GRAPHENE BASED THERMAL MANAGEMENT DEVICES

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Appl. No.: 14/433,320
PCT Filed: Oct. 3, 2013
PCT No.: PCT/US13/63333
§ 371 (c)(1), (2) Date: Apr. 2, 2015

Related U.S. Application Data

Publication Classification
Int. Cl.
F28F 21/02 (2006.01)
U.S. Cl.
CPC .................................................................... F28F 21/02 (2013.01)

ABSTRACT
Thermal management devices comprising compositions comprising graphene sheets and compositions comprising graphene sheets and at least one thermally conductive, non-electrically conductive compound. The thermal management devices of the present invention comprise compositions comprising graphene sheets, and other components such as electrically conductive materials. By thermal management device is meant a device or component of a device that is designed or used to generate, spread, disperse, otherwise handle or manage the flow of heat. Examples include heaters, heating elements, heat sinks, thermal diffusion devices, heat spreaders, coolers, thermally conductive adhesives, thermally conductive gaskets and seals. The thermal management devices can be flexible and made to conform to surfaces. They can be crease resistant and thin. They can be used in items such as apparel, bags, gear, etc.
GRAPHENE BASED THERMAL MANAGEMENT DEVICES

REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. Provisional Applications 61/709,117, filed on Oct. 2, 2012 and 61/709,122, filed on Oct. 2, 2012, the entire contents of which are hereby incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to thermal management devices comprising graphene sheets.

SUMMARY OF THE INVENTION

The graphene sheets composition may further comprise one or more additional components. Examples of other materials include polymers, other thermally and/or electrically conductive materials, etc. The composition can be a polymer composite, a coating or ink, or the like.

Thermal management devices can be formed from the compositions using any suitable method. For example, they may be molded, extruded, or the like or applied in the form of a coating. The compositions can be overmolded or coated onto a heat source, heating element, cooling element, etc. A heat or cooling source or element can be partially or fully embedded into the compositions.

The devices can be formed by creating an electrically conductive heating or cooling element from a metallic (such as silver, copper, aluminum, steel, etc.) or non-metallic material and overcoating or overmolding the heating or cooling element with a form of the graphene sheets composition that is more electrically resistive than the heating or cooling element. Alternatively, the graphene sheets composition can be coated, molded, etc. over the more electrically conductive material. The composition can act as a heat spreader. The heating or cooling element can also be formed from a graphene sheet composition. The heating or cooling element can be a wire or filament, a trace, a printed trace, a metalized or plated surface, a metallic adhesive, etched, etc. The heating or cooling elements can be connected to a voltage source and act as bus bars.

Fig. 3 shows heating or cooling elements 30 printed on a surface 32 and overcoated with graphene sheets composition 34. Overcoating 34 can heat up as a current is applied to the heating elements and can serve as a heat spreader or diffuser.

The more electrically conductive materials can be made of any suitable electrically conductive material. They can be metals or metal alloys (e.g. copper, aluminum, silver, gold, etc.), organic, polymeric, and/or carbon-based conductors, coatings or inks, etc. Conductive material can be in any suitable form, including strips, sheets, foils, tapes, wires, tapes, threads, etc. Conductive materials can be deposited, such as by sputtering, plating, etching, molding, printing, coating, metallization, vapor deposition, adhering, gluing, taping, or other deposition techniques.

Fig. 5 shows a heater 50 comprising a surface 52 that is coated with graphene sheets composition 54. The graphene sheets composition is overcoated with heating elements/bus bars 56, which are connected to a voltage source 58, and heating element 60, which is not connected to a voltage source.

Fig. 6 shows a heater 70 comprising a surface 72 that is coated with graphene sheets composition 74. The graphene sheets composition is overcoated with heating elements/bus bars 76, which are connected to a voltage source 78, and heating element 80, which is not connected to a voltage source.

In some embodiments, the graphene sheets composition is applied to a substrate and overcoated with an ink or coating (e.g. silver, copper, etc. ink) to form a heating or cooling element. Alternatively, a heating or cooling element can be formed on a substrate from an ink or coating (e.g. silver, copper, etc. ink) and then overcoated with the graphene sheets composition. In some cases, some parts of the substrate may be coated with the graphene sheets composition and overcoated with the element, while other parts of the substrate are coated with the element and overcoated with the graphene
sheets composition. The resulting article can be laminated with other materials and substrates and formed into a heating/cooling device. The other materials and substrates can be laminated on top of the coated surface (e.g. elements and graphene sheets composition) or the device can be overcoated to create a sandwich structure. Substrates can include fabrics, textiles, films, sheets, and other flexible substrates. In some cases, the laminated article can be thermally sealed.

[0021] The thermal management devices can be heat sinks, thermally conductive adhesives, thermal traces, heaters, coolers, passive solar heaters (such as hot water heaters), thermostats, thermally conductive channels, etc. Heaters and coolers can be used for portable heaters and coolers (such as those run off batteries), components of buildings, heaters and coolers for tents, heaters and coolers for clothing (such as underwear), buildings and building components (such as windows, doors, floors, etc.), pipes (such as outdoor water pipes), medical devices, heating pads, heating patches, heaters and window defrosters for vehicles (such as cars, trucks, motorcycles, forklifts, airplanes, farm equipment), packaging, hot or cold food and beverage packaging, etc.

[0022] The thermal management device may be used to heat or cool some portion of the body. Heating or cooling may be desired for a variety of purposes, such as medical treatment, therapy, rehabilitation, comfort, thermal conditioning, bio-feedback, etc. The thermal management device may be applied to any part of the body or combination of parts, such as joints, muscles, extremities, head, abdomen, skin, etc.

[0023] Examples of types of thermal management devices include medical and health-related devices, portable heaters and coolers, heaters and coolers for food and beverages (such as coffee, Carbonated drinks, alcoholic drinks, etc.), chemical curing devices, etc. Examples of medical devices include heating and cooling pads, bandages (such as ace bandages), splints, braces, casts, etc.

[0024] The thermal management devices can be flexible and made to conform to surfaces. They can be crease resistant and thin. They can be used in items such as apparel, bags, gear, etc. Examples include shirts, jackets, coats, vests, shirts, pants, shorts, hats, helmets, shoes, belts, gloves and mittens, socks, underwear, sweat shirts and pants, athletic apparel and gear, hand bags, purses, backpacks, briefcases, messenger bags, computer bags, sachets, luggage, sports bags (golf bags, gym bags, etc.), tents, sleeping bags, sleeping pads and mattresses, hunting and sports equipment, ski apparel (such as ski jackets, pants, boots, etc.) chairs, cushions, upholstered objects, seats (such as car or vehicle seats), ballistic protection equipment (e.g. bullet-proof vests), scuba diving equipment, etc. They can be used as pocket warmers.

[0025] Devices (such as heaters) can be incorporated into or onto the items by any suitable method, such as by sewing, snaps, buttons, tape, adhesive, hook and loop fasteners (e.g. Velcro®), zippers, etc. They can be embedded into the object either permanently or removable. They can be placed in pockets, slits, hems, between layers of components of the objects, etc. They can be placed within the padding of bags such as backpacks, computer bags, messenger bags, etc. They can be sewn, taped, laminated, etc. into place. They can be washable in some embodiments.

[0026] FIG. 4 shows a jacket 40 having a pocket 42 into which a heater 44 comprising graphene sheets has been incorporated.

[0027] Devices can be printed onto fabrics that can be incorporated into apparel or other gear. The fabrics can be laminated with other fabric materials.

[0028] The devices can be used with alternating and direct current power sources, such as energy from an electrical grid, batteries (rechargeable and non-rechargeable), solar power, fuel cells, capacitors, solar power, etc. The power source can be a low voltage power source such as a USB port, 12 V power supplies and batteries, 24 and 42 V batteries and power supplies, cell phone batteries, 9 V batteries, AAA batteries, AA batteries, coin cells, etc. Laptop computer batteries, car batteries, etc. can be used as power sources. Power may be supplied to the device using, for example, a USB connection from a computer (such as laptop computers), from a wall plug or other source (e.g. a 12 V car battery) USB power adapter, etc.

[0029] In some cases, the devices can have anisotropic thermal and/or electrical conductivities.

[0030] In one embodiment, a metallic heating element is formed on a heat sealable substrate by any suitable method, such as printing, metal deposition, using a conductive adhesive, applying cut (such as die-cut) shapes, etc. The heating element is overcoated at least in part with a graphene sheets coating composition, where the coating composition is less thermally conductive than the heating element material. The heat sealable substrate containing the overcoated heating element can then be adhered to one or more layers of other materials, such as fabrics. It can be directly adhered to an article of apparel or other item.

[0031] Examples of electrically and/or thermally conductive additives include metals (including metal alloys), conductive metal oxides, conductive carbons, polymers, metal coated materials, inorganic compounds, ceramics, etc. These components can take a variety of forms, including particles, powders, flakes, foils, needles, etc.

[0032] Metals can be pure metals, alloys, etc. Examples of metals include, but are not limited to silver, copper, aluminum, platinum, palladium, nickel, chromium, gold, zinc, tin, iron, gold, lead, steel, stainless steel, rhodium, titanium, tungsten, magnesium, brass, bronze, colloidal metals, etc. Examples of metal oxides include antimony tin oxide and indium tin oxide and materials such as fillers coated with metal oxides. Metal and metal-oxide coated materials include, but are not limited to metal coated carbon and graphite fibers, metal coated glass fibers, metal coated glass beads, metal coated ceramic materials (such as beads), etc. These materials can be coated with a variety of metals, including nickel.

[0033] Examples of conductive polymers include, but are not limited to, polyacetylene, polyethylene dioxythiophene (PEDOT), poly(styrenesulfonate) (PSS), PEDOT: PSS copolymers, polythiophene and polythiophenes, poly(3-alklythiophenes), poly(2,5-bis(3-tetradecyliothien-2-yl)thieno[3,2-b]thiophene) (PBTDT), poly(phenylenevinylene), polypyrrene, polycarbazole, polyaniline, polypyrrole, polyaniline, polypyrrole, poly(pheonilene sulfide), polycarbazoles, polyanines, polypyrroles, copolymers of one or more of the foregoing, etc., and their derivatives and copolymers. The conductive polymers can be doped or undoped. They can be doped with boron, phosphorous, iodine, etc.

[0034] Examples of conductive carbons include, but are not limited to, graphite (including natural, Kish, and synthetic, annealed, pyrolytic, highly oriented pyrolytic, etc. graphites),
graphitized carbon, carbon black, carbon fibers and fibrils, carbon whiskers, vapor-grown carbon nanofibers, metal coated carbon fibers, carbon nanotubes (including single- and multi-walled nanotubes), fullerences, activated carbon, carbon fibers, expanded graphite, expandable graphite, graphite oxide, hollow carbon spheres, carbon foams, etc.

[0035] Thermally conductive additives can be dielectrics. Thermally conductive additives can be metal based. They can be electrically conducting, insulating or semiconducting. In some embodiments, the additives have electrical conductivities of no more than about 10^2 S/cm, or of no more than about 10^3 S/cm, or of no more than about 10^4 S/cm, or of no more than about 10^5 S/cm, or of no more than about 10^6 S/cm, or of no more than about 10^7 S/cm, or of no more than about 10^8 S/cm, or of no more than about 10^9 S/cm, or of no more than about 10^10 S/cm, or of no more than about 10^11 S/cm, or of no more than about 10^12 S/cm, or of no more than about 10^13 S/cm, or of no more than about 10^14 S/cm, or of no more than about 10^15 S/cm, or of no more than about 10^16 S/cm, or of no more than about 10^17 S/cm, or of no more than about 10^18 S/cm, or of no more than about 10^19 S/cm, or of no more than about 10^20 S/cm.

[0036] Examples of thermally conductive additives include metal oxides, nitrides, ceramics, minerals, silicates, etc. Examples include boron nitride, aluminum nitride, alumina, aluminum nitride, beryllium oxide, nickel oxide, titanium dioxide, copper(I) oxide, copper(II) oxide, iron(II) oxide, iron(III) oxide (magnetite), iron(III) oxide, iron(II) sulfide, silicon dioxide, zinc oxide, magnesium oxide (MgO), etc.

[0037] In some embodiments, additives have a thermally conductivity at 25°C of at least about 0.5 W/m-K, of at least about 0.7 W/m-K, of at least about 1 W/m-K, of at least about 3 W/m-K, or of at least about 5 W/m-K, or at least about 10 W/m-K, or at least about 20 W/m-K, or at least about 30 W/m-K.

[0038] The compositions comprising graphene sheets can comprise graphene sheets and at least one inorganic thermally conductive additive that is non-electrically conductive. The non-electrically conductive additives can be metal based. In some embodiments, they have a thermally conductivity at 25°C of at least about 0.5 W/m-K, of at least about 0.7 W/m-K, of at least about 1 W/m-K, at least about 3 W/m-K, at least about 5 W/m-K, at least about 10 W/m-K, at least about 20 W/m-K, or at least about 30 W/m-K.

[0039] The non-electrically conductive additive can be electrically insulating or semiconducting. In some embodiments, the additives have electrical conductivities of no more than about 10^3 S/cm, or of no more than about 10^4 S/cm, or of no more than about 10^5 S/cm, or of no more than about 10^6 S/cm, or of no more than about 10^7 S/cm, or of no more than about 10^8 S/cm, or of no more than about 10^9 S/cm, or of no more than about 10^10 S/cm, or of no more than about 10^11 S/cm, or of no more than about 10^12 S/cm, or of no more than about 10^13 S/cm, or of no more than about 10^14 S/cm, or of no more than about 10^15 S/cm, or of no more than about 10^16 S/cm, or of no more than about 10^17 S/cm, or of no more than about 10^18 S/cm, or of no more than about 10^19 S/cm, or of no more than about 10^20 S/cm.

[0040] Examples of non-electrically conductive additives include Examples of thermally conductive additives include metal oxides, nitrides, ceramics, minerals, silicates, etc. Examples include boron nitride, aluminum nitride, alumina, aluminum nitride, beryllium oxide, nickel oxide, titanium dioxide, copper(I) oxide, copper(II) oxide, iron(II) oxide, iron(III) oxide (magnetite), iron(III) oxide, iron(II) sulfide, silicon dioxide, zinc oxide, magnesium oxide (MgO), etc.

[0041] The graphene sheets are graphite sheets preferably having a surface area of from about 100 to about 2630 m²/g. In some embodiments, the graphene sheets primarily, almost completely, or completely comprise fully exfoliated single sheets of graphite (these are approximately 1 nm thick and are often referred to as “graphene”), while in other embodiments, at least a portion of the graphene sheets can comprise partially exfoliated graphite sheets, in which two or more sheets of graphite have not been exfoliated from each other. The graphene sheets can comprise mixtures of fully and partially exfoliated graphite sheets. Graphene sheets are distinct from carbon nanotubes. Graphene sheets can have a “platy” (e.g., two-dimensional) structure and do not have the needle-like form of carbon nanotubes. The two longest dimensions of the graphene sheets can each be at least about 10 times greater, or at least about 50 times greater, or at least about 100 times greater, or at least about 1000 times greater, or at least about 5000 times greater, or at least about 10,000 times greater than the shortest dimension (i.e. thickness) of the sheets.

[0042] Graphene sheets are distinct from expanded, exfoliated, vermicular, etc. graphite, which has a layered or stacked structure in which the layers are not separated from each other. The graphene sheets do not need to be entirely made up of carbon, but can have heteroatoms incorporated into the lattice or as part of functional groups attached to the lattice. The lattice need not be a perfect hexagonal lattice and may contain defects (including five- and seven-membered rings).

[0043] Graphene sheets can be made using any suitable method. For example, they can be obtained from graphite (including natural, Kish, and synthetic, pyrolytic, highly oriented pyrolytic, etc. graphites), graphite oxide, expandable graphite, expanded graphite, etc. They may be obtained by the physical exfoliation of graphite, by for example, peeling, grinding, milling, graphene sheets. They may be made by sonication of precursors such as graphite. They may be made by opening carbon nanotubes. They may be made from inorganic precursors, such as silicon carbide. They may be made by chemical vapor deposition (such as by reacting a methane and hydrogen on a metal surface). They may be made by epitaxial growth on substrates such as silicon carbide and metal substrates and by growth from metal-carbon melts. They are made by them They may be by the reduction of an alcohol, such as ethanol, with a metal (such as an alkali metal like sodium) and the subsequent pyrolysis of the alkoxide product (such a method is reported in Nature Nanotechnology (2009), 4, 30-33). They may be made from small molecule precursors such as carbon dioxide, alcohols (such as ethanol, methanol, etc.), alkoxides (such as ethoxides, methoxides, etc., including sodium, potassium, and other alkoxides). They may be made by the exfoliation of graphite in dispersions or exfoliation of graphite oxide in dispersions and the subsequently reducing the exfoliated graphite oxide. Graphene sheets may be made by the exfoliation of expandable graphite, followed by intercalation, and ultrasonication or other means of separating the intercalated sheets (see, for example, Nature Nanotechnology (2008), 3, 538-542). They may be made by the intercalation of graphite and the subsequent exfoliation of the product in suspension, thermally, etc. Exfoliation processes may be thermal, and include exfoliation by rapid heating, using microwaves, furnaces, hot baths, etc.

[0044] Graphene sheets can be made from graphite oxide (also known as graphitic acid or graphite oxide). Graphite can be treated with oxidizing and/or intercalating agents and exfoliated. Graphite can also be treated with intercalating
agents and electrochemically oxidized and exfoliated. Graphene sheets can be formed by ultrasonically exfoliating suspensions of graphite and/or graphite oxide in a liquid (which can contain surfactants and/or intercalants). Exfoliated graphite oxide dispersions or suspensions can be subsequently reduced to graphene sheets. Graphene sheets can also be formed by mechanical treatment (such as grinding or milling) to exfoliate graphite or graphite oxide (which would subsequently be reduced to graphene sheets).

Graphene sheets may be made by the reduction of graphite oxide. Reduction of graphite oxide to graphene may be done by thermal reduction/annealing, chemical reduction, etc. and may be carried out on graphite oxide in a solid form, in a dispersion, etc. Examples of useful chemical reducing agents include, but are not limited to, hydrazines (such as hydrazine or liquid or vapor forms, N,N-dimethylhydrazine, etc.), sodium borohydride, citric acid, hydroquinone, isocyanates (such as phenyl isocyanate), hydrogen, hydrogen plasma, etc. A dispersion or suspension of exfoliated graphite oxide in a carrier (such as water, organic solvents, or a mixture of solvents) can be made using any suitable method (such as ultrasonication and/or mechanical grinding or milling) and reduced to graphene sheets. Reduction can be solvothermal reduction, in solvents such as water, ethanol, etc. This can for example be done in an autoclave at elevated temperatures (such as those above about 200°C).

Graphite oxide can be produced by any method known in the art, such as by a process that involves oxidation of graphite using one or more chemical oxidizing agents and, optionally, intercalating agents such as sulfuric acid. Examples of oxidizing agents include nitric acid, nitrates (such as sodium and potassium nitrates), per chlorates, potassium chlorate, sodium chlorate, chromic acid, potassium permanganates, sodium chromate, potassium dichromate, sodium dichromate, hydrogen peroxide, sodium and potassium permanganates, phosphoric acid (H₃PO₄), phosphorus pentoxide, bisulphites, etc. Preferred oxidants include KClO₄, HNO₃ and KClO₃, KMnO₄ and/or NaMnO₄, KMnO₄ and NaNO₃, K₂S₂O₇ and P₂O₅, KMnO₄ and KNO₃, KMnO₄ and HNO₃, and KNO₃. Preferred intercalating agents include sulfuric acid. Graphite can also be treated with intercalating agents and electrochemically oxidized. Examples of methods of making graphite oxide include those described by Staudenmaier (Ber. Dtsch. Chem. Ges., (1898), 31, 1481) and Hummers (J. Am. Chem. Soc., (1958), 80, 1539).

One example of a method for the preparation of graphene sheets is to oxidize graphite to graphite oxide, which is then thermally exfoliated to form graphene sheets (also known as thermally exfoliated graphite oxide), as described in US 2007/0092432, the disclosure of which is hereby incorporated herein by reference. The thusly formed graphene sheets can display little or no signature corresponding to graphite or graphite oxide in their X-ray diffraction pattern.

The thermal exfoliation can be carried out in a continuous, semi-continuous, batch, etc. process.

Heating can be done in a batch process or a continuous process and can be done under a variety of atmospheres, including inert and reducing atmospheres (such as nitrogen, argon, and/or hydrogen atmospheres). Heating times can range from under a few seconds or several hours or more, depending on the temperatures used and the characteristics desired in the final thermally exfoliated graphite oxide. Heating can be done in any appropriate vessel, such as a fused silica, miner, metal, carbon (such as graphite), ceramic, etc. vessel. Heating can be done using a flash lamp or with microwaves. During heating, the graphite oxide can be contained in an essentially constant location in a batch reaction vessel, or can be transported through one or more vessels during the reaction in a continuous or batch mode. Heating can be done using any suitable means, including the use of furnaces and infrared heaters.

Examples of temperatures at which the thermal exfoliation and/or reduction of graphite oxide can be carried out are at least about 150°C, at least about 200°C, at least about 300°C, at least about 400°C, at least about 450°C, at least about 500°C, at least about 600°C, at least about 700°C, at least about 750°C, at least about 800°C, at least about 850°C, at least about 900°C, at least about 950°C, at least about 1000°C, at least about 1100°C, at least about 1500°C, at least about 2000°C, and at least about 2500°C. Preferred ranges include between about 750 and about 3000°C, between about 850 and 2500°C, between about 950 and 2500°C, between about 950 and about 1500°C, between about 750 and about 3100°C, between about 850 and 2500°C, or between about 950 and about 2500°C.

The time of heating can range from less than a second to many minutes. For example, the time of heating can be less than about 0.5 seconds, less than about 1 second, less than about 5 seconds, less than about 10 seconds, less than about 20 seconds, less than about 30 seconds, or less than about 1 minute. The time of heating can be at least about 1 minute, at least about 2 minutes, at least about 5 minutes, at least about 15 minutes, at least about 30 minutes, at least about 45 minutes, at least about 60 minutes, at least about 90 minutes, at least about 120 minutes, at least about 150 minutes, at least about 240 minutes, from about 0.01 seconds to about 240 minutes, from about 0.05 seconds to about 240 minutes, from about 0.1 seconds to about 240 minutes, from about 0.25 seconds to about 240 minutes, from about 0.5 seconds to about 240 minutes, from about 1 second to about 240 minutes, from about 1 minute to about 60 minutes, from about 1 minute to about 60 minutes, from about 0.01 seconds to about 10 minutes, from about 0.01 seconds to about 10 minutes, from about 0.01 seconds to about 1 minute, from about 0.01 seconds to about 1 minute, from about 1 second to about 1 minute, no more than about 30 minutes, no more than about 30 minutes, no more than about 60 minutes, no more than about 60 minutes, no more than about 15 minutes, no more than about 10 minutes, no more than about 5 minutes, no more than about 1 minute, no more than about 30 seconds, or no more than about 1 second. During the course of heating, the temperature can vary.

Examples of the rate of heating include at least about 120°C/minute, at least about 200°C/minute, at least about 300°C/minute, at least about 400°C/minute, at least about 600°C/minute, at least about 800°C/minute, at least about 1000°C/minute, at least about 1200°C/minute, at least about 1500°C/minute, at least about 1800°C/minute, and at least about 2000°C/minute.

Graphene sheets can be annealed or reduced to graphene sheets having higher carbon to oxygen ratios by heating under reducing atmospheric conditions (e.g., in systems purged with inert gases or hydrogen). Reduction/anneal-
The heating can be done under a variety of conditions, including in an inert atmosphere (such as argon or nitrogen) or a reducing atmosphere, such as hydrogen (including hydrogen diluted in an inert gas such as argon or nitrogen), or under vacuum. The heating can be done in any appropriate vessel, such as a fused silica or a mineral or ceramic vessel or a metal vessel. The materials being heated including any starting materials and any products or intermediates can be contained in an essentially constant location in single batch reaction vessel, or can be transported through one or more vessels during the reaction in a continuous or batch reaction. Heating can be done using any suitable means, including the use of furnaces and infrared heaters.

The graphene sheets preferably have a surface area of at least about 100 m²/g, or of at least about 200 m²/g, or of at least about 300 m²/g, or of at least about 350 m²/g, or of least about 400 m²/g, or of least about 500 m²/g, or of least about 600 m²/g, or of least about 700 m²/g, or of least about 800 m²/g, or of least about 900 m²/g, or of least about 1100 m²/g. The theoretical maximum surface area can be calculated to be 2630 m²/g. The surface area includes all values and subvalues therebetween, especially including 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, 2400, 2500, and 2630 m²/g.

The graphene sheets can have number average aspect ratios of from about 100 to about 100,000, or of about 100 to about 100,000, or of about 100 to about 10,000 (where “aspect ratio” is defined as the ratio of the longest dimension of the sheet to the shortest).

Surface area can be measured using either the nitrogen adsorption/BET method at 77 K or a methylene blue (MB) dye method in liquid solution.

The dye method is carried out as follows: A known amount of graphene sheets is added to a flask. At least 1.5 g of MB are then added to the flask per gram of graphene sheets. Ethanol is added to the flask and the mixture is ultrasonicated for about fifteen minutes. The ethanol is then evaporated and a known quantity of water is added to the flask to re-dissolve the free MB. The undissolved material is allowed to settle, preferably by centrifuging the sample. The concentration of MB in solution is determined using a UV-vis spectrophotometer by measuring the absorption at λ_max = 298 nm relative to that of standard concentrations.

The difference between the amount of MB that was initially added and the amount present in solution as determined by UV-vis spectrophotometry is assumed to be the amount of MB that has been adsorbed onto the surface of the graphene sheets. The surface area of the graphene sheets are then calculated using a value of 2.54 m² of surface covered per one mg of MB adsorbed.

The graphene sheets can have a bulk density of from about 0.01 to at least about 200 kg/m³. The bulk density includes all values and subvalues therebetween, especially including 0.05, 0.1, 0.5, 1, 5, 10, 15, 20, 25, 30, 35, 50, 75, 100, 125, 150, and 175 kg/m³.

Graphene sheets can be used in a dry or powder form (with little or no solvent), as a blend/dispersion/etc. in one or more solvents.
70 percent, or from about 1 to about 60 percent, or from about 10 to about 60 percent, or from about 20 to about 60 percent, from about 30 to about 60 percent, or from about 40 to about 60 percent, or from about 50 to about 60 percent, or from about 1 to about 50 percent, or from about 10 to about 50 percent, or from about 20 to about 50 percent, from about 30 to about 50 percent, or from about 40 to about 50 percent, or from about 1 to about 40 percent, or from about 10 to about 40 percent, or from about 20 to about 40 percent, from about 30 to about 40 percent, from about 1 to about 30 percent, or from about 10 to about 30 percent, or from about 20 to about 30 percent, or from about 1 to about 20 percent, or from about 10 to about 20 percent, or from about 1 to about 10 percent, based on the total weight of graphene sheets and graphite.

[0066] The graphene sheets can comprise two or more graphene powders having different particle size distributions and/or morphologies. The graphite can also comprise two or more graphite powders having different particle size distributions and/or morphologies.

[0067] If one or more additional thermally and/or electrically conductive additives are used, they can be present in the composition in from about 1 to about 99 weight percent, or about 5 to about 95 weight percent, or about 5 to about 80 weight percent, or about 5 to about 70 weight percent, or about 5 to about 50 weight percent, or about 15 to about 99 weight percent, or about 15 to about 95 weight percent, or about 15 to about 90 weight percent, or about 15 to about 80 weight percent, or about 15 to about 70 weight percent, or about 15 to about 50 weight percent, or about 15 to about 30 weight percent, or about 30 to about 99 weight percent, or about 20 to about 98 weight percent, or about 20 to about 97 weight percent, or about 20 to about 96 weight percent, or about 20 to about 95 weight percent, or about 20 to about 94 weight percent, or about 20 to about 93 weight percent, or about 20 to about 92 weight percent, or about 20 to about 91 weight percent, based on the total weight of the conductive additive and graphene sheets or graphene sheet and graphite, if present.

[0068] They graphene sheets and other components can be combined with polymers to make composites, inks and coatings, and the like. They can be dispersed in one or more solvents with or without a polymer binder.

[0069] The compositions can be in the form of polymer composites, such as those made from thermoplastics and thermosetting polymers. The compositions can be in the form of inks and coatings. By the terms “ink” and “coating” are meant composition that are in a form that is suitable for application to a substrate as well as the material after it is applied to the substrate, while it is being applied to the substrate, and both before and after any post-application treatments (such as evaporation, cross-linking, curing, etc.). The components of the ink and coating compositions can vary during these stages. The inks and coatings can optionally further comprise at least one polymeric binder. They can be in the form of paints.

[0070] When used, the polymeric binders can be thermosets, thermoplastics, non-melt processable polymers, etc. Polymers can also comprise monomers that can be polymerized before, during, or after the application of the coating to the substrate. Polymeric binders can be crosslinked or otherwise cured after the coating has been applied to the substrate. Examples of polymers include, but are not limited to acrylic polymers, polyolefins (such as polyethylene, linear low density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene, polypropylene, and olefin copolymers), styrene/butadiene rubbers (SBR), styrene/ethylene/butadiene/styrene copolymers (SEBS), butyl rubbers, ethylene/propylene copolymers (EPR), ethylene/propylene/diene monomer copolymers (EPDM), polystyrene (including high impact polystyrene), poly(vinyl acetate), ethylene/vinyl acetate copolymers (EVA), poly(vinyl alcohol), ethylene/vinyl alcohol copolymers (EVOH), poly(vinyl butyral) (PVB), poly(vinyl formal), poly(methyl methacrylate) and other acrylate polymers and copolymers (such as methyl methacrylate polymers, methacrylate copolymers, polymers derived from one or more acrylates, methacrylates, ethyl acrylates, ethyl methacrylates, butyl acrylates, butyl methacrylates, glycidyl acrylates and methacrylates and the like), olefin and styrene copolymers, acrylonitrile/butadiene/styrene (ABS), styrene/acylonitrile polymers (SAN), styrene/maleic anhydride copolymers, isobutylene/maleic anhydride copolymers, ethylene/acrylic acid copolymers, poly(acrylonitrile), poly(vinyl acrylate) and poly(vinyl acetate) copolymers, poly(vinyl pyrrolidone) and poly(vinyl pyrrolidone) copolymers, vinyl acetate and vinyl pyrrolidone copolymers, polycarbonates (PC), polyamides, polyesters, liquid crystaline polymers (LCPs), poly(lactic acid) (PLA), poly(phenylene oxide) (PPO), PPO-polyamide alloys, polysulphones (PSU), polysulides, polyetherketones (PEK), polyetheretherketone (PEEK), polyimides, polyoxymethylene (POM) homo- and copolymers, polyetherimides, fluorinated ethylene propylene polymers (FEP), poly(vinyl fluoride), poly(vinylidene fluoride), poly(vinylidene chloride), and poly(vinyl chloride), polyurethanes (thermoplastic and thermosetting (including crosslinked polyurethanes such as those crosslinked with amines, etc.), aramides (such as Kevlar® and Nomex®, polysulides, polytetrafluoroethylene (PTFE), polyisoxazoles (including polydimethylenesiloxane, dimethylsiloxane/vinylmethyldimethylsiloxane/vinylidemethyldimethylsiloxane copolymers, vinylmethyldimethyldimethylsiloxane terminated poly(dimethyldimethyldimethyldimethylsiloxane), etc.), elastomers, epoxy polymers (including crosslinked epoxy polymers such as those crosslinked with polysiloxanes, amines, etc.), decalin polymers, polynorbornes, aldehydes, cellulose polymers (such as nitrocellulose, ethyl cellulose, ethyl hydroxyethyl cellulose, carboxymethyl cellulose, cellulose acetate, cellulose acetate propionates, and cellulose acetate butyrates), polyethers (such as poly(ethylene oxide), poly(propylene oxide), poly(propylene glycol), oxirane/propylene oxide copolymers, etc.), acrylic latex polymers, polyester acrylate oligomers and polymers, polyester diol diacrylate polymers, UV-curable resins, etc.

[0071] Examples of elastomers include, but are not limited to, polyurethanes, copolyuretheresters, rubbers (including butyl rubbers and natural rubbers), styrene/butadiene copolymers, styrene/ethylene/butadiene/styrene copolymer (SEBS), polysisoprene, ethylene-propylene copolymers (EPR), ethylene/propylene/diene monomer copolymers (EPDM), polysiloxanes, and polyethers (such as poly(ethylene oxide), poly(propylene oxide), and their copolymers).

[0072] Examples of polyamides include, but are not limited to, aliphatic polyamides (such as polyamide 4,6; polyamide 6,6; polyamide 6; polyamide 11; polyamide 12; polyamide 6,9; polyamide 6,10; polyamide 6,12; polyamide 10,10; polyamide 10,12; and polyamide 12,12), aliphatic poly-
mides, and aromatic polyamides (such as poly(m-xylylene adipamide) (polyamide MXD.6)) and polyterephthalamides such as poly(dodecamethylene terephthalamide) (polyamide 12, T), poly(decamethylene terephthalamide) (polyamide 10, T), poly(nonamethylene terephthalamide) (polyamide 9, T), the polyamide of hexamethylene terephthalamide and hexamethylene adipamide, the polyamide of hexamethylene-terephthalamide, and 2-methylpentamethylene-terephthalamide), etc. The polyamides can be copolymers and copolymerms (i.e., polyamides having at least two different repeat units) having melting points between about 120 and 255°C including aliphatic copolyamides having a melting point of about 230°C or less, aliphatic copolyamides having a melting point of about 210°C or less, aliphatic copolyamides with a melting point of about 200°C or less, or aliphatic copolyamides having a melting point of about 180°C or less, etc. Examples of these include those sold under the trade names Macromelt by Henkel and Versamid by Cognis.

[0073] Examples of acrylate polymers include those made by the polymerization of one or more acrylic acids (including acrylic acid, methacrylic acid, etc.) and their derivatives, such as esters. Examples include methyl acrylate polymers, methyl methacrylate polymers, and methacrylate copolymers. Examples include polymers derived from one or more acrylates, methacrylates, acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, glycidyl acrylate, glycidyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, hydroxyethyl acrylate, hydroxyethyl (methyl) acrylate, acrylonitrile, and the like. The polymers can comprise repeat units derived from other monomers such as olefins (e.g., ethylene, propylene, etc.), vinyl acetates, vinyl alcohols, vinyl pyrrolidones, etc. They can include partially neutralized acrylate polymers and copolymers (such as ionomer resins).

[0074] Examples of polymers include Elvacite® polymers supplied by Lucite International, Inc., including Elvacite® 2009, 2010, 2013, 2014, 2016, 2028, 2042, 2045, 2046, 2550, 2552, 2614, 2669, 2697, 2776, 2823, 2895, 2927, 3001, 3003, 3004, 4018, 4021, 4026, 4028, 4044, 4059, 4400, 4075, 4060, 4102, etc. Other polymer families include Bynel® polymers (such as Bynel® 2222 supplied by DuPont) and Joncryl® polymers (such as Joncryl® 678 and 682).

[0075] Examples of polyesters include, but are not limited to, poly(butylene terephthalate) (PBT), poly(ethylene terephthalamide) (PET), poly(1,3-propylene terephthalamide) (PPT), poly(ethylene naphthalate) (PEN), poly(cyclohexanedimethanol terephthalamide) (PCT), etc.

[0076] In some embodiments, the polymer has a acid number of at least about 5, or at least about 10, or at least about 15, or at least about 20.

[0077] In some embodiments, the glass transition temperature of at least one polymer is no greater than about 100°C, 90°C, or no greater than about 80°C, or no greater than about 70°C, or no greater than about 60°C, or no greater than about 50°C, or no greater than about 40°C.

[0078] Examples of solvents into which the graphene sheets and, optionally, other components can be dispersed include water, distilled or synthetic isoparaffinic hydrocarbons (such as Ispar® and Norpar® (both manufactured by Exxon) and Dowanol® (manufactured by Dow)), citrus terpenes and mixtures containing citrus terpenes (such as Purogen, Electron, and Posiron (all manufactured by Exolink)), terpenes and terpene alcohols (including terpineols, including alpha-terpineol), limonene, aliphatic petroleum distillates, alcohols (such as methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, sec-butanol, tert-butanol, pentanols, i-amyl alcohol, hexanols, heptanols, octanols, decanols, diacetone alcohol, butyl glycol, etc.), ketones (such as acetone, methyl ethyl ketone, cyclohexanone, i-butyl ketone, 2,6,8-trimethyl-4-nonanone etc.), esters (such as methyl acetate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, tert-butyl acetate, carbaryl acetate, etc.), glycol ethers, ester and alcohols (such as 2-(2-ethoxyethoxy)ethanol, propylene glycol monomethyl ether and other propylene glycol ethers; ethylene glycol monobutyl ether, 2-methoxyethyl ether (diglyme), propylene glycol methyl ether (PGME); and other ethylene glycol ethers; ethylene and propylene glycol ether acetates, diethylene glycol monoethyl ether acetate, 1-methoxy-2-propanol acetate (PGMEA); and hexylene glycol (such as Hexasol™ supplied by Special-Chem), dibasic esters (such as dimethyl succinate, dimethyl glutarate, dimethyl adipate), dimethyl sulfoxide (DMSO), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), imides, amides (such as dimethylformamide (DMF), dimethylacetamide, etc.), cyclic amides (such as N-methylpyrrolidone and 2-pyrrolidone), lactones (such as beta-propiolactone, gamma-valerolactone, delta-valerolactone, gamma-butyrolactone, epsilon-caprolactone), cyclic imides (such as imidazolidinones such as N,N'-dimethylimidazolidinone (1,3-dimethyl-2-imidazolidinone)) (DMI), aromatic solvents and aromatic solvent mixtures (such as toluene, xylene, mesitylene, cumene, etc.), petroleum distillates, naphthas (such as VM&P naphtha), and mixtures of two or more of the foregoing and mixtures of one or more of the foregoing with other carriers. Solvents can be low- or non-VOC solvents, non-hazardous air pollution solvents, and nonhalogenated solvents.

[0079] The compositions can contain additives such as dispersion aids (including surfactants, emulsifiers, and wetting aids), adhesion promoters, thickening agents (including clays), defoamers and anti-foamers, biocides, additional fillers, floe enhancers, stabilizers, crosslinking and curing agents, conductive additives, etc.

[0080] Examples of dispersing aids include glycol ethers (such as poly(ethylene oxide)), block copolymers derived from ethylene oxide and propylene oxide (such as those sold under the trade name Pluronic® by BASF), acetylenic diols (such as 2,5,8,11-tetramethyl-6-dodecyn-5,8-diol ethoxylate and others sold by Air Products under the trade names Surfynol® and Dynol®), salts of carboxylic acids (including alkali metal and ammonium salts), and polysiloxanes.

[0081] Examples of grinding aids include stearates (such as Al, Ca, Mg, and Zn stearates) and acetylenic diols (such as those sold by Air Products under the trade names Surfynol® and Dynol®).

[0082] Examples of adhesion promoters include titanium chlorides and other titanium compounds such as titanium phosphate complexes (including butyl titanium phosphate), titinate esters, diisopropoxy titanium bis(ethyl-3-oxobutanoate, isopropoxy titanium acetylaconate, and others sold by Johnson-Matthey Catalysts under the trade name Vertec.

[0083] The compositions can optionally comprise at least one "multi-chain lipid", by which term is meant a naturally-occurring or synthetic lipid having a polar head group and at least two nonpolar tail groups connected thereto. Examples of polar head groups include oxygen-, sulfur-, and halogen-containing, phosphates, amidines, ammonium groups, amino
acids (including α-amino acids), saccharides, polysaccharides, esters (including glyceryl esters), zwitterionic groups, etc.

[0084] The tail groups can be the same or different. Examples of tail groups include alkanes, alkenes, alkynes, aromatic compounds, etc. They can be hydrocarbons, functionalized hydrocarbons, etc. The tail groups can be saturated or unsaturated. They can be linear or branched. The tail groups can be derived from fatty acids, such as oleic acid, palmitic acid, stearic acid, arachidic acid, erucic acid, arachidonic acid, linoleic acid, limononic acid, oleic acid, etc.

[0085] Examples of multi-chain lipids include, but are not limited to, lecithin and other phospholipids (such as phosphatidylcholine, phosphoglycerides (including phosphatidylserine, phosphatidylinositol, phosphatidylethanolamine (cephalin), and phosphatidylglycerol) and sphingomyelins); glycolipids (such as glucosyl-cerebroside); saccharolipids; sphingolipids (such as cerebrosides, di- and triglycerides, phosphatidylglycerol, and glycosphingolipids); etc. They can be amphoteric, including zwitterionic.

[0086] Examples of thickening agents include glycol ethers (such as polyethylene oxide), block copolymer derived from ethylene oxide and propylene oxide (such as those sold under the trade name Pluronic® by BASF), long-chain carboxylate salts (such as calcium carbonate, zinc, etc. salts of stearates, oleates, palmitates, etc.), alimentary inorganic compounds (such as those sold under the trade name Antinal® by Unimicron Specialty Minerals and Aerosil®, 9200 by Evonik Degussa), fumed silica, natural and synthetic zeolites, etc.

[0087] Examples of crosslinking agents include radical initiators such as radical polymerization initiators, radical sources, etc., including organic and inorganic compounds. Coagents and crosslinking promoters may be used as well. Examples include organic and inorganic peroxides (such as hydrogen peroxide, dialkyl peroxides, hydroperoxides, peracids, diacetyl peroxides, perylene esters, ketone peroxides, hydrocarbon peroxides, organometallic peroxides, organic polyoxides, organic polyoxides, dialkyl trioxides, hydrotrioxide, tetroxides, alkali metal peroxides (such as lithium peroxide), etc.), azo compounds, polyphenyldiacarbons, substituted hydrazines, alkoxyamines, nitrocompounds, nitrates, nitrites, nitroso compounds, polysulfides, persulfates (e.g., potassium persulfate, etc.), etc.

[0088] Examples of peroxides include, but are not limited to dibenzoyl peroxide, diethyl peroxide, acetone peroxide, methyl ethyl ketone peroxide, t-butyl peroxide, t-butyl peracetate, di-t-butyl peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, 1,3-bis(tert-butylperoxy-1-propyl) benzene, bis-(tert-butylperoxy) valerate, bis-(2,4-dichlorobenzoyl peroxide), etc.

[0089] Examples of azo compounds include azobisisobutanoylimine (AIBN); 1'-azobis(cyclohexanonecarbodimide) (ABCN); 2,2'-azo-bis(2-methylbutyronitrile); 2,2'-azo-bis(2-methylpropionitrile); 2,2'-azo-bis(2-methylpropionitrile); N-tert-butyl-N-(2-methyl-1-phenylpropyl)-O-(1-phenylethyl) hydroxylamine, etc.

[0090] In one embodiment, graphene sheets are used without a binder or with minimal amounts of a binder when used with a crosslinking agent.

[0091] The compositions can be made using any suitable method, including wet or dry methods and batch, semi-continuous, and continuous methods. They can be made using melt-processing methods (using, for example, a single or twin-screw extruder, a blender, a kneader, a Banbury mixer, etc.) and solution/dispersing blending. Dispersions, suspensions, solutions, etc. of graphene sheets and thermally conductive additives (including inks and coatings formulations) can be made or mechanically processed (e.g., milled/ground, blended, dispersed, suspended, etc.) by using suitable mixing, dispersing, stirring, and/or compounding techniques.

[0092] Components of the compositions, such as one or more of the graphene sheets, conductive additives (if used), graphite (if used), binders, carriers, and/or other components can be processed (e.g., milled/ground, blended, etc. by using suitable mixing, dispersing, and/or compounding techniques and apparatus, including ultrasonic devices, high-shear mixers, ball mills, attrition equipment, sandmills, two-roll mills, three-roll mills, cryogenic grinding crushers, extruders, kneaders, double planetary mixers, triple planetary mixers, high pressure homogenizers, horizontal and vertical wet grinding mills, etc.) Processing (including grinding) technologies can be wet or dry and can be continuous or discontinuous. Suitable materials for use as grinding media include metals, carbon steel, stainless steel, ceramics, stabilized ceramic media (such as cerium yttrium stabilized zirconium oxide), PTFE, glass, tungsten carbide, etc. Methods such as these can be used to change the particle size and/or morphology of the graphene, graphene sheets, thermally conductive additives, other components, and blends of two or more components.

[0093] Components can be processed together or separately and can go through multiple processing (including mixing/blending) stages, each involving one or more components (including blends).

[0094] There is no particular limitation to the way in which the graphene sheets, graphite (if used), additives (if used), and other components are processed and combined. For example, graphene sheets and/or graphite can be processed into given particle size distributions and/or morphologies separately and then combined for further processing with or without the presence of additional components. Unprocessed graphene sheets and/or graphite can be combined with processed graphene sheets and/or graphite and further processed with or without the presence of additional components. Processed and/or unprocessed graphene sheets and/or processed and/or unprocessed graphite can be combined with other components, such as one or more binders and then combined with and/or unprocessed graphene sheets and/or processed and/or unprocessed graphite. Two or more combinations of processed and/or unprocessed graphene sheets and/or processed and/or unprocessed graphite that have been combined with other components can be further combined or processed.

[0095] Graphene sheets and/or graphite can be processed (e.g., milled or ground) in the presence of the metal particles, or the graphene and/or graphite (if present) can be processed separately from some or all of the thermally conductive additives, and the components later blended. The graphene sheets and/or graphite and/or thermally conductive additives can be separately processed in the presence of binders and then later combined.

[0096] In one embodiment, if a multi-chain lipid is used, it can be added to graphene sheets (and/or graphite if present) before processing.

[0097] After blending and/or grinding steps, additional components can be added to the compositions, including, but
not limited to, thickeners, viscosity modifiers, binders, etc. The compositions can also be diluted by the addition of more carrier.

[0098] Inks and coatings can be formed by blending the graphene sheets with at least one solvent and/or binder and, optionally, other additives. Blending can be done using one or more of the preceding methods.

[0099] The compositions can be formed by polymerizing monomers in the presence of graphene sheets and, optionally, other additives.

[0100] Polymer composite compositions can be made using any suitable melt-mixing method, such as using a single or twin-screw extruder, a blender, a kneader, or a Banbury mixer. In one embodiment of the invention, the compositions are melt-mixed blends wherein the non-polymeric ingredients are well-dispersed in the polymer matrix, such that the blend forms a unified whole.

[0101] Polymer composite compositions may be formed into thermal management devices using any suitable technique, including compression molding, extrusion, run extrusion, injection molding, extrusion, co-extrusion, rotational molding, blow molding, injection blow molding, thermoforming, vacuum forming, casting, solution casting, centrifugal casting, overmolding, resin transfer molding, vacuum assisted resin transfer molding, spinning, printing, etc. Thermoset compositions can be formed by mixing resin precursors with graphene sheets and, optionally, other additives in a mold and curing.

[0102] Inks and coatings can be applied to a wide variety of substrates to form the thermal management device, including, but not limited to, flexible and/or stretchable materials, silicones and other elastomers and other polymeric materials, metals (such as aluminum, copper, steel, stainless steel, etc.), adhesives, heat-sealable materials (such as cellulose, biaxially oriented polypropylene (BOPP), poly(lactic acid), polyurethanes, etc.), fabrics (including cloths and textiles (such as cotton, wool, polyesters, rayon, etc.), clothing, glasses and other minerals, ceramics, silicon surfaces, wood, paper, cardboard, paperboard, cellulose-based materials, glassine, labels, silicon and other semiconductors, laminates, corrugated materials, concrete, bricks, fiber-reinforced materials (such as glass fiber reinforced materials, glass fiber-reinforced epoxy resins, fiberglass, etc.), fiber mats, paper-reinforced phenolic resins, building materials, etc. Substrates can be in the form of films, papers, waters, larger three-dimensional objects, etc.

[0103] The substrates can have been treated with other coatings (such as paints) or similar materials before the inks and coatings are applied. Examples include substrates (such as PET coated with indium tin oxide, antimony tin oxide, etc. They can be woven, nonwoven, in mesh form; etc. They can be woven, nonwoven, in mesh form; etc.

[0104] The substrates can be paper-based materials generally (including paper, paperboard, cardboard, glassine, etc.). Paper-based materials can be surface treated, impregnated, etc. Examples of surface treatments include coatings such as polymeric coatings, which can include PET, polyethylene, polypropylene, biaxially oriented polypropylene (BOPP), acetates, nitrocellulose, etc. Coatings can be adhesives. Paper based materials can be sized.

[0105] Examples of polymeric materials include, but are not limited to, those comprising thermoplastics and thermosets, including elastomers and rubbers (including thermoplastics and thermosets), phenolic resins, paper-reinforced phenolic resins, silicones, fluorinated polysiloxanes, natural rubber, butyl rubber, chlorosulfonated polyethylene, chlorinated polyethylene, styrene/butadiene copolymers (SBR), styrene/ethylene/butadiene/styrene copolymers (SEBS), styrene/ethylene/butadiene/styrene copolymers (SBS), polyisoprene, nitrile rubbers, hydrogendonated nitrile rubbers, neoprene, ethylene/propylene copolymers (EPR), ethylene/propylene/diene copolymers (EPDM), ethylene/vinyl acetate copolymer (EVA), hexafluoropropylene/vinylidene fluoride/tetrafluoroethylene copolymers, tetrafluoroethylene/propylene copolymers, fluoroelastomers, polyesters (such as poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate), liquid crystalline polyesters, poly(lactic acid), etc; polystyrene; polyamides (including polyterephthalamides); polyimides (such as Kapton®); aramids (such as Kevlar® and Nomex®); fluoropolymers (such as fluorinated ethylene propylene (FEP), polytetrafluoroethylene (PTFE), poly(vinyl fluoride), poly(vinylidene fluoride), etc.); polyetherimides; poly(vinyl chloride); poly(vinylidene chloride); polyurethanes (such as thermoplastic polyurethanes (TPU)); spandex, cellulose polymers (such as cellulose, nitrocellulose, cellulose acetate, etc.); styrene/ acrylic polymers (SAN); acrylonitrile/butadiene/styrene polymers (ABS); polycarbonates; polyacrylates; poly(methyl methacrylate); ethylene/vinyl acetate copolymers; thermoset epoxies and polyurethanes; polyolefins (such as polyethylene (including low density polyethylene, high density polyethylene, ultrahigh molecular weight polyethylene, etc.); polypropylene (such as biaxially-oriented polypropylene, etc.); Mylar; etc). They can be non-woven materials, such as DuPont Tyvek®. They can be adhesive or adhesive-backed materials (such as adhesive-backed papers or paper substitutes). They can be mineral-based paper substitutes such as Teslin® from PPG Industries. The substrate can be a transparent or translucent or optical material, such as glass, quartz, polymer (such as polycarbonate or poly(methyl methacrylate) (such as poly(methyl methacrylate)).

[0106] The inks and coatings can be applied to the substrate using any suitable method, including, but not limited to, painting, pouring, spin coating, solution casting, dip coating, powder coating, by syringe or pipette, spray coating, curtain coating, laminating, co-extrusion, electrophoretic deposition, ink-jet printing, spin coating, thermal transfer (including laser transfer) methods, doctor blade printing, screen printing, rotary screen printing, gravure printing, lithographic printing, intaglio printing, digital printing, capillary printing, offset printing, electrohydrodynamic (EHD) printing (a method of which is described in WO 2007/053621, which is hereby incorporated herein by reference), microprinting, pad printing, tampon printing, stencil printing, wire rod coating, drawing, flexographic printing, stamping, xerography, microcontact printing, dip pen nanolithography, laser printing, via pen, via brush, via sponge, or similar means, etc. The compositions can be applied in multiple layers.

[0107] After they have been applied to a substrate, the inks and coatings can be cured using any suitable technique, including drying and oven-drying (in air or another inert or reactive atmosphere), UV curing, IR curing, drying, crosslinking, thermal curing, laser curing, ion curing, micro-wave curing or drying, sintering, and the like.

[0108] The cured inks and coatings can have a variety of thicknesses. For example, they can optionally have a thickness of at least about 2 mm, or at least about 5 mm. In various
embodiments, the coatings can optionally have a thickness of about 2 nm to 2 mm, about 5 nm to 1 mm, about 2 nm to about 100 nm, about 2 nm to about 200 nm, about 2 nm to about 500 nm, about 2 nm to about 1 micrometer, about 5 nm to about 200 nm, about 5 nm to about 500 nm, about 5 nm to about 1 micrometer, about 5 nm to about 50 micrometers, about 5 nm to about 200 micrometers, about 10 nm to about 200 nm, about 50 nm to about 500 nm, about 50 nm to about 1 micrometer, about 100 nm to about 10 micrometers, about 1 micrometer to about 2 mm, about 1 micrometer to about 1 mm, about 1 micrometer to about 500 micrometers, about 1 micrometer to about 200 micrometers, about 1 micrometer to about 100 micrometers, about 50 micrometers to about 1 mm, about 100 micrometers to about 2 mm, about 100 micrometers to about 1 mm, about 100 micrometers to about 750 micrometers, about 100 micrometers to about 500 micrometers, about 500 micrometers to about 2 mm, or about 500 micrometers to about 1 mm.

[0109] When applied to a substrate, the inks and coatings can have a variety of forms. They can be present as a film or lines, patterns, letters, numbers, circuitry, logos, identification tags, and other shapes and forms. The inks and coatings can be covered in whole or in part with additional material, such as overcoatings, varnishes, polymers, fabrics, etc.

[0110] The inks and coatings can be applied to the same substrate in varying thicknesses at different points and can be used to build up three-dimensional structures on the substrate.

[0111] The compositions, including those in the form of polymer composites, dispersions, inks and coatings, etc. can be electrically and/or thermally conductive. In some embodiments, the composition can have a conductivity of at least about $10^{-6}$ S/m. It can have a conductivity of about $10^{-3}$ S/m, or of about $10^{-2}$ S/m to about $10^{-1}$ S/m. In other embodiments of the invention, the coating has conductivities of at least about 0.001 S/m, of at least about 0.01 S/m, of at least about 0.1 S/m, or of at least about 1 S/m, of at least about 10 S/m, or of at least about 100 S/m, or at least about 1000 S/m, or at least about 10,000 S/m, or at least about 20,000 S/m, or at least about 30,000 S/m, or at least about 40,000 S/m, or at least about 50,000 S/m, or at least about 60,000 S/m, or at least about 75,000 S/m, or at least about 100,000 S/m.

[0112] In some embodiments, the surface resistivity of the composition (including polymer composites, cured inks and coatings, etc.) can be no greater than about 10 mega$\Omega$/square/mil, or no greater than about 1 mega$\Omega$/square/mil, or no greater than about 500 kilo$\Omega$/square/mil, or no greater than about 200 kilo$\Omega$/square/mil, or no greater than about 100 kilo$\Omega$/square/mil, or no greater than about 50 kilo$\Omega$/square/mil, or no greater than about 25 kilo$\Omega$/square/mil, or no greater than about 10 kilo$\Omega$/square/mil, or no greater than about 10$\Omega$/square/mil, or no greater than about 5$\Omega$/square/mil, or no greater than about 1$\Omega$/square/mil, or no greater than about 0.1$\Omega$/square/mil, or no greater than about 0.01$\Omega$/square/mil, or no greater than about 0.001$\Omega$/square/mil.

[0113] In some embodiments, the composition can have a thermal conductivity of about 0.1 to about 50 W/mK, or of about 0.5 to about 30 W/mK, or of about 0.1 to about 0.5 W/mK, or of about 0.1 to about 1 W/mK, or of about 0.1 to about 5 W/mK, or of about 0.5 to about 2 W/mK, or of about 0.1 to about 0.5 W/mK, or of about 0.1 to about 50 W/mK, or of about 1 to about 10 W/mK, or of about 1 to about 15 W/mK, or of about 0.1 to about 10 W/mK, or of about 1 to about 15 W/mK, or of about 0.1 to about 10 W/mK, or of about 1 to about 15 W/mK, or of about 0.1 to about 10 W/mK, or of about 1 to about 15 W/mK.

1. A thermal management device, comprising a composition comprising graphene sheets.

2. The device of claim 1, wherein the composition further comprises at least one polymer.

3. The device of claim 1, wherein the composition further comprises at least one electrically and/or thermally conductive additive.

4. The device of claim 3, wherein the thermally conductive additive is at least one metal oxide.

5. The device of claim 4, wherein the metal oxide is one or more selected from iron(II) oxide, iron(III) oxide (magnetite), iron (III) oxide, and alumina.

6. The device of claim 1, wherein the graphene sheets have a surface area of at least about 300 m$^2$/g.

7. The device of claim 1, wherein the graphene sheets have a surface area of at least about 400 m$^2$/g.

8. The device of claim 1, wherein the graphene sheets have a carbon to oxygen molar ratio of at least about 25:1.

9. The device of claim 1, wherein the graphene sheets have a carbon to oxygen molar ratio of at least about 75:1.

10. The device of claim 1, wherein the composition further comprises at least one polymeric binder.

11. The device of claim 1, wherein the composition is in the form of an ink or coating.

12. The device of claim 1, wherein the thermal management device is a heater or heater component.

13. The device of claim 1, in the form of a heat spreader, heat diffuser, or heat sink.

14. The device of claim 1, in the form of a cooling device.

15. The device of claim 1, wherein the composition is an ink or coating.

16. The device of claim 1, wherein the device comprises an ink or coating applied to at least a portion of a polymeric substrate.

17. An article of apparel comprising the device of claim 1.

18. A composition, comprising graphene sheets and at least one thermally conductive, non-electrically conductive compound.

19. The composition of claim 18, wherein the thermally conductive compound is at least one metal oxide.

20. The composition of claim 19, wherein the non-electrically conductive compound is one or more selected from iron(II) oxide, iron(III) oxide (magnetite), iron (III) oxide, iron(II) sulfide, and alumina.

21. The composition of claim 18, further comprising at least one polymer.