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~~ consisting essentially of one or more molten thermoplastic polymers to form a graphite-molten thermoplastic polymer phase; and (b) applying a succession of shear strain events to the graphite-molten thermoplastic polymer phase so that shear stress within said molten polymer phase exceeds the Interlayer Shear Strength (ISS) of said graphite microparticles and said molten polymer phase exfoliates ~~the~~ graphene from the graphite microparticles successively with each event~~,~~ until said graphite microparticles are at least partially exfoliated to form a distribution in the molten polymer phase of single- and/or multiplayer graphene nanoparticles less than 50 nm thick in a c-axis direction, and further continuing the shear strain events until tearing of said exfoliated single and/or multilayer graphene sheets occurs and produces reactive free radical graphenic carbon bonding sites on the torn edges ~~on~~ of said single and/or multilayer graphene sheets that react with ~~and cross-link~~ said one or more molten thermoplastic polymers to provide a composite where the thermoplastic polymer chains are directly covalently bonded to, and inter-molecularly cross-linked by, said single and/or multiplayer graphene sheets; wherein said one or more molten 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,

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

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

In a ~~fifth~~ third aspect, there is provided a thermoplastic polymer composite comprising thermoplastic polymer chains which are directly covalently bonded to, and inter-molecularly cross-linked by, reactive free radical graphenic carbon bonding sites on the torn edges of single- and/or multi-layer graphene sheets ~~having carbon atoms with reactive bonding sites on the torn edges of said sheets~~.

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

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

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

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

CLAIMS

What is claimed is:

1. A method for forming a graphene-reinforced polymer matrix composite, comprising:

(a) distributing graphite microparticles into a molten thermoplastic polymer phase ~~comprising~~ consisting essentially of one or more molten thermoplastic polymers to form a graphite-molten thermoplastic polymer phase; and

(b) applying a succession of shear strain events to the graphite-molten thermoplastic polymer phase so that shear stress within said molten polymer phase exceeds the Interlayer Shear Strength (ISS) of said graphite microparticles and said molten polymer phase exfoliates ~~the~~ graphene from the graphite microparticles successively with each event, until said graphite microparticles are at least partially exfoliated to form a distribution in the molten polymer phase of single- and/or multiplayer graphene nanoparticles less than 50 nm thick in a c-axis direction, and further continuing the shear strain events until tearing of said exfoliated single and/or multilayer graphene sheets occurs and produces reactive free radical graphenic carbon bonding sites on the torn edges of~~on~~ said single and/or multilayer graphene sheets that react with ~~and cross-link~~ said one or more molten thermoplastic polymers to provide a composite where the thermoplastic polymer chains are directly covalently bonded to, and inter-molecularly cross-linked by, said single and/or multiplayer graphene sheets;

wherein said one or more molten thermoplastic polymers are selected from the group consisting of thermoplastic polymers subject to UV degradation.

2. The method of Claim 1, wherein at least one of said one or more molten thermoplastic polymers is an aromatic polymer.

3. The method of Claim 2, wherein said aromatic polymer comprises phenyl groups, optionally substituted, in either the backbone or as substituents.

4. The method of Claim 3, wherein the optionally substituted phenyl groups are contained within the polymer backbone as optionally substituted phenylene groups.

5. The method of Claim 3, wherein the optionally substituted phenyl groups are substituents on the polymer.

6. The method of any one of Claims 1 to 5, wherein said one or more thermoplastic polymers are selected from the group consisting of polyetheretherketone (PEEK), polyetherketone (PEK), polyphenylene sulfide (PPS), polyethylene sulfide (PES), polyetherimide (PEI), polyvinylidene fluoride (PVDF), polycarbonate (PC), ~~polyphenylene ether,~~ aromatic thermoplastic polyesters, thermoplastic polyimides, liquid crystal polymers, thermoplastic elastomers, polyethylene, polypropylene, polystyrene (PS),

polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), ultra-high-molecular-weight polyethylene (UHMWPE), polytetrafluoroethylene (PTFE), acrylonitrile butadiene styrene (ABS), polyamides (PA), polyphenylene oxide (PPO), polyoxy-methylene plastic (POM/Acetal), ~~polyimides,~~ polyaryletherketones, polyvinylchloride (PVC), acrylics, and mixtures thereof.

7. A method for forming a high-strength graphene-reinforced polymer matrix composite, comprising:

(a) forming the composite of any one of Claims 1 to 6 into cross-linked polymer particles; and

(b) distributing the polymer particles into another non-cross-linked molten host thermoplastic matrix polymer.

8. The method of any one of Claims 1 to 7, wherein said molten thermoplastic polymer phase comprises two or more molten thermoplastic polymers.

9. The method of any one of Claims 1 to 8, wherein the graphite microparticles are prepared by crushing and grinding a graphite-containing mineral to millimeter-sized dimensions, followed by milling to a micron-sized particle mixture.

10. The method of Claim 9, wherein the graphite microparticles are extracted from the micron-sized particle mixture by a flotation method.

11. The method of Claim 2 or Claim 6, wherein said one or more molten thermoplastic polymers is polyetheretherketone (PEEK).

12. The method of any one of Claims 1 to 11, wherein the graphite is expanded graphite.

~~13. A graphene-reinforced polymer matrix composite prepared according to the method of any one of Claims 1 to 12.~~

~~14. The graphene-reinforced polymer matrix composite of Claim 13, wherein said polymer is polyetheretherketone.~~

~~15. A high strength graphene-reinforced polymer matrix composite prepared according to the method of Claim 7.~~

~~16. The graphene-reinforced polymer matrix composite of Claim 15, wherein said polymer is polyetheretherketone.~~

~~17~~13. A thermoplastic polymer composite comprising thermoplastic polymer chains which are directly covalently bonded to, and inter-molecularly cross-linked by, reactive free radical graphenic carbon bonding sites on the torn edges of single- and/or multi-layer graphene sheets ~~having carbon atoms with reactive bonding sites on the torn edges of said sheets~~.

~~18~~14. The thermoplastic polymer composite of Claim ~~17~~13, wherein said thermoplastic polymers are selected from the group consisting of polyetheretherketone (PEEK), polyether-ketone (PEK), polyphenylene sulfide (PPS), polyethylene sulfide (PES), polyetherimide (PEI), polyvinylidene fluoride (PVDF), polycarbonate (PC), ~~polyphenylene ether,~~ aromatic thermoplastic polyesters, thermoplastic polyimides, liquid crystal polymers, thermoplastic elastomers, polyethylene, polypropylene, polystyrene (PS), polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), ultra-high-molecular-weight polyethylene (UHMWPE), polytetra-fluoroethylene (PTFE), acrylonitrile butadiene styrene (ABS), polyamides (PA), poly-phenylene oxide (PPO), polyoxymethylene plastic (POM/Acetal), ~~polyimides,~~ polyarylether-ketones, polyvinylchloride (PVC), acrylics, and mixtures thereof.

~~19~~15. An automotive, aircraft or aerospace part formed from the composite of Claim ~~17~~13.

~~20~~16. The part of Claim ~~19~~15, wherein said part is an engine part.

~~21~~17. Graphene cross-linked polymer particles formed from the composite of Claim ~~17~~13.

~~22~~18. A polymer composition comprising a host thermoplastic polymer and the graphene cross-linked polymer particles of Claim ~~21~~ 17 dispersed therein.

~~23~~19. The polymer composition of Claim ~~22~~18, wherein said host thermoplastic polymer is selected from the group consisting of polyetheretherketone (PEEK), polyether-ketone (PEK), polysulfones (PS), polyphenylene sulfide (PPS), polyethylene sulfide (PES), polyetherimide (PEI), polyvinylidene fluoride (PVDF), polycarbonate (PC), ~~polyphenylene ether,~~ aromatic thermoplastic polyesters, thermoplastic polyimides, liquid crystal polymers, thermoplastic

elastomers, polyethylene, polypropylene, polystyrene (PS), polymethyl-methacrylate (PMMA), polyacrylonitrile (PAN), ultra-high-molecular-weight polyethylene (UHMWPE), polytetra-fluoroethylene (PTFE), acrylonitrile butadiene styrene (ABS), polyamides (PA), poly-phenylene oxide (PPO), polyoxymethylene plastic (POM/Acetal), ~~polyimides,~~ polyarylether-ketones, polyvinylchloride (PVC), acrylics, and mixtures thereof.

~~24~~20. An automotive, aircraft or aerospace part formed from the polymer composition of Claim ~~22~~18.