

FOAMABLE COMPOSITIONS, FOAMS AND ARTICLES THEREOF

FIELD OF THE INVENTION

[1] This invention relates to foams comprising polyolefin blends and methods of making and using the foams in various applications.

BACKGROUND OF THE INVENTION

[2] Conventional wet suits which have heretofore been employed for skin-diving, scuba-diving, surfing, fishing, kayaking and other such activities are generally laminates made of materials comprising a closed-cell sponge sheet as a core layer and stretch fabrics adhesively bonded to the sheet at one or two surfaces. The sponge sheet provides good heat retention properties and good workability for movement of human body. Neoprene (chloroprene rubber - CR) has been the dominate material for about 60 years to make the foam due to excellent softness, flexibility, handfeel, mechanical strength (such as low compression set), weatherability, insulation and waterproof properties. A nylon jersey or tricot having good stretchability provides good wearability for the wet suit. The exterior surface of the laminate is smooth or embossed and usually adhesive coated with a polyurethane film that provides water-repellence, durability, colorance, etc.

[3] It would be useful to provide a lighter, chlorine free material suitable for wetsuits, particularly for sustainability reasons.

SUMMARY OF THE INVENTION

[4] The invention provides a composition suitable for use in wetsuit and related applications. In particular, the invention provides a foamable composition comprising: one or more olefin block copolymers; one or more olefin copolymers; an oil; a crosslinking agent; and, a blowing agent. The invention also provides a foam, a laminate, an article and a wetsuit made from the foamable composition.

DETAILED DESCRIPTION OF THE INVENTION

[5] "Polymer" means a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term "polymer" embraces the terms "homopolymer," "copolymer," "terpolymer" as well as "interpolymer."

[6] "Interpolymer" means a polymer prepared by the polymerization of at least two different types of monomers. The generic term "interpolymer" includes the term

"copolymer" (which is usually employed to refer to a polymer prepared from two different monomers) as well as the term "terpolymer" (which is usually employed to refer to a polymer prepared from three different types of monomers). It also encompasses polymers made by polymerizing four or more types of monomers.

[7] The term "crystalline" if employed, refers to a polymer that possesses a first order transition or crystalline melting point (T_m) as determined by differential scanning calorimetry (DSC) or equivalent technique. The term may be used interchangeably with the term "semicrystalline". The term "amorphous" refers to a polymer lacking a crystalline melting point as determined by differential scanning calorimetric (DSC) or equivalent technique.

[8] The foams and foamable compositions of the invention comprise an olefin block copolymer. The term "olefin block copolymer" or "OBC" is an ethylene/ α -olefin multi-block copolymer and includes ethylene and one or more copolymerizable α -olefin comonomer in polymerized form, characterized by multiple blocks or segments of two or more polymerized monomer units differing in chemical or physical properties. The terms "interpolymer" and "copolymer" are used interchangeably herein. In some embodiments, the multi-block copolymer can be represented by the following formula:



where n is at least 1, preferably an integer greater than 1, such as 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, or higher, "A" represents a hard block or segment and "B" represents a soft block or segment. Preferably, As and Bs are linked in a substantially linear fashion, as opposed to a substantially branched or substantially star-shaped fashion. In other embodiments, A blocks and B blocks are randomly distributed along the polymer chain. In other words, the block copolymers usually do not have a structure as follows.



[9] In still other embodiments, the block copolymers do not usually have a third type of block, which comprises different comonomer(s). In yet other embodiments, each of block A and block B has monomers or comonomers substantially randomly distributed within the block. In other words, neither block A nor block B comprises two or more sub-segments (or sub-blocks) of distinct composition, such as a tip segment, which has a substantially different composition than the rest of the block.

[10] Preferably, ethylene comprises the majority mole fraction of the whole block copolymer, i.e., ethylene comprises at least 50 mole percent of the whole polymer. More

preferably ethylene comprises at least 60 mole percent, at least 70 mole percent, or at least 80 mole percent, with the substantial remainder of the whole polymer comprising at least one other comonomer that is preferably an α -olefin having 3 or more carbon atoms. For many ethylene/octene block copolymers, the preferred composition comprises an ethylene content greater than 80 mole percent of the whole polymer and an octene content of from 10 to 15, preferably from 15 to 20 mole percent of the whole polymer.

[11] The olefin block copolymer includes various amounts of "hard" and "soft" segments. "Hard" segments are blocks of polymerized units in which ethylene is present in an amount greater than 95 weight percent, or greater than 98 weight percent based on the weight of the polymer. In other words, the comonomer content (content of monomers other than ethylene) in the hard segments is less than 5 weight percent, or less than 2 weight percent based on the weight of the polymer. In some embodiments, the hard segments include all, or substantially all, units derived from ethylene. "Soft" segments are blocks of polymerized units in which the comonomer content (content of monomers other than ethylene) is greater than 5 weight percent, or greater than 8 weight percent, greater than 10 weight percent, or greater than 15 weight percent based on the weight of the polymer. In some embodiments, the comonomer content in the soft segments can be greater than 20 weight percent, greater than 25 weight percent, greater than 30 weight percent, greater than 35 weight percent, greater than 40 weight percent, greater than 45 weight percent, greater than 50 weight percent, or greater than 60 weight percent.

[12] The term 'delta comonomer' means the difference in mole percent comonomer between the hard segment and the soft segment of the olefin block copolymer. In some embodiments, the delta comonomer is greater than 18.5 mol%, greater than 20 mol% or greater than 30 mol%. The delta comonomer can be from 18.5 mol% to 70 mol%, from 20 mol% to 60 mol% or from 30 mol% to 50 mol%. The delta comonomer can be measured using ^{13}C NMR such as described below and in US Patent No. 7,947,793. The term, "mesophase separation" means a process in which polymeric blocks are locally segregated to form ordered domains. Crystallization of the ethylene segments in these systems is primarily constrained to the resulting mesodomains and such systems may be referred to as "mesophase separated". These mesodomains can take the form of spheres, cylinders, lamellae, or other morphologies known for block copolymers. The narrowest dimension of a domain, such as perpendicular to the plane of lamellae, is generally greater than about 40 nm in the mesophase separated block copolymers of the instant invention. In some embodiments, the olefin block copolymer is mesophase separated.

[13] The soft segments can be present in an OBC from 1 weight percent to 99 weight percent of the total weight of the OBC, or from 5 weight percent to 95 weight percent, from 10 weight percent to 90 weight percent, from 15 weight percent to 85 weight percent, from 20 weight percent to 80 weight percent, from 25 weight percent to 75 weight percent, from 30 weight percent to 70 weight percent, from 35 weight percent to 65 weight percent, from 40 weight percent to 60 weight percent, or from 45 weight percent to 55 weight percent of the total weight of the OBC. Conversely, the hard segments can be present in similar ranges. The soft segment weight percentage and the hard segment weight percentage can be calculated based on data obtained from DSC or NMR. Such methods and calculations are disclosed in, for example, U.S. Patent No. 7,608,668, entitled "Ethylene/ α -Olefin Block Interpolymers," filed on March 15, 2006, in the name of Colin L. P. Shan, Lonnie Hazlitt, et. al. and assigned to Dow Global Technologies Inc., the disclosure of which is incorporated by reference herein in its entirety. In particular, hard and soft segment weight percentages and comonomer content may be determined as described in Column 57 to Column 63 of US 7,608,668.

[14] The olefin block copolymer is a polymer comprising two or more chemically distinct regions or segments (referred to as "blocks") preferably joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined end-to-end with respect to polymerized ethylenic functionality, rather than in pendent or grafted fashion. In an embodiment, the blocks differ in the amount or type of incorporated comonomer, density, amount of crystallinity, crystallite size attributable to a polymer of such composition, type or degree of tacticity (isotactic or syndiotactic), region-regularity or regio-irregularity, amount of branching (including long chain branching or hyper-branching), homogeneity or any other chemical or physical property. Compared to block interpolymers of the prior art, including interpolymers produced by sequential monomer addition, fluxional catalysts, or anionic polymerization techniques, the present OBC is characterized by unique distributions of both polymer polydispersity (PDI or M_w/M_n or MWD), block length distribution, and/or block number distribution, due, in an embodiment, to the effect of the shuttling agent(s) in combination with multiple catalysts used in their preparation.

[15] In an embodiment, the OBC is produced in a continuous process and possesses a polydispersity index, PDI, from 1.7 to 3.5, or from 1.8 to 3, or from 1.8 to 2.5, or from 1.8 to 2.2. When produced in a batch or semi-batch process, the OBC possesses PDI from 1.0 to 3.5, or from 1.3 to 3, or from 1.4 to 2.5, or from 1.4 to 2.

[16] In addition, the olefin block copolymer possesses a PDI fitting a Schultz-Flory distribution rather than a Poisson distribution. The present OBC has both a polydisperse block distribution as well as a polydisperse distribution of block sizes. This results in the formation of polymer products having improved and distinguishable physical properties. The theoretical benefits of a polydisperse block distribution have been previously modeled and discussed in Potemkin, Physical Review E (1998) 57 (6), pp. 6902-6912, and Dobrynin, J. Chem.Phys. (1997) 107 (21), pp 9234-9238.

[17] In an embodiment, the present olefin block copolymer possesses a most probable distribution of block lengths. In an embodiment, the olefin block copolymer is defined as having:

(A) Mw/Mn from 1.7 to 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, where in the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2, \text{ and/or}$$

(B) Mw/Mn from 1.7 to 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest Crystallization Analysis Fractionation ("CRYSTAF") peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299 \Delta H + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C ; and/or

(C) elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolmer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolmer is substantially free of crosslinked phase:

$$Re > 1481 - 1629(d); \text{ and/or}$$

(D) has a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content greater than, or equal to, the quantity $(-0.2013) T + 20.07$, more preferably greater than or equal to the quantity

(-0.2013) $T + 21.07$, where T is the numerical value of the peak elution temperature of the TREF fraction, measured in $^{\circ}\text{C}$; and/or,

(E) has a storage modulus at 25°C , $G'(25^{\circ}\text{C})$, and a storage modulus at 100°C , $G'(100^{\circ}\text{C})$, wherein the ratio of $G'(25^{\circ}\text{C})$ to $G'(100^{\circ}\text{C})$ is in the range of 1:1 to 9:1.

5 [18] The olefin block copolymer may also have:

(F) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to 1 and a molecular weight distribution, M_w/M_n , greater than 1.3; and/or

(G) average block index greater than zero and up to 1.0 and a molecular weight
10 distribution, M_w/M_n greater than 1.3. It is understood that the olefin block copolymer may have one, some, all, or any combination of properties (A)-(G). Block Index can be determined as described in detail in US Patent No. 7,608,668 herein incorporated by reference for that purpose. Analytical methods for determining properties (A) through (G) are disclosed in, for example, US Patent No 7,608,668, Col. 31, line 26 through Col. 35, line
15 44, which is herein incorporated by reference for that purpose.

[19] Suitable monomers for use in preparing the present OBC include ethylene and one or more addition polymerizable monomers other than ethylene. Examples of suitable comonomers include straight-chain or branched α -olefins of 3 to 30, preferably 3 to 20, carbon atoms, such as propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-
20 methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; cyclo-olefins of 3 to 30, preferably 3 to 20, carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene; di- and polyolefins, such as butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-
25 pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, ethylenenorbornene, vinyl norbornene, dicyclopentadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene; and 3-phenylpropene, 4-phenylpropene, 1,2-difluoroethylene, tetrafluoroethylene, and 3,3,3-trifluoro-1-propene.

30 [20] The olefin block copolymer has a density of from 0.850 g/cc to 0.925 g/cc, or from 0.860 g/cc to 0.88 g/cc or from 0.860 g/cc to 0.879 g/cc. The OBC has a Shore A value of 40 to 70, preferably from 45 to 65 and more preferably from 50 to 65. In an embodiment, the olefin block copolymer has a melt index (MI) from 0.1 g/10 min to 30 g/10, or from 0.1

g/10 min to 20 g/10 min, or from 0.1 g/10 min to 15 g/10 min, as measured by ASTM D 1238 (190°C/2.16 kg). The olefin block copolymer is present in an amount of 5 wt% to 45 wt%, preferably 10 wt% to 30 wt%, more preferably 10 wt% to 25 wt%. The composition may comprise more than olefin block copolymer.

5 [21] The olefin block copolymers are produced via a chain shuttling process such as described in US Patent No. 7,858,706, which is herein incorporated by reference. In particular, suitable chain shuttling agents and related information are listed in Col. 16, line 39 through Col. 19, line 44. Suitable catalysts are described in Col. 19, line 45 through Col. 46, line 19 and suitable co-catalysts in Col. 46, line 20 through Col. 51 line 28. The process is described throughout the document, but particularly in Col. 51, line 29 through Col. 54, line 56. The process is also described, for example, in the following: US Patent Nos. 7,608,668; US 7,893,166; and US 7,947,793.

[22] The foams and foamable compositions of the invention may also include another olefin copolymer. Any other olefin copolymer known to a person of ordinary skill in the art may be used in the invention disclosed herein. Non-limiting examples of olefin copolymers include copolymers derived from ethylene and a monoene having 3 or more carbon atoms. Non-limiting examples of the monoene having 3 or more carbon atoms include propene; butenes (*e.g.*, 1-butene, 2-butene and isobutene) and alkyl substituted butenes; pentenes (*e.g.*, 1-pentene and 2-pentene) and alkyl substituted pentenes (*e.g.*, 4-methyl-1-pentene); hexenes (*e.g.*, 1-hexene, 2-hexene and 3-hexene) and alkyl substituted hexenes; heptenes (*e.g.*, 1-heptene, 2-heptene and 3-heptene) and alkyl substituted heptenes; octenes (*e.g.*, 1-octene, 2-octene, 3-octene and 4-octene) and alkyl substituted octenes; nonenes (*e.g.*, 1-nonene, 2-nonene, 3-nonene and 4-nonene) and alkyl substituted nonenes; decenes (*e.g.*, 1-decene, 2-decene, 3-decene, 4-decene and 5-decene) and alkyl substituted decenes; dodecenes and alkyl substituted dodecenes; and butadiene. In some embodiments, the olefin copolymer is an ethylene/alpha-olefin (EAO) copolymer or ethylene/propylene copolymer (EPM). In some embodiments, the olefin copolymer is a homogeneous ethylene-based random copolymer, and is preferably an ethylene/ α -olefin copolymer, more preferably an ethylene/octene copolymer. Such polymers are commercially available under the tradenames ENGAGE (The Dow Chemical Company) and EXACT (ExxonMobil Chemical Company). The olefin copolymer has a density of 0.850 g/cc to 0.908 g/cc, preferably from 0.850 g/cc to 0.900 g/cc and a Shore A value of 40 to 70, preferably from 45 to 65 and more preferably from 50 to 65. The olefin copolymer can be present in an amount of 0 wt% to 60 wt%, 15 wt% to 60 wt%,

preferably 20 wt% to 60 wt%, more preferably 30 wt% to 55 wt%, based on total weight of the composition.

[23] In an embodiment, the foam or foamable composition comprises an ethylene-propylene-diene monomer rubber (EPDM). EPDM materials are linear interpolymers of ethylene, propylene, and a nonconjugated diene such as 1,4-hexadiene, dicyclopentadiene, or ethylidene norbornene. A preferred class of interpolymers having the properties disclosed herein is obtained from polymerization of ethylene, propylene, and a non-conjugated diene to make an EPDM elastomer. Suitable non-conjugated diene monomers can be a straight chain, branched chain or cyclic hydrocarbon diene having from 6 to 15 carbon atoms. Examples of suitable non-conjugated dienes include, but are not limited to, straight chain acyclic dienes, such as 1,4-hexadiene, 1,6-octadiene, 1,7-octadiene, 1,9-decadiene, branched chain acyclic dienes, such as 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 3,7-dimethyl-1,7-octadiene and mixed isomers of dihydromyricene and dihydroocinene, single ring alicyclic dienes, such as 1,3-cyclopentadiene; 1,4-cyclohexadiene; 1,5-cyclooctadiene and 1,5-cyclododecadiene, and multi-ring alicyclic fused and bridged ring dienes, such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicyclo-(2,2,1)-hepta-2,5-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes, such as 5-methylene-2-norbornene (MNB); 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene, and norbornadiene. Of the dienes typically used to prepare EPDMs, the particularly preferred dienes are 1,4-hexadiene (HD), 5-ethylidene-2-norbornene (ENB), 5-vinylidene-2-norbornene (VNB), 5-methylene-2-norbornene (MNB), and dicyclopentadiene (DCPD). The especially preferred dienes are 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene (HD).

[24] In some embodiments, the EPDM polymers have an ethylene content of from 50% to 75% by weight, a propylene content of from 20% to 49% by weight, and a nonconjugated diene content from 1% to 10% by weight, all weights based upon the total weight of the polymer. Examples of representative EPDM polymers for use include Nordel IP 3640, Nordel IP 4520 and Nordel IP 4570 available from The Dow Chemical Company, Midland, MI, Vistalon 2504 available from ExxonMobil, Baton Rouge, LA, and Keltan 4550 available from DSM Elastomers Americas, Addis, LA.

[25] The EPDM polymers, also known as elastomeric copolymers of ethylene, a higher- α -olefin and a polyene, have molecular weights from 20,000 to 2,000,000 daltons or more. Their physical form varies from waxy materials to rubbers to hard plastic-like polymers. They have dilute solution viscosities (DSV) from 0.5 to 10 dl/g, measured at 30 °C

on a solution of 0.1 gram of polymer in 100 cc of toluene. The EPDM polymers also have a Mooney viscosity of 10 to 100 ML(1+4) at 125 °C, preferably from 10 to 70 ML(1+4) at 125 °C or 10 to 50 ML(1+4) at 125 °C. The EPDM polymers have a density of 0.850 g/cc to 0.90 g/cc, from 0.855 g/cc to 0.885 g/cc or from 0.860 g/cc to 0.880 g/cc.

5 [26] In some embodiments, the EPDM has a crystallinity of less than 10% as measured by DSC, preferably greater than 0 % to 10%, from 0.001 % to 10% or from 0.001 % to 5%.

[27] In some embodiments, the EPDM is present in an amount of 0 wt% to 50 wt%, preferably 5 wt% to 40 wt%, more preferably 5wt% to 30 wt% based on total weight of the
10 composition.

[28] The composition can also include a styrenic block copolymer. Generally speaking, styrenic block copolymers include at least two monoalkenyl arene blocks, preferably two polystyrene blocks, separated by a block of a saturated conjugated diene, preferably a saturated polybutadiene block. The preferred styrenic block copolymers
15 have a linear structure, although branched or radial polymers or functionalized block copolymers make useful compounds. The total number average molecular weight of the styrenic block copolymer is preferably from 30,000 to 250,000 if the copolymer has a linear structure. Such block copolymers may have an average polystyrene content from 10% by weight to 40% by weight. Suitable block copolymers having unsaturated
20 rubber monomer units include, but are not limited to, styrene-butadiene (SB), styrene-ethylene/butadiene (SEB), styrene-isoprene(SI), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), α -methylstyrene-butadiene- α -methylstyrene and α -methylstyrene-isoprene- α -methylstyrene. The styrenic block copolymer can be present in an amount of 0 wt% to 50 wt%, preferably 5 wt% to 40 wt%, more preferably 5wt%
25 to 30 wt% based on total weight of the composition.

[29] The composition may also include an acrylonitrile-butadiene rubber, silicon rubber or a chlorinated polyethylene rubber that may be present in amounts of 0 wt% to 50 wt%, preferably 5 wt% to 40 wt%, more preferably 5wt% to 30 wt% based on total weight of the composition

30 [30] The composition includes an oil. The oil can be an aromatic oil, a mineral oil, a naphthenic oil, a paraffinic oil, a triglyceride-based vegetable oil such as castor oil, a synthetic hydrocarbon oil such as polypropylene oil, a silicone oil, or any combination thereof. A nonlimiting example of a suitable oil is a white mineral oil sold under the

tradename HYDROBRITE® 550 (Sonneborn). The oil is present in an amount of 10 wt% to 45 wt%, preferably 20 wt% to 40 wt%, more preferably 25 wt% to 35 wt% based on total weight of the composition.

[31] The foams disclosed herein can be prepared from a foamable composition comprising at least one blowing agent, at least one cross-linking agent and at least one of the polyolefins described above and optionally at least one other additive or a combination thereof. Non-limiting examples of suitable other additives include grafting initiators, cross-linking catalysts, blowing agent activators (*e.g.*, zinc oxide, zinc stearate and the like), coagents (*e.g.*, triallyl cyanurate, trimethylolpropane trimethylacrylate), plasticizers, colorants or pigments, stability control agents, nucleating agents, fillers, antioxidants, acid scavengers, ultraviolet stabilizers, flame retardants, lubricants, processing aids, extrusion aids, and combinations thereof. Some suitable additives have been described in Zweifel Hans *et al.*, “*Plastics Additives Handbook*,” Hanser Gardner Publications, Cincinnati, Ohio, 5th edition (2001), which is incorporated herein by reference in its entirety. The blowing agent is present in an amount of 1 phr to 8 phr, preferably 2 phr to 6 phr. The crosslinking agent is present in an amount of 1 phr to 6 phr, preferably 2 phr to 5 phr. When present, blowing agent activators can be present in an amount of greater than 0 phr to 2.0 phr, preferably 0.05 phr to 1.0 phr. When present, filler can be present in an amount of greater than 0 phr to 20 phr, preferably 0.05 phr to 10 phr. When present, processing aids can be present in an amount of 0.1 phr to 2.0 phr; antioxidant in an amount of 0.1 phr to 1.0 phr; and, UV stabilizer in an amount of 0.1 phr to 1.0 phr. The term “phr” means parts per hundred resin, as commonly understood in the art.

[32] The foams disclosed herein can be substantially cross-linked. A foam is substantially cross-linked when the foam contains more than 5 % of gel per ASTM D-2765-84 Method A. In some embodiments, the foam disclosed herein contains more than 5 % of gel, more than 10 % of gel, more than 15 % of gel, more than 20 % of gel, more than 25 % of gel, more than 30 % of gel, more than 35 % of gel, or more than 40 % of gel per ASTM D-2765-84 Method A. In other embodiments, the foam disclosed herein contains less than 99 % of gel. In further embodiments, the foam disclosed herein contains less than 85 % of gel. In further embodiments, the foam disclosed herein contains less than 75 % of gel. The foam can have from 5% of gel to 99 % of gel, 15% of gel to 85% of gel, or from 25% of gel to 75% of gel.

[33] The foams or foamable compositions disclosed herein can have a density of 0.05 g/cc to 0.2 g/cc, preferably 0.06 g/cc to 0.16 g/cc, more preferably 0.08 g/cc to 0.16 g/cc, as measured according to ASTM 792. The foams can have a 60% modulus of 0.60 kg/cm² to 1.50 kg/cm², preferably 0.60 kg/cm² to 0.8 kg/cm², more preferably 0.65 kg/cm² to 0.75 kg/cm². The foams can have a compression set of 15% to 35%, preferably 15% to 30%.

[34] The foams or foamable compositions disclosed herein can be either closed-celled or open-celled. Disclosed herein, a foam is a closed cell foam when the foam contains 80 % or more closed cells or less than 20 % open cells according to ASTM D2856-A.

[35] The blowing agents suitable for making the foams disclosed herein can include, but are not limited to, inorganic blowing agents, organic blowing agents, chemical blowing agents and combinations thereof. Some blowing agents are disclosed in Sendjarevic *et al.*, "Polymeric Foams And Foam Technology," Hanser Gardner Publications, Cincinnati, Ohio, 2nd edition, Chapter 18, pages 505-547 (2004), which is incorporated herein by reference.

[36] Non-limiting examples of suitable inorganic blowing agents include carbon dioxide, nitrogen, argon, water, air, nitrogen, and helium. Non-limiting examples of suitable organic blowing agents include aliphatic hydrocarbons having 1-6 carbon atoms, aliphatic alcohols having 1-3 carbon atoms, and fully and partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms. Non-limiting examples of suitable aliphatic hydrocarbons include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, and the like. Non-limiting examples of suitable aliphatic alcohols include methanol, ethanol, n-propanol, and isopropanol. Non-limiting examples of suitable fully and partially halogenated aliphatic hydrocarbons include fluorocarbons, chlorocarbons, and chlorofluorocarbons. Non-limiting examples of suitable fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoro-ethane (HFC-134a), pentafluoroethane, difluoromethane, perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane. Non-limiting examples of suitable partially halogenated chlorocarbons and chlorofluorocarbons include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-trichloroethane, 1,1-dichloro-1-fluoroethane (HCFC-141b), 1-chloro-1,1 difluoroethane (HCFC-142b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124). Non-limiting examples of suitable fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11),

dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), 1,1,1-trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane. Non-limiting examples of suitable chemical blowing agents include azodicarbonamide, azodiisobutyro-nitrile, benzenesulfonhydrazide, 4,4-oxybenzene
5 sulfonfyl-semicarbazide, p-toluene sulfonfyl semi-carbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and trihydrazino triazine. In some embodiments, the blowing agent is azodicarbonamide isobutane, CO₂, or a mixture of thereof. Preferably, the blowing agent has a decomposition temperature of 150 °C to 210 °C.

[37] The cross-linking of the foams can be induced by activating the cross-
10 linking agent in the foamable composition. The cross-linking agent can be activated by exposing it to a temperature above its decomposition temperature. Alternatively, the cross-linking agent can be activated by exposing it to a radiation that causes the generation of free radicals from the cross-linking agent. Similarly, the foaming or expansion of the foams disclosed herein can be induced by activating the blowing agent
15 in the foamable composition. In some embodiments, the blowing agent is activated by exposing it to a temperature above its activation temperature. Generally, the activations of the cross-linking and foaming can occur either simultaneously or sequentially. In some embodiments, the activations occur simultaneously. In other embodiments, the activation of the cross-linking occurs first and the activation of the foaming occurs next.
20 In further embodiments, the activation of the foaming occurs first and the activation of the cross-linking occurs next.

[38] The foamable composition can be prepared or processed at a temperature of less than 150 °C to prevent the decomposition of the blowing agent and the cross-linking agent. When radiation cross-linking is used, the foamable composition can be prepared or
25 processed at a temperature of less than 160 °C to prevent the decomposition of the blowing agent. In some embodiments, the foamable composition can be extruded or processed through a die of desired shape to form a foamable structure. Next, the foamable structure can be expanded and cross-linked at an elevated temperature (*e.g.*, from 150 °C to 250 °C) to activate the blowing agent and the cross-linking agent to form a foam structure. In some
30 embodiments, the foamable structure can be irradiated to cross-link the polymer material, which can then be expanded at the elevated temperature as described above.

[39] Some suitable cross-linking agents have been disclosed in Zweifel Hans *et al.*, "Plastics Additives Handbook," Hanser Gardner Publications, Cincinnati, Ohio,

5th edition, Chapter 14, pages 725-812 (2001); *Encyclopedia of Chemical Technology*, Vol. 17, 2nd edition, Interscience Publishers (1968); and Daniel Seern, "Organic Peroxides," Vol. 1, Wiley-Interscience, (1970), all of which are incorporated herein by reference. In some embodiments, there is no cross-linking agent in the foamable

compositions or foams disclosed herein.

[40] Non-limiting examples of suitable cross-linking agents include peroxides, phenols, azides, aldehyde-amine reaction products, substituted ureas, substituted guanidines; substituted xanthates; substituted dithiocarbamates; sulfur-containing compounds, such as thiazoles, sulfenamides, thiuramidisulfides, paraquinonedioxime, dibenzoparaquinonedioxime, sulfur; imidazoles; silanes and combinations thereof.

[41] Non-limiting examples of suitable organic peroxide cross-linking agents include alkyl peroxides, aryl peroxides, peroxyesters, peroxycarbonates, diacylperoxides, peroxyketals, cyclic peroxides and combinations thereof. In some embodiments, the organic peroxide is dicumyl peroxide, t-butylisopropylidene peroxybenzene, 1,1-di-t-butyl peroxy-3,3,5-trimethylcyclohexane, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, t-butyl-cumyl peroxide, di-t-butyl peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexyne or a combination thereof. In one embodiment, the organic peroxide is dicumyl peroxide. Additional teachings regarding organic peroxide cross-linking agents are disclosed in C. P. Park, "Polyolefin Foam", Chapter 9 of *Handbook of Polymer Foams and Technology*, edited by D. Klemperer and K. C. Frisch, Hanser Publishers, pp. 198-204, Munich (1991), which is incorporated herein by reference.

[42] Optionally, the foamable composition disclosed herein may comprise a catalyst. Any cross-linking catalyst that can promote the cross-linking of the ethylene/ α -olefin interpolymer or the polymer blend can be used. Non-limiting examples of suitable catalysts include organic bases, carboxylic acids, and organometallic compounds. In some embodiments, the catalyst includes organic titanates and complexes or carboxylates of lead, cobalt, iron, nickel, zinc and tin. In other embodiments, the catalyst is or comprises dibutyltin dilaurate, dioctyltin maleate, dibutyltin diacetate, dibutyltin dioctanoate, stannous acetate, stannous octanoate, lead naphthenate, zinc caprylate, cobalt naphthenate or a combination thereof. In further embodiments, the catalyst is or comprises a tin carboxylate such as dibutyltin dilaurate and dioctyltin maleate.

[43] Alternatively, the cross-linking of the foams or foamable compositions disclosed herein can be effected by using radiation. Non-limiting examples of suitable radiation include electron beam or beta ray, gamma rays, X-rays, or neutron rays. Radiation is believed to activate the cross-linking by generating radicals in the polymer which may subsequently combine and cross-link. Additional teachings concerning radiation cross-linking are disclosed in C. P. Park, *supra*, pages 198-204, which is incorporated herein by reference. In some embodiments, the foam or foamable composition is not cross-linked by radiation.

[44] Radiation dosage generally depends upon many factors. Those skilled in the art will be readily able to select suitable radiation levels based on thickness and geometry of the article to be irradiated, as well as the characteristics of the foamable composition or components, such as molecular weight, molecular weight distribution, comonomer content, the presence of cross-linking enhancing coagents, additives (*e.g.*, oil), and the like. In general, the dosage does not exceed what is required to effect the desired level of cross-linking. In some embodiments, the dosage causes more than 5 % gel in the foam per ASTM D-2765-84 Method A.

[45] In some embodiments, dual cure systems, which comprises at least two activation methods selected from cross-linking agents and radiation, can be effectively employed. For instance, it may be desirable to employ a peroxide cross-linking agent in conjunction with a silane cross-linking agent, a peroxide cross-linking agent in conjunction with radiation, a sulfur-containing cross-linking agent in conjunction with a silane cross-linking agent, or the like.

[46] The foams or foamable compositions disclosed herein may optionally comprise a stability control agent or gas permeation modifier. Any stability control agent that can enhance the dimensional stability of the foams can be used. Non-limiting examples of suitable stability control agents include amides and esters of C_{10-24} fatty acids. Such agents are described in U.S. Patent Nos. 3,644,230 and 4,214,054, both of which are incorporated herein by reference. In some embodiments, the stability control agents include stearyl stearamide, glycerol monostearate, glycerol monobehenate, sorbitol monostearate and combinations thereof. In general, the amount of the stability control agents is from 0.1 to 10 parts, from 0.1 to 5 parts, or from 0.1 to 3 parts by weight per hundred parts by weight of the polymer. In some embodiment, the stability control agent is glycerol monostearate.

[47] The foams or foamable compositions disclosed herein may optionally comprise a nucleating agent. Any nucleating agent that can control the size of foam cells can be used. Non-limiting examples of suitable nucleating agents include inorganic substances such as calcium carbonate, talc, clay, titanium oxide, silica, barium sulfate, diatomaceous earth, citric acid, sodium bicarbonate, sodium carbonate, and combinations thereof. In some embodiments, the nucleating agent is a combination of citric acid and sodium bicarbonate or a combination of citric acid and sodium carbonate. In other embodiments, the nucleating agent is HYDROCEROL[®] CF 20 from Clariant Corporation, Charlotte, NC. The amount of nucleating agent employed can range from 0.01 to 5 parts by weight per hundred parts by weight of the polymer.

[48] In some embodiments, the foams or foamable compositions disclosed herein comprise an antioxidant. Any antioxidant that can prevent the oxidation of polymer components and organic additives in the foams can be added to the foams disclosed herein. Non-limiting examples of suitable antioxidants include aromatic or hindered amines such as alkyl diphenylamines, phenyl- α -naphthylamine, alkyl or aralkyl substituted phenyl- α -naphthylamine, alkylated p-phenylene diamines, tetramethyl-diaminodiphenylamine and the like; phenols such as 2,6-di-t-butyl-4-methylphenol; 1,3,5-trimethyl-2,4,6-tris(3',5'-di-t-butyl-4'-hydroxybenzyl)benzene; tetrakis[(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate))]methane (*e.g.*, IRGANOX[™] 1010, from Ciba Geigy, New York); acryloyl modified phenols; octadecyl-3,5-di-t-butyl-4-hydroxycinnamate (*e.g.*, IRGANOX[™] 1076, commercially available from Ciba Geigy); phosphites and phosphonites; hydroxylamines; benzofuranone derivatives; and combinations thereof. Some antioxidants have been described in Zweifel Hans *et al.*, "*Plastics Additives Handbook*," Hanser Gardner Publications, Cincinnati, Ohio, 5th edition, Chapter 1, pages 1-140 (2001), which is incorporated herein by reference.

[49] In other embodiments, the foams or foamable compositions disclosed herein comprise a UV stabilizer. Any UV stabilizer that may prevent or reduce the degradation of the foams by UV radiations can be added to the foams disclosed herein. Non-limiting examples of suitable UV stabilizers include benzophenones, benzotriazoles, aryl esters, oxanilides, acrylic esters, formamidines, carbon black, hindered amines, nickel quenchers, hindered amines, phenolic antioxidants, metallic salts, zinc compounds and combinations thereof. Some UV stabilizers have been

described in Zweifel Hans *et al.*, “*Plastics Additives Handbook*,” Hanser Gardner Publications, Cincinnati, Ohio, 5th edition, Chapter 2, pages 141-426 (2001), which is incorporated herein by reference.

[50] In further embodiments, the foams or foamable compositions disclosed herein comprise a colorant or pigment. Any colorant or pigment that can change the look of the foams to human eyes can be added to the foams disclosed herein. Non-limiting examples of suitable colorants or pigments include inorganic pigments such as metal oxides such as iron oxide, zinc oxide, and titanium dioxide, mixed metal oxides, carbon black, organic pigments such as anthraquinones, anthanthrones, azo and monoazo compounds, arylamides, benzimidazolones, BONA lakes, diketopyrrolopyrroles, dioxazines, disazo compounds, diarylide compounds, flavanthrones, indanthrones, isoindolinones, isoindolines, metal complexes, monoazo salts, naphthols, b-naphthols, naphthol AS, naphthol lakes, perylenes, perinones, phthalocyanines, pyranthrones, quinacridones, and quinophthalones, and combinations thereof. Where used, the amount of the colorant or pigment in the foam can be from greater than 0 to 10 wt%, from 0.1 to 5 wt%, or from 0.25 to 2 wt% of the total weight of the foam. Some colorants have been described in Zweifel Hans *et al.*, “*Plastics Additives Handbook*,” Hanser Gardner Publications, Cincinnati, Ohio, 5th edition, Chapter 15, pages 813-882 (2001), which is incorporated herein by reference.

[51] Optionally, the foams or foamable compositions disclosed herein can comprise a filler. Any filler which can be used to adjust, *inter alia*, volume, weight, costs, and/or technical performance can be added to the foams disclosed herein. Non-limiting examples of suitable fillers include talc, calcium carbonate, chalk, calcium sulfate, clay, kaolin, silica, glass, fumed silica, mica, wollastonite, feldspar, aluminum silicate, calcium silicate, carbon black, alumina, hydrated alumina such as alumina trihydrate, glass microsphere, ceramic microsphere, thermoplastic microsphere, barite, wood flour, glass fibers, carbon fibers, marble dust, cement dust, magnesium oxide, magnesium hydroxide, antimony oxide, zinc oxide, barium sulfate, titanium dioxide, titanates and combinations thereof. In some embodiments, the filler is barium sulfate, talc, calcium carbonate, silica, glass, glass fiber, alumina, titanium dioxide, or a mixture thereof. In other embodiments, the filler is talc, calcium carbonate, barium sulfate, glass fiber or a mixture thereof. Some fillers have been disclosed in U.S. Patent No. 6,103,803 and Zweifel Hans *et al.*, “*Plastics Additives Handbook*,” Hanser Gardner

Publications, Cincinnati, Ohio, 5th edition, Chapter 17, pages 901-948 (2001), both of which are incorporated herein by reference.

[52] Optionally, the foams or foamable compositions disclosed herein can comprise a lubricant. Any lubricant that can be used, *inter alia*, to modify the rheology of the molten foamable compositions, to improve the surface finish of molded foamed articles, and/or to facilitate the dispersion of fillers or pigments can be added to the foams disclosed herein. Non-limiting examples of suitable lubricants include fatty alcohols and their dicarboxylic acid esters, fatty acid esters of short-chain alcohols, fatty acids, fatty acid amides, metal soaps, oligomeric fatty acid esters, fatty acid esters of long-chain alcohols, montan waxes, polyethylene waxes, polypropylene waxes, natural and synthetic paraffin waxes, fluoropolymers and combinations thereof. Where used, the amount of the lubricant in the foam can be from greater than 0 to 5 wt%, from 0.1 to 4 wt%, or from 0.1 to 3 wt% of the total weight of the foam. Some suitable lubricants have been disclosed in Zweifel Hans *et al.*, "*Plastics Additives Handbook*," Hanser Gardner Publications, Cincinnati, Ohio, 5th edition, Chapter 5, pages 511-552 (2001), both of which are incorporated herein by reference.

[53] Optionally, the foams or foamable compositions disclosed herein can comprise an antistatic agent. Any antistatic agent that can increase the conductivity of the foams and to prevent static charge accumulation can be added to the foams disclosed herein. Non-limiting examples of suitable antistatic agents include conductive fillers (*e.g.*, carbon black, metal particles and other conductive particles), fatty acid esters (*e.g.*, glycerol monostearate), ethoxylated alkylamines, diethanolamides, ethoxylated alcohols, alkylsulfonates, alkylphosphates, quaternary ammonium salts, alkylbetaines and combinations thereof. Where used, the amount of the antistatic agent in the foam can be from greater than 0 to 5 wt%, from 0.01 to 3 wt%, or from 0.1 to 2 wt% of the total weight of the foam. Some suitable antistatic agents have been disclosed in Zweifel Hans *et al.*, "*Plastics Additives Handbook*," Hanser Gardner Publications, Cincinnati, Ohio, 5th edition, Chapter 10, pages 627-646 (2001), both of which are incorporated herein by reference.

[54] The processes of making polyolefin foams are described in C. P. Park, "*Polyolefin Foam*", Chapter 9 of *Handbook of Polymer Foams and Technology*, edited by D. Klempner and K. C. Frisch, Hanser Publishers, Munich (1991), which is incorporated herein by reference.

[55] The ingredients of the foamable composition can be mixed or blended in any suitable mixing or blending devices known to skilled artisans. The ingredients in the foamable composition can then be mixed at a temperature below the decomposition temperature of the blowing agent and the cross-linking agent to ensure that all ingredients are
5 homogeneously mixed and remain intact. After the foamable composition is relatively homogeneously mixed, the composition is shaped and then exposed to conditions (*e.g.* heat, pressure, shear, *etc.*) over a sufficient period of time to activate the blowing agent and the cross-linking agent to make the foam.

[56] In some embodiments, the ingredients of the foamable composition can be
10 mixed and melt blended by any mixing or blending device known to a person of ordinary skill in the art. Non-limiting examples of suitable mixing or blending devices include extruders, mixers, blenders, mills, dispersers, homogenizers and the like. In other embodiments, the blowing agent is dry-blended with the ethylene/ α -olefin interpolymers or the polymer blend before the foamable composition is heated to a molten form. In further
15 embodiments, the blowing agent is added when the foamable composition is in a molten phase. In some embodiments, the foamable composition disclosed herein is extruded through a die where the cross-linking is activated. Next, the extruded foamable composition may be exposed to an elevated temperature to activate the blowing agent to form the foams.

[57] The foams disclosed herein can be prepared by conventional extrusion
20 foaming processes. The foam can generally be prepared by heating the polymer components to form a plasticized or melt polymer material, incorporating therein a blowing agent to form a foamable composition, and extruding the foamable composition through a die to form foam products. Prior to mixing with the blowing agent, the polymers can be heated to a temperature at or above their glass transition temperatures or melting points. The blowing
25 agent can be incorporated or mixed into the molten polymer by any means known in the art such as with an extruder, mixer, blender, and the like. The blowing agent can be mixed with the molten polymer at an elevated pressure sufficient to prevent substantial expansion of the molten polymer and to generally disperse the blowing agent homogeneously therein. Optionally, a nucleating agent can be blended in the polymer melt or dry blended with the
30 polymer prior to plasticizing or melting. The foamable composition can be cooled to a lower temperature to optimize physical characteristics of the foam structure. The foamable composition can then be extruded or conveyed through a die of desired shape to a zone of reduced or lower pressure to form the foam structure. The zone of lower pressure can be at a

pressure lower than that in which the foamable composition is maintained prior to extrusion through the die. The lower pressure can be super-atmospheric or sub-atmospheric (vacuum), but is preferably at an atmospheric level.

[58] In some embodiments, the foams disclosed herein are formed in a coalesced strand form by extrusion of the polymer through a multi-orifice die. The orifices can be arranged so that contact between adjacent streams of the molten extrudate occurs during the foaming process and the contacting surfaces adhere to one another with sufficient adhesion to result in a unitary foam structure. The streams of the molten extrudate exiting the die can take the form of strands or profiles, which can desirably foam, coalesce, and adhere to one another to form a unitary structure. Desirably, the coalesced individual strands or profiles should remain adhered in a unitary structure to prevent strand delamination under stresses encountered in preparing, shaping, and using the foams. Apparatuses and methods for producing foam structures in coalesced strand form are disclosed in U.S. Patent Nos. 3,573,152 and 4,824,720, both of which are incorporated herein by reference.

[59] In other embodiments, the foams disclosed herein are formed by an accumulating extrusion process as seen in U.S. Patent No. 4,323,528, which is incorporated by reference herein. In the accumulating extrusion process, low density foams having large lateral cross-sectional areas are prepared by: 1) forming under pressure the foamable composition of the polymers and a blowing agent at a temperature at which the viscosity of the foamable composition is sufficient to retain the blowing agent when the foamable composition is allowed to expand; 2) extruding the foamable composition into a holding zone maintained at a temperature and pressure which does not allow the foamable composition to foam, the holding zone having an outlet die defining an orifice opening into a zone of lower pressure at which the foamable composition foams, and an openable gate closing the die orifice; 3) periodically opening the gate; 4) substantially concurrently applying mechanical pressure by a movable ram on the foamable composition to eject it from the holding zone through the die orifice into the zone of lower pressure, at a rate greater than that at which substantial foaming in the die orifice occurs and less than that at which substantial irregularities in cross-sectional area or shape occurs; and 5) permitting the ejected foamable composition to expand unrestrained in at least one dimension to produce the foam structure.

[60] In some embodiments, the foams disclosed herein can be prepared by either compression molding or injection molding. In other embodiments, the foams are prepared by compression molding at a temperature above the decomposition temperatures of the peroxide

and the blowing agent and under pressure for a defined time which is followed by an expansion step when the mold opens and pressure is released. In further embodiments, the foams are prepared by injection molding the compound comprising the polymers which melt at temperatures below the decomposition temperatures of the peroxide and the blowing agent into molds at temperatures above the decomposition temperatures of the peroxide and the blowing agent. The material remains at temperature and under pressure until the mold opens and the pressure is reduced at which point the material will expand.

Blending of the Ingredients Of the Foams

[61] The ingredients of the foamable composition can be mixed or blended using methods known to a person of ordinary skill in the art. Non-limiting examples of suitable blending methods include melt blending, solvent blending, extruding, and the like.

[62] In some embodiments, the ingredients of the foams are melt blended by a method as described by Guerin *et al.* in U.S. Patent No. 4,152,189. First, all solvents, if there are any, are removed from the ingredients by heating to an appropriate elevated temperature of 100°C to 200°C or 150°C to 175°C at a pressure of 5 torr (667 Pa) to 10 torr (1333 Pa). Next, the ingredients are weighed into a vessel in the desired proportions and the foam is formed by heating the contents of the vessel to a molten state while stirring.

[63] In other embodiments, the ingredients of the foams are processed using solvent blending. First, the ingredients of the desired foam are dissolved in a suitable solvent and the mixture is then mixed or blended. Next, the solvent is removed to provide the foam.

[64] In some embodiments, physical blending devices that can provide dispersive mixing, distributive mixing, or a combination of dispersive and distributive mixing can be used in preparing homogenous blends. Both batch and continuous methods of physical blending can be used. Non-limiting examples of batch methods include those methods using BRABENDER[®] mixing equipments (*e.g.*, BRABENDER PREP CENTER[®], available from C. W. Brabender Instruments, Inc., South Hackensack, N.J.) or BANBURY[®] internal mixing and roll milling (available from Farrel Company, Ansonia, Conn.) equipment. Non-limiting examples of continuous methods include single screw extruding, twin screw extruding, disk extruding,

reciprocating single screw extruding, and pin barrel single screw extruding. In some embodiments, the additives can be added into an extruder through a feed hopper or feed throat during the extrusion of the polymers or the foam. The mixing or blending of polymers by extrusion has been described in C. Rauwendaal, "*Polymer Extrusion*",
5 Hanser Publishers, New York, NY, pages 322-334 (1986), which is incorporated herein by reference.

[65] When one or more additives are required in the foams, the desired amounts of the additives can be added in one charge or multiple charges to any of the polymer components separately or together. Furthermore, the addition can take place
10 in any order.

[66] Embodiments of the invention also comprise articles comprising the foam or foamable composition as described above. In particular, the articles can be wetsuits for skin-diving, scuba-diving, surfing, fishing, kayaking and other such activities. Wetsuits can be constructed from the inventive foam compositions by
15 laminating the foams to appropriate fabrics via methods known in the art. Wetsuit articles are described in, for example, US Patent No. 3,660,849 and US Patent No. 4,274,158.

[67] The following examples are presented to exemplify embodiments of the invention. All numerical values are approximate. When numerical ranges are given, it
20 should be understood that embodiments outside the stated ranges may still fall within the scope of the invention. Specific details described in each example should not be construed as necessary features of the invention.

EXAMPLES

Test Methods

Compression Set

[68] Compression set is measured based on ASTM D 395 method B. The sample thickness is around 19 mm, diameter 29 ± 0.5 mm, cut from the foamed sheet with thickness 19 ± 0.5 mm. The samples were tested under constant depression of 50% at around 23 ± 1 °C for 23 hours and then taken out and relaxed at around 23 ± 1 °C for 1
30 hour and then measured. Compression Set = [(original thickness-final thickness)/original thickness] x 100%.

¹³C NMR Analysis

[69] The samples are prepared by adding approximately 3g of a 50/50 mixture of tetrachloroethane-d²/orthodichlorobenzene to 0.4 g sample in a 10 mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150°C. The data are collected using a JEOL Eclipse™ 400MHz spectrometer or a Varian Unity Plus™ 400MHz spectrometer, corresponding to a ¹³C resonance frequency of 100.5 MHz. The data are acquired using 4000 transients per data file with a 6 second pulse repetition delay. To achieve minimum signal-to-noise for quantitative analysis, multiple data files are added together. The spectral width is 25,000 Hz with a minimum file size of 32K data points. The samples are analyzed at 130 °C in a 10 mm broad band probe. The comonomer incorporation is determined using Randall's triad method (Randall, J.C.; JMS-Rev. Macromol. Chem. Phys., C29, 201-317 (1989), which is incorporated by reference herein in its entirety.

Density

[70] Samples for foam density measurement are prepared from the bun foams with or without a skin layer attached. The foam density is measured on using the bun foam sample after any integral skin layer is removed by accurately measuring the length (L) x width(W) and height (H) of the foam and the mass to the nearest 0.1g. The density is calculated by dividing the mass of the foam sample by the product of the L x W x H, all in centimeters.

[71] The density of polymers may be measured by preparing the samples according to ASTM D 1928 and then measuring density within one hour of sample pressing according to ASTM D792, Method B.

Melt Temperature, T_m, via DSC

[72] Differential Scanning Calorimetry results are determined using a TAI model Q1000 DSC equipped with an RCS cooling accessory and an autosampler. A nitrogen purge gas flow of 50 ml/min is used. The sample is pressed into a thin film and melted in the press at about 175°C and then air-cooled to room temperature (25°C). 3-10 mg of material is then cut into a 6 mm diameter disk, accurately weighed, placed in a light aluminum pan (ca 50 mg), and then crimped shut. The thermal behavior of the sample is investigated with the following temperature profile. The sample is rapidly heated to 180°C and held isothermal for 3 minutes in order to remove any previous thermal history. The sample is then cooled to -

40°C at 10°C/min cooling rate and held at -40°C for 3 minutes. The sample is then heated to 150 °C at 10°C/min. heating rate. The cooling and second heating curves are recorded.

[73] The DSC melting peak is measured as the maximum in heat flow rate (W/g) with respect to the linear baseline drawn between -30°C and end of melting. The heat of fusion is measured as the area under the melting curve between -30°C and the end of melting using a linear baseline.

GPC (Mw/Mn determination)

[74] The gel permeation chromatographic system can be either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220 instrument. The column and carousel compartments are operated at 140 °C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4 trichlorobenzene. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160°C. The injection volume used is 100 microliters and the flow rate is 1.0 ml/minute.

[75] Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80°C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)): $M_{\text{polyethylene}} = 0.431(M_{\text{polystyrene}})$.

[76] Polyethylene equivalent molecular weight calculations are performed using Viscotek TriSEC software Version 3.0.

Table 1. Additional Test methods

Property	Unit	Method
Shore A/000	-	ASTM D-2240
MI	g/10min	ASTM D-1238 (190°C/2.16 Kg)
Tensile strength	Kg/cm ²	ASTM D638
Ultimate Elongation	%	ASTM D638
Tensile Secant Modulus (60% and 300%)	Kg/cm ²	ASTM D638
Tear strength	Kg/cm	ASTM D624, type C
Mooney viscosity	ML1+4, 125 deg C	ISO289 (or ASTM D1646)

5 Components

- POE: ENGAGETM 8842: density 0.857 g/cm³ (ASTM D792), MI 1 g/10min (ASTM D1238, at 190 deg C/2.16Kg), Shore A = 54 (ASTM D2240).
- OBC1: INFUSETM 9807, density 0.866 g/cm³ (ASTM D792), MI 15 g/10min (ASTM D1238, at 190 deg C/2.16Kg), Shore A = 55 (ASTM D2240).
- 10 • OBC2: INFUSETM 9107, density 0.866 g/cm³ (ASTM D792), MI 1 g/10min (ASTM D1238, at 190 deg C/2.16Kg), Shore A = 60 (ASTM D2240).
- OBC3: density 0.870 g/cm³ (ASTM D792), MI 0.5 g/10min (ASTM D1238, at 190 deg C/2.16Kg), Shore A = 51 (ASTM D2240); 1-octene content in the soft segment of 27 mol%.
- 15 • Crosslinking agent: LuperoxTM DC40 SP2 (40 wt% active percent) from Arkema.
- Mineral oil: paraffin oil, Hydrobrite 550, available from SONNEBORN.
- Blowing agent: AC3000, from Kum Yang Chemical Company.
- Mica: particle size around 205 microns; locally sourced
- ZnO: zinc oxide; Horsehead Corporation
- 20 • ZnSt: zinc stearate; Fisher Scientific
- EPDM1: NordelTM IP 3430, Mooney viscosity (ML1+4, 125 deg C) = 27 MU, available from The Dow Chemical Company.
- EPDM2: NordelTM IP 3640, Mooney viscosity (ML1+4, 125 deg C) = 40 MU, available from The Dow Chemical Company.
- 25 • Comparative A: neoprene rubber foam

Table 2. Inventive formulations for bun foam preparation

Example	OBC1	OBC2	OBC3	POE	EPDM 1	EPDM 2	Mineral oil	Crosslinking agent	Blowing agent	Mica	ZnO	ZnSt
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	PHR	PHR	PHR	PHR	PHR
1	30.0	/	12.0	/	30.0	/	28.0	5.0	5.0	5.0	0.5	0.5
2	/	/	12.0	30.0	30.0	/	28.0	5.0	5.0	5.0	0.5	0.5
3	/	/	10.0	35.0	/	20.0	35.0	5.5	5.0	5.0	0.5	0.5
4	/	10.0	/	35.0	/	20.0	35.0	5.5	5.0	5.0	0.5	0.5
5	/	/	15.0	55.0	/	/	30.0	6.0	5.0	5.0	0.5	0.5

PHR – parts per hundred of resin

5

Sample Preparation

1. Batch Mixing

[77] The ingredients were added to the Kobelco 3.5L internal mixer in the following order: Polymer followed by ZnO, ZnSt, Talc and Oil in 3 successive pours after the polymer melted. The blowing agent and peroxide were added next and mixed for an additional 3 to 5 minutes for a total mix time of 15 minutes keeping the batch temperature below 125°C. The resulting batch was finished on a two roll mill to completely mix any ingredients remaining on the surface when dropped from the mixer.

15

2. Foam Preparation

[78] The finished milled blankets were cut into squares such that 200 grams would fit into the compression molding chase used to make the bun foams. The pre-foams were preheated for 8 minutes at 120°C and pressed at 20 tons for 4 minutes to form a solid mass in the mold before foaming. The preheated mass was transferred to the foaming press and held for 8 minutes at 66K psi and 180°C. Once the pressure was released, the foam was removed, measured and allowed to cool. The foams were cut and sliced into thin layers or desired shape for testing.

25

Table 3. Inventive Example foams vs. Comparative foam (3 mm foam sheet)

Example	Elongation at break	Tensile Strength at break	60% modulus	300% modulus	Density	Tear Strength	Compression Set
	(%)	(Kg/cm ²)	(Kg/cm ²)	(Kg/cm ²)	g/cc	(Kg/cm)	%
1	345.8	3.06	0.64	2.70	0.092	1.27	33
2	314.2	3.96	0.74	3.88	0.123	1.45	22
3	300.0	3.80	0.68	3.76	0.142	1.34	16
4	294.8	3.59	0.67	3.56	0.154	1.31	18
5	324.0	4.60	0.70	1.50	0.090	1.37	28
Comparative A	> 400	> 5.0	0.60-0.75	>1.10	0.17- 0.21	>1.10	20-30

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[79] From the test results in Table 3, it can be seen that surprisingly lower density (light weight) foams made from the inventive formulations showed physical properties that are comparable to the benchmark neoprene foam, which is typical for wet suit applications, especially for the 60% modulus and compression set, which are key requirements for application such as wetsuits. Although the tensile strength and elongation are somewhat lower than that of the neoprene foam, these can be compensated for by laminating with elastic fabrics.

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[80] While the invention has been described with respect to a limited number of embodiments, the specific features of one embodiment should not be attributed to other embodiments of the invention. No single embodiment is representative of all aspects of the invention. In some embodiments, the compositions or methods may include numerous compounds or steps not mentioned herein. In other embodiments, the compositions or methods do not include, or are substantially free of, any compounds or steps not enumerated herein. Variations and modifications from the described embodiments exist. Finally, any number disclosed herein should be construed to mean approximate, regardless of whether the word "about" or "approximately" is used in describing the number. The appended claims intend to cover all those modifications and variations as falling within the scope of the invention.

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CLAIMS

What is claimed is:

1. A foamable composition comprising:

a) one or more olefin block copolymers having a Mw/Mn from 1.7 to 3.5, and at least one melting point, T_m, in degrees Celsius, and a density, d, in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2;$$

b) one or more olefin copolymers;

c) an oil;

d) a crosslinking agent; and,

e) a blowing agent.

2. The foamable composition of Claim 1 wherein one or more of the olefin block copolymers is mesophase separated and has a delta comonomer of greater than 18.5 mol%.

3. The foamable composition of Claim 1 wherein the olefin copolymer comprises ethylene-propylene-diene monomer rubber and/or an ethylene/ α -olefin copolymer.

4. The foamable composition of Claim 3 wherein

a) the olefin block copolymer is present in an amount of 5 wt% to 40 wt%, preferably 10 wt% to 30 wt%, more preferably 10 wt% to 25 wt%;

b) the ethylene-propylene-diene- monomer rubber is present in an amount of 5 wt% to 40 wt%, preferably 5 wt% to 30 wt%;

c) the mineral oil is present in an amount of 15 wt% to 45 wt%, preferably 20 wt% to 40 wt%, more preferably 25 wt% to 35wt%;

d) the crosslinking agent is present in an amount of 1 – 6 phr, preferably 2-5 phr.

e) the blowing agent is present in an amount of 1-8 phr, preferably 2-6.

5. A foam made from the foamable composition of Claim 1.

6. The foam of Claim 5 having a density of 0.05 g/cc to 0.2 g/cc, a 60% modulus of 0.60 Kg/cm² to 1.50 Kg/cm², and a compression set of 15% to 35%.

7. A laminate comprising the foam of Claim 5.

8. An article comprising the laminate of Claim 7.

9. An article comprising the foam of Claim 5.

10. A wetsuit comprising the foam of Claim 5.