

COMPOSITIONS, SYSTEMS AND METHODS FOR TURBOSTRATIC GRAPHENE ASPHALT CEMENT AND CONCRETE MODIFIERS

Technical Field

[0001] The embodiments disclosed herein relate to asphalt cement and asphalt concrete mixtures, and, in particular, to compositions of graphene and graphene-based polymers composites and asphalt cement modifiers for asphalt cement and methods of manufacture of the same.

Background

[0002] Asphalt cement is commonly used in the pavement, construction, and roofing industries. For example, asphalt cement is often used as a binder for mineral aggregates in asphalt concretes or pavements. However, over time and with exposure to weather and traffic asphalt cement and compositions thereof, become damaged due to factors such as temperature-induced deformation or rutting, thermal cracking caused by low temperatures, and fatigue from heavy loads. This can lead to costly repairs such as frequent road repaving. While, in some existing systems, mineral aggregates make up most of these mixtures the effect of the asphalt cement-containing binder on these properties is significant. Furthermore, the prices of asphalt cement and polymer modifiers have increased based on, at least, the decline of crude oil reserves globally, the demand for petroleum products, and the increase in applications of asphalt cement. Therefore, is beneficial to optimize the asphalt cement's rheology, and strength to minimize cost and improve longevity of the asphalt.

[0003] In existing systems, modifiers such as fibrous reinforcements, surfactants, adhesion promoters, nanofillers, or polymers are included in the asphalt concrete mixtures to improve performance, such as the durability and environmental resilience of pavement construction. Performance improvements depend substantially on the modifier selected and the dosage of each modifier. The compatibility of the modifier and incorporation method is also a factor effecting phase separation during storage, transportation, application, and service.

[0004] In some existing systems, a wet method is used to mix a solid modifier with neat asphalt cement. The solid modifier is mixed with asphalt cement at high temperatures resulting in a modified binder. The modified binder is mixed with aggregates to obtain asphalt concrete or pavement. Mixing temperature and duration will depend on the type of modifier and neat asphalt. The wet process may also change the rheological response of polymer-modified asphalt due to the aging and oxidation of asphalt components, yielding an increase in the linear viscoelastic functions and steady-state viscosity. The wet method may require a high energy mixing process and/or the addition of a crosslinker to stabilize and disperse the modifier in the asphalt cement, particularly where the modifier is a high molecular weight polymer.

[0005] In other existing systems, a dry method is used to mix polymer granules or chips of the modifier are first mixed with aggregates and then neat asphalt cement is added to the mix. The dry method may be more difficult to implement due to lower mixing energy used to disperse the polymer phase in the asphalt concrete mixture compared to the wet method one.

[0006] In some existing systems, the modifier is a polymer modifier, such as styrene-butadiene block copolymers (SBSs). Polymer modifiers enhance the elasticity, strength, durability, cohesion, and adhesion of asphalt cement. The polymer modifiers enable or improve the asphalt cement binder's resistance to deformation, rutting, cracking, and fatigue, and distributes stresses more effectively. Polymer-modified asphalt cement often exhibits improved performance in terms of temperature susceptibility, with increased stiffness at high temperatures and reduced brittleness at lower temperatures. They also demonstrate enhanced resistance to aging, oxidative degradation, and moisture damage.

[0007] The growing interest in sustainable technology has encouraged the use of more recycled materials in pavement. This interest is supported by regulations at the local, state, and federal levels. Existing systems, directed to sustainability, include those using blends of plastic waste and ground tire rubber (GTR) can be found. For example, A composition of asphalt, comprising aggregates, granular or powder material derived from rubber scrap, for example, tires, and a mixture of thermoplastic polymers and

copolymers, as well as additional additives and filling materials, is described in the international patent application WO2015179553. Also, U.S. Patent No. 2022/0186032A1 describes a road pavement asphalt concrete mix that includes a blend of GTR and elastomeric polymers as a modifier for asphalt cement. However, using stock materials, such as polymers, from a recycled stream in compounds presents stability and mixing challenges.

[0008] In some existing systems nanomaterials, such as ZnO, clay, TiO₂, CaCO₃, SiO₂, graphene, and graphene oxide, significantly enhance the mechanical, aging, fatigue, and adhesion properties of asphalt cement. The level of improvement varies depending on the specific nanomaterial used.

[0009] In existing systems, as described in patent document WO2020034822A1, modifiers including graphene material improve three key performance metrics: penetration, softening point, and ductility. Described therein, partially oxidized graphene powder and a surface graft modifier enhance the phase stability and compatibility of the graphene nanoparticles when mixed with asphalt cement. However, modifiers such as graphene based modifiers can be costly, require specialized incorporation methods, and produce various levels of quality in the resultant compound such as asphalt cement.

[0010] In further existing systems, specially engineered graphene-reinforced polymer blending methods and compositions utilize graphene and polymer modifiers for enhanced performance of asphalt cement. This technique is described, for example, in U.S. Patent Application 2020/0354275 A1 where a blend of thermoplastic materials (preferably a combination of polyethylene and polypropylene), polyvinyl butyral (PVB), and graphene nanoparticles appear to demonstrate improved performance in high tensile strength, high stiffness, and high fatigue resistance of asphalt concrete conglomerates.

[0011] In some existing systems, graphene being used as an asphalt cement modifier or in polymer composites as an asphalt cement modifier is obtained through physical or chemical processing of graphite or graphite oxides. The physical method includes peeling, grinding, milling graphite, and sonicating graphite in suitable solvents. The chemical process normally involves the chemical oxidation/intercalation of graphite, exfoliation of graphite oxide by sonication, and chemical reduction of exfoliated graphene

oxide into reduced graphene oxide. The exfoliation and reduction in the chemical approach can also be done by a rapid heating process using microwaves, furnaces, hot baths, and lasers. Other graphene preparation methods include chemical/physical vapour deposition, carbon nanotube opening, etc.

[0012] Graphene obtained using the above-mentioned methods has a two dimensional (2D) sheet-like morphology with a range of lateral size and thickness that can be used to define its aspect ratio. Generally, graphene fabricated by these methods has layers that are Bernal stacked (all graphene produced from graphite), predominately have 15 layers up to > 30 layers of graphene stacked, have low 2D/G ratios < 0.3, and have carbon content from 90 to 95%. The Bernal stacking between the graphene layers of the existing graphene means that it is very difficult to exfoliate the layers. The large number of layers means that the inner layers contribute to the composite mass but are not bound with the polymer composite and therefore do not contribute to the performance of the composite. In addition to the loss of performance, the concentration of existing graphene in a composite needed to make a useful polymer composite is higher, making the composite less economical to make.

[0013] Accordingly, there is a need for compositions, for asphalt cement and concrete modifiers and systems and methods for manufacturing the same that overcome the difficulties described above.

Summary

[0014] An asphalt modifier for modifying the asphalt cement is provided. The modifier is configured to be added to the asphalt cement or concrete and composed of graphene obtained via flash joule heating of a carbon source.

[0015] In an embodiment, the modifier is further configured to be added as an additive directly to an aggregate of the asphalt concrete.

[0016] In an embodiment, the modifier is further configured to be blended with an asphalt cement, wherein the blending is via a wet mixing tool.

[0017] In an embodiment, a surface functionality of the graphene is modified by one or more of a flash process, a post-process, a post-treatment, a surfactant, a dispersant, an organic or inorganic ligand, and a coupling agent.

[0018] In an embodiment, the modifier is a graphene-polymer composite further comprising a polymer and wherein the polymer is obtained from one or more of a non-used polymer material and recycled polymer material.

[0019] In an embodiment, the polymer comprises one or more of linear, branched polymers, homopolymers, copolymers, grafted polymers, block polymers, random polymers, polyethylene, polypropylene, poly vinyl butyral, ethylene vinyl acetate, ethylene acrylate, ethylene alkyl acrylate, ethylene propylene diene monomer rubber, ground tire rubber, polyethylene terephthalate, and resin.

[0020] In an embodiment, the polymer is functionalized with one or more of maleic anhydride, or glycidyl methacrylate, grafted with polyethylene, polypropylene, and ethylene vinyl acetate.

[0021] In an embodiment, the graphene-polymer composite is added into the asphalt concrete by dry mixing directly to one or more of a hot mix asphalt (HMA) and warm mix asphalt (WMA).

[0022] In an embodiment, the addition of the graphene-polymer composite into the asphalt concrete is via one or more of aggregates drum heater, RAP feeder, aggregate and asphalt cement mixer at one or more of an asphalt cement plant or an in-field asphalt mobile mixer.

[0023] In an embodiment, the modifier further includes one or more of sulfur or sulfur-based crosslinker, Isocyanate crosslinker, or a peroxide crosslinker, reactive elastomeric terpolymers, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions, amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, phenylpropanolamine, gilsonite, Polyphosphoric Acid (PPA), peroxide crosslinkers, sulfur less agents, functional fillers, antioxidants, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, and carbon fibers.

[0024] In an embodiment, a morphology of the graphene is one or more of turbostratic, polyhedral, flake, or flake like.

[0025] In an embodiment, the carbon source is one or more of coal, met coke, pet coke, carbon black, recycled plastics, recycled rubber, biomass/biomass waste, waste tire carbon black, petroleum coke, tire carbon black, carbon black, metallurgical coke, plastic ash, plastic powder, ground coffee, anthracite coal, biomass, low-cost feedstocks, biomass wastes, low-cost fibrous feedstocks, corn starch, pine bark, polyethylene microwax, wax, chemplex 690, cellulose, naptenic oil, asphaltenes, gilsonite, and carbon nanotubes.

[0026] A method of modifying asphalt is provided. The method includes adding to asphalt cement or concrete an asphalt modifier composed of graphene obtained via flash joule heating of a carbon source.

[0027] In an embodiment, the asphalt modifier is added as an additive directly to an aggregate of the asphalt concrete.

[0028] In an embodiment, the method further includes blending the asphalt modifier with the asphalt cement via a wet mixing tool.

[0029] In an embodiment, the method further includes modifying a surface functionality of the graphene by one or more of a flash process, a post-process, a post-treatment, a surfactant, a dispersant, an organic or inorganic ligand, and a coupling agent.

[0030] In an embodiment, the asphalt modifier is a graphene-polymer composite further comprising a polymer and wherein the polymer is obtained from one or more of a non-used polymer material and recycled polymer material.

[0031] In an embodiment, the polymer comprises one or more of linear, branched polymers, homopolymers, copolymers, grafted polymers, block polymers, random polymers, polyethylene, polypropylene, poly vinyl butyral, ethylene vinyl acetate, ethylene acrylate, ethylene alkyl acrylate, ethylene propylene diene monomer rubber, ground tire rubber, polyethylene terephthalate, and resin.

[0032] In an embodiment, the method further includes functionalizing the polymer with one or more of maleic anhydride, or glycidyl methacrylate, grafted with polyethylene, polypropylene, and ethylene vinyl acetate.

[0033] In an embodiment, adding the graphene-polymer composite into the asphalt concrete by dry mixing directly to one or more of a hot mix asphalt (HMA) and warm mix asphalt (WMA).

[0034] In an embodiment, adding the graphene-polymer composite into the asphalt concrete is via one or more of aggregates drum heater, RAP feeder, aggregate and asphalt cement mixer at one or more of an asphalt cement plant or an in-field asphalt mobile mixer.

[0035] In an embodiment, the method further includes adding one or more of other polymers, polyolefins, SBS, SBR, SB, GTR (ground tire rubber) PET, RET- Reactive elastomeric terpolymers, hybrids thereof, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions – amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, crosslinkers- sulfur, polyphosphoric acid (PPA), Isocyanate based, sulfur less agents, antioxidants, functional fillers, gilsonite, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, carbon fibers, pigments, antioxidants, UV light absorbers, flame retardants, radical scavengers, plasticizers, or other modifiers.

[0036] In an embodiment, a morphology of the graphene is one or more of turbostratic, polyhedral, flake, or flake like.

[0037] In an embodiment, the carbon source is one or more of coal, met coke, pet coke, carbon black, recycled plastics, recycled rubber, biomass/biomass waste, waste tire carbon black, petroleum coke, tire carbon black, carbon black, metallurgical coke, plastic ash, plastic powder, ground coffee, anthracite coal, biomass, low-cost feedstocks, biomass wastes, low-cost fibrous feedstocks, corn starch, pine bark, polyethylene microwax, wax, chemplex 690, cellulose, naptenic oil, asphaltenes, gilsonite, and carbon nanotubes.

[0038] A modified asphalt cement is provided. The modified asphalt is composed of an asphalt modifier, the asphalt modifier composed of graphene obtained via flash joule heating of a carbon source.

[0039] In an embodiment, the asphalt modifier is configured to be added as an additive directly to an aggregate of an asphalt concrete such that the asphalt modifier of the modified asphalt cement is asphalt modifier of the asphalt modifier and aggregate mixture.

[0040] In an embodiment, the asphalt cement is configured to be blended with the asphalt modifier via a wet mixing tool.

[0041] In an embodiment, a surface functionality of the graphene is modified by one or more of a flash process, a post-process, a post-treatment, a surfactant, a dispersant, an organic or inorganic ligand, and a coupling agent.

[0042] In an embodiment, the asphalt modifier is a graphene-polymer composite further comprising a polymer and wherein the polymer is obtained from one or more of a non-used polymer material and recycled polymer material.

[0043] In an embodiment, the polymer comprises one or more of linear, branched polymers, homopolymers, copolymers, grafted polymers, block polymers, random polymers, polyethylene, polypropylene, poly vinyl butyral, ethylene vinyl acetate, ethylene acrylate, ethylene alkyl acrylate, ethylene propylene diene monomer rubber, ground tire rubber, polyethylene terephthalate, and resin.

[0044] In an embodiment, the polymer is functionalized with one or more of maleic anhydride, or glycidyl methacrylate, grafted with polyethylene, polypropylene, and ethylene vinyl acetate.

[0045] In an embodiment, the graphene-polymer composite is added into the asphalt concrete by dry mixing directly to one or more of a hot mix asphalt (HMA) and warm mix asphalt (WMA).

[0046] In an embodiment, the addition of the graphene-polymer composite into the asphalt concrete is via one or more of aggregates drum heater, RAP feeder, aggregate

and asphalt cement mixer at one or more of an asphalt cement plant or an in-field asphalt mobile mixer.

[0047] In an embodiment, the modified asphalt cement further includes one or more of other polymers, polyolefins, SBS, SBR, SB, GTR (ground tire rubber) PET, RET- Reactive elastomeric terpolymers, hybrids thereof, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions – amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, crosslinkers-sulfur, polyphosphoric acid (PPA), Isocyanate based, sulfur less agents, antioxidants, functional fillers, gilsonite, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, carbon fibers, pigments, antioxidants, UV light absorbers, flame retardants, radical scavengers, plasticizers, or other modifiers. .

[0048] In an embodiment, a morphology of the graphene is one or more of turbostratic, polyhedral, flake, or flake like.

[0049] In an embodiment, the carbon source is one or more of coal, met coke, pet coke, carbon black, recycled plastics, recycled rubber, biomass/biomass waste, waste tire carbon black, petroleum coke, tire carbon black, carbon black, metallurgical coke, plastic ash, plastic powder, ground coffee, anthracite coal, biomass, low-cost feedstocks, biomass wastes, low-cost fibrous feedstocks, corn starch, pine bark, polyethylene microwax, wax, chemplex 690, cellulose, naptenic oil, asphaltenes, gilsonite, and carbon nanotubes.

[0050] Other aspects and features will become apparent, to those ordinarily skilled in the art, upon review of the following description of some exemplary embodiments.

Brief Description of the Drawings

[0051] The drawings included herewith are for illustrating various examples of articles, methods, and apparatuses of the present specification. In the drawings:

[0052] Figure 1 is a flow diagram of a framework to modify and test asphalt cement and asphalt concrete, according to an embodiment;

[0053] Figure 2 is images of a compatibilization effect of polyhedral graphene in multi-component matrix polymers, according to an embodiment;

[0054] Figure 3 is a block diagram of a general description for processes available to modify turbostratic graphene, according to an embodiment;

[0055] Figure 4 is a flow diagram of a general description for producing a graphene-polymer composite asphalt modifier, according to an embodiment;

[0056] Figure 5 is a comparison table of the control asphalt cements and two polyhedral graphene modified asphalt cements, according to an embodiment;

[0057] Figure 6 is a comparison table of various example asphalt cement compositions, according to an embodiment; and

[0058] Figure 7 is a table of example results of testing performed on a base or neat asphalt concrete and base or neat asphalt concrete modified with graphene-based modifiers, according to an embodiment.

Detailed Description

[0059] Various apparatuses or processes will be described below to provide an example of each claimed embodiment. No embodiment described below limits any claimed embodiment and any claimed embodiment may cover processes or apparatuses that differ from those described below. The claimed embodiments are not limited to apparatuses or processes having all of the features of any one apparatus or process described below or to features common to multiple or all of the apparatuses described below.

[0060] While the above description provides examples of one or more compositions, apparatus, methods, or systems, it will be appreciated that other compositions, apparatus, methods, or systems may be within the scope of the claims as interpreted by one of skill in the art.

[0061] Provided herein are graphene-polymer composite-based, and graphene-based asphalt cement modifiers, the composition and method of making and using these modifiers, within Asphalt cement and Asphalt concrete mixtures. The graphene is a flash/resistive joule heating graphene of any morphology, preferably polyhedral morphology.

[0062] Referring to Figure 1, shown therein is a flow diagram 100 of a framework to modify and test asphalt cement 105 and asphalt concrete 110, according to an embodiment.

[0063] Definitions

[0064] The term “asphalt cement”, also known as and referred to herein as “asphalt binder”, “binder” or “pitch” is a mixture obtained by refining a complex mixture such as crude oil, tar, coal, or biomass, or a modified asphalt cement. The asphalt cement may be for road pavement and road surface repair. It may also be for shingles or roof applications, and any other asphalt cement based composite. The asphalt cement may be, without any limitation, a natural product. Asphalt cement examples include sticky, black, highly viscous liquid or semi-solid forms of hydrocarbons obtained naturally or synthetically as a residue from petroleum distillation. Asphalt cement may further contain various petrochemical components. Between 0% and 10% of an asphalt cement may contain sulfur, nitrogen, and oxygen, with the remaining portion primarily composed of carbon and hydrogen. Asphalts may be classified by the SARA method into four fractions defined as saturates (S), aromatics (A_1), resins (R), and asphaltenes (A_2) with the molecular weight (MW), aromaticity, polarity, and heteroatomic content increasing in the order $S < A_1 < R < A_2$. It will be appreciated may be used generally “asphalt cement” to describe neat asphalt cement or modified asphalt cement as defined below.

[0065] The term “neat asphalt cement” refers to “asphalt cement” to be modified with a modifier as described below.

[0066] The term “modified asphalt cement” refers to asphalt cement including a modifier as described below.

[0067] The term “asphalt concrete” or “asphalt concrete mixture” as used herein refers to the mixture of asphalt cement and mineral aggregates. Asphalt concrete is also known as “asphalt”, “asphalt concrete”, “blacktop”, “asphalt concrete conglomerates” or “pavement”. The amount of asphalt cement may be between 4-10% of the asphalt concrete, preferably to be 4-5%.

[0068] The term “mineral aggregates” used herein is also known as “construction aggregates” or simply “aggregates” refers to a broad category of medium to coarse-grained mineral particles used in constructions. Example mineral aggregates include, but are not limited to, sand, gravel, crushed stone, slag, recycled asphalt, recycled concrete, and geosynthetic aggregates. In an asphalt concrete mixture, the amount of aggregate may be between 90-96%, preferably to be 95-96%.”

[0069] The term “asphalt terminal” as used herein refers to a site where asphalt cement is handled.

[0070] The term “asphalt plant” as used herein refers to a site where asphalt concrete is handled.

[0071] The term “graphene” refers to any carbon-based structure comprising graphitic structural units present in various forms and morphologies. Existing forms and morphologies include 2D sheets, fiber-like structures, and polyhedral morphologies. The term “graphene” further refers to a material which is a one-atom-thick planar sheet of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice, and, further, contains an intact ring structure of carbon atoms and aromatic bonds throughout at least a majority of the interior sheet and lacks significant oxidation modification of the carbon atoms. Graphene has a predominately crystalline structure and its quality is measured by its degree of crystallinity. Graphene is distinguishable from graphene oxide in that it has a lower degree of oxygen-containing groups such as OH, COOH and epoxide.

[0072] The term “a graphene monolayer” refers to graphene that is a single layer of graphene.

[0073] The term “very few-layer graphene” refers to a graphene that is between 1 to 3 layers of graphene.

[0074] The term “a few-layer graphene” refers to graphene that is between 2 to 5 layers of graphene.

[0075] The term “multilayer graphene” refers to a graphene that is between 2 to 10 layers of graphene.

[0076] The term “Flash Joule Heating” refers to quickly and intensely heating a resistive carbon source, as defined below, by passing an electric current through the resistive carbon source. Examples of flash joule heating are described in the flash joule heating synthesis method and compositions thereof of Patent Cooperation Treaty Application having International Publication Number WO 2020/051000 A1 to Tour et al., having an international publication date of March 12, 2020, which is herein incorporated by reference in its entirety and a system and methods for producing graphene by joule heating described in Patent Cooperation Treaty Application having International Application Number WO2023044569A1 to Mancevski et al., having an international publication date of March 03, 2023, which is herein incorporated by reference in its entirety and Device and method for continuous synthesis of graphene described in Patent Cooperation Treaty Application having International Application Number WO2021092705A1 to Mancevski publication date of May 20, 2021, which is herein incorporated by reference in its entirety. This process converts via rapid graphitization an amorphous carbon to a crystalline carbon made of a single to few layers of carbon atoms arranged in a hexagonal pattern. Opposed to AB-stacked (Bernal) graphene that is normally available on the market, the turbostratic graphene is featured with a relative rotation angle between adjacent layers, which decouples the interlayer interaction and increases the interlayer spacing along the c axial.

[0077] The term “carbon source” generally refers to any carbon-based material typically amorphous (non-crystalline in nature) or with some degree of crystallinity, which may be converted into a predominately crystalline graphene material, preferably turbostratic graphene. The carbon source may include, without limitation, coal, anthracite coal, metallurgical coke (met coke), petroleum coke (pet coke), carbon black, plastic and rubber, recycled plastic, plastic ash, plastic powder, recycled rubber, waste tire carbon black, tire carbon black, biomass, biomass waste, ground coffee, corn starch, pine bark, cellulose, wax, polyethylene microwax, chemplex 690, , naptenic oil, asphaltenes, gilsonite, and carbon nanotubes, etc.

[0078] The term “turbostratic graphene” (TG) 115 refers to a graphene that has little order between the graphene layers. Each graphene layer of the turbostratic graphene 115 structure is predominately crystalline in nature. Other terms which may be

used include misoriented, twisted, rotated, rotationally faulted, and weakly coupled. The turbostratic nature of graphene may be observed and confirmed by Raman spectroscopy, Transmission Electron Microscopy (TEM), selected area electron diffraction (SAED), scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), and X-ray diffraction (XRD) analysis. Predominate morphologies of TG that are produced as a result of a joule heating process include flake-like turbostratic graphene structure (FTG), polyhedral-like turbostratic graphene structure (PG), and combinations thereof, further defined below.

[0079] The term “polyhedral graphene (PG)” refers to TG graphene with a polyhedral morphology prepared by a Flash-Joule Heating process. Polyhedral Graphene may be prepared from different feedstocks such as: carbon black, hydrocarbons, plastics, rubber, recycled tires, recycled plastics, etc. PG shows a unique three dimensional (3D) branched structure compared to AB-stacked or turbostratic flake graphene. PG is a closed form of graphene that forms a polyhedral cage, wherein multiple cages are nested within each other. Spherical cage is also possible. Typical PG graphene ranges from 10 nm to 300 nm in (diameter) size and has from 2 to more than 100 layers wall thickness. Polyhedral graphene nanoparticles can self-organize in a branched structure made from multiple PG nano sized primary particles, ranging in length from a few nm to a few microns. In some embodiments, polyhedral graphene is used in a pellet for a light process to deagglomerate to ease the dispersion of polyhedral graphene modifier into asphalt cement. The light process may be manually smearing, blade smearing, crushing, or any other process that deagglomerates graphene pellets into fine powders.

[0080] The term “flake-like turbostratic graphene (FTG)” refers to TG graphene with a flake morphology prepared by a Flash-Joule Heating process. In some embodiments, the FTG is processed to achieve a reasonable particle size, thickness, and exfoliation for an easy and stable dispersion in asphalt cement. Typical FTG graphene ranges from 100 nm to 2 μ m in lateral size and from 2 graphene layers to more than 10 layers in thickness.

[0081] Graphene-Based Modifiers for Asphalt Cement and Asphalt Concrete

[0082] Asphalt concrete 110 or asphalt cement 105 may include modifiers 120 for improving the performance of the neat asphalt cement or asphalt concrete, respectively. Modifiers 120 may undergo polymer formulation 125 whereby 2-4 components, along with additives, are used to formulate polymers for modifiers 120. Asphalt concrete 110 and asphalt cement 105 may provide a variety of field applications 130, such as rutting resistance and creaking resistance. In some embodiments, described herein, the modifiers 120 are graphene based. Graphene based modifiers include but are not limited to, graphene modifiers and graphene-polymer composite modifiers. It will be appreciated that the performance improvement of graphene-based modifiers may correlate to the quality, composition, or morphology of the graphene.

[0083] Referring to Figure 2, shown therein are images 200 of a compatibilization effect of PG in multi-component matrix polymers, according to an embodiment.

[0084] Image 202 shows a control scenario in which only a blend of 3 polymers is present, while image 204 shows a scenario in which polyhedral graphene (PG) is added to the blend of 3 polymers.

[0085] In an example, graphene-based modifiers include graphene produced using flash joule heating. These flash graphene-based modifiers, such as FTG and PG modifiers, exhibit superior benefits in comparison with existing graphene-based or polymer based asphalt cement modifiers. For example, flash joule heated graphene and optional polymer matrix and additives provide additional compatibility and microstructure to matrix polymers. Specifically, when multi-component matrix polymers are used, the joule-flashed graphene may compatibilize and optimize the phase separations between different components to get a finer phase morphology that contributes to phase stability and combined synergistic improvement in modifier performance.

[0086] The joule flash graphene may also initiate and/or accelerate the crosslinking of elastomer or unsaturated polymer-based matrix. These benefits allow current modifiers to be applicable to a variety of polymers, including, without any limitation, homopolymer, copolymer, neat polymer, mixed polymer, virgin polymer, recycled or reproduced polymer.

[0087] The 3D branched structure of PG promotes the 3-dimensional spatial interaction in the matrix when used in composite materials such as thermoplastics,

thermosets, rubber as described in WO2022123499A1 and coating resins, cement, polyurethane foams as described in WO2021077233A1, and the like. The 3-dimensional spatial structure may also provide a tortuous or labyrinthine pathway. The tortuous pathway may slow down the diffusion of gas, vapour, salt, ions or other molecules or species. In a liquid and/or melt dispersion, the 3D branched morphology of PG and its spatial interaction with a media can also alter the media's viscosity, density, and rheology, and contribute to improvements in mechanical performance. Such a liquid can be an asphalt cement, asphalt binder, melt thermoplastic polymer, resin, thermoset rubber, etc.

[0088] The rotational stacking of turbostratic graphene helps mitigate interlayer coupling and increases interplanar spacing, thereby yielding superior physical properties relative to competitive graphene structures when compared on a similar weight basis. The subtle difference in adjacent layer stacking orientation expresses itself with important differences in product performance attributes. An important performance benefit evident with turbostratic graphene is that multi-layer graphene structures separate into few and individual graphene layers more easily and the graphene layers tend not to recouple.

[0089] Turbostratic graphene provides various advantages over conventional graphene due to its turbostratic nature. For example, turbostratic graphene is easier to delaminate and/or exfoliate compared to conventional graphene which can contribute to an improvement in preparing graphene dispersions. The relative rotation between adjacent layers may also alter the surface energy of TG, allowing it to interact with a media differently from AB-stacked graphene. Such an interaction can be better in certain cases to promote graphene wetting and dispersion in a media, solvent, or matrix. Such interaction may also improve the anchoring and functionalization by ligands, coupling agents, linkers, or chemicals to improve the performance in application.

[0090] The unique graphene morphology and chemistry of the PG obtained from flashing recycled tire carbon black have properties that enable the graphene to chemically bond with the functional groups in asphalt cement. When PG is compounded in a composite of a graphene-polymer blend and used as an additive/modifier, the unique graphene morphology and chemistry have properties that also enable the compatibilization and stabilization of multiple polymer blends that would otherwise not be

easily blended and will separate. The graphene interactions with the polymer and asphalt cement are essential for maintaining the asphalt cement phase stability during a wet mixing process to modify asphalt cement at the asphalt terminal level, as well as improve its dispersion during a dry mixing process at the asphalt plant level further described below. The 3-D spatial interaction and tortuous of PG reduce the diffusion of air and improve the aging performance. Where PG is added separately or as a graphene-polymer composite it also improves the rheology and mechanical stability of the asphalt cement and/or asphalt concrete mixtures to provide better flexibility, cracking resistance, and rutting resistance.

[0091] Referring to Figure 3, shown therein is a block diagram of a general description 300 for processes available to modify turbostratic graphene 315.

[0092] The graphene based modifier may include turbostratic flake graphene or polyhedral graphene. The turbostratic flake graphene may be processed to achieve a reasonable particle size, thickness, agglomeration size, and exfoliation for easy and stable dispersion in asphalt cement.

[0093] The process of the description 300 may include the production of pristine PG 305.

[0094] The process may be mechanical milling using a ball mill, rod mill, or via any milling method known in the art to obtain milled PG 325. Polyhedral graphene may need a light process to deagglomerate to ease the dispersion of polyhedral graphene modifier into asphalt cement. The light process may be manually smearing, blade smearing, crushing, or any other process that deagglomerates graphene pellets into fine powders.

[0095] Moreover, the surface of graphene may be modified or functionalized to create a hybrid graphene 330 to obviate the functionalization of graphene surface or improve its affinity to base asphalt cement. A higher affinity may improve the asphalt cement's stability and rheology performance. The functionalization may be a mechanical milling, a wet chemical treatment, a solid chemical treatment, or a plasma treatment. In some embodiments, the functionalization may be a surface modification with a ligand, a resin, a dispersant, or a surfactant.

[0096] The graphene may be functionalized 320 or modified, either using an in situ or ex situ joule heating functionalization, or post-treatment, with a functional group. The functional groups may include, without limitation, oxygen, hydroxide, carbonyl, carboxylic acid, ketone, ether, unsaturated carbons, silane, chlorine, bromine, fluorine, or any combination thereof. The functional groups also include any heteroatom dopants, islands, and heterostructures that branch or attach to the surface of graphene or partially cover or replace graphene surfaces. The in-situ joule heating functionalization is related to creating graphene surface functional group during the joule heating process, by controlling the joule heating condition and parameters, flash environment, atmosphere, or addition of chemicals. The parameters include, without limitations, the current, voltage, power, duration, flash batch size, flash device, and feedstock condition. The environment includes, but is not limited to, pressure, ventilation, and environmental temperature control/adjustment. The atmosphere may be any gas flow, ambient or pressurized gas blanket, inert or reactive gas, or gas mixture. The chemical may be any chemical that may react with carbon at elevated temperatures to yield heteroatom dopants, islands, additional structures, and branches on the graphene surface. Examples of these chemicals include, without any limitation, sulfur, boron, boric acid, PTFE, SF₆, melamine, et al. The post-treatment includes mechanical milling, wet chemistry, hydrothermal and thermal treatment, plasma reaction/oxidation, etc.

[0097] *Graphene-Polymer Composite Modifiers*

[0098] Referring to Figure 4, shown therein is flow diagram of a general description 400 for producing a graphene-polymer composite asphalt modifier 405, according to an embodiment.

[0099] In some embodiments, the graphene-based modifier 405 is a graphene-polymer composite. The compounding process may be via any melt-mixing method known in the art. The method includes but is not limited to single- or twin-screw extruder, blender, kneader, Haake mixer, Banbury mixer, Brabender mixer, twin-roll mill, roll mixer, etc.

[0100] The graphene-polymer composite includes joule/resistive heating flashed graphene with any morphology. The joule heating flashed graphene, matrix polymer, and

polymeric additives are compounded as the graphene-polymer based asphalt cement modifier 405. Flake turbostratic morphology and polyhedral morphology, particularly polyhedral morphology may provide improvements over other morphologies. The flake turbostratic graphene 415 or graphene with turbostratic flake morphology may be of 1 – 500 nm in thickness and 1 to 200 μm in lateral size. The polyhedral graphene is ensembled with turbostratic graphene polygons having walls and a hollow center. The turbostratic graphene 415 wall is at least 2 to 3 layers, up to several hundred layers. The overall diameter of polyhedral graphene is between 10 to 500 nm. The polyhedral graphene may be aggregated into secondary structures of 100nm to 20 μm . The aggregates may be agglomerated into clusters of 200nm to 200 μm . The agglomeration can be deagglomerated by means of shear, smear, milling, vibration, sonication, or any other methods known to the art. The graphene is used in the polymer composite in an amount of from 0.0001% to 20%, preferably from 0.0001% to 5%, and more preferably from 0.01% to 1%

[0101] The graphene-polymer composite further comprises a matrix of polymers blend. The matrix polymers may be a thermoplastic polymer, an elastomer, or a thermoplastic elastomer. The matrix polymer may comprise one composition or multiple components that are compatible with each other or are compatibilized by the addition of TG. The matrix polymer may be a naturally produced polymer or a synthetic polymer. Furthermore, the matrix polymer may be a virgin polymer or recycled or reproduced polymer.

[0102] One example of matrix polymer is a thermoplastic polymer, such as polyolefins. Polyolefins used in the present innovation may be, but not limited to, polyethylene (PE) 450, polypropylene (PP) 455, polybutene (PB), polyisobutylene (PIB), poly-4-methyl-1-pentene (PMP), or any combination thereof, preferably to be PE, or PP, or a compounding of both, where the amount of PE is from 20% to 80%. Various types of PE may be used, for example, ultra low-density polyethylene (ULDPE), very low-density polyethylene (VLDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), medium density polyethylene (MDPE), high-density polyethylene (HDPE), ultrahigh-molecular-weight polyethylene (UHMWPE), or metallocene polyethylene (MPE). In the same concept, various types of PP may be used, including but not limited

to, isotactic polypropylene (iPP), syndiotactic polypropylene (sPP), atactic polypropylene (aPP), random copolymer polypropylene (PP-R), block copolymer polypropylene (PP-B), high-melt strength polypropylene (HMS-PP).

[0103] The graphene-based polymer composite modifier 405 also may comprise a polymeric additive 460. The polymeric additive may be a thermoplastic resin, a thermoplastic elastomer, a thermosetting elastomer, a rubber, or any combination thereof. A preferred polymeric additive 460 includes polyvinyl butyral (PVB), polyvinyl alcohol, polyvinyl acetate, ethylene-vinyl acetate (EVA), ethylene propylene diene rubber, ethylene propylene rubber, acrylic resin, tackifiers resin, or any combination thereof.

[0104] Another example of matrix polymer is elastomer or rubber. The elastomer in the present innovation includes, but not limited to, thermoplastic elastomer, thermoset elastomer, natural rubber, and synthetic rubber. The thermoplastic elastomer may be EPR, SBR, EVA, or any other thermoplastic as known in the art. The synthetic rubber may, without limitations, be SBR, BR, IR, EPDM. The elastomer may be in its virgin state, or maybe at an end-use rubber produce, a recycled rubber product, or a reproduced product, for example, a ground tire rubber, a recycled rubber, a devulcanized rubber, or any combination thereof. Polymeric additives may also be added with an elastomer polymer matrix to improve the stability and compatibility. The polymeric additives herein refer to oxidized or functionalized polymers with improved polarities, preferably to be functionalized polyolefins, including but not limited to, oxidized polyethylene (OPE), polyethylene wax (PE-wax), oxidized polypropylene (OPP), maleic anhydride-grafted polyolefins (MA-g-PO), maleic anhydride-grafted polyethylene (MAPE), metallocene polyethylene (mPE), ethylene butene copolymer based (EBC), Glycidyl Methacrylate (GMA), adhesive resins, polyolefin-based adhesive resins.

[0105] The matrix polymer, and any combination of polymeric additives may adjust the surface energy at the interface, improve the stability of the matrix polymer, improve the interaction with the asphalt cement and/or asphalt concrete mixture, facilitate graphene and filler dispersion, improve mechanical performance and aging stability.

[0106] *Wet Mixing:*

[0107] In some embodiments, the graphene-based modifier is blended into base asphalt cement. The incorporation or blending of graphene polymer composite modifier into base asphalt cement may be done via a well-known “wet mixing” step, using any method that falls in the concept of agitation mixing, for example, without any limitation, rod or stick stirrer, overhead stirrer, impeller agitator, vortex mixer, rotary drum mixer, high shear mixer, static mixer, planetary mixer, homogenizer, asphalt cement mill, etc.

[0108] The joule heating flashed graphene may improve the dispersibility and stability of polymer modifier 405 in base asphalt cement, to yield a more uniform and stable modified asphalt cement. The graphene based modifiers provide improved asphalt cement stability, reduce polymer separations in the “wet mixing” or in modified asphalt cement and improve the rheology properties of asphalt cement and its mechanical performance. The improved rheology properties may extend the service temperature range at both the high end and low end as measured by the standard performance grading scale as described by American Association of State Highway and Transportation Officials (AASHTO) and American Society for Testing and Materials (ASTM) testing methods.

[0109] According to some embodiments, the joule heating flashed graphene is further incorporated with surface functionalities, for example, with Zn- or S-based doping, islands, domains, and heterogeneous structures that may accelerate and/or initiate the crosslinking of polymer networks, specifically when elastomer-based matrix polymer is employed, as well as with the asphalt cement binder.

[0110] There is no specific requirement on the physical form of the matrix polymer or polymeric additives 422, which may be in pellet form, or flake form, or fine powder form, or wax form. The joule heating flashed graphene used in the compounding may be in pellet form or fine powders, preferably to be fine powders for ease of combination with the matrix polymer. According to some embodiments, graphene may be pre-mixed with the matrix polymer, polymeric additives 422, or both, before being fed into the extruder 418 or any other mixing tool. Alternatively, graphene may be fed directly into the extruder 418. Moreover, graphene may be first compounded with polymeric additives, matrix polymer, or a component of matrix polymer at high concentrations as a masterbatch 420

and then let down with an additional extrusion 425 step. The graphene concentration in masterbatch 420 may be 5 to 70%, preferably 10 to 20%. Subsequently, the graphene-polymer composite modifier may be processed into pellet, flake, granular, or fine powders.

[0111] The graphene-polymer composite modifier in the “wet mixing” step may be 0.01 – 20% of the base asphalt cement asphalt cement. The graphene-polymer composite modifier may be mixed in asphalt cement at high concentrations as masterbatches that are diluted to lower concentrations by mixing with more base asphalt cement in a later process.

[0112] In some embodiments according to the present innovation, joule heating flashed graphene may be used directly as graphene modifier to asphalt cement, without pre-compounding into a graphene-polymer composite modifier. The graphene modifier may improve the rheology of asphalt binder in terms of rheology and low-temperature stiffness. It may also improve asphalt cement’s aging performance by reducing the oxidation and enable a longer service life. The graphene modifier may also improve the thermal conductivity and UV resistance of asphalt cement. The graphene is used in asphalt cement binder in an amount of from 0.0001% to 20%.

[0113] *Dry Mixing*

[0114] In some embodiments, asphalt concrete mixture including a flash graphene based modifier is fabricated using the “dry mixing” method. Dry mixing is a standard operation done at asphalt plants, particularly in a feeding location. The graphene-based modifier can be introduced as one material and/or with an additional materials/additives and will be introduced via initial mixing with warm aggregate to yield a uniform aggregate mixture. The latter is further maintained at an elevated temperature to allow the graphene-based modifier to turn into a uniform coating. The graphene-based modifier and/or additives can also be introduced with a RAP (recycled asphalt) stream that is further mixed with fresh hot aggregates or any other plausible feeding port to introduce sufficient mixing and contact between the graphene polymer- composite pellets and the aggregate prior to mixing with asphalt cement.

[0115] Additional filler or solid additives may also be mixed in this step. The filler and additives include, without any limitation, clay, limestone, talc, mica, polymer fibers,

carbon fibers, carbon nanotubes, metal fiber, glass fiber, glass whiskers. The asphalt cement is subsequently mixed with the marinated graphene-based modifier/aggregate mixture that will result in a homogenous mixture of the coated aggregates, fillers, and asphalt cement. The asphalt cement may be a virgin base asphalt cement (i.e. neat asphalt cement), or one modified by polymers or pre-blended with other additives.

[0116] The “dry mixing” of graphene-based modifiers further mitigates any issues that can arise from phase separation between polymer modifiers and asphalt cement with low compatibility and improves the stability and service life of asphalt concrete mixture. Furthermore, the polyhedral graphene modifier may also improve the rheology and aging performance of asphalt cement, without any matrix polymer.

[0117] The graphene-polymer composite modifier in the “dry mixing” step may be 0.1 – 10% of the base asphalt cement.

[0118] *Additives*

[0119] Any additional bitumen additives may be added in the “wet mixing” or “dry mixing” process. These additives include, without any limitation, other polymers, polyolefins, SBS, SBR, SB, GTR (ground tire rubber) PET, RET- Reactive elastomeric terpolymers, hybrids of these, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions – amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, crosslinkers- sulfur, polyphosphoric acid (PPA), Isocyanate based, sulfur less agents, antioxidants, functional fillers, gilsonite, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, carbon fibers, pigments, antioxidants, UV light absorbers, flame retardants, radical scavengers, plasticizers, or other modifiers.

[0120] The asphalt cement binder used may be 2 – 10% of the base asphalt cement, preferably 4 – 8%, more preferably 4 – 5%.

[0121] The graphene-polymer composite used may be composed of 10-99% polyethylene, 10-50% polypropylene, 0-50% ethyl vinyl acetate or poly vinyl butyral.

[0122] **Performance Examples:**

[0123] Performance-Verification of the embodiments described herein were done following specialty laboratory test methods, as well as well-accepted by the US DOTs and Canadian MTO as described. These tests are well known in North America (i.e. FHWA) and are being utilized by DOTs/MTO for their performance testing.

[0124] Asphalt Cements:

[0125] Referring to Figures 5 through 6, shown therein are tables of example results of testing performed on a neat asphalt cement and asphalt cement modified with SBS or graphene based modifiers. The asphalt cement modified with graphene based modifiers were exemplar embodiments according to the disclosure provided herein. Binder stiffness was measured by Dynamic Shear Rheometer (DSR) (AASHTO T315) and low temperature flexibility as measured by Bending Beam Rheometer (BBR) (AASHTO T313).

[0126] To obtain the tested embodiments, the modification of the asphalt cement with SBS polymer or graphene-based modifiers was prepared by using a typical wet mixing procedure. A rotor-stator type of shear mixing tool was used to mix the asphalt cement.

[0127] The asphalt cements modified with graphene-based modifiers were compared to control asphalt cements including a base asphalt cement (Example 1) and an SBS polymer modified asphalt cement (Example 2). The base binder was performance grade 52-34. The SBS polymer modified asphalt cement was a wet mixing of a 2.5% SBS standard polymer modifier such as LG 501 and a 0.25% crosslinker such as ReactiLINK™ into the base asphalt cement. The crosslinker was a standard crosslinking agent to crosslink SBS and provide better stability.

[0128] The graphene-based modifiers of Examples 3, 4, 6 and 8 were added into asphalt cement using a wet mixing method. The wet mixing method included pre-heating the asphalt cement and dispersing graphene modifier into the asphalt cement. The pre-heating of asphalt cement was done using an oven or other heating tools. The pre-heat temperature was allowed to vary between 130 to 180°C, preferably 160 – 170°C. Temperature was maintained using a heating mantel or hot plate with a temperature probe to monitor and control the binder's temperature.

[0129] Improvements to the asphalt cement included improved rheology of asphalt cement in terms of stiffness (including binder stiffness), low temperature flexibility/stiffness, aging performance to allow the asphalt cement or asphalt pavement such as HMA or WMA to have a longer service life, and thermal conductivity and UV resistance of asphalt cement or concrete.

[0130] *Polyhedral Graphene Modifiers*

[0131] Referring specifically to Figure 5, shown therein is the comparison table 500 of the control asphalt cements and two PG modified asphalt cements. The first PG modified asphalt cement (Example 3) was graphene manufactured via flash joule heating from a high-quality carbon black feedstock (PG-1) blended into the neat asphalt cement at 2 wt% concentrations. The second PG modified asphalt cement (Example 4) was graphene manufactured via flash joule heating from a recycled tire carbon feedstock (PG-2) blended into the neat asphalt cement at 2 wt% concentrations.

[0132] The asphalt cement formulated with graphene modifier in this invention is suitable for pavement applications such as hot mix asphalt (HMA) or warm mix asphalt (WMA). The asphalt cement of the present example may also find use in other asphalt applications such as roofing, shingles, asphalt emulsions. Etc.

[0133] The average ash content of the neat asphalt cement and modified asphalt cement were compared following Ontario Ministry of Transportation (MTO) LS-227. Compared to the neat asphalt cement and asphalt cement modified by SBS and cross-linker, the PG-modified asphalt cement shows some minimal increase in ash content.

[0134] The rotational viscosity of the neat asphalt cement and modified asphalt cement were compared following AASHTO T316. Compared to the neat asphalt cement and asphalt cement modified by SBS and cross-linker, the PG-modified asphalt cement shows comparable viscosity, indicating no impact on pumpability and workability during operation.

[0135] The storage stability of the neat asphalt cement and modified asphalt cement were compared following ASTM D7173 and evaluated by dynamic shear rheometer following AASHTO T315. Compared to the neat asphalt cement and asphalt

cement modified by SBS and cross-linker, the PG-modified asphalt cement showed very similar stabilities, indicating the PG is easily dispersed in the asphalt cement with very good compatibility.

[0136] The performance grade of the neat asphalt cement, asphalt cement modified with SBS and cross-linker, and asphalt cement modified with two PG variables were compared following ASTM D7643 and evaluated by AASHTO T315 and AASHTO T313. Both asphalt cement modified by PGs showed at least a one bump (6° C) increase in high continuous grading temperature compared with neat asphalt cement, without impacting the low continuous grading temperature.

[0137] *PG Polymer Composite Modifiers*

[0138] Referring back to Figure 6, shown therein is the comparison table 600 of the control asphalt cements, two polymer composite modified asphalt cements (Example 5: thermoplastic polymer composite (TPC) and Example 7: thermoplastic elastomer composite (TEC)), and two PG polymer composite modified asphalt cements (Example 6: PG:TPC and Example 8: PG:TEC). The TPC of Example 6 included a thermoplastic blend of polyethylene, polypropylene, polyvinyl butyral with loading of 2.5% with respect to the binder. The TEC of Example 8 included an elastomer blend of polyethylene, polypropylene, ethyle vinyl acetate with loading of 2.0 % with respect to the binder. The polyethylene (PE), polypropylene (PP), and polyvinyl (PVB) was either in pellet form or powder form.

[0139] The asphalt cement formulated with graphene modifier in this invention is suitable for pavement applications such as hot mix asphalt (HMA) or warm mix asphalt (WMA).

[0140] The graphene-polymer composite was made via a polymer extrusion process. The polymer was a thermoplastic, homo-polymer, a co-polymer, thermoplastic elastomer, thermoset, or a mix of multiple polymers. The polymer composite and graphene – polymer composite were compounded using a twin-screw extruder using a specific temperature profile, screw design, screw speed and feed rate to accommodate the proper blending of polymers and optimal graphene dispersion. Polymer blends were in powder or pellet forms and fed directly via the main feeding port along with the

graphene powder also fed via a side feeder. When using polymer in powder form, the graphene was pre-blended via mechanical mixing with one or more polymers and the mixture was fed via main or side feeder. Graphene powder was also separately extruded with one of the polymers to make a high-concentration master batch that was then further let down in the next extrusion with the other polymer composition.

[0141] For Example 6, polyhedral graphene produced from a recycled tire carbon feedstock was compounded with PE, PP, and PVB referred to collectively as graphene – polymer composite UM-1. For Example 8, polyhedral graphene produced from a recycled tire carbon feedstock was compounded with PE, PP, and EVA referred to collectively as graphene – polymer composite UM-2.

[0142] The average ash content of the neat asphalt cement and modified asphalt cement were compared following MTO LS-227. Compared to the neat asphalt cement and asphalt cement modified by SBS and cross-linker, the graphene-polymer composite modified asphalt cement showed comparable level of ash content with no increase.

[0143] The rotational viscosity of the neat asphalt cement and modified asphalt cement were compared following AASHTO T316. Compared to the neat asphalt cement, the graphene-polymer composite modified asphalt cement showed slight increase viscosity compared to asphalt cement modified by SBS and cross-linker, indicating no impact on pumpability and workability during operation.

[0144] The storage stability of the neat asphalt cement and modified asphalt cement were compared following ASTM D7173 and evaluated by dynamic shear rheometer following AASHTO T315. Compared to the neat asphalt cement and asphalt cement modified by SBS and cross-linker, the graphene- polymer composite modified asphalt cement showed minimal reduction in stabilities (Examples 6, 8), while the control polymer composite without graphene (Examples 5, 7) were much less stable, indicating the graphene-polymer composite modifier contributed to the compatibilization of the polymers composite and was easily dispersed in the asphalt cement with very good compatibility.

[0145] The performance grade of the neat asphalt cement, asphalt cement modified with SBS and cross-linker, and asphalt cement modified with different graphene – polymer composites variables were compared following ASTM D7643 and evaluated by AASHTO T315 and AASHTO T313. The asphalt cement modified by graphene-polymer composite with PVB showed a 2 bumps (12°C) increase in high continuous grading temperature compared with neat asphalt cement, without impacting the low continuous grading temperature. The asphalt cement modified by graphene-polymer composite with EVA showed 1 bump (6°C) increase in high continuous grading temperature compared with neat asphalt cement, with minimal impact on the low continuous grading temperature.

[0146] Asphalt Concretes

[0147] Referring to Figure 7, shown therein is a table 700 of example results of testing performed on a base or neat asphalt concrete and base or neat asphalt concrete modified with graphene-based modifiers. The asphalt concrete modified with graphene based modifiers were exemplar embodiments according to the disclosure provided herein. Rutting in terms of binder stiffness at high temperatures was measured by Hamburg Wheel-Track Testing (HWWT) according to AASHTO T324, resistance to cracking susceptibility in terms of low temperature fracture energy was measured by Disk-shaped Compact Tension (DCT) according to AASHTO T393, and resistance to cracking by differentials in traffic frequency in terms of intermediate temperature flexibility was measured by Semi-Circular Bend (SCB) according to ASTM D7313.

[0148] Hamburg Wheel-Track Testing (HWWT): rutting and moisture susceptibility

[0149] Hamburg Wheel Tracking (HWT) Test in accordance with AASHTO T324 at one (1) temperature of 50°C. This test provides insight into the aggregate skeleton stability and binder stiffness in relation to rutting/shoving resistance. The HWT test was conducted while specimens are submerged in hot water, which could provide further insight into any performance issues related to moisture susceptibility.

[0150] Disk-shaped Compact Tension (DCT): fracture energy over low temperatures, cracking

[0151] Disk-Shaped Compact Tension Test (DCT) Test in accordance with AASHTO T393 is used to characterize the low temperature flexibility at cold testing temperature of -24°C. This testing temperature represents the performance grade XX-34 climate zone.

[0152] Semi-Circular Bend (SCB): intermediate cracking, differentials in traffic frequency.

[0153] Semi-Circular Bend Test (SCB) in accordance with ASTM D7313 is used to characterize the intermediate temperature flexibility at testing temperature of 25° C.

[0154] Control asphalt concrete samples (Example 9) were prepared by blending a base asphalt cement with aggregates using a wet mixing method as described previously. This type of hot mix asphalt is used in existing systems on residential roads and lower volume arterial roads. The base asphalt concrete mix design was 12.5 – Category C– with the same performance grade 52-34 binder include Mix volumetrics Evaluation with One Point Design Check (OPDC) using Superpave volumetrics properties.

[0155] For Examples 10 and 11 a graphene-polymer composite modifier, TPC and TEC respectively, was added into asphalt cement prior to blending of the modified asphalt with the asphalt concrete into a hot mix asphalt. The modifier was added using a wet mixing method previously described with a loading of 2.5% with respect to the binder.

[0156] For Examples 12 through 14, a graphene-polymer composite modifier was added into asphalt concrete using a dry mixing method during the preparation of hot mix asphalt. The dry mixing method included pre heating the aggregates at 139°C overnight, and the asphalt cement to 139°C for 1.5 hr. The graphene -polymer composite modifier was then added and mixed with hot aggregate in a standard mixing container for 45 seconds for adequate distribution of the composite. The container and the aggregate mix were then conditioned in the oven at a temperature of 160°C, for 30 min in order to soften and melt the composite till some coating was observed on the aggregate before adding the asphalt cement and further mix. Asphalt cement was then added to the mixture for a total mixing time of 1 min and until full coating was observed. The mix was further

conditioned at a compaction temperature of 127°C for four hours as recommended by the testing standard for lab-produced mixes.

[0157] In Example 12 the graphene-polymer composite modifier was a TPC blend with loading of 5% with respect to the binder. In Examples 13 and 14 the graphene-polymer composite modifier was a TEC blend with loading of 5% and 3.5%, respectively with respect to the binder.

[0158] In some embodiments, the addition of graphene-polymer composite modifiers provides improved resistance to rutting in terms of better binder stiffness at higher temperatures, improved resistance to cracking susceptibility in terms of low temperature fracture energy, and improved resistance to cracking by differentials in traffic frequency, in terms of intermediate temperature flexibility. The asphalt concrete formulated with graphene-polymer composite modifier may be used in hot mix asphalt (HMA) or warm mix asphalt (WMA) using both “wet mixing” and “dry mixing” for pavement applications with improved performance.

[0159] Based on the findings from the Illinois Flexibility Index Test (I-FIT), Disk-Shape Compaction Tensile Test (DCT), and Hamburger Rut Test (HDWT) conducted on three asphalt mixes via wet mix method, the graphene- polymer composite modifier made with PVB demonstrated improvements over the neat asphalt concrete in fatigue cracking resistance (27.72%) and rut resistance (7.1%) of the asphalt mix when added (Example 10). The Fracture Energy was not impacted compared to the control mix value, suggesting no impact on thermal cracking resistance. The graphene- polymer composite modifier made with EVA demonstrated improvements over the neat asphalt concrete in fatigue cracking resistance (38.61%) and significant rut resistance (82.6%) of the asphalt mix. However, the Fracture Energy decreased by -3.8% from the control mix value, suggesting a slight reduction in thermal cracking resistance. The most significant improvement was observed in rut resistance, with a percentage change of 82.6% in HDWT (Passes at 12.5 mm rut depth). This indicates that the mix gained stiffness, leading to better resistance against rutting, but potentially reduced ability to withstand cracking at low temperatures (Example 11).

[0160] Based on the findings from the Illinois Flexibility Index Test (I-FIT), Disk-Shape Compaction Tensile Test (DCT), and Hamburger Rut Test (HDWT) conducted on three asphalt mixes via dry mix method, the graphene- polymer composite modifier made with PVB demonstrated more positive effects over the neat asphalt concrete and compared to the wet mix on fatigue cracking resistance (27.72% ->31.68%), thermal cracking resistance (0.7%->4.5%), and rut resistance (7.1%->59.6%) (Example 12). The graphene- polymer composite modifier made with EVA demonstrated either less or negative effects over the neat asphalt concrete and compared to the wet mix on overall mix performance properties. Fatigue cracking resistance reduced (38.61%->7.92%), minimal change to thermal cracking resistance (-3.8->-5%), and some minimal reduction in rut resistance (82.6%->70.3%) (Example 13).

[0161] Further testing to evaluate the impact of higher levels of graphene-polymer composite modifier loading on the increased stiffness and reduced flexibility needed for cracking resistance was done at lower loading levels for the graphene- polymer composite modifier made with EVA.

[0162] Based on the findings from the Illinois Flexibility Index Test (I-FIT), Disk-Shape Compaction Tensile Test (DCT), and Hamburger Rut Test (HDWT) conducted on three asphalt mixes via dry mix method, reducing the loading of the graphene- polymer composite modifier made with EVA to 3.5% demonstrates a notable improvement over the neat asphalt, with a 34.9% enhancement in in fatigue cracking resistance and a 26.5% improvement in thermal cracking resistance. This improvement is consistent with the role of the graphene-polymer composite modifier as a stiffness provider. The loading levels of the graphene-polymer composite modifier should be considered at optimal levels as to low loading level as also recued the rutting resistance over the neat asphalt (70.32% -> 10.09%).

[0163] Embodiments

[0164] According to some embodiments, there is a graphene asphalt cement composite. The graphene asphalt cement composite includes an asphalt cement, also known as asphalt, asphalt binder, or asphalt cement. The graphene serves as an additive, modifier, or performance promoter.

[0165] In some embodiments, graphene may be a turbostratic flake graphene. The turbostratic flake graphene can be made from a natural material, for example, coke or coal; or from a processed material, for example, petroleum-based coke, processed biomass, etc.

[0166] In some embodiments, graphene may be a polyhedral graphene. The polyhedral graphene may be made from a carbon black.

[0167] In some embodiments, turbostratic flake graphene and polyhedral graphene may be made from recycled materials, such as recycled rubbers, tire rubbers, or plastics.

[0168] In some embodiments, turbostratic flake graphene and polyhedral graphene may be made from biomass wastes or low-cost feedstocks.

[0169] In some embodiments, turbostratic fiber graphene and flake graphene may be made from biomass wastes or low-cost fibrous feedstocks.

[0170] In some embodiments, graphene can be added directly as an additive at low concentrations to asphalt cement to adjust asphalt cement's rheology and improve its mechanical performance and aging performance when used in asphalt concrete. The temperature performance can be fatigue cracking resistance, thermal cracking resistance, rutting-resistant, higher grading temperatures, lower grading temperature, etc. The aging performance can be a longer service life with improved mechanical durability, improved stability to oxidation, improved resistance to stripping by moisture damage, drain down, etc.

[0171] In some embodiments, the graphene is modified to have surface functionalities different from pristine graphene. Such a modification can improve the affinity of graphene and asphalt cement, and result in a better dispersion and stability, and an enhanced binder performance.

[0172] According to some embodiments, the modification can be controlled by the flash process. The flash process can be a control of defects density, flash with a chemical or chemicals to create selective dopants, or flash in a gas or gases to create selective dopants.

[0173] According to some embodiments, the modification can be a post-process or post-treatment. Such a post-process or post-treatment can be a mechanical mill or chemical functionalization, or plasma etching.

[0174] According to some embodiments, the modification can be achieved by a surfactant, dispersant, organic or inorganic ligand, coupling agent, etc.

[0175] In some embodiments, graphene is blended in asphalt cement using a typical wet mixing tool at temperatures above asphalt cement's melting temperature. The mixing tool can be a high-shear mixer, standard high shear mil such as commonly used in asphalt terminals or similar.

[0176] In some embodiments, graphene can be compounded into polymer at low concentrations or as a master batch to make a graphene-polymer composite as an additive to asphalt cement to improve the mechanical and aging performance.

[0177] In some embodiments, polymer can be a neat polymer or blends of several types of polymers. The polymer can be Polyethylene, Polypropylene, Poly Vinyl Butyral, Ethylene Vinyl Acetate, Ethylene Acrylate, Ethylene Alkyl Acrylate, EPDM rubber, GTR (Ground Tire Rubber), Polyethylene Terephthalate, or a resin, such as Escorez resin, or a blend of these polymers.

[0178] In some embodiments, polymer can be functionalized, for example, with maleic anhydride, or Glycidyl Methacrylate, grafted with Polyethylene, Polypropylene, Ethylene Vinyl Acetate

[0179] In some embodiments, the polymers could be linear, branched, homopolymers, copolymers, grafted polymers, block polymers, random polymers, or any possible polymer configuration with different crystallinity levels and density levels.

[0180] According to some embodiments, the polymer(s) can be non-used neat polymer or from recycled polymer material.

[0181] In some embodiments, the polymer(s) can be crosslinked by compounding with a crosslinker. Such a crosslink can be a sulfur or sulfur-based crosslinker, Isocyanate crosslinker, or a peroxide crosslinker,

[0182] In some embodiments, the graphene – polymer composite can be used in parallel to other asphalt modifiers and additives such as, other polymers, polyolefins, SBS, SBR, SB, GTR (ground tire rubber) PET, RET- Reactive elastomeric terpolymers, hybrids thereof, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions – amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, crosslinkers- sulfur, polyphosphoric acid (PPA), Isocyanate based, sulfur less agents, antioxidants, functional fillers, gilsonite, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, carbon fibers, pigments, antioxidants, UV light absorbers, flame retardants, radical scavengers, plasticizers, or other modifiers.

[0183] According to some embodiments, the graphene-polymer composite is added into asphalt cement by wet mixing directly in the asphalt terminal using a typical wet mixing tool at temperatures above asphalt cement's melting temperature. The mixing tool can be a high-shear mixer, standard high shear mil such as commonly used in asphalt terminals or similar.

[0184] In some embodiments, the graphene-polymer composite is added into asphalt cement by wet mixing to adjust asphalt cement's rheology and improve its mechanical performance and aging performance when used in asphalt concrete. The temperature performance can be fatigue cracking resistance, thermal cracking resistance, rutting-resistant, higher grading temperatures, lower grading temperature, etc. The aging performance can be a longer service life with improved mechanical durability, improved stability to oxidation, improved resistance to stripping by moisture damage, drain down, etc.

[0185] In some embodiments, the wet mixing is done with the addition of a crosslinker. Such crosslink can be a sulfur, sulfur-based chemical, Polyphosphoric Acid (PPA) or a peroxide crosslinker. The crosslinker creates 3D polymer network to improve the asphalt cement's stability.

[0186] According to some embodiments, the graphene-polymer composite is added into asphalt concrete by dry mixing directly to Hot Mix Asphalt (HMA) and Warm

mix asphalt (WMA) in asphalt plant via aggregates drum heater, RAP feeder, aggregate and asphalt cement mixer, etc.

[0187] According to some embodiments, the graphene-polymer composite is added into asphalt concrete by dry mixing directly to Hot Mix Asphalt (HMA) and Warm mix asphalt (WMA) in field asphalt mobile mixer via aggregates drum heater, RAP feeder, aggregate and asphalt cement mixer, etc.

[0188] In some embodiments, the graphene-polymer composite is added into asphalt concrete by dry mixing to improve its mechanical performance and aging performance. The temperature performance can be fatigue cracking resistance, thermal cracking resistance, rutting-resistant, higher grading temperatures, lower grading temperature, etc. The aging performance can be a longer service life with improved mechanical durability, improved stability to oxidation, improved resistance to stripping by moisture damage, drain down, etc.

[0189] While the above description provides examples of one or more apparatus, methods, or systems, it will be appreciated that other apparatus, methods, or systems may be within the scope of the claims as interpreted by one of skill in the art.

Claims:

1. An asphalt modifier for modifying the asphalt cement, the modifier configured to be added to the asphalt cement or concrete and composed of graphene obtained via flash joule heating of a carbon source.
2. The modifier of claim 1 further configured to be added as an additive directly to an aggregate of the asphalt concrete.
3. The modifier of claim 1 further configured to be blended with an asphalt cement, wherein the blending is via a wet mixing tool.
4. The modifier of claim 1, wherein a surface functionality of the graphene is modified by one or more of a flash process, a post-process, a post-treatment, a surfactant, a dispersant, an organic or inorganic ligand, and a coupling agent.
5. The modifier of claim 1, wherein the modifier is a graphene-polymer composite further comprising a polymer and wherein the polymer is obtained from one or more of a non-used polymer material and recycled polymer material.
6. The modifier of claim 5, wherein the polymer comprises one or more of linear, branched polymers, homopolymers, copolymers, grafted polymers, block polymers, random polymers, polyethylene, polypropylene, poly vinyl butyral, ethylene vinyl acetate, ethylene acrylate, ethylene alkyl acrylate, ethylene propylene diene monomer rubber, ground tire rubber, polyethylene terephthalate, and resin.
7. The modifier of claim 5, wherein the polymer is functionalized with one or more of maleic anhydride, or glycidyl methacrylate, grafted with polyethylene, polypropylene, and ethylene vinyl acetate.

8. The modifier of claim 5, wherein the graphene-polymer composite is added into the asphalt concrete by dry mixing directly to one or more of a hot mix asphalt (HMA) and warm mix asphalt (WMA).
9. The modifier of claim 8, wherein the addition of the graphene-polymer composite into the asphalt concrete is via one or more of aggregates drum heater, RAP feeder, aggregate and asphalt cement mixer at one or more of an asphalt cement plant or an in-field asphalt mobile mixer.
10. The modifier of claim 1 further comprising one or more of additional bitumen additives including, other polymers, polyolefins, SBS, SBR, SB, GTR (ground tire rubber) PET, RET- Reactive elastomeric terpolymers, hybrids thereof, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions – amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, crosslinkers- sulfur, polyphosphoric acid (PPA), Isocyanate based, sulfur less agents, antioxidants, functional fillers, gilsonite, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, carbon fibers, pigments, antioxidants, UV light absorbers, flame retardants, radical scavengers, plasticizers.
11. The modifier of claim 1, wherein a morphology of the graphene is one or more of turbostratic, polyhedral, flake, or flake like.
12. The modifier of claim 1, wherein the carbon source is one or more of coal, met coke, pet coke, carbon black, recycled plastics, recycled rubber, biomass/biomass waste, waste tire carbon black, petroleum coke, tire carbon black, carbon black, metallurgical coke, plastic ash, plastic powder, ground coffee, anthracite coal, biomass, low-cost feedstocks, biomass wastes, low-cost fibrous feedstocks, corn starch, pine bark, polyethylene microwax, wax, chemplex 690, cellulose, naptenic oil, asphaltenes, gilsonite, and carbon nanotubes.

13. A method of modifying asphalt comprising adding to asphalt cement or concrete an asphalt modifier composed of graphene obtained via flash joule heating of a carbon source.
14. The method of claim 13, wherein the asphalt modifier is added as an additive directly to an aggregate of the asphalt concrete.
15. The method of claim 13 further comprising blending the asphalt modifier with the asphalt cement via a wet mixing tool.
16. The method of claim 13 further comprising modifying a surface functionality of the graphene by one or more of a flash process, a post-process, a post-treatment, a surfactant, a dispersant, an organic or inorganic ligand, and a coupling agent.
17. The method of claim 13, wherein the asphalt modifier is a graphene-polymer composite further comprising a polymer and wherein the polymer is obtained from one or more of a non-used polymer material and recycled polymer material.
18. The method of claim 17, wherein the polymer comprises one or more of linear, branched polymers, homopolymers, copolymers, grafted polymers, block polymers, random polymers, polyethylene, polypropylene, poly vinyl butyral, ethylene vinyl acetate, ethylene acrylate, ethylene alkyl acrylate, ethylene propylene diene monomer rubber, ground tire rubber, polyethylene terephthalate, and resin.
19. The method of claim 17 further comprising functionalizing the polymer with one or more of maleic anhydride, or glycidyl methacrylate, grafted with polyethylene, polypropylene, and ethylene vinyl acetate.
20. The method of claim 17, wherein adding the graphene-polymer composite into the asphalt concrete by dry mixing directly to one or more of a hot mix asphalt (HMA) and warm mix asphalt (WMA).

21. The method of claim 20, wherein adding the graphene-polymer composite into the asphalt concrete is via one or more of aggregates drum heater, RAP feeder, aggregate and asphalt cement mixer at one or more of an asphalt cement plant or an in-field asphalt mobile mixer.
22. The method of claim 13 further comprising adding one or more of additional bitumen additives including, other polymers, polyolefins, SBS, SBR, SB, GTR (ground tire rubber) PET, RET- Reactive elastomeric terpolymers, hybrids thereof, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions – amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, crosslinkers- sulfur, polyphosphoric acid (PPA), Isocyanate based, sulfur less agents, antioxidants, functional fillers, gilsonite, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, carbon fibers, pigments, antioxidants, UV light absorbers, flame retardants, radical scavengers, plasticizers.
23. The method of claim 13, wherein a morphology of the graphene is one or more of turbostratic, polyhedral, flake, or flake like.
24. The method of claim 13, wherein the carbon source is one or more of coal, met coke, pet coke, carbon black, recycled plastics, recycled rubber, biomass/biomass waste, waste tire carbon black, petroleum coke, tire carbon black, carbon black, metallurgical coke, plastic ash, plastic powder, ground coffee, anthracite coal, biomass, low-cost feedstocks, biomass wastes, low-cost fibrous feedstocks, corn starch, pine bark, polyethylene microwax, wax, chemplex 690, cellulose, naptenic oil, asphaltenes, gilsonite, and carbon nanotubes.
25. A modified asphalt cement composed of an asphalt modifier, the asphalt modifier composed of graphene obtained via flash joule heating of a carbon source.
26. The modified asphalt cement of claim 25, wherein the asphalt modifier is configured to be added as an additive directly to an aggregate of an asphalt

concrete such that the asphalt modifier of the modified asphalt cement is asphalt modifier of the asphalt modifier and aggregate mixture.

27. The modified asphalt cement of claim 25, wherein the asphalt cement is configured to be blended with the asphalt modifier via a wet mixing tool.
28. The modified asphalt cement of claim 25, wherein a surface functionality of the graphene is modified by one or more of a flash process, a post-process, a post-treatment, a surfactant, a dispersant, an organic or inorganic ligand, and a coupling agent.
29. The modified asphalt cement of claim 25, wherein the asphalt modifier is a graphene-polymer composite further comprising a polymer and wherein the polymer is obtained from one or more of a non-used polymer material and recycled polymer material.
30. The modified asphalt cement of claim 29, wherein the polymer comprises one or more of linear, branched polymers, homopolymers, copolymers, grafted polymers, block polymers, random polymers, polyethylene, polypropylene, poly vinyl butyral, ethylene vinyl acetate, ethylene acrylate, ethylene alkyl acrylate, ethylene propylene diene monomer rubber, ground tire rubber, polyethylene terephthalate, and resin.
31. The modified asphalt cement of claim 29, wherein the polymer is functionalized with one or more of maleic anhydride, or glycidyl methacrylate, grafted with polyethylene, polypropylene, and ethylene vinyl acetate.
32. The modified asphalt cement of claim 29, wherein the graphene-polymer composite is added into the asphalt concrete by dry mixing directly to one or more of a hot mix asphalt (HMA) and warm mix asphalt (WMA).

33. The modified asphalt cement of claim 32, wherein the addition of the graphene-polymer composite into the asphalt concrete is via one or more of aggregates drum heater, RAP feeder, aggregate and asphalt cement mixer at one or more of an asphalt cement plant or an in-field asphalt mobile mixer.
34. The modified asphalt cement of claim 25 further comprising one or more of additional bitumen additives including, other polymers, polyolefins, SBS, SBR, SB, GTR (ground tire rubber) PET, RET- Reactive elastomeric terpolymers, hybrids thereof, warm mix additives, foaming technologies, wax additives, chemical additives, adhesion promotions – amines, phosphate esters, silanes, recycling agents, rejuvenators, stiffening agents, crosslinkers- sulfur, polyphosphoric acid (PPA), Isocyanate based, sulfur less agents, antioxidants, functional fillers, gilsonite, hydrated lime, portland cement, fly ash, steel slag, fibers, cellulose, minerals, aramid, carbon fibers, pigments, antioxidants, UV light absorbers, flame retardants, radical scavengers, plasticizers.
35. The modified asphalt cement of claim 25, wherein a morphology of the graphene is one or more of turbostratic, polyhedral, flake, or flake like.
36. The modified asphalt cement of claim 25, wherein the carbon source is one or more of coal, met coke, pet coke, carbon black, recycled plastics, recycled rubber, biomass/biomass waste, waste tire carbon black, petroleum coke, tire carbon black, carbon black, metallurgical coke, plastic ash, plastic powder, ground coffee, anthracite coal, biomass, low-cost feedstocks, biomass wastes, low-cost fibrous feedstocks, corn starch, pine bark, polyethylene microwax, wax, chemplex 690, cellulose, naptenic oil, asphaltenes, gilsonite, and carbon nanotubes.