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(54) **SULFONATED POLYOLEFIN-BASED FLAME
RETARDANT MATERIAL**

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(57) **ABSTRACT**

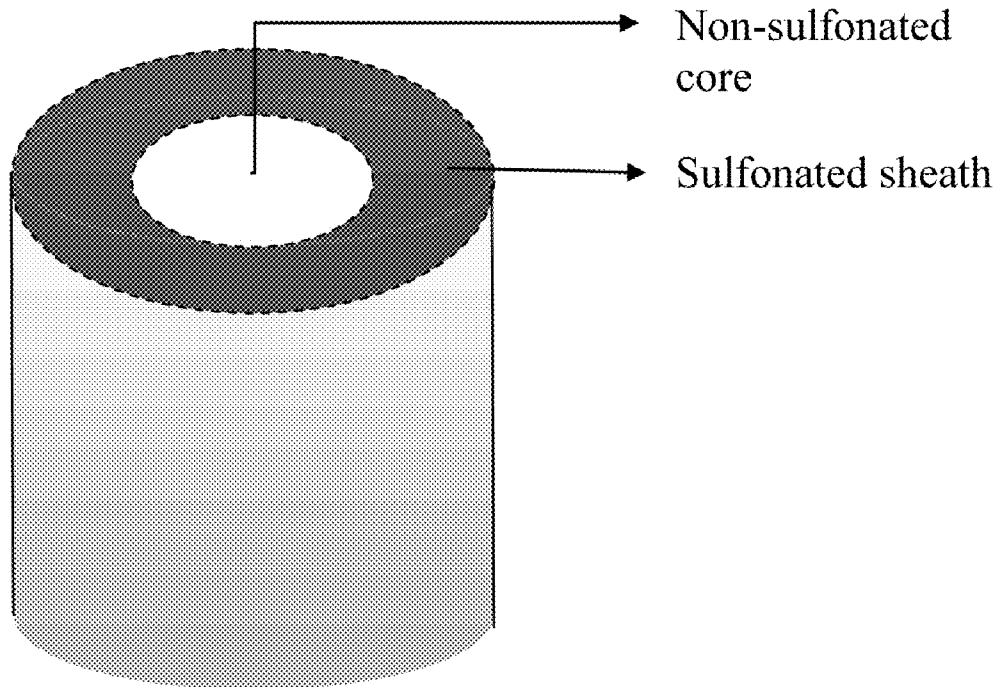
(21) Appl. No.: **14/175,218**

Disclosed herein is a flame retardant composition comprising sulfonated polyolefin and a SO₂-scavenging material and/or a flame retardant material that is not a sulfonated polyolefin. Also disclosed is a flame-resistant composite comprising a host material in which is incorporated sulfonated polyolefin as a flame retardant composition. Further disclosed are methods for producing the flame retardant composition and flame-resistant composites.

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Related U.S. Application Data

(60) Provisional application No. 61/762,489, filed on Feb. 8, 2013.



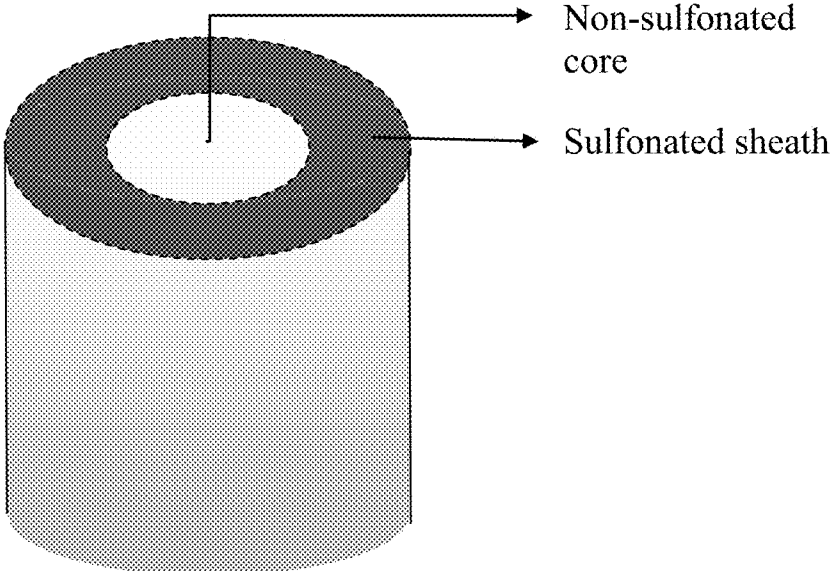


FIG. 1

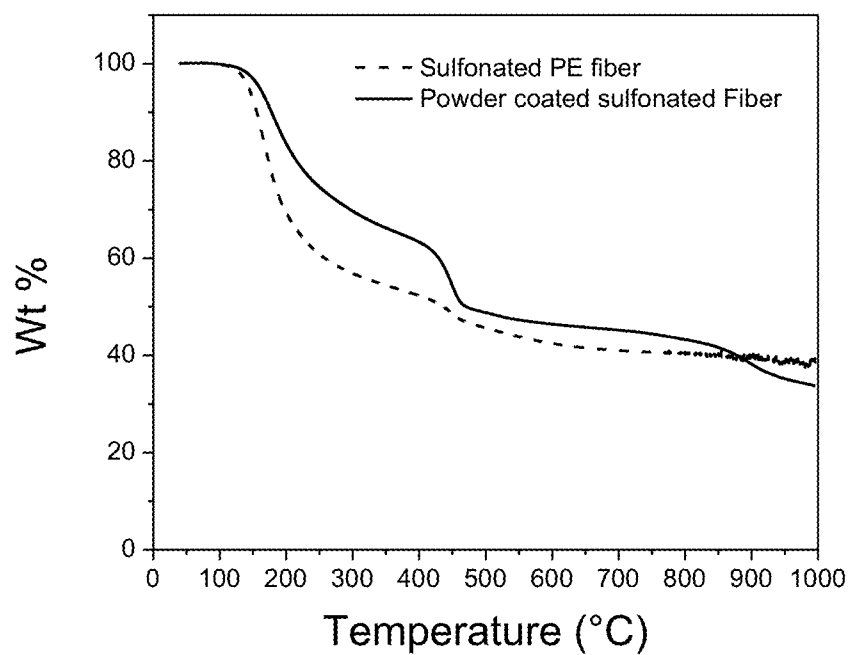


FIG. 2

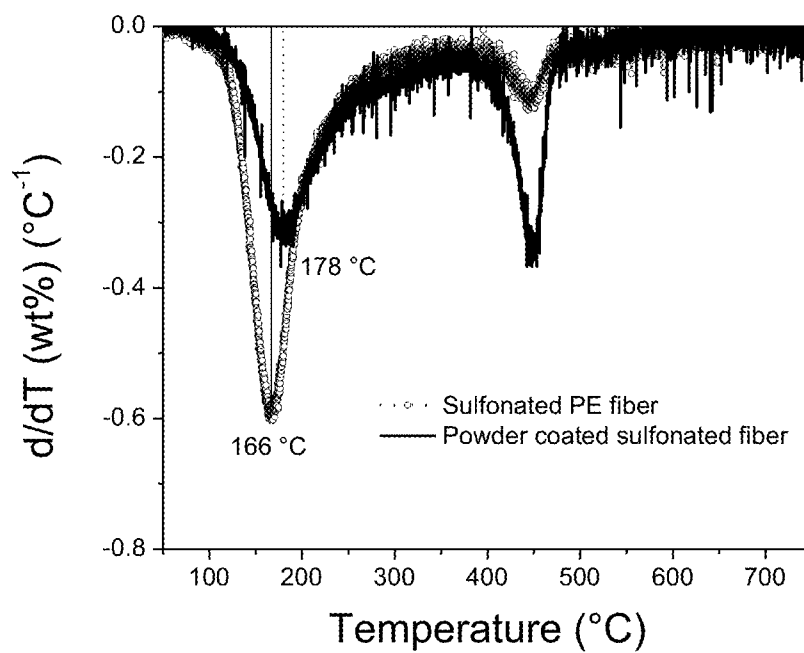


FIG. 3

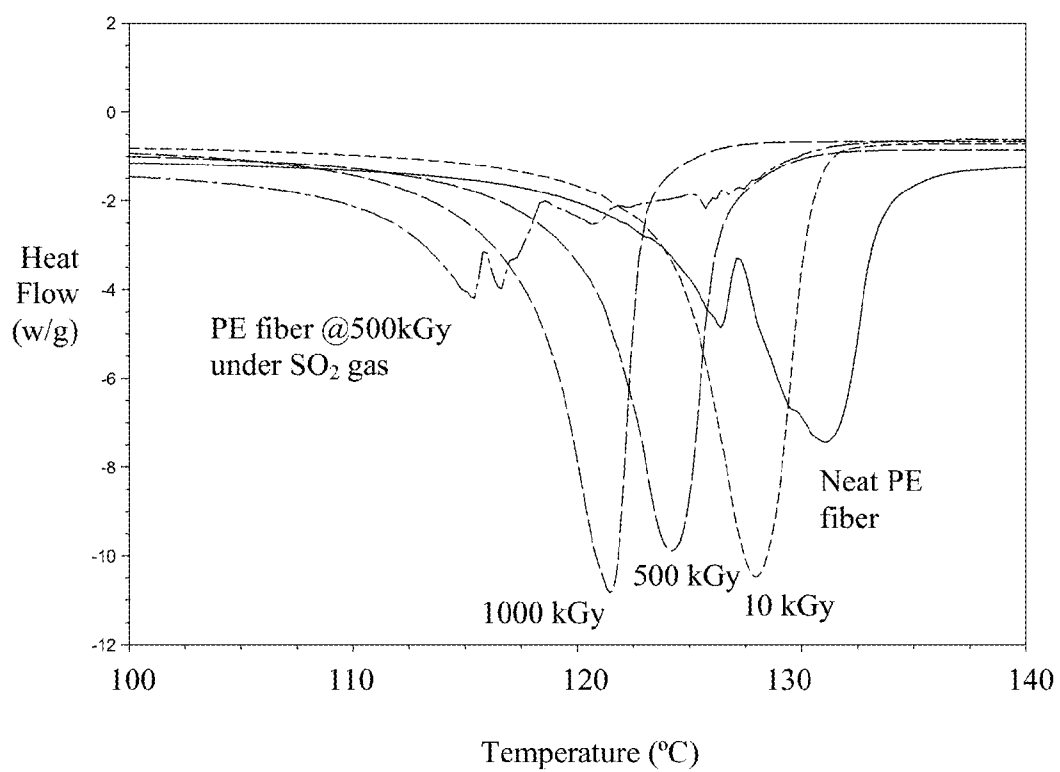


FIG. 4

SULFONATED POLYOLEFIN-BASED FLAME RETARDANT MATERIAL

[0001] The present application claims benefit of U.S. Provisional Application No. 61/762,489, filed on Feb. 8, 2013, all of the contents of which are incorporated herein by reference.

[0002] This invention was made with government support under Prime Contract No. DE-AC05-000R22725 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates, generally, to flame retardant materials, and more particularly, to sulfonated forms of such compositions.

BACKGROUND OF THE INVENTION

[0004] Flame retardant materials are produced in large quantities and incorporated into numerous everyday articles in order to meet fire safety codes and regulations. Nevertheless, numerous drawbacks and concerns exist with their use. For example, many flame retardant substances are either too costly, toxic, or difficult to incorporate into a particular material of interest. Thus, there is a continuing effort to find flame retardant materials that are effective, economical, non-toxic, and can be readily incorporated into other materials, such as textiles and fabrics.

SUMMARY OF THE INVENTION

[0005] The instant disclosure describes a new class of flame retardant compositions based on sulfonated forms of neat or recycled polyolefin-based fibers. The flame retardant compositions described herein are advantageously highly effective, cost efficient, and can be readily incorporated into a range of materials to render them flame resistant. In particular, since the developed fibers can typically exhibit elongation characteristics of >8%, or 12-15%, the filaments can be weaved to form flame retardant fabric. Moreover, by appropriate measures, as further described below, these flame retardant compositions can be rendered substantially non-toxic without a deleterious effect on their flame retardant abilities. In particular embodiments, the sulfonated polyolefin fiber is combined with a SO₂-scavenging material in order to decompose toxic SO₂ fumes formed when the sulfonated polyolefin fiber is subjected to a high temperature, such as provided by a flame.

[0006] In another aspect, the invention is directed to a flame-resistant composite that includes the sulfonated polyolefin flame retardant composition described above incorporated into a material in need of flame resistance. The invention is also directed to an article (e.g., a textile or fabric) composed completely of the flame retardant composition described above, or in combination with at least one other material in need of flame resistance.

[0007] In yet other aspects, the invention is directed to methods for producing the flame retardant composition described above, or for producing a flame-resistant article, such as a flame-resistant textile or fabric. In a method for producing a flame retardant composition, the method includes combining sulfonated polyolefin with a material selected from a SO₂-scavenging material, a flame retardant material that is not a sulfonated polyolefin, and combination thereof. For example, the SO₂-scavenging material and/or flame retardant material can be incorporated into the sul-

fonated polyolefin or can be coated onto the sulfonated polyolefin, or both. The SO₂-scavenging material in the composition helps to avoid the deleterious exposure to thermal decomposition products resulting from sulfonated polyolefins. In a method for forming a flame-resistant composite, the method includes forming a composite of a sulfonated polyolefin and a host material in need of flame resistance. For example, in the case where the flame-resistant composite is a flame-resistant textile, the flame-resistant textile can be formed by a process including weaving or bonding a sulfonated polyolefin fiber having an elongation at break of at least 8%, 9%, or 10% with itself and/or other fibers of a textile. The fibers can also be rendered flame resistant before or after weaving into fabric form.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1. Schematic of a polyolefin fiber that is partially sulfonated by diffusion of sulfonating agent(s) from outside, thus resulting in a sheath-core morphology, where sheath is sulfonated polyolefin and core is neat or unreacted polyolefin.

[0009] FIG. 2. Thermogravimetric analysis (TGA) data of sulfonated polyolefin and sulfonated polyolefin coated with SO₂-scavenger material (ZnO).

[0010] FIG. 3. Derivative thermogravimetric analysis data of sulfonated polyolefin and sulfonated polyolefin coated with SO₂-scavenger material (ZnO).

[0011] FIG. 4. DSC melting endotherms of polyethylene fibers before and after e-beam irradiation, and DSC melting endotherms after e-beam irradiation under reactive sulfonation conditions.

DETAILED DESCRIPTION OF THE INVENTION

[0012] As used herein, the term "about" generally indicates within +0.5, 1, 2, 5, or 10% of the indicated value. For example, a temperature of about 25° C. generally indicates in its broadest sense 25° C. ± 10%, which indicates 22.5-27.5° C.

[0013] The flame retardant composition described herein includes or is composed entirely of a sulfonated form of a polyolefin (i.e., sulfonated polyolefin). The sulfonated polyolefin is typically in the form of a fiber; however, particularly as the fiber can be broken down into particles or powder form, and with appropriate molding techniques (e.g., melt pressing or extrusion), numerous other shapes of the sulfonated polyolefin are possible, including powder, particles, pellets, flakes, platelets, spheres, and the like.

[0014] The sulfonated polyolefin may, in some embodiments, be any of the completely or partially sulfonated polyolefin fiber compositions known in the art as intermediates in the preparation of carbon fiber, although the sulfonated polyolefin fiber compositions of the art have heretofore never been considered as flame retardants since the necessary or optimal characteristics of sulfonated polyolefins as precursors for carbon fiber vs. their use as flame retardants are mutually exclusive and generally in conflict. Significantly, it has herein been found that the sulfonated polyolefin compositions, optimized as flame retardants, would, in many cases, be essentially useless as precursors for carbon fiber. More specifically, many of the sulfonated polyolefin compositions described herein, effective as flame retardants, would produce carbon fibers with an extreme degree of brittleness, and with unacceptably low strength and modulus. Conversely, many of the sulfonated polyolefin fiber compositions known in the art as

useful precursors for carbon fiber may be substantially sub-optimal, inferior, or even ineffective as a flame retardant for the instant purposes.

[0015] The sulfonated polyolefin can be produced by any of the methods and conditions known in the art, particularly those methods known in the art for sulfonating polyolefin fibers. The sulfonation methods and conditions considered herein can be any of the processes known in the art in which a polymer fiber is exposed to a source of SO_x species (typically, SO_2 , preferably in an oxidizing environment, such as O_3 , and/or SO_3 in an inert environment) for the purpose of sulfonating the polymer fiber. The sulfonation methods and conditions considered herein can be, for example, any of the processes known in the art in which a polymer fiber is submerged in a sulfonation bath of, for example, sulfuric acid, fuming sulfuric acid, or chlorosulfonic acid, or their mixtures, in order to sulfonate the polymer fiber. As further discussed below, the conditions of the sulfonation step can be selected to either completely sulfonate or partially sulfonate the polyolefin fiber. For example, adjustments in residence time, processing temperature, and reactivity or concentration of the sulfonating species will also adjust the degree of sulfonation. Therefore, one or more of these variables can be suitably modified to achieve a complete, partial, or specific degree of sulfonation. The foregoing methods, commonly used in the sulfonation of polyolefin fiber, may also be used in the sulfonation of a polyolefin object of another shape, such as polyolefin powder, particles, sheets, pellets, rods, tubes, spheres, flakes, platelets, and the like.

[0016] When sulfonated by diffusion of sulfonating agents, as described above, a fiber of cylindrical shape can possess a morphology characterized by a sulfonated sheath and unsulfonated core. Such a sheath-core texture of a fiber is schematically shown in FIG. 1.

[0017] As used herein, the terms “partially sulfonated,” “partial sulfonation,” “incompletely sulfonated,” or “incomplete sulfonation” all have equivalent meanings and are defined as an amount of sulfonation below a saturated (or “complete”) level of saturation. The degree of sulfonation can be determined by, for example, measuring the thermal characteristics (e.g., softening or charring point, or decomposition temperature associated with pyrolysis of incompletely sulfonated polyolefin) or physical characteristics (e.g., density, rigidity, or weight fraction of decomposable unsulfonated-polymer segment, or limiting oxygen index) of the partially sulfonated polyolefin (typically fiber). Since rigidity, as well as the softening and charring point (and thermal infusibility, in general) all increase with an increase in sulfonation, monitoring of any one or combination of these characteristics can be correlated with a level of sulfonation relative to a saturated level of sulfonation. In particular, a polyolefin fiber or other object can be considered to possess a saturated level of sulfonation by exhibiting a constant thermal or physical characteristic with increasing sulfonation treatment time. In contrast, a fiber that has not reached a saturated level of sulfonation will exhibit a change in a thermal or physical characteristic with increasing sulfonation treatment time. Moreover, if the fiber with a saturated degree of sulfonation is taken as 100% sulfonated, fibers with a lesser degree of sulfonation can be ascribed a numerical level of sulfonation below 100%, which is commensurate or proportionate with the difference in thermal or physical characteristic between the partially sulfonated fiber and completely sulfonated fiber. In different embodiments, the polyolefin precursor is sul-

fonated up to or less than a sulfonation degree of 95%, 90%, 85%, 80%, 75%, 70%, 65%, 60%, 55%, 50%, 45%, 40%, 35%, 30%, 25%, 20%, 15%, 10%, or 5% relative to a saturated level of sulfonation taken as 100%. The level of sulfonation can be further verified or made more accurate by an elemental analysis. In some embodiments, the polyolefin fiber may be hyper-sulfonated by use of longer sulfonation time or high pressure in a gas phase reaction. In such cases, the degree of sulfonation (in wt %) can be greater than 100%.

[0018] In one embodiment, to sulfonate the polyolefin object (e.g., powder, fiber, or a mat or paper preform thereof), the polyolefin object is submerged into or passed through a liquid containing sulfur trioxide (SO_3), a sulfur trioxide precursor (e.g., chlorosulfonic acid, HSO_3Cl), sulfur dioxide (SO_2), or a mixture thereof. In particular embodiments, polyolefin fiber is passed through the liquid by pulling the fiber into the liquid from a creel of fiber spool either unconstrained or held at a specified tension. Typically, the liquid containing sulfur trioxide is fuming sulfuric acid (i.e., oleum, which typically contains 5-30% (or more particularly, 15-30%) free SO_3) or chlorosulfonic acid, or a liquid solution thereof.

[0019] In other embodiments, to sulfonate the polyolefin object, the polyolefin object is contacted with a sulfonating gas in a gaseous atmosphere (i.e., not in a liquid). For example, the polyolefin object can be introduced into a chamber containing SO_2 or SO_3 gas, or a mixture thereof, or a gaseous reactive precursor thereof, or mixture of the SO_2 and/or SO_3 gas with another gas, such as oxygen, ozone, or an inert gas, such as nitrogen or a noble gas (e.g., helium or argon).

[0020] In some specific embodiments, hot melt-spun fiber jets below the spinneret are exposed to sulfonating gas in a gaseous atmosphere (i.e., not in a liquid). The hot melt stream of fiber reacts with the sulfonating gas mixture. The hot, less crystalline or non-crystalline melt reacts faster with reactive gas to yield sulfonated polyolefin fiber.

[0021] The sulfonating liquid or gas may also include (i.e., be admixed with) one or more additional oxidants that may favorably adjust the density or type of oxidized groups formed on the surface of the polyolefin object. Some examples of additional oxidants include ozone, air, oxygen, an inorganic or organic peroxide (e.g., hydrogen peroxide, cumene peroxide, or benzoyl peroxide), a peroxy acid (e.g., a peroxy-sulfuric or peroxy-carboxylic acid), a chromate or dichromate (e.g., $\text{K}_2\text{Cr}_2\text{O}_7$), permanganate (e.g., KMnO_4), hypochlorite (e.g., HOCl or NaOCl), chlorite, perchlorate (e.g., NaClO_4), or nitrate (e.g., HNO_3 or KNO_3).

[0022] In other embodiments, to sulfonate the polyolefin object, a polyolefin precursor resin is melt-mixed with a sulfonation additive that evolves a SO_x gas at elevated temperatures in order to effect sulfonation at the elevated temperature. To form a precursor fiber, the melt-mixed composite can be spun to produce a melt-mixed composite fiber, wherein the melt-mixed composite fiber contains polyolefin precursor resin as an unsulfonated matrix material within which the sulfonation additive is incorporated. The resulting melt-mixed composite fiber (i.e., “melt-spun fiber”) or other object is then heated to a desulfonation temperature effective for the liberation of SO_x gas from the sulfonation additive. Liberation of SO_x gas from the sulfonation additive results in complete or partial sulfonation of the polyolefin matrix under an inert or oxic environment. A particular advantage of this melt-mixing methodology is that the amount of sulfonation of the fiber material or other object can be carefully controlled

by precisely quantifying the amount of sulfonation material (e.g., by weight or molar ratio of the sulfonation material with respect to total amount of composite material). In some embodiments, a completely sulfonated object exhibits 1 mole of sulfonate or sulfate per mole of polyethylene repeat unit. In some embodiments, a completely sulfonated object gains 0.5 moles of sulfonate or sulfate per mole of polyethylene repeat unit, through a diffusion-controlled process. In some embodiments, when hypersulfonation is conducted, the sulfonated object may gain greater than 0.5 moles, or at or greater than 0.55 moles, of sulfonate or sulfate per mole of polyethylene repeat unit.

[0023] The sulfonation additive can be any solid-state compound or material bearing reactive SO_x -containing groups (typically, $-\text{SO}_3\text{H}$, or sulfone, i.e., $-(\text{SO}_2-\text{O})-$, or sulfate $-(\text{O}-\text{SO}_2-\text{O})-$ groups) that function to liberate SO_2 and/or SO_3 under elevated temperatures. In particular embodiments, the sulfonation additive is an organic (i.e., carbon-containing or carbonaceous) sulfonated compound or material. Some examples of organic sulfonated compounds or materials include sulfonated graphene, sulfonated diene rubber, sulfonated polyolefin, polyvinyl sulfate, sulfonated polystyrene, sulfonated lignin, and sulfonated mesophase pitch. Such organic sulfonated compounds are either commercially available or can be produced by methods well known in the art (e.g., by any of the liquid or gas sulfonation processes known in the art, as discussed above). Inorganic non-metallic sulfates, such as ammonium sulfate, ammonium bisulfate, or other such sulfates, can also be used as a sulfonation additive in the precursor matrix. Moreover, to increase compatibility of the additive with the polyolefin polymer, the sulfonation additive (e.g., graphene or other polycyclic aromatic compound or material) may be functionalized with hydrophobic aliphatic chains of sufficient length (e.g., hexyl, heptyl, octyl, or a higher alkyl chain) by methods well known in the art.

[0024] In a particular embodiment, the sulfonation additive is elemental sulfur, which can be melt-mixed with polyolefin precursor. To form precursor fibers, the elemental sulfur-mixed polyolefin resin can be spun into fiber or non-woven mat form. Then the precursor object is oxidized, such as in air, ozone, or in oxidizing liquid bath, as described above, to obtain the sulfonated precursor. In other embodiments, fibers are exposed to electron beam, microwave, or UV radiation during reaction with sulfonating agents.

[0025] In still other embodiments, to produce a sulfonated polyolefin fiber, fibers are produced (e.g., drawn) from a sulfonated polyolefin resin. The sulfonated polyolefin resin can be produced by, for example, sulfonating a polyolefin resin by any of the techniques described above. Fibers can be produced from the sulfonated polyolefin resin by any of the fiber-producing techniques known in the art and as herein described, e.g., by solution spinning, gel-spinning, solvent or plasticizer-assisted melt-spinning, or melt processing.

[0026] In another embodiment, completely or partially sulfonated polyolefins are plasticized with a suitable (i.e., plasticizing) solvent, such as dimethyl sulfoxide, dimethyl formamide, an oil (e.g., an inorganic oil, such as silicone oil, or an organic oil, such as vegetable oil) or concentrated or dilute sulfuric acid, at varied dilutions and processed in the form of a gel at low temperature in a coagulation bath to obtain solution-spun completely- or partially-sulfonated fibers. In particular embodiments, sulfonated additives, such as organic sulfonated compounds, are incorporated into the fiber by

doping them into the plasticized polymer gel. Sulfonated additives serve as a source of SO_x gas at elevated temperatures and serve as sulfonating agents in an oxidic environment.

[0027] The period of time (i.e., residence time) that the polyolefin fiber or other object is exposed to the sulfonating species at the sulfonating temperature, as well as the temperature during exposure to the sulfonating species (i.e., sulfonation temperature) can be suitably adjusted to provide a complete sulfonation or a level of sulfonation below a complete sulfonation (i.e., partial sulfonation). In some embodiments, the degree of sulfonation (DS) can be determined or monitored at points during the process by use of thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), density measuring device, or other suitable analytical technique.

[0028] The sulfonation temperature is generally below a carbonization temperature, and more typically, at least 0°C ., 10°C ., 20°C ., 30°C ., 40°C ., or 50°C ., and up to 300°C . In different embodiments, the sulfonation temperature is precisely or about 30°C ., 40°C ., 50°C ., 60°C ., 70°C ., 80°C ., 90°C ., 100°C ., 110°C ., 120°C ., 130°C ., 140°C ., 150°C ., 160°C ., 170°C ., 180°C ., 190°C ., 200°C ., 210°C ., 220°C ., 230°C ., 240°C ., 250°C ., 260°C ., 270°C ., 280°C ., 290°C ., or 300°C ., or a sulfonation temperature within a range bounded by any two of the foregoing values (for example, at least or above 30°C ., 40°C ., 50°C . and up to or less than 200°C ., 250°C ., or 300°C .; or at least or above 50°C . and up to or less than 160°C ., 170°C ., or 180°C .; or at least or above 70°C . and up to or less than 120°C ., 140°C ., 160°C ., or 180°C .).

[0029] The residence time at sulfonation is very much dependent on several variables, including the sulfonation temperature used, concentration of sulfonating agent in the reaction medium, level of applied tension (if any), crystallinity of the precursor polymer, and the thickness of the polyolefin fiber or other object. The residence time is also dependent on the sulfonation method used (i.e., liquid or gas phase processes). As would be appreciated by one skilled in the art, the degree of sulfonation achieved at a particular sulfonating temperature and residence time can be replicated by use of a higher sulfonation temperature at a shorter residence time, or by use of a lower sulfonation temperature at a longer residence time. Similarly, the residence time required to achieve a degree of sulfonation in a polyolefin fiber or other object of a certain thickness may result in a higher degree of sulfonation in a thinner fiber or smaller object and a lower degree of sulfonation in a thicker fiber or larger object with all other conditions and variables normalized.

[0030] Generally, for polyolefin fibers having a thickness in the range of 0.5 to 50 microns, a residence time at sulfonation of up to about 90 minutes provides a partial sulfonation (i.e., where sulfonation has not occurred through the entire diameter of the fiber through the core, thus producing a surface-sulfonated polyolefin fiber), whereas a residence time above 90 minutes generally provides a complete sulfonation for the indicated thickness. In different embodiments, depending on such variables as the sulfonation temperature and fiber thickness or object size, the residence time at sulfonation may be suitably selected as precisely, about, up to, or less than 360 minutes, 300 minutes, 240 minutes, 180 minutes, 150 minutes, 120 minutes, 90 minutes, 60 minutes, 30 minutes, 20 minutes, 10 minutes, 5 minutes, or 1 minute, or a residence time within a range bounded by any two of the foregoing values. During sulfonation, which is a diffusion controlled process, a tensile stress of any suitable degree can be

employed, such as a tensile stress of 0, 1, 5, 10, or 15 MPa, or within a range thereof. Precursor crystallinity depends on the nature of the polymer and molecular orientation in the fiber form and typically has a value from 0 to 80%.

[0031] Generally, for polyolefin fibers having a thickness in the range of 15 to 20 microns, complete sulfonation (i.e., to the core of the fiber) will occur at: a sulfonation temperature of 150° C. or greater when employing a sulfonation residence time of about 5-10 minutes or greater; or a sulfonation temperature of 140° C. or greater when employing a residence time of about 10-15 minutes or greater; or a sulfonation temperature of 130° C. or greater when employing a residence time of about 15-20 minutes or greater; or a sulfonation temperature of 120° C. or greater when employing a residence time of about 20-25 minutes or greater; or a sulfonation temperature of 110° C. or greater when employing a residence time of about 25-30 minutes or greater; or a sulfonation temperature of 100° C. or greater when employing a residence time of about 30-35 minutes or greater; or a sulfonation temperature of 90° C. or greater when employing a residence time of about 35-40 minutes or greater; or a sulfonation temperature of 70° C. or greater when employing a residence time of about 40-45 minutes or greater. Therefore, for any of the foregoing examples, a reduction in sulfonation temperature or residence time should generally have the effect of achieving a partial sulfonation (i.e., a surface sulfonation) for polyolefin fibers having a thickness in the range of 15 to 20 microns.

[0032] The above exemplary sulfonation temperatures and residence times are not meant to be taken precisely, but as approximate and typical for polyolefin fibers having a thickness in the range of 15 to 20 microns. For polyolefin fibers having a thickness below the aforesaid range, lower sulfonation temperatures and/or lower residence times may be used to achieve the same effect or if a partial sulfonation is desired; and likewise, for polyolefin fibers having a thickness above the aforesaid range, higher sulfonation temperatures and higher residence times can be used to achieve the same effect, or the same or lower sulfonation temperatures and/or residence times may be used to achieve a partial sulfonation. Moreover, generally, for polyolefin fibers having a thickness in the range of 15 to 20 microns, a residence time at sulfonation of 2 minutes is too short to achieve complete sulfonation (to the core of the fiber) at a sulfonation temperature of 160° C. or less, and a residence time of 1 minute or less is generally too short to achieve complete sulfonation at a sulfonation temperature of 200° C. or less. In particular embodiments, a partially sulfonated tow of filaments of 1 to 30 micron thicknesses is produced by varying one or more of the above parameters. The foregoing exemplary combinations of sulfonation temperatures and residence times are particularly relevant to liquid phase and gas phase sulfonation processes described above.

[0033] In particular embodiments, a partial sulfonation process is employed on the polyolefin object. Particularly when a liquid phase or gas phase sulfonation process is used, the partial sulfonation process results in a surface-sulfonated polyolefin fiber or other object (i.e., which possesses an unsulfonated core). The surface-sulfonated polyolefin object is achieved by judicious selection of sulfonation temperature and residence time, appropriate for the fiber thickness or object size, that halts sulfonation before the entire core of the object becomes sulfonated. Generally, this is achieved by limiting the residence time at a particular sulfonation tem-

perature to a time below that which would result in complete sulfonation through the core. Moreover, by adjusting the residence time, the thickness of the unsulfonated core and sulfonated surface can be correspondingly adjusted. For example, increasing the residence time at a particular sulfonation temperature would have the effect of thickening the sulfonated surface and narrowing the unsulfonated core, while decreasing the residence time at a particular sulfonation temperature would have the effect of reducing the thickness of the sulfonated surface and thickening the unsulfonated core.

[0034] If desired, the thickness of the sulfonated surface and unsulfonated core can be further adjusted by including an autocatalytic solid-state desulfonation-sulfonation step (i.e., “desulfonation step” or “desulfonation process”) at the interface of the sulfonated sheath and unsulfonated core (i.e., “sheath-core interface”). During the desulfonation-sulfonation process, the aforesaid interface gradually propagates towards the core. In the desulfonation process, the surface-sulfonated polyolefin object is heated to a desulfonation temperature effective for the liberation of SO_x gas from the sulfonated surface. As the sulfonated sheath is rigid and becomes crosslinked after desulfonation, in the sulfonation phase, SO_x gas molecules liberated from the surface migrate toward the core of the object, thereby partially sulfonating additional polymeric material toward the core. This results in a narrower unsulfonated core and thicker sulfonated surface, or eventually, partial sulfonation throughout the object including through the core. The higher the temperature and the longer the residence time at the desulfonation temperature, the narrower the unsulfonated core and the thicker the crosslinked sheath. In some embodiments, the desulfonation temperature is employed for a period of time less than the time required for the entire polyolefin object to be partially sulfonated through the core. The instant application also includes the possibility of employing a desulfonation step for a period of time effective to partially sulfonate the polyolefin object through the core. In the foregoing embodiment, no unsulfonated core remains.

[0035] When a desulfonation process is employed, the desulfonation temperature can independently be selected from any of the sulfonation temperatures and residence times provided above (e.g., at least 30° C., 40° C., 50° C., 60° C., or 70° C., and up to or less than 120° C., 140° C., 160° C., 180° C., 200° C., 250° C., or 300° C.). Moreover, a desulfonation (inverse sulfonation) process is generally practiced herein in the absence of an external sulfonating source, thereby not further adding sulfonating species to the polyolefin object, but limiting the amount of sulfonating species to the amount present in the sulfonated surface or the amount incorporated into the sulfonated polyolefin object on completion of the sulfonation process. The desulfonation process is generally practiced herein in an oxygen-containing (i.e., O₂-containing or oxidic) environment, such as air or an artificial oxygen-inert gas atmosphere, which may be conducted at either standard pressure (e.g., 0.9-1.2 bar), elevated pressure (e.g., 2-10 bar), or reduced pressure (e.g., 0.1-0.5 bar). In other embodiments, a pressure of precisely, about, or at least 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 bar, or a pressure within a range therein, is employed.

[0036] In some embodiments, the sulfonation and/or desulfonation process includes exposing the fiber or other object (before, during, and/or after the sulfonation or desulfonation process) to radiative energy. The radiative energy can be, for

example, electromagnetic radiation (e.g., ultraviolet, X-ray, infrared, or microwave radiation) or energetic particles (e.g., electron or neutron beam). In the case of electromagnetic radiation, the radiation may be dispersed or collimated, as in a laser. In some embodiments, the radiative energy is ionizing, while in other embodiments it is not ionizing. The polyolefin fiber or other object may alternatively or additionally be exposed to radiative energy before, during, or after sulfonation. In some embodiments, electromagnetic or energetic particle radiation is not employed.

[0037] In some embodiments, in the case of a polyolefin fiber, the sulfonation and desulfonation processes are practiced without applying a stress (tension) along the length of the fiber. In other embodiments, either the sulfonation or desulfonation process, or both, are practiced by applying a stress along the fiber length. The stress can be applied to, for example, avoid fiber shrinkage or to improve the strength or modulus of the fiber.

[0038] The polyolefin precursor to be sulfonated can be, for example, a poly- α -olefin, such as polyethylene, polypropylene, polybutylene, polyisobutylene, ethylene propylene rubber, or a chlorinated polyolefin (e.g., polyvinylchloride, or PVC), or a polydiene, such as polybutadiene (e.g., poly-1,3-butadiene or poly-1,2-butadiene), polyisoprene, dicyclopentadiene, ethylidene norbornene, or vinyl norbornene, or a homogeneous or heterogeneous composite thereof, or a copolymer thereof (e.g., EPDM rubber, i.e., ethylene propylene diene monomer). In the case of polyethylene, the polyethylene can be any of the types of polyethylene known in the art, e.g., low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), high density polyethylene (HDPE), medium density polyethylene (MDPE), high molecular weight polyethylene (HMWPE), and ultra high molecular weight polyethylene (UHMWPE). In the case of polypropylene, the polypropylene can also be any of the types of polypropylenes known in the art, e.g., isotactic, atactic, and syndiotactic polypropylene. The polyolefin precursor may or may not also be derived from, or include segments or monomeric units of other addition monomers, such as styrene, acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, vinyl acetate (as well as partially or fully hydrolyzed derivatives of vinyl acetate, such as vinyl alcohol), terephthalate (e.g., as polyethylene terephthalate, or PET), and acrylonitrile. In some embodiments, these other addition monomers are included in no more than, or less than, for example, 50, 60, or 70% by monomer number or weight in the polyolefin precursor. The polyolefin may also be either in virgin, compounded, or recycled form.

[0039] The sulfonated polyolefin object (or polyolefin precursor) can have any desired thickness (i.e., diameter, particularly for the case of a fiber) or size. For example, in different embodiments, the fiber can have a thickness of precisely, about, at least, above, up to, or less than, for example, 0.1, 0.2, 0.5, 1, 2, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, or 100 microns, or a thickness within a range bounded by any two of these values. In some embodiments, the fiber is in the form of a tow, while in other embodiments the fiber is in the form of a single filament. Continuous filaments or tows from very low count (<500) to very high counts (>50 k) are considered herein. Such fibers may also be stapled or chopped (short-segment). The polyolefin fiber precursor may also be in the form of a fiber, film, yarn, fabric, mesh, or felt. In the case of a non-fibrous sulfonated polyolefin object, the object may

have one or more of its dimensions independently selected from any of the thicknesses provided above, or it may have one, two, or all of its dimensions substantially larger, e.g., 250, 500, 750, 1000, or 1500 microns.

[0040] The polyolefin fiber precursor can be produced by any of the methods known in the art. In some embodiments, the fiber precursor is produced by a melt-spinning (i.e., melt-extrusion) or other variants of melt-processing (i.e., melt-blowing). In other embodiments, the fiber precursor is produced by a solution-spinning process (fiber is produced by coagulation of solid fiber from solution of the polymer in a solvent). The conditions and methodology employed in melt-spinning and solution-spinning processes are well-known in the art. Moreover, the fiber precursor may be produced by a single or bi-component extrusion process. The conditions and methodology employed in single or bi-component extrusion processes are also well-known in the art.

[0041] The sulfonation of polyolefin materials induces flame retardancy. The higher the degree of sulfonation, the higher the flame-resistance. Thus, depending on the degree of sulfonation, or depending on the composition of the material, the limiting oxygen index of the material can be tailored. However, a sulfonated material during thermal exposure (above 100° C.) generally produces SO_x. For example, a sulfonic acid derivative of a polyolefin is known to produce SO₂ and H₂O. The release of SO_x is generally known to induce toxic effects in a human; thus, its mitigation, as described herein, is of great importance.

[0042] In some embodiments, the sulfonated polyolefin object, described above, is combined with a SO₂-scavenging material. The SO₂-scavenging material can be any material, generally a solid, but possibly a liquid, that functions to scavenge SO₂ and/or a related gas (e.g., any sulfur-containing or SO_x gas or liquid) formed during decompositional heating of the sulfonated polyolefin.

[0043] In a first set of embodiments, the SO₂-scavenging material is selected from one or a combination of metal oxides, particularly those having an effective or pronounced ability to scavenge SO₂ and related gases. The metal oxide can be, for example, an alkaline earth oxide (e.g., MgO or CaO), or a transition metal oxide, particularly oxides of the first row of transition metals, such as oxides of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn, wherein ZnO is particularly preferred.

[0044] In a second set of embodiments, the SO₂-scavenging material is a carbonate or bicarbonate compound, such as a metal, ammonium, or phosphonium carbonate or bicarbonate. Any of the metals described above are considered herein in their carbonate or bicarbonate form, such as the alkaline earth metal carbonates and bicarbonates (e.g., MgCO₃ and CaCO₃, e.g., limestone), as well as the alkali metal carbonates and bicarbonates (e.g., Na₂CO₃ and NaHCO₃).

[0045] In a third set of embodiments, the SO₂-scavenging material is a hydroxide compound, such as a metal, ammonium, or phosphonium hydroxide. Any of the metals described above are considered herein in their hydroxide form, particularly the alkali metal hydroxides (e.g., LiOH, NaOH, and KOH), alkaline earth hydroxides (e.g., Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂), main group hydroxides (e.g., Al(OH)₃), and transition metal hydroxides.

[0046] In a fourth set of embodiments, the SO₂-scavenging material is a compound containing ammonium or phosphonium groups. When such compounds are combined with the sulfonated polyolefin, it is believed that the positively

charged ammonium or phosphonium groups form a complex with negatively charged sulfur-containing (e.g., sulfonate) groups in the sulfonated polyolefin. Without being bound by any theory, it is believed that the formed complex substantially inhibits the sulfur-containing groups from decomposing into SO₂ fumes.

[0047] The ammonium group can be, for example, inorganic ammonium (i.e., NH₄⁺), or an organic ammonium of the formula NR₄⁺, wherein the four R groups are independently selected from H and hydrocarbon groups (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, t-butyl, benzyl, and phenyl), with at least one R group being a hydrocarbon group. Some specific examples of organic ammonium groups include methylammonium, dimethylammonium, trimethylammonium, and tetramethylammonium, and ammonium groups in which one or more of the methyl groups in the foregoing examples are independently replaced with any of the other exemplary hydrocarbon groups mentioned above.

[0048] The phosphonium group can be, for example, of the formula PR₄⁺, wherein the four R groups are independently selected from H and hydrocarbon groups (e.g., as provided above) with at least one R group being a hydrocarbon group. Some specific examples of phosphonium groups can be derived by substituting nitrogen with phosphorus in examples provided above for ammonium groups.

[0049] In other embodiments, the ammonium or phosphonium group is cyclic or bicyclic in nature, i.e., a cyclic hydrocarbon group having one or more ring nitrogen or phosphorus atoms. Some examples of ammonium ring groups include piperidinium, pyrrolidinium, imidazolium, pyridinium, and pyrazinium groups. An example of a phosphonium ring group is a charged phosphabenzene or P-spiro bicyclic phosphonium group.

[0050] The anion in the ammonium and phosphonium compound can be any anion, but preferably an anion that permits the facile exchange with sulfur-containing anions in the sulfonated polyolefin and that does not adversely affect the flame-resisting and physical properties of the sulfonated polyolefin. The anion can be, for example, a halide (e.g., chloride, bromide, or iodide), hydroxide, nitrate, sulfate, hydrogensulfate, phosphate, hexafluorophosphate, carbonate, formate, acetate, and triflate.

[0051] In some embodiments, any two or more of the above SO₂-scavenging materials can be used in combination. In other embodiments, one or more of any of the above-mentioned classes or specific types of SO₂-scavenging materials are excluded from the above-described sulfonated flame retardant composition or excluded from a flame-resistant composite in which the sulfonated flame retardant composition is incorporated.

[0052] By having the sulfonated polyolefin and SO₂-scavenging material in a combined state is meant that the SO₂-scavenging material is in physical contact with at least a portion of the sulfonated polyolefin composition. The sulfonated polyolefin composition is made to be in contact with the SO₂-scavenging material in any suitable manner and by any suitable means, provided that the SO₂-scavenging material is not substantially hindered or obviated from scavenging SO₂ gas produced by the sulfonated polyolefin at a temperature at which SO₂ gas is produced. Moreover, as the development of SO₂ fumes is desirably substantially eliminated or prevented, the SO₂-scavenging material is preferably included in an amount and spatial arrangement that permits

the substantial elimination or prevention of SO₂ fumes from the entire sulfonated polyolefin object used monolithically or as a fire retardant in another material.

[0053] By a first particular embodiment, the SO₂-scavenging material can be incorporated within the sulfonated polyolefin object by, for example, admixing, blending, or compounding (i.e., combining) a sulfonated polyolefin and SO₂-scavenging material to form a sulfonated composite. The resulting composite may be substantially homogeneous or relatively or substantially heterogeneous in its distribution of SO₂-scavenging material. A substantially homogeneous distribution of SO₂-scavenging material generally possesses particles of SO₂-scavenging material having a size of up to or less than, for example, 1 micron, 500 nm, 100 nm, 50 nm, or 20 nm in size evenly distributed in the sulfonated polyolefin matrix. Alternatively, the substantially homogeneous distribution may not be a distribution of SO₂-scavenging particles, but a distribution of SO₂-scavenging molecules. A heterogeneous distribution of SO₂-scavenging material generally possesses particles having a size greater than 1 micron, or at least or greater than 2, 5, 10, 50, 100, 200, or 500 microns in the sulfonated polyolefin matrix. Using shaping techniques, such as cutting, powderizing, molding, and/or pressing techniques known in the art, various shapes of the sulfonated composite material can be made.

[0054] By a second particular embodiment, the SO₂-scavenging material is in the form of a coating (i.e., layer) on the surface of the sulfonated polyolefin fiber or other object. The coating may, in some embodiments, completely cover the entire surface of the sulfonated polyolefin object, whereas in other embodiments, the coating may cover a portion, typically at least 50%, 60%, 70%, 80%, 90%, or 95% of the surface, of the sulfonated polyolefin object. In different embodiments, the coating of the SO₂-scavenging material can have a uniform or average thickness of about, at least, greater than, up to, or less than, for example, 0.1, 0.2, 0.5, 1, 2, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, or 100 microns, or a thickness within a range bounded by any two of these values.

[0055] The SO₂-scavenging material can be coated onto the sulfonated polyolefin object by any suitable means. In particular embodiments, the sulfonated polyolefin object is contacted with a fluidized bed of a powderized form of the SO₂-scavenging material in order to deposit a layer of the SO₂-scavenging material onto the sulfonated polyolefin object. The powderized form of the SO₂-scavenging material can be made of particles having any suitable uniform or average diameter, including diameters corresponding to any of the exemplary coating thicknesses provided above, or a smaller uniform or average diameter of at least, greater than, up to, or less than, for example, 5, 10, 15, 20, 30, 40, or 50 nm. In other embodiments, a layer of the SO₂-scavenging material is deposited by contacting the sulfonated polyolefin object with a liquid solution in which the SO₂-scavenging material is dissolved, dispersed, or suspended, and then drying the liquid coating, with optional re-application of the liquid solution followed by drying, if desired, to provide a coating of desired thickness. Thus, the SO₂-scavenging material can be applied on sulfonated fibers, films, or fabrics by deploying a method similar to that of the textile sizing or finish application process.

[0056] In some embodiments, after an initial or final layer of the SO₂-scavenging material has been deposited, the layer may be subjected to a post-processing step in which the layer

is made to coalesce into a resilient layer and/or become strongly adhered with the sulfonated polyolefin. The post-processing step may include, for example, exposure to a crosslinkable resin, followed by curing. In some embodiments, curing can be achieved by alternative cross-linking methods similar to deposition of external energy (such as electron beam) for short duration. Alternatively, the sulfonated polyolefin object may be pre-treated, prior to deposition of a layer of the SO₂-scavenging material, with a substance that forms or facilitates a strong bonding interaction between the sulfonated polyolefin and the SO₂-scavenging material.

[0057] The SO₂-scavenging material can be included in or on the sulfonated polyolefin object in any suitably effective amount. In different embodiments, the SO₂-scavenging material is included in or on the sulfonated polyolefin object in an amount of about, at least, above, up to, or less than, for example, 1, 2, 3, 4, 5, 10, 12, 15, 18, 20, 25, 30, 35, 40, 45, or 50 wt %, or a wt % within a range bounded by any two of the foregoing exemplary values, wherein the wt % is with respect to the combined weight of the SO₂-scavenging material and sulfonated polyolefin.

[0058] In some embodiments, the sulfonated polyolefin object, described above, with or without a SO₂-scavenging material, is combined with a flame retardant material that is not a sulfonated polyolefin. The term "combined", used herein, may have any of the same meanings as provided above for the SO₂-scavenging material, such as being incorporated within (e.g., dispersed as particles, fibers, or molecules in the sulfonated polyolefin matrix) or as a layer on the sulfonated polyolefin object. Moreover, any of the methods for incorporating an SO₂-scavenging material into the sulfonated polyolefin, as described above, are also applicable for incorporating the flame retardant material into the sulfonated polyolefin. In some embodiments, the flame retardant material has the same composition as the SO₂-scavenging material; thus, one substance may function as both a SO₂-scavenging material and a flame retardant material. In other embodiments, the flame retardant material has a composition different than the SO₂-scavenging material. In the latter embodiment, the flame retardant material normally does not have SO₂-scavenging ability, and the SO₂-scavenging material normally does not have flame retarding ability.

[0059] The flame retardant material can be any of the inorganic or organic flame retardant materials known in the art, except that it preferably does not adversely affect the physical properties of the sulfonated polyolefin for use as a flame retardant, and can be easily integrated into or on the sulfonated polyolefin. Some examples of flame retardant materials include metal hydroxides or hydrates (e.g., aluminum hydroxide or magnesium hydroxide), red phosphorus, boron compounds (e.g., borates and boric acid), organochlorides, organobromides (e.g., decabromodiphenylether and tetrabromobisphenol A), organophosphorus compounds (e.g., organophosphates), carbonate minerals (e.g., huntite), antimony compounds (e.g., antimony trioxide, sodium antimonate, and antimony pentoxide), and combinations thereof. In other embodiments, the flame retardant material is a silicate-containing compound or material, such as a silicate-containing mineral, such as silica, feldspar, talc, olivine, tourmaline, serpentine, chrysotile, amphibole, crocidolite, asbestiform, asbestos, mullite, or a clay (e.g., a kaolin, serpentine, montmorillonite, illite, mica, glauconite, chlorite, vermiculite, attapulgite, or sepiolite). In yet other embodiments, the flame

retardant material is a form of elemental carbon with significant barrier properties, such as graphenes, exfoliated graphite, carbon black, amorphous carbon, or carbon nanofibers (e.g., nanotubes), or a carbide (e.g., silicon carbide).

[0060] It is well known in the art that some flame retardant materials may not work alone, but may need to be in combination with another flame retardant chemical to function effectively or optimally as a flame retardant. For example, halogenated flame retardants are often used in combination with antimony oxide. In other embodiments, one or more of any of the above-mentioned classes or specific types of flame retardants are excluded from the above-described sulfonated flame retardant composition or excluded from a flame-resistant composite in which the sulfonated flame retardant composition is incorporated.

[0061] The flame retardant is typically either in solid or liquid form when incorporated in or onto the sulfonated polyolefin object. In solid form, the flame retardant is typically incorporated as particles or fibers, which are preferably homogeneously dispersed throughout the sulfonated polyolefin matrix or formed as a layer on the surface of the sulfonated polyolefin fiber. The flame retardant particles or fibers can have any suitable diameters, such as any of the diameters provided above for the SO₂-scavenging material. In fibrous form, the flame retardant can have any suitable length, which may correspond to the diameters provided above, or may be significantly longer, e.g., at least, above, or up to 200, 300, 400, or 500 microns.

[0062] The flame retardant material can be included in or on the sulfonated polyolefin object in any suitably effective amount. In different embodiments, the flame retardant material is included in or on the sulfonated polyolefin object in an amount of about, at least, above, up to, or less than, for example, 1, 2, 3, 4, 5, 10, 12, 15, 18, 20, 25, 30, 35, 40, 45, or 50 wt %, or a wt % within a range bounded by any two of the foregoing exemplary values, wherein the wt % is with respect to the combined weight of the flame retardant material and sulfonated polyolefin.

[0063] Significantly, the inclusion of a flame retardant can advantageously permit a significantly lowered amount of sulfonation for the sulfonated polyolefin object. The lower required amount of sulfonation can be particularly advantageously by, for example, reducing the time and cost of the sulfonation process.

[0064] By controlling the conditions used in the sulfonation process, as well as choice and manner of integration of the SO₂-scavenging material or flame retardant, the mechanical properties of the sulfonated polyolefin object, which may or may not be combined with a SO₂-scavenging material or flame retardant material (other than a sulfonated polyolefin), can be tailored. Some mechanical properties that can be tailored, as particularly applicable to a sulfonated polyolefin fiber, include tensile strength, modulus, elongation at break (i.e., break strain), and toughness. The sulfonated polyolefin object produced herein, which may or may not be combined with a SO₂-scavenging material or flame retardant material (other than a sulfonated polyolefin), can have a tensile strength of about, at least, greater than, up to, or less than, for example, 2, 5, 7, 10, 12, 15, 18, 20, 25, or 30 ksi. In different embodiments, the sulfonated polyolefin object, which may or may not be combined with a SO₂-scavenging material or flame retardant material (other than a sulfonated polyolefin), has a modulus of precisely, about, at least, greater than, up to, or less than, for example, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, or 0.8

Msi. The sulfonated polyolefin object, which may or may not be combined with a SO₂-scavenging material or flame retardant material (other than a sulfonated polyolefin), can have an elongation at break of precisely, about, at least, greater than, up to, or less than, for example, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, or 25%.

[0065] In another aspect, the invention is directed to flame-resistant composites that contain the above-described sulfonated polyolefin as a flame retardant component incorporated into or integrated with a host material to be rendered flame resistant, wherein the sulfonated polyolefin may or may not be combined with a SO₂-scavenging material or flame retardant material (other than a sulfonated polyolefin) when it is incorporated in the material to be rendered flame resistant. The host material can be any material requiring flame resistance in which the sulfonated polyolefin fibers can be incorporated. The host material can be, for example, a layer, sheet, film, or other shape of a plastic, polymer, fabric, or cellulosic material. If the host material is meltable, the sulfonated polyolefin can be mixed with the melted host followed by solidification. If the host material is not meltable, or melting is to be avoided, the sulfonated polyolefin can be introduced by, for example, powderizing or pelletizing the host material, mixing it with the sulfonated polyolefin fiber or other object, and melt-pressing or pressure-welding. The sulfonated polyolefin can be included in any suitable amount in the flame resistant composite, which can be an amount over 0% and under 100%. In different embodiments, the sulfonated polyolefin can be included in an amount of precisely, about, at least, above, up to, or less than, for example, 1%, 2%, 5%, 10%, 15%, 20%, 25%, 30%, 40%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, or 95% by weight of the flame resistant composite. The amount of sulfonated polyolefin may also be within a range bounded by any of the foregoing exemplary values.

[0066] In a first set of embodiments of the flame resistant composite, if a SO₂-scavenging material or flame retardant material is included in the flame resistant composite, either or both of these materials are either incorporated into the sulfonated polyolefin objects or are a coating on the sulfonated polyolefin objects that are incorporated into or integrated with the host material. In a second set of embodiments of the flame resistant composite, if a SO₂-scavenging material or flame retardant material is included in the flame resistant composite, either or both of these materials, or a portion thereof, are not in contact with the sulfonated polyolefin objects, but instead are incorporated (e.g., dispersed) separately in the host material. Any of the means, described above, for incorporating sulfonated polyolefin into a host material can be used for incorporating a SO₂-scavenging material or flame retardant material into the host material.

[0067] In particular embodiments, the material to be rendered flame resistant is a textile. The textile can be, for example, a woven or non-woven fabric composed of strands of a textile material. In particular embodiments, the fabric is a fabric used in clothing, furniture, upholstery, flooring, rugs, or mats. Some examples of fabrics that can be rendered flame resistant include cotton, polyester, nylon, silk, wool, rayon, cellulose acetate, spandex, and blends thereof. In other embodiments, the strands of the fabric are composed solely of sulfonated polyolefin fiber, which may also include a SO₂-scavenging material or flame retardant material. The flame resistant textile can be produced by, for example, weaving sufficiently flexible sulfonated (or partially sulfonated) poly-

olefin in fiber form with either itself or other fibers of a textile by methods well known in the art.

[0068] In another embodiment, the flame resistant textile or other flame resistant article is made by chemical or physical bonding of the sulfonated polyolefin objects (e.g., powder, particles, pellets, or fibers) with each other and/or with a material to be rendered flame resistant. Chemical bonding can be accomplished by, for example, including a bonding agent, such as a curable polymeric resin, that bonds the sulfonated polyolefin objects with each other and/or with a material to be rendered flame resistant. Physical bonding can be accomplished by, for example, pressure, heat, or a radiative source (e.g., electromagnetic or particle bombardment) to induce bonding.

[0069] In a particular embodiment, the sulfonated polyolefin objects are bonded with each other by inducing strong inter-object or interfilament bonding between sulfonated polyolefin objects, such as particles or fibers. In some embodiments, the strong interfilament bonding is induced by contacting the sulfonated polyolefin objects with water. Without being bound by any theory, the strong interfilament bonding is believed to be mediated by the presence of sulfur-containing and possibly other oxidized groups on the surface of the sulfonated polyolefin objects that likely form extensive hydrogen bonding interactions with each other particularly when they interact with water molecules.

[0070] As used herein, the term “water” can be relatively or substantially pure water, or alternatively, an aqueous solution. Relatively or substantially pure water is generally composed completely of water, except for trace elements that may normally be found in water of relative or substantial purity. In some embodiments, the water may be ultrapure (i.e., up to 14, 16, or 18 MOhm). An aqueous solution, if used, may include one or more additional solvents or a solute, as long as the additional components in the water do not substantially hinder or adversely affect the ability of the sulfonated polyolefin objects to bond. The additional solvent or solute may function, for example, as wetting agents, surfactants, agglomerating agents, or bonding agents. The solvent is necessarily a polar protic or aprotic solvent miscible in water, such as an alcohol (e.g., methanol, ethanol, or isopropanol), dimethylformamide, dimethylacetamide, dimethylsulfoxide, acetone, glycerol, or ethylene glycol. The solute can be, for example, an inorganic compound or salt (e.g., lithium, sodium, and potassium salts of a halide, hydroxide, nitrate, or mineral acid), an inorganic polymeric material (e.g., a polysiloxane or sol-gel), an organic polymeric material (e.g., a polyacrylate or polyacrylamide), or an organic compound (e.g., a fluorinated surfactant, wetting agent, polyol, or polyalkylene glycol). In some embodiments, any one or all of the additional solvents or solutes described above (or any additional solvent or solute altogether) are excluded. In other embodiments, any one or a combination of the above-listed solvents may be used instead of water to make contact with the sulfonated objects in order to effect a strong inter-object (or interfilament) bonding.

[0071] In some embodiments, the sulfonated fibers or other objects are soaked in aqueous mineral acids such as hydrochloric acid, sulfuric acid, nitric acid, chlorosulfonic acid, or aqueous alkaline solutions of metal hydroxides or nonmetallic hydroxide (e.g., ammonium hydroxide) in order to effect hydrogen or ionic bonding in dried agglomerations or filament bundles of preferred orientation or random orientation.

In embodiments where sulfonated filaments are used, the filaments can be in continuous or chopped forms of finite lengths.

[0072] In some embodiments, the sulfonated polyolefin objects are contacted with water by immersing the sulfonated polyolefin objects in water or an aqueous solution. The sulfonated polyolefin objects can be immersed in water or aqueous solution by, for example, submerging the sulfonated objects into water or an aqueous solution, passing water or an aqueous solution over the sulfonated objects, or spraying the sulfonated objects with water or an aqueous solution. Generally, excess water (i.e., water or aqueous solution beyond that which coats the fibers) is removed either by filtration, draining, or drying, or a combination of these. The resulting sulfonated objects, after removal of excess water, become strongly bonded to form a mat or paper preform. In embodiments where sulfonated polyolefin fibers are used, the sulfonated polyolefin fibers can be passed through a slit die, during or after contact with water, in order to orient the fibers in a special arrangement to make a mat or paper preform. When being passed through a slit die, the fibers are generally in the form of a viscous suspension and then placed under pressure in a hot chamber where solvents volatilize. Generally, after excess water is removed, the sulfonated polyolefin objects are dried or annealed either under ambient conditions (e.g., 20-35° C.) or at an elevated temperature, such as a temperature of precisely, about, at least, up to, or less than 40, 50, 60, 70, 80, 90, 100, 120, 150, 175, 200, 250, or 300° C., or a temperature within a range bounded by any two of the foregoing values.

[0073] In other embodiments, the sulfonated polyolefin objects are contacted with water by contacting the sulfonated polyolefin fibers with water vapor. Any gaseous atmosphere containing water vapor is applicable herein. Typically, the humidity level of the water-containing atmosphere is precisely, about, or at least, for example, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, or 100%. The water-containing atmosphere generally includes, besides water vapor, those gases normally found in air, or an inert atmosphere, such as nitrogen, argon, or carbon dioxide. The water-containing atmosphere may or may not also include one or more reactive gases that function, for example, to further encourage inter-object (or interfilament) bonding or alter the surface chemistry of the sulfonated objects.

[0074] The sulfonated polyolefin objects and/or the water contacting the sulfonated polyolefin objects may be held at any suitable temperature during contact of the sulfonated objects with water or an aqueous solution. In some embodiments, the sulfonated objects and/or water are at room temperature, such as precisely or about 20, 25, 30, or 35° C. In other embodiments, the sulfonated objects and/or water are at an elevated temperature, such as precisely or about 40, 50, 60, 70, 80, 90, or 100° C. In other embodiments, the sulfonated objects and/or water are at a depressed temperature, such as precisely or about 0, 10, or 15° C. In some embodiments, the temperature of the sulfonated objects and/or water is within a range bounded by any two of the exemplary temperatures provided above.

[0075] One or more additional steps or conditions can be employed, besides contact with water, to promote inter-object or interfilament bonding in the sulfonated polyolefin objects. The one or more additional steps or conditions can be, for

example, any of the chemical or physical bonding techniques generally discussed above and as known in the art. In a particular embodiment, a hot stamping process or mechanical pinning, as well known in the art, is applied to the sulfonated polyolefin objects. The sulfonated polyolefin objects may also be coated with a plasticizer, which can be any suitable plasticizing compound or material, such as a polyol (e.g., ethylene glycol, diethyleneglycol, or glycerol) or organic solvent. In some embodiments, the sulfonated polyolefin objects are subjected to a hot stamping process, mechanical pinning, or plasticization without first exposing (or ever exposing) the sulfonated objects to water.

[0076] To produce the mat or paper preform, partially or completely sulfonated polyolefin fibers may be arranged in a non-woven mat or paper form, and then bonded, as described above, to form the preform. In other embodiments, unsulfonated polyolefin fibers are arranged in a non-woven mat or paper form, and then bonded, by any of the chemical or physical techniques described above (e.g., hot stamping, partial melting, or plasticization) to form a preform that is then subjected to sulfonation conditions to partially or completely sulfonate the preform. In yet other embodiments, a non-woven mat or paper preform composed of partially sulfonated polyolefin fibers is subsequently further sulfonated. In particular embodiments, unsulfonated polyolefin fibers are arranged in a non-woven mat or paper form, and then bonded by any of the processing techniques known in the art for producing a spun-bonded or melt-blown mat, before being sulfonated.

[0077] Examples have been set forth below for the purpose of illustration and to describe certain specific embodiments of the invention. However, the scope of this invention is not to be in any way limited by the examples set forth herein.

Example 1

Preparation of Sulfonated Polyolefin (LLDPE) Fiber

[0078] An as-spun tow of neat LLDPE of 1560 filaments (18 micrometer filament diameter) was continuously processed through a two-part reactor containing (1) concentrated sulfuric acid, and (2) oleum with 20% SO₃. The speed of the fiber was adjusted to attain proper residence time. A tensile stress of 5 MPa was applied to the fiber during semi-continuous processing. For the concentrated sulfuric acid bath, the temperature was maintained at 115° C. A temperature below 100° C. in the concentrated sulfuric acid bath did not result in an infusible fiber even after 12 hours of treatment. For the oleum bath (which is a concentrated sulfuric acid bath containing dissolved SO₃ gas), the temperature was maintained at 90° C. A residence time of 4 hours and 40 minutes was used for the concentrated sulfuric acid and oleum baths, respectively, which resulted in infusible fibers that were found to be hygroscopic under ambient conditions.

[0079] The oleum-based sulfonated LLDPE fibers treated at 70, 80, 90, and 97° C. resulted in 1.21, 1.49, 1.55, and 1.61 g/cc densities, respectively, in the resulting sulfonated fibers. The mechanical properties of the fibers are displayed in the table below.

TABLE 1

Mechanical properties of the sulfonated LLDPE fibers					
Fiber	Density (g/cc)	Diameter (mm)	Tensile strength (ksi)	Modulus (Msi)	Elongation (%)
As-spun LLDPE	0.94	16-20	20-25	0.1-0.3	100
Sulfonated by conc. H ₂ SO ₄ at 97° C. for 12 hours	—	20	12	0.1	12
Stabilized by oleum at 97° C. for 4 hours	1.61	20-25	7	0.2	15

[0080] As shown in Table 1, the sulfonated filaments exhibit greater than 10% ultimate elongation, which is important for conversion of tow into fabric by proper fabrication technique, such as knitting or weaving. The completely sulfonated fibers with high densities are thermally infusible and do not catch fire in open flame under ambient conditions. Sulfonated filaments with a density above 1.45 g/cc tend to exhibit flame-resistance.

[0081] However, the thermal treatment causes release of SO₂ gas, which is known to be toxic. For sequestration or adsorption of SO₂ gas, the sulfonated fiber was coated with ZnO powder by passing the fiber through a fluidized bed of ZnO. The sulfonated filaments were dispersed in ZnO suspension in tetrahydrofuran solvent. After soaking for 2 minutes in ZnO suspension, the fibers were removed from the liquid medium by use of a tweezer.

[0082] The TGA data (scanned at 10° C./min under nitrogen) of the sulfonated fiber and ZnO coated sulfonated fibers are shown in FIG. 2. It was observed that the presence of a ZnO coating reduced the SO₂ release kinetics, and the derivative thermogravimetric (DTG) analysis peak maxima (as shown in FIG. 3) shifted to higher temperature by 12° C. The pyrolysis of ZnO coated sulfonated fibers above 400° C. was found to be more intense than that in neat sulfonated fibers. Thus, the presence of a SO₂-scavenger retards desulfonation and forms an adduct containing SO_x that finally decomposes above 850° C. (FIG. 2).

Example 2

Preparation of Sulfonated Polyolefin (LLDPE) Fiber Using E-beam Irradiation

[0083] The LLDPE fiber tow discussed in Example 1 was e-beam irradiated at 10-1000 kGy to reduce the melting temperature, which in turn accelerated the sulfonation kinetics during subsequent sulfonation reaction. As shown in FIG. 4, increasing radiation dosage results in a reduction in melting temperature of polyethylene fibers with overall heat of fusion, i.e., crystallinity, of the fibers remaining unchanged, even when they were irradiated at 1000 kGy dosage. However, when polyethylene fiber was irradiated in the presence of a SO₂ gas and at 500 kGy dose, a significant reduction in crystallinity was observed, as also shown in FIG. 4. This indicates crosslinking of the polymer by the SO₂ gas and e-beam. The highly irradiated fibers were dissolved in the sulfonation bath due to vigorous reaction. However, unlike the neat PE fiber sample described in Example 1, the 10 kGy irradiated fiber, when treated with concentrated H₂SO₄ for 12 hours at 97° C., resulted in an infusible fiber. Thus, it was

herein found that generation of free radicals in the polyolefin accelerates the sulfonation kinetics and more quickly converts the flame retardant material.

[0084] While there have been shown and described what are at present considered the preferred embodiments of the invention, those skilled in the art may make various changes and modifications which remain within the scope of the invention defined by the appended claims.

What is claimed is:

1. A flame retardant composition comprising sulfonated polyolefin and a SO₂-scavenging material.

2. The composition of claim 1, wherein said SO₂-scavenging material is incorporated within the sulfonated polyolefin.

3. The composition of claim 1, wherein said sulfonated polyolefin is in the form of an object which has on its surface a layer of said SO₂-scavenging material.

4. The composition of claim 1, wherein said SO₂-scavenging material is comprised of a metal oxide.

5. The composition of claim 4, wherein said metal oxide is a transition metal oxide.

6. The composition of claim 5, wherein said transition metal oxide is zinc oxide.

7. The composition of claim 4, wherein said metal oxide is an alkaline earth oxide.

8. The composition of claim 1, wherein said SO₂-scavenging material is comprised of ammonium or phosphonium groups serving as countercations to sulfonate groups residing on or in the sulfonated polyolefin.

9. The composition of claim 1, wherein said flame retardant composition is further comprised of a flame retardant material that is not a sulfonated polyolefin.

10. The composition of claim 9, wherein said flame retardant material is comprised of a silicate-containing material.

11. The composition of claim 10, wherein said silicate-containing material is a clay.

12. The composition of claim 1, wherein said polyolefin is selected from polyethylene, polypropylene, polybutadiene, polyisoprene, and combinations thereof.

13. The composition of claim 1, wherein the flame retardant composition exhibits an elongation at break of at least 5%.

14. The composition of claim 1, wherein the flame retardant composition exhibits an elongation at break of at least 15%.

15. A flame-resistant composite comprised of a host material requiring flame resistance in which is incorporated sulfonated polyolefin as a flame retardant composition.

16. The flame-resistant composite of claim 15, wherein said flame-resistant composite further comprises a SO₂-scavenging material incorporated therein.

17. The flame-resistant composite of claim 16, wherein said SO₂-scavenging material is comprised of a metal oxide.

18. The flame-resistant composite of claim 15, wherein said flame retardant composition further comprises a flame retardant material incorporated therein, wherein said flame retardant material is not a sulfonated polyolefin.

19. The flame-resistant composite of claim 18, wherein said flame retardant material is comprised of a silicate-containing material.

20. The flame-resistant composite of claim 15, wherein said host material requiring flame resistance is a fabric.

21. The flame-resistant composite of claim 15, wherein said host material requiring flame resistance is a plastic.

22. A method for producing a flame retardant composition, the method comprising combining sulfonated polyolefin with a material selected from a SO₂-scavenging material, a flame retardant material that is not a sulfonated polyolefin, and combination thereof.

23. The method of claim **22**, wherein said SO₂-scavenging material is incorporated into said sulfonated polyolefin.

24. The method of claim **22**, wherein said SO₂-scavenging material is coated onto said sulfonated polyolefin fiber. said sulfonated polyolefin is in the form of an object which has on its surface a layer of said SO₂-scavenging material.

25. The method of claim **22**, further comprising producing the sulfonated polyolefin fiber by sulfonating a polyolefin fiber.

26. The method of claim **22**, wherein said SO₂-scavenging material is comprised of a metal oxide.

27. The method of claim **22**, wherein said SO₂-scavenging composition is comprised of ammonium or phosphonium groups serving as counterions to sulfonate groups residing on the surface of the sulfonated polyolefin fiber.

28. The method of claim **22**, wherein said flame retardant material is comprised of a silicate-containing material.

29. A method for forming a flame-resistant composite, the method comprising forming a composite of a sulfonated polyolefin and a host material in need of flame resistance.

30. The method of claim **29**, further comprising incorporating a SO₂-scavenging material into said flame-resistant composite.

31. The method of claim **30**, wherein said SO₂-scavenging material is comprised of a metal oxide.

32. The method of claim **30**, further comprising incorporating a flame retardant material that is not a sulfonated polyolefin into said flame-resistant composite.

33. The method of claim **32**, wherein said flame retardant material is comprised of a silicate-containing material.

34. The method of claim **29**, wherein said flame-resistant composite is a flame-resistant textile, and said flame-resistant textile is formed by a process comprising weaving or bonding a flame retardant composition comprising sulfonated polyolefin fiber having an elongation at break of at least 10% with itself and/or other fibers of a textile.

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