(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 July 2009 (09.07.2009)

PCT

(10) International Publication Number
WO 2009/085814 A2

(51) International Patent Classification:
C08J 9/00 (2006.01) ***C08J 9/10*** (2006.01)
C08J 9/08 (2006.01) *C08L 23/16* (2006.01)

(21) International Application Number:
PCT/US2008/087149

(22) International Filing Date:
17 December 2008 (17.12.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/015,006 19 December 2007 (19.12.2007) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,

[Continued on next page]

(54) Title: COMPOSITIONS USEFUL FOR PREPARING FOAMED ARTICLES FROM LOW MELT INDEX RESINS

(57) Abstract: Foamed articles are prepared from a composition comprising a low MI polymer, e.g., an ethylene/alpha-olefin copolymer with a density of less than 0,91 g/cc and an MI of less than 3 g/10 min, a chemical blowing agent, e.g., azodicarbonamide, a scorch inhibitor, e.g, a TEMPO compound, and, optionally, a free radical initiator, e.g., peroxide. If the composition does not comprise a free radical initiator, then it is exposed to a source of free radicals before and/or during the foaming process, e.g., e-beam or UV-light. The composition is compounded and foamed using conventional process equipment and conditions.

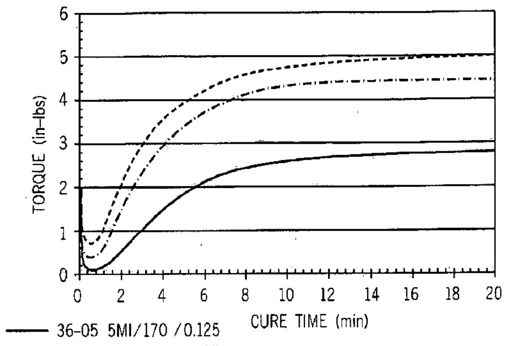

FIG. 1A

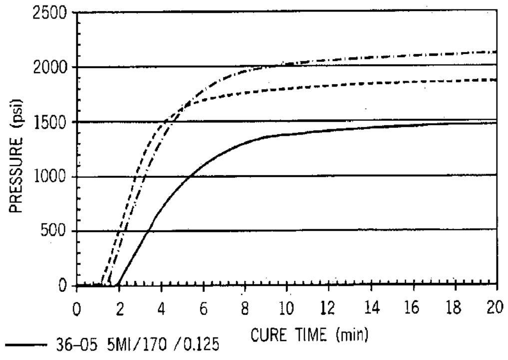

FIG. 1B

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ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

64747A

COMPOSITIONS USEFUL FOR PREPARING FOAMED ARTICLES FROM LOW MELT INDEX RESINS

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 61/015,006, filed December 19, 2007, which application is fully incorporated herein by reference.

FIELD OF THE INVENTION

[0001] This invention relates to foamed articles. In one aspect, the invention relates to foamed articles made from low melt index resins while in another aspect, the invention relates to foamed articles made from crosslinked, low melt index resins. In still another aspect, the invention relates to a continuous process for making foamed articles from low melt index resins while in yet another aspect, the invention relates to such a process that uses a scorch inhibitor.

BACKGROUND OF THE INVENTION

[0002] Crosslinked, foamed articles are of use in a variety of applications in which lightweight, cushioned materials are needed. These applications include footwear, gaskets, sports foams, weather stripping, acoustic management foams and insulating foams. Foams prepared by the expansion of peroxide-initiated, crosslinked polyolefins have attractive mechanical properties, but the manner in which they are processed depends, in part, upon their melt index (MI, expressed in grams per 10 minutes or g/10 min).

[0003] In one process, i.e., a batch process, the polyolefin is compounded with one or more other materials (e.g., filler, various additives, etc.), fabricated into a sheet or other shape, diced, fed to an extruder or other mixing device in which it is compounded with peroxide, blowing agent, etc., and then fabricated into a molded part. In another process, i.e., a continuous process, the polyolefin, filler, additives, peroxide and blowing agent are fed in a single operation to an extruder or other mixing device from which a fabricated article is molded. While polyolefins with an MI of 3 g/10 min or more are useful in either process, those with an MI of less than 3 g/10 min do not lend themselves well to preparation in the continuous process.

[0004] This limitation on MI is due, at least in part, to shear heating, i.e., an increase in processing temperature in response to the mechanical action applied to the polymer during mixing. Polymers compounded in the continuous process are exposed to considerably more shear heating than polymers compounded in a batch process. Polymers with a low MI (e.g., less than 3 g/10 min) exhibit a large degree of shear heating as compared with like polymers with an MI of 3 g/10 min or more. This increase in shear heating can result in premature polymer crosslinking (i.e., scorch) during compounding or secondary molding or foaming processes and this, in turn, can create gel particles in the mass of the compounded polymer. These gel particles can adversely impact the homogeneity of the final product. Moreover, excessive scorch can so reduce the plastic properties of the material that it cannot be efficiently processed with the likely possibility that the entire batch will be lost.

[0005] One method of reducing the temperature during compounding is to reduce the production rate, but this leads to higher unit costs. Another method of minimizing scorch is the incorporation of scorch inhibitors into the compositions. For example, British patent 1,535,039 discloses the use of organic hydroperoxides as scorch inhibitors for peroxide-cured ethylene polymer compositions. USP 3,751,378 discloses the use of N-nitroso diphenylamine or N,N'-dinitroso-para-phenylamine as scorch retardants incorporated into a polyfunctional acrylate crosslinking monomer for providing long Mooney scorch times in various copolymer formulations. USP 3,202,648 discloses the use of nitrites such as isoamyl nitrite, tert-decyl nitrite and others as scorch inhibitors for polyethylene. USP 3,954,907 discloses the use of monomeric vinyl compounds as protection against scorch. USP 3,335,124 describes the use of aromatic amines, phenolic compounds, mercaptothiazole compounds, bis(N,N-disubstituted-thiocarbamoyl) sulfides, hydroquinones and dialkyldithiocarbamate compounds. USP 4,632,950 discloses the use of mixtures of two metal salts of disubstituted dithiocarbamic acid in which one metal salt is based on copper.

[0006] One commonly used scorch inhibitor for use in free radical, particularly peroxide, initiator-containing compositions is 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl also known as nitroxyl 2, or NR 1, or 4-oxypiperidol, or tanol, or tempol, or tmpn, or probably most commonly, 4-hydroxy-TEMPO or even more simply, h-TEMPO or just TEMPO. The addition of 4-hydroxy-TEMPO minimizes scorch by "quenching" free radical crosslinking of the crosslinkable polymer at melt processing temperatures.

[0007] The use of low MI polymers in the preparation of crosslinked, foamed articles is desirable at several levels not the least of which is an improvement in a number of different mechanical properties, e.g., tensile and Type C tear. However, low MI polymers require more energy for compounding and this, in turn, increases shear heating. Accordingly, the ability to manufacture crosslinked, foamed articles at conventional production rates with acceptable levels of scorch is of continuing interest to the foam industry.

SUMMARY OF THE INVENTION

[0008] In one embodiment of this invention, foamed articles are prepared in a continuous process from a composition comprising a low MI polymer, a chemical blowing agent, a scorch inhibitor and, optionally, a free radical initiator. If the composition does not comprise a free radical initiator, then it is exposed to a source of free radicals before and/or during the foaming process. The low MI polymer is typically and preferably an ethylene/alpha-olefin copolymer with a density of less than 0.91 grams per cubic centimeter (g/cc) and an MI of less than 3 g/10 min. The chemical blowing agent is typically and preferably an organic compound, such as azodicarbonamide, and the scorch inhibitor is a tetramethylpiperidinyl oxy compound, i.e., a TEMPO compound. The free radical initiator is typically and preferably peroxide but if the composition does not contain a free radical initiator, then before and/or during the foaming process it is exposed to a source of free radicals such as e-beam or UV-light. The composition is compounded and foamed using conventional process equipment and conditions.

[0009] In another embodiment, the invention is a foamed article made from a composition comprising a low MI polymer, a chemical blowing agent, a free radical initiator and a scorch inhibitor. The article can take any shape and size, and is useful in a wide array of applications, e.g., footwear, gaskets, sports foams, weather stripping, acoustic management and insulation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1A is a line graph reporting the cure behavior (torque vs. cure time) of compositions comprising ENGAGE® ethylene/1-butene copolymers of different MI.

[0011] Figure 1B is a line graph reporting the cure behavior (pressure vs. cure time) of compositions comprising ENGAGE® ethylene/1-butene copolymers of different MI.

[0012] Figure 2 is a line graph reporting the apparent viscosity vs. MI of compositions comprising ENGAGE® ethylene/1-butene copolymers of different MI.

[0013] Figure 3 is a bar graph reporting the foam density, tensile and tear strength of foams made from compositions comprising ENGAGE® ethylene/1-butene copolymers of different MI.

[0014] Figure 4 is a bar graph reporting the skin density, tensile and tear strength of skins made from compositions comprising ENGAGE® ethylene/1-butene copolymers of different MI.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0015] The numerical ranges in this disclosure include all values from and including the lower and the upper values, in increments of one unit, provided that there is a separation of at least two units between any lower value and any higher value. As an example, if a compositional, physical or other property, such as, for example, molecular weight, viscosity, melt index, etc., is from 100 to 1,000, it is intended that all individual values, such as 100, 101, 102, etc., and sub ranges, such as 100 to 144, 155 to 170, 197 to 200, etc., are expressly enumerated. For ranges containing values which are less than one or containing fractional numbers greater than one (e.g., 1.1, 1.5, etc.), one unit is considered to be 0.0001, 0.001, 0.01 or 0.1, as appropriate. For ranges containing single digit numbers less than ten (e.g., 1 to 5), one unit is typically considered to be 0.1. These are only examples of what is specifically intended, and all possible combinations of numerical values between the lowest value and the highest value enumerated, are to be considered to be expressly stated in this disclosure. Numerical ranges are provided within this disclosure for, among other things, MI, molecular weight, and the amount of various components in the compositions used in the practice of this invention.

[0016] "Polymer" means a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer, usually employed to refer to polymers prepared from only one type of monomer, and the term interpolymer as defined below.

[0017] "Copolymer" means a polymer prepared by the polymerization of at least two different types of monomers. This generic term includes the traditional definition of copolymers, i.e., polymers prepared from two different types of monomers, and the more expansive definition of copolymers, i.e., polymers prepared from more than two different types of monomers, e.g., terpolymers, tetrapolymers, etc.

[0018] "Blend" and like terms mean a composition of two or more materials. Such a blend may or may not be miscible. Such a blend may or may not be phase separated. Such a blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and any other method known in the art.

[0019] "Composition" and like terms means a mixture or blend of two or more components. In the context of a mix or blend of materials from which foam is fabricated, the composition includes all the components of the mix, e.g., polymer, blowing agent, free radical initiator, scorch inhibitor and any other additives such as free radical crosslinking coagents, i.e. promoters or co-initiators or cure catalysts, nucleating agents, anti-oxidants, fillers, flame retardants, colorants, pigments, lubricants, etc.

[0020] "Blowing agent" and like terms mean a substance incorporated into a mixture for the purpose of producing a foam.

[0021] "Foam" and like terms mean a substance that is formed by trapping many gas bubbles in a liquid or solid. Solid foams form an important class of lightweight cellular engineering materials, and are often classified into two types based on their pore structure. One type is an open cell structure in which many, if not most, of the pores are connected to each other and forms an interconnected network. The other type is a closed cell structure in which the majority, typically the vast majority, of cells is not connected to one another.

[0022] "Continuous process" and like terms mean, in the context of this invention, a process for making a molded foam article in which a low MI polymer, a chemical blowing agent, a scorch inhibitor, optionally, a free radical initiator, and optionally, one or more additives, are compounded in a single mixing device, e.g., an extruder, into an essentially homogeneous composition from which a foamed article is fabricated.

[0023] The polymers encompassed in the present invention are those natural or synthetic polymers which are thermoplastic and/or elastomeric in nature, and which can be crosslinked (cured) through the action of a crosslinking agent. These polymers include polyolefins, polyesters, polyethers, polyamides, polyurethanes and others, but the polyolefins are the preferred low MI polymers for use in this invention. Polyolefins suitable for use in this invention are described in Modern Plastics Encyclopedia 89 pp 63-67, 74-75. Illustrative polymers include LLDPE, LDPE, HDPE, medium density polyethylene, ultralow density polyethylene, chlorinated polyethylene, ethylene-propylene terpolymers (e.g., ethylene-propylene-butadiene, EPDM), polybutadiene, styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), ethylene vinyl acetate (EVA), functionalized polyolefins such as ethylene ethyl acrylate (EEA), ethylene acrylic acid (EAA) and ethylene methacrylic acid (EMA), ethylene-propylene copolymers (EP), silicone rubber, chlorosulfonated polyethylene, fluoroelastomers and the like.

[0024] The polymers useful in the practice of this invention have an MI of less than 3, preferably less than about 2.5, and more preferably less than about 2, g/10 min. The polymers typically have an MI greater than about 0.1, and more preferably greater than about 0.2, g/10 min. The MI of ethylene-based polymers is measured by the procedure of ASTM D-1238 (190C/2.16kg).

[0025] The polyolefin copolymers useful in the practice of this invention preferably have a density of less than about 0.95, more preferably less than about 0.93 and more even preferably less than about 0.91, grams per cubic centimeter (g/cc). The polyolefin copolymers typically have a density greater than about 0.85, and more preferably greater than about 0.86, g/cc. The density of polyolefin polymers is measured by the procedure of ASTM D-792.

[0026] The polyolefin copolymers particularly useful in the practice of this invention include ethylene/α-olefin copolymers having a α-olefin content of between about 15, preferably at least about 20 and even more preferably at least about 25, wt% based on the weight of the interpolymer. These copolymers typically have an α-olefin content of less than about 50, preferably less than about 45, more preferably less than about 40 and even more preferably less than about 35, wt% based on the weight of the copolymer. The α-olefin content is measured by 13C nuclear magnetic resonance (NMR) spectroscopy using the procedure described in Randall (Rev. Macromol. Chem. Phys., C29 (2&3)).

[0027] The α-olefin is preferably a C3-20 linear, branched or cyclic α-olefin. Examples of C3-20 α-olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. The α-olefins can also contain a cyclic structure such as cyclohexane or cyclopentane, resulting in an α-olefin such as 3-cyclohexyl-1-propene (allyl cyclohexane) and vinyl cyclohexane. Although not α-olefins in the classical sense of the term, for purposes of this invention certain cyclic olefins, such as norbornene and related olefins, are α-olefins and can be used in place of some or all of the α-olefins described above. Similarly, styrene and its related olefins (for example, α-methylstyrene, etc.) are α-olefins for purposes of this invention. Acrylic and methacrylic acid and their respective ionomers, and acrylates and methacrylates, however, are not α-olefins for purposes of this invention. Illustrative polyolefin copolymers include ethylene/propylene, ethylene/butene, ethylene/1-hexene, ethylene/1-octene, ethylene/styrene, EAA, EEA, EMA and the like. Illustrative terpolymers include ethylene/propylene/1-octene, ethylene/propylene/-butene, ethylene/butene/1-octene, and ethylene/butene/styrene. The copolymers can be random or blocky.

[0028] More specific examples of olefinic copolymers useful in this invention include very low density polyethylene (VLDPE) (e.g., FLEXOMER® ethylene/1-hexene polyethylene made by The Dow Chemical Company), homogeneously branched, linear ethylene/α-olefin copolymers (e.g. TAFMER® by Mitsui Petrochemicals Company Limited and EXACT® by Exxon Chemical Company), and homogeneously branched, substantially linear ethylene/α-olefin polymers (e.g., AFFINITY® and ENGAGE® polyethylene available from The Dow Chemical Company). The more preferred polyolefin copolymers are the homogeneously branched linear and substantially linear ethylene copolymers. The substantially linear ethylene copolymers are especially preferred, and are more fully described in USP 5,272,236, 5,278,272 and 5,986,028.

[0029] The polyolefin copolymers useful in the practice of this invention also include propylene, butene and other alkene-based copolymers, e.g., copolymers comprising a majority of units derived from propylene and a minority of units derived from another α-olefin (including ethylene). Exemplary polypropylenes useful in the practice of this invention include the VERSIFY® polymers available from The Dow Chemical Company, and the VISTAMAXX® polymers available from ExxonMobil Chemical Company.

[0030] In addition, blends of two or more polymers may be employed. The polymers described above and the foamed, crosslinkable compositions prepared from these polymers may contain various other additives known to those skilled in the art including, but not limited to, fillers such as carbon black, titanium dioxide, and the alkaline earth metal carbonates, and monomeric co-agents such as triallylcyanurate, allyldiglycolcarbonate, triallylisocyanurate, trimethylolpropane, diallylether, trimethylolpropane trimethacrylate, and various allylic compounds. Methacrylate and acrylate compounds may also be added separately to the various polymers identified above. The crosslinkable compositions of this invention may also contain such conventional additives as antioxidants, stabilizers, plasticizers, processing oils and the like.

[0031] Typically the polymers used in the practice of this invention comprise at least 50, preferably at least 70 and more preferably at least 80, percent by weight of the composition to be foamed.

[0032] The free radical initiators used in the practice of this invention include any thermally activated compound that is relatively unstable and easily breaks into at least two radicals. Representative of this class of compounds are the peroxides, particularly the organic peroxides, and the azo initiators. Of the free radical initiators used as crosslinking agents, the dialkyl peroxides and diperoxyketal initiators are preferred. These compounds are described in the Encyclopedia of Chemical Technology, 3rd edition, Vol. 17, pp 27-90. (1982).

[0033] In the group of dialkyl peroxides, the preferred initiators are: dicumyl peroxide, di-t-butyl peroxide, t-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane, 2,5-dimethyl-2,5-di(t-amylperoxy)-hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(t-amylperoxy)hexyne-3, α,α-di[(t-butylperoxy)-isopropyl]-benzene, di-t-amyl peroxide, 1,3,5-tri-[(t-butylperoxy)-isopropyl]benzene, 1,3-dimethyl-3-(t-butylperoxy)butanol, 1,3-dimethyl-3-(t-amylperoxy)butanol and mixtures of two or more of these initiators.

[0034] In the group of diperoxyketal initiators, the preferred initiators are: 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(t-butylperoxy)cyclohexane n-butyl, 4,4-di(t-amylperoxy)valerate, ethyl 3,3-di(t-butylperoxy)butyrate, 2,2-di(t-amylperoxy)propane, 3,6,6,9,9-pentamethyl-3-ethoxycarbonylmethyl-1,2,4,5-

tetraoxacyclononane, n-butyl-4,4-bis(t-butylperoxy)-valerate, ethyl-3,3-di(t-amylperoxy)-butyrate and mixtures of two or more of these initiators.

[0035] Other peroxide initiators, e.g., 00-t-butyl-0-hydrogen-monoperoxysuccinate; 00-t-amyl-0-hydrogen-monoperoxysuccinate and/or azo initiators e.g., 2,2'-azobis-(2-acetoxypropane), may also be used to provide a crosslinked polymer matrix. Other suitable azo compounds include those described in USP 3,862,107 and 4,129,531. Mixtures of two or more free radical initiators may also be used together as the initiator within the scope of this invention. In addition, free radicals can form from shear energy, heat or radiation.

[0036] The amount of peroxide or azo initiator present in the crosslinkable compositions of this invention can vary widely, but the minimum amount is that sufficient to afford the desired range of crosslinking. The minimum amount of initiator is typically at least about 0.05, preferably at least about 0.1 and more preferably at least about 0.25, wt% based upon the weight of the polymer or polymers to be crosslinked. The maximum amount of initiator used in these compositions can vary widely, and it is typically determined by such factors as cost, efficiency and degree of desired crosslinking desired. The maximum amount is typically less than about 10, preferably less than about 5 and more preferably less than about 3, wt% based upon the weight of the polymer or polymers to be crosslinked.

[0037] In those embodiments of the invention in which the composition does not comprise a free radical initiator, or at least a thermally activated free radical initiator such as peroxide, then free radical crosslinking initiation via electromagnetic radiation, e.g., sunlight, ultraviolet (UV) light, infrared (IR) radiation, electron beam, beta-ray, gamma-ray, x-ray and neutron rays, can be employed. Radiation is believed to affect crosslinking by generating polymer radicals, which may combine and crosslink. The Handbook of Polymer Foams and Technology, supra, at pp. 198-204, provides additional teachings. Elemental sulfur may be used as a crosslinking agent for diene containing polymers such as EPDM and polybutadiene. The amount of radiation used to cure the copolymer will vary with the chemical composition of the copolymer, the composition and amount of initiator, if any, the nature of the radiation, and the like, but a typical amount of UV light is at least about 0.05, more typically at about 0.1 and even more typically at least about 0.5, Joules/cm^2, and a typical amount of E-beam radiation is at least about 0.5, more typically at least about 1 and even more typically at least about 1.5, megarads. Of course, free radical crosslinking initiation via electromagnetic radiation can be used in combination with thermal initiated free radical crosslinking.

[0038] If sunlight or UV light is used to effect cure or crosslinking, then typically and preferably one or more photoinitiators are employed. Such photoinitiators include organic carbonyl compounds such as such as benzophenone, benzanthrone, benzoin and alkyl ethers thereof, 2,2-diethoxyacetophenone, 2,2-dimethoxy, 2 phenylacetophenone, p-phenoxy dichloroacetophenone, 2-hydroxycyclohexylphenone, 2-hydroxyisopropylphenone, and 1-phenylpropanedione-2-(ethoxy carboxyl) oxime. These initiators are used in known manners and in known quantities, e.g., typically at least about 0.05, more typically at least about 0.1 and even more typically about 0.5, wt% based on the weight of the copolymer.

[0039] If moisture, i.e., water, is used to effect cure or crosslinking, then typically and preferably one or more hydrolysis/condensation catalysts are employed. Such catalysts include Lewis acids such as dibutyltin dilaurate, dioctyltin dilaurate, stannous octonoate, and hydrogen sulfonates such as sulfonic acid.

[0040] Free radical crosslinking coagents, i.e. promoters or co-initiators, include multifunctional vinyl monomers and polymers, triallyl cyanurate and trimethylolpropane trimethacrylate, divinyl benzene, acrylates and methacrylates of polyols, allyl alcohol derivatives, and low molecular weight polybutadiene. Sulfur crosslinking promoters include benzothiazyl disulfide, 2-mercaptobenzothiazole, copper dimethyldithiocarbamate, dipentamethylene thiuram tetrasulfide, tetrabutylthiuram disulfide, tetramethylthiuram disulfide and tetramethylthiuram monosulfide.

[0041] These coagents are used in known amounts and known ways. The minimum amount of coagent is typically at least 0.05, preferably at least 0.1 and more preferably at least 0.5, wt% based upon the weight of the polymer or polymers to be crosslinked. The maximum amount of coagent used in these compositions can vary widely, and it is typically determined by such factors as cost, efficiency and degree of desired crosslinking desired. The maximum amount is typically less than 10, preferably less than 5 and more preferably less than 3, wt% based upon the weight of the polymer or polymers to be crosslinked.

[0042] Free radical crosslinking processes for crosslinkable polymers are well known in the art, and are well described generally in PCT applications WO 2005/063896, WO 2005/066280 and WO 2005/066282. Rubber World, "Elastomer Crosslinking with

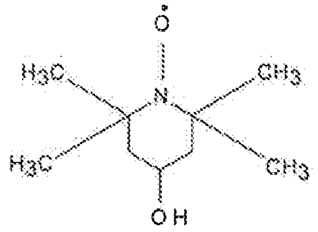
Diperoxyketals," October, 1983, pp.26-32, Rubber and Plastic News, "Organic Peroxides for Rubber Crosslinking," Sep. 29, 1980, pp. 46-50, and the PCT publications cited above all describe the crosslinking action and representative crosslinkable polymers.

[0043] In order to produce a foam product with a greater degree of foaming, compositions referred to as "blowing agents" are often added to the reaction mixture. Blowing agents are available in two basic forms, physical and chemical. Physical blowing agents simply do not undergo a chemical reaction to vaporize, and are either mixed with the polymer as a gas or are mixed with the polymer as a solid or liquid and then converted to a gas. Chemical blowing agents are also mixed with the polymer as a solid or liquid, but undergo a chemical reaction of which at least one product is a gas.

[0044] The blowing agent used in the practice of this invention comprises a chemical blowing agent although a minor amount of physical blowing agent can be used in combination with a chemical blowing agent. Suitable chemical blowing agents include azodicarbonamide, azodiisobutyronitrile, benzenesulfo-hydrazide, 4,4-oxybenzene sulfonyl semi-carbazide, p-toluene sulfonyl semi-carbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, trihydrazino triazine and sodium bicarbonate.

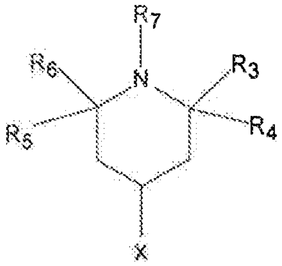
[0045] The blowing agent composition is typically present in the polymer composition at a concentration of 3, preferably 4 and more preferably 5, parts per hundred (pph) or more based on polymer resin weight. The blowing agent composition is typically present in the polymer composition at a concentration of 18, preferably 15 and more preferably 12, pph or less based on polymer resin weight. Blowing agents and their use are more fully described in, among others, USP 6,872,757 and 6,750,264.

[0046] "TEMPO compound" and like terms mean compounds represented by formulae (I), (II) and (III). 4-Hydroxy-TEMPO has the chemical structural formula of (I):



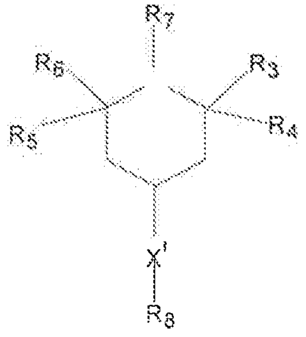
(I)

The TEMPO compounds from which a derivative, particularly the ether, ester and urethane derivates, can be prepared are of formula (II):



(II)

The ether, ester and urethane derivatives of a TEMPO compound that are used as scorch inhibitors in the compositions of this invention have the chemical structural formula of (III):



(III)

in which

X of formula II is any group that can react with another compound, e.g., an alcohol, a carboxylic acid, an alkyl sulfate, an isocyanate, etc., to form the ether, ester or urethane group (or corresponding sulfur, phosphorus or amine derivative) of formula III, and preferably X is hydroxyl, amine, mercaptan, phosphino (H_2P-), phosphinyl ($H_2P(O)$-) or silyl (H_3Si-) group, and more preferably X is hydroxyl;

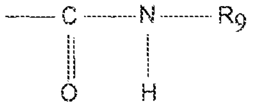
X' of formula III is at least a divalent atom, preferably an atom of oxygen, sulfur, nitrogen, phosphorus or silicon, more preferably an atom of oxygen or sulfur and most preferably an atom of oxygen;

and with respect to both formulae II and III

R_3-R_6 are each independently a C_{1-12} hydrocarbyl or inertly-substituted hydrocarbyl group, or any of the R_3-R_6 groups can join with one or more of the other R_3-R_6 groups to form one or more hydrocarbyl or inertly-substituted hydrocarbyl rings, preferably with at least a 5 carbon atoms;

R_7 is an oxyl (O•) or a C_{1-20} hydrocarbyloxy group;

R_8 is a hydrogen or C_{1-12} hydrocarbyl or inertly-substituted hydrocarbyl or carboxyl group, or a urethane group of the formula



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R_9 \qquad (IV)$$

with the proviso that if the R_3-R_6 groups are methyl, then R_8 is not hydrogen; and

R_9 is a C_{2-30} hydrocarbyl or inertly-substituted hydrocarbyl group.

[0047] As here used, "ether, ester and urethane derivatives" are the compounds of formula III in which X' is a divalent oxygen radical. The hydrocarbyl groups of R_3-R_9 include, but are not limited to, alkyl, aryl, aralkyl, cycloalkyl, alkenyl, and the like. Preferably, R_3-R_6 are each independently a C_{1-4} alkyl group and more preferably, R_3-R_6 are each independently methyl groups. Preferably R_7 is an oxyl or a C_{1-12} alkyloxy group, and more preferably an oxyl group. Preferably R_8 is a C_{1-12} alkyl, or a C_{1-12} alkyl carboxyl or an aryl carboxyl group, or a urethane group, and more preferably a C_{1-8} alkyl group, or benzoic acid group, or a urethane group. Preferably R_9 is a C_{5-30} alkyl group, more preferably a C_{5-20} alkyl group. Representative ether and urethane derivatives of 4-hydroxy-TEMPO include methyl ether TEMPO, butyl ether TEMPO, hexyl ether TEMPO, allyl ether TEMPO, amino-TEMPO, PAPI-TEMPO adduct, MDI-urethane-bis-TEMPO and stearyl urethane TEMPO.

[0048] The scorch inhibitors of this invention are used in the same manner as known scorch inhibitors. The amount of scorch inhibitor used in the compositions of this invention will vary with its molecular weight and the amount and nature of the other components of the composition, particularly the free radical initiator, but typically the minimum amount of scorch inhibitor used is at least 0.01, preferably at least 0.05, more preferably at least 0.1 and most preferably at least 0.15, wt% based on the weight of the polymer. The maximum amount of scorch inhibitor can vary widely, and it is more a function of cost and efficiency than anything else. The typical maximum amount of scorch inhibitor does not exceed 20, preferably does not exceed 10 and more preferably does not exceed 7, wt% based on the weight of the polymer.

[0049] In one embodiment of the invention, the compositions from which the foamed articles are fabricated are prepared by mixing in a single vessel, typically an extruder but other mixing vessels can be used, a low MI polymer, a chemical blowing agent, a scorch inhibitor, optionally, a free radical initiator, and optionally one or more other additives. These components can be added in any order, but typically the polymer and scorch inhibitor are added first. The scorch inhibitor, blowing agent, free radical initiator and optional additives are typically first compounded into individual or collective masterbatchs, and then added to the low MI polymer. All components of the mix are blended until an essentially homogeneous composition is formed. The conditions of blending are such to minimize early activation of the peroxide and/or blowing agent but with the presence of sufficient scorch inhibitor these conditions can be more aggressive and can be maintained for a longer period of time than without the scorch inhibitor. Once fully blended, the composition is then fabricated, e.g., extruded, molded, cast, etc., into the desired articles and subjected to crosslinking and/or foaming conditions which are well known to those of ordinary skill in the art.

[0050] The compositions of this invention are further described by the following examples. Unless otherwise noted, all parts and percentages are by weight.

SPECIFIC EMBODIMENTS

Compounding Protocol:

[0051] The composition ingredients are added to a laboratory scale Banbury mixer in the order described in Table 1, i.e., polymer, zinc oxide (ZnO) and zinc stearate (ZnSt) for blowing agent activation, calcium carbonate ($CaCO_3$), MB1 (a TEMPO compound), peroxide (ROOR) and lastly, blowing agent (BA).

Table 1A

Ingredient Addition Sequence

Ex.	Time (min)	RMP	Temp (F)	Addition/Action
1	0	75	101.7	Add Polymer
	1.5	50	151.5	Add ZnO/ZnSt as a mixture
	3	50	157.5	Add $CaCO_3$
	4	50	157.8	Sweep (Raise the ram, scrape surface of the ram, and feed the throat)
	5	50	163.6	Add MB1
	6	50	162.2	Add BA/ROOR as a mixture
	7	50	170.5	Sweep (as above)
	10	50	178.4	Drop, open the mixer and remove batch for milling, pass batch once through a 2-roll mill at a temperature of 60/61C.
2	0	75	159.1	Add Polymer
	1.5	50	180.2	Add ZnO/ZnSt as a mixture
	3	50	210.7	Add $CaCO_3$
	4	50	213.8	Sweep (as above)
	5	50	220.6	Add MB1
	6	50	219.5	Add BA/ROOR
	7	35	225.8	Sweep (as above)
	11.5	35	223.7	Drop (as above)
3	0	75	116.3	Add Polymer
	1.5	50	135.5	Add ZnO/ZnSt as a mixture
	3	50	174.5	Add $CaCO_3$
	4	50	187.5	Sweep (as above)
	5	50	195.9	Add MB1
	6	50	200.4	Add BA/ROOR sequentially
	7	50	209.9	Sweep (as above0

Ex.	Time (min)	RMP	Temp (F)	Addition/Action
	9	30	231.4	Lowered RPM during continued mixing
	10.5	30	217.3	Drop (as above)

The polymer is linear ethylene/1-butene copolymer.

ELVAX 265 is a poly(ethylene-co-vinylacetate) linear copolymer, 28% vinyl acetate by weight, 3 MI from DuPont.

INSTEP MB1 is a mixture of 2.5% 4-hydroxytetramethylpipiridinyl-1-oxyl with 97.5% Elvax 260, a poly(ethylene-co-vinylacetate) with 28% vinyl acetate, 6MI.

AZ 130 is azodicarbonamide, a chemical blowing agent from Akzo Nobel.

DiCup 40 KE is dicumyl peroxide, 40 weight percent.

[0052] Table 1B below lists the ingredient levels for the example compounds.

Table 1B

Foam Density, Rheology and Cure Results

Ingredient	Description/Analysis	Ex. 1	Ex. 2	Ex. 3
ENGAGE® 7340	5MI. 0.875g/cc	100		
ENGAGE® 7360	1MI, 0.875g/cc		100	
ENGAGE® 7370	0.5 0.875g/cc			100
ELVAX 265	3MI, 0.940g/cc	6.8	6.8	6.8
INSTEP MB1		7	7	7
DiCup 40KE		3	3	3
AZ130		1.8	2.6	3.2
ZnO		0.260	0.375	0.462
ZnSt		0.260	0.375	0.462
CaCO3		5	5	5
170 MDRP-Min	20min	0.1	0.4	0.7
170 MDRP-Max		2.8	4.4	5.0
170 MDRP-Delta	In-lbs	2.7	4.0	4.2
170 MDRP-Pr (Delta)	psi	1574	2100	1874
180 MDRP-Min	10min	0.1	0.33	0.6

Ingredient	Description/Analysis	Ex. 1	Ex. 2	Ex. 3
180 MDRP-Max		2.3	3.91	4.7
180 MDRP-Delta	In-lbs	2.2	3.58	4.1
180 MDRP-Pr (Delta)	psi	1270	1885	2070

Each batch is run through a cool two-roll mill to make sheets ready for compression molding into foams.

Bun Foam Preparation:

[0053] Roll milled blankets are cut into 7" x 7" squares and placed inside a pre-heated mold of dimensions 9.0" x 9.0" x 0.25" at 110°C. The vertical walls have a large draft angle of 30 degrees so the foam can expand without resistance. Top and bottom mold surfaces consist of thin metal sheets with a non-stick sheet against the compound. The charge weight is determined by calculating mold volume multiplied by compound specific gravity + 10% to achieve a slight overfill.

[0054] Samples are pre-heated at 110°C for 4 to 8 minutes and pressed at 20,000 psi for 4 minutes. The sample and mold assembly is then quickly transferred to the curing press.

[0055] The mold is immediately closed under 30,000 psi of pressure using a Carver press model 3467-0 with heated platens. Platen temperature is typically set at 170°C for 10 minutes. After the desired cure time, the press is opened and the foam expanded. Although the foam is essentially cool after a few hours, it continues to shrink and solidify for about 24 hours.

[0056] The benefits are described below.

- MB1 enabled the use of lower MI Engage in typical foam compounds by protecting the polymer from premature crosslinking during higher temperature compounding and assumed subsequent processing including injection molding.
- Foams made with lower MI polymers showed higher tensile and tear (Type C) strength, higher cure response and lower compression set at 23 and 50C.
- MB1 enables compounding at higher temperatures that would normally cause noticeable changes in viscosity. This translates into higher throughputs (lower costs) in the compounding equipment.

- The use of MB1 and lower MI polymers allows for the production of lighter, lower density, foams that have similar performance to current foam compounds.
- The use of MB1 and lower MI polymers allows for reduction in the amount of the peroxide and blowing agent loading in the compound, and thus for lower cost formulations.

[0057] Table 2 lists the foam layer properties of the various compounds tested.

Table 2

Foam Density and Physical and Mechanical Property Results

Ingredient/Analysis	**Description**	**Ex. 1**	**Ex. 2**	**Ex. 3**
ENGAGE® 7340	5MI. 0.875g/cc	100		
ENGAGE® 7360	1MI, 0.875g/cc		100	
ENGAGE® 7370	0.5MI, 0.875g/cc			100
ELVAX 265	3MI, 0.940g/cc	6.8	6.8	6.8
INSTEP MB1		7	7	7
DiCup 40KE		3	3	3
AZ130		1.8	2.6	3.2
ZnO		0.260	0.375	0.462
ZnSt		0.260	0.375	0.462
CaCO3		5	5	5
Foam Density x 1000	Foam	202.8	207.4	212.2
Robound (%)	Foam	65.6	67.8	67.8
CSET 22h/23C,%	Foam	38.3	22.3	33.1
CSET 4h/50C, %	Foam	110.9	94.2	85.1
Tensile, psi	Foam	275.6	684.6	638.1
Elongation, %	Foam	518.6	390.8	374.1
Modulus, psi	Foam	151.4	277.3	296.6
100%Mod,psi	Foam	78.9	109.4	171.7
Type C Tear, pli x 10	Foam	506.0	570.0	577.2
Skin Density x 1000	Skin	244.2	253.7	251.3

Ingredient/Analysis	Description	Ex. 1	Ex. 2	Ex. 3
Rebound (%)	Skin	69.0	70.4	69.8
Tensile, psi	Skin	570.1	701.7	762.5
Type C Tear, pli	Skin	102.3	111.4	115.9

[0058] Figures 1A and 1B show the cure behavior (torque and corrected pressure, respectively) of the compounds made with the different MI ENGAGE® polymers. The lower MI compounds showed a higher torque corresponding to higher cure state and the pressure response was higher due to the higher level of blowing agent needed to reach the same final foam density. Reducing the levels of peroxide and blowing agent in the lower MI compounds would help reduce the foam density and cost of the compound.

[0059] Figure 2 shows the effect of temperature and polymer MI on the apparent viscosity at constant shear rate. The apparent viscosity increased with decreasing MI as expected. A polymer MI of 3 is used to show a typical foam compound viscosity at current compounding and injection molding processing temperatures (100-110C). From this point, the compounds made from lower MI ENGAGE® require higher processing temperatures to have similar or lower viscosity. The use of Instep MB1 enables the higher temperatures to be used without premature crosslinking. The level of Instep needed to protect the different MI ranges will change slightly as discussed below.

[0060] The apparent viscosity of the 0.5MI compound run at 140C is higher than expected due to depletion of Instep MB1 throughout the mixing, molding and testing of the compound. The lower MI compounds generated more shear heat in the mixer and started the consumption of the Instep sooner than the higher MI compound. This helps explain the difference observed in the cure behavior.

[0061] Figures 3 and 4 show a few property specific performance values for the foam and skin layers at each MI tested. The goal of this study is to determine the difference in performance between foams made with different MI polymers at the same overall foam density. Figures 3 shows the tensile and tear strength of the foam layer at similar foam density, across the 3 MI polymers used. Decreasing the polymer MI produced foams with significantly higher tensile strengths and slightly higher tear strength. Optimization of the lower MI compounds to achieve the same foam density at lower peroxide and blowing agent loading might help improve these results. The data shows lower MI compounds can produce improved foam properties at similar foam density. Another aspect of this would be the ability to produce lighter (lower density) foams that have the same properties as the current compounds. Blending different MI and density polymers can also be used to improve the properties but the enabling technology is the use of Instep MB1 to achieve the mixing and processing temperatures needed to produce foam compounds and parts. Similar results were observed looking at the skin layer of the foams with slightly less difference seen in the tear strength.

[0062] Although the invention as been described in considerable detail by the preceding examples, this detail is for illustration and is not to be construed as a limitation on the spirit and scope of the invention as it is described in the following claims. All U.S. patents, U.S. patent application publications, allowed U.S. patent applications and all other references cited above are incorporated herein by reference.

What is claimed is:

1. A composition comprising a low MI polymer, a chemical blowing agent, a scorch inhibitor and, optionally, a free radical initiator.

2. The composition of Claim 1 in which the low MI polymer is an ethylene/alpha-olefin copolymer with a density of less than 0.91 g/cc and an MI of less than 3 g/10 min.

3. The composition of Claim 2 in which the blowing agent comprises at least one of azodicarbonamide, azodiisobutyronitrile, benzenesulfo-hydrazide, 4,4-oxybenzene sulfonyl semi-carbazide, p-toluene sulfonyl semi-carbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, trihydrazino triazine and sodium bicarbonate.

4. The composition of Claim 3 in which the scorch inhibitor is a TEMPO compound.

5. The composition of Claim 4 in which the TEMPO compound is 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl.

6. The composition of Claim 4 comprising a free radical initiator.

7. The composition of Claim 6 in which the free radical initiator is peroxide.

8. Foam made from the composition of Claim 1.

9. An article made from the foam of Claim 8.

10. Footwear, gaskets, sport foams, weather stripping, acoustic management foam or insulation comprising the foam of Claim 8.

11. The composition of Claim 1 in which the low MI polymer is an ethylene/alpha-olefin copolymer with an MI of 2.5 g/10 min or less.

12. The composition of Claim 11 in which the low MI ethylene/alpha-olefin copolymer comprises units derived from at least one C_{3-20} olefin.

13. The composition of Claim 12 in which the C_{3-20} olefin is at least one of propene, 1-butene, 1-hexene and 1-octene.

14. The composition of Claim 11 in which the ethylene-alpha-olefin polymer comprises at least 50 weight percent of the composition.

15. The composition of Claim 14 in which the initiator is present in an amount of at least 0.05 percent based on the weight of the polymer.

16. The composition of Claim 15 further comprising a free radical crosslinking coagent.

17. A continuous process of for fabricating a foamed article, the process comprising mixing in a single vessel a low MI polymer, a chemical blowing agent, a scorch inhibitor and, optionally, a free radical initiator to form an essentially homogeneous composition.

18. The process of Claim 17 in which the mixing vessel is an extruder.

19. The process of Claim 18 in which the low MI polymer is an ethylene/alpha-olefin copolymer with a density of less than 0.91 g/cc and an MI of less than 3 g/10 min, the blowing agent comprises at least one of azodicarbonamide, azodiisobutyronitrile, benzenesulfo-hydrazide, 4,4-oxybenzene sulfonyl semi-carbazide, p-toluene sulfonyl semi-carbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, trihydrazino triazine and sodium bicarbonate, and the scorch inhibitor is a TEMPO compound.

20. The process of Claim 19 comprising the further steps of extruding the essentially homogeneous composition into a desired shape and subjecting the extruded composition to crosslinking and/or foaming conditions.

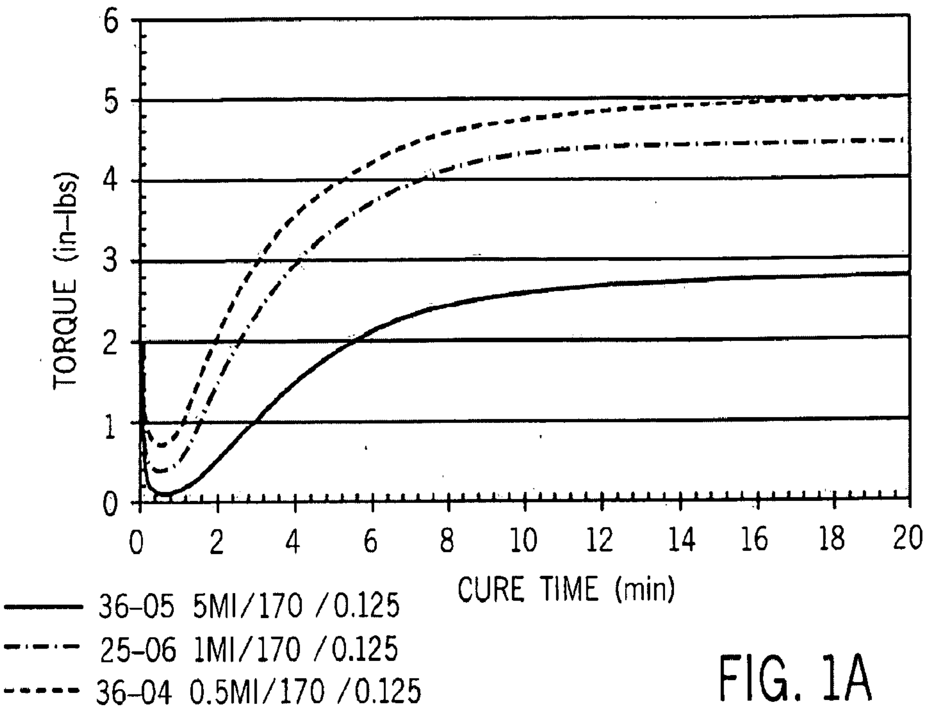

TORQUE (in-lbs)
0
1
2
3
4
5
6
CURE TIME (min)
0
2
4
6
8
10
12
14
16
18
20
36-05 5MI/170 /0.125
25-06 1MI/170 /0.125
36-04 0.5MI/170 /0.125

FIG. 1A

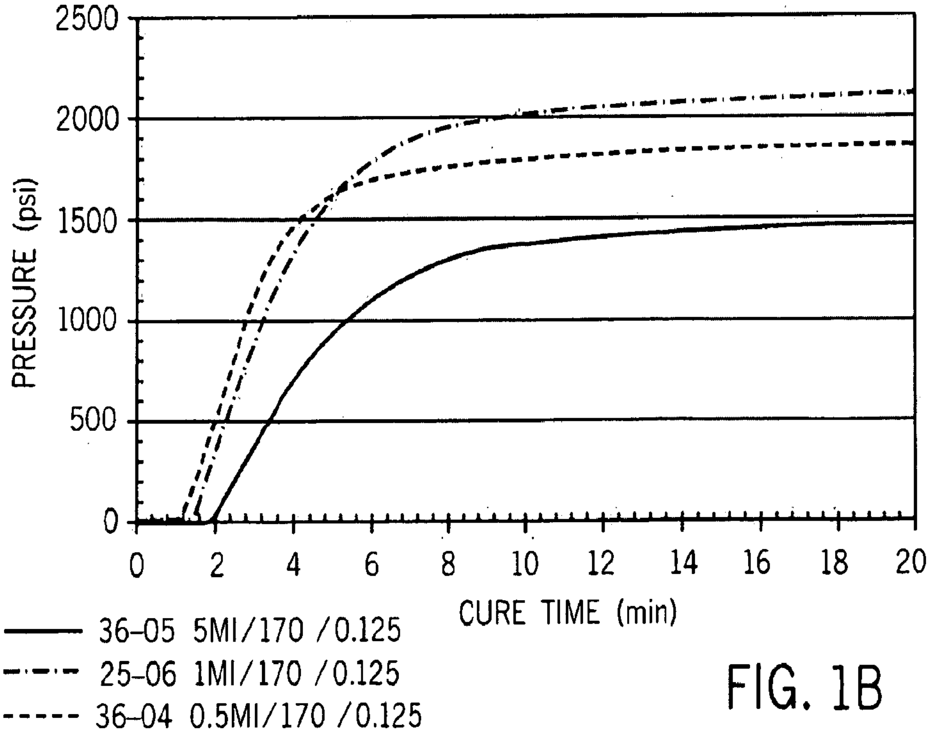

PRESSURE (psi)
0
500
1000
1500
2000
2500
CURE TIME (min)
0
2
4
6
8
10
12
14
16
18
20
36-05 5MI/170 /0.125
25-06 1MI/170 /0.125
36-04 0.5MI/170 /0.125

FIG. 1B

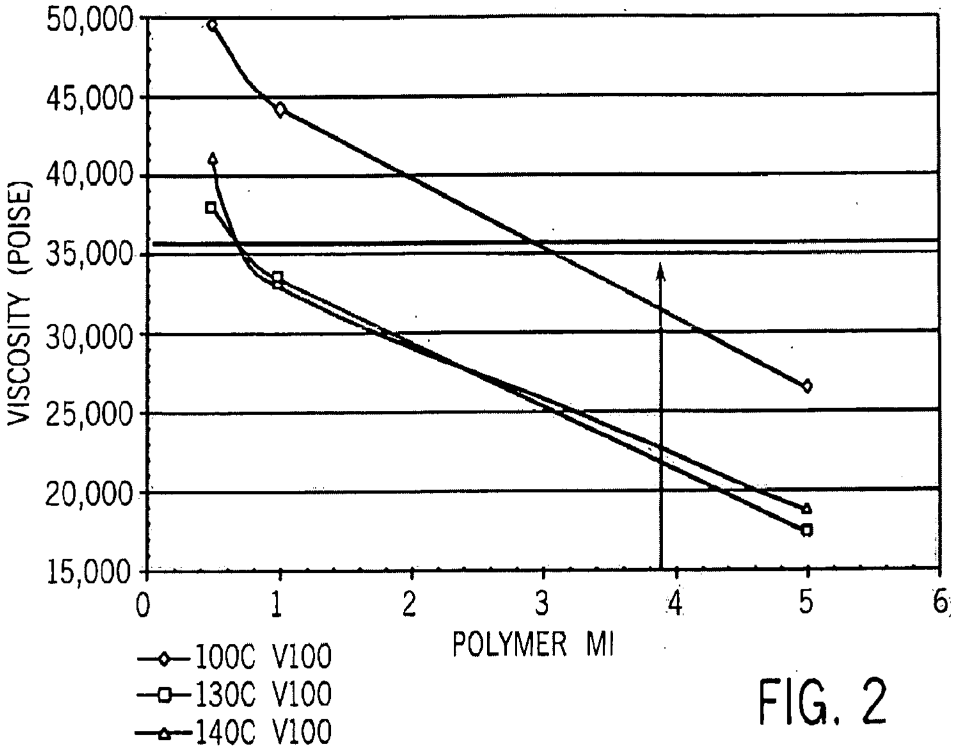
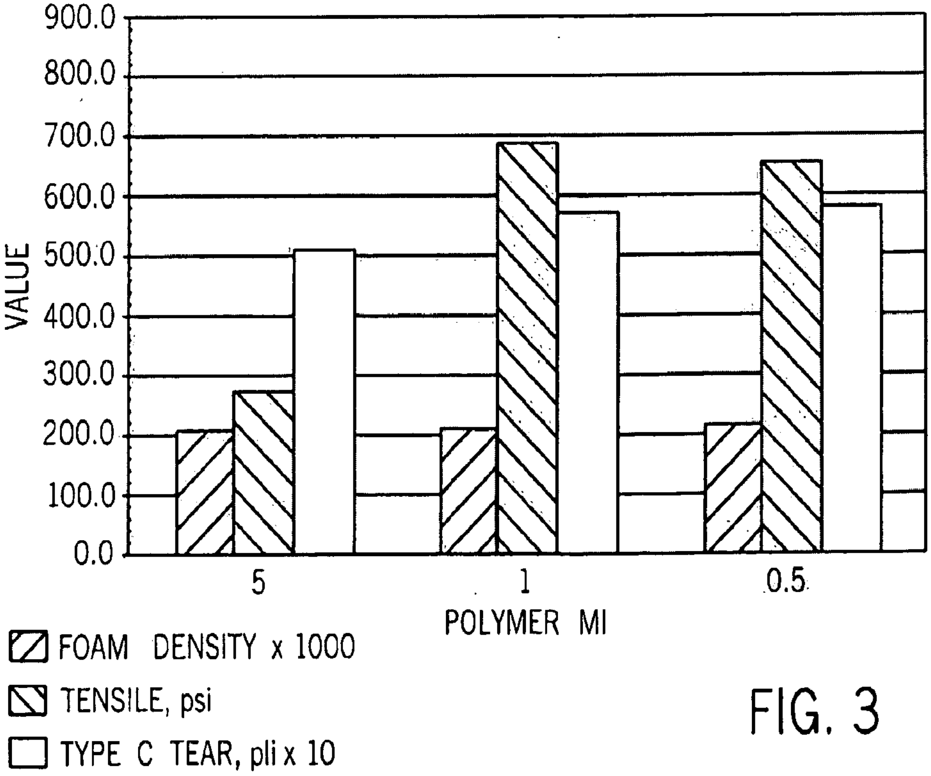

50,000
45,000
40,000
35,000
30,000
25,000
20,000
15,000
VISCOSITY (POISE)
0
1
2
3
4
5
6
POLYMER MI
100C V100
130C V100
140C V100

FIG. 2


900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
VALUE
5
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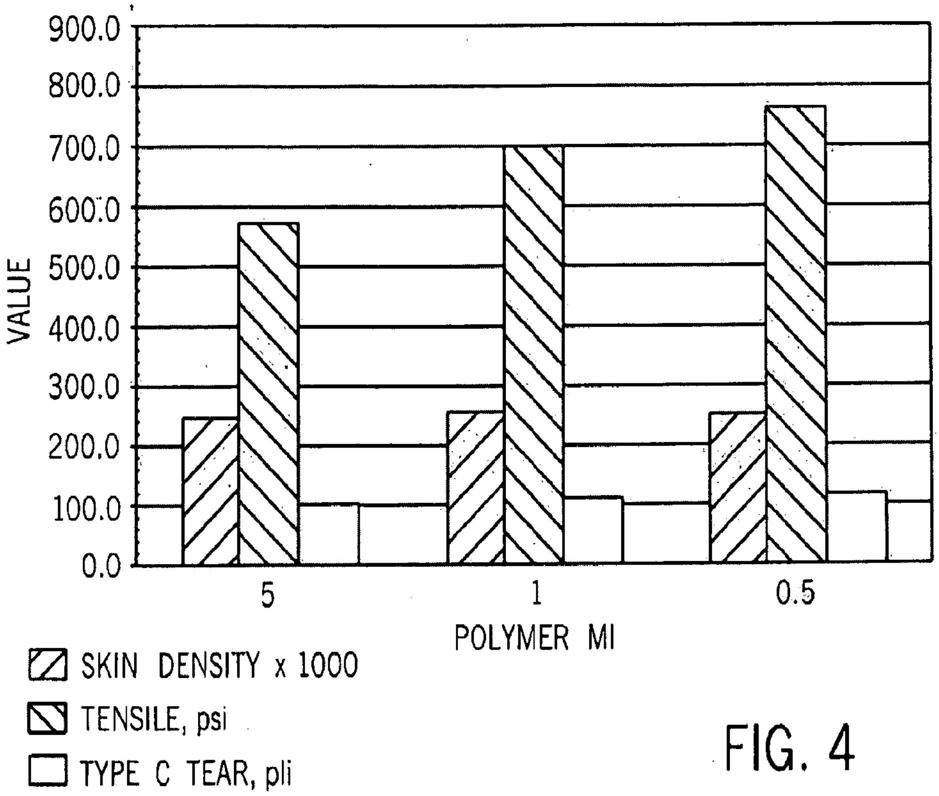
0.5
POLYMER MI
FOAM DENSITY x 1000
TENSILE, psi
TYPE C TEAR, pli x 10

FIG. 3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800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
VALUE
5
1
0.5
POLYMER MI
▨ SKIN DENSITY x 1000
▧ TENSILE, psi
☐ TYPE C TEAR, pli

FIG. 4