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(54) Title: CONTAINER WITH BARRIER COMPOSITION

(57) Abstract: The present disclosure provides a container. In an embodiment, the container includes a sidewall. The sidewall is composed of a barrier composition. The barrier composition is composed of (i) a low density polyethylene (LDPE), and (ii) a nucleator. The sidewall has an oxygen transmission rate from 100 cc-mil/100 in²/day to less than 400 cc-mil/100 in²/day.

CONTAINER WITH BARRIER COMPOSITION

BACKGROUND

[0001] An ampoule or bottle for medical applications can be made by a blow molding process or a blow fill seal (BFS) process. Known is low density polyethylene (LDPE) for use in Blow fill Seal (BFS) applications, as LDPE meets the requirements of low hexane extractables, squeezability, and suitable melt strength for processability. However, LDPE exhibits high oxygen transmission rates which is detrimental for medical applications.

[0002] Thus, the art recognizes the need for LDPE with increased barrier properties, and a low oxygen transmission rate, in particular. Specifically, a need exists for LDPE with low oxygen transmission rate suitable for medical applications, and for BFS containers in particular.

SUMMARY

[0003] The present disclosure provides a container. In an embodiment, the container includes a sidewall. The sidewall is composed of a barrier composition. The barrier composition is composed of (i) a low density polyethylene (LDPE), and (ii) a nucleator. The sidewall has an oxygen transmission rate from 100 cc-mil/100 in²/day to less than 400 cc-mil/100 in²/day.

DEFINITIONS

[0004] Any reference to the Periodic Table of Elements is that as published by CRC Press, Inc., 1990–1991. Reference to a group of elements in this table is by the new notation for numbering groups.

[0005] For purposes of United States patent practice, the contents of any referenced patent, patent application or publication are incorporated by reference in their entirety (or its equivalent U.S. version is so incorporated by reference) especially with respect to the disclosure of definitions (to the extent not inconsistent with any definitions specifically provided in this disclosure).

[0006] The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranges containing explicit values (e.g., from 1 or 2, or 3 to 5, or 6, or 7), any subrange between any two explicit values is included (e.g., the range 1-7 above includes subranges of from 1 to 2; from 2 to 6; from 5 to 7; from 3 to 7; from 5 to 6; etc.).

[0007] Unless stated to the contrary, implicit from the context, or customary in the art, all parts

and percents are based on weight and all test methods are current as of the filing date of this disclosure.

[0008] The terms “blend” or “polymer blend,” as used, refers to a mixture of two or more polymers. A blend may or may not be miscible (not phase separated at molecular level). A blend may or may not be phase separated. A blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and other methods known in the art. The blend may be affected by physically mixing two or more polymers on the macro level (for example, melt blending resins or compounding), or the micro level (for example, simultaneous forming within the same reactor).

[0009] The term "composition" refers to a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

[0010] The terms "comprising," "including," "having" and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term "comprising" may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step, or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step, or procedure not specifically delineated or listed. The term "or," unless stated otherwise, refers to the listed members individually as well as in any combination. Use of the singular includes use of the plural and vice versa.

[0011] An "ethylene-based polymer" is a polymer that contains more than 50 weight percent (wt%) polymerized ethylene monomer (based on the total amount of polymerizable monomers) and, optionally, may contain at least one comonomer. Ethylene-based polymer includes ethylene homopolymer, and ethylene copolymer (meaning units derived from ethylene and one or more comonomers). The terms "ethylene-based polymer" and "polyethylene" may be used interchangeably.

[0012] The term “ethylene monomer,” or “ethylene,” as used herein, refers to a chemical

unit having two carbon atoms connected with a double bond, and each carbon atom is bonded to two hydrogen atoms, wherein the chemical unit polymerizes with other such chemical units.

[0013] High density polyethylene (or "HDPE") is an ethylene homopolymer or an ethylene/ α -olefin copolymer with at least one C_4 – C_{10} α -olefin comonomer, or at least one C_4 – C_8 α -olefin comonomer and a density from 0.940 g/cc, or 0.945 g/cc, or 0.950 g/cc, 0.953 g/cc to 0.955 g/cc, or 0.960 g/cc, or 0.965 g/cc, or 0.970 g/cc, or 0.975 g/cc, or 0.980 g/cc.

[0014] The term "linear low density polyethylene," (or "LLDPE") as used herein, refers to a linear ethylene/ α -olefin copolymer containing heterogeneous short-chain branching distribution comprising units derived from ethylene and units derived from at least one C_3 – C_{10} α -olefin, or C_4 – C_8 α -olefin comonomer. LLDPE is characterized by little, if any, long chain branching, in contrast to conventional LDPE. LLDPE has a density from 0.910 g/cc to less than 0.940 g/cc. Nonlimiting examples of LLDPE include TUFLIN™ linear low density polyethylene resins (available from The Dow Chemical Company), DOWLEX™ polyethylene resins (available from the Dow Chemical Company), and MARLEX™ polyethylene (available from Chevron Phillips).

[0015] The term "low density polyethylene" (or "LDPE") may also be referred to as "high pressure ethylene polymer" or "highly branched polyethylene" and is an ethylene homopolymer and is typically produced by way of high pressure free radical polymerization (≥ 100 MPa (for example, 100–400 MPa), tubular reactor or autoclave reactor with free radical initiator). LDPE resins typically have a density in the range of 0.915 to 0.935 g/cc. LDPE is distinct from LLDPE.

[0016] An "olefin" is an unsaturated, aliphatic hydrocarbon having a carbon-carbon double bond.

[0017] The term "polymer" or a "polymeric material," as used herein, refers to a compound prepared by polymerizing monomers, whether of the same or a different type, that in polymerized form provides the multiple and/or repeating "units" or "mer units" that make up a polymer. 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 copolymer, usually employed to refer to polymers prepared from at least two types of monomers. It also embraces all forms of copolymer, e.g., random, block, etc. The terms "ethylene/ α -olefin polymer" and "propylene/ α -olefin polymer" are indicative of copolymer as described above prepared from polymerizing ethylene or propylene

respectively and one or more additional, polymerizable α -olefin monomer. It is noted that although a polymer is often referred to as being "made of" one or more specified monomers, "based on" a specified monomer or monomer type, "containing" a specified monomer content, or the like, in this context the term "monomer" is understood to be referring to the polymerized remnant of the specified monomer and not to the unpolymerized species. In general, polymers herein are referred to as being based on "units" that are the polymerized form of a corresponding monomer.

TEST METHODS

[0018] Density. Density is measured by the displacement (Archimedes) method, ASTM method D792 Method B. A sample is weighed in air (dry weight) and immersed in a fluid (wet weight). Knowing the density of the immersion fluid, the loss in weight of the sample on immersion allows the sample density to be calculated. A sheet of material is molded under per ASTM D4703 per Annex A.1 Procedure C (15°C cooling). On removal from the press, 3 (three) coupons (~1.5" x ~0.5" x ~0.125") are cut from the sheet and density is measured. For Method B, the samples are weighed in air and then immersed in the fluid. The fluid (IPA, isopropyl alcohol) is contained in a double walled vessel and the temperature is controlled to 23°C +/- 0.1°C. The samples are allowed to soak in the fluid for 8 minutes to ensure the samples have equilibrated to the bath temperature. The samples are then weighed while still immersed in the fluid. A glass sinker of known dry weight and volume is then weighed while immersed in the fluid. The density of the immersion fluid is calculated from the known and measured values for the glass sinker (this corrects for any small deviations in the fluid density in the allowable temperature range). The density of the samples may then be calculated from the known fluid density and the measured wet and dry sample weights.

[0019] Triple Detector Gel Permeation Chromatography (TD-GPC). The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 160° Celsius and the

column and detector compartment were set at 150^o Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene (TCB) and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[0020] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were 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 were pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160°C for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

$$M_{polyethylene} = A \times (M_{polystyrene})^B \quad (EQ1)$$

where M is the molecular weight, A has a value of 0.401 and B is equal to 1.0.

[0021] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[0022] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns.

[0023] Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the

PolymerChar high temperature autosampler. The samples were dissolved for 3 hours at 160°C Celsius under “low speed” shaking.

[0024] The calculations of $Mn_{(cc)}$, $Mw_{(cc)}$, and $Mz_{(cc)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

$$M_n(CC) = \frac{\sum^i IR_i}{\sum^i \left(IR_i / M_{polyethylene_i} \right)} \quad (EQ2)$$

$$M_w(CC) = \frac{\sum^i (IR_i * M_{polyethylene_i})}{\sum^i IR_i} \quad (EQ3)$$

$$M_z(CC) = \frac{\sum^i (IR_i * M_{polyethylene_i}^2)}{\sum^i (IR_i * M_{polyethylene_i})} \quad (EQ4)$$

[0025] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)}) \quad (EQ5)$$

[0026] For the determination of the viscometer and light scattering detector offsets from the IR5 detector, the systematic Approach for the determination of multi-detector offsets is done in a manner consistent with that published by Balke, Mourey, et. al. (Mourey and Balke, Chromatography Polym. Chpt 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, Chromatography Polym. Chpt 13, (1992)), optimizing triple detector log (MW and IV) results from a linear homopolymer polyethylene standard ($3.5 > Mw/Mn > 2.2$) with a molecular weight in the range of 115,000 to 125,000 g/mol to the narrow standard column calibration results from the narrow standards calibration curve using PolymerChar GPCOne™ Software.

[0027] The absolute molecular weight data was obtained in a manner consistent with that published by Zimm (Zimm, B.H., J. Chem. Phys., 16, 1099 (1948)) and Kratochvil (Kratochvil, P., Classical Light Scattering from Polymer Solutions, Elsevier, Oxford, NY (1987)) using PolymerChar GPCOne™ software. The overall injected concentration, used in the determination of the molecular weight, was obtained from the mass detector area and the mass detector constant, derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards of known weight-average molecular weight. The calculated molecular weights (using GPCOne™) were obtained using a light scattering constant, derived from one or more of the polyethylene standards mentioned below, and a refractive index concentration coefficient, dn/dc , of -0.104. Generally, the mass detector response (IR5) and the light scattering constant (determined using GPCOne™) should be determined from a linear standard with a molecular weight in excess of about 50,000 g/mole. The viscometer calibration (determined using GPCOne™) can be accomplished using the methods described by the manufacturer, or, alternatively, by using the published values of suitable linear standards, such as Standard Reference Materials (SRM) 1475a (available from National Institute of Standards and Technology (NIST)). A viscometer constant (obtained using GPCOne™) is calculated which relates specific viscosity area (DV) and injected mass for the calibration standard to its intrinsic viscosity. The chromatographic concentrations are assumed low enough to eliminate addressing 2nd virial coefficient effects (concentration effects on molecular weight).

[0028] The absolute weight average molecular weight ($MW_{(Abs)}$) is obtained (using GPCOne™) from the Area of the Light Scattering (LS) integrated chromatogram (factored by the light

scattering constant) divided by the mass recovered from the mass constant and the mass detector (IR5) area. The molecular weight and intrinsic viscosity responses are linearly extrapolated at chromatographic ends where signal to noise becomes low (using GPCOne™). Other respective moments, $M_{n(abs)}$, $M_{w(abs)}$, and $M_{z(abs)}$ are be calculated according to equations 6-8 as follows:

$$M_n(abs) = \frac{\sum^i IR_i}{\sum^i (IR_i / M_{Absolute_i})} \quad (EQ6)$$

$$M_w(abs) = \frac{\sum^i IR_i \times M_{Absolute_i}}{\sum^i IR_i} \quad (EQ7)$$

$$M_z(abs) = \frac{\sum^i (IR_i \times M_{Absolute_i}^2)}{\sum^i (IR_i \times M_{Absolute_i})} \quad (EQ8)$$

[0029] Cumulative Detector Fraction (CDF) Calculation Method

[0030] The calculation of the cumulative detector fraction from the internal infrared detector IR5 (CDF_{IR}) is accomplished using the following steps:

- 1). Linearly flow correct the chromatogram based on decane flow marker injection as described above.
- 2). Calculate molecular weights from the IR5 measurement channel as described above.
- 3). Calculate the cumulative detector of the IR5 (CDF_{IR}) chromatogram (measurement channel) based on its baseline-subtracted peak height (H) from high to low molecular weight (low to high retention volume) at each data slice (j) according to Equation 9.

$$CDF_{IR} = \frac{\sum_{j=RV \text{ at } 316,228 \text{ MW}}^{j=RV \text{ at Lowest Integrated Volume}} H_j}{\sum_{j=RV \text{ at Lowest Integrated Volume}}^{j=RV \text{ at Highest Integrated Volume}} H_j} \quad (EQ9)$$

[0031] gpcBR Branching Index by TD-GPC

[0032] The gpcBR branching index is determined by first calibrating the light scattering, viscosity, and infrared IR5 detectors as described previously. Baselines are then subtracted from the light scattering, viscometer, and IR5 (measurement channel) chromatograms. Integration

windows are then set to ensure integration of all of the low molecular weight retention volume range in the light scattering and viscometer chromatograms that indicate the presence of detectable polymer from the infrared (IR5) chromatogram. Linear polyethylene standards are then used to establish polyethylene and polystyrene Mark-Houwink constants. Upon obtaining the constants, the two values are used to construct two linear reference conventional calibrations for polyethylene molecular weight and polyethylene intrinsic viscosity as a function of elution volume, as shown in Equations (10) and (11):

$$M_{PE} = \left(\frac{K_{PS}}{K_{PE}}\right)^{\frac{1}{\alpha_{PE}+1}} \times M_{PS}^{\frac{\alpha_{PS}+1}{\alpha_{PE}+1}} \quad (\text{EQ10})$$

$$[\eta]_{PE} = \frac{K_{PS} \times M_{PS}^{\alpha_{PS}+1}}{M_{PE}} \quad (\text{EQ11})$$

[0033] The gpcBR branching index is a robust method for the characterization of long chain branching as described in Yau, Wallace W., “Examples of Using 3D-GPC—TREF for Polyolefin Characterization,” *Macromol. Symp.*, 2007, 257, 29-45. The index avoids the “slice-by-slice” TD-GPC calculations traditionally used in the determination of g' values and branching frequency calculations, in favor of whole polymer detector areas. From TD-GPC data, one can obtain the sample bulk absolute weight average molecular weight ($MW_{(Abs)}$) by the light scattering (LS) detector, using the peak area method. The method avoids the “slice-by-slice” ratio of light scattering detector signal over the concentration detector signal, as required in a traditional g' determination.

[0034] With TD-GPC, sample intrinsic viscosities are also obtained independently using Equations (12). The area calculation in (12) offers more precision, because, as an overall sample area, it is much less sensitive to variation caused by detector noise and TD-GPC settings on baseline and integration limits. More importantly, the peak area calculation is not affected by the detector volume offsets. Similarly, the high-precision sample intrinsic viscosity ($[\eta]$) is obtained by the area method shown in Equation (12):

$$[\eta] = \frac{\sum_i c_i \times [\eta]_i}{\sum_i c_i} = \frac{\sum_i \eta_{spi}}{\sum_i c_i} = \frac{\text{Viscometer Area}}{\text{Conc. Area}} \quad (\text{EQ12})$$

where n_{spi} stands for the specific viscosity as acquired from the viscometer detector.

[0035] To determine the gpcBR branching index, the light scattering elution area for the sample polymer is used to determine the absolute molecular weight of the sample ($MW_{(Abs)}$). The viscosity detector elution area for the sample polymer is used to determine the intrinsic viscosity ($[\eta]$) of the sample.

[0036] Initially, the molecular weight and intrinsic viscosity for a linear polyethylene standard sample, such as SRM1475a or an equivalent, are determined using the conventional calibrations (“cc”) for both molecular weight and intrinsic viscosity as a function of elution volume, per Equations (3) and (13):

$$[\eta]_{cc} = \frac{\sum_i c_i \times [\eta]_{i,cc}}{\sum_i c_i} = \frac{\sum_i c_i \times K \times (M_{i,cc})^\alpha}{\sum_i c_i} \quad (EQ13)$$

[0037] Equation (14) is used to determine the gpcBR branching index:

$$gpcBR = [(\frac{[\eta]_{cc}}{[\eta]}) \times (\frac{MW_{(Abs)}}{M_w(cc)})^{\alpha_{PE}} - 1] \quad (EQ14)$$

wherein $[\eta]$ is the measured intrinsic viscosity, $[\eta]_{cc}$ is the intrinsic viscosity from the conventional calibration, $MW_{(Abs)}$ is the measured weight average molecular weight, and $M_w(cc)$ is the weight average molecular weight of the conventional calibration. The weight average molecular weight by light scattering (LS) is commonly referred to as “absolute weight average molecular weight”. The $M_w(cc)$ from Equation (3) using conventional GPC molecular weight calibration curve (“conventional calibration”) is often referred to as “polymer chain backbone molecular weight,” “conventional weight average molecular weight”.

[0038] All statistical values with the “cc” subscript are determined using their respective elution volumes, the corresponding conventional calibration as previously described, and the concentration (c_i). The values of “ $MW_{(Abs)}$ ” and “ $[\eta]$ ” are measured values based on the mass detector, LALLS, and viscometer areas. The value of K_{PE} is adjusted iteratively, until the linear reference sample has a gpcBR measured value of zero. For example, the final values for α and $\log K$ for the determination of gpcBR in this particular case are 0.725 and -3.391 , respectively, for polyethylene, and 0.722 and -3.993 , respectively, for polystyrene. These polyethylene coefficients (α and K) were then entered into Equation 14.

[0039] Once the K and α values have been determined using the procedure discussed previously, the procedure is repeated using the branched samples. The branched samples are analyzed using the final Mark-Houwink constants obtained from the linear reference as the best “cc” calibration values.

[0040] Melt Index. The term “melt index,” or “MI” as used herein, refers to the measure of how easily a thermoplastic polymer flows when in a melted state. Melt index, or I_2 , is measured in accordance with ASTM D 1238, Condition 190°C/2.16 kg, Method B, and is reported in grams eluted per 10 minutes (g/10 min).

[0041] Oxygen transmission rate. The measurement of oxygen transmission rate (OTR) is measure in accordance with the standard ASTM D3985. In this method, each test specimen in the form of a flat sheet is mounted and hermetically sealed (with the help of O-rings and Apiezon T Grease) in a diffusion cell. The diffusion cell consists of two chambers separated by the specimen. The permeant (test) gas (i.e., O_2) at a desired concentration and a flow rate is plumbed into and out of one side. An inert carrier gas (Nitrogen (98% N_2 and 2% H_2)) is plumbed into and out of the other side at the same flow rate. In its path, the carrier gas picks up oxygen molecules that have permeated through the film. The carrier gas, upon its exit from the cell, flows through a Coulometric sensor which is designed to produce an electric signal whose amplitude is proportional to the oxygen content in the carrier gas. The result is given in terms of volume of oxygen per unit area of the specimen per unit time. For OTR, a typical unit after normalizing to thickness (often referred to as ‘Permeation’) is cc-mil/100in²/day. The OTR of a specimen is the equilibrated value read after several hours, when its difference relative to the last measurement is less than 1%. For the samples used in these studies, the MOCON instrument OX-TRAN 2/22ML was used and two specimens were used for each sample. The concentration of the test gas used was 10% and the result was reported by compensating to 100% gas concentration by multiplying the measured value by 10. The conditions used were 23°C and 0% relative humidity (“RH”) for both test and carrier gases. The specimens were cut from blow-molded bottles and their surface area (exposed to test gas) within the diffusion cell was 50 cm².

BRIEF DESCRIPTION OF THE DRAWING

[0042] FIG. 1 is a perspective view of a blow-fill-seal (“BFS”) ampoule in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

[0043] The present disclosure is directed to container. In an embodiment, the container includes a sidewall. The sidewall is composed of a barrier composition. The barrier composition is composed of (i) a low density polyethylene (LDPE), and (ii) a nucleator. The sidewall has an oxygen transmission rate from 100 cc-mil/100 in²/day to less than 400 cc-mil/100 in²/day.

[0044] The barrier composition includes (A) a low density polyethylene (LDPE). The LDPE is an ethylene homopolymer having one, some, or all of the following properties:

- (i) a density from 0.910 g/cc to 0.930 g/cc; and/or
- (ii) a melt index from 0.1 g/10 min to 2.4 g/10 min, or from 0.5 g/10 min to 2.2 g/10 min; and/or
- (iii) Mw(abs) from 50,000 g/mol to 220,000 g/mol, or from 100,000 g/mol to 220,000 g/mol; and/or
- (iv) CDF_{IR} from 0.010 to less than 0.060; and/or
- (v) a gpcBR value from 0.50 to 2.10, or from 1.00 to 2.10, or from 1.50 to 2.10, or from 1.80 to 2.10; and/or
- (vi) a Mw(cc)/Mn(cc)polydispersity index (PDI) from 1.00 to less than 7.50.

[0045] The barrier composition includes a nucleator. Examples can be metal carboxylates, metal aromatic carboxylates, hexahydrophthalic acid metal salts, stearates, organic phosphates, sorbitols, bisamides, or mixtures thereof.

[0046] In an embodiment, the nucleator is 1,2-cyclohexanedicarboxylic acid.

[0047] In an embodiment, the nucleator is blended, or is melt blended, with the LDPE by way of a nucleator masterbatch.

[0048] In an embodiment, the nucleator masterbatch includes HPN-20E (HPN-20E is 67 wt% of calcium salt of 1,2-cyclohexanedicarboxylic acid and 33 wt% of zinc stearate, based on the total

weight of the HPN-20E). The nucleator masterbatch includes 3 wt% of HPN-20E, 1.5 wt% silica, 0.5 wt % hydrotalcite, 5 wt% of antioxidants, and 90 wt% weight percent of a carrier resin. The carrier resin is a second ethylene-based polymer different than the LDPE. In an embodiment, the second ethylene-based polymer is a high-density polyethylene homopolymer (HDPE). In an embodiment, the second ethylene-based polymer is a high-density polyethylene homopolymer (HDPE) with a narrow molecular weight distribution having a density from 0.945 g/cc to 0.970 g/cc, and a melt index from 4 g/10 minutes to 15 g/10 minutes. In a further embodiment, the sidewall (with or without the second ethylene-based polymer) is void of, or otherwise excludes, LLDPE.

[0049] The barrier composition may include one or more optional additives. Nonlimiting examples of suitable additives include antioxidants, ultraviolet light stabilizers, thermal stabilizers, slip agents, antiblock, pigments or colorants, processing aids, crosslinking catalysts, flame retardants, fillers, foaming agents, and combinations thereof. In an embodiment, the barrier composition includes 0 wt%, or from 0.5 wt% to 3 wt%, or from 1.0 wt% to 2.5 wt%, or from 1.0 wt% to 2.0 wt% total amount of additives. Weight percent is based on total weight of the barrier composition.

[0050] In an embodiment, the sidewall of the container is a monolayer structure composed solely of the barrier composition, and the barrier composition comprises, consists essentially of, or consists of:

(A) from 94 wt% to 99 wt%, or from 95 wt% to 98 wt% an LDPE ethylene homopolymer having one, some, or all of the following properties:

(i) a density from 0.910 g/cc to 0.930 g/cc; and/or

(ii) a melt index from 0.1 g/10 min to 2.4 g/10 min, or from 0.5 g/10 min to 2.2 g/10 min; and/or

(iii) Mw (abs) from 50,000 g/mol to 220,000 g/mol, or from 100,000 g/mol to 220,000 g/mol, and/or

(iv) CDF_{IR} from 0.010 to less than 0.060, and/or

(v) a gpcBR value from 0.50 to 2.10, or from 1.00 to 2.10, or from 1.50 to 2.10, or from 1.80 to 2.10; and/or

(vi) a $M_w(cc)/M_n(cc)$ polydispersity index (PDI) from 1.00 to less than 7.50;

(B) from 0.01 wt% to 0.2 wt%, or from 0.05 wt% to 0.015 wt% of a nucleator that is 1,2-cyclohexanedicarboxylic acid;

(C) 0 wt%, or from 0.1 wt% to 0.5 wt%, or from 0.2 wt% to 0.4 wt% additives; and

(D) 0 wt%, or from 1 wt% to 5 wt%, or from 1.5 wt% to 4.5 wt% of a second polymer that is a HDPE wherein weight percent is based on total weight of the barrier composition; and the sidewall can have variable thickness and has a OTR from 100 cc-mil/100 in²/day to less than 400 cc-mil/100 in²/day (hereafter *sidewall1*).

[0051] In an embodiment, the sidewall of the container is a monolayer structure composed solely of the barrier composition, and the barrier composition comprises, consists essentially of, or consists of

(A) from 94 wt% to 99 wt%, or from 95 wt% to 98 wt% of an LDPE ethylene homopolymer having one, some, or all of the following properties:

(i) a density from 0.91 g/cc to 0.93 g/cc; and/or

(ii) a melt index from 0.1 g/10 min to 2.4 g/10 min, or from 0.5 g/10 min to 2.2 g/10 min; and/or

(iii) M_w (abs) from 50,000 g/mol to 220,000 g/mol, or from 100,000 g/mol to 220,000 g/mol; and/or

(iv) CDF_{IR} from 0.010 to less than 0.060; and/or

(v) a gpcBR value from 0.50 to 2.10, or from 1.00 to 2.10, or from 1.50 to 2.10, or from 1.80 to 2.10; and/or

(vi) a $M_w(cc)/M_n(cc)$ polydispersity index (PDI) from 1.00 to less than 7.50;

(B) from 0.01 wt% to 0.2 wt%, or from 0.05 wt% to 0.15wt% of a nucleator that is 1,2-cyclohexanedicarboxylic acid;

(C) an additive that is 75 ppm to 1500 ppm silica (silicon dioxide); and

(D) 0 wt%, or from 1 wt% to 5 wt%, or from 1.5 wt% to 4.5 wt% of a second polymer that is a HDPE wherein weight percent is based on total weight of the barrier composition; and the sidewall can have a variable thickness, and the sidewall has an OTR from 100 cc-mil/100in²/day to less than 400 cc-mil/100in²/day (hereafter *sidewall2*).

[0052] The present container can be a flexible package, a pouch, and/or a stand-up pouch.

[0053] In an embodiment, the container is a Blow-Fill-Seal container (“BFS” container). A “BFS container,” as used herein, is a container produced in an automated manufacturing process by which polymeric containers, such as bottles or ampoules, are, in a continuous operation, blow-formed, filled, and sealed. The BFS container is manufactured in a sterile, enclosed area inside a machine. An advantage of the BFS manufacturing process is that the process is a closed and automated system. The BFS container is formed within the BFS machine, filled with sterile solution, and the BFS container is closed, with limited, or no, human intervention.

[0054] FIG. 1 shows a BFS container 10. In the BFS container manufacturing process, the present barrier composition (*i.e.*, LDPE, nucleator, and optional additives) is melted, extruded into a sidewall 12 which is shaped in the form of a cylindrical tube (a “parison,” or a continuous sidewall), and formed into a container by blowing sterile air or nitrogen into the cylindrical tube to force the present barrier composition (in the melted state) into the shape of the mold. Cooling of the container begins within seconds after it is formed, as the mold is chilled. A medicament 14 (typically a liquid, a semi-liquid or a gel) is then filled into the just-formed polymeric container while still inside the mold. The BFS machine then closes sidewall 12 upon itself by sealing the top end and the bottom end of the cylindrical tube, thereby forming a sealed BFS container 10 with sidewall 12 defining a body portion 16, a top portion 18, a bottom portion 20, and a closed chamber 22 with medicament 14 therein. In other words, BFS container 10 is made from a single continuous sidewall 12. BFS container also includes a tab 24 (also made from the present barrier composition) for opening container 10 and dispensing, or otherwise discharging, medicament 14 from chamber 22.

[0055] Nonlimiting examples of medicament present in chamber 22 and in direct contact with sidewall 12 include liquid ophthalmics (such as sterile eye drops), inhalational anesthetics, biologics, lavaging agents, and vaccines.

[0056] Sidewall 12 may be uniform thickness or may vary in thickness along a length of BFS container 10, from top portion 18, to body portion 16, and to bottom portion 20. In an embodiment, continuous sidewall 12 forms closed top portion 18, body portion 16, and bottom portion 20.

[0057] In an embodiment, sidewall 12 is a continuous sidewall with no seam, and/or with no seal, and/or with no heat seal.

[0058] In an embodiment, body portion 16 is a continuous body portion and has no seam, and/or body portion 16 has no heat seal.

[0059] By way of example, and not limitation, some embodiments of the present disclosure will now be described in detail in the following examples.

EXAMPLES

[0060] Materials used in the inventive examples (“IE”) and comparative samples (“CS”) are set forth in Table 1 below.

[0061] Table 1

Material	Description	Source
LDPE 1	LDPE ethylene homopolymer MI 1.85 g/10 min, d – 0.925 g/cc	Dow
LDPE 2	LDPE ethylene homopolymer MI 1.93 g/10 min, d – 0.924 g/cc	Dow
LDPE 3	LDPE ethylene homopolymer MI 1.97 g/10 min, d – 0.920 g/cc	Dow
LDPE 4	LDPE ethylene homopolymer MI 1.57 g/10 min, d – 0.919 g/cc	Dow
LDPE 5	LDPE ethylene homopolymer MI 1.90 g/10 min, d – 0.919 g/cc	Dow
LDPE 6	LDPE ethylene homopolymer MI 2.3 g/10 min, d – 0.918 g/cc	Dow
HDPE 1	HDPE MI 12 8.25 g/10 min, I21.6 180 g/10 min, d – 0.965 g/cc	Dow
HPN-20E	Nucleator composition 66 wt% of calcium salt of 1,2-cyclohexanedicarboxylic acid and 34 wt% of zinc stearate/zinc palmitate (based on total weight of the nucleator composition)	Milliken
Sylobloc 45	Amorphous silicon dioxide	WR Grace
Hycite 713	Aluminum magnesium carbonate hydroxide (hydrate)	Clariant
Irganox 1076	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	BASF
Irgafos 168	Tris(2,4-di-tert-butylphenyl)phosphite	BASF

[0062] Table 1a: Composition of nucleator masterbatch (MB)

Nucleator masterbatch (MB)	wt%
HDPE 1	90
Hyperform HPN-20E	3
Sylobloc 45	1.5
Hycite 713	0.5
Irganox 1076	1
Irgafos 168	4
Total (based on total weight MB)	100

[0063] Containers in the form of blow molded bottles (14 oz “Boston Round”-shaped bottles with a target bottle weight of 26 ± 0.5 grams) were made using a Bekum H-111 continuous extrusion blow molding machine equipped with a 50 mm extruder and MACO 6500 digital readout controller. Nucleator masterbatch pellets with the composition shown in Table 1a were added to base LDPE in a bag, to create a barrier composition with 95 wt% of the LDPE and 5 wt% of the nucleator MB, based on the total weight of the barrier composition. The pellet bag was hand-shaken and then fed into extruder. The blow molding equipment was run using parison programming to ensure that a consistent uniform sidewall thickness distribution was maintained in the bottles produced. The extruder barrel temperatures were maintained at 350° F. The extrusion rate was 120 g/min to 140 g/min. Head weight was used to adjust the weight throughout the parison. This can be used to compensate for the added weight of profiling the bottle. A higher head weight is correlated with a wider die gap and vice versa. The target bottle weight for each produced bottle was 26 grams. The sidewall (and the entire bottle) is composed solely of the barrier composition and contains (i) 95 wt% LDPE, (ii) 4.5 wt% HDPE 1, 0.15 wt% HPN-20E, 0.075 wt% Sylobloc 45, 0.025 wt% Hycite 713, 0.05 wt% Irganox 1076, and 0.2 wt% Irgafos 168, based on total weight of the container sidewall.

[0064] Blow molded bottles with a chamber volume of 14 ounces and a sidewall thickness from 20 mil to 40 mil were formed from the barrier compositions in Table 2 below. The properties (i) of the initial LDPE (prior to blending with nucleator MB) and (ii) the OTR for the sidewall for each sample container (inventive examples (“IE”) and comparative samples (“CS”)) are provided in Table 2 below.

[0065] Table 2: Container Sidewall Properties

Sample	Bottle sidewall thickness without MB/with MB	OTR* without MB/with MB	OTR improv ement	Density ^{&}	MI ^{&}	Mw ^{&} (abs)	CDF _{IR}	gpcBR ^{&}	Mn(cc) ^{&}	Mw(cc) ^{&}	Mw(cc) /Mn(cc)
Unit	mil	cc-mil/100in ² /day	%	g/cc	g/10 min	g/mol			g/mol	g/mol	
IE1 LDPE 1	31.8/27.4	402/320	20.4	0.9246	1.85	184,800	0.042	1.83	15,300	90,300	5.90
IE2 LDPE 2	27.5/17.9	404/332	17.9	0.9236	1.93	198,000	0.052	1.94	15,000	95,800	6.38
IE3 LDPE 3	26.9/28.4	437/367	15.9	0.9199	1.97	194,200	0.055	1.87	16,900	99,700	5.90
CS1 LDPE 4	25.9/30.0	477/406	14.8	0.9192	1.57	254,800	0.068	2.38	13,400	107,300	8.01
CS2 LDPE 5	30.2/36.2	510/471	7.61	0.9193	1.90	258,800	0.080	2.31	25,500	120,300	4.72
CS3 LDPE 6	28.4/27.9	514/431	16.2	0.9171	2.41	653,800	0.188	4.55	16,300	223,700	13.69

*OTR – cc-mil/100in²/day[&]LDPE properties prior to blending LDPE with nucleator MB

[0066] Applicant discovered that container sidewall composed of the unique LDPE (LDPE1-LDPE3) in combination with the nucleator exhibit low OTR (100 cc-mil/100 in²/day to less than 400 cc-mil/100 in²/day). Bounded by no particular theory, the specific structural features of the unique LDPE in inventive examples IE1-IE3 that enabled low OTR values include, low levels for high MW tail (as quantified by $CDF_{IR} < 0.055$), $M_w(ABS) (< 220,000)$, $gpcBr (< 2.1)$, $PDI (< 7.5)$ as compared to comparative samples LDPE4-LDPE6. Each of LDPE4-LDPE6 is deficient in at least one property and each of LDPE4-LDPE6 fail to provide a container sidewall composition a barrier composition wherein the sidewall has an OTR from 100 cc-mil/100 in²/day to less than 400 cc-mil/100 in²/day.

[0067] It is specifically intended that the present disclosure not be limited to the embodiments and illustrations contained herein, but include modified forms of those embodiments including portions of the embodiments and combinations of elements of different embodiments as come within the scope of the following claims.

CLAIMS

1. A container comprising:

a sidewall, the sidewall composed of a barrier composition comprising

(i) a low density polyethylene (LDPE), and

(ii) a nucleator; and

the sidewall has an oxygen transmission rate from 100 cc-mil/100 in²/day to less than 400 cc-mil/100 in²/day.
2. The container of claim 1 wherein the LDPE is an ethylene homopolymer and has a property selected from the group consisting of

(i) a density from 0.91 g/cc to 0.93 g/cc,

(ii) a melt index from 0.1 g/10 min to 2.4 g/10 min,

(iii) Mw (abs) from 50,000 g/mol to 220,000 g/mol,

(iv) a CDF_{IR} from 0.010 to less than 0.060,

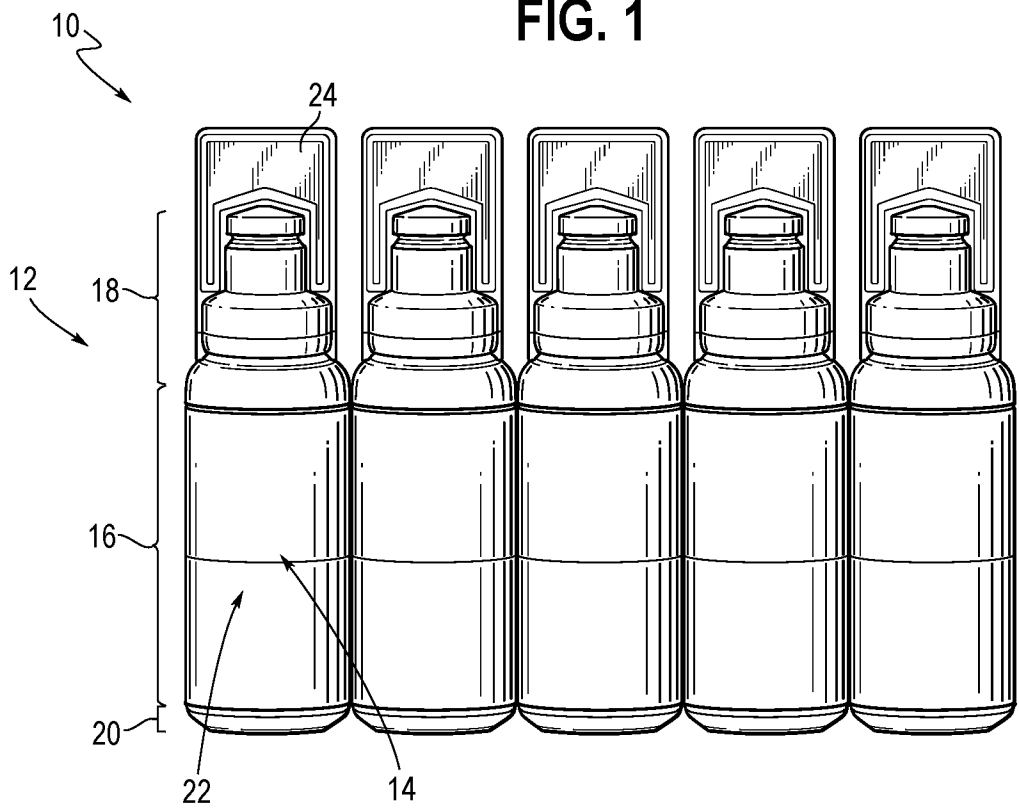
(v) a gpcBR value from 0.50 to 2.10,

(vi) a Mw(cc)/Mn(cc) from 1.00 to less than 7.50, and

(vii) combinations thereof.
3. The container of any of claims 1-2 wherein the nucleator is calcium salt of 1,2-cyclohexanedicarboxylic acid.
4. The container of any of claims 1-3 wherein the barrier composition further comprises a second ethylene-based polymer different than the LDPE.
5. The container of any of claims 1-4 wherein the barrier composition further comprises silica.

6. The container of any of claims 1-5 comprising
from 94 wt% to 99 wt% of the LDPE;
from 100 ppm to 2000 ppm of the nucleating agent that is 1,2-cyclohexanedicarboxylic acid;
from 1 wt% to 5wt% of the second ethylene-based polymer that is a high density polyethylene; and
from 75 ppm to 1500 ppm silica.
7. The container of any of claims 1-6 wherein the sidewall defines a closed chamber; and a medicament is present in the closed chamber.
8. The container of any of claims 1-7 wherein the sidewall is a monolayer structure and has a thickness from 0.3 mm to 1.5 mm.
9. The container of any of claims 7-8 wherein the closed chamber has a volume from 0.1 cc to 100 cc.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER INV. C08K5/098 C08K3/36 C08L23/06 B65D1/02 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B65D C08K Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 20 September 2024		Date of mailing of the international search report 14/10/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Russell, Graham

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