

ELASTOMER COMPOSITIONS AND METHODS THEREOF

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5 **CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of U.S. Provisional Application No. 63/520,120, filed August 17, 2023, entitled “Elastomer Compositions and Methods Thereof”, the entirety of which is incorporated by reference herein.

FIELD

10 [0002] The present disclosure relates to elastomer compositions and methods thereof.

BACKGROUND

[0003] The tire industry is interested in developing novel ways of extending the useful lifetime of tire products and materials, as such products and materials are ubiquitous in commercial and consumer applications. However, such high utilization inevitably means that
15 a tire product may become punctured or damaged which can result in the substantial or total loss of air pressure of one or more tires. This unfortunately limits a vehicle’s ability to travel, and has been an issue dating back from the very start of the use of inflated tires.

[0004] For decades, the spare wheel was considered to be the only universal solution to sudden, irreversible loss of air pressure. However, recent technological advancements have
20 arisen that could potentially dispense with the need for having a spare tire. Specifically, the concept of “extended mobility” has been developed and is associated with techniques which allow the vehicle to run on the same tire after being damaged. However, in many cases, this concept comes with some limitations. For example, once damaged, the tire would not be able to traverse to a point of repair without having to stop. The damaged tire would then have to be
25 changed before travel is to continue.

[0005] Thus, self-healing and/or self-sealing compositions for tires have become an active area of intrigue and research. The goal of such work is to produce a tire composition that is capable of automatically sealing a tire in the event of it being punctured by a foreign body, such as a nail. In addition, the automatic sealing properties should be able to proceed without
30 any external intervention.

[0006] While there have been reports of elastomeric polymers being implemented in self-healing or self-sealing compositions, it is difficult to provide both of these properties within the same composition. In addition, many of these compositions and tires thereof lack physical and mechanical property retention once the material is damaged. In particular, retaining gas

barrier properties of the material once damaged is particularly troublesome, as poor retention in gas barrier properties can result in tire deflation.

[0007] There is a need to develop novel compositions to be used in tires, such that upon receiving damage, the tire can autonomously self-heal and self-seal to extend the usable lifetime of the tire. Specifically, there is a need to develop novel compositions that upon self-healing/sealing, the gas barrier properties retained will be comparable to that of the original material.

[0008] References for citing in an information disclosure statement (37 C.F.R. 1.97(h)): U.S. Patent Nos. 8,883,415; 11,312,094; 8,602,075; 10,919,242; 7,674,344; 8,703,832; U.S. Publication Nos. 2016/0068031; 2021/0354407.

SUMMARY

[0009] The present disclosure relates to elastomer compositions and methods thereof.

[0010] In some embodiments, an elastomer composition includes a first elastomer and a second elastomer. The first elastomer is a copolymer comprising p-methylstyrene, p-halomethylstyrene, and isobutylene derived repeat units and comprises about 30 phr to about 100 phr of the elastomeric composition. The second elastomer comprises about 30 phr to about 75 phr of the elastomeric composition.

[0011] In some embodiments, an elastomeric network includes a first elastomer, a second elastomer, and a nucleophilic compound. The first elastomer is a copolymer comprising p-methylstyrene, p-halomethylstyrene, and isobutylene derived repeat units and comprises about 30 phr to about 100 phr of the elastomeric composition, the second elastomer comprises about 30 phr to about 75 phr of the elastomeric composition, and the nucleophilic compound is a crosslinking agents, the nucleophilic compound comprising about 1.4 phr to about 2.7 phr of the elastomeric composition.

[0012] In some embodiments, a method of making a tire component includes mixing a first elastomer and a second elastomer to form an elastomer composition in a mixing bowl at about 40 rpm. The first elastomer is a copolymer comprising p-methylstyrene, p-halomethylstyrene, and isobutylene derived repeat units and comprises about 30 phr to about 100 phr of the elastomeric composition. The second elastomer is butyl rubber and comprises about 30 phr to about 75 phr of the elastomeric composition. The method further comprises blending the elastomer composition with a nucleophilic compound to form an elastomeric network. The nucleophilic compound comprises about 1.4 phr to about 2.7 phr of the elastomeric network and the nucleophile to halide ratio is about 1:0.7 to about 1:1.3. The method further comprises integrating the elastomeric network into one or more components of a tire of a tire.

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DETAILED DESCRIPTION

[0013] Multiple pathways have been developed to produce highly impermeable self-healing and self-sealing compositions suitable for tire sealing applications. Those pathways include the implementation and crosslinking of elastomeric blends comprising one or more halogenated species. It was found that semi-interpenetrating elastomer network components with dual sealing mechanisms and in-situ formed low molecular weight ionomer containing compositions showed good resealing performances and retention of gas after puncture and reseal.

[0014] The interpenetrating elastomer networks of the present disclosure can implement an ionomeric network component, thereby providing the material with self-healing capabilities via the breaking and formation of the ion pair aggregations. The ionomeric network possesses dynamic mechanical properties that are comparable to thermoset vulcanizates.

[0015] The interpenetrating elastomer networks can further implement a second rubber component to provide the material with viscoelastic properties. Such properties allow the material to form a gas impermeable seal if the material were to become damaged and subsequently self-healed.

[0016] The second rubber component may also be partially crosslinked, so as to provide the interpenetrating elastomeric network with increased mechanical properties.

[0017] Additionally, in-situ low molecular weight ionomer formation was found to provide easier flow characteristics, prepared by chain breaking the halogenated elastomer with a peroxide. The network is then reformed via the ionomer forming reagent reacting with higher amounts of halobutyl elastomers or blends thereof, and a second elastomer.

Definitions

[0018] Elastomer refers to a polymer or blend of polymers consistent with the ASTM D1566 definition: "a material that is capable of recovering from large deformations, and can be, or already is, modified to a state in which it is essentially insoluble, if vulcanized, (but can swell) in a solvent." Elastomers are often also referred to as rubbers; the term elastomer may be used herein interchangeably with the term rubber. Elastomers may have a melting point that cannot be measured by Differential Scanning calorimetry (DSC) or if it can be measured by DSC is less than 40° C., such as less than 20° C., such as less than 0° C. Elastomers may have a glass transition temperature (T_g) of -50° C. or less as measured by DSC.

[0019] As used herein, "polymer" may be used to refer to homopolymers, copolymers, terpolymers, etc. As used herein, the term "copolymer" is meant to include polymers having two or more monomers. Polymers, in some embodiments, may be produced (1) by mixing all multiple monomers at the same time or (2) by sequential introduction of the different

comonomers. The mixing of comonomers may be done in one, two, or possible three different reactors in series and/or in parallel. 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. 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.

[0020] As used herein, “diolefin” refers to an unsaturated hydrocarbon having at least two unsaturated bonds between carbon atoms. While normally, a diolefin will have two double bonds, a molecule with additional double bonds or with one or more triple bonds may also function as a diolefin for purposes of the present disclosure.

[0021] The term “composition” or “blend” as used herein refers to a mixture of two or more polymers, optionally including additional materials such as curing agents. A composition can include the components of the compositions and/or reaction product(s) of two or more of the components. Blends may be produced by, for example, solution blending, melt mixing, or compounding in a shear mixer. A composition/blend can be cured to form a “vulcanizate”. The vulcanizate can be used as a tire liner of the present disclosure.

[0022] The term “monomer” or “comonomer,” as used herein, can refer to the monomer used to form the polymer (*i.e.*, the unreacted chemical compound in the form prior to polymerization) and can also refer to the monomer after it has been incorporated into the polymer, also referred to herein as a “[monomer]-derived unit”. Different monomers are discussed herein including C₄-C₇ isoolefin monomers, non-halogenated alkylstyrene monomers, halogenated styrene monomers, and diolefin monomers.

[0023] As used herein, “phr” means “parts per hundred parts rubber,” where the “rubber” is the total rubber content of the composition. Herein, both the elastomers (such as BIMSM) of the present disclosure and additional rubbers, when present, are considered to contribute to the total rubber content. Thus, for example, a composition having 30 parts by weight of elastomer of the present disclosure and 70 parts by weight of a second rubber (*e.g.*, butyl rubber) may be referred to as having 30 phr elastomer and 70 phr second rubber. Other components added to the composition are calculated on a phr basis. That is, addition of 50 phr of oil means, for example, that 50 g of oil are present in the composition for every 100 g of total rubber. Unless specified otherwise, phr should be taken as phr on a weight basis.

[0024] “Mooney viscosity” as used herein is the Mooney viscosity of a polymer or polymer composition. The polymer composition analyzed for determining Mooney viscosity should be substantially devoid of solvent. For instance, the sample may be placed on a boiling-water steam table in a hood to evaporate a large fraction of the solvent and unreacted monomers, and

then, dried in a vacuum oven overnight (12 hours, 90 °C) prior to testing, 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 D1646-19, but with the following modifications/clarifications of that procedure. First, sample polymer is pressed between two hot plates of a compression press prior to testing. The plate temperature is 125 °C $\pm$ 10 °C instead of the 50 $\pm$ 5 °C recommended in ASTM D1646-19, because 50 °C is unable to cause sufficient massing. Further, although ASTM D1646-19 allows for several options for die protection, should any two options provide conflicting results, PET 36 micron should be used as the die protection. Further, ASTM D1646-19 does not indicate a sample 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 $\pm$ 2.7 g in the D1646-19 Section 8 procedures will govern. Finally, the rest procedures before testing set forth in D1646-19 Section 8 are 23 $\pm$ 3 °C for 30 min in air; Mooney values as reported herein are determined after resting at 24 $\pm$ 3 °C for 30 min in air. Samples are placed on either side of a rotor according to the ASTM D1646-19 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 M is the Mooney viscosity number, L denotes large rotor (defined as ML in ASTM D1646-19), 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.

Elastomers and compositions thereof

[0025] In one or more embodiments, the compositions can be comprised of at least one elastomeric network and can exhibit self-healing and self-sealing behavior. In some embodiments, the self-healing and self-sealing compositions comprise a blend of at least one elastomeric network and an additional elastomeric component, where the additional elastomeric component is optionally crosslinked. Without being bound by theory, the at least one elastomeric network participates predominantly in the self-healing behavior of the composition, while the additional elastomeric component participates predominantly in the

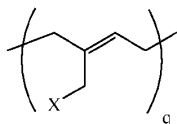
self-sealing behavior. In addition, in some embodiments, the physical and rheological properties of the optionally crosslinked additional elastomeric component are considered, as those physical and rheological properties should be tailored to provide the overall composition added mechanical benefit without sacrificing self-sealing properties and efficiency.

5 [0026] In at least one embodiment, an elastomer comprises a polymer made up of at least one olefinic monomer. The olefinic monomer is selected from any one or more C₄-C₁₄ olefin monomers having at least one unsaturation, such as isoprene, butadiene, 1-methylbutadiene, 2-methylbutadiene, 2,3-dimethyl-1,3-butadiene, 2,4-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-
10 pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 3-methyl-1,3-hexadiene, 4-methyl-1,3-hexadiene, 5-methyl-1,3-hexadiene, 2,3-dimethyl-1,3-hexadiene, 2,4-dimethyl-1,3-hexadiene, 2,5-dimethyl-1,3-hexadiene, 2-neopentylbutadiene, 1,3-cyclopentadiene, 1,3-cyclohexadiene, 1-vinyl-1,3-cyclohexadiene, isobutylene, isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene, and combinations thereof. In at least one embodiment,
15 an elastomer is butyl rubber.

[0027] In at least one embodiment, an elastomer comprises halogenated butyl rubber. As used herein, “halogenated butyl rubber” refers to both butyl rubber and so-called “star-branched” butyl rubber. In some embodiments, the halogenated rubber component is a halogenated copolymer of a C₄-C₁₄ isoolefin and a C₄-C₁₄ multiolefin. In another embodiment,
20 the halogenated rubber component is a blend of a polydiene or block copolymer, and a copolymer of a C₄-C₁₄ isoolefin and a conjugated, or a “star-branched” butyl polymer. The halogenated butyl polymer of the present disclosure can thus be described as a halogenated elastomer comprising C₄-C₁₄ isoolefin derived units, multiolefin derived units, and halogenated multiolefin derived units, and includes both “halogenated butyl rubber” and so called
25 “halogenated star-branched” butyl rubber. In one embodiment, the halogenated butyl rubber is brominated butyl rubber, and in another embodiment is chlorinated butyl rubber.

[0028] In some embodiments, the halogenated butyl or star-branched butyl rubber may be halogenated such that the halogenation is primarily allylic in nature. This is typically achieved by free radical bromination, free radical chlorination, ionic bromination, or by such methods
30 as secondary treatment of electrophilically halogenated rubbers, such as by heating the rubber, to form the allylic halogenated butyl and star-branched butyl rubber. Common methods of forming the allylic halogenated polymer are disclosed by Gardner et al. in U.S. Pat. Nos. 4,632,963, 4,649,178, and 4,703,091. Thus, in some embodiments, the halogenated butyl rubber is such that the halogenated multiolefin units are primary allylic halogenated units, and
35 wherein the primary allylic configuration is present to at least 20 mole percent (relative to the

total amount of halogenated multiolefin) in some embodiments, and at least 30 mole percent in other embodiments. This arrangement can be described by the structure:



where X is a halogen, such as chlorine or bromine, and q is a positive integer.

- 5 [0029] A commercial embodiment of the halogenated butyl rubber is Bromobutyl 2222 (Exxon Mobil Corporation) which has a Mooney viscosity of 27 to 37 (ML 1+8 at 125° C., ASTM 1646-17), and the bromine content is 1.8 to 2.2 weight percent relative to the Bromobutyl 2222. Further, cure characteristics of Bromobutyl 2222 are as follows: MH is from 28 to 40 dN·m, ML is from 7 to 18 dN·m (ASTM D2084-17). Another commercial
- 10 embodiment of the halogenated butyl rubber is Bromobutyl 2255 (Exxon Mobil Corporation). Its Mooney viscosity is 41 to 51 (ML 1+8 at 125° C., ASTM 1646-17), and the bromine content is 1.8 to 2.2 weight percent. Further, cure characteristics of Bromobutyl 2255 are as follows: MH is from 34 to 48 dN·m, ML is from 11 to 21 dN·m (ASTM D2084-17).
- [0030] Examples of isobutylene-isoprene copolymers, include EXXON™ BUTYL 065, EXXON™ BUTYL 065S, EXXON™ BUTYL 365, EXXON™ BUTYL 068, EXXON™ BUTYL 068S, EXXON™ BUTYL 268, EXXON™ BUTYL 268S, or combinations thereof. Examples of non-halogenated and halogenated rubbers are provided in Table 1 (all available from ExxonMobil Chemical Company), where the balance of the composition is isobutylene.

TABLE I Exemplary Isobutylene Based Polymers						
Elastomer	Mooney Viscosity (ML1 + 8 @ 125° C)	Isoprene (mol. %)	Para-Methylstyrene (wt. %)	Halogen	Halogen (wt. %)	Halogen (mol. %)
EXXON™ BUTYL 065	32	1.05	--	--	--	--
EXXON™ BUTYL 365	33	2.30	--	--	--	--
EXXON™ BUTYL 068	51	1.15	--	--	--	--
EXXON™ BUTYL 268	51	1.70	--	--	--	--
EXXON™ CHLORO-BUTYL 1066	38	1.95	--	Cl	1.26	--
EXXON™ BROMO-BUTYL 2222	32	1.70	--	Br	2.00	--
EXXON™ BROMO-BUTYL 2235	39	1.70	--	Br	2.00	--
EXXON™ BROMO-BUTY 2255	46	1.70	--	Br	2.00	--
EXXON™ BROMO-BUTYL 2211	32	1.70	--	Br	2.10	--

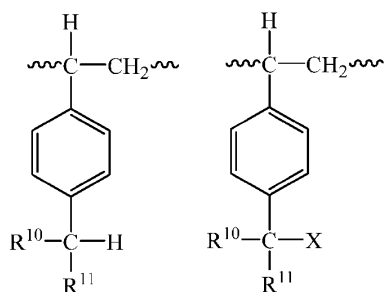
EXXON TM BROMO-BUTYL 2244	46	1.70	–	Br	2.10	–
EXXON TM BROMO-BUTYL 7211	32	1.70	–	Br	2.00	–
EXXON TM BROMO-BUTYL 7244	46	1.7	–	Br	2.00	–
EXXON TM BROMO-BUTYL 6222	32	1.70	–	Br	2.40	–
EXXON TM CHLORO-BUTYL 5066	32	–	–	Cl	1.26	–
EXXPRO® 3035	45	–	5.00	Br	–	0.47
EXXPRO® 3433	35	–	5.00	Br	–	0.75
EXXPRO® 3745	45	–	7.50	Br	–	1.20
EXXPRO® 3563	35	–	10	Br	–	0.85

[0031] In at least one embodiment, an elastomer comprises a polymer made up of at least one non-halogenated styrene monomer and/or halogenated styrene monomer. In at least one embodiment, the non-halogenated styrene monomer unit is selected from α -methylstyrene, tert-butylstyrene, styrene units substituted in the ortho, meta, or para position with a C₁ to C₅ alkyl or branched chain alkyl, and combinations thereof. In some embodiments, the styrene monomer is a halogenated styrene monomer selected from halomethylstyrene, styrene units substituted in the ortho, meta, or para position with a halogenated C₁ to C₅ alkyl or branched chain alkyl, and combinations thereof wherein the halogen may be chlorine or bromine. In one or more embodiments, the at least one non-halogenated alkylstyrene and/or halogenated alkylstyrene monomers independently comprise about 0.2 mol % to about 20 mol % para-isomer, such as about 0.3 mol % to about 10 mol %, such as about 0.4 mol % to about 7 mol %, such as about 0.5 mol % to about 5 mol %.

[0032] In one or more embodiments, an elastomer is a copolymer comprising a backbone architecture of at least one of a random copolymer, a block copolymer, an alternating copolymer, or a gradient copolymer. In one or more embodiments, the elastomer is a random copolymer. In one or more embodiments, the elastomer is a block copolymer.

[0033] In one or more embodiments, an elastomer is random copolymer of at least one C₄-C₁₄ isooolefin monomer (*e.g.*, isobutylene), at least one non-halogenated alkylstyrene monomer (*e.g.*, p-methylstyrene), and at least one halogenated alkylstyrene monomer (*e.g.*, p-bromomethylstyrene). In some embodiments, non-halogenated alkylstyrene and halogenated alkylstyrene monomers each contain at least 80 wt%, such as at least 90 wt% para-isomer. In some embodiments, non-halogenated alkylstyrene and halogenated alkylstyrene monomers each contain about 0.2 mol % to about 20 mol % para-isomer based on the total mol % of alkylstyrene based monomers, such as about 0.3 mol % to about 10 mol %, such as about 0.4 mol % to about 7 mol %, such as about 0.5 mol % to about 5 mol %.

[0034] In some embodiments, elastomers of the present disclosure may contain the following monomer units randomly spaced along the polymer chain:



wherein R¹⁰ and R¹¹ are independently hydrogen, alkyl, such as C₁ to C₇ alkyl, or primary or secondary alkyl halides and X is a functional group such as halogen.

[0035] In some embodiments, R¹⁰ and R¹¹ are hydrogen. Up to 60 mole percent of the para-substituted styrene present in the elastomer structure may be functionalized, and in other
5 embodiments from 0.1 to 5 mol %. In yet another embodiment, the amount of functionalized para-substituted styrene units of an elastomer is 0.4 to 1 mol %.

[0036] The functional group X may be halogen or a combination of a halogen and some other functional group which may be incorporated by nucleophilic substitution of benzylic halogen with other groups such as carboxylic acids; carboxy salts; carboxy esters, amides, and imides;
10 hydroxy; alkoxide; phenoxide; thiolate; thioether; xanthate; cyanide; nitrile; amino and mixtures thereof. These functionalized isoolefin copolymers, their method of preparation, methods of functionalization, and cure are more particularly disclosed in U.S. Pat. No. 5,162,445, and in particular, the functionalized amines as described below.

[0037] In at least one embodiment, an elastomer is an elastomeric random copolymer of
15 isobutylene, p-methylstyrene, and p-bromomethylstyrene where the p-methylstyrene and the p-bromomethylstyrene are present in a combined amount of 0.2 mol % to about 20 mol%, such as about 0.3 mol % to about 10 mol%, such as about 0.4 mol % to about 7 mol%, such as about 0.5 mol % to about 5 mol%, alternatively about 0.2 to about 40 wt %, alternatively about 0.5 to about 20 wt %. These halogenated elastomers are commercially available as EXXPRO™
20 Elastomers (Exxon Mobil Corporation), and abbreviated as “BIMSM.” These elastomers can, if desired, have a substantially homogeneous compositional distribution such that at least about 95% by weight of the polymer has a combined p-methylstyrene and p-bromomethylstyrene content within about 15% of the combined p-methylstyrene and p-bromomethylstyrene content of the overall polymer.

[0038] In some embodiments, an elastomer contains about 0.1 mol % to about 7.5 mol %
25 halogenated alkylstyrene derived units, relative to the combined non-halogenated and halogenated alkylstyrene derived units in the polymer. In one or more embodiments, the amount of halogenated alkylstyrene derived units is about 0.2 mol % to about 3 mol %, such as about 0.3 mol % to about 2.8 mol %, such as about 0.3 mol % to about 2 mol %, such as
30 about 0.4 mol % to about 1 mol %, wherein a desirable range may be any combination of any upper limit with any lower limit. Expressed another way, elastomeric copolymers contain about 0.3 wt % to about 4.5 wt % of bromine, based on the weight of the polymer, such as about 0.4 wt % to about 4 wt % bromine, such as about 0.6 wt % to about 1.5 wt % bromine. In at least one embodiment, the elastomer is a copolymer of C₄ to C₁₄ isoolefin derived units

(or isomonoolefin), p-methylstyrene derived units, and p-halomethylstyrene derived units, wherein the p-halomethylstyrene units are present in the elastomer from about 0.4 mol % to about 1 mol % based on the total number of p-methylstyrene and p-halomethylstyrene derived units, and wherein the p-methylstyrene derived units are present from about 3 wt % to about 15 wt % based on the total weight of the polymer, or about 10 wt % to about 12 wt %. In at least one embodiment, the p-halomethylstyrene is p-bromomethylstyrene.

[0039] In at least one alternative embodiment, the elastomers can further include one or more diolefin monomers, where the C₄ to C₁₄ isoolefin is not the same as the diolefin. Examples of diolefins include isoprene; cis-1,3-pentadiene; trans-1,3-pentadiene; cyclopentadiene; beta-pinene; limonene; or combinations thereof. The diene monomers can be present in the elastomers in an amount of about 0.5 wt % to about 10 wt% of the polymer, such as about 1 wt% to about 8 wt%, such as about 2 wt% to about 5 wt%.

[0040] In one or more embodiments, an elastomer includes at least one C₄ to C₁₄ isoolefin-derived monomer present at about 60 wt % to about 99 wt%, at least one non-halogenated alkylstyrene-derived monomer, and at least one halogenated alkylstyrene-derived monomer wherein the cumulative total of halogenated and non-halogenated alkylstyrene derived monomer comprises about 0.5 wt % to about 30 wt % of the elastomer. In at least one embodiment, the at least one halogenated alkylstyrene-derived monomer comprises about 0.1 mol % to about 7.5 mol % of the combined content of the cumulative total of alkylstyrene-derived monomers. In some embodiments, the at least one halogenated alkylstyrene-derived monomer can be present at about 0.5 wt % to about 10 wt %.

[0041] In one or more embodiments, an elastomer can have a (ML, 1+8 @ 100 °C) Mooney viscosity less than about 65, such as about 20 to about 60, such as about 25 to about 50, such as about 30 to about 45, such as about 32 to about 37.

[0042] In some embodiments, elastomers of the present disclosure can have a molecular weight distribution (MWD) of about 1 to about 5, such as about 1.5 to about 2.5.

[0043] In some embodiments, elastomers can be characterized by a weight average molecular weight of about 2,000 g/mol to about 2,000,000 g/mol, and a number average molecular weight of about 2,500 g/mol to about 750,000 g/mol as determined by gel permeation chromatography.

In some embodiments, it may be advantageous to utilize two or more elastomers each having a similar polymer backbone composition but different molecular weight profiles, for example, a low molecular weight elastomer having a weight average molecular weight less than about 150,000 g/mol being blended with a high molecular weight elastomer having a weight average molecular weight greater than about 250,000 g/mol.

Elastomeric and interpenetrating networks

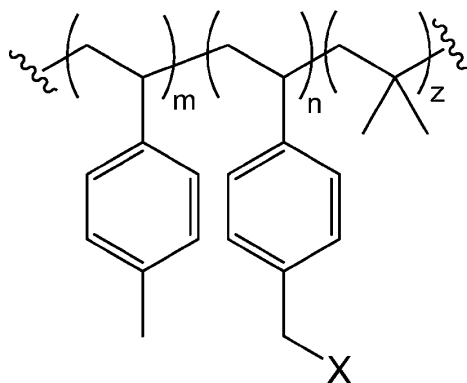
[0044] Elastomer compositions of the present disclosure can be composed of multiple elastomer components, as have been previously disclosed. Without being bound by theory, blending various elastomer materials into an elastomeric composition allow the operator to

5 tailor various physical and mechanical properties of the overall composition.

[0045] In some embodiments, one or more halogenated elastomers (denoted hereinafter as “component A”) are blended with one or more uncured secondary elastomers (denoted hereinafter as “component B”) to form a blend thereof, wherein the uncured secondary elastomer does not participate in ionomeric network formation. Furthermore, a nucleophilic

10 compound can be blended therewith to induce ionomeric network formation of the one or more halogenated elastomers, thereby forming an interpenetrating network composed of the one or more halogenated elastomers and the one or more uncured secondary elastomers.

[0046] In one or more embodiments, component A can be represented by



15 where X is a halogen and each of m, n, and z is independently a numerical value representing the number of respective repeat units along the polymer backbone. In at least one embodiment, each X is independently either bromine or chlorine. In some embodiments, the elastomeric polymer of component A has a number average molecular weight (M_n) of about 500,000 g/mol to about 5,000 g/mol, such as about 300,000 g/mol to about 6,000 g/mol, such as about 200,000

20 g/mol to about 7,000 g/mol, such as about 150,000 g/mol to about 10,000 g/mol, such as about 100,000 g/mol to about 15,000 g/mol, such as about 15,000 g/mol. In some embodiments, the ratio of m to n is about 1:0.7 to about 1:0.3, such as about 1:0.7 to about 1:0.5, such as about 1:0.5. In at least one alternative embodiment, the ratio of m to n is about 1:0.5 to about 1:0.3. In some embodiments, the ratio of m+n to z is about 40:60 to about 5:95, such as about 30:70 to

25 about 10:90, such as about 20:80. In at least one alternative embodiment the ratio of m+n to z is about 40:60 to about 30:70, alternatively about 30:70 to about 20:80, alternatively about

20:80 to about 10:90, alternatively about 10:90 to about 5:95. In at least one embodiment, the halogenated poly(isobutylene-co-p-methylstyrene) is any one or more commercially available halogenated poly(isobutylene-co-p-methylstyrene), such as Exxpro® 3035, Exxpro® 3433, Exxpro® 3745, and combinations thereof, available from Exxon Mobil Corporation.

5 [0047] In at least one embodiment, component A is halogenated butyl rubber or isomer thereof.

[0048] In at least one embodiment, component A is present in the elastomeric composition at about 100 phr. In one or more embodiments, component A is present in the composition at about 80 phr to about 30 phr, such as about 70 phr to about 30 phr, such as about 60 phr to
10 about 40 phr, such as about 55 phr to about 45 phr.

[0049] In one or more embodiments, component B is selected from natural rubber, polyisoprene rubber, poly(styrene-co-butadiene) rubber (SBR), polybutadiene rubber (BR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber, propylene oxide polymers,
15 halobutyl rubber, star-branched butyl rubber, halogenated star-branched butyl rubber, ionic butyl rubber, and combinations thereof. Many of these rubbers are described by Subramaniam in RUBBER TECHNOLOGY 179-208 (M. Morton, Chapman & Hall 1995), THE VANDERBILT RUBBER HANDBOOK 105-122 (R. F. Ohm ed., R.T. Vanderbilt Co., Inc. 1990), or E. Kresge and H. C. Wang in 8 KIRK-OTHMER ENCYCLOPEDIA
20 OF CHEMICAL TECHNOLOGY 934-955 (John Wiley & Sons, Inc. 4th ed. 1993).

[0050] Natural rubbers can include Malaysian rubber such as SMR CV, SMR 5, SMR 10, SMR 20, SMR 50, and combinations thereof, wherein the natural rubbers have a Mooney viscosity at 100 °C (ML 1+4) of about 30 to about 120, such as about 40 to about 65. The Mooney viscosity test referred to herein is in accordance with ASTM D1646-19.

25 [0051] Polybutadiene rubber (BR) can have a Mooney viscosity as measured at 100 °C (ML 1+4) of about 35 to about 70, such as about 40 to about 65, such as about 45 to about 60. A desirable rubber is high cis-polybutadiene (cis-BR). By “cis-polybutadiene” or “high cis-polybutadiene,” it is meant that 1,4-cis polybutadiene is used, where the amount of cis component is at least 95%. An example of a high cis-polybutadiene commercial product used
30 in the composition is BUDENE™ 1207 (available from Goodyear Chemical).

[0052] Secondary rubbers of ethylene and propylene derived units such as EPM and EPDM are also suitable as polymers in component B of the present disclosure. Examples of suitable comonomers in making EPDM are ethylidene norbornene, 1,4-hexadiene, dicyclopentadiene,

as well as others. A suitable ethylene-propylene rubber is commercially available as VISTALON™ (ExxonMobil Chemical Company).

[0053] In some embodiments, the elastomeric polymer of component B has a number average molecular weight (M_n) of about 300,000 g/mol to about 500 g/mol, such as about 200,000 g/mol to about 7,000 g/mol, such as about 150,000 g/mol to about 10,000 g/mol, such as about 100,000 g/mol to about 15,000 g/mol, such as about 15,000 g/mol.

[0054] In at least one embodiment, the elastomeric polymer of component B is treated with a peroxide to allow for vis-breaking of the polymer chain. Once vis-broken, the elastomeric polymer of component B has an M_n of about 150,000 g/mol to about 7000 g/mol, such as about 100,000 g/mol to about 10,000 g/mol, such as about 50,000 g/mol to about 15,000 g/mol.

[0055] In one or more embodiments, components B is present in the elastomeric composition at about 75 phr to about 30 phr, such as about 60 phr to about 40 phr, such as about 50 phr to about 40 phr.

[0056] In some embodiments, the elastomeric composition includes one or more additives such as fillers, dyes, pigments, antioxidants, heat and light stabilizers, plasticizers, oils, and/or other ingredients.

[0057] Examples of fillers include 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, such as N330 and N660), or combinations thereof. The fillers may be any suitable size, shape, and/or any aggregate size range thereof that is typical for use in the tire industry, such as about 1,000 nm to about 25 nm, such as about 700 nm to about 50 nm, such as about 500 nm to about 100 nm, such as about 300 nm to about 200 nm. In some embodiments, fillers can be present within the elastomeric composition at about 10 phr to about 100 phr, such as about 25 phr to about 80 phr, such as about 30 phr to about 70 phr. In at least one alternative embodiments, fillers can be present within the elastomeric composition about 10 phr to about 30 phr.

[0058] As used herein, silica refers to any type or particle size silica or another silicic acid derivative, or silicic acid, processed by solution, pyrogenic, or like methods, including untreated, precipitated silica, crystalline silica, colloidal silica, aluminum or calcium silicates, fumed silica, and the like. Precipitated silica can be conventional silica, semi-highly dispersible silica, or highly dispersible silica.

[0059] The compositions of the present disclosure may also include clay as a filler. The clay may be, for example, montmorillonite, nontronite, beidellite, vokoskoite, laponite, hectorite, saponite, sauconite, magadite, kenyaite, stevensite, vermiculite, halloysite, aluminate oxides,

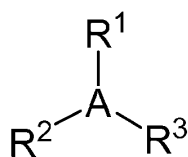
hydrotalcite, or mixtures thereof, optionally, treated with modifying agents. The clay may contain at least one silicate. Alternatively, the filler may be a layered clay, optionally, treated or pre-treated with a modifying agent such as organic molecules; the layered clay may comprise at least one silicate.

5 [0060] In some embodiments, components of the present disclosure include an extender oil. The extender oil can be any suitable extender oil that is capable of extending or plasticizing elastomers. In some embodiments, the extender oil is chosen from the group consisting of polyolefin oils, paraffinic oils, naphthelnic oils, aromatic oils, mineral oils, and combinations thereof. In some embodiments, extender oil is present within the elastomeric composition at
10 about 100 phr to about 1 phr, such as about 75 phr to about 5 phr, such as about 50 phr to about 10 phr, such as about 30 phr to about 20 phr. In at least one embodiment, the extender oil is a polybutene oil having an M_n of about 100,000 g/mol to about 1,000 g/mol, such as about 75,000 g/mol to about 5,000 g/mol, such as about 50,000 g/mol to about 10,000 g/mol, such as about 30,000 g/mol to about 20,000 g/mol.

15 [0061] In some embodiments, it is desirable to incorporate crosslinks into the elastomer composition. In such instances, a curing system comprising a nucleophilic compound can be introduced to an elastomeric composition consisting of a halogen functionalized monomer, such as a halogenated alkylstyrene or a halobutyl rubber, to cause ionic interactions thereby forming an ionomeric network. Without being bound by theory, the resulting elastomeric network is
20 the result of ion-pair aggregation.

[0062] When forming the interpenetrating network, a curing system comprising a nucleophilic species is introduced to the elastomeric composition to induce ionomeric network formation with component A. In some embodiments, it is important that components A and B be adequately blended such that upon the introduction of the nucleophilic species to the
25 elastomeric composition, the newly formed ion pairs and ion-pair aggregates form substantially throughout the elastomeric composition. Further, since component B is incapable of interacting with the nucleophilic species, component B remains dispersed within the ionomeric network formed by component A.

[0063] In at least one embodiment, a nucleophilic compound introduced to an elastomeric
30 composition to form an elastomeric network is one or more of a nitrogen or phosphorus nucleophile. In one or more embodiments, the nucleophilic compound can be represented by



wherein:

A is a nitrogen or phosphorus; and

R¹, R², and R³ are independently selected from the group consisting of an alkyl substituent, an aryl substituent, a heteroatom, and combinations thereof, wherein:

the alkyl substituent is any one or more linear or branched C₁-C₁₈ alkyl substituents,

the aryl substituent is monocyclic or composed of fused C₄-C₈ rings, and

the heteroatom is selected from B, N, O, Si, P, and S.

[0064] In general and without being bound by theory, the appropriate nucleophile will contain at least one neutral nitrogen or phosphorus center, both possessing a lone pair of electrons that are electronically and sterically accessible for participation in nucleophilic substitution reactions. Suitable nucleophiles include trimethylamine, triethylamine, triisopropylamine, tri-n-butylamine, trimethylphosphine, triethylphosphine, triisopropylphosphine, tri-n-butylphosphine, triphenylphosphine, and combinations thereof. In at least one embodiment, the nucleophilic compound is triphenyl phosphine.

[0065] Other suitable nucleophiles include substituted azoles as disclosed in US 2012/0157579, such as N-butyl imidazole, N-(trimethylsilyl)imidazole, N-decyl-2-methylimidazole, N-hydroxyethylimidazole, N-(3-trimethoxysilylpropyl)imidazole, N-vinylimidazole, 2-(imidazol-1-yl)ethyl 2-methyl-2-propenoate, 1-butylbenzimidazole, and combinations thereof.

[0066] The amount of nucleophile added to the elastomeric composition is determined based upon the molar equivalence ratio relative to the halide content therein. In one or more embodiments, the nucleophile is added to the elastomeric composition in an molar equivalent ratio of about 2:1 to about 0.1:1, such as about 1.1:1 to about 0.2:1, such as about 0.8:1 to about 0.5:1. In at least one alternative embodiment the nucleophile is added to the elastomeric composition in a molar equivalent ratio of about 2:1 to about 1.1:1, alternatively about 1.1:1 to about 0.8:1, alternatively about 0.8:1 to about 0.5:1, alternatively about 0.5:1 to about 0.2:1, alternatively about 0.2:1 to about 0.1:1. Alternatively, the nucleophilic composition is added to the elastomeric composition in an amount of about 2-7 phr to about 1-4 0.5 phr, such as about 5 phr to about 1 phr, such as about 3 phr to about 1.5 phr, such as about 2.1 phr.

[0067] Blending of component A, component B, fillers, additives, and curing system components may be carried out by combining the desired components and the elastomers of the present disclosure in any suitable mixing device such as a BANBURY™ mixer, BRABENDER™ mixer or an extruder and performed at temperatures of about 70 °C to 120 °C under conditions of shear sufficient to allow the components to become uniformly dispersed within the elastomer to form the elastomeric compositions thereof described herein.

[0068] In another embodiment, mixing of the components may be carried out by combining the elastomers, filler and clay in any suitable mixing device such as a two-roll open mill, BRABENDER™ internal mixer, BANBURY™ internal mixer with tangential rotors, Krupp internal mixer with intermeshing rotors, or a mixer/extruder. Mixing may be performed at temperatures up to the melting point of the elastomer(s) used in the composition in one embodiment, or 40 °C to 250 °C, or 100 °C to 200 °C. Mixing should generally be conducted under conditions of shear sufficient to allow any clay to exfoliate and become uniformly dispersed within the elastomer(s).

[0069] Typically, from 70% to 100% of the elastomer or elastomers is 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 mixing continues 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.

[0070] The compositions of the present disclosure may be compounded blended by any conventional means known to those skilled in the art. The mixing may occur in a single stage or in multiple stages. For example, the components are typically mixed in at least two stages, namely at least one non-productive stage followed by a productive mixing stage. The curatives are typically mixed in the final stage, which is conventionally called the “productive” mix stage. In the productive mix stage, the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) of the preceding non-productive mix stage(s). The elastomers, secondary rubbers, polymer additives, silica and silica coupler, and carbon black, if used, are generally mixed in one or more non-productive mix stages. The terms “non-productive” and “productive” mix stages are well known to those having skill in the rubber mixing art.

[0071] Without being bound by theory, the resulting elastomeric composition forms a self-healing network via the breaking and reformation of the ion-pairs. The resulting elastomeric network possesses dynamic mechanical properties that are comparable to thermoset vulcanizates. Additionally, both components of the interpenetrating elastomeric network can serve distinct purposes in the instance of the material being punctured or otherwise damaged. Without being bound by theory, the ionomeric network formed from the reaction between component A and the nucleophilic species provides the elastomeric composition a degree of structural integrity through the network structure thereof and gas impermeability, whilst also providing self-healing properties through the breaking and reformation of the ion-pairs. Furthermore, component B provides the elastomeric composition with a degree of viscoelasticity, such that the elastomeric composition is able to form a gas impermeable barrier upon receiving damage and undergoing subsequent self-healing. Without being bound by theory, these and other physical, mechanical, rheological, and chemical properties are able to be provided through careful selection of each component and/or additive input into the composition. As such, the overall composition of the elastomeric network is able to be tuned so as to provide the final material having physical and mechanical properties, and retention thereof upon receiving damage, as a result of the self-healing and self-sealing abilities provided by the composition. The virgin and retained material properties, as a result of self-healing and self-sealing, provide such elastomeric materials viability for implementation into any one or more intended commercial applications. Such commercial applications can include implementation into tire and tire tread compositions, such as a tire innerliner, a tire sidewall, and the like.

Elastomeric compositions with two or more curable components

[0072] In one or more embodiments, component B of the elastomeric composition comprises a partially crosslinked elastomer. Without being bound by theory, implementing a partially crosslinked elastomer as component B provides additional strength to the ionomeric network without significantly affecting the resealing characteristics and properties of the overall elastomeric composition.

[0073] In some embodiments, component B is partially crosslinked using any one or more conventional curing agents including sulfur and compounds comprising sulfur, metals, metal oxides such as zinc oxide, peroxides, organometallic compounds, radical initiators, fatty acids, accelerators, any other suitable curing agent and combinations thereof. As used herein, the term "curing system" refers to the combination of any one or more curative agents.

[0074] In at least one embodiment, the curing agent of component B is a bithiosulfate compound. A bithiosulfate compound can be represented by the formula $Z^1-R^1-Z^2$, where R^1 is substituted or unsubstituted C_1 to C_{15} alkyl, substituted or unsubstituted C_2 to C_{15} alkenyl, or substituted or unsubstituted C_6 to C_{12} cyclic aromatic moiety; and Z^1 and Z^2 are independently a thiosulfate group. In some embodiments, R^1 is selected from methylene, dimethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, and nonamethylene. Thiosulfate groups can include any suitable counteranion, such as an alkali metal counteranion, such as sodium or potassium. So-called bithiosulfate compounds are an example of a class of polyfunctional compounds included in the above formula. A non-limiting example of such polyfunctional curatives is hexamethylene bis(sodium thiosulfate).

[0075] Curing systems for composition B can include one or more additional accelerators. Additional accelerators may include mercaptobenzothiazole disulfide (MBTS), stearic acid, diphenyl guanidine (DPG), tetramethylthiuram disulfide (TMTD), N-t-butyl-2-benzothiazole sulfenamide (TBBS), N-cyclohexyl-2-benzothiazole-sulfenamide (CBS), thioureas, and combinations thereof.

[0076] Metal oxides can act as curing agents for composition B. Examples of metal oxides include zinc oxide, calcium oxide, lead oxide, magnesium oxide, and combinations thereof.

[0077] In one or more embodiments, metal oxide can be used alone or in conjunction with its corresponding metal fatty acid complex (e.g., zinc stearate, calcium stearate, etc.). In some embodiments, the organic and fatty acids, such as stearic acid, may be used alone or optionally with other curatives such as sulfur or a sulfur compound, an alkylperoxide compound, diamines, derivatives thereof, and combinations thereof.

[0078] In some embodiments, the curing system for component B is present in the elastomeric composition in an amount of about 0.1 phr to about 8 phr, such as about 0.5 phr to about 7.5 phr, such as about 1 phr to about 7 phr, such as about 2 phr to about 5.5 phr.

In-situ formation of low molecular weight resealing components

[0079] In some embodiments, it may be desired that the elastomeric composition possess a degree of flowability, such that the elastomeric composition exhibits improved self-sealing properties. For instance, when the elastomeric composition is punctured or damaged, the material would have the ability easily flow over the damaged area to thereby provide a sealant layer thereto. In the context of the present disclosure, this can be accomplished through the chain scission of one or more components of the interpenetrating network via the introduction of one or more peroxide catalysts.

[0080] Chain scission can occur in ionic butyl rubber, thereby producing low molecular weight ionomers. Such low molecular weight ionomers can also be called ionomeric oligomer. As used herein, "oligomer" refers to a material having molecular weight significantly lower than the original polymer/rubber. Oligomers are tacky to touch and often are viscous liquids
5 capable of flow. In some embodiments, the oligomeric ionomers have attached functional moieties, which can participate and/or facilitate ionic sealing. In some embodiments, the functional moiety is one or more of a bromine and chlorine.

[0081] Most rubbers, like natural rubber (NR), nitrile rubber (NBR), styrene-butadiene rubber (SBR), bromobutyl rubber (BIIR), chlorobutyl rubber (CDR), butadiene rubber (BR),
10 etc., crosslink when heated with suitable peroxide and storage modulus (G') increases after cure. In contrast, halobutyl rubber undergoes chain scission, resulting in decreased viscosity or G' after heating to a cure temperature.

[0082] In some embodiments, the elastomeric composition further comprises about 40 phr to about 10 phr of ionic butyl rubber, and about 3 phr to about 1 phr of peroxide catalyst, which
15 may be incorporated within the composition via either component A or component B. Without being bound by theory, incorporating ionic butyl rubber within the elastomeric composition provides self-sealing and gas impermeable properties.

[0083] In some embodiments, the elastomeric composition comprises at least one compound having at least one peroxide moieties. In one or more embodiments, the peroxide compound
20 can be any one or more of an aliphatic compound, a cycloaliphatic compound, or an aromatic compound. In at least one embodiment, the peroxide compound is any one or more of 2,5-bis(t-butyl peroxy)-2,5-dimethyl hexane, 1,1-di-t-butyl peroxy-3,3,5-trimethyl cyclohexane, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexyne-3, p-chlorobenzyl peroxide, 2,4-dichlorobenzyl peroxide; 2,2-bis-(t-butyl peroxy)-butane, di-t-butyl peroxide; benzyl peroxide, 2,5-bis(t-butyl
25 peroxy)-2,5-dimethyl hexane, dicumyl peroxide, and 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane. In one or more embodiments, the peroxide compound may be any appropriate commercially available peroxide compound, such as DI-CUP[®] Dicumyl Peroxide and/or Luperox[®] 101.

[0084] In some embodiments, the elastomeric composition comprises an activating agent,
30 such as 2,2,6,6-tetra alkyl piperidine based hindered amine, which will activate the organoperoxide, and in a sense, enable a reduction in the amount of the organoperoxide to more efficiently degrade the ionomeric network during the formation of the sealant layer. Such activating agents are described in U.S. Pat. No. 7,674,344 to D'Sidocky et al., the disclosure of which is incorporated by reference for that purpose.

[0085] In one or more embodiments, the 2,2,6,6-tetra alkyl piperidine based hindered amine is, for example, a 50/50 mixture of poly[[6-[1,1,3,3,-tetramethylbutyl)amino]-s-triazine-2,4-diyl][2,2,6,6,-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]] compound (referred to herein as "PTP") and bis(hydrogenated tallow alkyl),
5 amines oxidized and sold as Irgastab® FS410 FF from BASF.

[0086] In at least one embodiment, peroxide activating agent is a mixture of PTP, bis(hydrogenated tallow alkyl) amines oxidized, and bis(2,2,6,6-tetramethyl-4-piperidiny)l sebacate sold as Irgastab® FS811 from BASF.

[0087] In at least one embodiment, the peroxide activating agent is poly[[6-[1,1,3,3,-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][2,2,6,6,-tetramethyl-4-piperidyl)imino]-1,6-hexanedyl[(2,2,6,6-tetramethyl-4-piperidiny)l)imino]] available as Chimassorb® 944 FDL from BASF.

Physical properties

[0088] In some embodiments, the elastomeric compositions of the present disclosure
15 comprise a Shore A Hardness of about 5 to about 50, such as about 20 to about 38 such as about 27.5 to about 33.5. In one or more alternative embodiments, the elastomeric compositions of the present disclosure comprise a Shore A Hardness of about 5 to about 35, alternatively about 20.9 to about 43.3, alternatively about 22.2 to about 46, alternatively about 10.38 to about 41.1, alternatively about 12.2 to about 47.7.

[0089] In some embodiments, the elastomeric compositions of the present disclosure
20 comprise a M100 value of about 0.1 MPa to about 3.6 MPa, such as about 0.3 MPa to about 2.2 MPa, such as about 0.5 MPa to about 1.6 MPa, such as about 0.8 MPa to about 1.3 MPa. In one or more alternative embodiments, the elastomeric compositions of the present disclosure
25 comprise a M100 value of about 0.5 MPa to about 0.9 MPa, alternatively about 0.6 MPa to about 3.5 MPa, alternatively about 0.2 MPa to about 3.6 MPa, alternatively about 0.5 MPa to about 2.5 MPa, alternatively about 0.2 MPa to about 1.8 MPa, alternatively about 0.1 MPa to about 2.7 MPa.

[0090] In some embodiments, the elastomeric compositions of the present disclosure
30 comprise a tensile strength at break of about 0.03 MPa to about 15.1 MPa, such as about 1.1 MPa to about 8.3 MPa, such as about 3.0 MPa to about 7.0 MPa, such as about 4.3 MPa to about 6.3 MPa. In one or more alternative embodiments, the elastomeric compositions of the present disclosure comprise a tensile strength at break of about 2.7 MPa to about 12 MPa, alternatively about 1.5 MPa to about 15.1 MPa, alternatively about 0.9 MPa to about 8.3 MPa,

alternatively about 1.9 MPa to about 10.2 MPa, alternatively about 0.3 MPa to about 6.3 MPa, alternatively about 0.02 MPa to about 5.7 MPa.

[0091] In some embodiments, the elastomeric compositions of the present disclosure comprise an elongation at break of about 130 % to about 1380 %, such as about 350 % to about 1250 %, such as about 625 % to about 1150 %, such as about 800 % to about 1000 %. In one or more alternative embodiments, the elastomeric compositions of the present disclosure comprise an elongation at break of about 930 % to about 1300 %, alternatively about 315 % to about 1300 %, alternatively about 130 % to about 1280 %, alternatively about 240 % to about 1180 %, alternatively about 255 % to about 1380 %, alternatively about 235 % to about 1290 %.

[0092] In some embodiments, the elastomeric compositions of the present disclosure comprise an O₂ permeability coefficient of about 0.1 (mm)•(cc)/ m²•day•mmHg to about 1.4 (mm)•(cc)/ m²•day•mmHg, such as about 0.2 (mm)•(cc)/ m²•day•mmHg to about 0.4 (mm)•(cc)/ m²•day•mmHg, such as about 0.2 (mm)•(cc)/ m²•day•mmHg to about 0.3 (mm)•(cc)/ m²•day•mmHg. In one or more alternative embodiments, the elastomeric compositions of the present disclosure comprise an O₂ permeability coefficient of about 0.1 (mm)•(cc)/ m²•day•mmHg to about 1.3 (mm)•(cc)/ m²•day•mmHg, alternatively about 0.1 (mm)•(cc)/ m²•day•mmHg to about 1 (mm)•(cc)/ m²•day•mmHg, alternatively about 0.1 (mm)•(cc)/ m²•day•mmHg to about 0.3 (mm)•(cc)/ m²•day•mmHg, alternatively about 0.2 (mm)•(cc)/ m²•day•mmHg to about 0.3 (mm)•(cc)/ m²•day•mmHg, alternatively about 0.2 (mm)•(cc)/ m²•day•mmHg to about 0.4 (mm)•(cc)/ m²•day•mmHg.

[0093] In some embodiments, the elastomeric compositions of the present disclosure may be damaged as a result of commercial use. The elastomeric composition is capable of undergoing the self-healing and self-sealing behavior to produce a healed elastomeric composition.

[0094] In some embodiments, the healed elastomeric compositions of the present disclosure comprise a M100 value of about 0.02 MPa to about 1.4 MPa, such as about 0.4 MPa to about 0.9 MPa, such as about 0.5 MPa to about 0.7 MPa. In one or more alternative embodiments, the healed elastomeric compositions of the present disclosure comprise a M100 value of about 0.4 MPa to about 0.9 MPa, alternatively about 0.3 MPa to about 1.2 MPa, alternatively about 0.02 MPa to about 0.8 MPa, alternatively about 0.4 MPa to about 1.4 MPa, alternatively about 0.1 MPa to about 1 MPa, alternatively about 0.05 MPa to about 0.9 MPa.

[0095] In some embodiments, the healed elastomeric compositions of the present disclosure comprise a tensile strength at break of about 0.2 MPa to about 1.8 MPa, such as about 0.4 MPa to about 1.3 MPa, such as about 0.5 MPa to about 1 MPa, such as about 0.6 MPa to about 0.9

MPa. In one or more alternative embodiments, the healed elastomeric compositions of the present disclosure comprise a tensile strength at break of about 0.4 MPa to about 1.7 MPa, alternatively about 0.2 MPa to about 0.9 MPa, alternatively about 0.2 MPa to about 1.2 MPa, alternatively about 1 MPa to about 1.8 MPa, alternatively about 0.3 MPa to about 1.2 MPa, alternatively about 0.2 MPa to about 1.3 MPa.

[0096] In some embodiments, the healed elastomeric compositions of the present disclosure comprise a elongation at break of about 35 % to about 1165 %, such as about 55 % to about 520 %, such as about 85 % to about 265 %, such as about 110 % to about 180 %. In one or more alternative embodiments, the healed elastomeric compositions of the present disclosure comprise a elongation at break of about 120 % to about 1165 %, alternatively about 75 % to about 350 %, alternatively about 45 % to about 900 %, alternatively about 65 % to about 530 %, alternatively about 46 % to about 381 %, alternatively about 37 % to about 629 %.

[0097] In some embodiments, the healed elastomeric compositions of the present disclosure comprise an O₂ permeability coefficient of about 0.2 (mm)•(cc)/ m²•day•mmHg to about 0.4 (mm)•(cc)/ m²•day•mmHg, such as about 0.2 (mm)•(cc)/ m²•day•mmHg to about 0.3 (mm)•(cc)/ m²•day•mmHg, such as about 0.25 (mm)•(cc)/ m²•day•mmHg to about 0.26 (mm)•(cc)/ m²•day•mmHg.

Tires

[0098] In some embodiments, elastomeric compositions of the present disclosure can be used as a component of a tire. A tire (also referred to as a “tire product” herein) can be any suitable tire, such as a rubber tire having an outer (visible) rubber sidewall layer where the outer sidewall layer includes a composition of the present disclosure. The tire can be built, shaped, molded to include the outer sidewall (rubber sidewall layer) and cured by various methods which will be readily apparent to those having skill in such art.

[0099] Blends of highly saturated specialty elastomers blended with highly unsaturated polymers can be desired to improve the performance window of the blend (*e.g.*, oxygen & ozone resistance, thermal stability, tack, etc). For tire tread in particular, tire tread compounds in a tire dictate properties of the tire, such as wear, traction, and rolling resistance. It is a technical challenge to deliver excellent traction, low rolling resistance while providing good tread wear. The challenge lies in the trade-off between wet traction and rolling resistance/tread wear.

[0100] Generally, a tire comprises a supporting tire carcass comprised of one or more layers of ply, an outer circumferential tread, and a radially innermost innerliner layer, a pair of beads, sidewalls extending radially inward from the axial outer edges of the tread portion to join the

respective beads, a sealant layer, and a cover layer, disposed on said tire carcass innermost layer. The components of the interpenetrating networks described herein, may be tuned and modified to provide high mechanical and physical properties desirable suitable for application within a tire composition, such as the liner layer, while also maintaining the viscoelastic properties necessary for the material to retain the desired self-healing and self-sealing capabilities. As such, an appropriate balance of the parameters set forth for the elastomeric composition described herein, and implemented within a tire composition, reduces the downtime and cost commonly associated with tire maintenance and replacement.

Examples

10 *Formation of elastomeric interpenetrating networks:*

[0101] Elastomeric interpenetrating networks were formed by blending (one-step mixing) brominated poly(isobutylene-co-paramethylstyrene) and/or brominated poly(isobutylene-co-isoprene) with one or more of non-halogenated poly(isobutylene), butyl rubber, and/or poly(styrene-co-polyisobutylene), using a mixing bowl mixer at about 90 °C to 150 °C and mixed for approximately 2 minutes at about 40 rpm. The triphenyl phosphine, ZnO, salt mix, and/or any other additive was then added to the blend and allowed to mix for 5 minutes. Optionally, stearic acid was then added to the mixture, and the mixture was continuously blended for about 3 minutes to about 6 minutes. The resulting samples were then recovered for testing. Contents and amounts of the resulting elastomeric compositions are summarized in Tables 1A and 2A.

Table 1A:

	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C
Example	1	2	3	4	5	6	7	8	9	10	11	12
Material Name	Exxpro 3035 1:1 Meq TPP	Exxpro 3035 1:1 Meq TPP; 30 XP 50	Exxpro 3035 1:0.7 Meq TPP; 30 XP 50	Exxpro 3035 1:1 Meq TPP; 50 XP 50	Exxpro 3035 1:1 Meq TPP; 30 PIB	Exxpro 3035 1:1 Meq TPP; 50 365	Exxpro 3035 1:1 Meq TPP; 30 365	Exxpro 3035 1:1 Meq TPP; 30 068	Exxpro 3035 1:1 Meq TPP; 30 SIBSTAR	Exxpro 3035 1:1 Meq TPP; 30 XP 50 and more, BaO	Exxpro 3035 1:1 Meq TPP; 30 XP 50 and more, BaO	Exxpro 3035 1:1 Meq TPP; 30 068 and more, BaO
	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
	Expro 3035 Triphenyl phosphine	100.0	70.0	70.0	50.0	50.0	70.0	70.0	70.0	70.0	54.0	54.0
	XP 50	2.1	2.1	1.4	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Vistanexx 120ML		30.0	30.0	50.0	30.0					30.0	30.0	30.0
RB 365						50.0	30.0					
RB 068								30.0				
SIBSTAR (102TUCK282)									30.0			
Stearic acid										1.0	1.0	1.0
Barium Oxide										5.0	5.0	5.0
N660 (GPF)- Carbon Black												
ESCOREZ 1102												10.0
Indopol											20.0	20.0
Exxpro 3035/N660- 60phr MB												26.0
Total phr	102.1	102.1	101.4	102.1	102.1	102.1	102.1	102.1	102.1	108.1	138.1	148.1

Table 1A Contd.:

	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C
Example	13	14	15	16	17	18	19	20	21
Material Name	Exxpro 3745 1:1 Meq TPP	Exxpro 3745 1:1 Meq TPP; XP	Exxpro 3745 1:0.7 Meq TPP; XP	Exxpro 3745 1:1 Meq TPP; XP	Exxpro 3745 1:1 Meq TPP; 30 PIB	Exxpro 3745 1:1 Meq TPP; 50 365	Exxpro 3745 1:1 Meq TPP; 30 365	Exxpro 3745 1:1 Meq TPP; 30 068	Exxpro 3745 1:1 Meq TPP; 30 SIBS TAR
	phr	phr	phr	phr	phr	phr	phr	phr	phr
	100.0	70.0	70.0	50.0	70.0	50.0	70.0	70.0	70.0
	2.1	2.1	1.4	2.1	2.1	2.1	2.1	2.1	2.1
	XP 50	30.0	30.0	50.0					
Exxpro 3745					30.0	50.0	30.0		
Triphenyl phosphine									
RB 365									
RB 068								30.0	
SIBSTAR (102TUCK282)									30.0
Stearic acid									
Total phr	102.1	102.1	101.4	102.1	102.1	102.1	102.1	102.1	102.1

Table 2A:

	Mix at 150 C	22	Mix at 150 C	23	Mix at 150 C	24	Mix at 150 C	25	Mix at 150 C	26	Mix at 150 C	27	Mix at 150 C	28	Mix at 150 C	29	Mix at 150 C	30	Mix at 150 C	31	Mix at 150 C	32	Mix at 150 C	33	Mix at 150 C	34
Example																										
Material Name	Exxpro 3035 1:1 Meq TPP; 30 365	Exxpro 3035 1:1.3 Meq TPP; 30 365	Exxpro 3035 1:1 Meq TPP; 30 NR	Exxpro 3035 1:1 Meq TPP; 30 SBR	Exxpro 3035 1:1 Meq TPP; 15 NR, 15 SBR	Exxpro 3035 1:1.3 Meq TPP; 15 NR, 15 SBR	Exxpro 3035 1:1 Meq TPP; 30	Exxpro 3035 1:1 Meq TPP; SIBST AR 062	Exxpro 3035 1:1 Meq TPP; 30	Exxpro 3035 1:1 Meq TPP; SIBST AR 072	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1.3 Meq TPP; 15 NR, 30 365; 20 CB 660	Exxpro 3035 1:1.3 Meq TPP; 30 365; 20 CB 660	Exxpro 3035; 3035; NR, SBR, ZnO	
	Exxpro 3035	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 70.0	phr 30.0
Exxpro 3745																										
Butylimidazole																										
Armeen (Dialkyl Amine)																										
Triphenyl phosphine	2.1	2.7	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.7	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.7		
1-benzylimidazole																										
SMR 20			30.0		15.0	15.0						15.0														
SBR 1014				30.0	15.0	15.0						15.0														
RB 365	30.0	30.0																30.0		30.0						
Sibstar Kaneka (062TUP036)-Low Mw														30.0												
Sibstar Kaneka (072TUCPI30)-med Mw																										

[illegible]

Table 2A Contd.:

	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C
Example	35	36	37	38	39	40	41	42	43	44	45	46	47
Material Name	Exxpro 3745 1:1 Meq TPP; 30 365	Exxpro 3745 1:1.3 Meq TPP; 30 365	Exxpro 3745 1:1 Meq TPP; 30 NR	Exxpro 3745 1:1 Meq TPP; 30 SBR	Exxpro 3745 1:1 Meq TPP; 15 NR, 15 SBR	Exxpro 3745 1:1.3 Meq TPP; 15 NR, 15 SBR	Exxpro 3745 1:1 Meq TPP; 30 SIBST A 062	Exxpro 3745 1:1 Meq TPP; 30 SIBST A 072	Exxpro 3745 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3745 1:1 Meq TPP; 30 365; 20 CB 660; 1102 & Indopol 660	Exxpro 3745 1:1 Meq TPP; 15 NR, 15 SBR; 20 CB 660	Exxpro 3745 1:1.3 Meq TPP; 15 NR, 15 SBR; 20 CB 660	Exxpro 3745; NR, SBR, ZnO
	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
Exxpro 3745	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0	30.0
Triphenyl phosphine	2.1	2.7	2.1	2.1	2.1	2.7	2.1	2.1	2.1	2.1	2.1	2.7	
1- benzylimidazole													
SMR 20			30.0		15.0	15.0					15.0	15.0	30.0
SBR 1014				30.0	15.0	15.0					15.0	15.0	40.0
RB 365	30.0	30.0							30.0	30.0			
Sibstar Kaneka (062TUP036)- Low Mw							30.0						
Sibstar Kaneka (072TUCP130)- med Mw													
Stearic acid								30.0					
N660 (GPF)- Carbon Black									20.0	20.0	20.0	20.0	20.0

Formation of elastomeric components having two of more curable components:

- [0102] Elastomeric networks wherein both components A and B are, and/or could be, crosslinked, were formed by blending (one-step mixing) brominated poly(isobutylene-co-paramethylstyrene) and/or poly(isobutylene-co-isoprene) with a second elastomer that is
- 5 curable via any introducing any one or more conventional cure agents, using a mixing bowl at about 90 °C to 150 °C and mixed for approximately 2 minutes at about 40 rpm. The triphenyl phosphine is then added and allowed to blend for approximately 4 minutes. Subsequent the addition of the triphenyl phosphine, stearic acid, ZnO, and other additives are added and allowed to blend for approximately 2 minutes. The resulting samples were then recovered for testing.
- 10 Contents and amounts of the resulting elastomeric compositions are summarized in Table 3.

Table 3A:

	Mix at 150 C 48	Mix at 150 C 49	Mix at 150 C 50	Mix at 150 C 51	Mix at 150 C 52	Mix at 150 C 53	Mix at 150 C 54	Mix at 150 C 55	Mix at 150 C 56	Mix at 150 C 57	Mix at 150 C 58	Mix at 150 C 59	Mix at 160 C 60
Example													
Material Name	Exxpro 3035 1:1.3 Meq TPP; 50 365	Exxpro 3035 1:1.3 Meq TPP; 50 365; HSt; ZnO; 101	Exxpro 3035 1:1.3 Meq TPP; 50 365; HSt; ZnO	Exxpro 3035 1:1.3 Meq TPP; 50 365; S cure	Exxpro 3035 1:1.3 Meq TPP; 50 365; 1045 cure	Exxpro 3035 1:1.3 Meq TPP; 50 365; S cure 1102	Exxpro 3035 1:1.3 Meq TPP; 50 365; S cure CB, H100	Exxpro 3035 1:1.3 Meq TPP; 50 365; S cure CB, H100	Exxpro 3035 1:1.3 Meq TPP; 50 365; SBR; HSt; ZnO	Exxpro 3035 1:1.3 Meq TPP; 50 365; SBR; S MBTS	Exxpro 3035 1:1.3 Meq TPP; 30 365; 20 CB 660; 1102 & Indopol	Exxpro 3035 1:1.3 Meq TPP; 25 NR, S MBTS	Exxpro 3035 1:1.3 Meq TPP; 50 2502, HSt, ZnO
Exxpro 3035	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 70.0	phr 50.0	phr 50.0
Exxpro 3745													
Triphenyl phosphine	2.7	2.7	2.7		2.7	2.7	2.7	2.7	2.7	2.7	2.1	2.7	2.7
SMR 20												25.0	
SBR 1014								50.0	50.0	50.0		25.0	
RB 365	50.0	50.0	50.0	50.0	50.0	50.0	50.0				30.0		
RB 068													
Kraton G1652													
V 2502													50.0
PEDM, BCT#273667; M487C 12/18/18 2300 P-1													
Stearic acid		2.0	2.0		2.0	2.0	2.0	2.0	2.0	2.0		2.0	2.0
N660 (GPF)- Carbon Black						10.0	10.0			10.0	20.0		
ESCOREZ 1102						10.0					10.0		
Indopol H100							20.0				10.0		
ZnO			3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0		3.0	3.0

[illegible]

Table 3A Contd.:

Example	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C	Mix at 150 C
	61	62	63	64	65	66	67	68	69	70	
Material Name	Exxpro 3035 1:1.3 Meq TPP; 50 Kraton 1652	Exxpro 3035 1:1.3 Meq TPP; 50 Kraton, H100	Exxpro 3035 1:1.3 Meq TPP; 50 PEDM	Exxpro 3035 1:1.3 Meq TPP; 50 068	Exxpro 3035 1:1.3 Meq TPP; 50 068; HSt, ZnO; 101	Exxpro 3035 1:1.3 Meq TPP; 50 068; HSt, ZnO	Exxpro 3035 1:1.3 Meq TPP; 50 068; S cure	Exxpro 3745 1:1.3 Meq TPP; 50 068; HSt, ZnO; 101	Exxpro 3745 1:1.3 Meq TPP; 50 068; HSt, ZnO	Exxpro 3745 1:1.3 Meq TPP; 50 068; S cure	
Exxpro 3035	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	phr 50.0	
Exxpro 3745											
Triphenyl phosphine	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	
SMR 20											
SBR 1014											
RB 365											
RB 068				50.0	50.0	50.0	50.0	50.0	50.0	50.0	
Kraton G1652	50.0	50.0									
V 2502											
PEDM, BCT#273667; M487C 12/18/18 2300											
P-1			50.0								
Stearic acid	2.0	2.0	2.0		2.0	2.0	2.0	2.0	2.0	2.0	
N660 (GPF)- Carbon Black											
ESCOREZ 1102											
Indopol H100		20.0									
ZnO	3.0	3.0	3.0			3.0	3.0		3.0	3.0	
Sulfur		1.0	1.0				1.0			1.0	
TMTD		1.0	1.0				1.0			1.0	
MBTS		0.5	0.5				0.5			0.5	
SP1045											
Luperox 101	2	2	2		1.0			1.0			
Total phr	109.7	132.2	112.2	102.7	105.7	107.7	110.2	105.7	107.7	110.2	

Formation of elastomeric networks comprising peroxides:

[0103] Elastomeric interpenetrating networks were formed by blending (one-step mixing) brominated poly(isobutylene-co-paramethylstyrene) and/or poly(isobutylene-co-isoprene) with DICUP[®], and optionally a halogenated and/or non-halogenated butyl rubber, using a mixing bowl at about 100 °C and mixed for approximately 5 minutes at about 40 rpm. The temperature was then increased to a range of about 170 °C to about 190 °C, and allowed to mix for an additional 5 minutes. Optionally, samples may be produced in excess to be blended with other compositions at about 150 °C to form a mixture of blends. The triphenyl phosphine was then added to the blend, and/or mixture of blends, and allowed to mix for 5 minutes. The resulting samples were then recovered for testing. Contents and amounts of the resulting elastomeric compositions are summarized in Table 4.

Table 4A:

Example	Material Name	71	72	73	74	75	76	77	78	79	80	81
		Exxpro 3745 1:1 Meq TPP;	Exxpro 3745 1:1 Meq TPP; + Dicup 2	Exxpro 3745 1:1 Meq TPP; + Dicup 3	Exxpro 3745 1:1 Meq TPP; + Dicup 4	BB 2222 1:1 Meq TPP;	BB 2222 1:1 Meq TPP; + Dicup 2	BB 2222 1:1 Meq TPP; + Dicup 3	BB 2222 1:1 Meq TPP; + Dicup 4	BB 2255 1:1 Meq TPP;	BB 2255 1:1 Meq TPP; + Dicup 2	BB 2255 1:1 Meq TPP; + Dicup 3
	BB 2222	plhr	plhr	plhr	plhr	plhr	plhr	plhr	plhr	plhr	plhr	plhr
	Exxpro 3745	100.0	100.0	100.0	100.0		100.0	100.0	100.0			
	Butylimidazole											
	Armeen (Dialkyl Amine)											
	Triphenyl phosphine	5.0	5.0	5.0	5.0	4.2	4.2	4.2	4.2	4.2	4.2	4.2
	1- benzylimidazole											
	042-2021-09-02 (Exxpro 3745 + Dicup 2)											
	042-2021-09-03 (Exxpro 3745 + Dicup 3)											
	042-2021-09-06 (BB 2222 + Dicup 2)											
	042-2021-09-07 (BB 2222 + Dicup 3)											

Table 4A Contd.:

Example	82	83	84	85	86	87	88	89	90	91	92
Material Name	BB 2255 1:1 Meq TPP; + Dicup 4	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Dicup 2 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Dicup 3 (50%)	BB 2255 1:1 Meq TPP; 'Exxpro 3745 + Dicup 2 (50%)	BB 2255 1:1 Meq TPP; 'Exxpro 3745 + Dicup 3 (50%)	BB 2222 1:1 Meq TPP; 'BB 2222 + Dicup 2 (50%)	BB 2222 1:1 Meq TPP; 'BB 2222 + Dicup 3 (50%)	BB 2255 1:1 Meq TPP; 'BB 2255 + Dicup 2 (50%)	BB 2255 1:1 Meq TPP; 'BB 2255 + Dicup 3 (50%)	Exxpro 3745 1:1 Meq TPP; 'BB 2255 + Dicup 2 (50%)	Exxpro 3745 1:1 Meq TPP; 'BB 2255 + Dicup 2 (50%)
BB 2222	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
Exxpro 3745		50.0	50.0			50.0	50.0			50.0	50.0
Butylimidazole											
Armeen (Dialkyl Amine)											
Triphenyl phosphine	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	5.0
1-benzylimidazole											
042-2021-09-02 (Exxpro 3745 + Dicup 2)		50.0		50.0							
042-2021-09-03 (Exxpro 3745 + Dicup 3)			50.0		50.0						
042-2021-09-06 (BB 2222 + Dicup 2)						50.0				50.0	
042-2021-09-07 (BB 2222 + Dicup 3)							50.0				

Effect of visbreaking halobutyl using peroxide before ionomer reaction:

[0104] A master batch (MB) was first formed comprising a rubber component and DICUP®, wherein the rubber component was selected from Exxpro 3745, Exxpro 3035, BB 2222, or a blend of Exxpro 3745:RB068. The MB was first mixed at approximately 100 °C for about 5 minutes. The MB was then mixed for 5 min at a temperature range of about 160 °C to about 190 °C. An additional rubber component was then blended into the MB for approximately 2 minutes, followed by the addition of triphenyl phosphine. The resulting samples were then recovered for testing. Contents and amounts of the resulting elastomeric compositions are summarized in Table 5.

Table 5A:

Title:	Resealing Ionomer Compositions of Exxpro 3035 3745, 2222, and 2255-with low MW component by cracking													
Material Name	rubber with Dicup at ~100C, first; 2nd mix at 190C for Exxpro, 160C for 2222				Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C
	3745 Dicup 1.0 MB	3035 Dicup 1.0 MB	2222 Dicup 1.0 MB	3745:068 blend Dicup 1.0 MB	93	94	95	96	97	98	99	100	101	102
	Exxpro 3745, Dicup 1.0 MB	Exxpro 3035, Dicup 1.0 MB	Exxpro 2222, Dicup 1.0 MB	Exxpro 3745:068 blend Dicup 1.0 MB	Exxpro 3745 1:1 Meq TPP; Dicup 0.5 1.0 phr	Exxpro 3745 1:1 Meq TPP; Dicup 1.0 phr	Exxpro 3035 1:1 Meq TPP; Dicup 0.5 1.0 phr	Exxpro 3035 1:1 Meq TPP; Dicup 1.0 phr	BB 2222 1:1 Meq TPP; Dicup 0.5 1.0 phr	BB 2222 1:1 Meq TPP; Dicup 1.0 phr	BB 6222 1:1 Meq TPP; Dicup 0.5 1.0 phr	BB 6222 1:1 Meq TPP; Dicup 1.0 phr	Exxpro 3745:068 blend 1:1 Meq TPP; Dicup 1.0 phr	Exxpro 3035:068 blend 1:1 Meq TPP; Dicup 1.0 phr
	phr	phr	phr	phr										
	100.0	100.0		50.0	100.0	100.0	100.0	100.0					50.0	50.0
RB 068 Triphenyl phosphine				50.0									50.0	50.0
BB 6222					5.0	5.0	2.1	2.1	4.2	4.2	4.2	4.2	5.0	5.0
3745 Dicup 1.0 MB											100.0	100.0		
3035 Dicup 1.0 MB														
2222 Dicup 1.0 MB														
3745 068 Dicup 1.0 MB														

Table 5A Contd.:

[illegible]

3035 Dicup 1. 0 MB								50.0										50.0		
2222 Dicup 1. 0 MB									50.0											
3745 068 Dicup 1. 0 MB									50.0									50.0		
CB 1066																				
ZnO																				
Indopol H100																				
'DI- CUP® Dicumyl Peroxide																				
Total phr	105.2	105.5	106.0	105.0	104.2	102.1	102.1	102.1	104.2	104.2	104.2	104.2	105.0	154.2	114.2	112.1	115.0			

[0105] A master batch (MB) was first formed comprising a rubber component and Luperox 101, wherein the rubber component was selected from Exxpro 3745, Exxpro 3035, BB 2222, or a blend of Exxpro 3745:RB068. The MB was first mixed at approximately 100 °C for about 5 minutes. The MB was then mixed for 5 min at a temperature range of about 160 °C to about 190 °C. An additional rubber component was then blended into the MB for approximately 2 minutes, followed by the addition of triphenyl phosphine. The resulting samples were then recovered for testing. Contents and amounts of the resulting elastomeric compositions are summarized in Table 6.

10

Table 6A:

				Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	
	3745 Lupero x 101 1.0 MB	3035 Lupero x 101 1.0 MB	2222 Lupero x 101 1.0 MB	3745:06 8 blend Luperox 101 1.0 MB	118	119	120	121	122	123	124	125	126	127	
042- 2021-31															
Material Name	Exxpro 3745, Lupero x 101 1.0 MB	Exxpro 3035, Lupero x 101 1.0 MB	Exxpro 2222, Lupero x 101 1.0 MB	Exxpro 3745:06 8 blend Luperox 101 1.0 MB	Exxpro 3745 1:1 Meq TPP; Lupero x 101 0.5	Exxpro 3745 1:1 Meq TPP; Lupero x 101 1.0	Exxpro 3035 1:1 Meq TPP; Lupero x 101 0.5	Exxpro 3035 1:1 Meq TPP; Lupero x 101 1.0	BB 2222 1:1 Meq TPP; Lupero x 101 0.5	BB 2222 1:1 Meq TPP; Lupero x 101 1.0	Exxpro 3745:06 8 blend 1:1 Meq TPP; Luperox 101 1.0	Exxpro 3035:06 8 blend 1:1 Meq TPP; Luperox 101 1.0	BB 2222:06 8 blend 1:1 Meq TPP; Luperox 101 1.0	CB 1066 1:1 Meq TPP; Lupero x 101 0.5	
	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
BB 2222			100.0						100.0	100.0			50.0		
Exxpro 3745	100.0			50.0		100.0					50.0				
Exxpro 3035		100.0					100.0	100.0				50.0			
RB 068				50.0							50.0	50.0	50.0		
Triphenyl phosphine					5.0	5.0	2.1	2.1	4.2	4.2	5.0	5.0	4.2	5.0	

Table 6A Contd.:

	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C	Mix TPP at 150 C
Example	128	129	130	131	132	133	134	135	136	137	138	139
Material Name	CB1066 1:1 Meq TPP; Luperox 101 1.0	Exxpro 3745 1:1 Meq TPP; 'Exxpro 3745 + Luperox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Luperox 101 1 (50%)	Exxpro 3035 1:1 Meq TPP; 'Exxpro 3035 + Luperox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3035 + Luperox 101 1 (50%)	BB 2222 1:1 Meq TPP; 2222 + Luperox 101 1 (50%)	BB 2222 1:1 Meq TPP; 3745 + Luperox 101 1 (50%)	Exxpro 3745 1:1 Meq TPP; 'Exxpro 3745:068 + Luperox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745:068 + Luperox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Luperox 101 1 (50%), H100	BB 2222 1:1 Meq TPP; 'Exxpro 3035 + Luperox 101 1 (50%), H100	Exxpro 3745 1:1 Meq TPP; 'Exxpro 3745:068 + Luperox 101 1 (50%), H100
BB 2222	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
Exxpro 3745		50.0			50.0	50.0			50.0	50.0	50.0	
Exxpro 3035				50.0			50.0	50.0				50.0
RB 068												
Triphenyl phosphine	5.0	5.0	4.2	2.1	2.1	4.2	4.2	5.0	4.2	4.2	2.1	5.0

3745 Luperox 101 1.0 MB		50.0	50.0							50.0									
3035 Luperox 101 1.0 MB						50.0	50.0				50.0								
2222 Luperox 101 1.0 MB										50.0	50.0								
3745 068 Luperox 101 1.0 MB											50.0	50.0							50.0
ZnO																			
Indopol H100																	10.0	10.0	10.0
Luperox 101	1.0																		
Total phr	6.0	105.0	104.2	102.1	102.1	104.2	104.2	104.2	105.0	154.2	114.2	112.1	115.0						

Hardness testing: Hardness measurements were taken on test specimens in accordance with ASTM D2240, which is incorporated herein as reference.

Tensile testing:

[0106] Stress/Strain measurements were taken on test specimens using ASTM D412 die.

- 5 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 20mm as the gauge length. Sample information, operator name, date, lab temperature, and humidity were all recorded. Specimen thickness was measured at three places in the test area and the average value was entered when prompted. The lab temperature and humidity were measured.
- 10 Specimen was carefully loaded in the grips to ensure grips clamp on the specimen symmetrically. The extensometer grips was then attached to the sample in the test area. The test was prompted to start. A pre-load of 0.1N was applied. Testing began with the crosshead at 20 inches/minute until a break is detected. 3 specimens from each sample were tested and the median values were reported.

15 O₂ permeability:

[0107] Permeation rates of gases and permeation coefficients may be measured by a number of methods including coulometric (ASTM D 3895), manometric (ASTM D 1434), and carrier gas (ISO 15105-1). Instruments that measure permeation, and permeation testing services are provided by companies such as Mocon Inc., of Minneapolis, MN, USA. Oxygen transmission

20 rate can be tested using ASTM D 3985-05 and an OX-TRAN® 2/61 MJ module (an oxygen transmission rate test system, available from Mocon, Inc.). The specimen for Mocon testing was a circular disk having a diameter of about 0.2 mm to about 0.3 mm.

Elastomeric network self-healing and self-sealing:

- [0108] Elastomeric network materials were cut and/or punctured, so as to mimic potential
- 25 damage the material may receive during commercial use. For example, tensile test specimens were cut to form damaged components. After damaging the material, the damaged components were then compressed together under about 5 tons of pressure at about 50 °C for about 10 minutes, so as to self-heal the material. The pressure was then released from the sample, and the sample was allowed to cool for about 5 minutes on a cool platen. Samples were then
- 30 retested, via any one or more of the previously described material testing methods, and compared to their original undamaged counterpart to determine the degree of mechanical and physical property retention. To determine the self-sealing properties of the elastomeric network materials, select samples were studied using Mocon instrument after puncture and reseal to illustrate the air retention capabilities after puncture and reseal formation. Mocon test

specimens were punctured using a nail, then resealed similar to the cut tensile specimen preparation. The resealed samples were then used for impermeability testing, using Mocon instrument. The results are summarized in Tables 1B through 6B, wherein Tables denoted with B represent the corresponding properties of each of the respective formulations as summarized
5 in Tables denoted with A.

Table 1B:

Formulation Number	1	2	3	4	5	6	7	8	9	10	11	12
Name	Exxpro 3035 1:1 Meq TPP	Exxpro 3035 1:1 Meq TPP; 30 XP 50	Exxpro 3035 1:0.7 Meq TPP; 30 XP 50	Exxpro 3035 1:1 Meq TPP; 50 XP 50	Exxpro 3035 1:1 Meq TPP; 30 PIB	Exxpro 3035 1:1 Meq TPP; 50 365	Exxpro 3035 1:1 Meq TPP; 30 365	Exxpro 3035 1:1 Meq TPP; 30 068	Exxpro 3035 1:1 Meq TPP; 30 SIBSTAR	Exxpro 3035 1:1 Meq TPP; 30 XP 50 and more	Exxpro 3035 1:1 Meq TPP; 30 XP 50 and more, BaO	Exxpro 3035 1:1 Meq TPP; 30 068 and more, BaO
Physical Properties												
Hardness, Shore A	29.8	24.4	20.7	19.5	28.9	18.7	24.3	25.8	31.6	too soft	too soft	too soft
M100, MPa - Original	0.63	0.52	0.45	0.44	0.61	0.44	0.55	0.56	0.74	NA	NA	NA
Tensile Strength at Break, MPa Original	8.28	7.38	5.07	3.45	2.71	4.21	7.675	6.46	13.41	NA	NA	NA
Elongation at Break, % Original	1206	1292	1292	1291	1020	1291	1256	1235	1165	NA	NA	NA
Cut seal testing results												
M100, MPa - Cut Seal	0.63	0.55	0.47	0.47	0.62	0.47	0.57	0.59	0.72	NA	NA	NA
Tensile Strength at Break, MPa Cut Seal	0.44	0.7	0.68	1.70	0.76	0.61	0.66	1.61	1.03	NA	NA	NA
Elongation at Break, % Cut Seal	179	278	472	1161	216	358	202	791.4	141	NA	NA	NA

Table 1B Contd.:

Formulation Number	13	14	15	16	17	18	19	20	21
Name	Exxpro 3745 1:1 Meq TPP	Exxpro 3745 1:1 Meq TPP; 30 XP 50	Exxpro 3745 1:0.7 Meq TPP; 30 XP 50	Exxpro 3745 1:1 Meq TPP; 50 XP 50	Exxpro 3745 1:1 Meq TPP; 30 PIB	Exxpro 3745 1:1 Meq TPP; 50 365	Exxpro 3745 1:1 Meq TPP; 30 365	Exxpro 3745 1:1 Meq TPP; 30 068	Exxpro 3745 1:1 Meq TPP; 30 SIBSTAR
Physical Properties									
Hardness, Shore A	32.3	29.4	23.7	29.1	32.1	28.1	29.6	32.4	36.4
M100, MPa - Original	0.83	0.70	0.52	0.69	0.66	0.61	0.76	0.78	0.93
Tensile Strength at Break, MPa Original	6.33	8.29	6.01	4.135	3.72	4.55	7.18	5.58	11.94
Elongation at Break, % Original	1278	1231	1291	1181	929	998	1136	1070	1221
Cut seal testing results									
M100, MPa - Cut Seal	0.89	0.7	0.53	0.88	0.75	0.76	0.69	0.75	0.87
Tensile Strength at Break, MPa Cut Seal	1.04	0.96	0.78	1.07	0.98	1.13	0.83	1	0.91
Elongation at Break, % Cut Seal	150	165	234	142	182	185	139	165	121

Table 2B:

Formulation Number	22	23	24	25	26	27	28	29	30	31	32	33	34
Name	Exxpro 3035 1:1 Meq TPP; 30 365	Exxpro 3035 1:1.3 Meq TPP; 30 365	Exxpro 3035 1:1 Meq TPP; 30 NR	Exxpro 3035 1:1 Meq TPP; 30 SBR	Exxpro 3035 1:1 Meq TPP; 15 NR, 15 SBR	Exxpro 3035 1:1.3 Meq TPP; 15 NR, 15 SBR	Exxpro 3035 1:1 Meq TPP; 30 SIBSTAR 062	Exxpro 3035 1:1 Meq TPP; 30 SIBSTAR 072	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3035 1:1 Meq TPP; 30 365; 20 CB 660; 1102 & Indopol	Exxpro 3035 1:1 Meq TPP; 15 NR, 15 SBR; 20 CB 660	Exxpro 3035 1:1.3 Meq TPP; 30 365; 20 CB 660	Exxpro 3035; NR, SBR, ZnO
Physical Properties													
Hardness, Shore A	25.4	25.9	27.7	21.3	22.5	21.9	33.2	33.2	35.2	24.8	34.5	32.7	20.9
M100, MPa (original)	0.62	0.75	1.13	0.70	0.91	0.97	0.74	0.72	0.88	0.58	1.04	1.68	0.99
Tensile Strength at Break, MPa (original)	6.7	8.9	3.3	5.6	7.0	6.0	13.6	15.1	5.5	3.7	4.7	5.3	1.5
Elongation at Break, % (original)	1223	1291	754	1291	1291	1280	1201	1190	854	993	884	837	599
M100, MPa (cut)	0.55	0.55	0.45	0.47	0.58	0	0.69	0.67	0.91	0.56	1.04	0.84	0.54
Tensile Strength at Break, MPa (cut)	0.59	0.56	0.36	0.55	0.45	0.37	0.50	0.61	0.66	0.45	0.60	0.55	0.52
Elongation at Break, % (cut)	251	320	108	352	173	176	164	250	171	191	117	130	304
O ₂ Permeability Coefficient; (mm) ³ •(cc)/ m ² •day•mmHg	0.238	0.246	NA	0.357	0.487	0.356	0.242	0.236	0.208	0.255	NA	0.460	1.329

Table 2B Contd.:

Formulation Number	35	36	37	38	39	40	41	42	43	44	45	46	47
Name	Exxpro 3745 1:1 Meq TPP; 30 365	Exxpro 3745 1:1.3 Meq TPP; 30 365	Exxpro 3745 1:1 Meq TPP; 30 NR	Exxpro 3745 1:1 Meq TPP; 30 SBR	Exxpro 3745 1:1 Meq TPP; 15 NR, 15 SBR	Exxpro 3745 1:1.3 Meq TPP; 15 NR, 15 SBR	Exxpro 3745 1:1 Meq TPP; 30 SIBST A 062	Exxpro 3745 1:1 Meq TPP; 30 SIBST A 072	Exxpro 3745 1:1 Meq TPP; 30 365; 20 CB 660	Exxpro 3745 1:1 Meq TPP; 30 365; 20 CB 660; 1102 & Indopol	Exxpro 3745 1:1 Meq TPP; 15 NR, 15 SBR; 20 CB 660	Exxpro 3745 1:1.3 Meq TPP; 15 NR, 15 SBR; 20 CB 660	Exxpro 3745; NR, SBR, ZnO
Physical Properties													
Hardness, Shore A	29.96	33.44	27.10	29.84	27.62	32.98	40.88	40.08	43.32	34.54	41.64	40.40	33.82
M100, MPa (original)	1.16	1.69	1.10	1.43	1.09	2.14	2.68	2.91	3.53	2.11	2.46	2.38	1.95
Tensile Strength at Break, MPa (original)	4.81	7.98	2.93	6.71	3.47	5.47	11.19	11.10	6.84	4.76	5.21	4.31	4.94
Elongation at Break, % (original)	892	965	510	1292	858	878	902	872	654	737	580	315	530
M100, MPa (cut)	0.75	0.90	0.66	0.85	0.75	0.30				0.91	1.15		1.21

Tensile Strength at Break, MPa (cut)	0.50	0.53	0.31	0.61	0.52	0.29	0.63	0.66	0.85	0.57	0.65	0.51	0.68
Elongation at Break, % (cut)	141	127	95	169	128	92	90	78	78	99	109	78	99
O ₂ Permeability Coefficient; (mm) ³ /(cc)/ m ² •day•mmHg	0.230	0.224	0.701	0.334	NA	NA	0.213	0.212	0.199	0.274	0.420	NA	1.135

Table 3B:

Formulation Number	48	49	50	51	52	53	54	55	56	57	58	59	60
Name	Exxpro 3035 1:1.3 Meq; TPP; 50 365	Exxpro 3035 1:1.3 Meq; TPP; 50 365; HSt, ZnO; 101	Exxpro 3035 1:1.3 Meq; TPP; 50 365; HSt, ZnO	Exxpro 3035 1:1.3 Meq; TPP; 50 365; S cure	Exxpro 3035 1:1.3 Meq; TPP; 50 365; 1045 cure	Exxpro 3035 1:1.3 Meq; TPP; 50 365; S cure CB, 1102	Exxpro 3035 1:1.3 Meq; TPP; 50 365; S cure CB, H100	Exxpro 3035 1:1.3 Meq; TPP; 50 SBR; HSt, Zn	Exxpro 3035 1:1.3 Meq; TPP; 50 SBR; S MBTS	Exxpro 3035 1:1.3 Meq; TPP; 50 SBR; CB, S MBTS	Exxpro 3035 1:1 Meq; TPP; 30 365; 20 CB; 660; 1102 & Indopol	Exxpro 3035 1:1.3 Meq; TPP; 25 SBR; 25 NR, S MBTS	Exxpro 3035 1:1.3 Meq; TPP; 50 2502, Hst, Zn
Physical Properties													
Hardness, Shore A	19.20	16.80	18.40	29.30	25.90	36.50	25.00	17.90	39.50	13.90	25.60	39.10	30.50
M100, MPa (original)	0.37	0.37	0.68	1.81	1.25	1.57	1.30	1.84	3.58	2.22	2.37	1.74	0.78
Tensile Strength at Break, MPa (original)	3.11	4.01	4.17	6.09	2.61	8.24	3.59	4.52	5.11	2.31	5.58	4.31	1.86
Elongation at Break, % (original)	1230	1280	1280	760	702	815	455	1280	247	130	914	337	281
M100, MPa (cut)	0.39	0.34	0.36	0.56	0.65	0.52	0.42	0.37	0.00	0.00	0.52	0.00	0.00
Tensile Strength at Break, MPa (cut)	0.50	0.47	0.40	0.56	0.68	0.67	0.44	0.43	0.54	0.38	0.60	0.90	0.57
Elongation at Break, % (cut)	562	904	517	105	111	76	241	485	47	47	191	67	83
O2 Permeability Coefficient: (mm)•(cc)/m ² •day•mmHg	0.177	0.180	0.164	0.256	0.279	NA	NA	0.414	0.551	NA	0.189	NA	1.09

Table 3B Contd.:

Formulation Number	61	62	63	64	65	66	67	68	69	70
Name	Exxpro 3035 1:1.3 Meq TPP; 50 Kraton 1652	Exxpro 3035 1:1.3 Meq TPP; 50 Kraton, HI100	Exxpro 3035 1:1.3 Meq TPP; 50 PEDM	Exxpro 3035 1:1.3 Meq TPP; 50 068	Exxpro 3035 1:1.3 Meq TPP; 50 068; HSt, ZnO; 101	Exxpro 3035 1:1.3 Meq TPP; 50 068; HSt, ZnO	Exxpro 3035 1:1.3 Meq TPP; 50 068; S cure	Exxpro 3745 1:1.3 Meq TPP; 50 068; HSt, ZnO; 101	Exxpro 3745 1:1.3 Meq TPP; 50 068; HSt, ZnO	Exxpro 3745 1:1.3 Meq TPP; 50 068; S cure
Physical Properties										
Hardness, Shore A	53.30	47.30	37.30	22.90	11.50	24.90	24.10	18.10	31.80	31.40
M100, MPa (original)	1.57	1.26	0.75	0.36	0.23	1.29	1.32	0.69	1.20	1.64
Tensile Strength at Break, MPa (original)	6.54	6.54	3.34	2.99	0.98	1.94	1.61	1.05	1.41	2.88
Elongation at Break, % (original)	571	650	503	1040	761	244	137	203	152	194
M100, MPa (cut)	0.00	0.00	0.80	0.43	0.21	0.49	0.02	0.31	0.62	0.09
Tensile Strength at Break, MPa (cut)	1.20	1.21	0.70	0.58	0.24	0.71	0.31	0.33	0.76	0.26
Elongation at Break, % (cut)	64	65	85	273	349	208	60	282	115	111
O2 Permeability Coefficient; (mm) ³ •(cc)/ m ² •day•mmHg	0.749	0.807	0.780	0.252	NA	NA	NA	0.357	NA	NA

Table 4B:

Formulation Number	71	72	73	74	75	76	77	78	79	80	81
Name	Exxpro 3745 1:1 Meq TPP;	Exxpro 3745 1:1 Meq TPP; + Dicup 2	Exxpro 3745 1:1 Meq TPP; + Dicup 3	Exxpro 3745 1:1 Meq TPP; + Dicup 4	BB 2222 1:1 Meq TPP;	BB 2222 1:1 Meq TPP; + Dicup 2	BB 2222 1:1 Meq TPP; + Dicup 3	BB 2222 1:1 Meq TPP; + Dicup 4	BB 2255 1:1 Meq TPP;	BB 2255 1:1 Meq TPP; + Dicup 2	BB 2255 1:1 Meq TPP; + Dicup 3
Physical Properties											
Hardness, Shore A	46.0	42.8	44.0	42.4	26.1	24.0	23.0	22.5	25.6	25.8	23.3
M100, Mpa (Original)	1.6	1.4	2.0	1.7	0.5	0.5	0.5	0.6	0.5	0.7	0.6
Tensile Strength at Break, Mpa (Original)	10.2	3.8	3.7	3.2	5.4	3.8	3.1	2.1	7.2	3.4	2.7
Elongation at Break, % (Original)	816	457	242	265	1183	1140	1153	891	1138	764	848
M100, Mpa (Reseal)	1.4		1.2		0.5	0.5	0.4	0.7	0.5	0.5	0.6
Tensile Strength at Break, Mpa (Reseal)	1.1	1.0	1.8	1.4	1.0	1.4	1.2	1.4	1.3	1.2	1.2
Elongation at Break, % (Reseal)	67	70	73	81	494	355	472	220	533	279	192

O ₂ permeability coefficient Original (mm)•(cc)/ m ² •day•mmHg	0.189	0.226	0.226	0.226	0.226	0.269	0.293	0.247	0.276	0.272	0.290	0.252
O ₂ permeability coefficient after puncture and rescal (mm)•(cc)/ m ² •day•mmHg	0.270	NA	0.242	NA	0.324	NA	NA	NA	0.268	0.235	NA	NA

Table 4B Contd.:

Formulation Number	82	83	84	85	86	87	88	89	90	91	92
Name	BB 2255 1:1 Meq TPP; 'Exxpro 3745 + Dicup 2 (50%) + Dicup 4	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Dicup 2 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Dicup 3 (50%)	BB 2255 1:1 Meq TPP; 'Exxpro 3745 + Dicup 2 (50%)	BB 2255 1:1 Meq TPP; 'Exxpro 3745 + Dicup 3 (50%)	BB 2222 1:1 Meq TPP; 'BB 2222 + Dicup 2 (50%)	BB 2222 1:1 Meq TPP; 'BB 2222 + Dicup 3 (50%)	BB 2255 1:1 Meq TPP; 'BB 2255 + Dicup 2 (50%)	BB 2255 1:1 Meq TPP; 'BB 2255 + Dicup 3 (50%)	Exxpro 3745 1:1 Meq TPP; 'BB 2255 + Dicup 2 (50%)	Exxpro 3745 1:1 Meq TPP; 'BB 2255 + Dicup 2 (50%)
Physical Properties											
Hardness, Shore A	22.2	38.6	35.9	38.4	37.0	24.7	24.3	26.6	25.0		40.5
M100, Mpa (Original)	0.5	1.1	0.9	1.3	0.9	0.6	0.5	0.6	0.7	NA	2.5
Tensile Strength at Break, Mpa (Original)	1.9	7.1	7.1	7.6	4.3	4.8	4.4	6.3	4.8	NA	6.5
Elongation at Break, % (Original)	789	1167	1153	1107	891	1132	1183	1103	1081	NA	666
M100, Mpa (Reseal)	0.6	1.0	1.0	1.1	1.0	0.5	0.5	0.7	0.7		
Tensile Strength at Break, Mpa (Reseal)	1.2	1.5	1.5	1.3	1.3	1.4	1.3	1.5	1.5		1.300
Elongation at Break, % (Reseal)	197	202	233	142	180	446	408	264	236		83.800
O ₂ Permeability Coefficient Original	0.239	0.204	0.214	0.201	0.168	0.213	0.188	0.209	0.241	NA	NA

O ₂ Permeability Coefficient after puncture and reseal puncture and reseal	0.305	NA	0.216	NA	NA	0.255	NA	0.218	NA	NA	NA
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Table 5B:

Example	3745 Dicup 1.0 MB	3035 Dicup 1.0 MB	2222 Dicup 1.0 MB	3745:068 blend Dicup 1.0 MB	93	94	95	96	97	98	99	100	101	102
Name					Exxpro 3745 1:1 Meq TPP; Dicup 0.5	Exxpro 3745 1:1 Meq TPP; Dicup 1.0	Exxpro 3035 1:1 Meq TPP; Dicup 0.5	Exxpro 3035 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; Dicup 0.5	BB 2222 1:1 Meq TPP; Dicup 1.0	BB 6222 1:1 Meq TPP; Dicup 0.5	BB 6222 1:1 Meq TPP; Dicup 1.0	Exxpro 3745:068 blend 1:1 Meq TPP; Dicup 1.0	Exxpro 3035:068 blend 1:1 Meq TPP; Dicup 1.0
Physical Properties														
Hardness, Shore A					38.02	37.32	25.88	23.52	28.18	N/A	22.64	10.38	12.32	N/A
M100, Mpa (Original)					2.15	1.62	0.88	0.79	0.56		0.37	0.16	0.37	
Tensile Strength at Break, Mpa (Original)					5.10	3.26	3.88	1.96	5.17		1.15	0.35	1.15	
Elongation at Break, % (Original)					282	258	1320	834	1170		727	983	727	
M100, Mpa (Reseal)					0.000	0.000	0.790	0.682	0.576		0.163	0.285	0.338	
Tensile Strength at Break, Mpa (Reseal)					0.830	1.010	0.681	0.728	1.170		0.426	0.267	0.506	
Elongation at Break, % (Reseal)					46	69	106	123	381		92	289	183.	
O2 Permeability Coefficient; (mm) ³ •(cc)/ m ² •day•mm Hg					0.241	0.237	0.224	0.224	0.269	0.394	0.274	NA	0.383	NA

Table 5B Contd.:

Example	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117
Name	BB 2222:0 68 blend 1:1 Meq TPP; Dicup 1.0	CB 1066 1:1 Meq TPP; Dicu p 0.5	CB10 66 1:1 Meq TPP; Dicup 1.0	Exxpro 3745 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; Exxpro 3745 1:1 Meq TPP; Dicup 1.0	Exxpro 3035 1:1 Meq TPP; Exxpro 3035 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; Exxpro 3035 1:1 Meq TPP; Dicup 1.0	BB 2222 2 1:1 Meq TPP; Exxpro 3035 1:1 Meq TPP; Dicup 1.0	BB 6222 1:1 Meq TPP; Exxpro 3035 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; Exxpro 3745 1:1 Meq TPP; Dicup 1.0	Exxpro 3745 1:1 Meq TPP; Exxpro 3745 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; Exxpro 3745 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; Exxpro 3035 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; Exxpro 3035 1:1 Meq TPP; Dicup 1.0	Exxpro 3745 1:1 Meq TPP; Exxpro 3745 1:1 Meq TPP; Dicup 1.0
Physical Properties															
Hardness, Shore A	N/A	41.0 2	34.94	27.64	26.04	35.00	38.18	32.3 2	26.2 4	27.62	28.46	36.14			
M100, Mpa (Original)		1.80	1.12	0.68	0.74	1.27	1.55	1.45	0.77	0.55	0.90	1.42			
Tensile Strength at Break, Mpa (Original)		4.26	2.91	4.25	4.30	3.23	4.34	3.23	2.33	6.29	3.11	2.94			
Elongation at Break, % (Original)		292	448	1380	1350	413	440	342	540	1110	987	301			
M100, Mpa (Reseal)		0.00 0	0.923	0.758	0.850	0.944	0.000		0.00 0	0.584	0.000	-0.010			
Tensile Strength at Break, Mpa (Reseal)		1.19 0	1.090	0.797	0.950	0.959	0.898		0.53 1	0.673	0.583	0.441			

Table 5B Contd.:

Example	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117
Name	BB 2222:0 68 blend 1:1 Meq TPP; Dicup 1.0	CB 1066 1:1 Meq TPP; Dicu p 0.5	CB10 66 1:1 Meq TPP; Dicup 1.0	Exxpr o 3745 1:1 Meq TPP; Dicup 1.0	BB 2222 1:1 Meq TPP; 'Exxp ro 3745 + Dicup 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxp ro 3035 + Dicup 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxp ro 3035 + Dicup 1 (50%)	BB 222 2 1:1 Meq TPP; Dicu p 1 (50%)	BB 6222 1:1 Meq TPP; TPP; 2222 + Dicu p 1 (50%)	BB 2222 1:1 Meq TPP; 3745 + Dicup 1 (50%)	Exxpro 3745 1:1 Meq TPP; 'Exxpr o 3745:0 68 + Dicup 1 (50%), H100	BB 2222 1:1 Meq TPP; 'Exxpr o 3745:0 68 + Dicup 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxp ro 3745 + Dicup 1 (50%), H100	BB 2222 1:1 Meq TPP; 'Exxp ro 3035 + Dicup 1 (50%), H100	Exxpro 3745 1:1 Meq TPP; 'Exxpr o 3745:0 68 + Dicup 1 (50%), H100
Physical Properties															
Hardness, Shore A	N/A	41.0 2	34.94	27.64	26.04	35.00	38.18	32.3 2	26.2 4	27.62	28.46	36.14			
M100, Mpa (Original)		1.80	1.12	0.68	0.74	1.27	1.55	1.45	0.77	0.55	0.90	1.42			
Tensile Strength at Break, Mpa (Original)		4.26	2.91	4.25	4.30	3.23	4.34	3.23	2.33	6.29	3.11	2.94			
Elongation at Break, % (Original)		292	448	1380	1350	413	440	342	540	1110	987	301			
M100, Mpa (Reseal)		0.00 0	0.923	0.758	0.850	0.944	0.000		0.00 0	0.584	0.000	-0.010			
Tensile Strength at		1.19 0	1.090	0.797	0.950	0.959	0.898		0.53 1	0.673	0.583	0.441			

Table 6B:

Formulation Number	118	119	120	121	122	123	124	125	126	127
Name	Exxpro 3745 1:1 Meq TPP; Luperox 101 0.5	Exxpro 3745 1:1 Meq TPP; Luperox 101 1.0	Exxpro 3035 1:1 Meq TPP; Luperox 101 0.5	Exxpro 3035 1:1 Meq TPP; Luperox 101 1.0	BB 2222 1:1 Meq TPP; Luperox 101 0.5	BB 2222 1:1 Meq TPP; Luperox 101 1.0	Exxpro 3745:068 blend 1:1 Meq TPP; Luperox 101 1.0	Exxpro 3035:068 blend 1:1 Meq TPP; Luperox 101 1.0	BB 2222:068 blend 1:1 Meq TPP; Luperox 101 1.0	CB 1066 1:1 Meq TPP; Luperox 101 0.5
Physical Properties										
Hardness, Shore A	39,800	46,300	26,200	18,800	27,200	30,700	15,300	N/A	12,200	N/A
M100, Mpa (Original)	2.65	2.03	0.381	0.433	0.594	0.598	0.355	0.122	0.243	0.168
Tensile Strength at Break, Mpa (Original)	4.84	3.74	1.99	1.15	2.470	1.860	0.833	0.025	0.826	0.373
Elongation at Break, % (Original)	247	235	891	682	625	416	388	758	807	283
M100, Mpa (Rescal)			0.534	0.449	0.768	0.653	0.055	0.410	0.269	N/A
Tensile Strength at Break, Mpa (Rescal)	1,290	0,934	0,590	0,539	0,950	0,875	0,305	0,226	0,361	
Elongation at Break, % (Rescal)	55	56	87	139	132	134	182	629	271	
O ₂ Permeability Coefficient; (mm) ³ •(cc)/m ² •day•mmHg	NA	NA	0.222	0.239	0.344	NA	0.307	NA	0.438	NA

Table 6B Contd.:

Formulation Number	128	129	130	131	132	133	134	135	136	137	138	139
Name	CBI066 1:1 Meq TPP; Luperrox 101 1.0	Exxpro 3745 1:1 Meq TPP; 'Exxpro 3745 + Luperrox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Luperrox 101 1 (50%)	Exxpro 3035 1:1 Meq TPP; 'Exxpro 3035 + Luperrox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3035 + Luperrox 101 1 (50%)	BB 2222 1:1 Meq TPP; 2222 + Luperrox 101 1 (50%)	BB 2222 1:1 Meq TPP; 3745 + Luperrox 101 1 (50%)	Exxpro 3745 1:1 Meq TPP; 'Exxpro 3745:068 + Luperrox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745:068 + Luperrox 101 1 (50%)	BB 2222 1:1 Meq TPP; 'Exxpro 3745 + Luperrox 101 1 (50%), H100	BB 2222 1:1 Meq TPP; 'Exxpro 3035 + Luperrox 101 1 (50%), H100	Exxpro 3745 1:1 Meq TPP; 'Exxpro 3745:068 + Luperrox 101 1 (50%), H100
Physical Properties												
Hardness, Shore A	N/A	47.700	35.700	28.100	25.100	30.800	38.900	43.300	27.700	31.000	19.700	29.600
M100, Mpa (Original)	0.127	2.650	0.988	0.725	0.658	0.816	1.510	1.610	0.696	0.702	0.486	0.786
Tensile Strength at Break, Mpa (Original)	0.264	5.680	3.950	3.910	3.280	2.940	3.700	5.380	1.840	2.880	2.530	3.280
Elongation at Break, % (Original)	617	398	827	1280	1230	651	340	429	500	725	1290	770
M100, Mpa (Reseal)	N/A		0.915	0.790	0.654	0.890			0.603	0.804	0.577	
Tensile Strength at Break, Mpa (Reseal)		1.190	0.945	0.784	0.719	1.040	0.715	0.966	0.641	0.868	0.588	0.718
Elongation at Break, % (Reseal)		54	108	92	123	124	52	56	100	120	106	37
O ₂ Permeability Coefficient: (mm) ³ /(cc)/m ² •day•mm Hg	NA	NA	0.259	0.254	0.295	0.302	0.232	NA	0.273	0.314	0.325	0.260

[0109] Overall, the present disclosure provides compositions of self-healing and self-sealing interpenetrating networks and methods thereof. The interpenetrating networks can include a first component, a second component, and a curing system. The overall composition of the interpenetrating networks, as disclosed herein, can provide physical and mechanical properties for implementation within tire components. Additionally, the overall composition of the interpenetrating networks can provide the material with self-healing and self-sealing properties to extend the usable lifetime of the tire component.

[0110] The phrases, unless otherwise specified, "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the present disclosure, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

[0111] 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.

[0112] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0113] All numerical values within the detailed description herein are modified by "about" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0114] All documents described herein are incorporated by reference herein, including any priority documents and or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the present disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including" for purposes of United

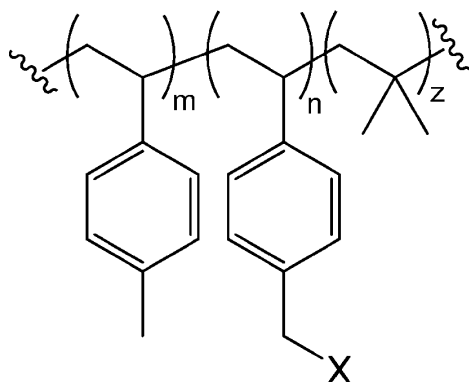
States law. Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase “comprising,” it is understood that we also contemplate the same composition or group of elements with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of
5 the composition, element, or elements and vice versa.

[0115] While the present disclosure has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the present disclosure.

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CLAIMS

1. An elastomer composition, comprising:
 - a first elastomer, a second elastomer, and a nucleophile, wherein;
 - the first elastomer is a copolymer comprising p-methylstyrene, p-halomethylstyrene, and isobutylene derived units, the first elastomer comprising about 30 phr to about 100 phr of the elastomeric composition; and
 - the second elastomer comprises isobutylene derived repeat units and comprises about 30 phr to about 75 phr of the elastomeric composition.
2. The elastomer composition claim 1, wherein the first elastomer is a halogenated poly(isobutylene-co-p-methylstyrene) that can be represented by



wherein:

- x is a halogen; and
 - each of m, n, and z is independently a numerical value representing the number of respective repeat units along the polymer backbone.
3. The elastomer composition of claim 2, wherein X is selected from bromine and chlorine.
 4. The elastomer composition of claim 3, wherein X comprises about 0.3 wt % to about 4.5 wt % of the first elastomer.
 5. The elastomer composition of claim 2, wherein the first elastomer comprises about 0.1 mol % to about 7.5 mol % p-halomethylstyrene units, relative to total of p-methylstyrene and p-halomethylstyrene derived units.

6. The elastomer composition of claim 2, wherein the combination of the p-halomethylstyrene units and the p-methylstyrene units comprise about 0.5 wt % to about 30 wt % of the first elastomer.

7. The elastomer composition of claim 1, wherein the second elastomer is partially crosslinked.

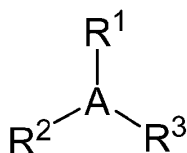
8. The elastomer composition of claim 1, wherein the second elastomer is a vis-broken polymer capable of ionomer formation.

9. The elastomer composition of claim 1, wherein the composition further comprises one or more additives selected from the group consisting of fillers, dyes, pigments, antioxidants, heat and light stabilizers, plasticizers, oils, and combinations thereof.

10. An elastomeric composition, comprising:

a first elastomer, a second elastomer, and a nucleophilic compound, wherein;
the first elastomer is a copolymer comprising p-methylstyrene, p-halomethylstyrene, and isobutylene derived repeat units;
the first elastomer comprises about 30 phr to about 100 phr of the elastomeric composition;
the second elastomer comprises about 30 phr to about 75 phr of the elastomeric composition;
the nucleophilic compound is a crosslinking agent, the nucleophilic compound comprising about 1 phr to about 5 phr of the elastomeric composition.

11. The elastomeric network of claim 10, wherein the nucleophilic compound is represented by



wherein:

A is a nitrogen or phosphorus; and

R¹, R², and R³ are independently selected from the group consisting of an alkyl substituent, an aryl substituent, a heteroatom, and combinations thereof, wherein:
the alkyl substituent is any one or more linear or branched C₁-C₁₈ alkyl substituents,
the aryl substituent is monocyclic or composed of fused C₄-C₈ rings,

and the heteroatom is selected from B, N, O, Si, P, and S.

12. The elastomeric network of claim 11, wherein the nucleophilic compound is selected from the group consisting of trimethylamine, triethylamine, triisopropylamine, tri-n-butylamine, trimethylphosphine, triethylphosphine, triisopropylphosphine, tri-n-butylphosphine, triphenylphosphine, and combinations thereof.

13. The elastomeric network of claim 10, wherein the nucleophilic compound is triphenylphosphine.

14. The elastomeric network of claim 10, wherein a molar ratio of the nucleophilic compound to halide of the first elastomer is about 0.2:1 to about 1.2:1.

15. The elastomeric network of claim 10, wherein the second elastomer is selected from the group consisting of natural rubber, polyisoprene rubber, poly(styrene-co-butadiene) rubber (SBR), polybutadiene rubber (BR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber, propylene oxide polymers, halobutyl rubber, star-branched butyl rubber, halogenated star-branched butyl rubber, ionic butyl rubber, and combinations thereof.

16. The elastomeric network of claim 10, wherein the second elastomer is crosslinked.

17. A method of making a tire component, the method comprising:

mixing a first elastomer and a second elastomer to form an elastomer composition in a mixer, wherein:

the first elastomer is a copolymer comprising p-methylstyrene, p-halomethylstyrene, and isobutylene derived repeat units;

the first elastomer comprises about 30 phr to about 100 phr of the elastomeric composition;

the second elastomer is butyl rubber; and

the second elastomer comprises about 30 phr to about 75 phr of the elastomeric composition;

blending the elastomer composition with a nucleophilic compound to form an elastomeric network, wherein:

the nucleophilic compound comprises about 1.4 phr to about 2.7 phr of the elastomeric network, and

a molar ratio of the nucleophilic compound to halide of the first elastomer is about 0.2:1 to about 1.2:1; and

integrating the elastomeric network into one or more components of a tire.

18. The method of claim 17, wherein the elastomeric network has a M100 value of about 0.1 MPa to about 3.6 MPa.

19. The method of claim 17, wherein the elastomeric network has a tensile strength at break of about 0.03 MPa to about 15.1 MPa.

20. The method of claim 17, wherein the elastomeric network has an elongation at break of about 130 % to about 1380%.

21. The method of claim 17, wherein the elastomeric network has an O₂ permeability coefficient of about 0.1 (mm)•(cc)/ m²•day•mmHg to about 1.4 (mm)•(cc)/ m²•day•mmHg.

22. The method of claim 17, wherein the elastomeric network has a Shore A Hardness value of about 5 to about 50.

23. The method of claim 17, wherein the nucleophilic compound is triphenylphosphine.