and the like (e.g., carbon nano-tubes are generally thought of as graphene sheets rolled up into nanometer-sized cylinders). Graphene is a single planar sheet of sp^2 bonded carbon atoms. Graphene is not an allotrope of carbon because the sheet is of finite size and other elements can be attached at the edge in non-vanishing stoichiometric ratios.

When used to reinforce polymers, graphene in any form increases polymer toughness by inhibiting crack propagation. Graphene can also be added to polymers and other compositions to provide electrical and thermal conductivity. The thermal conductivity of graphene makes it an ideal additive for thermal management (e.g., planar heat dissipation) for electronic devices and lasers. Some commercial applications of carbon fiber-reinforced polymer matrix composites (CF-PMCs) include aircraft and aerospace systems, automotive systems and vehicles, electronics, government defense/security, pressure vessels, and reactor chambers, among others.

Progress in the development of low cost methods to effectively produce graphene-reinforced polymer matrix composites (G-PMCs) remains very slow. Currently, some of the challenges that exist affecting the development of G-PMCs viable for use in real world applications include the expense of the materials and the impracticality of the presently used chemical and/or mechanical manipulations for large-scale commercial production. It would thus be desirable for a low cost method to produce a G-PMC suitable for large-scale commercial production that offers many property advantages, including increased specific stiffness and strength, enhanced electrical/thermal conductivity, and retention of optical transparency.

SUMMARY ~~OF THE INVENTION~~

The present disclosure provides polymer processing methods to fabricate a graphene-reinforced polymer matrix composite (G-PMC) by elongational flow and folding of well-crystallized graphite particles dispersed in a molten polymer matrix.

In one ~~aspect~~embodiment, there is provided herein a method for forming a graphene-reinforced polymer matrix composite, including: distributing graphite microparticles into a molten thermoplastic polymer phase; and applying a succession of shear strain events to the molten polymer phase so that the molten polymer phase exfoliates the graphite successively with each event until at least

50% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nano-particles less than 50 nanometers thick along a c-axis direction. In a first aspect, there is provided herein a method for forming a graphene-reinforced polymer matrix composite, comprising: (a) distributing graphite microparticles into a molten thermoplastic polymer phase comprising one or more molten thermoplastic polymers; and (b) applying a succession of shear strain events to the molten polymer phase so that said molten polymer phase exfoliates the graphene successively with each event, until tearing of exfoliated multilayer graphene sheets occurs and produces reactive edges on said multilayer sheets that react with and cross-link said one or more thermoplastic polymers; wherein said one or more thermoplastic polymers are selected from the group consisting of thermoplastic polymers subject to UV degradation.

In certain embodiments, the graphite particles may be prepared by crushing and grinding a graphite-containing mineral to millimeter-sized dimensions.

In certain embodiments, the millimeter-sized particles may be reduced to micron-sized dimensions using any known method, such as ball milling or attritor milling.

In certain embodiments, the graphite particles are extracted from the micron-sized particle mixture, preferably by a flotation method.

In certain embodiments, the extracted graphite particles may be incorporated in a polymer matrix using a single screw extruder with axial fluted extensional mixing elements or spiral fluted extensional mixing elements.

In certain embodiments, the graphite-containing polymer matrix is subjected to repeated extrusion to induce exfoliation of the graphitic material, thus forming a uniform dispersion of graphene nanoparticles in the polymer matrix.

In certain embodiments, the thermoplastic polymer is an aromatic polymer. The aromatic polymer preferably comprises phenyl groups, optionally substituted, either as part of the backbone or as substituents on the backbone. In certain embodiments the optionally substituted phenyl groups are contained within the polymer backbone as optionally

substituted phenylene groups. In certain other embodiments the optionally substituted phenyl groups are substituents on the polymer. In specific embodiments, the thermoplastic polymer is selected from polyetheretherketones, polyether-ketones, polyphenylene sulfides, polyethylene sulfides, polyetherimides, polyvinylidene fluorides, polysulfones, polycarbonates, polyphenylene ethers or oxides, polyamides such as nylons, aromatic thermoplastic polyesters, aromatic polysulfones, thermoplastic polyimides, liquid crystal polymers, thermoplastic elastomers, polyethylenes, polypropylenes, polystyrene, acrylics, such as polymethylmethacrylate, polyacrylonitrile, acrylonitrile butadiene styrene, and the like, ultra-high-molecular-weight polyethylene,

polytetrafluoroethylene, polyoxymethylene plastic, polyaryletherketones, polyvinylchloride, and mixtures thereof.

In certain embodiments, in combination with other embodiments, the succession of shear strain events may be applied until at least 50% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nanoparticles less than 25 nanometers thick along the c-axis direction.

In certain embodiments, in combination with other embodiments, the succession of shear strain events may be applied until at least 50% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nanoparticles less than 10 nanometers thick along the c-axis direction.

In certain embodiments, in combination with other embodiments, the succession of shear strain events may be applied until at least 90% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nanoparticles less than 10 nanometers thick along the c-axis direction.

In certain embodiments, in combination with other embodiments, the succession of shear strain events may be applied until at least 80% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nanoparticles less than 10 nanometers thick along the c-axis direction.

In certain embodiments, in combination with other embodiments, the succession of shear strain events may be applied until at least 75% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nanoparticles less than 10 nanometers thick along the c-axis direction.

In certain embodiments, in combination with other embodiments, the succession of shear strain events may be applied until at least 70% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nanoparticles less than 10 nanometers thick along the c-axis direction.

In certain embodiments, in combination with other embodiments, the succession of shear strain events may be applied until at least 60% of the graphite is exfoliated to form a distribution in the molten polymer phase of single- and multi-layer graphene nanoparticles less than 10 nanometers thick along the c-axis direction.

In certain embodiments, in combination with other embodiments, the graphite may be doped with other elements to modify the surface chemistry of the exfoliated graphene nanoparticles.

In certain embodiments, in combination with other embodiments, the graphite is expanded graphite.

In certain embodiments, in combination with other embodiments, the surface chemistry or nanostructure of the dispersed graphite may be modified to enhance bond strength with the polymer matrix to increase strength and stiffness of the graphene composite.

In certain embodiments, in combination with other embodiments, directional alignment of the graphene nanoparticles is used to obtain one-, two- or three-dimensional reinforcement of the polymer matrix phase.

In another ~~aspect~~ embodiment of the ~~disclosed invention~~disclosure, there is provided herein a method for forming a cross-linked G-PMC, including: distributing graphite microparticles into a molten thermoplastic polymer phase comprising one or more molten thermoplastic polymers; and applying a succession of shear events to said molten polymer phase, so that said molten polymer phase exfoliates the grapheme with each event, until tearing of exfoliated multilayer graphene sheets occurs and produces reactive edges on said multilayer sheets that react with and cross-link said thermoplastic polymer.

In another ~~aspect~~ embodiment of the ~~disclosed invention~~disclosure, there is provided herein a method for forming a high strength cross-linked G-PMC, including: distributing graphite microparticles into a molten thermoplastic polymer phase comprising one or more molten thermoplastic polymers; applying a succession of shear strain events to the molten polymer phase so that said molten polymer phase exfoliates the graphene successively with each event, until tearing of exfoliated multilayer graphene sheets occurs and produces reactive edges on said multilayer sheets that react with and cross-link said thermoplastic polymer, to form a graphene-reinforced polymer matrix composite;

and further grinding and distributing the graphene-reinforced polymer matrix composite with another non-cross-linked thermoplastic polymer.

In a second aspect, there is provided herein a method for forming a high-strength graphene-reinforced polymer matrix composite, comprising: (a) forming the composite as disclosed herein into cross-linked polymer particles; and (b) distributing the polymer particles into another non-cross-linked molten host thermoplastic matrix polymer.

In certain embodiments, the graphite particles may be prepared by crushing and grinding a graphite-containing mineral to millimeter-sized dimensions, followed by reduction to micron-sized particles by milling.

In certain embodiments, the graphite particles are extracted from the micron-sized particle mixture, preferably by a flotation method, to obtain Separated Mineral Graphite ("SMG").

In certain embodiments, the molten thermoplastic polymer phase comprises two molten thermoplastic polymers.

In certain embodiments, the thermoplastic polymers are selected from polyether-etherketone (PEEK), polyetherketone (PEK), polyphenylene sulfide (PPS), polyethylene sulfide (PES), polyetherimide (PEI), polyvinylidene fluoride (PVDF), polycarbonate (PC), poly-phenylene ether, aromatic thermoplastic polyesters, thermoplastic polyimides, liquid crystal polymers, thermoplastic elastomers, polyethylene, polypropylene, polystyrene (PS), acrylics, such as polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), acrylonitrile butadiene styrene (ABS), and the like, ultra-high-molecular-weight polyethylene (UHMWPE), polytetra-fluoroethylene (PTFE/Teflon®), polyamides (PA) such as nylons, polyphenylene oxide (PPO), polyoxymethylene plastic (POM/Acetal), polyaryletherketones, polyvinylchloride (PVC), and mixtures thereof.

In a third aspect, there is provided herein a graphene-reinforced polymer matrix composite prepared according to the methods of the first and second aspects.

In a fourth aspect, there is provided herein a high strength graphene-reinforced polymer matrix composite prepared according to the method of the second aspect.

In a fifth aspect, there is provided a thermoplastic polymer composite comprising thermoplastic polymer chains inter-molecularly cross-linked by torn single- and/or multi-layer graphene sheets having carbon atoms with reactive bonding sites on the torn edges of said sheets.

In a sixth aspect, there is provided an automotive, aircraft or aerospace part formed from the composite of the sixth aspect.

In a seventh aspect, there is provided graphene cross-linked polymer particles formed from the composite of the sixth aspect.

In an eighth aspect, there is provided a polymer composition comprising a host thermoplastic polymer and the graphene cross-linked polymer particles of the seventh aspect dispersed therein.

In a ninth aspect, there is provided an automotive, aircraft or aerospace part formed from the polymer composition of the eighth aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the morphology analysis of 2% graphite exfoliated in polysulfone at mixing times of 3 minutes, 30 minutes, and 90 minutes according to an *in situ* exfoliation method of the present disclosure.

FIG. 2 illustrates micrographs of 90G-PMC at various scales and magnification levels according to an *in situ* exfoliation method of the present disclosure.