

TIRE CURING BLADDERS WITH BROMINATED POLY(ISOBUTYLENE-CO-PARAMETHYLSTYRENE)

INVENTORS: Paul Tu Quang Nguyen; Sunny Jacob

5 **CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims priority to and the benefit of U.S. Provisional Patent Application 63/405,934, filed 13 September 2022, entitled TIRE CURING BLADDERS WITH BROMINATED POLY(ISOBUTYLENE-CO-PARAMETHYLSTYRENE), the disclosure of which is incorporated herein by reference in its entirety.

10 **FIELD OF INVENTION**

[0002] This application relates to tire curing bladders with enhanced processability properties and, in particular, tire curing bladders comprising brominated poly(isobutylene-co-paramethylstyrene) compounds having a molecular weight distribution (MWD) ranging from about 2.5 to about 10 (*e.g.*, from about 2.5 to about 4).

15 **BACKGROUND**

[0003] Vehicle tires are typically manufactured by building, molding, and/or curing a green (*e.g.*, uncured) tire in a molding press. For example, a green tire construct is pressed against a mold surface by a tire curing bladder. The tire curing bladder is a fluid-expandable bladder positioned along an inner surface of the green tire construct. As fluid (*e.g.*, air) is introduced
20 into the tire curing bladder, the green tire construct is forced against a surface of the mold that defines a tire tread pattern and/or configuration of the tire sidewalls. Further, heat and pressure can be applied via the tire curing bladder to mold and vulcanize the tire at elevated temperatures.

[0004] Tire curing bladders typically comprise elastomers and compounding materials; the
25 selection of which can influence the durability, service life, and operational efficiency of the bladders. Traditionally, butyl rubbers, such as isobutylene-isoprene copolymers, have been the preferred elastomers for tire curing bladder formulations due to excellent heat aging resistance, good flex and tear resistance, and fluid impermeability (*e.g.*, impermeability to air, inert gases, and/or water vapor). Additionally, brominated poly(isobutylene-co-paramethylstyrene)
30 compounds have been employed in tire curing bladder applications. For example, tire curing bladders have been constructed using brominated poly(isobutylene-co-paramethylstyrene) with a low bromine content (*e.g.*, 0.45 mole percent or less) in a vulcanized curing system of 1,6-hexamethylene-bis(sodium thiosulfate) and zinc oxide.

SUMMARY

[0005] In various non-limiting embodiments described herein, a tire curing bladder is provided. The tire curing bladder can comprise a brominated poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio greater than or equal to 2.5 and less than
5 or equal to 10; mercaptobenzothiazole disulfide; a phenolic resin; and a curative agent.

[0006] In various non-limiting embodiments described herein, a composition is provided. The composition can comprise an elastomeric composition formed into a tire curing bladder. Further, the elastomeric composition can comprise a brominated poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio greater than or equal to 2.5 and less than
10 or equal to 10; and a cure package comprising: mercaptobenzothiazole disulfide; a phenolic resin; and a curative agent.

[0007] In various non-limiting embodiments described herein, a method of making a tire curing bladder is provided. The method can comprise forming a mixture of a brominated poly(isobutylene-co-paramethylstyrene) elastomer and a cure package, where the brominated
15 poly(isobutylene-co-paramethylstyrene) elastomer has a Mw/Mn ratio greater than or equal to 2.5 and less than or equal to 10, and where the cure package comprises mercaptobenzothiazole disulfide, a phenolic resin, and a curative agent; and curing the mixture into a shape of the tire curing bladder.

[0008] These and other features and attributes of the disclosed tire curing bladders
20 comprising broad MWD brominated poly(isobutylene-co-paramethylstyrene) elastomers of the present disclosure and their advantageous applications and/or uses will be apparent from the detailed description which follows.

DETAILED DESCRIPTION

[0009] This application relates to tire curing bladders that comprise brominated
25 poly(isobutylene-co-paramethylstyrene), and/or blended compositions thereof, having a broad MWD to lower compound Mooney viscosity and improve processability and, in particular, tire curing bladders comprising brominated poly(isobutylene-co-paramethylstyrene) having a MWD (Mw/Mn) ranging from about 2.5 to about 10 (e.g., from about 2.5 to about 4), thereby resulting in a compound Mooney viscosity of less than about 100 (ML, 1+4 @ 100°C).

[0010] The MWD (e.g., a ratio of moments characterized by Mw/Mn, where Mw is the
30 molecular weight value and Mn is the number average value) of an elastomer can significantly affect the mechanical and/or processability properties of tire curing bladder. For instance, the fraction of higher molecular weight polymer species can contribute to desired mechanical properties, while the fraction of low-molecular weight polymer species can contribute to the

processability properties (*e.g.*, as the low molecular weight fraction can act as a plasticizer). In a further instance, an elastomer's MWD can affect the Mooney viscosity of the compound (*e.g.*, broadening the MWD of brominated poly(isobutylene-co-paramethylstyrene) elastomers can result in a reduced compound Mooney viscosity). By reducing the Mooney viscosity, the processability of the tire curing bladder compounds can be improved (*e.g.*, due to faster stress relaxation rates). Thus, it is important to have a controlled, broad MWD for commercial polymers so that the tire producers/converters/fabricators can process the products with faster cycle time, good surface appearance, splice integrity, strength, etc. in the final product. However, brominated poly(isobutylene-co-paramethylstyrene) elastomers are typically characterized by a narrow MWD (*e.g.*, less than 2.5), resulting in tire curing bladders with high compound Mooney viscosity.

[0011] The present disclosure provides tire curing bladder compositions that include brominated poly(isobutylene-co-paramethylstyrene) elastomers with broad MWD and thereby a low compound Mooney viscosity. In various embodiments, the tire curing bladder compositions can comprise brominated poly(isobutylene-co-paramethylstyrene) elastomers, and/or compositions thereof, having a MWD ranging from, for example, about 2.5 to about 10 (*e.g.*, from about 2.5 to about 4). For example, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be copolymers modified by a post-polymerization treatment that chemically induces thermal breaking of the backbone to increase the fraction of low molecular weight species. Additionally, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be blends of modified and unmodified polymer species to achieve a "tailor-made" MWD.

Definitions

[0012] As used herein, the term "polymer," and grammatical variants thereof, refers to homopolymers, copolymers, interpolymers, terpolymers, etc. The term "copolymer," and grammatical variants thereof, is meant to include polymers having two or more monomers. The term "interpolymer," and grammatical variants thereof, means any polymer or oligomer having a number average molecular weight of 500 or more prepared by the polymerization or oligomerization of at least two different monomers. As used herein, when a polymer is referred to as "comprising" a monomer, the monomer is present in the polymer in the polymerized form of the monomer or in the derivative form of the monomer. Likewise, when catalyst components are described as comprising neutral stable forms of the components, it is well understood by one skilled in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers.

[0013] As used herein, the term “olefin,” and grammatical variants thereof, refers to a hydrocarbon containing a carbon-carbon double bond. An “isoolefin,” and grammatical variants thereof, refers to any olefin monomer having two substitutions on the same carbon. The term “diolefin,” and grammatical variants thereof, refers to any olefin monomer having
5 two double bonds.

[0014] As used herein, the term “elastomer” or “elastomeric composition,” and grammatical variants thereof, refers to any polymer or composition of polymers consistent with the ASTM D1566-21A (November 2021) definition. Elastomer may be used herein interchangeably with the term “rubber(s)”.

10 [0015] As used herein, the term “Mooney viscosity,” and grammatical variants thereof, is the Mooney viscosity of a polymer or polymer composition. The polymer composition analyzed for determining Mooney viscosity should be substantially devoid of diluent and solvent. For instance, the sample may be placed on a boiling-water steam table in a hood to evaporate a large fraction of the diluent and unreacted monomers, and then, dried in a vacuum oven
15 overnight (12 hours, 90°C) prior to testing, in accordance with laboratory analysis techniques, or the sample for testing may be taken from a devolatilized polymer (*i.e.*, the polymer post-devolatilization in industrial-scale processes). Unless otherwise indicated, Mooney viscosity is measured using a Mooney viscometer according to ASTM D1646-19A (November 2019, but with the following modifications/clarifications of that procedure. First, sample polymer is
20 pressed between two hot plates of a compression press prior to testing. The plate temperature is 125°C +/- 10°C instead of the 50 +/- 5°C as recommended in ASTM D1646-17, because 50°C is unable to cause sufficient massing. Further, although ASTM D1646-17 allows for several options for die protection, should any two options provide conflicting results, PET 36 micron is used as the die protection. Further, ASTM D1646-17 does not indicate a sample
25 weight in Section 8; thus, to the extent results may vary based upon sample weight, Mooney viscosity determined using a sample weight of 21.5 +/- 2.7 grams (g) per D1646-17 Section 8 procedures will govern. Finally, the rest procedures before testing set forth in D1646-17 Section 8 are 23 +/- 3°C for 30 minutes in air; Mooney values as reported herein were determined after resting at 24 +/- 3°C for 30 minutes in air. Samples are placed on either side
30 of a rotor according to the ASTM D1646-17 test method; torque required to turn the viscometer motor at 2 rpm is measured by a transducer for determining the Mooney viscosity. The results are reported as Mooney Units (ML, 1+4 @ 125°C or ML, 1+8 @ 125°C), where MU is the Mooney viscosity number, L denotes large rotor (defined as ML in ASTM D1646-17), 1 is the pre-heat time in minutes, 4 or 8 is the sample run time in minutes after the motor starts, and

125°C is the test temperature. Thus, a Mooney viscosity of 90 determined by the aforementioned method would be reported as a Mooney viscosity of 90 MU (ML, 1+8 @ 125°C) or 90 MU (ML, 1+4 @ 125°C). Alternatively, the Mooney viscosity may be reported as 90 MU; in such instance, it should be assumed that the just-described (ML, 1+4 @ 125°C) method is used to determine such viscosity, unless otherwise noted. In some instances, a lower test temperature may be used (*e.g.*, 100°C), in which case Mooney is reported as Mooney Viscosity (ML, 1+8 @ 100°C), or @ T°C where T is the test temperature.

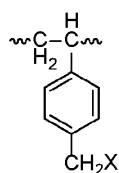
[0016] As used herein, the term “blended”, and grammatical variants thereof, refers to a mixture of two or more polymers. Blends can be produced by, for example: solution blending, melt mixing, shear mixing, a combination thereof, and/or the like.

[0017] As used herein, the term “curing system,” and grammatical variants thereof, refers to the combination of curative agents. Examples of curative agents include, but are not limited to: sulfur; metals; metal oxides such as zinc oxide, peroxides, organometallic compounds, radical initiators, fatty acids, accelerators, a combination thereof, and/or the like.

[0018] Numerical ranges used herein include the numbers recited in the range. For example, the numerical range “from 1 wt% to 10 wt%” includes 1 wt% and 10 wt% within the recited range.

Brominated Poly(isobutylene-co-paramethylstyrene) Elastomers

[0019] As used herein, the term “brominated poly(isobutylene-co-paramethylstyrene) elastomer” can refer to a brominated polyolefin copolymer composition of isobutylene and paramethylstyrene having a MWD ranging from, for example, about 2.5 to about 10 (*e.g.*, from about 2.5 to about 4). For example, the paramethylstyrene block of the brominated poly(isobutylene-co-paramethylstyrene) elastomer can be represented by the following Formula 1.



Formula 1

Where “X” is a halogen (*e.g.*, bromine or chlorine) or a combination of a halogen and another functional group such which can be incorporated by nucleophilic substitution of benzylic halogen with other groups such as: carboxylic acids; carboxy salts, carboxy esters, amides, and imides; hydroxyl, alkoxide, phenoxide, thiolate, thioether, xanthate; cyanide; nitrile; amino,

and mixtures thereof. The “~” indicate covalent bonds to isobutylene blocks of the copolymer backbone.

- [0020] The brominated poly(isobutylene-co-paramethylstyrene) elastomers described herein have a MWD ranging from, for example, about 2.5 to about 10 (*e.g.*, from about 2.5 to about 4). In various embodiments, the brominated poly(isobutylene-co-paramethylstyrene) elastomers described herein have a MWD ranging from, for example, about 6.1 to about 10. Additionally, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can have a Mw ranging from, for example, about 10,000 Daltons (Da) to about 1,000,000 Da (*e.g.*, from about 25,000 Da to about 500,000 Da). In one or more embodiments, the brominated poly(isobutylene-co-paramethylstyrene) elastomers have a substantially homogenous compositional distribution comprising between about 80 and about 99.5 mole percent of the isobutylene and about 0.5 to about 20 mole percent of the paramethylstyrene. Further, in various embodiments, brominated poly(isobutylene-co-paramethylstyrene) elastomers can comprise at least 0.25 wt% (*e.g.*, from about 0.25 wt% to about 4 wt%) bromine. Expressed another way, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can comprise from about 0.1 to about 7.5 mole percent of brominated paramethylstyrene derived units. Moreover, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can have a Mooney viscosity (ML, 1+8 at 125°C) from about -10 to about 60 (*e.g.*, about 20 to about 50 and/or from about 30 to about 48).
- [0021] In various embodiments, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be copolymers derived from poly(isobutylene-co-paramethylstyrene) compositions (*e.g.* halogenated or non-halogenated) having a MWD of about 2.5 or less, which were subjected to a post-polymerization modification to broaden the MWD. For example, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be copolymers derived from halogenated elastomers that are commercially available as Exxpro™ elastomers (ExxonMobil Product Solutions Company, Houston TX), and abbreviated as “BIMSM.” For instance, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be copolymers derived from Exxpro™ 3035, 3433, 3563, and/or 3745 (*e.g.*, where the Exxpro™ 3035, 3433, 3563, and/or 3745 was subjected to a chemically induced thermal breaking along the copolymer backbone).

Curing System

[0022] The tire curing bladders described herein are formed by curing the brominated poly(isobutylene-co-paramethylstyrene) elastomers with a curing system that comprises: a phenolic resin; mercaptobenzothiazole disulfide (MBTS); and one or more additional curative

agents, such as: sulfur; metals; metal oxides such as zinc oxide, peroxides, organometallic compounds, radical initiators, fatty acids, accelerators, a combination thereof, and/or the like.

[0023] The phenolic resin can be present in the curing system at a range from about 1 phr to about 7.5 phr (*e.g.*, about 2 to about 6 phr or about 3 to about 5 phr). In one or more
5 embodiments, phenolic resin can be an alkyl phenol formaldehyde resin including, but not limited to: octyl phenol formaldehyde resin (SP-1045TM), brominated octyl phenol formaldehyde resin (SP-1055TM), a combination thereof, and/or the like.

[0024] The mercaptobenzothiazole disulfide (MBTS) can be present in the curing system in a range from about 0.5 phr to about 5 phr (*e.g.*, 0.75 to 4 phr, 1 to 3 phr, or 1.4 to 2 phr). In
10 various embodiments, the mercaptobenzothiazole disulfide (MBTS) and/or one or more additional curative agents within the curing system can be utilized to minimize post curing aging.

[0025] In one or more embodiments, the curing system can further comprise one or more additional accelerators in individual ranges from about 0.1 to about 5 phr (*e.g.*, 0.5 to 4 phr or
15 1 to 3 phr). Example accelerators include, but are not limited to: stearic acid, diphenyl guanidine, tetramethylthiuram disulfide, N-t-butyl-2-benzothiazole sulfonamide, N-cyclohexyl-2-benzothiazole-sulfen amide, thioureas, a combination thereof, and/or the like. For instance, the curing system can comprise stearic acid. In one or more embodiments, the curing system can further comprise sulfur or a sulfur compound in a range from about 0.5 phr
20 to about 2.5 phr.

[0026] In one or more embodiments, the curing system can further comprise a metal oxide in a range from about 0.01 to about 5.0 phr (*e.g.*, 0.1 to 4 phr, 1 to 3 phr, 0.01 to 0.5 phr, or 2 to 4 phr). Example metal oxides can include, but are not limited to: zinc oxide, calcium oxide, lead oxide, magnesium oxide, a combination thereof, and/or the like. For instance, the curing
25 system can comprise zinc oxide. Additionally, the metal oxide can be utilized alone or in conjunction with its corresponding metal fatty acid complex (*e.g.*, zinc stearate, calcium stearate, and/or the like).

Other Additives

[0027] In various embodiments, the tire curing bladder formulations can further comprise
30 one or more additional additives, including, but not limited to: fillers, dyes, pigments, antioxidants, heat and light stabilizers, plasticizers, oils, a combination thereof, and/or the like. For example, the one or more additional additives can be individually present in a range from, for example, about 10 to about 100 phr (*e.g.*, 25 to 80 phr or 30 to 70 phr).

[0028] Example fillers can include, but are not limited to: calcium carbonate, clay, mica, silica, silicates, talc, titanium dioxide, aluminum oxide, starch, wood flour, carbon black (*e.g.*, N110 to N990 per ASTM D1765-17), a combination thereof, and/or the like. Examples of carbon black that can be included in the tire curing bladder formulations can include, but are not limited to: carbon black ISAF (*e.g.*, N220 per ASTM D1765-17), carbon black HAF (*e.g.*, N330 per ASTM D1765-17), carbon black GPF, combinations of carbon black with acetylene black compounds, a combination thereof, and/or the like. Examples of silica can include any type or particle size silica, a silicic acid derivative, and/or silicic acid. For instance, the silica can be processed by solution or pyrogenic means, including: precipitated silica (*e.g.*, conventional silica, semi-highly dispersible silica, and/or highly dispersible silica), crystalline silica, colloidal silica, aluminum silicates, calcium silicates, fumed silica, a combination thereof, and/or the like. Examples of clay can include, but are not limited to: montmorillonite, nontronite, beidellite, vokoskoite, laponite, hectorite, saponite, sauconite, magadite, kenyaite, stevensite, vermiculite, halloysite, aluminate oxides, hydrotalcite, a combination thereof, and/or the like. Further, the clay filler can include one or more modifying agents, such as a silicate and/or organic molecules. In one or more embodiments, the filler can be a layered clay.

Blends

[0029] In one or more embodiments, the tire curing bladder formulations described herein can comprise the brominated poly(isobutylene-co-paramethylstyrene) elastomers as part of a blended elastomer composition comprising multiple species of elastomers. For example, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be blended with one or more other elastomer species. For example, the other elastomer species can have a narrower respective MWD. For instance, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be blended with one or more other poly(isobutylene-co-paramethylstyrene) elastomers (*e.g.*, halogenated or non-halogenated) that have a respective MWD of 2.5 or less. In one or more embodiments, a blending ratio of the brominated poly(isobutylene-co-paramethylstyrene) elastomers (*e.g.*, having a broad MWD) to other poly(isobutylene-co-paramethylstyrene) elastomers (*e.g.*, halogenated or non-halogenated, and having a narrower MWD) can range from, for example, about 0.1:1 to about 1:0.1. In various embodiments, the blended composition can have a low molecular weight fraction (*e.g.*, characterizing the amount of species having a molecular weight less than 100,000 Da) ranging from, for example, about 10 wt% to about 90 wt%, and a high molecular weight fraction (*e.g.*, characterizing the amount of species having a molecular weight greater than 100,000 Da) ranging from, for example, about 10 wt% to about 90 wt%.

[0030] In another instance, the brominated poly(isobutylene-co-paramethylstyrene) elastomers can be blended with one or more butyl rubbers (*e.g.*, isobutylene-isoprene copolymers) such as, but not limited to, EXXONTM BUTYL 065, 065S, 365, 068, 068S, 268, and/or 268S. In various embodiments, the butyl rubber can be present at a range from, for
5 example, about 0.5 to about 30 phr (*e.g.*, from 1 to 25 phr, 5 to 20 phr, or 10-15 phr).

[0031] Additionally, the tire curing bladder formulations can be formed by blending the one or more brominated poly(isobutylene-co-paramethylstyrene) elastomers, the curing system, and/or the additional additives together. In one or more embodiments, the components of the tire curing bladder formulation can be mixed via single mixing step or multiple mixing steps,
10 such as a non-productive mixing step and a productive mixing step. For example, a non-productive mixing step can include mixing the elastomer compounds and/or additional additives, while the productive mixing step can be performed at a lower temperature than the non-productive mixing step and can include introduction of the curing system. For example, the components can be blended via a suitable mixing device, such as a BANBURYTM mixer, a
15 BRABENDERTM mixer, and/or a mixer/extruder. In one or more embodiments, the elastomer species and/or the additional additives can be combined in a two-roll open mill, a BRABENDERTM internal mixer, a BANBURYTM internal mixer with tangential rotors, a Krupp internal mixer with intermeshing rotors, and/or a mixer/extruder device. Additionally, the mixing can be performed at temperatures up to the melting point of the elastomer species
20 (*e.g.*, the brominated poly(isobutylene-co-paramethylstyrene) elastomers). For instance, one or more of the components (*e.g.*, brominated poly(isobutylene-co-paramethylstyrene) elastomers, other elastomers, the curing system, and/or the additional additives) can be mixed at a temperature ranging from, for example, about 40°C to about 250°C (*e.g.*, from 100°C to 200°C) with conditions to uniformly disperse the components.

[0032] In one or more embodiments, the tire curing bladder formulations can include carbon black and zinc oxide added via different mixing stages. Additionally, processing materials such as the antioxidants and/or antioxidants can be added in a mixing stage after the carbon black has been processed with the elastomer components (*e.g.*, comprising the brominated poly(isobutylene-co-paramethylstyrene) elastomers), and the zinc oxide is added at a final
25 stage to maximize the compound modulus. Further, in one or more embodiments, clay can be added to the mixture at the same time as the carbon black. Also, one or more additional mixing stages can be performed to facilitate more of the additional additives.

[0033] For example, from 70% to 100% of the elastomers (*e.g.*, comprising the brominated poly(isobutylene-co-paramethylstyrene) elastomers) can be first mixed for 20 to 90 seconds,

or until the temperature reaches from 40 °C to 75 °C. Then, approximately 75% of the filler, and the remaining amount of elastomer, if any, can be added to the mixer; and the mixing can continue until the temperature reaches from 90 °C to 150 °C. Next, the remaining filler is added, as well as the processing aids, and mixing continues until the temperature reaches from 140 °C to 190 °C. The masterbatch mixture is then finished by sheeting on an open mill and allowed to cool, for example, to from 60 °C to 100 °C when the remaining components of the curing system may be added to produce a final batch mix.

[0034] In various embodiments, the tire curing bladder is a cylindrical bag made from the final batch mix, which is molded and/or cured. For example, the tire curing bladder formulations described herein can be cured, for example, in less than 30 minutes (*e.g.*, 15 to 30 minutes or 20 to 25 minutes) at 170 °C to 200 °C. In another example, the curing time can be 45 to 90 minutes (*e.g.*, 50 to 80 minutes, or 60 to 70 minutes) at 120 °C to 150 °C (*e.g.*, 125 °C to 145 °C, or 130 °C to 140 °C).

[0035] In use, the expandable tire curing bladder of the formulations described herein can be mounted in the lower section of a tire curing press; thereby forming a part of the press and mold assembly. The “green” unvulcanized tire is positioned over the curing bladder in the bottom half of the mold. When the mold is closed, pressurized steam, air, hot water, or inert gas (*e.g.*, nitrogen) is systematically introduced into the bladder to provide internal heat and pressure for the tire shaping and curing process. Two typical types of tire curing presses that can employ the tire curing bladders are: (1) a SLIDEBACK™ (tire curing press and loader, available from NRM) type press that requires an AUTOFORM™ (mechanical tire press, available from Bagwell) bladder, and (2) a TILTBACK™ (mechanical tire press, available from Bag-O-Matic) type press that requires a Bag-O-Matic bladder. Example applications for the tire curing bladders described herein can include wall curing bladders for passenger cars, light trucks and commercial trucks, toroidal curing bladders, closed end curing bladders, and the like.

[0036] For example, the expandable tire curing bladder of the formulations described herein can be used in conjunction with one or more of three types of tire cure cycles: a steam-high pressure hot water cure cycle, a steam-inert gas cure process, and/or a steam-steam cure cycle. During which, dome temperatures can reach 190 °C (*e.g.*, with mold sidewall plates at 180 °C), and the tire curing bladder temperature can reach up to 220 °C. An exemplary simple steam-hot water cure cycle time for a truck tire can be: (1) steam for 12 minutes; (2) high pressure hot water for 30 minutes; (3) cold water flush for 4 minutes; and (4) a drain operation for 30 seconds (*e.g.*, resulting in a total cure time of 46:30). The elastomeric compositions and blends

thereof described herein can be used for the curing bladder since they generally meet the basic property requirements: (1) a homogeneous, well mixed compound for ease of processing (mixing, extruding, and mold flow); (2) excellent heat aging resistance; (3) resistance to degradation due to saturated steam or high pressure hot water, or inert gas; (4) excellent flex and hot tear resistance; (5) low tension and compression set that maintains high elongation properties; and (6) impermeability to air, inert gas, and water vapor.

Additional Embodiments

[0037] Non-limiting example embodiments of the present disclosure include:

[0038] Embodiment A: A tire curing bladder, comprising: a brominated poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio greater than or equal to 2.5 and less than or equal to 10; mercaptobenzothiazole disulfide (MBTS); a phenolic resin; and a curative agent.

[0039] Non-limiting example embodiment A can include one or more of the following elements.

[0040] Element 1A: wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20 mole percent of paramethylstyrene.

[0041] Element 2A: wherein the curative agent is zinc oxide.

[0042] Element 3A: further comprising at least one filler selected from the group consisting of: calcium carbonate, clay, mica, silica, silicates, talc, titanium dioxide, aluminum oxide, starch, wood flour, carbon black, and a combination thereof.

[0043] Element 4A: wherein the filler is a carbon black N110 to N990 per ASTM D1765-17.

[0044] Element 5A: wherein the phenolic resin is at least one alkyl phenol formaldehyde resin selected from the group consisting of: octyl phenol formaldehyde resin, brominated octyl phenol formaldehyde resin, and a combination thereof.

[0045] Element 6A: further comprising a second poly(isobutylene-co-paramethylstyrene) elastomer, the second poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio less than 2.5.

[0046] Element 7A: wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is halogenated.

[0047] Element 8A: wherein the second poly(isobutylene-co-paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20 mole percent of paramethylstyrene.

- [0048] Element 9A: wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 parts per hundred rubber (phr), and wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 phr.
- [0049] Element 10A: wherein the tire curing bladder has a compound Mooney viscosity of less than 90 Mooney units (ML, 1+4 at 100°C).
- [0050] Element 11A: wherein the Mw/Mn ratio of the brominated poly(isobutylene-co-paramethylstyrene) elastomer is greater than or equal to 2.5 and less than or equal to 4.
- [0051] Each of Elements 1A through 11A can be combined in any combination, without limitation.
- [0052] Non-limiting example embodiments of the present disclosure also include:
- [0053] Embodiment B: A composition, comprising: an elastomeric composition formed into a tire curing bladder, the elastomeric composition comprising: a brominated poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio greater than or equal to 2.5 and less than or equal to 10; and a cure package comprising: mercaptobenzothiazole disulfide; a phenolic resin; and a curative agent.
- [0054] Non-limiting example embodiment B can include one or more of the following elements.
- [0055] Element 1B: wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20 mole percent of paramethylstyrene.
- [0056] Element 2B: wherein the cure package further comprises at least one filler selected from the group consisting of: calcium carbonate, clay, mica, silica, silicates, talc, titanium dioxide, aluminum oxide, starch, wood flour, carbon black, and a combination thereof.
- [0057] Element 3B: wherein the phenolic resin is at least one alkyl phenol formaldehyde resin selected from the group consisting of: octyl phenol formaldehyde resin, brominated octyl phenol formaldehyde resin, and a combination thereof.
- [0058] Element 4B: wherein the elastomeric composition further comprises a second poly(isobutylene-co-paramethylstyrene) elastomer, the second poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio less than 2.5.
- [0059] Element 5B: wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is halogenated.
- [0060] Element 6B: wherein the second poly(isobutylene-co-paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20 mole percent of paramethylstyrene.

[0061] Element 7B: wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 parts per hundred rubber (phr), and wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 phr.

5 [0062] Element 8B: wherein the tire curing bladder has a compound Mooney viscosity of less than 90 Mooney units (ML, 1+4 at 100 °C).

[0063] Each of Elements 1B through 8B can be combined in any combination, without limitation.

[0064] Non-limiting example embodiments of the present disclosure also include:

10 [0065] Embodiment C: A method of making a tire curing bladder, the method comprising: forming a mixture of a brominated poly(isobutylene-co-paramethylstyrene) elastomer and a cure package, wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer has a Mw/Mn ratio greater than or equal to 2.5 and less than or equal to 10, and wherein the cure package comprises mercaptobenzothiazole disulfide; a phenolic resin; and a curative agent; and curing the mixture into a shape of the tire curing bladder.

15 [0066] Non-limiting example embodiment C can include one or more of the following elements.

[0067] Element 1C: wherein the curing is performed for less than thirty minutes at a temperature greater than or equal to 170 °C and less than or equal to 200 °C.

20 [0068] Element 2C: wherein the wherein the curing is performed for less than forty-five minutes at a temperature greater than or equal to 120 °C and less than or equal to 150 °C.

[0069] Element 3C: wherein the forming the mixture further includes mixing a second poly(isobutylene-co-paramethylstyrene) elastomer with the brominated poly(isobutylene-co-paramethylstyrene) elastomer and the cure package, wherein the second poly(isobutylene-co-paramethylstyrene) elastomer has a Mw/Mn ratio less than 2.5.

25 [0070] Element 4C: wherein the phenolic resin is at least one alkyl phenol formaldehyde resin selected from the group consisting of: octyl phenol formaldehyde resin, brominated octyl phenol formaldehyde resin, and a combination thereof.

30 [0071] Element 5C: wherein the curing package further comprises at least one filler selected from the group consisting of: calcium carbonate, clay, mica, silica, silicates, talc, titanium dioxide, aluminum oxide, starch, wood flour, carbon black, and a combination thereof.

[0072] To facilitate a better understanding of the embodiments described herein, the following examples are provided. In no way should the following examples be read to limit, or to define, the scope of the present disclosure.

Examples

[0073] In the following examples, the brominated poly(isobutylene-co-paramethylstyrene) elastomers were obtained via a post polymerization treatment of Exxpro™ 3035, using various amounts of peroxide initiator under high temperature and high shear conditions. The post polymerization treatment chemically induced a thermal breaking of the copolymer backbone to increase the fraction of low molecular weight species, and thereby broaden the MWD (*e.g.*, increase the MWD to a value greater than 2.5).

[0074] To obtain example Elastomers 1-3, Exxpro™ 3035 was mixed with Luperox® 101 in a 280 gram mixing bowl at 100 °C. Then the temperature of the mixture was raised to 190 °C, and the mixing continued for 5 minutes. Table 1 characterizes the reactants for each of the example Elastomers 1-3.

Table 1

T = 190 °C 5 minutes	Exxpro™ 3035 (phr)	Luperox® (phr)	Total phr		Exxpro™ 3035 (grams (g))	Luperox® (g)
Elastomer 1	100.0	0.25	100.25		259.35	0.65
Elastomer 2	100.0	0.5	100.5		258.71	1.29
Elastomer 3	100.0	1.0	101.0		257.43	2.57

[0075] Table 2 evaluates the brominated poly(isobutylene-co-paramethylstyrene) in comparison to the unmodified Exxpro™ 3035. Each of the example Elastomers 1-3 and the Exxpro™ 3035 comprised 5 wt% of the paramethylstyrene (“PMS”), and the brominated PMS (“Br-PMS”) content was determined by FTIR. Further, the molecular weight and MWD data was determine by gel permeation chromatography (“GPC”).

[0076] GPC is an analytical procedure used for separating molecules by differences in size. The procedure as applied to polymers results in a concentration distribution of molecular weights. Most often, concentration is determined using differential refractive index (DRI) and the concentration v. time elution curve is related to molecular weight by means of a calibration curve based on a "known" standard. Utilizing low-angle laser light-scattering (LALLS) photometry in conjunction with DRI, direct determination of molecular weight can be made.

[0077] Molecular weight averages can be calculated based on the data obtained from a GPC test. Molecular weight averages include: number average (Mn), weight average (Mw) and Z-average (Mz). These averages are also referred to as the various moments of the distribution. Higher molecular weight species have a greater influence on the Z and weight averages whereas lower molecular weight species more greatly influence the number average. The breadth of the distribution overall as well as parts of it can be characterized by reference to various ratios,

e.g., M_w/M_n and M_z/M_w ; the higher the values of the ratio, the broader the distribution of molecular weights.

[0078] Molecular weights (weight average molecular weight (M_w) and number average molecular weight (M_n)) and molecular weight distribution ($MWD = M_w/M_n$), which is also sometimes referred to as the polydispersity index (PDI) of the polymer, were measured by GPC. Molecular weights were determined by Tosoh BioScience HLC-8320 GPC equipped with an internal DRI detector, an internal UV absorbance detector UV-8320 (254 nm absorbance Detector), a Wyatt Technology miniDawn TREOS light scattering detector with three angles (45°, 90°, and 135°), and a Wyatt Technology ViscoStar-II viscometer detector, a series of three of Polymer Labs PLgel Mixed-B with peak M_w ; range of 580-10,000,000. The columns were calibrated using Polymer Labs EasiVial polystyrene standards (high, medium, and low) standards. Approximately 20 mg of polymer dissolved in 10 mL tetrahydrofuran ("THF") stabilized with butylated hydroxyl toluene ("BHT") and with toluene as a flow marker, the solution was filtered by using a 0.45 μ m Acrodisc filter (membrane type PTFE), and 150 μ L samples were injected by the auto injector. Testing conditions: sample solvent: tetrahydrofuran containing 250-400 ppm of butylated hydroxyl toluene; sample concentration: 2.0 mg/mL; sample dissolution temperature: room temp (~23 °C); sample dissolution time: 3 hours minimum on dissolving wheel; GPC pump oven and column oven temperatures: 40°C; Flow rate: 1 mL/min; mobile phase solvent: THF (same as sample solvent); sample injection size: 150 μ L; sample elution time: 65 minutes. The Wyatt Technology's Astra 6.1 GPC software was used for data analysis. The universal calibration curve methodology data was primarily used for reporting the results. For detailed understanding of the molecular weights of the elastomers, the on-line light scattering measurements, using the laser light scattering ("LLS") detector connected on-line with the columns and other detectors were used. The dn/dc value for butyl rubber, 0.113 mL/g, was used for calculating the absolute molecular weights. Samples for light scattering were prepared with care to avoid the presence of particulate matter. The Wyatt Technology's Astra 6.1 GPC software was used for data analysis.

[0079] The quantification of the functional groups, the percent incorporation of paramethylstyrene and brominated paramethylstyrene (BrpMS) in the elastomer, and other components or additives present were determined using a PerkinElmer Frontier FTIR spectrometer with triglycine sulfate (TGS) detector and a sample shuttle. The spectrometer was controlled by the Spectrum™ 10.6.0 software. The infrared spectra of elastomers were acquired using a compression molded film specimen of thickness 0.060 cm, using an automated Carver

Hydraulic Press. FTIR spectra were collected at 4 cm⁻¹ resolution with 16 scans, scan range 6525-400 cm⁻¹. All FTIR spectra were normalized against a common region 4400-4250 cm⁻¹, and the base absorbance measured at 4980-2040 cm⁻¹. The paramethylstyrene concentration was quantified using an aromatic overtone band centered at 1894 cm⁻¹, and brominated paramethylstyrene units were quantified using the C-Br band centered 615 cm⁻¹. Spectral regions corresponding to structures or components of interest were correlated with their concentrations determined according to Beer's Law and multipoint calibrations to cover the range of paramethylstyrene and brominated paramethylstyrene concentrations, the calibration sets were prepared from standards with known concentration obtained by NMR. A model was developed to automatically calculate the mol% of paramethylstyrene and mol% brominated paramethylstyrene after the spectrum was collected.

Table 2

Samples*	Br-PMS Content (%)**	Mooney Viscosity ***	Mn (kDa)	Mw (kDa)	Mz (kDa)	Mw/Mn
Exxpro™ 3035	0.47	46.6	205.1	476.7	1556.5	2.32
Elastomer 1	0.45	32.2	156.4	470.3	1263	3.01
Elastomer 2	0.42	31.9	110.4	338.1	935.6	3.06
Elastomer 3	0.35	24.6	65.8	208.4	559.9	3.17

*All samples contain 5 wt% paramethylstyrene

**Determined by FTIR

***ML, 1+8 @ 125 °C

[0080] Additionally, the example Elastomers 1-3 were blended with Exxpro™ 3035, as characterized by Table 3, below. In particular, the example Elastomer Blends 1-3 are 50:50 blends of: Exxpro™ 3035 and Elastomer 1 (*i.e.*, Elastomer Blend 1), Exxpro™ 3035 and Elastomer 2 (*i.e.*, Elastomer Blend 2), and Exxpro™ 3035 and Elastomer 3 (*i.e.*, Elastomer Blend 3).

Table 3

Samples	Blending Ratio*	Mn (kDa)	Mw (kDa)	Mz (kDa)	Mw/Mn
Exxpro™ 3035	N/A	205.1	476.7	1556.5	2.32
Elastomer Blend 1	1:1	146	498.2	1506.8	3.41
Elastomer Blend 2	1:1	124	411.7	992.8	3.32

Elastomer Blend 3	1:1	94.9	380.2	927.1	4.01
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* Ratio of Exxpro™ 3035 to example Elastomer 1, 2, or 3.

- [0081] Utilizing the example Elastomers 1-3 as the brominated poly(isobutylene-co-paramethylstyrene) elastomers described herein, examples of the tire curing bladder formulation were prepared using a BRABENDER™ intelli-torque internal mixer with a prep-mixer head in accordance with one or more embodiments described herein. Unless otherwise stated, the example tire curing bladder formulations include 100 parts by weight of the elastomer compounds and 50 phr N330 carbon black blended into the examples on a second pass in a BRABENDER™ intelli-torque internal mixer with roller type 6 blades and a temperature of less than 100 °C.
- [0082] The various example Elastomers 1-3, and/or blends thereof, characterized in Tables 1-3 were utilized in multiple example tire bladder formulations in accordance with one or more embodiments described herein. For instance, Table 4 depicts the tire bladder formations of three example tire bladder compounds (e.g., Example Compounds 1-3), prepared in accordance with various embodiments described herein.

Table 4

Ingredient	Control Compound	Example Compound 1	Example Compound 2	Example Compound 3
Exxpro™ 3035 [PHR]	100	50	50	50
Elastomer 1 [PHR]	0	50	0	0
Elastomer 2 [PHR]	0	0	50	0
Elastomer 3 [PHR]	0	0	0	50
Carbon Black N330 [PHR]	50	50	50	50
MBTS [PHR]	1.85	1.6	1.23	0.7
Stearic acid [PHR]	0.5	0.5	0.5	0.5
Phenolic resin SP-1045 [PHR]	3	3	3	3
Zinc Oxide (ZnO) [PHR]	0.5	0.5	0.5	0.5
Total PHR	155.85	155.6	155.23	154.7

[0083] To assess the impact on processability of tire bladder formulations comprising the brominated poly(isobutylene-co-paramethylstyrene) elastomer described herein (*e.g.*, Example Compounds 1-3, having elastomer species with broader MWD than Exxpro™ 3035), the Mooney viscosity of Example Compounds 1-3 were obtained and the results are summarized in Table 5. The compound Mooney values in Table 5 are directly correlated ($r^2 = 0.95$) to the Mn values of the example elastomers (*e.g.*, Elastomers 1-3) shown in Table 2. Further, the Example Compounds 1-3 demonstrate an unexpected magnitude of correlation between the MWD and compound Mooney viscosity, where a relatively small change in MWD resulted in a significant improvement in compound Mooney viscosity. For example, comparing the Control Compound to Example Compound 2, a change of Mw/Mn of only from 2.32 to 3.32 resulted in a large reduction of the compound Mooney viscosity from 94 ML to 74 ML, which represents a significant improvement in processability.

Table 5

Compound	Compound Mooney Viscosity*
Control Compound	94.1
Example Compound 1	85.3
Example Compound 2	74.2
Example Compound 3	69.4

*ML 1+4@100°C

[0084] Cure characteristics of Example Compounds 1-3 were evaluated using an Alpha Technologies MDR rheometer 2000 at 190 °C and 1 °arc. The cure characteristics are included in Table 6, below, where: delta torque (MH-ML) is the maximum torque (“MH”) minus minimum torque (“ML”), scorch safety (“TS2”) is the time at which torque rises 2 torque units (dNm) above ML; cure time “TC(90)” is the time to 90 percent of delta torque above minimum torque. Additionally, stress/strain measurements were performed on test specimens using ASTM D4482 die. Specimens were tested on an Instron 5565 with a long travel mechanical extensometer. The load cell and extensometer are calibrated before each day of testing with 20 mm as the gauge length. Sample information, operator name, date, lab temperature, and humidity were all recorded and specimen thickness was measured at three places in the test area. The lab temperature and humidity were measured. Specimen was carefully loaded in the grips to ensure grips clamp on the specimen symmetrically. A pre-load of 0.1 N was applied during the stress/strain tests, which began with the crosshead at 20 inches/minute until a break is detected. Three specimens from each sample (*e.g.*, Example Compounds 1-3) were tested

and the median values were reported. Samples were oven aged for 48 hours at 177 °C., followed by resting for 24 hours before the strain/strain measurement.

Table 6

190 °C	Control Compound	Example Compound 1	Example Compound 2	Example Compound 3
Test Time (min)	60	60	60	60
Test Temp (°C)	190	190	190	190
ML (dNm)	3.7	2.9	2.6	2.3
MH (dNm)	16.2	15.3	15.4	14.6
MH-ML (dNm)	12.5	12.5	12.8	12.4
Scorch Time TS2(min)	1.5	1.6	1.6	1.6
Cure Time TC90 (min)	11.2	13.4	10.3	7.4

5

[0085] To assess the physical properties of Example Compounds 1-3, in comparison to the Control Compound, all compounds were cured at 190 °C for TC90+5 minutes. As shown in Table 7, formulations comprising the brominated poly(isobutylene-co-paramethylstyrene) elastomer described herein (e.g., Example Compounds 1 and/or 2) exhibit comparable moduli, ultimate tensile strength and/or elongation to the Control Compound.

10

Table 7

	Control Compound	Example Compound 1	Example Compound 2	Example Compound 3
Stress @ 100% [Mpa]	1.71	1.75	1.69	1.86
Stress @ 200% [Mpa]	3.2	3.52	3.55	4.21
Stress @ 300% [Mpa]	5.01	5.57	5.75	6.79
Ultimate Tensile Strength [Mpa]	12.6	12.5	13.1	12.1
% Elongation at Break [%]	765	686	683	568
Energy at Break [J]	7.68	6.47	7.14	5.21

[0086] The aging properties of the vulcanizates of the Example Compounds were evaluated in Table 8 by conducting stress/strain measurements after air aging at 177 °C for 48 hours. Similarly, the Example Compounds 1 & 2 show comparable aging tensile properties to the Control Compound.

5

Table 8

	Control Compound	Example Compound 1	Example Compound 2	Example Compound 3
Stress @ 100% [Mpa]	2.01	2.09	2.02	2.44
Stress @ 200% [Mpa]	3.72	3.88	3.75	4.91
Stress @ 300% [Mpa]	5.65	5.84	5.72	7.38
Ultimate Tensile Strength [Mpa]	11.2	10.0	10.4	10.4
% Elongation at Break [%]	640	608	587	455
Energy at Break [J]	5.84	5.00	5.08	3.73

[0087] As demonstrated via Tables 5-8, a relatively small change in molecular weight distribution (MWD) can impart a surprisingly significant improvement in compound Mooney viscosity while maintaining good physical and aging properties. For instance, a change from
 10 Mw/Mn = 2.32 to 3.32 can effectively reduce the compound Mooney viscosity from 94 ML to 74 ML, resulting an unexpectedly large difference of 20 Mooney units leading to marked improvement in processability for tire bladder formulations comprising the brominated poly(isobutylene-co-paramethylstyrene) elastomer described herein.

[0088] Unless otherwise indicated, all numbers expressing quantities of ingredients,
 15 properties such as molecular weight, reaction conditions, and so forth used in the present specification and associated claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the incarnations of the present
 20 inventions. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claim, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0089] One or more illustrative incarnations incorporating one or more invention elements are presented herein. Not all features of a physical implementation are described or shown in this application for the sake of clarity. It is understood that in the development of a physical embodiment incorporating one or more elements of the present invention, numerous implementation-specific decisions must be made to achieve the developer's goals, such as compliance with system-related, business-related, government-related and other constraints, which vary by implementation and from time to time. While a developer's efforts might be time-consuming, such efforts would be, nevertheless, a routine undertaking for those of ordinary skill in the art and having benefit of this disclosure.

[0090] While compositions and methods are described herein in terms of “comprising” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular examples and configurations disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative examples disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles “a” or “an,” as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

CLAIMS

What is claimed is:

1. A tire curing bladder, comprising:
 - 5 a brominated poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio greater than or equal to 2.5 and less than or equal to 10; mercaptobenzothiazole disulfide; a phenolic resin; and a curative agent.
2. The tire curing bladder of claim 1, wherein the brominated poly(isobutylene-co-
10 paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20 mole percent of paramethylstyrene.
3. The tire curing bladder of claim 1, wherein the curative agent is zinc oxide.
- 15 4. The tire curing bladder of claim 1, further comprising at least one filler selected from the group consisting of: calcium carbonate, clay, mica, silica, silicates, talc, titanium dioxide, aluminum oxide, starch, wood flour, carbon black, and a combination thereof.
5. The tire curing bladder of claim 4, wherein the filler is a carbon black N110 to N990
20 per ASTM D1765-17.
6. The tire curing bladder of claim 4, wherein the phenolic resin is at least one alkyl phenol formaldehyde resin selected from the group consisting of: octyl phenol formaldehyde resin, brominated octyl phenol formaldehyde resin, and a combination thereof.
- 25 7. The tire curing bladder of claim 1, further comprising:
 - a second poly(isobutylene-co-paramethylstyrene) elastomer, the second poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio less than 2.5.
- 30 8. The tire curing bladder of claim 7, wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is halogenated.

9. The tire curing bladder of claim 8, wherein the second poly(isobutylene-co-paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20 mole percent of paramethylstyrene.
- 5 10. The tire curing bladder of claim 7, wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 parts per hundred rubber (phr), and wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 phr.
11. The tire curing bladder of claim 7, wherein the tire curing bladder has a compound
10 Mooney viscosity of less than 90 Mooney units (ML, 1+4 at 100°C).
12. The tire curing bladder of claim 11, wherein the Mw/Mn ratio of the brominated poly(isobutylene-co-paramethylstyrene) elastomer is greater than or equal to 2.5 and less than or equal to 4.
- 15 13. A composition, comprising:
an elastomeric composition formed into a tire curing bladder, the elastomeric composition comprising:
a brominated poly(isobutylene-co-paramethylstyrene) elastomer having a
20 Mw/Mn ratio greater than or equal to 2.5 and less than or equal to 10; and
a cure package comprising: mercaptobenzothiazole disulfide; a phenolic resin;
and a curative agent.
14. The composition of claim 13, wherein the brominated poly(isobutylene-co-
25 paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20 mole percent of paramethylstyrene.
15. The composition of claim 13, wherein the cure package further comprises at least one filler selected from the group consisting of: calcium carbonate, clay, mica, silica,
30 silicates, talc, titanium dioxide, aluminum oxide, starch, wood flour, carbon black, and a combination thereof.

16. The composition of claim 15, wherein the phenolic resin is at least one alkyl phenol formaldehyde resin selected from the group consisting of: octyl phenol formaldehyde resin, brominated octyl phenol formaldehyde resin, and a combination thereof.
- 5 17. The composition of claim 13, wherein the elastomeric composition further comprises:
a second poly(isobutylene-co-paramethylstyrene) elastomer, the second poly(isobutylene-co-paramethylstyrene) elastomer having a Mw/Mn ratio less than 2.5.
- 10 18. The composition of claim 17, wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is halogenated.
19. The composition of claim 18, wherein the second poly(isobutylene-co-paramethylstyrene) elastomer comprises 80 to 99.5 mole percent of isobutylene and 0.5 to 20
15 mole percent of paramethylstyrene.
20. The composition of claim 17, wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 parts per hundred rubber (phr), and wherein the second poly(isobutylene-co-paramethylstyrene) elastomer is present in 50 phr.
20
21. The composition of claim 17, wherein the tire curing bladder has a compound Mooney viscosity of less than 90 Mooney units (ML, 1+4 at 100 °C).
22. A method of making a tire curing bladder, the method comprising:
25 forming a mixture of a brominated poly(isobutylene-co-paramethylstyrene) elastomer and a cure package, wherein the brominated poly(isobutylene-co-paramethylstyrene) elastomer has a Mw/Mn ratio greater than or equal to 2.5 and less than or equal to 10, and wherein the cure package comprises mercaptobenzothiazole disulfide, a phenolic resin, and a curative agent; and
30 curing the mixture into a shape of the tire curing bladder.

23. The method of claim 22, wherein the curing is performed for less than thirty minutes at a temperature greater than or equal to 170 degrees Celsius (°C) and less than or equal to 200 °C.
24. The method 22, wherein the wherein the curing is performed for less than forty-five
5 minutes at a temperature greater than or equal to 120 degrees Celsius (°C) and less than or equal to 150 °C.
25. The method of claim 22, wherein the forming the mixture further includes:
mixing a second poly(isobutylene-co-paramethylstyrene) elastomer with the
10 brominated poly(isobutylene-co-paramethylstyrene) elastomer and the cure package, wherein the second poly(isobutylene-co-paramethylstyrene) elastomer has a Mw/Mn ratio less than 2.5.
26. The method of claim 25, wherein the phenolic resin is at least one alkyl phenol
15 formaldehyde resin selected from the group consisting of: octyl phenol formaldehyde resin, brominated octyl phenol formaldehyde resin, and a combination thereof.
27. The method of claim 26, wherein the curing package further comprises at least one
20 filler selected from the group consisting of: calcium carbonate, clay, mica, silica, silicates, talc, titanium dioxide, aluminum oxide, starch, wood flour, carbon black, and a combination thereof.