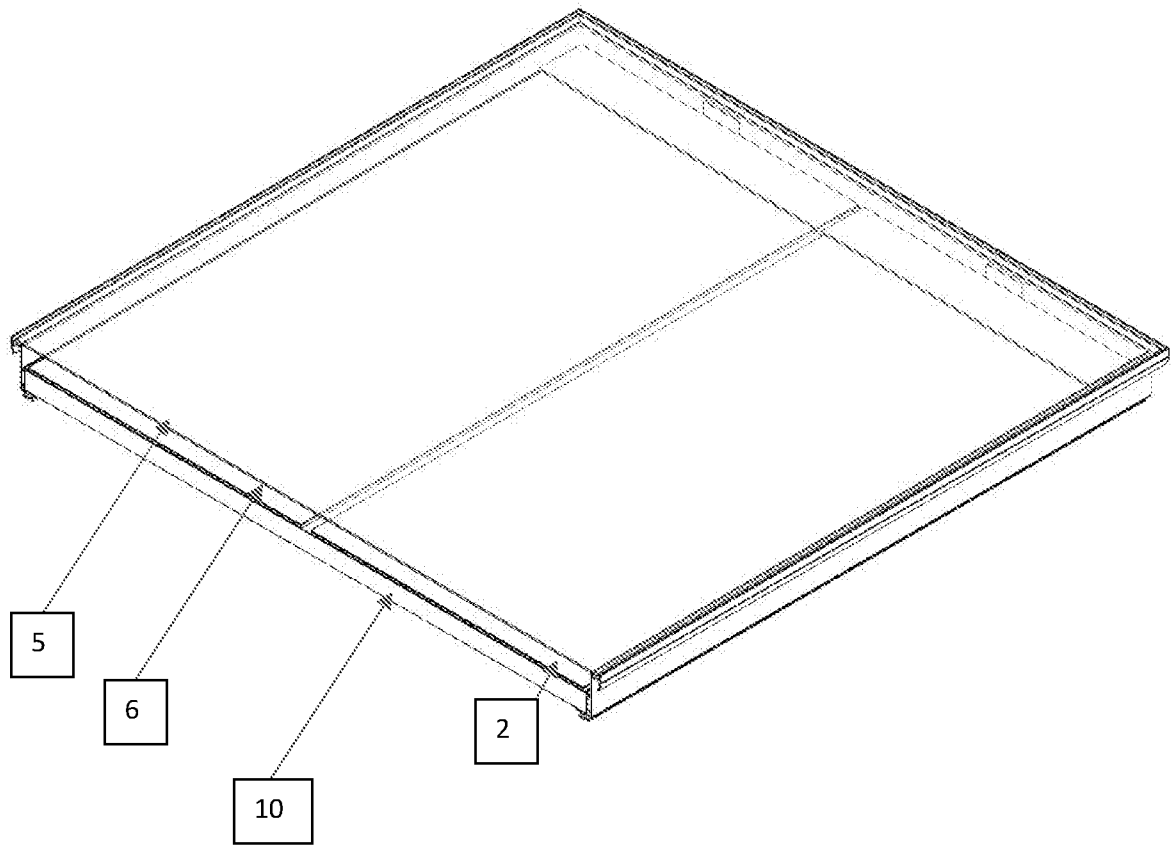


Figure 2

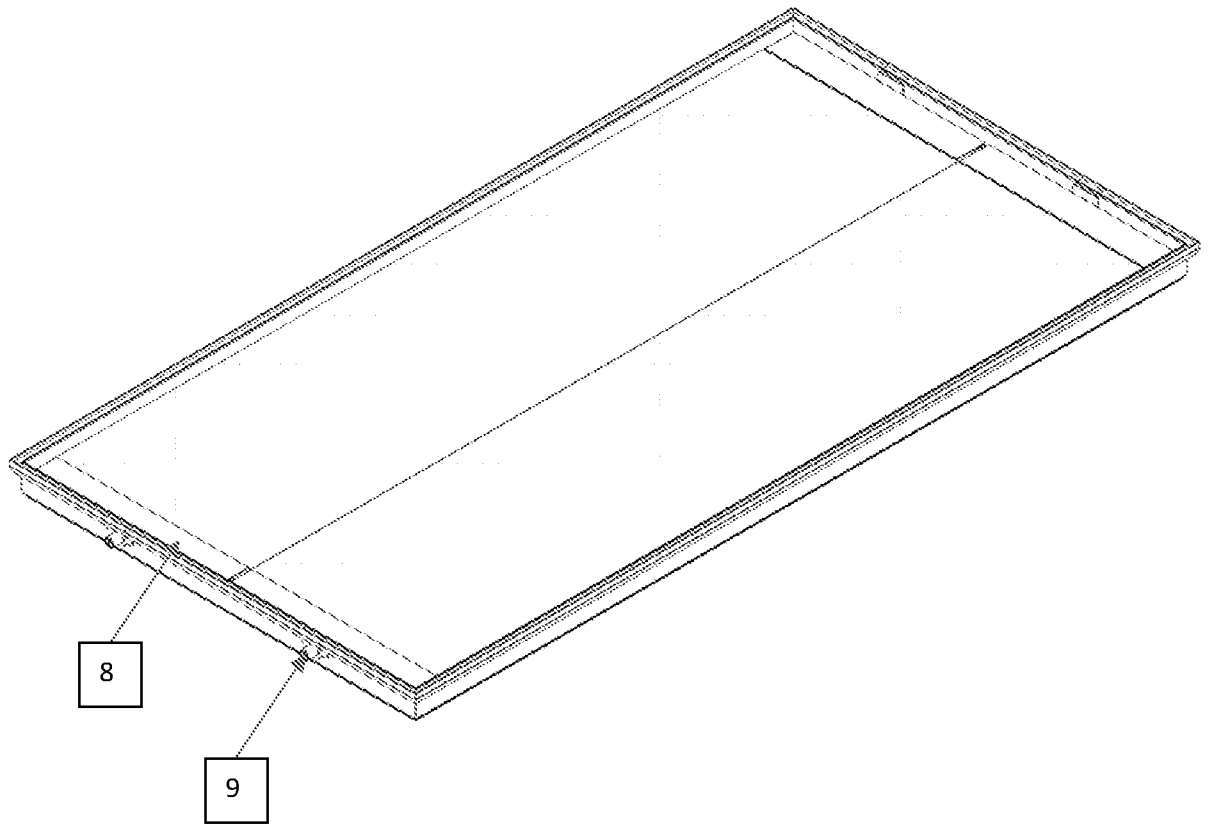


Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2022/052926

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/04 C08K3/28 C08K3/38
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)
C08K

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 109 206 896 B (ZHEJIANG EXPO NEW MAT CO LTD) 30 March 2021 (2021-03-30)	1, 4, 6-11, 13, 14
A	paragraph [0001] examples 1-3 claims 1-5	2, 3, 5, 12
X	CN 105 238 044 A (BENGBU GAOHUA RESOLUTION TECHNOLOGY CO LTD) 13 January 2016 (2016-01-13)	1, 4, 6, 7, 11-14
A	paragraph [0001] example 1 claims 1-2	2, 3, 5, 8-10
	----- -/--	

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 7 February 2023	Date of mailing of the international search report 14/02/2023
---	---

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 Neumeier, Michael
--	--

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2022/052926

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	CN 113 604 036 A (UNIV EAST CHINA SCIENCE & TECH ET AL.) 5 November 2021 (2021-11-05) paragraph [0001] examples 7, 9 claims 1-7	1, 3, 4, 6, 7, 9, 13, 14 2, 5, 8, 10-12
X A	----- CN 111 378 226 A (TAIXI NEW MATERIAL TECH ZHEJIANG CO LTD) 7 July 2020 (2020-07-07) paragraphs [0001], [0039], [0105] example 2 claims 1-10	1, 4-7, 13, 14 2, 3, 8-12
X A	----- CN 110 669 317 A (UNIV FUJIAN) 10 January 2020 (2020-01-10) paragraph [0001] example 2 claims 1-7	1, 2, 4-7, 11, 13, 14 3, 8-10
X A	----- CN 109 280 387 A (XINAO GRAPHENE TECH CO LTD) 29 January 2019 (2019-01-29) paragraphs [0001], [0004] example 2 claims 1-10	1, 6, 7, 11-14 2-5, 8-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2022/052926

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 109206896	B	30-03-2021	NONE
CN 105238044	A	13-01-2016	NONE
CN 113604036	A	05-11-2021	NONE
CN 111378226	A	07-07-2020	NONE
CN 110669317	A	10-01-2020	NONE
CN 109280387	A	29-01-2019	NONE