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(54) Title: NON-HYDROGENATED STYRENE BLOCK COPOLYMERS WITH IMPROVED PROCESSING AND MECHANICAL PROPERTIES AND METHODS FOR MAKING SAME

(57) Abstract: Films and methods for making the same. The film can include at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%, and a at least one hydrogenated resin having a MWD of from about 1.5 to about 3.5.

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# NON-HYDROGENATED STYRENE BLOCK COPOLYMERS WITH IMPROVED PROCESSING AND MECHANICAL PROPERTIES AND METHODS FOR MAKING SAME

## CROSS REFERENCE TO RELATED APPLICATIONS

**[0001]** This application claims the benefit of U.S. provisional application Serial No. 61/140,453 filed December 23, 2008 which is hereby incorporated by reference in its entirety.

## BACKGROUND

**[0002]** Embodiments of the present invention generally relate to films and method for making same. In particular, embodiments of the present invention relate to films and method for making same that comprise blends of styrene block copolymers and hydrogenated resins.

**[0003]** Styrenic block polymers are frequently used in elastomeric films for hygiene and personal care applications where highly elastic properties are required. Being thermoplastic elastomers, stryenic block polymers do not require cross-linking to develop strength. They may be free of the taste, odor and nitrosamines that often accompany conventional rubber vulcanizates.

**[0004]** There is a need, therefore, for improving the processability of the styrenic block copolymer without adversely affecting the performance of the styrenic block copolymer composition.

## SUMMARY

**[0005]** Films and methods for making the same are provided. The film can include at least one rubber component and at least one hydrogenated resin. In at least one specific embodiment, the film can include: at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%, and at least one hydrogenated resin having a MWD of from about 1.5 to about 3.5.

**[0006]** In at least one other specific embodiment, the film can include: at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%; and at least one hydrogenated resin having a MWD of from about 1.5 to about 3.0.

**[0007]** In at least one other specific embodiment, the film can include: of from 5 wt.% to 95 wt.% at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%; and of from 5 wt.% to 20 wt.% of at least one hydrogenated resin having a MWD of from about 1.5 to about 3.0.

## DETAILED DESCRIPTION

**[0008]** Each of the appended claims defines a separate invention, which for infringement purposes is recognized as including equivalents to the various elements or limitations specified in the claims. Depending on the context, all references below to the "invention" may in some cases refer to certain specific embodiments only. In other cases it will be recognized that references to the "invention" will refer to subject matter recited in one or more, but not necessarily all, of the claims. Each of the inventions will now be described in greater detail below, including specific embodiments, versions and examples, but the inventions are not limited to these embodiments, versions or examples, which are included to enable a person having ordinary skill in the art to make and use the inventions, when the information in this patent is combined with available information and technology.

Rubber Component

**[0009]** The rubber component can be or include any one or more block copolymers. Block copolymers generally include a thermoplastic block portion A and an elastomeric block portion B. Block copolymers are elastomeric in the sense that they generally form a three-dimensional physical crosslinked or entangled structure below the glass transition temperature ($T_g$) of the thermoplastic block portion, and because they exhibit elastic memories in response to external forces. Block copolymers are thermoplastic in the sense that they can be melted above the endblock $T_g$, formed, and resolidified several times with little or no change in physical properties, assuming minimum oxidative degradation. Illustrative block copolymers include linear block copolymers, A-B diblock copolymers, A-B-A triblock copolymers, A-B-A-B tetrablock copolymers, A-B-A-B-A pentablock copolymers, and the like.

**[0010]** The block portion A may be derived from materials which have a sufficiently high glass transition temperature to form crystalline or glassy domains at the use temperature of the polymer. The A-block may thus be regarded as a hard rock. Such hard blocks generally form strong physical entanglements or agglomerates with other hard blocks in the copolymers. The hard block portion A may be a polyvinylarene derived from monomers such as styrene, alpha-methyl styrene, other styrene derivates, or mixtures thereof. The block portion A may also be a copolymer derived from styrenic monomers and olefinic monomers such as ethylene, propylene, butylene, isoprene, butadiene, and mixtures thereof.

**[0011]** In one or more embodiments, the block portion A is polystyrene, having a number-average molecular weight between from about 1,000 to about 200,000, preferably

from about 2,000 to about 100,000, more preferably from about 5,000 to about 60,000. The block portion A may be present in amount of from about 10% to about 80%, preferably from about 20% to about 50%, more preferably from about 25 to about 35% of the total weight of the copolymer.

**[0012]** The material forming the B-block preferably has a sufficiently low glass transition temperature at the use temperature of the polymer such that crystalline or glassy domains are not formed at these working temperatures. The B-block may thus be regarded as a soft block. The soft block portion B is preferably an olefinic polymer derived from conjugated aliphatic diene monomers of from about 4 to about 6 carbon atoms or linear alkene monomers of from about 2 to about 6 carbon atoms. Suitable diene monomers include butadiene, isoprene, and the like. Suitable alkene monomers include ethylene, propylene, butylene, and the like. In one or more embodiments, the soft block portion B includes a substantially amorphous polyolefin such as ethylene/propylene polymers, ethylene/butylene polymers, polyisoprene, polybutadiene, and the like or mixtures thereof. The number-average molecular weight of the soft block B is typically from about 1,000 to about 300,000, preferably from about 10,000 to about 200,000, and more preferably from about 20,000 to about 100,000. The soft block portion B may be present in the amount of from about 20% to about 90%, preferably from about 50% to about 80%, more preferably from about 65% to about 75% of the total weight of the copolymer.

**[0013]** In one or more embodiments, the B-block may represent at least about 50 wt.% of the total weight of the block copolymer. The unsaturation in olefinic double bonds may be selectively hydrogenated to reduce sensitivity to oxidative degradation and may have beneficial effects on the elastomeric properties. For example, a polyisoprene block can be selectively reduced to form an ethylene-propylene block. In one or more embodiments, the vinylarene block typically comprises at least about 10 percent by weight of the block copolymer. However, higher vinylarene contents may be selected for high elastic and low stress relaxation properties.

**[0014]** In one or more embodiments, the block copolymer is a triblock copolymer having an elastomeric midblock B and thermoplastic endblocks A and A', wherein A and A' may be derived from different vinylarene monomers. In one or more embodiments, the block copolymer has more than one A block and/or more than one B block, wherein each A block may be derived from the same or different vinylarene monomers and each B block may be derived from the same or different olefinic monomers.

**[0015]** In one or more embodiments, the block copolymer is radial, having three or more arms, each arm being an B-A, B-A-B-A, or the like type copolymer and the B blocks being at or near the center portion of the radial polymer. In other embodiments, the block copolymer may have four, five, or six arms.

**[0016]** Preferably, the block copolymer is or includes a styrenic block copolymer ("SBC"). Illustrative SBCs include, but are not limited to, styrene-olefin-styrene triblock copolymers such as styrene-butadiene-styrene (S-B-S), styrene-ethylene/butylene-styrene (S-EB-S), styrene-ethylene/propylene-styrene (S-EP-S), styrene-isoprene-styrene (S-I-S), hydrogenated polystyrene-isoprenelbutadiene-styrene (S-IB-S), derivatives thereof, and blends thereof. Typical styrenic block copolymers that are useful are Vector™ 4111A, 4211, 4411A, 8508 and 8508A commercially available from Dexco Polymer L.P.

**[0017]** In one or more embodiments, the SBC can contain of from 10 wt.% to 49 wt.% styrene. The SBC can have a styrene content of from 15wt.% to 49 wt.%. In one or more embodiments, the styrene content can range from a low of about 10 wt.%, 15 wt.%, or 20 wt.% to a high of about 30 wt.%, 40 wt.%, or 45 wt.%. In one or more embodiments, the styrene content can be of from 15 wt.% to 47 wt.%; 18 wt.% to 47 wt.%; 29 wt.% to 47 wt.%; 30 wt.% to 47 wt.%; or 44 wt.% to 47 wt.%.

**[0018]** In one or more embodiments, the SBC can have a Shore A hardness (ASTM D2240) of from 20 to 150. The Shore A hardness can also range from a low of about 20, 25, or 30 to a high of about 65, 75, or 90. In one or more embodiments, the Shore A hardness can range from a low of about 39, 49 or 59 to a high of about 69, 79, or 89. In one or more embodiments, the Shore A hardness can be of from 39 to 87; 39 to 65; or 39 to 62.

**[0019]** In one or more embodiments, the SBC can have a melt flow rate ("MFR") at 190°C/2.16 kg of from 2.0 g/10min to about 10.0 g/10 min. The MFR can also range from a low of about 2.0, 2.2, or 2.4 g/10min to a high of about 5.0, 6.0 or 7.0 g/10min. In one or more embodiments, the MFR can be of from 3.4 g/10 min to 6.6 g/10 min; 3.4 g/10 min to 4.0 g/10 min; or 3.4 g/10 min to 3.9 g/10 min. In one or more embodiments, the MFR can be about 3.0 g/10 min; about 3.5 g/10 min; about 4.0 g/10 min; about 4.5 g/10 min; about 5.0 g/10 min; about 5.5 g/10 min; about 6.0 g/10 min; about 6.5 g/10 min; or about 7.0 g/10 min.

**[0020]** In one or more embodiments, the SBC is a triblock copolymer having substantially no diblock content wherein "substantially no diblock content" is defined as having less than 1 wt % diblock content. Preferably, the diblock content can be less than 0.5

wt.%. Linear block content such as diblock content is measured by gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC).

Hydrocarbon Resin

**[0021]** The hydrocarbon resin ("HCR") can be derived from petroleum, and may be hydrogenated or non-hydrogenated resins. Useful hydrocarbon resins include, but are not limited to, aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, aliphatic/aromatic resins, polycyclic resins, hydrogenated polycyclic resins, hydrogenated polycyclic aromatic resins, hydrogenated aromatic resins in which a substantial portion of the benzene rings are converted to cyclohexane rings, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, and combinations thereof.

**[0022]** In one or more embodiments, the hydrocarbon resin contains one or more petroleum resins, terpene resins, styrene resins, and/or cyclopentadiene resins. In one or more embodiments, the hydrocarbon resin can be selected from the group consisting of aliphatic hydrocarbon resins, hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, hydrogenated aliphatic aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, hydrogenated cycloaliphatic/aromatic hydrocarbon resins, hydrogenated aromatic hydrocarbon resins, polyterpene resins, terpene-phenol resins, rosins and rosin esters, hydrogenated rosins and rosin esters, and combinations thereof. Preferred aliphatic olefins are $C_4$ to $C_{20}$, preferably $C_4$ to $C_7$, even more preferably $C_5$ to $C_6$, linear, branched, or alicyclic olefins or non-conjugated diolefins. Preferred aromatic olefins include one or more of styrene, indene, derivatives of styrene and derivatives of indene. Particularly preferred aromatic olefins include styrene, alpha-methylstyrene, beta-methylstyrene, indene and methylindenes, and vinyl toluenes. In preferred embodiments, the HCR comprises monomers derived from piperylene, isoprene, amylene, cyclics, styrene, indene, or combinations thereof.

**[0023]** The hydrocarbon resin may include one or more styrenic components, such as styrene, derivatives of styrene, and substituted styrenes. In general, styrenic components do not include fused-rings, such as indene. The hydrocarbon resin may include one or more indenic components, such as indene and derivatives of indene. In some embodiments, the styrenic component may have a lowering effect on the HCR's softening point. Other aromatics (especially indenics) may tend to increase the HCR's softening point. In other

embodiments, the hydrocarbon resin may include cyclopentadiene (CPD) and di-cyclopentadiene (DCPD) which have a broadening effect on molecular weight distribution and tend to increase the HCR's softening point.

**[0024]** The hydrocarbon resin may be produced by methods generally known in the art for the production of hydrocarbon resins. See for example, the Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., Vol. 13, pp. 717-744. For example, in some embodiments, the hydrocarbon resin is produced by thermal polymerization, while in other embodiments the hydrocarbon resin may be produced by catalytic polymerization. The polymerization and stripping conditions may be adjusted according to the nature of the feed to obtain the desired resin.

**[0025]** In one or more embodiments, the hydrocarbon resin may be prepared by thermal polymerization. For example, the resin may be thermally polymerized from a feed containing cyclopentadiene in a benzene or toluene solvent for 2.0 to 4.0 hours at 220°C to 280°C and about 14 bars pressure, with conditions being adjusted to control the molecular weight and softening point of the resin. The feed may further contain alkyl cyclopentadienes, dimers and codimers of cyclopentadiene and methylcyclopentadiene, and other acyclic dienes such as 1,3-piperylene and isoprene. Other copolymerizable unsaturated monomers such as vinyl aromatics including styrene, α-methylstyrene, indene, and vinyl toluene may also be present.

**[0026]** In one or more embodiments, the hydrocarbon resin may be catalytically polymerized. A preferred method for production of the resins is combining the feed stream in a polymerization reactor with a Friedel-Crafts or Lewis Acid catalyst at a temperature between 0°C and 200°C, preferably between 20°C and 80 °C. Friedel-Crafts polymerization is generally accomplished by use of known catalysts in a polymerization solvent, and removal of solvent and catalyst by washing and distillation. The polymerization process may be in a batchwise or continuous mode, continuous polymerization may be in a single stage or in multiple stages. The Friedel-Crafts catalysts to be used are generally Lewis Acids such as boron trifluoride ($BF_3$), complexes of boron trifluoride ($BF_3$), aluminum trichloride ($AlCl_3$), or alkyl-aluminum halides, particularly chloride. The amount of Lewis Acid to be used in the catalyst is in the range of from 0.3 to 3.0 wt.%, based upon the weight of the feed blend, preferably 0.5 to 1.0 wt.%. The aluminum trichloride catalyst is preferably used as a powder.

**[0027]** In a preferred embodiment, the resins may be hydrogenated. Any known process for catalytically hydrogenating hydrocarbon resins may be used to hydrogenate the resin. The hydrogenation of hydrocarbon resins may be carried out via molten or solution based

processes by either a batchwise or, more commonly, a continuous process. Catalysts employed for the hydrogenation of hydrocarbon resins are typically supported monometallic and bimetallic catalyst systems. The catalysts which may be used may include Group VIII metals such as nickel, palladium, ruthenium, rhodium, cobalt, and platinum, Group VI metals such as tungsten, chromium, and molybdenum, Group VII metals such as rhenium, manganese, and copper, other catalysts may be based on group 9, 10, or 11 elements. These metals maybe used singularly or in combination of two or more metals, in the metallic form or in an activated form and may be used directly or carried on a solid support such as alumina or silica-alumina. The support material is typically comprised of such porous inorganic refractory oxides such as silica, magnesia, silica-magnesia, zirconia, silica-zirconia, titanic silica-titania, alumina, silica-aluminun alumino-silicate, etc. Preferably, the supports are essentially free of crystalline molecular sieve materials. Mixtures of the foregoing oxides are also contemplated, especially when prepared as homogeneously as possible. Preferred supports include alumina, silica, carbon, MgO, $TiO_2$, $ZrO_2$, $FeO_3$, or mixtures thereof.

**[0028]** The hydrocarbon resin can have a number average molecular weight less than 5000, preferably less than 2000, most preferably in the range of from 500 to 1000. Preferably, the hydrocarbon resin has a softening point in the range of from 60°C to 180°C. The hydrocarbon resin preferably has a ring and ball softening point of 10 °C to 140 °C, more preferably 80°C to 120°C. In one or more embodiments, the hydrocarbon resin has a weight average molecular weight (Mw) of 4000 or less, preferably between 500 and 4000, preferably from 500 to 2500. In one or more embodiments, the hydrocarbon resin has a Mw/Mn of 3 or less, preferably between 1 and 2.4, or more preferably between 1 and 2. In one or more embodiments, the hydrocarbon resin has a Mw/Mn of between about 1.5 and about or between about 1.5 to about 3.5.

**[0029]** In at least one specific embodiment, the hydrocarbon resin can include 50-90 wt.% piperylene, 0-5 wt.% isoprene, 10-30 wt.% amylene, 0-5 wt.% cyclics, 0-10 wt.% styrenic components, and 0-10 wt.% indenic components. The resin may have a melt viscosity at 160°C of from 375 cPs to 515 cPs, a Mn of 700-900 g/mole, a Mw of 1400-1800 g/mole, a Mz of 3000-5000 g/mole, and a Tg of 45°C to 50°C.

**[0030]** In at least one other specific embodiment, the hydrocarbon resin can include 60-90 wt.% piperylene, 0-5 wt.% isoprene, 0-10 wt.% amylene, 5-15 wt.% cyclics, 5-20 wt.% styrenic components, and 0-5 wt.% indenic components. The hydrocarbon resin may have a

melt viscosity at 160 °C of from 375 cPs to 615 cPs, a Mn of 520-650 g/mole, a Mw of 1725-1890 g/mole, a Mz of 6000-8200 g/mole, and a Tg of 48 °C to 53 °C.

**[0031]** In at least one other specific embodiment, the hydrocarbon resin can include dicyclopentadiene and methyl substituted dicyclopentadiene. The hydrocarbon resin can have a softening point of from about 115 to 130°C, a Tg of about 70°C, a Mn of about 410 g/mole, a Mw of about 630 g/mole, and a Mz of about 1020 g/mole.

**[0032]** Commercially available hydrocarbon resins that are suitable herein include Oppera™ series of polymeric additives from ExxonMobil Chemical Company; ARKON™ M90, M100, M115 andM135 and SUPER ESTER™ rosin esters (commercially available from Arakawa Chemical Company of Japan); SYLVARES™ phenol modified styrene, methyl styrene resins, styrenated terpene resins, ZONATAC™ terpene-aromatic resins, and terpene phenolic resins (commercially available from Arizona Chemical Company of Jacksonville, FL); SYLVATAC™ and SYLVALITE™ rosin esters (commercially available from Arizona Chemical Company of Jacksonville, FL); NORSOLENE™ aliphatic aromatic resins (commercially available from Cray Valley of France); DERTOPHENE™ terpene phenolic resins (commercially available from DRT Chemical Company of Landes, France); EASTOTAC™ resins, PICCOTAC™ $C_5/C_9$ resins, REGALITE™ and REGALREZ™ aromatic and REGALITE™ cycloaliphatic/aromatic resins (commercially available from Eastman Chemical Company of Kingsport, TN); WINGTACK™ ET and EXTRA™ (commercially available from Sartomer of Exton, PA); FORAL™, PENTALYN™, and PERMALYN™ rosins and rosin esters (commercially available from Hercules, now Eastman Chemical Company of Kingsport, TN); QUINTONE™ acid modified $C_5$ resins, $C_5/C_9$ resins, and acid modified $C_5/C_9$ resins (commercially available from Nippon Zeon of Japan); and LX™ mixed aromatic/cycloaliphatic resins (commercially available from Neville Chemical Company of Pittsburgh, PA); CLEARON™ hydrogenated terpene aromatic resins (commercially available from Yasuhara of Japan); and PICCOLYTE™ (commercially available from Loos & Dilworth, Inc. of Bristol, PA). Other suitable hydrocarbon resins can be found in U.S. Patent 5,667,902, incorporated herein by reference. The preceding examples are illustrative only and by no means limiting.

**[0033]** In at least one other specific embodiment, the hydrocarbon resin can be or include saturated alicyclic resins. Such resins, if used, can have a softening point in the range of from 85 to 140°C, or preferably in the range of 100°C to 140°C, as measured by the ring and ball technique. Examples of suitable, commercially available saturated alicyclic resins are

ARKON-P® (commercially available from Arakawa Forest Chemical Industries, Ltd., of Japan).

**[0034]** Preferred hydrocarbon resins are hydrocarbon polymer additives ("HPA"). "Hydrocarbon Polymer Additives" as used herein are complex copolymers that include monomers derived from piperylene, isoprene, amylenes, cyclics, styrene, indenic, or combinations thereof. Hydrocarbon polymer additives are polar or non-polar. "Non-polar" means the hydrocarbon polymer additive is substantially free of monomers having polar groups.

**[0035]** The properties of hydrocarbon polymer additives are manipulated by controlling the copolymer microstructure, i.e., type and amount of monomers. Monomer placement in the polymer chain is random leading to further complexity in the polymer microstructure. Differences in the hydrocarbon polymer additives are largely due to the olefins in the feedstock from which the hydrocarbon components are derived. Hydrocarbon polymer additives may contain aliphatic hydrocarbon components which have a hydrocarbon chain formed from $C_4$ – $C_6$ fractions containing variable quantities of piperylene, isoprene, mono-olefins, and non-polymerizable paraffinic compounds. Such hydrocarbon polymer additives are based on pentene, butane, isoprene, piperylene, and contain reduced quantities of cyclopentadiene or dicyclopentadiene. Hydrocarbon polymer additives may also contain aromatic hydrocarbon structures having polymeric chains which are formed of aromatic units, such as styrene, xylene, α-methylstyrene, vinyl toluene, and indene.

**[0036]** Piperylenes are generally a distillate cut or synthetic mixture of $C_5$ diolefins, which include, but are not limited to, cis-1,3-pentadiene, trans-1,3-pentadiene, and mixed 1,3-pentadiene. In general, piperylenes do not include branched $C_5$ diolefins such as isoprene. In one embodiment, hydrocarbon polymer additives have from 40 to 90 wt.% piperylene, or from 50 to 90 wt.%, or more preferably from 60 to 90 wt.% piperylene, based on the weight of the hydrocarbon polymer additive. In a particularly preferred embodiment, hydrocarbon polymer additives are from 70 to 90 wt.% piperylene.

**[0037]** Cyclics are generally a distillate cut or synthetic mixture of $C_5$ and $C_6$ cyclic olefins, diolefins, and dimers therefrom. Cyclics include, but are not limited to, cyclopentene, cyclopentadiene, dicyclopentadiene, cyclohexene, 1,3-cycylohexadiene, and 1,4-cyclohexadiene. A preferred cyclic is cyclopentadiene. Dicyclopentadiene may be in either the endo or exo form. The cyclics may or may not be substituted. Preferred

substituted cyclics include cyclopentadienes and dicyclopentadienes substituted with a $C_1$ to $C_{40}$ linear, branched, or cyclic alkyl group, preferably one or more methyl groups.

**[0038]** In one embodiment, hydrocarbon polymer additives include up to 60 wt.% cyclics or up to 50 wt.% cyclics. Hydrocarbon polymer additives include at least about 0.1 wt.% cyclics, at least about 0.5 wt.% cyclics, or from about 1.0 wt.% cyclics. In at least one embodiment, hydrocarbon polymer additives include up to 20 wt.% cyclics or more preferably up to 30 wt.% cyclics. In a particularly preferred embodiments, hydrocarbon polymer additives comprises from about 1.0 to about 15 wt.% cyclics, or from about 5 to about 15 wt.% cyclics.

**[0039]** Hydrocarbon polymer additives optionally include isoprene. In some embodiments, hydrocarbon polymer additives are substantially free of isoprene, or may contain up to 5 wt.% isoprene, or more preferably up to 10 wt.% isoprene. In yet another embodiment, hydrocarbon polymer additives contain up to 15 wt.% isoprene.

**[0040]** Hydrocarbon polymer additives optionally include amylene. In some embodiments, hydrocarbon polymer additives are substantially free of isoprene, or may contain up to 10 wt.% amylene, or up to 25 wt.% amylene, or more preferably up to 30 wt.% amylene. In yet another embodiment, hydrocarbon polymer additives contain up to 40 wt.% amylene.

**[0041]** Preferred aromatics that may be in hydrocarbon polymer additives include one or more of styrene, indene, derivatives of styrene, and derivatives of indene. Particularly preferred aromatic olefins include styrene, alpha-methylstyrene, beta-methylstyrene, indene, and methylindenes, and vinyl toluenes.

**[0042]** Aromatic olefins are typically present in hydrocarbon polymer additives from 5 to 45 wt.%, or more preferably from 5 to 30 wt.%. In preferred embodiments, hydrocarbon polymer additives comprises from 10 to 20 wt.% aromatic olefins.

**[0043]** Styrenic components include styrene, derivatives of styrene, and substituted sytrenes. In general, styrenic components do not include fused-rings, such as indenics. In one embodiment, hydrocarbon polymer additives are composed of up to 60 wt.% styrenic components or up to 50 wt.% styrenic components. In one embodiment, hydrocarbon polymer additives are composed of from 5 to 30 wt.% styrenic components, or from 5 to 20 wt.% styrenic components. In a preferred embodiment, hydrocarbon polymer additives are composed of from 10 to 15 wt.% styrenic components.

**[0044]** Hydrocarbon polymer additives may include up to 5 wt.% indenic components, or up to 10 wt.% indenic components. Indenic components include indene and derivatives of indene. In one embodiment, hydrocarbon polymer additives include up to 15 wt.% indenic components. In another embodiment, the HPA is substantially free of indenic components.

**[0045]** Preferred hydrocarbon polymer additives have a melt viscosity of from 300 to 800 centipoise (cPs) at 160°C, or more preferably of from 350 to 650 cPs at 160°C. In a particularly preferred embodiment, the melt viscosity of hydrocarbon polymer additives is from 375 to 615 cPs at 160°C, or from 475 to 600 cPs at 160°C. The melt viscosity may be measured by a Brookfield viscometer with a type "J" spindle according to ASTM D-6267.

**[0046]** Generally hydrocarbon polymer additives have a Mw greater than about 600 g/mole or greater than about 1000 g/mole. In at least one embodiment, hydrocarbon polymer additives have a Mw of from 1650 to 1950 g/mole, or from 1700 to 1900 g/mole. Preferably hydrocarbon polymer additives have a weight average molecular weight of from 1725 to 1890 g/mole. Hydrocarbon polymer additives may have a Mn of from 450 to 700 g/mole, or from 500 to 675 g/mole, or more preferably from 520 to 650 g/mole. Hydrocarbon polymer additives may have a Mz of from 5850 to 8150 g/mole, or more preferably from 6000 to 8000 g/mole. Mw, Mn, and Mz may be determined by gel permeation chromatography (GPC).

**[0047]** In one embodiment hydrocarbon polymer additives have a polydispersion index ("PDI", PDI = Mw/Mn) of 4 or less. In a particularly preferred embodiment hydrocarbon polymer additives have a PDI of from 2.6 to 3.1.

**[0048]** Preferred hydrocarbon polymer additives have a glass transition temperature (Tg) of from about -30°C to about 200°C, or from about 0°C to 150°C, or from about 50°C to 160°C, or from about 50°C to 150°C, or from about 50°C to 140°C. In other embodiments, hydrogen polymer additives have a Tg of from about 0°C to 80°C, or from about 40-60°C, or from 45-55°C, or more preferably of from 48-53°C. Differential scanning calorimetry (DSC) is used to determine glass transition temperature.

**[0049]** Table A identifies ranges for preferred monomer combinations. The structures shown in Table A are representative only and not limiting. Typical physical and chemical properties of these exemplary hydrocarbon polymer additives are identified in Table B.

TABLE A

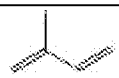
| | Exemplary HPA 1 | Exemplary HPA 2 | Representative Structure |
|---|---|---|---|
| %-Piperylene (P) | 50-90 | 60-90 |  |
| %-Isoprene (I) | 0-5 | 0-5 |  |
| %-Amylenes (A) | 10-30 | 0-10 |  |
| %-Cyclics (C) | 0-5 | 5-15 |  |
| %-Styrenic (St) | 0-10 | 5-20 |  |
| %-Indenic (In) | 0-10 | 0-5 |  |

TABLE B

| | Melt Viscosity at 160°C (cPs) | Mn (g/mole) | Mw (g/mole) | Mz (g/mole) | PDI | Tg °C |
|---|---|---|---|---|---|---|
| Exemplary HPA 1 | 375-515 | 700-900 | 1400-1800 | 3000-5000 | 1.5-2.5 | 45-50 |
| Exemplary HPA 2 | 375-615 | 520-650 | 1725-1890 | 6000-8200 | 2.6-3.1 | 48-53 |

**[0050]** Exemplary hydrocarbon polymer additives are commercially available as the Oppera™ series of polymeric additives from ExxonMobil Chemical Company.

POLYOLEFINIC THERMOPLASTIC RESIN

**[0051]** In one or more embodiments above or elsewhere herein, the hydrocarbon resin can include one or more polyolefins and/or polyolefinic thermoplastic resins. The terms "polyolefinic thermoplastic resin" and "polyolefin" as used herein refers to any material that is not a "rubber" and that is a polymer or polymer blend having a melting point of 70°C or more and considered by persons skilled in the art as being thermoplastic in nature, e.g., a polymer that softens when exposed to heat and returns to its original condition when cooled to room temperature. The polyolefinic thermoplastic resin can contain one or more polyolefins, including polyolefin homopolymers and polyolefin copolymers. Except as stated otherwise, the term "copolymer" means a polymer derived from two or more monomers

(including terpolymers, tetrapolymers, etc.), and the term "polymer" refers to any carbon-containing compound having repeat units from one or more different monomers.

**[0052]** Illustrative polyolefins can be prepared from mono-olefin monomers including, but are not limited to, monomers having 2 to 7 carbon atoms, such as ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 1-octene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, mixtures thereof and copolymers thereof with (meth)acrylates and/or vinyl acetates. Preferably, the polyolefinic thermoplastic resin component is unvulcanized or non crosslinked.

**[0053]** In one or more embodiments, the polyolefinic thermoplastic resin contains polypropylene. The term "polypropylene" as used herein broadly means any polymer that is considered a "polypropylene" by persons skilled in the art (as reflected in at least one patent or publication), and includes homo, impact, and random polymers of propylene. Preferably, the polypropylene used in the compositions described herein has a melting point above 110°C, includes at least 90 wt % propylene units, and contains isotactic sequences of those units. The polypropylene can also include atactic sequences or s syndiotactic sequences, or both. The polypropylene can also include essentially syndiotactic sequences such that the melting point of the polypropylene is above 110°C. The polypropylene can either derive exclusively from propylene monomers (i.e., having only propylene units) or derive from mainly propylene (more than 80% propylene) with the remainder derived from olefins, particularly ethylene, and/or $C_4$-$C_{10}$ alpha-olefins. As noted elsewhere herein, certain polypropylenes have a high MFR (e.g., from a low of 10, or 15, or 20 g/10 min to a high of 25 to 30 g/10 min. Others have a lower MFR, e.g., "fractional" polypropylenes which have an MFR less than 1.0. Those with high MFR can be preferred for ease of processing or compounding.

**[0054]** In one or more embodiments, the polyolefinic thermoplastic resin is or includes isotactic polypropylene. Preferably, the polyolefinic thermoplastic resin contains one or more crystalline propylene homopolymers or copolymers of propylene having a melting temperature greater than 105°C as measured by DSC. Preferred copolymers of propylene include, but are not limited to, terpolymers of propylene, impact copolymers of propylene, random polypropylene and mixtures thereof. Preferred comonomers have 2 carbon atoms, or from 4 to 12 carbon atoms. Preferably, the comonomer is ethylene. Such polyolefinic thermoplastic resin and methods for making the same are described in U.S. Pat. No. 6,342,565.

**[0055]** The term "random polypropylene" as used herein broadly means a copolymer of propylene having up to 9 wt %, preferably 2 wt % to 8 wt % of an alpha olefin comonomer. Preferred alpha olefin comonomers have 2 carbon atoms, or from 4 to 12 carbon atoms. Preferably, the alpha olefin comonomer is ethylene.

**[0056]** In one or more embodiments, the random polypropylene has a 1% secant modulus of about 100 kPsi to about 200 kPsi, as measured according to ASTM D790A. In one or more embodiments, the 1% secant modulus can be 140 kPsi to 170 kPsi, as measured according to ASTM D790A. In one or more embodiments, the 1% secant modulus can be 140 kPsi to 160 kPsi, as measured according to ASTM D790A. In one or more embodiments, the 1% secant modulus can range from a low of about 100, 110, or 125 kPsi to a high of about 145, 160, or 175 kPsi, as measured according to ASTM D790A.

**[0057]** In one or more embodiments, the random polypropylene can have a density of about 0.85 to about 0.95 g/cc, as measured by ASTM D792. In one or more embodiments, the random polypropylene can have a density of about 0.89 g/cc to 0.92 g/cc, as measured by ASTM D792. In one or more embodiments, the density can range from a low of about 0.85, 0.87, or 0.89 g/cc to a high of about 0.90, 0.91, 0.92 g/cc, as measured by ASTM D792.

**[0058]** In one or more embodiments, a blend of the one or more hydrocarbon resins and the one or more polyolefinic thermoplastic resins can have a glass transition temperature (Tg) of from 50°C to 120°C. The blend can also have a glass transition temperature ranging from a low of about 20°C, 30°C, or 40°C to a high of about 90°C, 100°C, or 120°C. In one or more embodiments, the blend can have a glass transition temperature ranging from a low of about 25°C, 35°C, or 45°C to a high of about 95°C, 105°C, or 115°C. In one or more embodiments, the blend can have a glass transition temperature of from 35°C to 90°C, 70°C to 90°C ; or 75°C to 90°C.

**[0059]** In one or more embodiments, a blend of the one or more hydrocarbon resins and the one or more polyolefinic thermoplastic resins can have a number average molecular weight (Mn) of from about 50 to about 1,000. The Mn of the blend can range from a low of about 50, 75, or 100 to a high of about 300, 400, or 500. The Mn of the blend can also range from a low of about 50, 100, or 150 to a high of about 300, 500, or 750.

**[0060]** In one or more embodiments, a blend of the one or more hydrocarbon resins and the one or more polyolefinic thermoplastic resins can have a weight average molecular weight (Mw) of from about 300 to about 1,000. The Mw of the blend can range from a low

of about 300, 375, or 390 to a high of about 400, 430, or 480. The Mw of the blend can also range from a low of about 180, 190, or 200 to a high of about 280, 300, or 320.

**[0061]** In one or more embodiments, a blend of the one or more hydrocarbon resins and the one or more polyolefinic thermoplastic resins can have a Mz of from about 500 to about 2,000. The Mz of the blend can range from a low of about 500, 600, or 700 to a high of about 1250, 1500, or 1750. The Mz of the blend can also range from a low of about 750, 800, or 850 to a high of about 900, 950, or 1000.

**[0062]** In one or more embodiments, a blend of the one or more hydrocarbon resins and the one or more polyolefinic thermoplastic resins can have a polydispersity index (PDI) or molecular weight distribution (Mw/Mn) or simply "MWD" of from about 1.0 to about 5.0. The MWD of the blend can range from a low of about 1.1, 1.4, or 1.6 to a high of about 2.0, 2.5, or 3.0. The MWD of the blend can also range from a low of about 1.3, 1.6, or 1.9 to a high of about 2.0, 2.3, or 2.6.

**[0063]** In one or more embodiments, a blend of the one or more hydrocarbon resins and the one or more polyolefinic thermoplastic resins can have a melt viscosity of from about 2,000 to about 10,000 at 160°C. The melt viscosity of the blend can range from a low of about 2,500, 3,000, or 3,500 to a high of about 4,000, 5,000, or 7,000 at 160°C. The melt viscosity of the blend can also range from a low of about 3,400, 3,800, or 4,200 to a high of about 4,800, 5,200, or 5,600 at 160°C. In one or more embodiments, the melt viscosity of the blend can range from a low of about 200, 300, or 400 to a high of about 500, 700, or 1,000 at 140°C. The melt viscosity of the blend can also range from a low of about 400, 550, or 700 to a high of about 750, 950, or 1,200 at 140°C.

**[0064]** In one or more embodiments, a blend of the one or more hydrocarbon resins and the one or more polyolefinic thermoplastic resins can contain of from 1 wt.% to 99 wt.% hydrocarbon resin and 99 wt.% to 1 wt.% polyolefinic thermoplastic resin. In one or more embodiments, the blend can contain 5 wt.% to 90 wt.%; 5 wt.% to 80 wt.%; 5 wt.% to 70 wt.%; 5 wt.% to 60 wt.%; 5 wt.% to 50 wt.%; 5 wt.% to 40 wt.%; 5 wt.% to 30 wt.%; 5 wt.% to 20 wt.%; 5 wt.% to 10 wt.%; 20 wt.% to 80 wt.% polyolefinic thermoplastic resin. In one or more embodiments, the blend can contain of from 30 wt.% to 70 wt.%; 30 wt.% to 65 wt.%; 30 wt.% to 60 wt.%; 30 wt.% to 55 wt.%; or 30 wt.% to 50 wt.% polyolefinic thermoplastic resin. In one or more embodiments, the blend can contain one or more polyolefinic thermoplastic resins in an amount ranging from a low of about 10 wt.%, 15 wt.%, or 25 wt.% to a high of about 40 wt.%, 50 wt.%, or 60 wt.%. In one or more

embodiments, the blend can contain 5 wt.% to 90 wt.%; 5 wt.% to 80 wt.%; 5 wt.% to 70 wt.%; 5 wt.% to 60 wt.%; 5 wt.% to 50 wt.%; 5 wt.% to 40 wt.%; 5 wt.% to 30 wt.%; 5 wt.% to 20 wt.%; 5 wt.% to 10 wt.%; 20 wt.% to 80 wt.% hydrocarbon resin. In one or more embodiments, the blend can contain of from 30 wt.% to 70 wt.%; 30 wt.% to 65 wt.%; 30 wt.% to 60 wt.%; 30 wt.% to 55 wt.%; or 30 wt.% to 50 wt.% hydrocarbon resin. In one or more embodiments, the blend can contain one or more hydrocarbon resins in an amount ranging from a low of about 10 wt.%, 15 wt.%, or 25 wt.% to a high of about 40 wt.%, 50 wt.%, or 60 wt.%.

**ADDITIVES**

**[0065]** The film may further include one or more additives. Illustrative additives include, but are not limited, to particulate fillers, lubricants, antioxidants, antiblocking agents, stabilizers, anti-degradants, anti-static agents, waxes, foaming agents, pigments, flame retardants, processing aids, adhesives, tackifiers, plasticizers, wax, and discontinuous fibers (such as world cellulose fibers). Exemplary particulate fillers are carbon black, silica, titanium dioxide, calcium carbonate, colored pigments, clay, and combinations thereof. When non-black fillers are used, it may be desirable to include a coupling agent to compatibilize the interface between the non-black fillers and polymers. Desirable amounts of carbon black, or other colorants, when present, are from about 5 to about 250 parts by weight per 100 parts by weight of rubber.

**[0066]** In one or more embodiments, the film can include of from 5 wt.% to 95% one or more rubber components and of from 95 wt.% to 5 wt.% a blend of one or more hydrocarbon resins and one or more polyolefinic thermoplastic resins. In one or more embodiments, the film can include of from 5 wt.% to 75% one or more rubber components and of from 5 wt.% to 25 wt.% a blend of one or more hydrocarbon resins and one or more polyolefinic thermoplastic resins. In one or more embodiments, the film can include of from 15 wt.% to 75% one or more rubber components and of from 5 wt.% to 20 wt.% a blend of one or more hydrocarbon resins and one or more polyolefinic thermoplastic resins. In one or more embodiments, the one or more rubber components can be present in an amount ranging from a low of about 20 wt.%, 30 wt.% or 40 wt.% to a high of about 60 wt.%, 70 wt.%, or 80 wt.%, based on the total weight of the composition. In one or more embodiments, a blend of the one or more hydrocarbon resins and one or more polyolefinic thermoplastic resins can be present in an amount ranging from a low of about 5 wt.%, 10 wt.% or 15 wt.% to a high of about 18 wt.%, 25 wt.%, or 35 wt.%, based on the total weight of the composition.

**[0067]** In one or more embodiments, the composition is composed of from 5 wt.% to 95 wt.% at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%; and from 5 wt.% to 20 wt.% a blend comprising 20 wt.% to 80 wt.% at least one hydrogenated resin having a MWD of from about 1.5 to about 3.0, and 80 wt.% to 20 wt.% at least one thermoplastic polyolefinic resin comprising at least 75 wt.% propylene derived units, wherein the blend has a glass transition temperature of from 35°C to about 95°C.

**[0068]** Provided are one or more embodiments:

A. An composition, comprising:

at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%; and

a blend comprising at least one hydrogenated resin having a MWD of from about 1.5 to about 3.0, and at least one thermoplastic polyolefinic resin comprising at least 75 wt.% propylene derived units, wherein the blend has a glass transition temperature of from 35°C to about 95°C.

B. The composition of embodiment A, wherein the styrenic block copolymer is non-hydrogenated.

C. The composition of embodiment A or B, wherein hydrogenated resin is present in an amount of about 5 wt.% or more, based on total weight of the composition.

D. The composition of embodiment A or B, wherein hydrogenated resin is present in an amount of from 5 wt.% to 20 wt.%, based on total weight of the composition.

E. The composition of any embodiment A-D, wherein the glass transition temperature of the blend is of from 35°C to about 90°C.

F. The composition of any embodiment A-D, wherein the glass transition temperature of the blend is of from 70°C to about 90°C.

G. The composition of any embodiment A-D, wherein the glass transition temperature of the blend is of from 75°C to about 90°C.

H. The composition of any embodiment A-G, wherein the hydrogenated resin comprises at least 10 wt.% aromatics, optionally at least 20 wt. % aromatics.

I. An composition, comprising:

at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%; and

a blend comprising 20 wt.% to 80 wt.% at least one hydrogenated resin having a MWD of from about 1.5 to about 3.0, and 80 wt.% to 20 wt.% at least one thermoplastic polyolefinic resin comprising at least 75 wt.% propylene derived units, wherein the blend has a glass transition temperature of from 35°C to about 95°C.

J. The composition of embodiment I, wherein the styrenic block copolymer is non-hydrogenated.

K. The composition of embodiment I or J, wherein hydrogenated resin is present in an amount of about 5 wt.% or more, based on total weight of the composition.

L. The composition of embodiment I or J, wherein hydrogenated resin is present in an amount of from 5 wt.% to 20 wt.%, based on total weight of the composition.

M. The composition of any of embodiments I or L, wherein the glass transition temperature of the blend is of from 35°C to about 90°C.

N. The composition of any of embodiments I or L, wherein the glass transition temperature of the blend is of from 70°C to about 90°C.

O. The composition of any of embodiments I or L, wherein the glass transition temperature of the blend is of from 75°C to about 90°C.

P. The composition of any of embodiments I or O, wherein the hydrogenated resin comprises at least 10 wt.% aromatics.

Q. An composition, comprising:

of from 5 wt.% to 95 wt.% at least one rubber component comprising at least one styrenic block copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.%; and

of from 5 wt.% to 20 wt.% a blend comprising 20 wt.% to 80 wt.% at least one hydrogenated resin having a MWD of from about 1.5 to about 3.0, and 80 wt.% to 20 wt.% at least one thermoplastic polyolefinic resin comprising at least 75 wt.% propylene derived units, wherein the blend has a glass transition temperature of from 35°C to about 95°C.

R. The composition of embodiment Q, wherein the glass transition temperature of the blend is of from 75°C to about 90°C.

S. The composition of embodiment Q or R, wherein the hydrogenated resin comprises at least 10 wt.% aromatics.

T. The composition of any of embodiments Q-S, wherein the rubber component is present in an amount of from 40 wt.% to 70 wt.%.

U. The composition of any of embodiments Q-T, wherein the hydrocarbon resin is a hydrocarbon polymer additive.

V. The composition of embodiment U, wherein the hydrocarbon polymer additive comprises comonomers of piperylene, isoprene, amylenes, cyclics, styrene, indenic, or combinations thereof.

W. The composition of embodiment U or V, wherein the hydrocarbon polymer additive comprises:

from 60 wt. % to 90 wt. % piperylene,

from 5 wt. % to 15 wt. % cyclic components, and

from 5 wt. % to 20 wt. % styrenic components.

X. The composition of embodiment U, wherein the hydrocarbon polymer additive comprises Exemplary HPA 1 from Table B.

Y. The composition of embodiment U, wherein the hydrocarbon polymer additive comprises Exemplary HPA 2 from Table B.

Z. A film comprising the composition of any of embodiments A-Y.

AA. An adhesive comprising the composition of any of the embodimenta A-Y.

EXAMPLES

**[0069]** The foregoing discussion can be further described with reference to the following non-limiting examples. The Examples provided below illustrate the surprising and unexpected increase in melt flow rate ("MFR") in addition to the surprising and unexpected decrease in hardness when a hydrocarbon resin ("HC resin") was added to a styrenic block copolymer ("SBC") according to one or more embodiments described herein.

**[0070]** Table 1A summarizes the SBC components and Table 1B summarizes the HC resins used in each example.

Table 1A: Rubber Component Physical Properties

| | % Styrene | Shore A | MFR |
|---|---|---|---|
| Vector 4111A (SIS) | 18 | 39 | 3.9 |
| Vector 4211A (SIS) | 30 | 62 | 4.0 |
| Vector 4411A (SIS) | 44 | 87 | 6.6 |
| Vector 8508A (SBS) | 29 | 65 | 3.4 |

Table 1B: Hydrogenated Resin Physical Properties

| HC Resin | %Aromatic | Tg (°C) | Molecular Weight (g/mol) | | | | Melt Viscosity | |
|---|---|---|---|---|---|---|---|---|
| | | | Mn | Mw | Mz | PDI | cP | Temp (°C) |
| Oppera PR100A | 0 | 90 | 299 | 477 | 841 | 1.6 | 5,200 | 160 |
| Oppera PR103 | 0 | 75 | 190 | 430 | 950 | 2.3 | 5,000 | 160 |
| Oppera PR106 | 0 | 35 | 190 | 370 | 800 | 1.9 | 700 | 140 |
| Oppera PR113 | 10 | 70 | 310 | 500 | 1,000 | 1.6 | 3,400 | 160 |

**[0071]** The HC resin melt viscosity reported in Table 1B was obtained at 160°C, except for PR106, which is reported at 140°C because the viscosity of PR106 is below the instrument detection limit at 160°C. Each HC resin in Table 2 was a hydrocarbon resin. The impact of the HC resin on the MFRs of the SBC is reported in Table 2.

Table 2: MFR of SBC and HC resin/SBC blends

| SBC | HC RESIN (wt.%) | MFR g/10 min 190°C/ 2.16 Kg | % Increase |
|---|---|---|---|
| Vector 4111A (SIS) | 0 | 3.93 | N/A |
| | 5 | 5.77 | 47 |
| | 10 | 7.12 | 81 |
| | 20 | 13.20 | 236 |
| | 5 | 5.63 | 43 |
| | 10 | 6.97 | 77 |
| | 20 | 13.24 | 237 |
| | 5 | 5.94 | 51 |
| | 10 | 8.20 | 109 |
| | 20 | 14.38 | 266 |
| | 5 | 5.62 | 43 |
| | 10 | 8.40 | 114 |
| | 20 | 14.89 | 279 |
| Vector 4211A (SIS) | 0 | 4.01 | N/A |
| | 5 | 5.46 | 36 |
| | 10 | 7.21 | 80 |
| | 20 | 16.50 | 311 |
| | 5 | 5.74 | 43 |
| | 10 | 7.20 | 80 |
| | 20 | 16.39 | 309 |
| | 5 | 6.00 | 50 |
| | 10 | 9.07 | 126 |
| | 20 | 20.77 | 418 |
| | 5 | 6.12 | 53 |
| | 10 | 9.40 | 134 |

| | | | |
|---|---|---|---|
| | 20 | 20.41 | 409 |
| Vector 4411A (SIS) | 0 | 6.62 | N/A |
| | 5 | 9.15 | 38 |
| | 10 | 11.32 | 71 |
| | 20 | 15.69 | 137 |
| | 5 | 9.70 | 47 |
| | 10 | 11.21 | 69 |
| | 20 | 16.06 | 143 |
| | 5 | 9.85 | 49 |
| | 10 | 13.95 | 111 |
| | 20 | 21.89 | 231 |
| | 5 | 10.50 | 59 |
| | 10 | 14.62 | 121 |
| | 20 | 22.71 | 243 |
| Vector 8508A (SBS) | 0 | 3.35 | N/A |
| | 5 | 4.44 | 33 |
| | 10 | 6.02 | 80 |
| | 20 | 11.02 | 229 |
| | 5 | 4.70 | 40 |
| | 10 | 5.83 | 74 |
| | 20 | 11.10 | 231 |
| | 5 | 4.55 | 36 |
| | 10 | 7.02 | 110 |
| | 20 | 13.57 | 305 |
| | 5 | 4.53 | 35 |
| | 10 | 7.13 | 113 |
| | 20 | 13.50 | 303 |

**[0072]** The presence of the HC resin increased the MFR of the polymer, meaning the polymer flowed easier. As the HC resin loadings increased so did the MFR. In general, the type of HC resin was not as important at the lower loadings (5 wt.%) as the impact of the HC resin on the MFR was approximately 40%, regardless of the SBC and HC resin grade. However, at higher loadings, the impact on MFR showed to be more dependent on the type of HC resin and the type of SBC. For example, at a 10 wt.%, HC resins PR100A and PR103 showed a similar increase in MFR (approximately 75%) and this increase was generally independent of the SBC type. At 10 wt.%, HC resins PR106 and PR113 had a similar increase on MFR (approximately 120%) which is approximately 45% greater than the increase measured for HC resins PR106 and PR113. In other words, HC resin PR106 and PR113 showed the greatest increase in MFR.

**[0073]** At 20 wt.%, the HC resins PR106 and PR113 continued to show a similar increase in MFR and HC resins PR100A and PR103 continued to show a similar impact on MFR. Also the trend of HC resins PR106 and PR113 having a greater increase in MFR continued to be observed in the SBCs. In general, we measured approximately 100% greater increase in MFR using HC resin PR106 and PR113 compared to HC resins PR100A and PR103. The smallest MFR increase was observed in SIS 4411 where HC resins PR100A and PR103 increased the MFR by approximately 140% and HC resins PR106 and PR113 increased the MFR by approximately 235%. The largest MFR increase was observed in SIS 4211 where HC resins PR100A and PR103 increased the MFR by approximately 310% and HC resins PR106 and PR113 increased the MFR by approximately 413%. A substantial increase in MFR was also observed in SBS 8508 where HC resins PR100A and PR103 increased the MFR by approximately 230% and HC resin PR106 and PR113 increased the MFR by approximately 303%. The MFR was less dependent on HC resin type in SIS 4111 where HC resins PR100A and PR103 increased the MFR by 236% and HC resins PR106 and PR113 increased MFR by 270%, which is an approximate 35% increase in MFR not a 100% increase as observed in the other SBCs.

**[0074]** As shown in Table 1B, HC resins PR100A and PR103 have similar melt viscosities at 160°C (5,000 to 5,200 cPs), PR113 has a lower viscosity at the same temperature (3,400 cPs), and HC resin PR106 has such a low viscosity that the temperature was lowered to 140°C in order to obtain a good measurement (700 cPs). Based on this information it was expected the MFR to increase the most by incorporating HC resin PR106, to a lesser degree with PR113, and the least but to a similar extent, with PR100A and PR103. However, as shown in Table 2 and discussed above, the HC resins PR106 and PR113 had a very similar impact on the MFR. All the HC resins were primarily hydrogentated aliphatic hydrocarbon resins where the Tg difference was primarily a result of cyclic content. The one exception was the HC resin PR113, which contained 10% aromatics. Accordingly, it is believed that the aromaticity increased the solubility of the HC resin, thus increasing the MFR to a greater extent than expected by comparing melt viscosities alone.

**[0075]** The impact of the HC resins on film elasticity was also determined. 10 micron films were compression molded then the elasticity and tensile were tested. The films were compression molded according to ASTM D4703. The following pressing conditions were used: preheat for 5 min with no pressure; increase pressure to 25 tons; hold at 350°F (177 °C)

for 6 min; cool under pressure at a cooling rate of 27°C/min; release pressure and remove films.

**[0076]** The films were cut to yield test specimens with dimensions of 1 in wide by 3 in long by 10 mil +/- 1.5 mil thick. Elasticity testing was conducted in an Instron under the following conditions: rubber grips; 10 in/mm crosshead speed; 500% pre-stretch; release and regrip specimen; and 200% stretch.

**[0077]** Tables 3-5 show that the incorporation of 10 wt.% HC resin resulted in an easier to stretch film (lower initial modulus, lower peak force/stress at 200%, lower and flatter stress/strain). There are two exceptions both involving HC resin PR103. Incorporation of HC resin PR103 had no impact in these properties when blended with SBS 8508 and created a harder to stretch film when blended with SIS 4211. In terms of these characteristics, incorporation of HC resin PR113 had the greatest impact on creating a softer stretching film; i.e., 5%-20% lower peak stress. There was one exception, however, when the base polymer was SIS 4111 then all HC resins yielded a film with similar stretching characteristics. In SIS 4211, incorporation of HC resins PR100A and PR113 resulted in a film with similar soft stretching properties. HC resin PR106 in SIS 4211 and in SBS 8508 had a slightly less impact than HC resin PR113 with a slightly higher initial modulus, peak forces/stress at 200%, and slope of the stress/strain curve.

**[0078]** Tables 3-5 also show that the permanent set decreased when adding 10 wt.% HC resin. A lower permanent set is often desirable in elastic films as it indicates the films have relaxed back to a dimension similar to the starting dimension of the film. A lower permanent set, relative to the control, was observed when incorporating any HC resin in SIS 4111 and PR100A in SBS 8508. In some cases, the HC resin had no impact on permanent set (PR100A and PR113 in SIS 4211, and PR103, PR106, and PR113 in SBS 8508).

Table 3: Elasticity data of films of pure SIS 4111 (control) and blends with 10 wt.% HC resin

| | | HYDROCARBON RESIN | | | | |
|---|---|---|---|---|---|---|
| | | None | PR100A, 10 wt.% loading | PR103, 10 wt.% loading | PR106, 10 wt.% loading | PR113, 10 wt.% loading |
| Permanent Set | % | 13.8 | 11.1 | 11.1 | 11.0 | 11.0 |
| Peak Stress @ 200% | psi | 113 | 88 | 93 | 90 | 97 |
| Load Loss @ 100% | % | 11.2 | 12.0 | 11.5 | 12.4 | 13.0 |
| Hysteresis | % | 15.3 | 16.1 | 13.7 | 15.6 | 15.4 |

Table 4. Elasticity data of films of pure SIS 4211 (control) and blends with 10 wt.% HC resin

| | | HYDROCARBON RESIN | | | | |
|---|---|---|---|---|---|---|
| | | None | PR100A, 10 wt.% loading | PR103, 10 wt.% loading | PR106, 10 wt.% loading | PR113, 10 wt.% loading |
| Permanent Set | % | 11.1 | 11.0 | 25.4 | 30.2 | 13.7 |
| Peak Stress @ 200% | psi | 163 | 127 | 230 | 147 | 122 |
| Load Loss @ 100% | % | 20.6 | 20.8 | 22.3 | 24.7 | 20.8 |
| Hysteresis | % | 26.4 | 28.3 | 29.0 | 29.6 | 25.3 |

Table 5. Elasticity data of films of pure SBS 8508 (control) and blends with 10 wt.% HC resin

| | | HYDROCARBON RESIN | | | | |
|---|---|---|---|---|---|---|
| | | None | PR100A, 10 wt.% loading | PR103, 10 wt.% loading | PR106, 10 wt.% loading | PR113, 10 wt.% loading |
| Permanent Set | % | 35.6 | 19.5 | 35.2 | 29.8 | 29.9 |
| Peak Stress @ 200% | psi | 295 | 228 | 288 | 217 | 230 |
| Load Loss @ 100% | % | 28.2 | 26.1 | 30.9 | 24.0 | 26.2 |
| Hysteresis | % | 31.5 | 29.7 | 33.1 | 28.5 | 29.7 |

**[0079]** The impact of the HC Resins on film tensile properties were also evaluated. Tensile tests were conducted according to ASTM D663 using a crosshead speed of 20 inlmin and on 10 mil film specimens. The Instron and specimen preparation is described above. Tables 6-8 show the tensile properties of the films.

Table 6: Tensile data of films of pure SIS 4111 (control) and blends with 10 wt.% HC resin

| | | HYDROCARBON RESIN | | | | |
|---|---|---|---|---|---|---|
| | | None | PR100A, 10 wt.% loading | PR103, 10 wt.% loading | PR106, 10 wt.% loading | PR113, 10 wt.% loading |
| Stress at 100% Strain | psi | 154 | 105 | 113 | 107 | 107 |
| Stress at Break | psi | 2338 | 2554 | 2502 | 1694 | 588 |
| Strain at Break | % | 2277 | 2634 | 2483 | 2229 | 1713 |

Table 7: Tensile data of films of pure SIS 4211 (control) and blends with 10 wt.% HC resin

| | | HYDROCARBON RESIN | | | | |
|---|---|---|---|---|---|---|
| | | None | PR100A, 10 wt.% loading | PR103, 10 wt.% loading | PR106, 10 wt.% loading | PR113, 10 wt.% loading |
| Stress at 100% Strain | psi | 600 | 306 | 457 | 533 | 151 |
| Stress at Break | psi | 3684 | 2285 | 2534 | 2122 | 1893 |
| Strain at Break | % | 2602 | 2095 | 2207 | 2281 | 1861 |

Table 8: Tensile data of films of pure SBS 8508 (control) and blends with 10 wt.% HC resin

| | | HYDROCARBON RESIN | | | | |
|---|---|---|---|---|---|---|
| | | None | PR100A, 10 wt.% loading | PR103, 10 wt.% loading | PR106, 10 wt.% loading | PR113, 10 wt.% loading |
| Stress at 100% Strain | psi | 318 | 387 | 366 | 403 | 410 |
| Stress at Break | psi | 2899 | 2799 | 2567 | 2838 | 3177 |
| Strain at Break | % | 2202 | 2002 | 1981 | 1999 | 2321 |

**[0080]** Referring to Tables 6-8, the incorporation of the HC Resins in the SBCs caused a 25% to 75% reduction in the Stress at 100% Strain, but in some cases an increase was measured. More specifically, the impact of the HC resin on the Stress at 100% Strain in SIS 4111 and SBS 8508 was independent of the HC resin type. In SIS 4111, the HC resin caused an approximate 25% decrease in the Stress at 100% Strain compared to the pure SIS 4111. However, in SBS 8508, the HC resin had the opposite impact with an approximate 25% increase in the Stress at 100% Strain. This could be interpreted as adding HC resin to SIS 4111 will create an easier to stretch product, where as incorporation of HC resin in SBS 8508 will create a harder to stretch product. In SIS 4211, HC resin did reduce the Stress at 100% Strain, but the reduction was dependent on the HC resin type. HC resin PR106 had the least impact (12% reduction) followed by PR103 (25%), PR100A (50%) and the greatest reduction in Stress at 100% Strain was measured when blended with HC resin PR113 (75%).

**[0081]** The impact of the HC resins on Stress and Strain at Break proved to be more dependent on the HC resin and SBC type than observed in the Stress at 100% Strain. Within standard uncertainty of the measurement, HC resins PR100A, PR103, and PR106 had little to no impact on the Strain at Break in any of the SBC tested. The impact of these same HC resins on the Stress at Break showed no impact in SBS 8508 and SIS 4111, except for PR106

which caused a 30% reduction in SIS 4111, and approximately 35% reduction in SIS 4211. Similar to HC resins PR100A, PR103, and PR106, the PR113 had no impact on Stress and Strain at Break in SBS 8508.

**[0082]** However, PR113 had the most significant impact on the tensile properties of any of the HC resins tests. The Stress at Break was reduced by 75% and 50% in SIS 4111 and SIS 4211, respectively. The Strain at Break was reduced by 21% and 28% in SIS 4111 and SIS 4211, respectively. A potential reason HC resin PR113 provided the greatest impact is it has 10% aromaticity which may increase the HC resin compatibility in the styrene phase. It is believed that the incorporation of the HC resin in the styrene helps compatibilize the rubber and styrene domains and/or the HC resin may lower the glass transition temperature of the styrene domain.

**[0083]** Shore A Hardness was measured according to ASTM D2240 on 125 mil specimens, Table 9 summarizes those results.

Table 9: Shore A hardness of 125 mil plaques of SBC and HC resin/SBC blends

| SBC | HC Resin (wt.%) | Shore A | % Decrease |
|---|---|---|---|
| SIS 4111 | 0 | 38.40 | N/A |
| | 5 | 35.60 | 7% |
| | 10 | 31.00 | 19% |
| | 20 | 28.00 | 27% |
| | 5 | 35.60 | 7% |
| | 10 | 33.80 | 12% |
| | 20 | 29.40 | 23% |
| | 5 | 34.80 | 9% |
| | 10 | 33.80 | 12% |
| | 20 | 26.40 | 31% |
| | 5 | 35.40 | 8% |
| | 10 | 33.60 | 13% |
| | 20 | 30.20 | 21% |
| SIS 4211 | 0 | 55.80 | N/A |
| | 5 | 55.80 | 0% |
| | 10 | 53.00 | 5% |
| | 20 | 46.00 | 18% |
| | 5 | 54.00 | 3% |
| | 10 | 53.40 | 4% |
| | 20 | 48.50 | 13% |
| | 5 | 54.00 | 3% |
| | 10 | 54.00 | 3% |
| | 20 | 46.50 | 17% |
| | 5 | 54.00 | 3% |
| | 10 | 54.00 | 3% |

| | | | |
|---|---|---|---|
| | 20 | 49.20 | 12% |
| SIS 4411 | 0 | 80.00 | N/A |
| | 5 | 80.40 | -1% |
| | 10 | 79.00 | 1% |
| | 20 | 75.60 | 6% |
| | 5 | 80.60 | -1% |
| | 10 | 78.80 | 2% |
| | 20 | 74.20 | 7% |
| | 5 | 79.20 | 1% |
| | 10 | 79.00 | 1% |
| | 20 | 78.50 | 2% |
| | 5 | 80.40 | -1% |
| | 10 | 82.10 | -3% |
| | 20 | 80.60 | -1% |
| SBS 8508 | 0 | 67.80 | N/A |
| | 5 | 66.50 | 2% |
| | 10 | 61.20 | 10% |
| | 20 | 55.40 | 18% |
| | 5 | 65.60 | 3% |
| | 10 | 62.40 | 8% |
| | 20 | 56.40 | 17% |
| | 5 | 67.00 | 1% |
| | 10 | 65.00 | 4% |
| | 20 | 55.00 | 19% |
| | 5 | 66.00 | 3% |
| | 10 | 65.00 | 4% |
| | 20 | 56.00 | 17% |

**[0084]** As shown in Table 9, adding HC resin showed no impact or decreased the hardness of the SBC, and the magnitude was related to the HC resin loading. Surprisingly, the magnitude of the hardness impact was generally independent of the HC resin type. For example, at a 5 wt.% loading, the HC resin had no impact on the Shore hardness of the SBCs tested, except for SIS 4111 where an approximate 8% decrease was measured. At 10 wt.% loading, the HC resins also had no impact on Shore A hardness of the SBCs tested, except for the PR100A and PR103 (10% decrease) in SBS 8508 and all HC resins in SIS 4211 (12%-l9% decrease). The 20 wt.% HC resin loading, however, provided a significant impact on hardness in all SBCs, except SIS 4411 but none of the HC resins at any loading provided an impact on hardness on SIS 4411. As shown in Table 9, the 20 wt.% HC resin loading provided a significant decrease in hardness, namely, approximately 26% in SIS 4111, 15% in SIS 4211, and 18% in SBS 8508.

**[0085]** Certain embodiments and features have been described using a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges from any lower limit to any upper limit are contemplated unless otherwise indicated. Certain lower limits, upper limits and ranges appear in one or more claims below. All numerical values are "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

**[0086]** Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

**[0087]** While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

## CLAIMS

*What is claimed is:*

1. A film, comprising:

at least one styrenic triblock copolymer having a styrene content of from 15.0 wt.% to 49.0 wt.% wherein the triblock copolymer has substantially no diblock content; and

at least one hydrogenated resin having a MWD of from about 1.5 to about 3.5.

2. The film of claim 1 further comprising at least one thermoplastic polyolefinic resin comprising at least 75 wt.% propylene derived units.

3. The film of claim 1 or 2 wherein the at least one styrenic block copolymer is a styrene-isoprene-styrene linear block copolymer.

4. The film of any preceding claims wherein the at least one styrenic block copolymer is a styrene-butadiene-styrene linear block copolymer.

5. The film of claim 2 wherein the at least one thermoplastic polyolefinic resin and the at least one hydrogenated resin is combined into a blend prior to compounding with the styrenic block copolymer wherein the blend has a glass transition temperature of from 35°C to about 95°C.

6. The film of any preceding claim wherein the styrenic block copolymer is non-hydrogenated.

7. The film of any preceding claim wherein the hydrogenated resin is present in an amount of from

5 wt.% to 20 wt.%, based on total weight of the composition.

8. The film of any preceding claim wherein the hydrogenated resin comprises at least 20 wt.% aromatics.

9. The film of any preceding claim wherein the hydrogenated resin comprises at least 10 wt.% aromatics.

10. The film of any preceding claim, wherein the hydrocarbon resin is a hydrocarbon polymer additive.