

MODIFIED BROMINATED POLYSTYRENES AS COMPATIBLE FLAME RETARDANTS FOR POLYMERIC COMPOSITIONS

BACKGROUND

[0001] Various commercial polymers from commodity to engineering plastics such as polyolefins, polystyrenes, polyesters and polyamides have been extensively used in many applications due to their versatile properties. However, poor flame resistance can preclude their use in some applications. This is because covalently bonded hydrocarbon back-bone chains are decomposed and burned when polymers are exposed fire. There are various types of fire-retardant materials that can impart fire-resistance properties to polymers. Among the many types of fire retardants, halogen compounds are widely applied for polyolefins due to their advantages such as cost-effectiveness, good processibility and efficient fire retardation. Brominated flame retardants (BrFRs) are primarily effective because of the acceptable range of the bond energy between aliphatic or aromatic carbon and bromine. The bond energy is neither too high nor low so that they are decomposed and perform the function of neutralization to hydrogen or hydroxyl radicals generated by fire.

[0002] Among different types of BrFRs, brominated polystyrene (BPS) is a polymeric BrFR with superior features such as excellent thermal stability. However, BPS causes a drop of mechanical properties such as tensile strength, flexural strength, and impact strength in polyolefins into which it is incorporated. The fracture toughness value (critical energy release rate, G_{IC}) for polypropylene containing BrFRs shows substantial reductions up to 50% compared to neat polypropylene under the impact condition.

[0003] Despite advances in flame-retardant materials research, there is still a scarcity of compositions including both brominated polystyrenes as flame retardants and polymers typically thought to be incompatible with brominated polystyrenes, where the compositions are adequately mixed and have excellent mechanical properties. Such compositions would be particularly useful as coatings for cables and wires, as well as components of other articles. These needs and other needs are satisfied by the present disclosure.

SUMMARY

[0004] In accordance with the purpose(s) of the present disclosure, as embodied and broadly described herein, the disclosure, in one aspect, relates to flame-retardant compositions including a brominated polystyrene reacted in the presence of a second monomer or a first portion of a second polymer and, optionally, at least a second portion of the second polymer that is not reacted with the brominated polystyrene. In some aspects, the first portion and the second portion of the second polymer can be selected from a polyamide, a polyolefin, a polyester, a styrenic polymer or copolymer, or any combination thereof. In any of these aspects, the flame-retardant compositions of the present disclosure are well-mixed and have excellent properties and can optionally include crosslinks for added mechanical strength. Also disclosed herein are methods for making the compositions and articles including the compositions.

[0005] Other systems, methods, features, and advantages of the present disclosure will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional systems, methods, features, and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims. In addition, all optional and preferred features and modifications of the described embodiments are usable in all aspects of the disclosure taught herein. Furthermore, the individual features of the dependent claims, as well as all optional and preferred features and modifications of the described embodiments are combinable and interchangeable with one another.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Many aspects of the present disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the principles of the present disclosure. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

[0007] FIG. 1 shows ^1H NMR spectroscopy used for calculating the M_n ratio in an XLPE/gBPS-0.4 wt% polymer blend.

[0008] FIG. 2 shows ^1H NMR spectroscopy used for calculating the M_n ratio in an XLPE/gBPS-2.1 wt% polymer blend.

[0009] FIG. 3 is a schematic demonstrating present mixtures of brominated polystyrenes and polyolefin resins do not mix well (left panel) but that modified brominated polystyrenes blend well with polyolefins and other resins.

[0010] FIG. 4A is a schematic showing a brominated polystyrene in one potential modified form to include a reactive group such as a trimethoxysilyl group, while FIG. 4B is a schematic of a commercial resin that can include, but is not limited to, a polyolefin, which is also modified to include a reactive group such as a trimethoxysilyl group.

[0011] FIG. 5 is a schematic showing crosslinking of the reactive groups on the brominated polystyrene (see FIG. 4A) and on the commercial resin (see FIG. 4B) according to one embodiment of a flame-retardant composition as described herein.

[0012] Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or can be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DETAILED DESCRIPTION

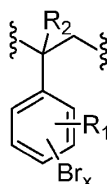
[0013] The present disclosure provides for flame-retardant compositions, methods of making flame-retardant compositions, and articles incorporating the flame-retardant compositions. The present disclosure is advantageous because it makes use of flame retardants that do not bioaccumulate and contribute to health problems in humans or animals. This may be particularly important since the flame-retardant compositions may be used as coverings for cables and wires, which may be exposed to the environment. The flame-retardant compositions have a homogeneous composition that enables the manufacture of articles with improved mechanical properties compared to materials currently used in molded parts and cable or wire applications. The flame-retardant compositions can also have improved appearance, including improved gloss.

[0014] Disclosed herein is a flame-retardant composition including a brominated polystyrene modified via a first portion of a second polymer. In some aspects, the composition further includes at least a second portion of the second polymer that is not reacted in the presence of the brominated polystyrene. In an aspect, the first portion and the second portion of the second polymer include a polyamide, a polyolefin, a polyester, a styrenic polymer or copolymer, or any combination thereof.

[0015] In one aspect, when the first and second portions of the second polymer include a polyamide, the polyamide is or includes nylon 6,6; nylon 6; nylon 6, 10; nylon 11; nylon 6,12; nylon 12; nylon 6,9; nylon 4,6; poly(m-phenylene isophthalamide); poly(p-phenylene

terephthalamide); copoly(p-phenylene/d,4'-diphenyl ether terephthalamide); PA66/6, PA6T, PA9T, PA10T, PA4T, poly(m-xylene sebacamide), poly(m-xylene adipamide), a copolymer thereof, or any combination thereof. In another aspect, when the first and second portions of the second polymer include a polyolefin, the polyolefin is or includes low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), very-low-density polyethylene (VLDPE), ultra-low-density polyethylene (ULDPE), medium-density polyethylene (MDPE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), ethylene-octene copolymer, stereo-block PP, olefin block copolymer, propylene-butane copolymer, polyisobutylene (PIB), poly(α -olefin), ethylene propylene rubber (EPR), ethylene propylene diene monomer rubber (EPDM rubber), high-density polyethylene (HDPE), ultra high density polyethylene (UHDPE), cross-linked polyethylene (PEX or XLPE), or any combination thereof. In still another aspect, when the first and second portions of the second polymer include a polyester, the polyester is or includes polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), polybutylene terephthalate (PBT), poly(cyclohexylenedimethylene terephthalate) (PCT), polylactic acid (PLA), polycaprolactone (PCL), polyethylene terephthalate glycol (PETG), polycyclohexylenedimethylene terephthalate glycol (PCTG), or any combination thereof. In yet another aspect, when the first and second portions of the second polymer include a styrenic polymer or copolymer, the styrenic polymer or copolymer is or includes poly(styrene-co-acrylonitrile) (SAN), poly(acrylonitrile-co-butadiene-styrene) (ABS), or any combination thereof.

[0016] In another aspect, the brominated polystyrene includes a plurality of monomer units having a structure of Formula I:



Formula I

wherein x in each monomer unit of the plurality is independently from 0 to 4;

wherein R₁ in each monomer unit of the plurality independently is selected from hydrogen, bromine, NR_{1a}R_{1b}, or a pendant group comprising at least 2 carbons;

wherein R_{1a} and R_{1b} are independently selected from C1 to C30 linear or branched hydrocarbons;

and wherein R_2 in each monomer unit of the plurality independently is selected from hydrogen or a pendant group comprising at least 2 carbons.

[0017] Further in this aspect, the pendant group connected to R_1 and/or R_2 can include at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 carbons, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values.

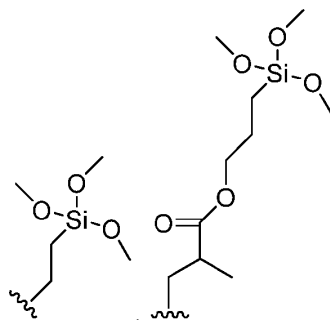
[0018] Also disclosed herein is a flame-retardant composition wherein each R_1 is hydrogen or bromine and each R_2 is independently hydrogen or the pendant group including at least 2 carbons. In another aspect, each R_2 is hydrogen and each R_1 is independently hydrogen, bromine, or the pendant group including at least 2 carbons.

[0019] In one aspect, an average value for x over the plurality of monomer units is from about 2 to about 5, or from about 2 to about 4, or from about 2 to about 3, or is about 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5, 3.75, 4, 4.25, 4.5, 4.75, or about 5, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values. Further in this aspect, x can be a whole number or may not be a whole number but rather a fractional or decimal value.

[0020] In one aspect, about one pendant group containing at least 2 carbons is present at R_1 or R_2 in levels from 0 to 250 of the total monomer units. In the brominated polystyrene represented in formula I there may be a pendant group on 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240 or about 250 monomer units in the plurality, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values.

[0021] In another aspect, the disclosed flame-retardant composition includes from about 0 to about 2.1 wt% pendant groups per total weight of the brominated polystyrene, about 0 to 0.75 wt%, about 0.5 to 0.7 wt%, about 1 to 2 wt%, or about 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, or about 2.1 wt% pendant groups, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values.

[0022] In some aspects, the pendant group having at least 2 carbons of at least one monomer unit of the plurality includes a trimethoxysilyl group. In one aspect, the pendant



group can be selected from , or any combination thereof.

[0023] In one aspect, the first portion of the second polymer includes at least one pendant group including a trimethoxysilyl group. In still another aspect, the flame-retardant composition includes at least one crosslink between a trimethoxysilyl group on a brominated polystyrene and a trimethoxysilyl group in the first portion of the second polymer.

[0024] In certain embodiments, the pendant groups at either R1 or R2 in formula I as described may be introduced to the brominated polystyrene during a modification reaction.

[0025] In certain embodiments, an acrylate or vinyl monomer possessing a pendant group that includes at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 carbons, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values, may be polymerized to form oligomers or homopolymers with a minimum of 2 repeat units during the modification reaction.

[0026] In some aspects, these acrylate or vinyl oligomers or homopolymers have between 2 and 1000 repeat units, including any whole number of repeat units in this range. The oligomers and homopolymers present may all have different numbers of repeat units, they may have the same number of repeat units, or they may have any distribution of repeat units within this range.

[0027] In some aspects, the flame-retardant compositions disclosed herein can also include a synergist. In a further aspect, the synergist can be antimony trioxide (herein Sb_2O_3 or ATO) or another synergist. In another aspect, the flame-retardant compositions can include from about 1% to about 10%, about 1% to about 5%, about 5% to about 10%, or about 3% to about 7% by weight of Sb_2O_3 or other synergist, or about 1, 2, 3, 4, 5, 6, 7,

8, 9, or about 10% by weight Sb_2O_3 or other synergist, a combination of any of the foregoing values, or a range encompassing any of the foregoing values.

[0028] In some aspects, the disclosed compositions also include a filler such as, for example, talc, calcium carbonate, AgO , ZnO , CaO , MnO , $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, $\text{Mg}(\text{OH})_2$, kaolinite, wollastonite, mica, glass beads, or any combination thereof. In one aspect, the disclosed compositions also include a reinforcing agent such as, for example, glass fibers.

[0029] In one aspect, disclosed herein are articles including the disclosed flame-retardant compositions. In one aspect, the articles have a flammability rating of V0 according to test method UL94. In one aspect, the articles can include molded parts for use in the housing, connectors, and/or circuit boards for electronics, various automotive uses such as, for example, parts in the engine compartment, seating, insulation, and interior components, and residential uses including insulation, carpeting, and wall coverings. In another aspect, the articles can be coverings for cables and/or wires. In yet another aspect the disclosed articles can be or include textiles and/or adhesives

[0030] The present disclosure provides for methods of making flame-retardant compositions. In an aspect, the method includes admixing an acrylate monomer with a brominated polystyrene to form a precursor mixture. The admixing step can be performed for a time period of from about 0.1 min to about 30 min, or from about 0.1 to about 5 min, from about 5 min to about 15 min, or from about 15 min to about 30 min, or can be about 0.1, 1, 2, 5, 10, 15, 20, 25, or about 30 min, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values. The admixing step can be conducted a temperature of about 160 °C to about 230 °C, about 160 °C to about 180 °C, about 175 to about 200 °C, about 200 to about 230 °C, or at about 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 225, or about 230 °C, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values.

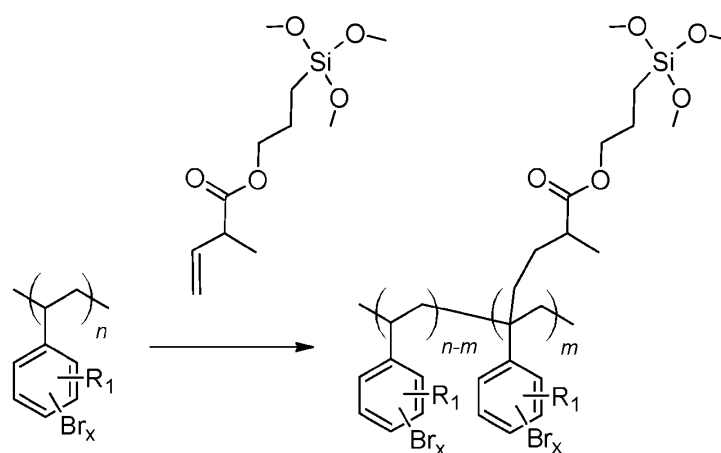
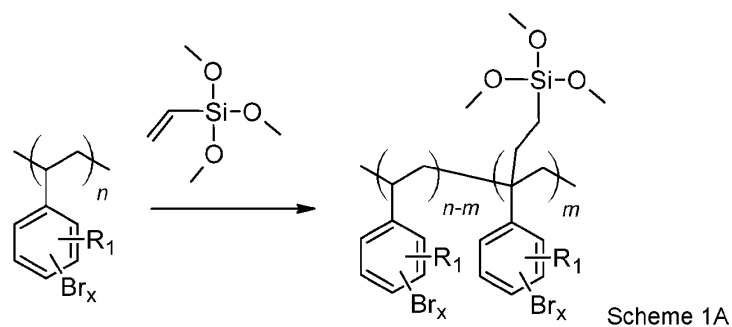
[0031] The precursor mixture is blended to produce the brominated polystyrene modified by the presence of first portion of the second polymer. The blending step can be performed for a time period of from about 0.1 min to about 30 min, or from about 0.1 to about 5 min, from about 5 min to about 15 min, or from about 15 min to about 30 min, or can be about 0.1, 1, 2, 5, 10, 15, 20, 25, or about 30 min, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values. The blending step can be conducted a temperature of about 160 °C to about 230 °C, about 160 °C to about 180 °C, about 175 to about 200 °C, about 200 to about 230 °C, or at about 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 225, or about 230 °C, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values.

[0032] The brominated polystyrene with the first portion of the second polymer can then be admixed with the second portion of the second polymer. This admixing step can be performed for a time period of from about 0.1 min to about 30 min, or from about 0.1 to about 5 min, from about 5 min to about 15 min, or from about 15 min to about 30 min, or can be about 0.1, 1, 2, 5, 10, 15, 20, 25, or about 30 min, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values. This admixing step can be conducted at a temperature of about 160 °C to about 230 °C, about 160 °C to about 180 °C, about 175 to about 200 °C, about 200 to about 230 °C, or at about 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 225, or about 230 °C, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values. The synergist such as, for example, antimony trioxide, can be added during any part of the mixing process.

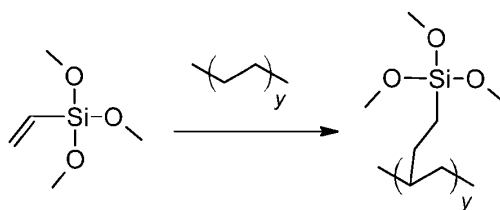
[0033] The method can also optionally include curing the flame-retardant composition in water. The curing can be performed for a time period of from about 1 hour to about 10 days, or from about 1 hour to about 24 hours, about 1 day to about 5 days, or about 5 days to about 10 days, or can be carried out for about 1, 2, 6, 12, 18, or 24 hours, or about 2, 3, 4, 5, 6, 7, 8, 9, or about 10 days, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values. In another aspect, the curing can be performed at a temperature of from about 25 °C to about 200 °C, from about 25 °C to about 50 °C, from about 50 to about 75 °C, or from about 75 °C to about 100 °C, or at about 25, 50, 100, 150, or about 200 °C, or a combination of any of the foregoing values, or a range encompassing any of the foregoing values.

[0034] In one aspect, the acrylate monomer can have at least 5 carbon atoms. For example, the acrylate monomer can be or include 3-(trimethoxysilyl) propyl methacrylate (TMSPMA), vinyltrimethoxy silane, vinyl triethoxy silane, or other vinyl containing species used by those skilled in the art of moisture cure wire and cable production, or a combination thereof. In some aspects, the precursor mixture further includes an initiator such as, for example, dicumyl peroxide, di(tert-butylperoxyisopropyl)benzene, cumyl hydroperoxide, 2,3-dimethyl-2,3-diphenylbutane, benzoyl peroxide, tert-butyl peroxybenzoate, di-tert butyl peroxide, azobisisobutyronitrile, or any combination thereof.

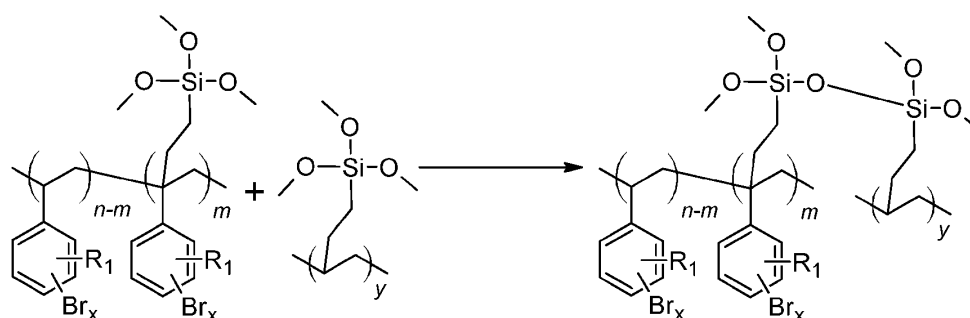
[0035] In certain embodiments, the brominated polystyrene may be modified to include a reactive group through reactive extrusion according to the procedure shown in Scheme 1A or Scheme 1B. A schematic diagram of this process is shown in **FIG. 4A**.



[0036] In certain embodiments, the resin such as, for example, a polyolefin resin may be modified to include a reactive group through reactive extrusion according to the procedure shown in Scheme 2. A schematic diagram of this process is shown in FIG. 4B.

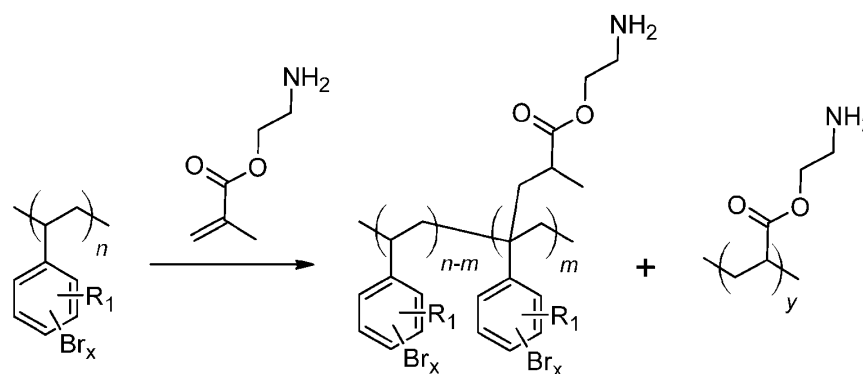


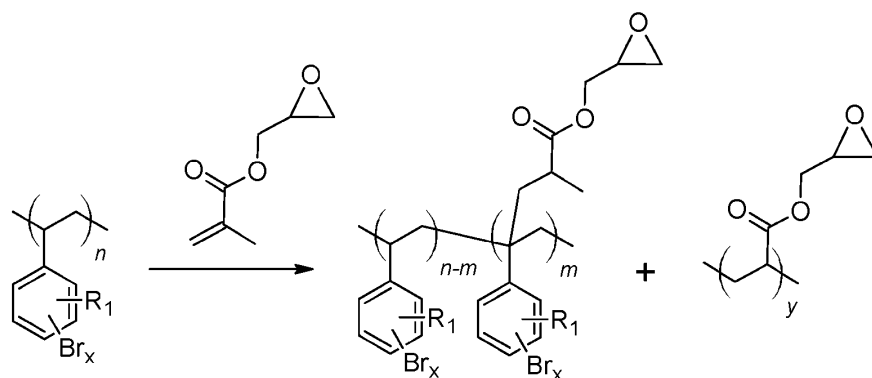
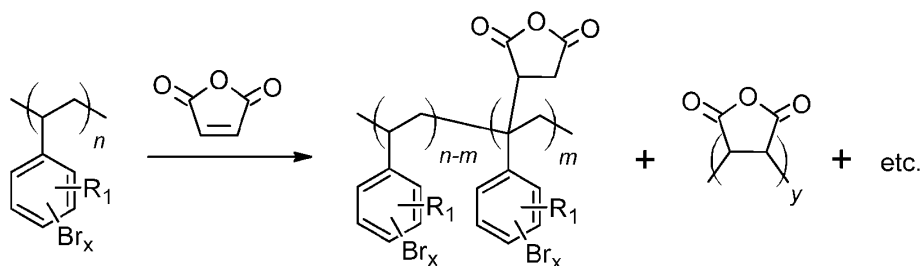
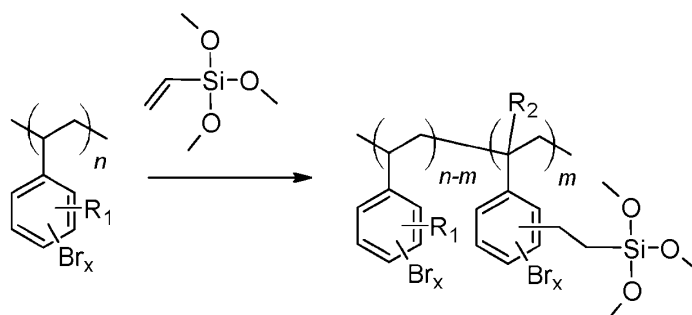
[0037] In certain embodiments, the grafted brominated polystyrene and resin can be crosslinked by water curing or another method according to the procedure shown in Scheme 3. A schematic diagram of this process is shown in FIG. 5.



Scheme 3

[0038] Schemes 4 to 7 depict some of the many modifications and other embodiments disclosed herein that will come to mind to one skilled in the art to which the disclosed compositions and methods pertain having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the disclosures are not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. The skilled artisan will recognize many variants and adaptations of the aspects described herein. These variants and adaptations are intended to be included in the teachings of this disclosure and to be encompassed by the claims herein.

Scheme 4 ($m \geq 0$, $y \geq 0$ and $m + y \geq 2$)

Scheme 5 ($m \geq 0$, $y \geq 0$ and $m + y \geq 2$)Scheme 6 ($m \geq 0$, $y \geq 0$ and $m + y \geq 2$)Scheme 7 ($m \geq 0$, $y \geq 0$ and $m + y \geq 2$)

[0039] Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

[0040] As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure.

[0041] Any recited method can be carried out in the order of events recited or in any other order that is logically possible. That is, unless otherwise expressly stated, it is in no way intended that any method or aspect set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not specifically state in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to arrangement of steps or operational flow, plain meaning derived from grammatical organization or punctuation, or the number or type of aspects described in the specification.

[0042] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The publications discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided herein can be different from the actual publication dates, which can require independent confirmation.

[0043] While aspects of the present disclosure can be described and claimed in a particular statutory class, such as the system statutory class, this is for convenience only and one of skill in the art will understand that each aspect of the present disclosure can be described and claimed in any statutory class.

[0044] It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the disclosed compositions and methods belong. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent

with their meaning in the context of the specification and relevant art and should not be interpreted in an idealized or overly formal sense unless expressly defined herein.

[0045] Prior to describing the various aspects of the present disclosure, the following definitions are provided and should be used unless otherwise indicated. Additional terms may be defined elsewhere in the present disclosure.

Definitions

[0046] As used herein, “comprising” is to be interpreted as specifying the presence of the stated features, integers, steps, or components as referred to, but does not preclude the presence or addition of one or more features, integers, steps, or components, or groups thereof. Moreover, each of the terms “by,” “comprising,” “comprises,” “comprised of,” “including,” “includes,” “included,” “involving,” “involves,” “involved,” and “such as” are used in their open, non-limiting sense and may be used interchangeably. Further, the term “comprising” is intended to include examples and aspects encompassed by the terms “consisting essentially of” and “consisting of.” Similarly, the term “consisting essentially of” is intended to include examples encompassed by the term “consisting of.”

[0047] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a monomer,” “a polyamide,” or “a filler,” include, but are not limited to, mixtures or combinations of two or more such monomers, polyamides, or fillers, and the like.

[0048] It should be noted that ratios, concentrations, amounts, and other numerical data can be expressed herein in a range format. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms a further aspect. For example, if the value “about 10” is disclosed, then “10” is also disclosed.

[0049] When a range is expressed, a further aspect includes from the one particular value and/or to the other particular value. For example, where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included

in the disclosure, e.g. the phrase “x to y” includes the range from ‘x’ to ‘y’ as well as the range greater than ‘x’ and less than ‘y.’ The range can also be expressed as an upper limit, e.g. ‘about x, y, z, or less’ and should be interpreted to include the specific ranges of ‘about x,’ ‘about y,’ and ‘about z’ as well as the ranges of ‘less than x,’ ‘less than y,’ and ‘less than z.’ Likewise, the phrase ‘about x, y, z, or greater’ should be interpreted to include the specific ranges of ‘about x,’ ‘about y,’ and ‘about z’ as well as the ranges of ‘greater than x,’ ‘greater than y,’ and ‘greater than z.’ In addition, the phrase “about ‘x’ to ‘y’”, where ‘x’ and ‘y’ are numerical values, includes “about ‘x’ to about ‘y’”.

[0050] It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a numerical range of “about 0.1% to 5%” should be interpreted to include not only the explicitly recited values of about 0.1% to about 5%, but also include individual values (e.g., about 1%, about 2%, about 3%, and about 4%) and the sub-ranges (e.g., about 0.5% to about 1.1%; about 5% to about 2.4%; about 0.5% to about 3.2%, and about 0.5% to about 4.4%, and other possible sub-ranges) within the indicated range.

[0051] As used herein, the terms “about,” “approximate,” “at or about,” and “substantially” mean that the amount or value in question can be the exact value or a value that provides equivalent results or effects as recited in the claims or taught herein. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art such that equivalent results or effects are obtained. In some circumstances, the value that provides equivalent results or effects cannot be reasonably determined. In such cases, it is generally understood, as used herein, that “about” and “at or about” mean the nominal value indicated $\pm 10\%$ variation unless otherwise indicated or inferred. In general, an amount, size, formulation, parameter or other quantity or characteristic is “about,” “approximate,” or “at or about” whether or not expressly stated to be such. It is understood that where “about,” “approximate,” or “at or about” is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0052] As used herein, the term “effective amount” refers to an amount that is sufficient to achieve the desired modification of a physical property of the composition or material. For

example, an “effective amount” of a brominated polystyrene refers to an amount that is sufficient to achieve the desired improvement in the property modulated by the formulation component, e.g. achieving the desired level of flame retardance while maintaining good mechanical properties. The specific level in terms of wt% in a composition required as an effective amount will depend upon a variety of factors including the amount and type of polymer, amount and type of brominated polystyrene including the degree of substitution of bromine atoms, amount and type of any fillers used, and end use of the article made using the composition.

[0053] As used herein, the terms “optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0054] “Test method UL94” refers to a test method produced by Underwriters Laboratories (UL) intended to serve as a preliminary indication of plastic acceptability for use as part of an article with respect to flammability. To achieve a V-0 flammability rating, for example, burning of an article stops within 10 seconds after two applications of ten seconds each of a flame set to a test bar. Flaming drips may not be present.

[0055] Unless otherwise specified, temperatures referred to herein are based on atmospheric pressure (i.e. one atmosphere).

[0056] Now having described the aspects of the present disclosure, in general, the following Examples describe some additional aspects of the present disclosure. While aspects of the present disclosure are described in connection with the following examples and the corresponding text and figures, there is no intent to limit aspects of the present disclosure to this description. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of the present disclosure.

EXAMPLES

[0057] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the disclosure and are not intended to limit the scope of what the inventors regard as their disclosure. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

Example 1: Preparation of XLPE/gBPS-0.4 wt% Polymer BlendModification Reaction

[0058] Dicumyl peroxide (DCP, 0.163 g) solid was dissolved in 0.326 g 3-(trimethoxysilyl)propyl methacrylate (TMSPMA). This solution of TMSPMA/DCP was then manually mixed with 6.20 g BPS powders. The mixture was added into a twin extruder (ThermoFisher Scientific HAAKE MiniCTW Micro-Conical Twin Screw Compounder) and blended at 185 °C for 10 minutes. The screw speed was 300 rpm. The modified product rBPS (reactive BPS) was produced in the amount of 6.21 g.

Calculation of Polymer Ratio

[0059] The modified product rBPS (0.5 g) was dissolved in 5 mL THF (tetrahydrofuran) via sonication. Then this solution was added drop by drop into 50 mL methanol solvent with stirring. The rBPS precipitates out. The solution was filtered and rBPS precipitates were collected. This purification process was repeated twice more to remove residual unreacted TMSPMA monomers and DCP decomposition products. The rBPS precipitates are dried in a vacuum oven at 120 °C overnight. The polymer ratio of rBPS was calculated using proton nuclear magnetic resonance (¹H NMR). 100 mg purified rBPS was dissolved in 1 mL deuterated chloroform (CDCl₃) and the solution is used for ¹H NMR measurement. The BPS had a bromine content of 68.5 wt.%, which meant in each repeat unit of BPS chemical structure, there were 2.75 Br atoms and 2.25 H atoms connecting to the benzene ring of BPS. The molar mass of a repeat unit of BPS was 321 g/mol while the molar mass of TMSPMA was 248 g/mol. The proton atoms in trimethoxy groups of TMSPMA were chosen as the characteristic peaks for the calculation. The ¹H NMR result is shown in FIG. 1 and the calculation procedure was as follows:

[0060] For every 9 proton atoms in the trimethoxy groups (chemical shift $\delta = 3.60$), there are 445.8 proton atoms connecting to benzene ring of BPS ($\delta = 5.6 \sim 8.0$). This means when there is a TMSPMA molecule in a rBPS polymer chain, there are $(445.8 \times 0.98) / 2.25 = 194$ BPS repeat units. Note that the coefficient 0.98 is applied here to account for the contribution from the peak area of deuterated chloroform. Then the polymer ratio, namely $w(\text{TMSPMA})/w(\text{rBPS})$ or $w(\text{TMSPMA})/(w(\text{TMSPMA})+w(\text{BPS}))$, is calculated:

$$248 / (248 + 194 \times 321) = 0.004 = 0.4\% \text{ by weight.}$$

[0061] The rBPS product with a polymer ratio of 0.4 wt% is named as rBPS-0.4 wt%.

Preparation of XLPE/rBPS-0.4 wt% Polymer Blend

[0062] Unlike the purification process in ^1H NMR measurement, the rBPS product obtained in step 1 was placed in a vacuum oven (10 mm Hg/180 °C/1 hour) to remove residual TMSPMA monomers. The purified rBPS was then used for polymer blending as follows:

[0063] The crosslinkable polyethylene (rPE) (LyondellBasell AQUATHENE 120000, 39.0 g) and rBPS-0.4 wt.% (13.0 g) were first blended in a twin-screw Haake mixer (Haake Buchler Rheocord system 40) at 225 °C for 7 minutes. The blend was further blended with a catalyst masterbatch (LyondellBasell AQUATHENE CM04482, 2.6 g) at 185 °C for 7 minutes with a weight composition of rPE/rBPS/Cat. = 75/25/5. The rPE/rBPS/Cat. blend was injection molded into rectangular bars and tensile bars for mechanical testing using ThermoFisher Scientific HAAKE MiniJet Pro Piston Injection Molding System. These bars were placed in a vial full of water and placed in an oven at 90 °C over night; the methoxysilane groups should react with each other in this water curing step and crosslinked samples are finally achieved, namely XLPE/rBPS-0.4 wt% polymer blend.

[0064] Izod testing showed an impact strength of 5.88 kJ/m² compared to 8.5 kJ/m² for XLPE/BPS and 84.8 kJ/m² for XLPE. Hot creep testing showed 2% $\pm$ 1% elongation, which is improved compared to 5% $\pm$ 2% for XLPE/BPS and 7% $\pm$ 2% for XLPE. A full description of Izod impact testing and hot creep testing can be found in Example 6.

Example 2: Preparation of XLPE/rBPS-2.1 wt% Polymer Blend

[0065] rBPS-2.1 wt.% was prepared following the procedure of Example 1 except using 6.00 g BPS, 1.50 g TMSPMA, and 0.30 g DCP. The grafting ratio is calculated using the ^1H NMR result shown in FIG. 2 following the same calculation procedure in Example 1.

[0066] XLPE/gBPS-2.1 wt.% polymer was prepared following Example 1 using 39.0 g rPE, 13.0 g rBPS-2.1 wt.%, and 2.6 g catalyst masterbatch.

[0067] Izod testing showed an impact strength of 8.81 kJ/m² compared to 8.5 kJ/m² for XLPE/BPS and 84.8 kJ/m² for XLPE. Hot creep testing showed 5% $\pm$ 2% elongation compared to 5% $\pm$ 2% for XLPE/BPS and 7% $\pm$ 2% for XLPE.

Example 3: Preparation of PP/rBPS2 (BPS-g-AMEH)/EBA-g-MAH Polymer Blend

Modification Reaction

[0068] Dicumyl peroxide (DCP, 0.7 g), 2-aminoethyl methacrylate hydrochloride (AMEH, 3.5 g) and 65.8 g of BPS powders were manually mixed in a plastic bag. The mixture was loaded into a twin-screw internal mixer (Haake Rheocord 40) and blended at 200 °C and 60 RPM for 10 minutes. Roughly, 50 g was collected from the internal mixer after reactive

extrusion. The produced material is mixture of rBPS2 (reactive BPS2, BPS-g-AMEH) and poly(AMEH) as generally represented in Scheme 4.

[0069] Preparation of PP/rBPS2/EBA-g-MAH Polymer Blend

[0070] 43 g of Polypropylene homopolymer (PP, LyondellBasell, Prfoax-6523), 5 g of modified rBPS2 and 2 g of maleic anhydride grafted ethylene butyl arylate copolymer (EBA-g-MAH, SK Functional Polymer, Lotader 3410) were blended in a twin-screw internal mixer (Haake Rheocord 40) at 230 °C and 50 RPM for 5 minutes. PP/rBPS2/EBA-g-MAH blend was injection-molded into Izod impact testing bars by ThermoFisher Minijet pro under injection mold pressure: 670 psi, barrel temperature: 230 °C, mold temperature: 50 °C, and cooling time: 10 seconds.

[0071] 43 g of PP (LyondellBasell, Prfoax-6523), 5 g of unmodified BPS and 2 g of EBA-g-MAH (SK Functional Polymer, Lotader 3410) were blended and injection-molded at the same condition as described for the preparation of PP/rBPS2/EBA-g-MAH.

[0072] Room temperature Izod impact testing showed an impact strength of 5.9 kJ/m² for PP/rBPS2/EBA-g-MAH, which had 12 % improvement, compared to that of 4.8 kJ/m² for PP/BPS/EBA-g-MAH. The morphological observations via a transmission electron microscope (JEOL-1200X) for PP/BPS/EBA-g-MAH and PP/rBPS2/EBA-g-MAH are shown in Fig. 6A and Fig. 6B, respectively. The elastomer (EBA-g-MAH) location is distinctly different between PP/BPS/EBA-g-MAH and PP/rBPS2/EBA-g-MAH. EBA-g-MAH is separately dispersed for PP/BPS/EBA-g-MAH (Fig. 6A). On the other hand, EBA-g-MAH is surrounding rBPS2 for PP/rBPS2/EBA-g-MAH (Fig. 6B).

Example 4: Preparation of PPA/rBPS3 Polymer Blend

Preparation of rBPS3 (BPS-g-GMA)

[0073] Dicumyl peroxide (DCP, 22.68 g) and Glycidyl methacrylate (GMA, 45.46 g) were premixed with 2199.96 g BPS powders. The premixed mixtures were fed to a Werner & Pfleider (Coperion) ZSK-30 twin-screw extruder (L/D 24, screw diameter 30 mm, barrel temperature 210 – 235 °C from hopper to die) with 175 RPM of screw speed and 14 kg/hr of feeding rate. The vacuum stack was used to remove unreacted GMA monomers. The manually chopped pellets produced from the die were mixtures of modified rBPS3 (reactive BPS3, BPS-g-GMA) and poly(GMA).

[0074] 39 g of PPA (Polyphthalamide, Dupont HTN-502, PA6T/66 type) and 11 g of rBPS3 were manually mixed in a plastic bag. The mixture was extruded in ThermoFisher Process 11 twin screw extruder with one feeder. The barrel temperature of the extruder is 285 to

320 °C from the hopper to the die. The twin screw speed was 150 RPM and feeding rate was 0.2 kg/h. Extruded strands were cool down in a conveying belt then chopped by a pelletizer. Chopped pellets after extrusion were injection-molded via ThermoFisher Minijet pro for Izod bars under injection pressure: 3,450 psi, barrel temperature: 345 °C, mold temperature: 90 °C, and cooling time: 15 seconds. PPA/BPS polymer blend (39 g of PPA and 11 g of unmodified BPS) was extruded and injection-molded in the same way for PPA/rBPS3 polymer blend.

[0075] Room temperature Izod impact testing showed an impact strength of 2.8 kJ/m² for PPA/rBPS3, which had 40 % improvement, compared to that of 2.0 kJ/m² for PPA/BPS. The average particle size and the total number of dispersed BPS in PPA/rBPS3 are 0.23 μm and 45, respectively (FIG. 8A and FIG. 8B), which had better dispersion, compared that the average particle size of dispersed and the total number of dispersed BPS in PPA/BPS are 2.08 μm and 7 (FIG. 7A and FIG. 8B).

Example 5: Preparation of PPA/rBPS4 Polymer Blend

Preparation of rBPS4 (BPS-g-MAH)

[0076] Dicumyl peroxide (DCP, 22.68 g) and Maleic Anhydride (MAH, 36.29 g) were premixed with 2209.3 g BPS powders. The final materials were produced in the same way as described for the preparation of rBPS3. The produced materials were mixtures of rBPS4 (reactive BPS4, BPS-g-MAH), poly(MAH) and etc., which includes 1,2,3,4-cyclobutanetetracarboxylic dianhydride, carbon dioxide and polyvinylketoneanhydride among other potential ring-opened and branched structures which could be envisioned by one skilled in the art.

[0077] 39 g of PPA and 11 g of rBPS4 were manually mixed in a plastic bag. The mixture was extruded and injection-molded in the same way as described for the preparation of PPA/rBPS3 polymer blend.

[0078] Room temperature Izod impact testing showed an impact strength of 2.9 kJ/m² for PPA/rBPS4, which had 45 % improvement, compared to that of 2.0 kJ/m² for PPA/BPS. The average particle size and the total number of dispersed BPS in PPA/rBPS4 are 0.02 μm and 271, respectively (FIG. 9A and FIG. 9B), which had better dispersion compared that the average particle size of dispersed and the total number of dispersed BPS in PPA/BPS are 2.08 μm and 7 (FIG. 7A and FIG. 8B).

Example 6: Test Procedures

Room and Low Temperature Notched Izod Impact Test

[0079] For room temperature Izod impact testing, Izod impact testing was carried out at 25 °C with a 2.7 J pendulum hammer for the injection molded Izod bars (63.5 mm × 10.2 mm × 3.2 mm with a 10.16 mm V notch depth) one day after their injection-mold. For low temperature Izod impact testing, fully crosslinked V-notched rectangular bars (63.5 mm × 10.2 mm × 3.2 mm with a 10.16 mm V notch depth) were dried in vacuum oven over night before testing. They were pre-cooled in an environmental chamber at -37 °C for 1 hour. Then these bars are immediately tested/impacted with a 11.3 J pendulum hammer. The resulting energy absorption is read. Izod impact strength is calculated following: Izod impact strength = Energy absorption/cross-sectional area.

Hot Creep Test

[0080] Tensile bars (3.0 mm width × 3.2 mm thickness in the gauge) were dried in vacuum oven over night before testing. Hot creep testing was conducted in accordance with UL-44 and UL-2556 standards. Before testing, the gauge length of tensile bar is measured and set at 1.0. Bars were pre-heated in an oven (150 °C) and then a loading stress of 0.2 MPa was applied by hanging an object of 196 g. Bars were tested under this condition (150 °C/0.2 MPa/15 minutes). After 15 minutes, the instantaneous length was measured, L. The elongation is calculated by $(L - L_0)/L_0$. In this test low creep was desirable.

Dynamic Mechanical Analysis

[0081] Specimens (35 mm × 8 mm × 3.2 mm) were tested from 30 °C to 200 °C with a ramping rate is 10 °C/min using a TA Instruments ARES-G2 rheometer. The testing frequency was 1 Hz and a small strain of 0.1% was applied.

Particle Size Analysis

[0082] Dispersed BPS phases were manually elliptical-selected in processed images via 'binary imaging' function in ImageJ software from transmission electron microscopic images taken by JEOL JEM-1400. The average particle size and total number of particles were analyzed by using 'Analyze particles' function in ImageJ software.

[0083] It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations set forth for a clear understanding of the principles of the disclosure. Many variations and modifications may be made to the above-described embodiment(s) without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

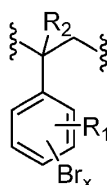
REFERENCES

1. Li, H. M.; et al, 2002, Polymer, 43:5455-5461.
2. Passaglia, E.; et al, 2004, Macromol Symp, 218:61-70.
3. Won Ho Jo, et al, 1996, Polymer, 37:1709-1714.

CLAIMS

What is claimed is:

1. A flame-retardant composition comprising a brominated polystyrene modified with a first portion of a monomer or a second polymer.
2. The flame-retardant composition of claim 1, further comprising at least a second portion of the second polymer.
3. The flame-retardant composition of claim 1 or 2, wherein the first portion and the second portion of the second polymer comprise a polyamide, a polyolefin, a polyester, a styrenic polymer or copolymer, or any combination thereof.
4. The flame-retardant composition of claim 3, wherein the polyamide comprises nylon 6,6; nylon 6; nylon 6, 10; nylon 11; nylon 6,12; nylon 12; nylon 6,9; nylon 4,6; poly(m-phenylene isophthalamide); poly(p-phenylene terephthalamide); copoly(p-phenylene/d,4'-diphenyl ether terephthalamide); PA66/6, PA6T, PA9T, PA10T, PA4T, poly(m-xylene sebacamide), poly(m-xylene adipamide), a copolymer thereof, or any combination thereof.
5. The flame-retardant composition of claim 3 or 4, wherein the polyolefin comprises low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), very-low-density polyethylene (VLDPE), ultra-low-density polyethylene (ULDPE), medium-density polyethylene (MDPE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), ethylene-octene copolymer, stereo-block PP, olefin block copolymer, propylene-butane copolymer, polyisobutylene (PIB), poly(α -olefin), ethylene propylene rubber (EPR), ethylene propylene diene monomer rubber (EPDM rubber), high-density polyethylene (HDPE), ultra high density polyethylene (UHDPE), cross-linked polyethylene (PEX or XLPE), or any combination thereof.
6. The flame retardant composition of any one of claims 3-5, wherein the polyester comprises polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), polybutylene terephthalate (PBT), poly(cyclohexylenedimethylene terephthalate) (PCT), polylactic acid (PLA), polycaprolactone (PCL), polyethylene terephthalate glycol (PETG), polycyclohexylenedimethylene terephthalate glycol (PCTG), or any combination thereof.
7. The flame retardant composition of any one of claims 3-6, wherein the styrenic polymer or copolymer poly(styrene-co-acrylonitrile) (SAN), poly(acrylonitrile-co-butadiene-styrene) (ABS), or any combination thereof.
8. The flame-retardant composition of any one of claims 1-7, wherein the brominated polystyrene comprises a plurality of monomer units having a structure of Formula I:



Formula I

wherein x in each monomer unit of the plurality is independently from 0 to 4;

wherein R_1 in each monomer unit of the plurality independently comprises hydrogen, bromine, $NR_{1a}R_{1b}$, or a pendant group comprising at least 2 carbons;

wherein R_{1a} and R_{1b} are independently selected from C1 to C30 linear or branched hydrocarbons;

and wherein R_2 in each monomer unit of the plurality independently comprises hydrogen or a pendant group comprising at least 2 carbons.

9. The flame-retardant composition of any one of claims 1-8, wherein each R_1 is hydrogen or bromine and each R_2 is independently hydrogen or the pendant group comprising at least 2 carbons, provided at least one pendant group is present in the first portion of the second polymer.

10. The flame-retardant composition of any one of claims 1-8, wherein each R_2 is hydrogen and each R_1 is independently hydrogen, bromine, or the pendant group comprising at least 2 carbons, provided at least one pendant group is present in the first portion of the second polymer.

11. The flame-retardant composition of any one of claims 1-10, wherein an average value for x over the plurality of monomer units is from about 2 to about 5.

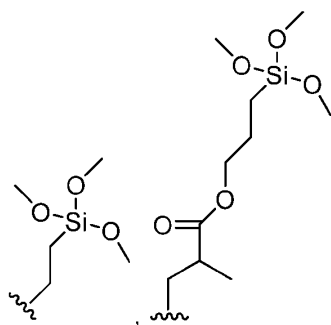
12. The flame-retardant composition of any one of claims 1-11, wherein about 1 pendant group comprising at least 5 carbons is present at R_1 or R_2 per every 5 to 150 monomer units of the plurality.

13. The flame-retardant composition of any one of claims 1-11, comprising from about 0 to about 2.1 wt% pendant groups per total weight of the brominated polystyrene.

14. The flame-retardant composition of any one of claims 1-11, with homopolymer polyacrylates of vinyl polymers containing pendant side chains polymerized in the presence of a brominated polystyrene.

15. The flame-retardant composition of any one of claims 8-14, wherein the pendant group comprising at least 2 carbons at an R_1 or R_2 of at least one monomer unit of the plurality comprises a trimethoxysilyl group.

16. The flame-retardant composition of claim 13-15, wherein the pendant group comprising at least 5 carbons has a structure selected from:



, or any combination thereof.

17. The flame-retardant composition of any one of claims 8-16, wherein the first portion of the second polymer comprises at least one pendant group comprising a trimethoxysilyl group.

18. The flame-retardant plastic composition of any one of claims 1-17, further comprising Sb_2O_3 .

19. The flame-retardant plastic composition of claim 18, wherein the flame retardant plastic composition comprises from about 1% to about 10% by weight of Sb_2O_3 .

20. The flame-retardant composition of any one of claims 1-19, further comprising a filler.

21. The flame-retardant composition of claim 20, wherein the filler comprises talc, calcium carbonate, AgO, ZnO, CaO, MnO, Al(OH)₃, AlO(OH), Mg(OH)₂, kaolinite, wollastonite, mica, glass beads, or any combination thereof..

22. The flame-retardant composition of any one of claims 1-21, further comprising a reinforcing agent.

23. The flame-retardant composition of claim 22, wherein the reinforcing agent comprises glass fibers.

24. An article comprising the flame-retardant composition of any one of claims 1-23.

25. The article claim 20 wherein the article has a flammability rating of V0 according to test method UL94.

26. The article of claim 20 or 21, wherein the article comprises a covering for a cable or a wire, an automotive component, an electronic component, insulation, carpeting, a wall covering, a textile, an adhesive, or any combination thereof.

27. A method of making the flame-retardant composition of any one of claims 2-23, the method comprising:

(a) admixing an acrylate monomer comprising at least 2 carbon atoms with a brominated polystyrene to form a precursor mixture and blending the precursor mixture to produce the brominated polystyrene modified by the presence of the first portion of the second polymer; and

(b) admixing the brominated polystyrene grafted to the first portion of the second polymer with the second portion of the second polymer.

28. The method of claim 27, wherein the acrylate monomer comprises 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) vinyltrimethoxy silane, vinyl triethoxy silane, or any combination thereof.

29. The method of claim 27 or 28, wherein the precursor mixture further comprises an initiator.

30. The method of claim 28, wherein the initiator comprises dicumyl peroxide, di(tert-butylperoxyisopropyl)benzene, cumyl hydroperoxide, 2,3-dimethyl-2,3-diphenylbutane, benzoyl peroxide, tert-butyl peroxybenzoate, di-tert butyl peroxide, azobisisobutyronitrile, or any combination thereof.

31. The method of any one of claims 27-30, further comprising adding Sb_2O_3 during step (a) or step (b).

32. The method of any one of claims 27-31, wherein blending in step (a), step (b), or both is conducted in a twin screw extruder.

33. The method of any one of claims 27-32, wherein blending in step (a), step (b), or both is conducted at from about 160 °C to about 230 °C.

34. The method of any one of claims 27-33, further comprising:

(c) curing the flame-retardant composition in water.

35. The method of claim 34, wherein curing is carried out for from about 1 hour to about 10 days.

36. The method of claim 34 or 35, wherein curing is carried out at a temperature of from about 25 °C to about 200 °C.